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AFL lithography and its application
to II-VI compound nanostructures

Adrian Stefan Avramescu

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March 2000

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Abstract

In this thesis we investigate the fabrication by atomic force microscope (AFM) of a mask with resolution down to a couple of tens of nanometers, which is suitable for selective area growth of II-VI compounds nanostructures. We introduce a new II-VI alloy system that is easy to be selectively grown at low temperature by metalorganic molecular beam epitaxy (MOMBE) and to be engineered with different bandgap energies while being lattice-matched to GaAs substrates. Based on these two ingredients we demonstrate II-VI compound nanostructures obtained by selective area growth.

High-resolution patterning is one of the key points for this approach. For this purpose a very thin carbonaceous mask deposited on a GaAs substrate is patterned by AFM. The carbonaceous film with a thickness of ~ 3 nm is locally deposited by electron-beam irradiation in a scanning electron microscope (SEM). The carbonaceous film is patterned by anodization activated by the electric field applied between the tip and the substrate. The highest resolution that was obtained is about 20 nm. This two-instruments combination provides unmatched advantages for patterning such as the continuous monitoring of the patterning status and the extension of the area and resolution of the patterning as compared with the case when only one is employed.

For the selective area growth, the II-VI compound semiconductors are chosen because they grow at low temperature and this system can cover a wide range of bandgap energies from UV to Green. In this direction, we propose for the first time the quaternary alloy ZnMgCdS and we demonstrate selective area growth of high-quality ZnMgCdS/ZnCdS heterostructures that are lattice-matched to GaAs substrates.

Using the highest-resolution patterning and the newly developed alloys, arrays of quantum dots (~ 26 nm) uniformly aligned (~ 100 -nm-pitch) providing densities as high as 10^{10} cm^{-2} are demonstrated.

The paper is structured as follows:

Chapter 1 is an introduction to the field of nanostructures and current status in developing nanostructures and applications based on them. The technologies based on scanning probe techniques are given a special attention.

Chapter 2 describes the AFM based lithography. AFM patterning by mechanic surface modification and electric-field induced anodization are treated. In the first section the mechanical approach is described. This is based on the plowing through a soft polymer resist for creating the

patterns, which are subsequently transferred into the underlying SiO_2 layer by wet etching. The second approach described is based on the combination of SEM and AFM. The local masking technology relies on the deposition by electron-beam of ~ 3 nm thick carbonaceous film directly on the substrate surface in the SEM followed by the high-resolution patterning by AFM anodization. In the mechanical patterning, the influences of the force value, the time sequence of the force application, and the SiO_2 thickness on the resolution of the patterns are discussed. In the electric field based patterning, the distribution of the electric field at the tip-film interface and the water meniscus geometry are estimated and the main parameters involved are discussed. The effects of modulation in polarity, amplitude, and frequency of the electric field during the patterning are analyzed in detail. A resolution of ~ 28 nm is demonstrated for the masks ready for selective area growth. A comparison between these two approaches is provided.

Chapter 3 discusses the design of II-VI compound semiconductors suitable for bandgap engineering and low-temperature selective area growth. After a brief introduction of the growth method, the main advantages of the II-VI materials are presented. A new alloy system $\text{ZnMgCdS}/\text{ZnCdS}$ that can be grown lattice-matched to GaAs is introduced. Structural, morphological and optical properties of the grown alloys and control of the Mg composition are discussed for different growth conditions. The influence of the nucleation and initial growth on the structural and optical properties of the alloys is emphasized.

Chapter 4 is focused on the nanoscale selective area growth. The specific points of the nanoscale selective area growth are presented. The nucleation issue is discussed together with the means to overcome it. MOMBE growth of arrays of dot-like nanostructures based on the $\text{ZnMgCdS}/\text{ZnCdS}$ alloys is demonstrated.

The summary of the current work and a proposal for future devices based on this technology are given in Chapter 5. As a future application of this research a new design for ultra-small cavity light emitting devices in the blue region that are ready for monolithic integration is proposed. The proposed ring structure will have a high coupling efficiency of the spontaneous emission into the cavity modes. This is achieved by minimizing the cavity volume to support a few resonance modes and by facilitating the light emission only at the antinodes of the cavity optical field. The fabrication of the ultra-small ring structure is possible only by AFM lithography and selective area growth since the geometrical and the structural quality requirements are very tight.

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Chapter 1

Introduction

1.1 Introductory Note

The human society at the beginning of a new millennium has reached a stage when it is more and more relying on different electronic products and services. This is a direct result of the tremendous developments achieved in science and technology. The computers and their networks are an everyday presence, electronic multimedia such as CDs or DVDs are currently used in every day life, just to enumerate a few. Most of these applications are employing small light emitting devices either for transmitting information without a wire or for reading or writing information from or on a media.

These optoelectronic devices that are now in everyday use show a similar trend as the simple electronic devices. There is a request to use smaller, less power consuming and more stable light emitting devices. In order to fulfill these requirements, a lot of research is necessary to be invested in many areas. A short list with these areas should include: the physics of the small size devices, the technology to produce the minute devices, the new materials to be used in these devices, and the design of the devices.

Each of this area has its own contribution to the final devices and each should be optimized to its best in order to succeed to obtain a state-of-art product.

1.2 Historical Background

1.2.1 Semiconductor Nanostructures

Semiconductor nanostructures are generally understood as crystalline structures of different shapes that possess at least one dimension on the nanometer scale, more typically below 100 nm. This feature, near the atomic scale of the dimension, will give quantum confinement of the electrons and thus will raise some unique properties.

Since the first quantum-confined structure, a superlattice, was proposed in 1970 by Esaki and Tsu [1], a lot of researches in the semiconductor area were focused on the nanostructures. The research on quantum well structures and superlattices was made possible by the

major advance in the thin film growth techniques, Molecular Beam Epitaxy (MBE) and Vapor Phase Epitaxy (VPE), which gave the possibility to fabricate routinely artificially layered semiconductor of high structural and purity perfections.

These nanostructures that feature 1-dimensional confinement have proved to have a tremendous impact on the advance in electronic devices and at least two applications are at this time in every-day-use: the quantum well lasers and the high electron mobility transistors (HEMT).

However, these structures have only a partial confinement, so the goal of many researchers developed into that of creating nanostructures with better confinements such as 2- and 3-dimension (2D and 3D), which will approach an atom-like behavior. These structures will have a more concentrated density of states and will improve the performance of laser diodes as was predicted by Arakawa and Sakaki back in 1982 [2].

Furthermore, the possibility to control the position and the size of the nanostructures will be of essential importance for the design of the optical devices. The optical devices, especially the laser diodes, have a special design that provides the light emission efficiently coupled the optical field to the optical active structure [3]. The ultimate combination would be a microcavity supporting only one resonance mode that contains a quantum dot situated at the antinode of the resonance mode, which is emitting light at the same wavelength with the cavity mode. In this case the quantum efficiency of light emission would be unity.

A lot of research efforts have been made in fabricating 3D nanostructures and several approaches were employed. With the state-of-the-art electronic fabrication technology it is possible to use a 1-dimensional nanostructures, which can be patterned and etched in order to reduce the other dimensions in the nanometer range. This technique could fabricate 3D nanostructures but the process damages were too extended in order to be able to observe the properties of the nanostructures without a defects-originating contribution.

In 1993, a breakthrough in fabrication of 3D nanostructures was done [4]. The growth of self-assembled quantum dots by Stranski-Krastanow mode provided 3D nanostructures that are damage-free and almost process-free. Since then the knowledge for producing quantum dots based active layers for laser diodes has advanced a lot and is possible to witness the apparition of the first commercial products not very far from now. However, these devices do not bring any innovation in the laser diodes design besides the replacement of the quantum well with the quantum dots. From the basic physics point of view, the studies on self-assembled quantum dots suffer from limitations due to the non-

uniformity in size and also the impossibility to control the spatial arrangement (i.e. inter-dot interactions).

Another approach to fabricate 3D nanostructures is the selective area growth on patterned substrates [5]. Providing that the initial patterns are small enough and the growth can be done selectively inside the patterns, this method would provide high-quality 3D nanostructures with uniform size and also easiness in positioning as desired. Also this approach opens the possibility for integration of photonic devices with high-speed electronic devices on the same substrate.

In order for this approach to be successful in creating 3D nanostructures the initial patterns should be in the nanometer range. This patterning resolution can be achieved only by a few methods that will be described in the next.

1.2.2 Scanning Probe Lithography

In the recent years a tremendous effort has been channeled into developing the technology for the fabrication of ultra-small structures and devices with dimensions in the sub-100-nm regime. In the mean time, the commercially available devices started to incorporate features down to 0.18 μm and will have features with the minimum size of 0.13 μm in the near future.

Figure 1.1 shows an overview of the main lithographic technologies and the respective minimum feature size that can be patterned. These will be categorized in three classes. The photon lithography is based on a conventional light source such as a Mercury lamp, a source of coherent light with a very short wavelength such as an excimer laser and a monochromized ultra short wavelength light source such as synchrotron radiation. The electron lithography is based on an electron beam that is accelerated, focused and irradiated to pattern the resist. Instruments very similar or identical with a scanning electron microscope are included in this category. The highest resolution patterning is obtained with a transmission scanning electron microscope. The scanning probe lithography is the last category. It is based on a scanning probe instrument and it will be explain in more detail in the following.

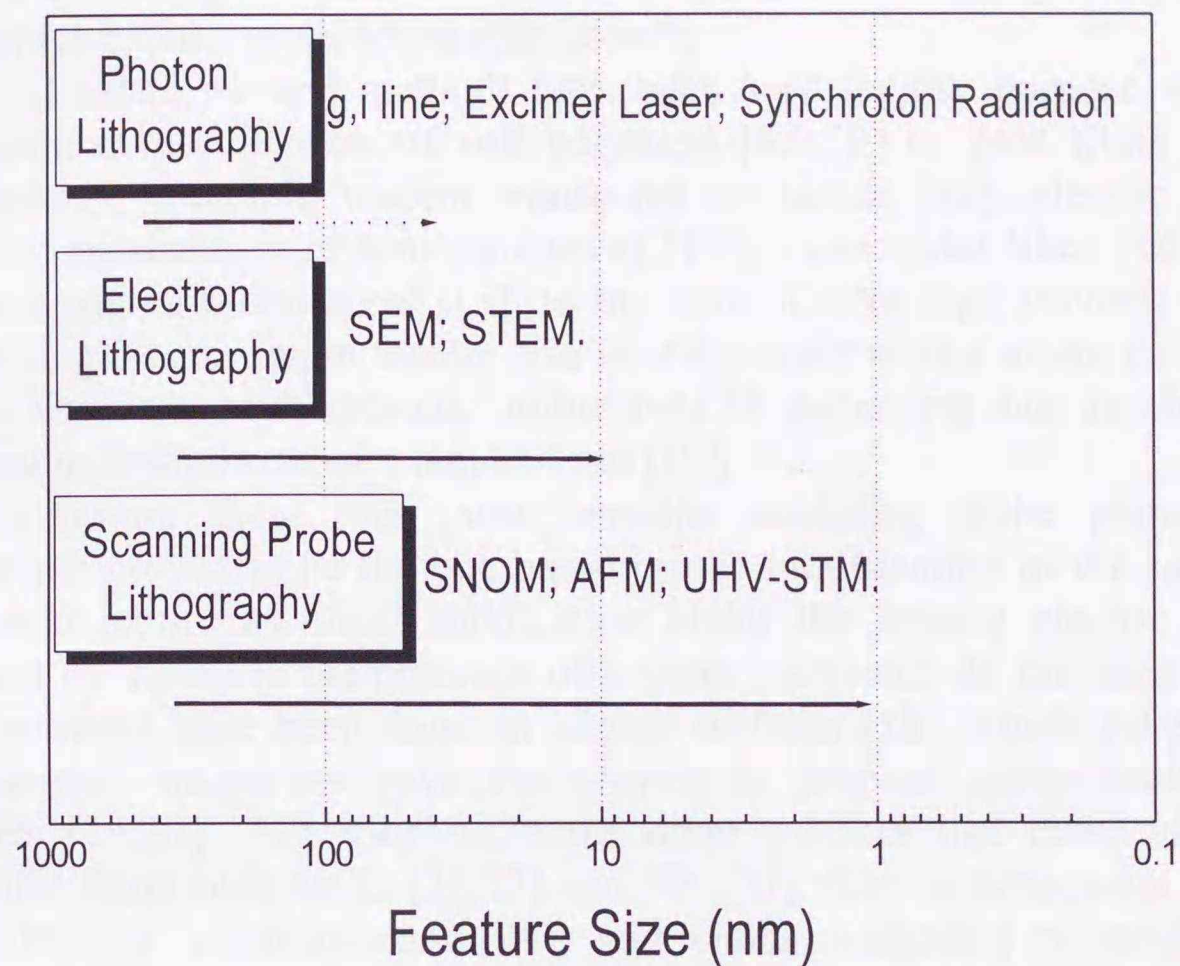


Fig.1. Lithography techniques and the minimum feature size

The “conventional” photolithography will be impossible to be applied in the sub-100-nm scale unless some unconventional photon sources, such as synchrotron radiation or X-rays, are developed. As can be seen from the chart, the electron-beam and the scanning probe techniques are the only two techniques that have capabilities to access the mentioned range of feature sizes.

The electron-beam lithography currently can pattern features with a minimum size of ~ 10 nm [6] but suffers from problems related to proximity effects and roughness of the pattern’s edges, both induced by the electrons scattering [7].

Scanning probe lithography was developed starting from techniques originally for surface characterization such as scanning tunneling microscope (STM), atomic force microscope (AFM), or scanning near-field optical microscope (SNOM). Soon after being developed, it was discovered that besides the surface characterization it was possible to induce modifications to the respective surface as well.

Scanning probe lithography is gradually maturing from its initial status of exotic technique for patterning and is gaining its unchallenged position in the fabrication of state-of-the-art devices and high-resolution masks for etching or selective area growth.

To date, several methods have been used for this purpose: direct mechanical modification of soft polymers [8,9,10] or gold films [11]; low-energy tunneling current irradiation of resists [12]; electric field assisted anodization of semiconductors [13], some metal films [14] and self-assembled monolayers [15]. In the case of ultra high vacuum STM patterning the minimum feature size is of the order of few atoms (<1 nm) [16]. The less sophisticated, ambient-AFM patterning has reached a minimum feature size of around 10 nm [17].

Among these, the most versatile scanning probe patterning technique proved to be the one based on the modification of the surface chemical nature by local anodization under the intense electric field applied by the tip in the presence of a water meniscus. In this area most of the works have been done on silicon surfaces [18], whose relatively well-known properties gave the chance to propose some analytical models [19,20]. Nevertheless, some other surfaces like those of thin metallic films such as Ti [21,22] and Nb [23], thin carbonaceous films deposited by electron-beam [24], and GaAs surfaces [25] could be successfully processed with the same technique.

Recently, several significant contributions for understanding the basic processes involved in the local anodization have been made. The *in situ* electric force characterization by scanning Maxwell-stress microscopy (SMM) gave some insights into the distribution and temporal evolution of the ionic species involved in the anodization and pointed out the possibility of charge accumulation in the oxide region [26]. Based on these findings it was suggested that a bias alternating its polarity during the patterning would remove some limiting factors of the oxide growth rate in the direction normal to the surface.

Another contribution in this field was given by the use of non-contact mode for patterning [20,27]. This approach opened the way for higher reliability during the patterning process and also gave additional information about the role played by the water meniscus [27].

The scanning probe lithography for device fabrication still has to overcome issues such as that of patterning on large areas and the very small aspect ratio of the patterns made by anodization. As a consequence, in order to achieve higher resolution very thin masks are necessary. More research is necessary in order to increase the aspect ratio and to fabricate very stable ultrathin masks. Also, new methods to

increase the reproducibility of this patterning technique need to be investigated.

1.2.3 Nanoscale selective area growth

Research in the area of selective area growth (SAG) was motivated by the current demand for monolithic integration of optical and electrical devices. The growth techniques that proved to be most suitable for this technology were metalorganic vapor phase epitaxy (MOVPE) and metalorganic molecular beam epitaxy (MOMBE). The latter, in special, is very attractive since the growth conditions to achieve selective area growth will cover a wider range due to the lower background pressure. The most representative semiconductor alloys that were grown selectively using a dielectric mask (usually SiO_2 or SiN_x) are the following: GaAs [28], InP [29,30], GaInAs [31,32], ZnSe [33,34].

The main requests for the selective area growth process to be successfully applied to integration of the devices are following: a low-temperature process in order to avoid any possible damages to the already fabricated devices, and the compatibility with the technology used for the first "layer" of devices.

From the more basic point of view, this selective growth technique offered the opportunities to understand the fundamental growth mechanisms like diffusion of the chemical species during the epitaxial growth and the growth kinetic of facets with different crystallographic orientation [35,36]. The crystalline and morphological properties of the mismatched epitaxial layers with a finite lateral size grown by SAG showed significant improvements as compared with the unrestricted epitaxial layers [37].

The nanoscale selective area growth deals with growth into sub-100-nm lateral size patterns. Research in this area is very recent and the semiconductors that were grown using patterns well below 100 nm are the following: GaAs [38], Si [36], GaN [39]. The main characteristic of the nanoscale selective area growth is that the pattern size is much smaller than the diffusion length of the species adsorbed on the surface at the growth temperature.

GaAs dot-like structures with a uniform size of $50 \times 50 \text{ nm}^2$ and 6-nm-height were fabricated for the first time [38]. The Si selective area growth could produce structures with sizes less than $50 \times 50 \text{ nm}^2$ and the STM studies revealed the formation of a double-layer stepped-structure and the formation of high-index facets formation [36]. In both cases a very thin mask layer was used in order to be able to pattern it. The

quality of the mask and the small thickness could not assure a perfect selectivity.

These results demonstrated the capability of nanoscale selective area growth to produce well-defined structures of Si or III-V compound semiconductors. However, the nanoscale selective area growth of II-VI compound semiconductors was not yet reported.

1.2.4 Ultra-small cavity light emitters

Light confinement in a cavity is very important for the operation of the light emitters because it provides the necessary feedback by allowing both enhancement and inhibition of the spontaneous emission from the active layer. Purcell first reported this property back in 1946 [40].

When the emitting dipole is placed at a node or an antinode of the cavity resonance, the optical transition will be suppressed or respectively enhanced. The enhancement or suppression factor of the spontaneous emission rate is given under the weak coupling approximation by the expression [41]:

$$\eta = \frac{Q}{4\pi V} \left(\frac{c}{n\nu} \right)^3$$

where c is the speed of light and ν optical transition frequency, $Q = \lambda/\Delta\lambda$ is the quality factor of the cavity and V is the volume of the confined optical mode. Based on this equation it can be directly concluded that Q/V ratio of the optical cavity will give the degree of the spontaneous emission enhancement. If the emission spectrum is broad, for the range of the spectrum that is overlapping with the cavity resonance the spontaneous emission will be enhanced while for the rest this will be suppressed. A narrow emission can be provided by nanostructures that have a discrete density of states such as quantum dots or localized states.

Up to date, high Q cavities were demonstrated with different shapes such as microdisks, pillars, rings and pyramids. In all these cavities, it is important that the surface roughness to be smaller than $\sim\lambda/10$ in order to avoid loss due to the light refraction.

An important condition for obtaining enhancement of the spontaneous emission is to position the emitting dipole at the antinodes of the cavity electric field vector and to be oriented parallel with it.

An example of a strong coupling regime was recently demonstrated by GaAs micro-disks that have a cavity Q factor as high as 12000 (linewidth ~ 0.1 meV). Self-assembled InAs quantum dots with an emission linewidth of ~ 80 μ eV were embedded in the cavity [42]. The spontaneous emission enhancement of the quantum dots in the disk cavity was estimated to be around 18.

The reported enhancement can be considered modest in comparison with the one expected from the high Q/V ratio and can be attributed mainly to the small probability to find the quantum dots at the antinodes of the cavity resonance.

To date the clear enhancement of the spontaneous emission in semiconductor microcavities that emit in the visible range was not yet reported.

1.3 Objective of this Work

The high-efficiency semiconductor light emitting devices can be obtained by fully employing the enhancement of the spontaneous emission in a cavity as described in Section 1.2.4. The enhancement of the spontaneous emission can be achieved by increasing the electron-photon coupling in a cavity. In order to achieve this regime, the 3D nanostructures with discrete density of states easily fulfills the condition of spectral overlap. 3D semiconductor nanostructures that are precisely positioned at the antinodes of the cavity resonance are essential for this purpose.

The selective area growth produces high-quality 3D nanostructures and facilitates the embedding in a microcavity as discussed in Section 1.2.1. In order to fabricate the 3D nanostructures, the mask should provide a minimum feature size well below 100 nm with a similar range of the inter-pattern distance. The state-of-the-art lithography cannot easily meet these requirements so that other techniques must be developed. The scanning probe lithography showed its potential for high-resolution patterning as was discussed in chapter 1.2.2. However, this technique was not able to fabricate masks for the perfect selective area growth. This was related with the difficulty to find the adequate mask material that can be patterned with the high resolution and is adequate for selective area growth, at the same time.

Provided these points are cleared, 3D semiconductor nanostructures will be fabricated by nanoscale selective area growth. As pointed out in Section 1.2.3 the nanoscale selective area growth of II-VI

compound semiconductors that emit in the visible has not yet been reported. Moreover, semiconductor alloys that are compatible with the low-temperature selective area growth and, at the same time, with properties appropriate for developing light emitting devices such as lattice matching to substrates and easy bandgap engineering were not available.

In this thesis we investigate the fabrication of a mask by atomic force microscope (AFM) with resolution down to a couple of tens of nanometers, which is suitable for selective area growth of II-VI compounds. We introduce a new II-VI alloy system that is easy to be selectively grown at low temperature by MOMBE and to be engineered with different bandgap energies while being lattice-matched to the GaAs substrate. Based on these two ingredients we demonstrate II-VI compound nanostructures obtained by selective area growth.

High-resolution patterning is one of the key points for this approach. For this purpose a very thin carbonaceous mask deposited on the GaAs substrate is patterned by AFM. The carbonaceous film with a thickness of ~ 3 nm is locally deposited by electron-beam irradiation in a scanning electron microscope (SEM). The carbonaceous film is patterned by anodization activated by the electric field applied between the tip and the substrate. The highest resolution that was obtained is about 20 nm. This two-instruments combination provides unmatched advantages for patterning such as the continuous monitoring of the patterning status and the extension of the area and resolution of the patterning as compared with the case when only one is employed. In order to increase the resolution of the patterns we theoretically reconsidered the basic phenomena involved in the patterning processes by electric field application and we proposed a new patterning method: the modulated-amplitude pulsed bias lithography.

For the selective area growth, the II-VI compound semiconductors are chosen because they grow at low temperature and this system can cover a wide range of bandgap energies from UV to Green. In this direction, we propose for the first time the quaternary alloy ZnMgCdS and we demonstrate selective area growth of high-quality ZnMgCdS/ZnCdS heterostructures that are lattice-matched to GaAs substrates.

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Chapter 2

AFM Lithography

2.1 Introduction

Lithography is the process of defining features on the substrate according to a specified pattern. A radiation sensitive material called resist is used to write in the pattern. The exposure radiation may be visible, deep ultraviolet or X-ray photons, or electron or ion beams of particles. The exposure can be made by a parallel process such as contact or projection printing from a mask or by serial scanning of one or more beams. The development of the pattern may be carried out with wet chemical etching, by dry plasma etching or by conversion to volatile compounds through the exposure radiation itself. Optical lithography is widely used mainly because of its high throughput. Its resolution can be written as $w = k_1 * \frac{\lambda}{NA}$, where k_1 is a constant depending on several lithographic tools and has a value around 0.6, λ is the light wavelength, and NA is the numerical aperture of the optical system. NA cannot be increased more than 0.4~0.5 because it will drastically reduce the depth of focus. The resolution will be intrinsically limited by the light wavelength at a value around 0.13 μm .

For this reason a lot of researches have started to focus on developing alternative technologies such as electron-beam lithography, imprint lithography, scanning probe lithography, and other more or less exotic techniques, with the aim to decrease the minimum features in the nanometer range. The driving force for this research was the continuous trend for miniaturization of the electronic and optoelectronic devices together with the expectation to access new physical properties associated with the quantum regime.

On this background, the scanning probe lithography has gained a pioneering position by demonstrating not only the ultimate resolution, manipulation of the atoms [1], but also proving to be adequate to assist the development of quantum-regime devices like the single electron transistors [2].

In the following, the atomic force microscope (AFM) lithography by two different methods will be treated after a brief introduction on the AFM.

2.2 The Atomic Force Microscope

Gerd Binnig, Calvin Quate, and Christopher Gerber made the first demonstration of the AFM in 1986 [3]. The Atomic Force Microscope proved to be a valuable tool in the research of surfaces or interfaces. Several types of commercial instruments have emerged but all of them are working based on similar basic principles. Simple schematic of the apparatus is given in Fig. 2.1.

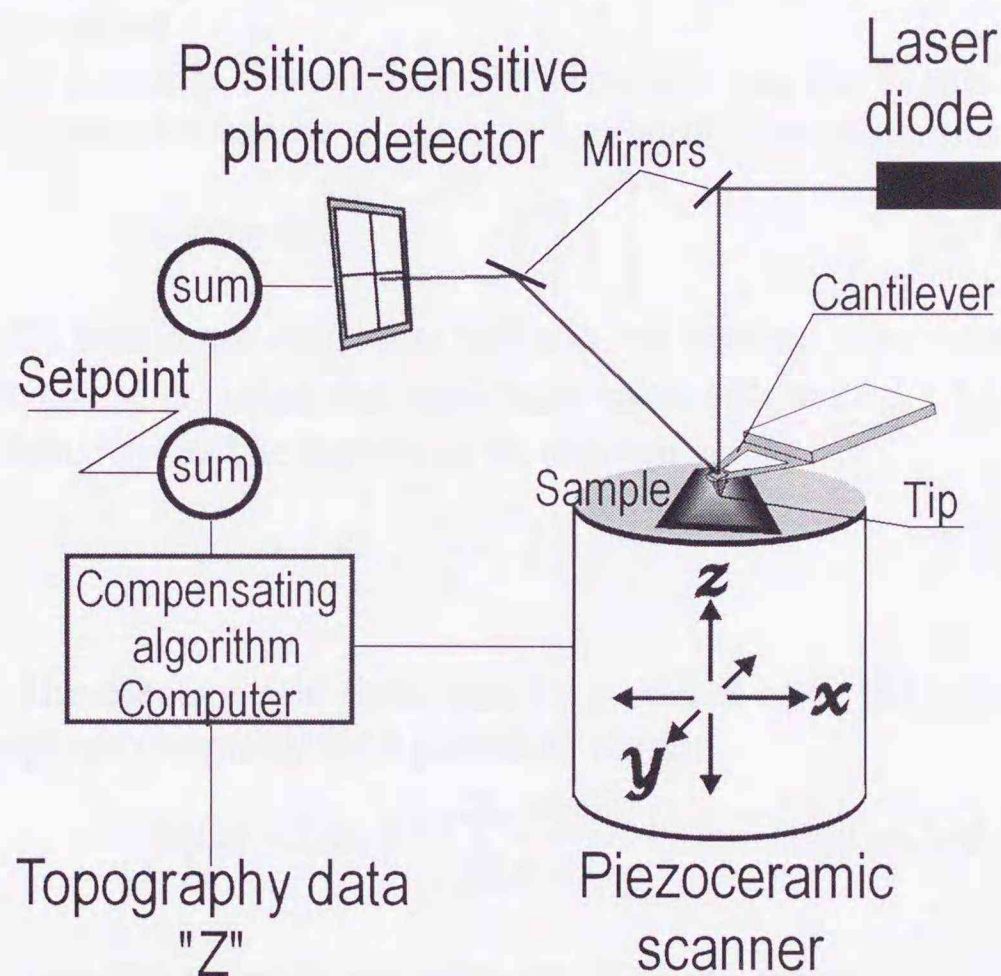


Fig. 2.1. Atomic Force Microscope basic diagram

The very thin cantilever has a very sharp tip at the end and a laser beam deflected by the back surface monitors its interaction with the surface. The reflected light is detected with a position-sensitive photodetector. This is providing the necessary feedback to the computer controller, which in turn is keeping a constant interaction (setpoint) by modifying the Z position of the sample surface. The raster scan and the vertical position are controlled by applying an electric bias to the piezoceramic scanner on which the sample is placed.

There are two basic modes for the AFM operation and these are differentiating by the way in which the tip is interacting with the surface:

continuous contact or intermittent contact. These are commonly called as contact mode and, respectively, tapping or non-contact mode AFM.

To provide a more quantitative description of the two interaction modes, one should consider the force, which appears when the sharp tip approaches the surface to be observed.

These forces depend on the chemical nature of the surface and tip and on the distance that separates them. The interaction force can include van der Waals, magnetic, electrostatic or capillarity forces. In addition to these, it is also necessary to consider the force exerted by the cantilever itself, which depends upon the deflection of the cantilever and upon its spring constant.

In a simple description, the attractive van der Waals and repulsive atomic potentials can be given by a Lennard-Jones potential

$$U(z) = 4U_0 \left[\left(\frac{\sigma}{z} \right)^{12} - \left(\frac{\sigma}{z} \right)^6 \right], \quad (2.1)$$

where U_0 and σ are constants and z is the vertical separation between tip and surface. $U(z)$ takes the minimum value $-U_0$ at $z=1.12\sigma$ and is zero at the distance $z=\sigma$. The force can be derived as [4] :

$$\vec{F}(z) = -24U_0 \left[\frac{\sigma^6}{z^7} - 2 \frac{\sigma^{12}}{z^{13}} \right] \vec{z}. \quad (2.2)$$

The electrostatic force can be modeled as in the approximation of sphere-plane geometry by a potential written

$$U_e(z) = 2\pi\epsilon_0 R V^2 \sum_{n=2}^{\infty} \frac{\sinh(\alpha)}{\sinh(n\alpha)}; \alpha = \text{Log} \left[1 + z' + \sqrt{z'^2 + 2z'} \right], \quad (2.3)$$

where ϵ_0 is the vacuum permittivity, R is the sphere radius and V is the sphere electric potential [4].

The capillarity forces may be approximated by

$$F_c = 2\pi R \gamma \cos \theta, \quad (2.4)$$

if the tip is considered as a sphere with the radius R and γ is the superficial tension coefficient. θ is the wetting angle of the water on the tip surface.

When the AFM is operated to display the change in the photodiode voltage as a function of the vertical displacement, one can obtain the "force curve". A typical force curve is given in Fig. 2.2. The shape of this force curve can be correlated with the forces described previously. As the tip is moved toward the sample surface, the cantilever deflection voltage remains unchanged until the tip is beginning to

interact with the surface (A to B). Just before the cantilever will start to contact the surface the tip probe can be pulled down to the surface by the attractive forces such as electrostatic and van der Waals ones (B to C). Further approach of the cantilever onto the surface deflects the laser beam and this gives an increased signal (C to D). When the cantilever is backward moved, the deflection will be decreased and so the signal (D to E). The adhesive forces such as electrostatic, van der Waals and capillarity ones will keep the cantilever deflecting in the opposite direction until the tip jumps out of contact (E to F).

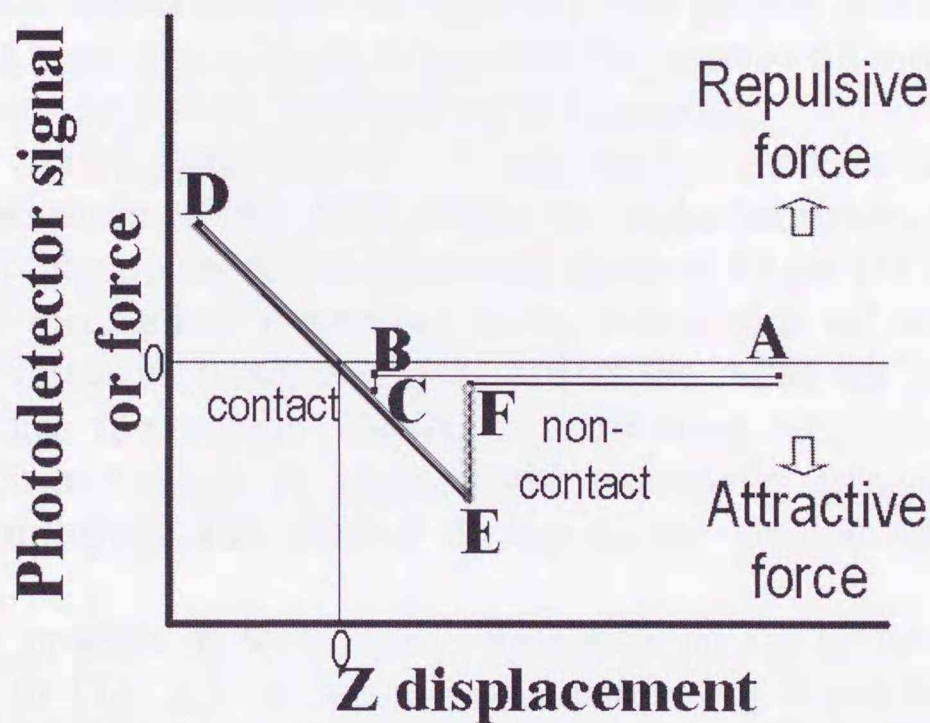


Fig. 2.2. Force curve as a function of the vertical displacement

Force curve gives the important information on the tip-surface interactions during the AFM scan and helps to minimize the applied forces in order to avoid any damage to the surface or to on purpose modify the surfaces by applying a well-controlled force.

The AFM can image the surfaces contact mode and non-contact mode depending on the interacting force. In the case of contact mode the interacting force can be set in the region D to E and in the tapping mode the force is set in the region E to F as it is shown in Fig. 2.2.

2.3 AFM Lithography by Mechanical Patterning on PMMA/SiO₂/GaAs Surfaces.

2.3.1 Introduction

Traditionally, the AFM has been used as an instrument for measuring the surface topography by contacting it with a probe. However, the degree of the tip-surface interaction can be controlled and this opens the possibility for intended modification of the surface.

AFM mechanical modification of the surface was demonstrated on several soft materials like polymers [5-8], gold [9], semiconductors such as GaSb [10] and demonstrated the AFM potential for performing lithography in the sub-100-nm range. However, the target of our research is to produce masks suitable for selective area growth and none of these materials is appropriate. A dielectric material such as SiO₂ or SiN_x that is much harder needs to be patterned for this purpose.

The AFM patterning of soft polymethyl methacrylate (PMMA) for the fabrication of thin SiO₂ masks on GaAs substrates was reported for the first time by us, with a resolution down to 40 nm [11].

The mechanical patterning is the indentation of surface with a sharp tip. Since the patterns mainly reflect the AFM tip geometry, this technique has the unique feature of fabricating rigorous geometrical shapes such as triangle or squares with nanometer precision if special tips are employed. The sharper the tip is, the smaller pattern can be obtained.

The process of SiO₂ mask fabrication on the GaAs substrates is illustrated in Fig. 2.3. A macroscopic patterning is performed on the surface of the GaAs wafer in order to be able to find the high-resolution AFM patterns. After the GaAs substrate surface is chemically cleaned, a bilayer system consisting of PMMA/SiO₂ is deposited onto. The SiO₂ is deposited by sputtering and the PMMA resist is deposited by spin coating. The soft PMMA layer is patterned mechanically with the tip of the AFM. These patterns are transferred into the SiO₂ layer by wet etching in buffered HF (BHF). The PMMA film is completely removed from the surface of the SiO₂ mask. The mask can be employed for selective area growth on GaAs.

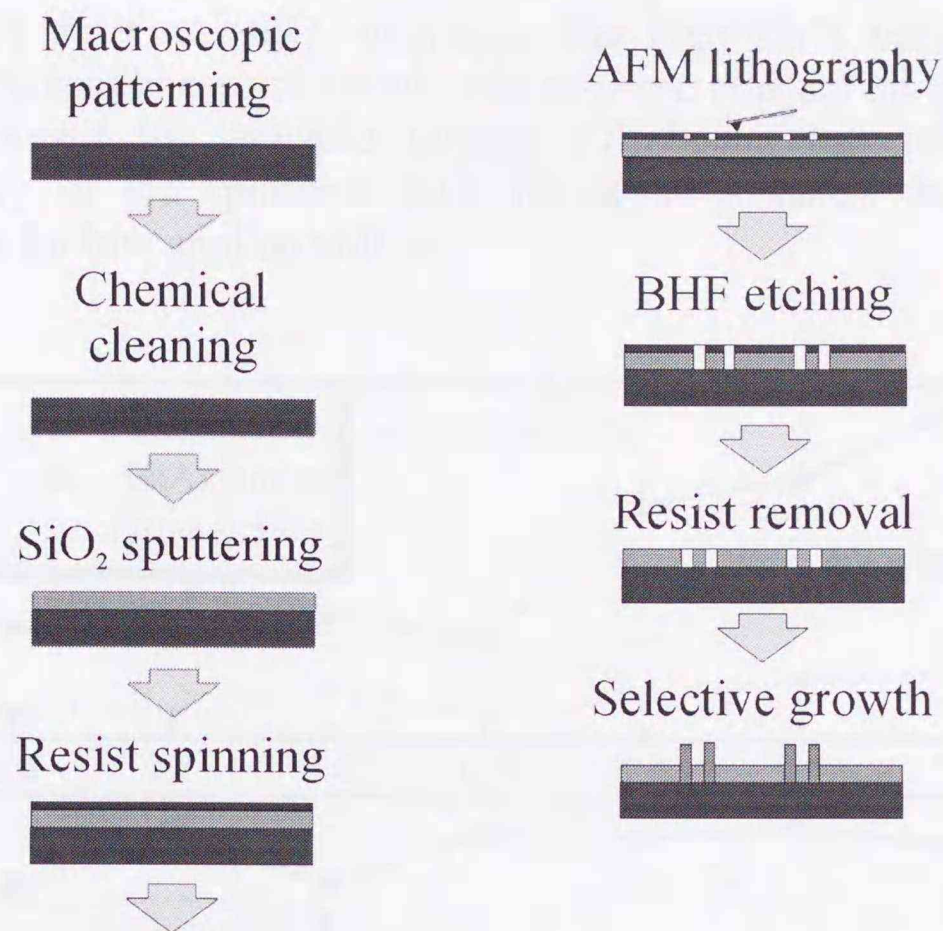


Fig. 2.3. Main steps in AFM based fabrication of the mask for selective area growth

2.3.2 Ultrathin SiO₂ and resist layers

In the above process there are several points that should be given a special attention: a) the PMMA layer should be thin enough to allow an easy patterning but thick enough to be able to withstand the wet-etching transfer of the patterns into the dielectric layer; b) the SiO₂ layer should be smooth and should leave a defect-free GaAs surface after is removed in order not to hinder the selective area growth process.

A macroscopic patterning of lines with 100 μm intervals is performed on the surface of the GaAs wafer in order to be able to position the further AFM made patterns. The GaAs (001) substrate is chemically cleaned using a $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (4:1:1) etchant. The SiO₂ film is sputtered with a thickness of 5 to 35 nm using a magnetron radio-frequency system with Ar or O plasma. The Ar or O₂ gasses were introduced in the sputter system with a partial pressure of 1×10^{-2} Torr. The roughness of the SiO₂ film and the roughness of the GaAs film after the mask removal were investigated as a function of the voltage applied for sputtering. The RMS data are given in Fig. 2.4. The RF power was between 50 to 100 W and increased with the applied voltage. A higher

voltage increases the kinetic energy of the plasma ions and also the roughness of the GaAs-SiO₂ interface. The high RMS values for the GaAs surface roughness are mainly due to some clusters on the surface, probably formed by interface mixing. O plasma can improve the stoichiometry of the sputtered SiO₂ but also increased the interface mixing even for low applied voltage.

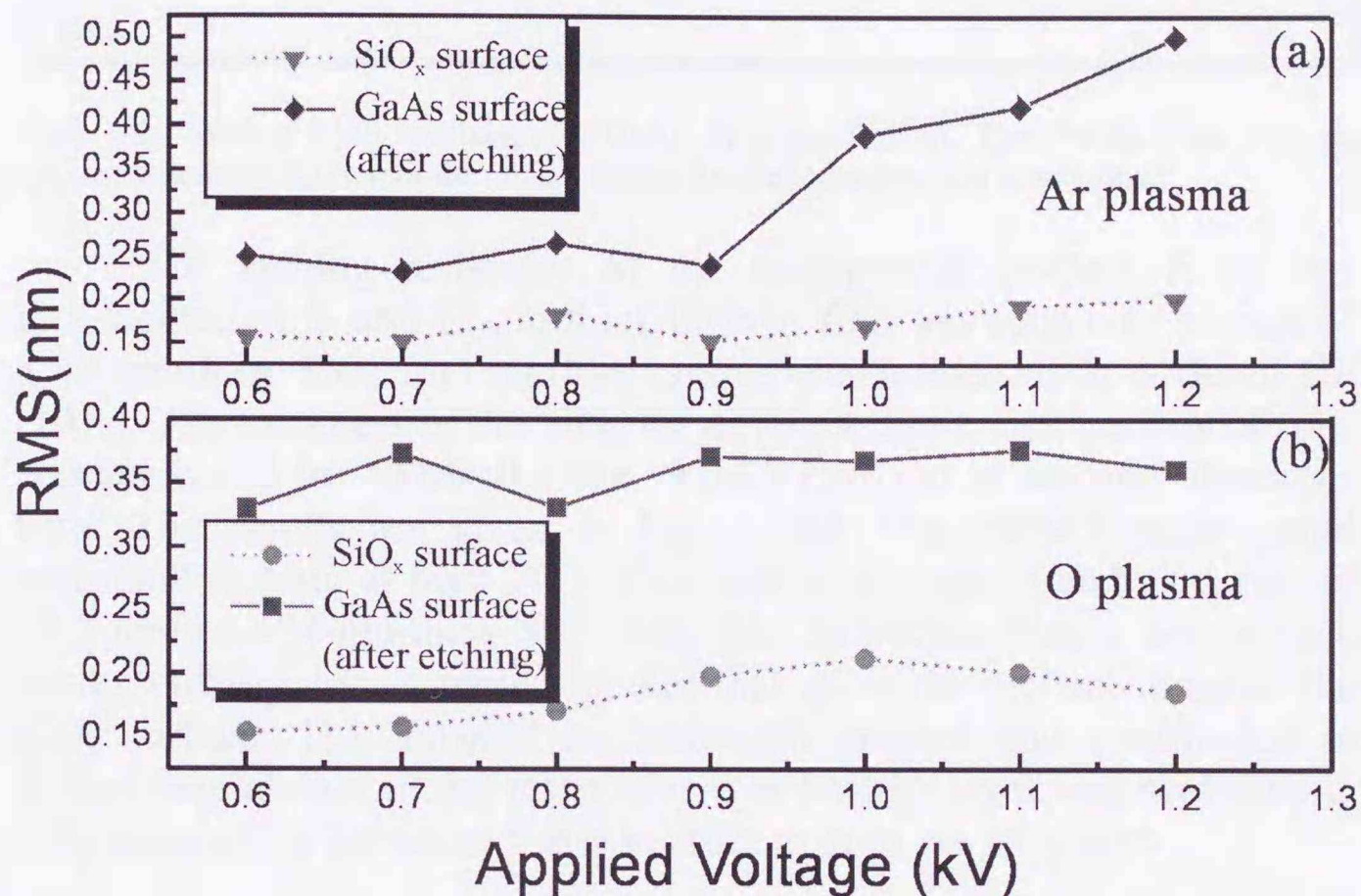


Fig. 2.4. Roughness of the SiO₂ and of the GaAs surface after SiO₂ mask removal in the case of (a) Ar plasma and (b) O plasma.

One can conclude that Ar plasma and an accelerating voltage of 0.9kV gave the best results for the GaAs surface smoothness after the SiO₂ removal. In this case the deposition rate was 43 nm/h.

The PMMA film is deposited on the SiO₂ surface by spinning a diluted solution of PMMA-based resist (OEBR-10cp) at 4000 rpm for 30 s after a first 10-s-step at 400 rpm. Resist films with different thickness in the range 2 to 15 nm were obtained by modifying the dilution of the PMMA from 1:20 to 1:5 in the thinner provided (ethyl cellosolve acetate). The thickness and the corresponding surface roughness (RMS) are provided in Table 2.1. The resist and SiO₂ thickness were measured

by AFM. The resist surface smoothness is almost as small as that of the the GaAs substrate.

Material <i>dilution</i>	GaAs	SiO ₂	OEBR 1:20	OEBR 1:10	OEBR 1:5	OEBR 10cp
Thickness (nm)	--	5-35	2-3	4-6	12-15	>20
RMS (nm)	0.1-0.12	0.12	0.17	0.20	0.22	0.23

Table 2.1. Surface RMS roughness for GaAs, SiO₂ and PMMA. The PMMA films become thinner with more dilution of the resist solution for the same spinning conditions.

The etching resistance of the as-deposited PMMA films was investigated. A 5- and 15-nm-thick PMMA film was spun on a surface of a 40-nm-thick SiO₂ film and the sample was immersed in buffered HF (10%). The thickness of the SiO₂ for different immersion periods of time was measured by AFM after the PMMA removal in acetone ultrasonic bath. The results are given in Fig. 2.5(a). The PMMA resist could withstand etching at least 20 s. This will be enough to etch at a rate of ~1.2 nm/s a ~24-nm-thick SiO₂ film. The thin resist film is deteriorated during etching due to some pinholes that allow the etchant to reach the SiO₂ surface. This favored an underetch process and contributed to further degradation of the resist. The thin PMMA layer was prebaked in a N₂ atmosphere for about 5 min in order to improve its quality.

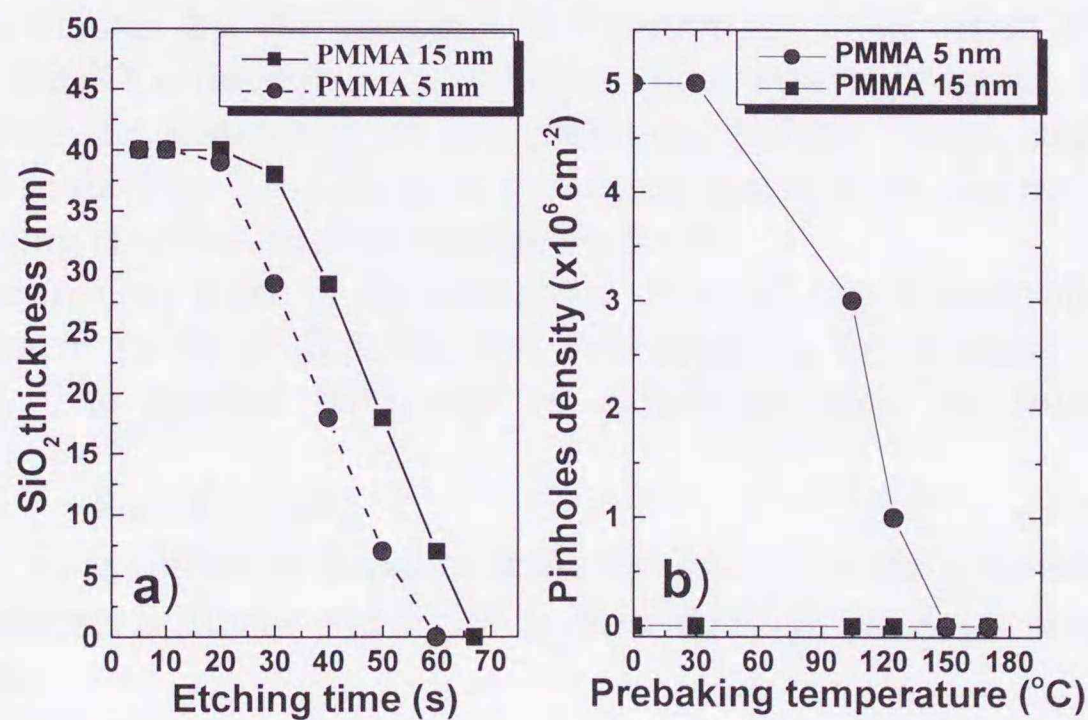


Fig. 2.5. The PMMA etching properties: a) etching resistance; b) pinholes density.

Figure 2.5(b) shows the density of hole-like defects in the SiO₂ layer after a 35 s etch for different prebaking temperatures. The quality of the 5-nm-thick PMMA film is greatly improved with this treatment. For temperatures higher than 100°C a reduction of the defect density is observed and it decreased to almost zero around 150°C. However, the prebaking should be used with precaution since it will also increase the hardness of the film besides its quality. About 125°C was considered the optimum temperature for prebaking.

2.3.3 AFM mechanical patterning on PMMA

The Atomic Force Microscope that was used in the lithography experiments is a commercial type, Nanoscope III manufactured by Digital Instruments, Santa Barbara, USA. The Si₃N₄ cantilevers that were employed for the patterning have 0.58 N/m stiffness and a top halfangle of 35°.

The software of the AFM has a special feature, which allows programming of the tip movement in any of the XYZ direction at a desired rate. A sample of the program written for the patterning is given in Appendix 1. The tip is used as a nanoscriber, which is moved across the surface to write the desired pattern under a higher load than that used for imaging.

The process of patterning can be divided in three major steps: cantilever positioning in the desired area and the capture of the surface plane coordinates by the imaging, the patterning itself when the tip moves in the XYZ directions according to the executed program, and in the last step the inspection of the patterning results. These steps are illustrated in the Fig. 2.6. The main parameter that is to be controlled for the patterning is the tip-surface interaction force.

The loading force in the contact mode AFM can be controlled by the movement in the Z direction that will result in the bending of the cantilever. The applied force can be calculated with the following formula:

$$F = k\Delta Z \cos \theta, \quad (2.5)$$

where ΔZ is the cantilever bending at the tip position in the Z direction, k is the cantilever stiffness and $\theta=10^\circ$ is the cantilever tilt angle from the (X Y) plan.

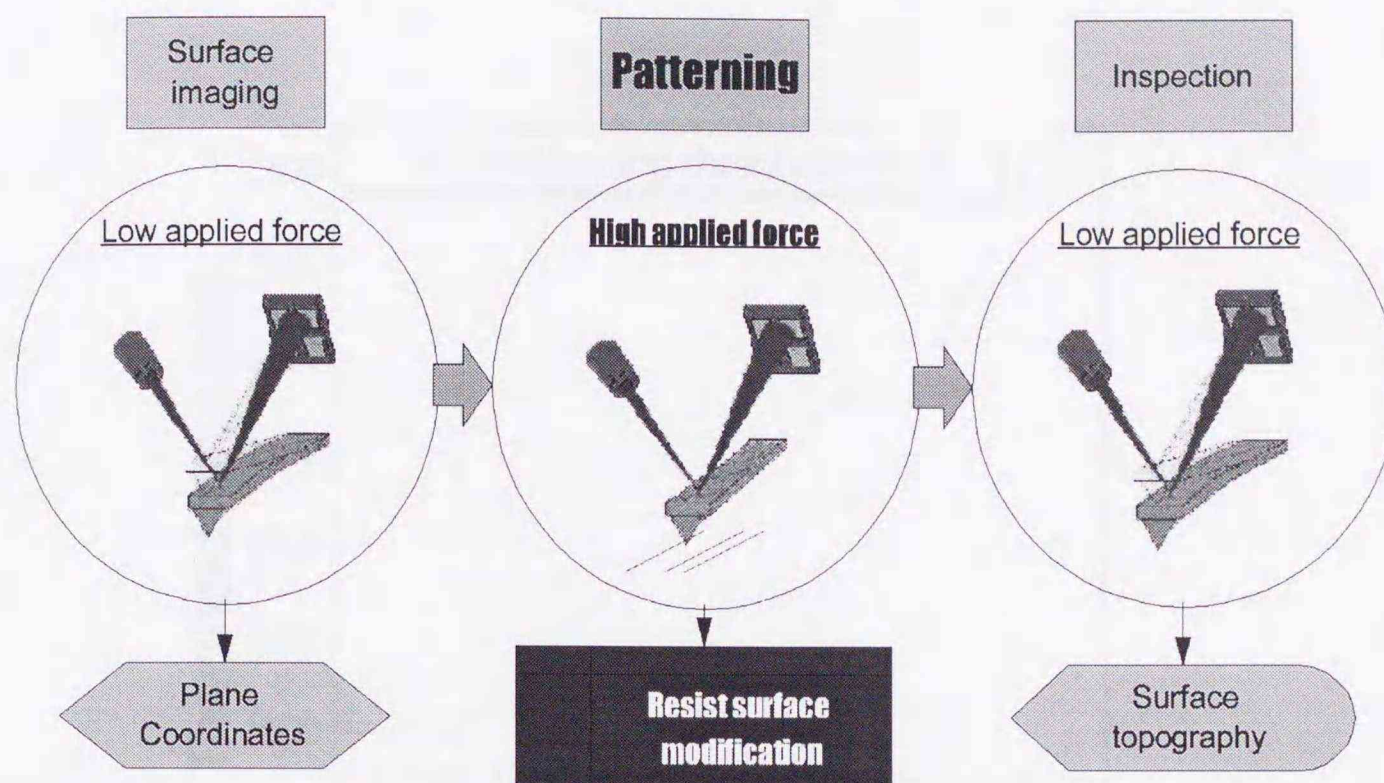


Fig. 2.6. Main steps in mechanical patterning of soft resists

The minimum force that gives reproducible modifications of the PMMA surface is considered as the threshold force. The threshold force was measured in a simple experiment. The cantilever was pressed against the PMMA surface with a determined force and then the surface was imaged in order to track any modifications in the surface topography. In the case of as-deposited PMMA (without any prebaking) this was measured to be approximately 1000nN. The dependence of the threshold force on the prebaking temperature was studied and the results are shown in Fig. 2.7. The prebaking process modified the hardness of the PMMA film and increased the threshold force.

The prebaking process is essential to reduce the defect density on the very thin PMMA film but prebaking at temperatures higher than 125-150°C will make difficult to pattern the film. A post-lithography baking process was tried as an alternative but resulted in deformation of the patterns. The strain incorporated in the thin film during the mechanical patterning can be considered as the main factor contributing to the deformation process.

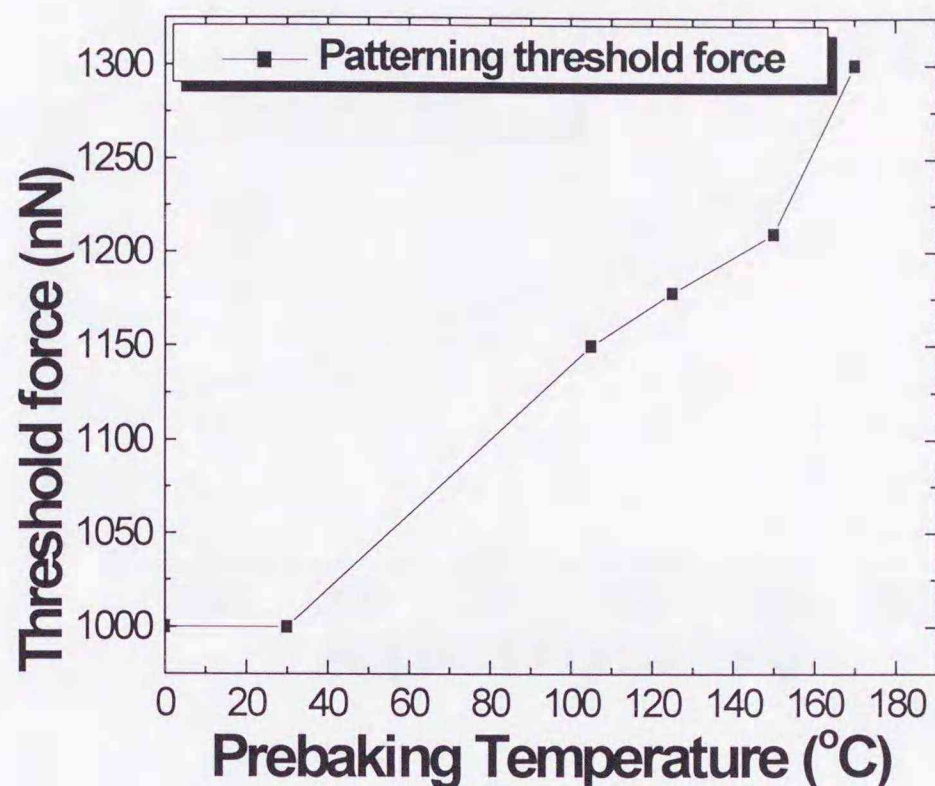


Fig. 2.7. Dependence of the threshold force on the prebaking temperature.

Two types of patterns were written on the PMMA films: wire-like and dot-like patterns. In the case of patterning simple lines, the linewidth of the pattern was measured for different applied forces and the results are given in Fig. 2.8. The patterning was performed at a constant linear velocity of $0.05 \mu\text{m/s}$. It will be worth to note that the linewidth increases as the patterning force is increased. The linewidth also increased for the 15-nm-thick film in comparison with 5-nm-thick one.

For the thicker film the penetration depth is higher and thus the lateral size of the pattern would increase by $\sim 14 \text{ nm}$, but because the film is not entirely plastically deformed the total lateral increase accounts for only a few nanometers. This is expected since the thicker the film, the more elastic stress can accommodate during deformation.

The plastic deformation of the PMMA film is depending on the film thickness. In the case of the 5-nm-thick film, the resist is not only deformed laterally but is also deposited as small hillocks, at random places along the edges of the line as shown in Fig. 2.9(a). In the case of thicker resist, the PMMA is deformed uniformly along the wire resulting in elevated edges with a height of 1-2 nm as shown in Fig. 2.9(b). This behavior can be also explained by the easiness of the thicker film to accommodate an increased strain during the patterning.

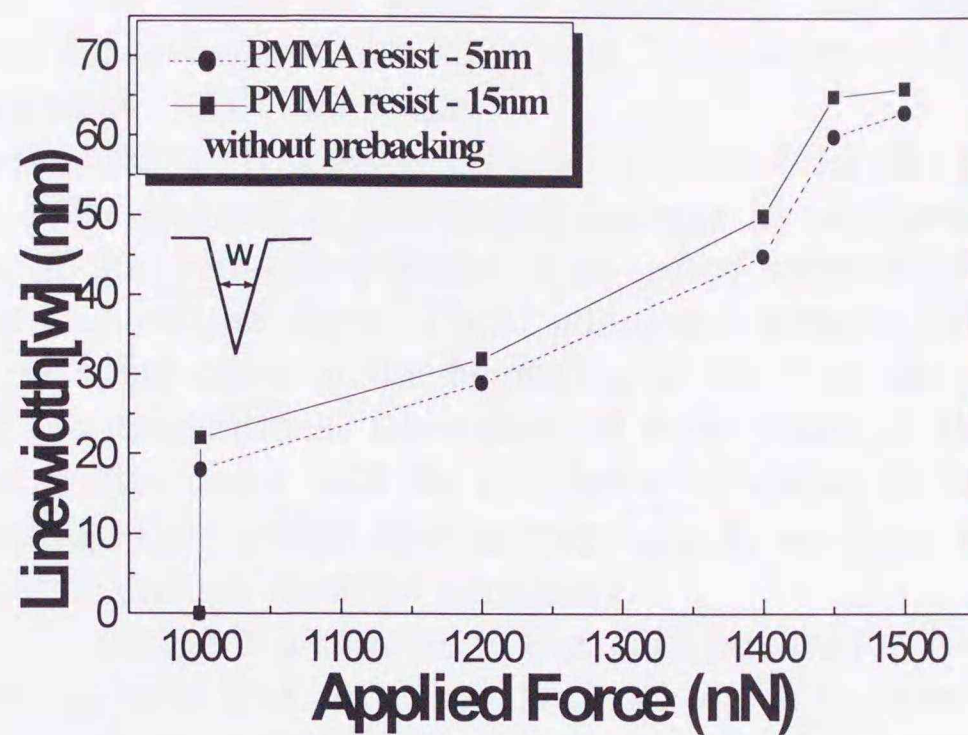


Fig. 2.8. Force dependence of pattern linewidth for the 5- and 15- nm-thick PMMA films.

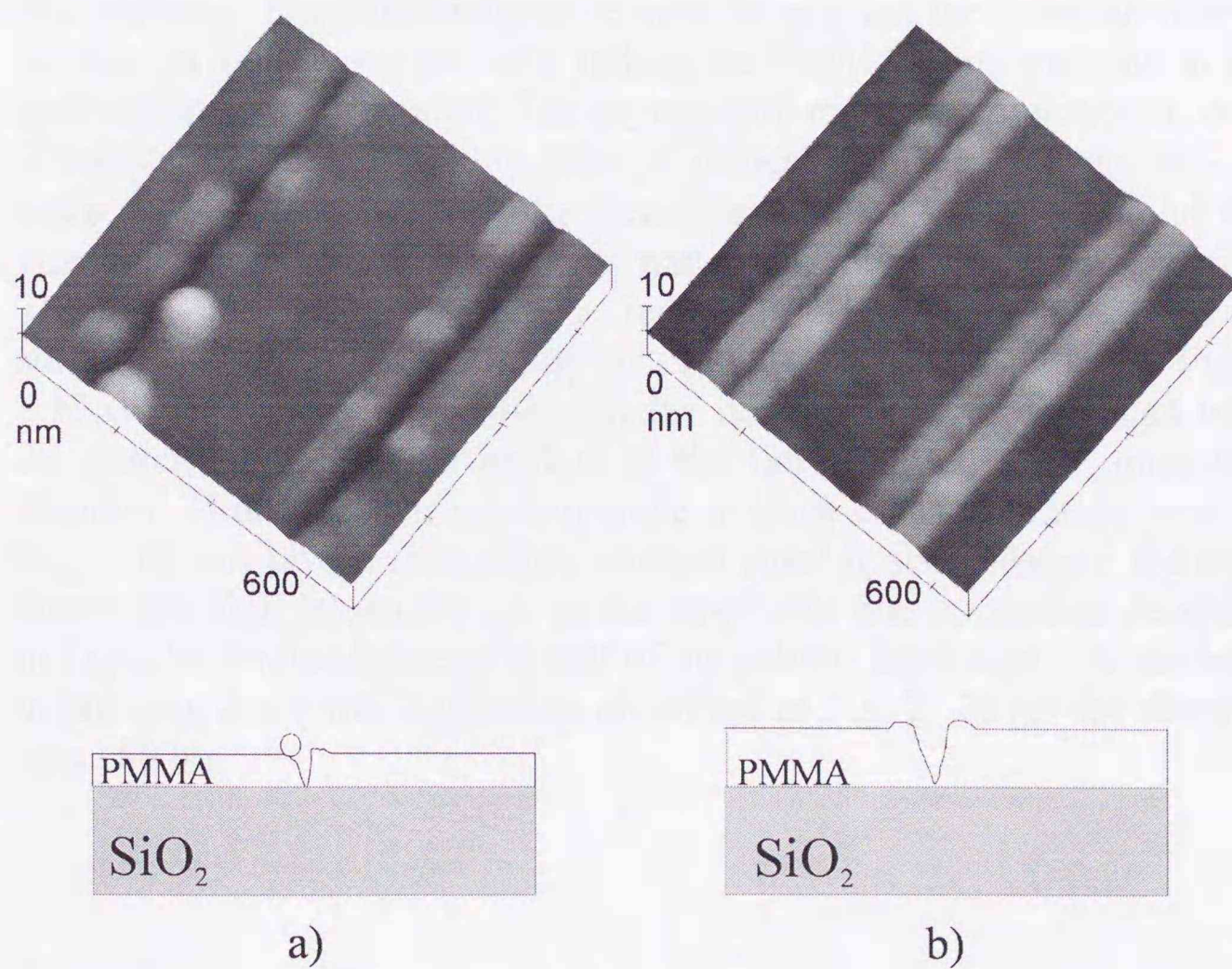


Fig. 2.9. (a) 18-nm-wide patterns drawn on the 5-nm-thick PMMA film. The PMMA debris is left at random places along the line. (b) 20-nm-wide patterns drawn on the 15-nm-thick PMMA film. Patterning results in uniformly elevated edges with a height of 1~2 nm.

The best results in terms of uniformity and linewidth were obtained in the case of patterns made onto 7- to 10-nm-thick PMMA that was prebaked at $\sim 125^{\circ}\text{C}$ for 5 min.

In the next we will discuss the fabrication of dot-like patterns. The patterned holes showed an increased diameter in comparison with the linewidth of the wire-like patterns. Very often some additional marks were observed around them. These additional patterns could be also observed in some cases at the beginning of the wire-like pattern. We attributed the unintentional fabrication of these marks to the tip lateral movement, which came with the cantilever deflection for large vertical displacements. The vertical displacement can be as large as $\sim 2\text{ }\mu\text{m}$ in order to obtain enough force for patterning.

This situation is illustrated in Fig. 2.10 (a) and the AFM image of the dot-like patterns that have the additional marks is given in Fig. 2.10 (b). In order to relax this problem a simple solution proved to be the control of the displacement rates in the vertical direction, the speed with which the patterning force is applied. Figure 2.10 (b) shows also the time variation of the patterning force that it was usually employed for the dot-like patterns. The patterning force must be applied for a certain interval of time in order to plastically indent the PMMA film and thus a low application rate is required. The asymmetric rate was employed in order to reduce the total patterning time. A vertical displacement rate of $\sim 0.2\text{ }\mu\text{m/s}$ assures application of the force for some period of time and thus guarantee that the PMMA film is patterned down to the SiO_2 surface. The high-speed force application reduces the tip "movement" over the surface and thus the possibility to produce additional patterns. Figure 2.10 (c) shows the AFM image of the dot-like patterns produced when the patterning force was applied at the rates shown in the force-time diagram. This approach could remove in most cases the lateral patterns but could not give a reasonable solution since it also enlarged the holes due to the high lateral forces. In the case force was applied as described in Fig. 2.10 (b) the diameter at half of the pattern depth was $\sim 50\text{ nm}$ while in the case force was applied as described in Fig. 2. 10 (c) the diameter was $\sim 80\text{ nm}$.

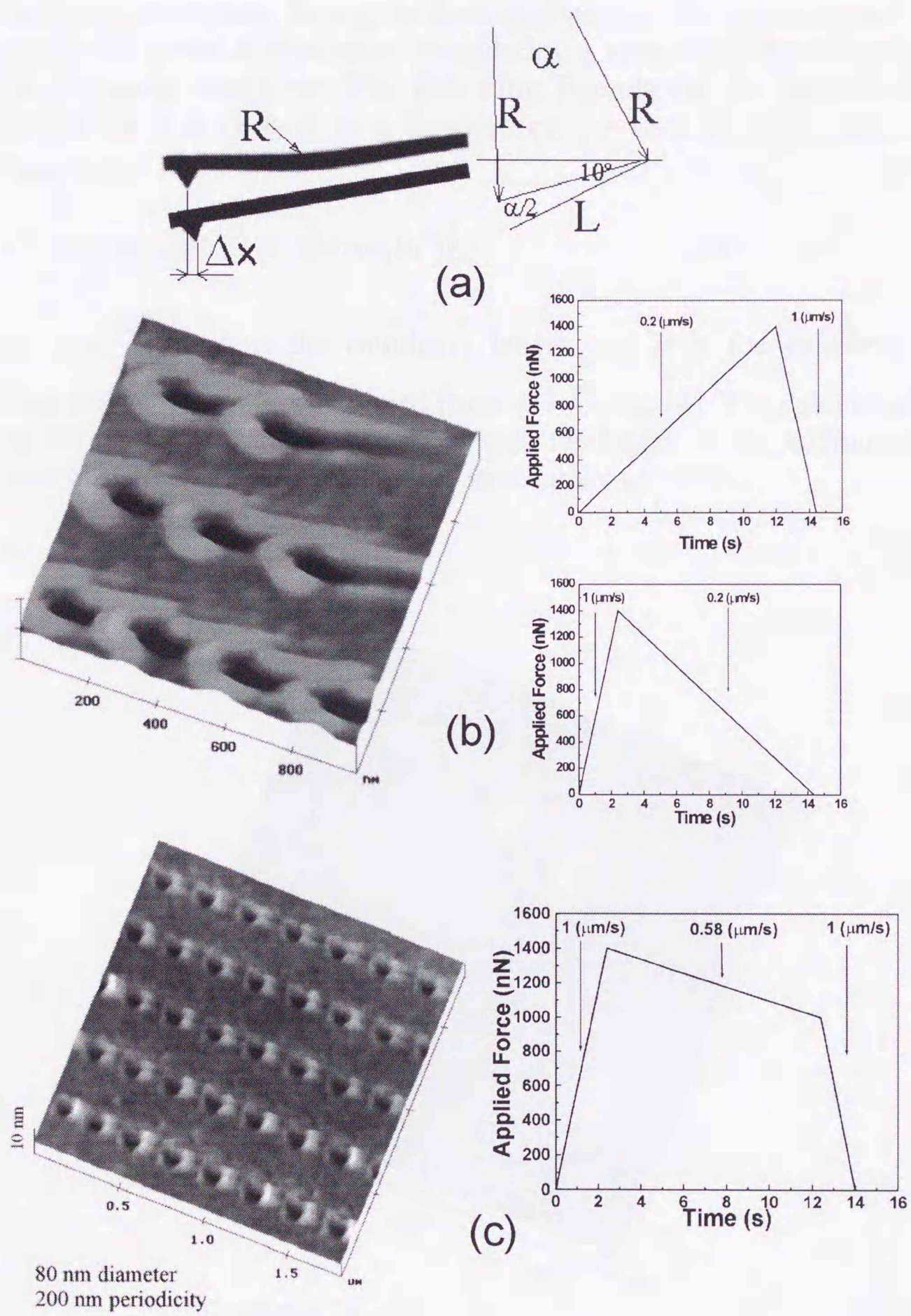


Fig. 2.10. (a) Cantilever deformation during load; (b) additional marks and the force variation in time while patterning. (c) patterns free of artifacts but enlarged and the time sequence for patterning.

A more viable solution to this problem proves to be the control of the lateral displacement during the load application. We approximately estimated the lateral displacement considering a very small deformation of the triangular cantilever. The following formula for the horizontal correction Δx was derived as a function of the vertical displacement $\Delta z = z_{final} - z_{initial}$:

$$\Delta x = L [\cos(10^\circ - \alpha/2) - \cos(10^\circ)], \quad (2.6)$$

where $\alpha = \frac{360}{2\pi} \frac{L}{R}$, L is the cantilever length and R is the cantilever bending radius. R can be calculated from $R = L^2 / 3\Delta z$ [4]. The calculated lateral displacements are in agreement with the length of the additional patterns observed experimentally with an accuracy of $\sim 30\%$.

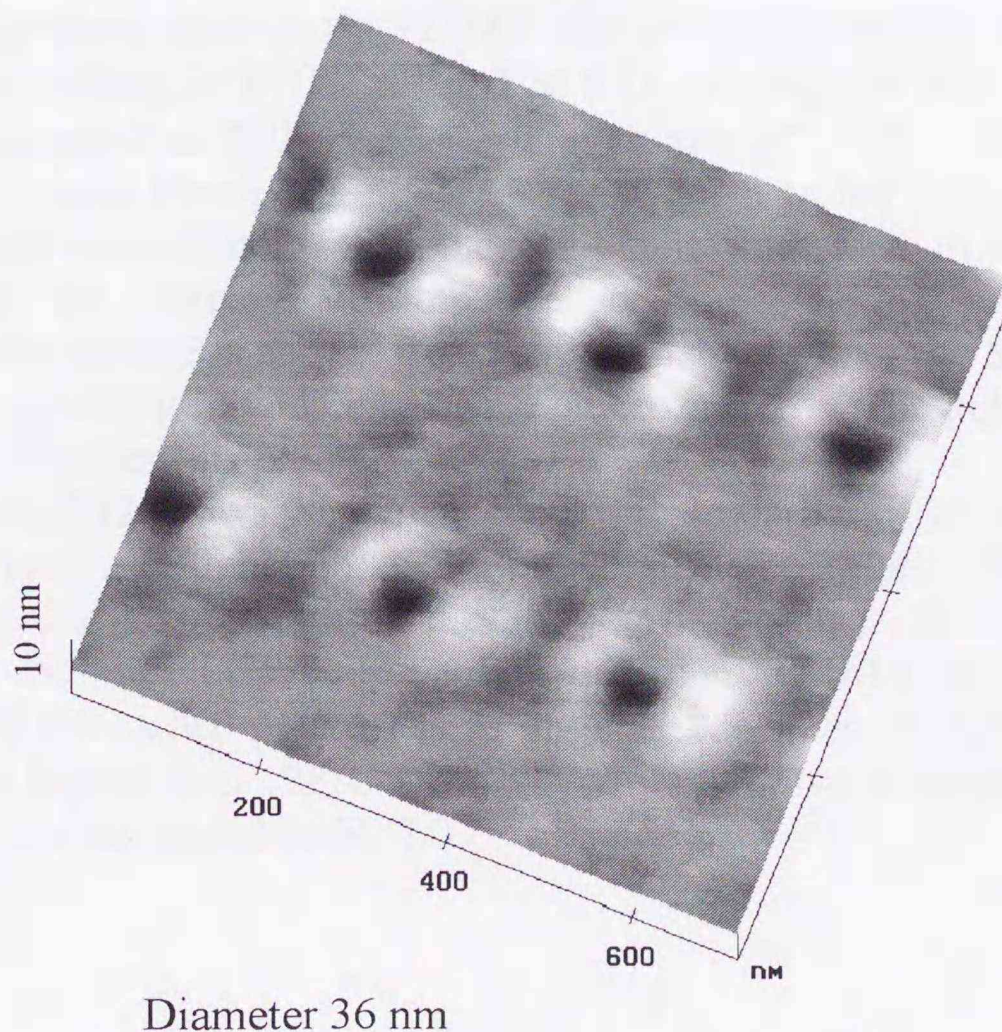


Fig. 2.11. Holes patterned in the PMMA film using the lateral displacement correction. The correction consisted in ten step of ~ 15 nm.

The correction for the lateral displacement $\Delta x_{threshold}$ is applied at the moment when the vertical movement reached the threshold, $z_{threshold}$,

to create enough load on the cantilever to indent into the resist. Starting with this point, the lateral correction Δx_i is applied in ten steps. This correction consisted in ~ 15 -nm-long steps in the -x direction so that this correction will not be very different from the tip diameter.

The application of this correction procedure could substantially improve the resolution and uniformity of the dot-like patterns simultaneously. An AFM image of the patterns written with this approach is presented in Fig. 2.11. Dot-like patterns with a diameter of ~ 36 nm were obtained in the 8-nm-thick PMMA film. The patterning was performed at a vertical displacement rate of $1 \mu\text{m/s}$ until the $z_{\text{threshold}}$ was reached; a 423 nm horizontal correction was applied at $1 \mu\text{m/s}$ followed by ten equal steps with a vertical displacement rate of $0.2 \mu\text{m/s}$ and with a horizontal correction rate of $1 \mu\text{m/s}$.

2.3.4. Transfer of the patterns into SiO_2 films by wet etching

The patterns made in the PMMA film are transferred into the SiO_2 film by wet etching in BHF (10%). The SiO_2 etching rate is ~ 1.2 nm/s when is immersed in BHF kept at a temperature of $\sim 22^\circ\text{C}$. When the patterns are made through the PMMA resist down to the SiO_2 surface, etching starts immediately after the sample is immersed in the BHF solution. If the patterns are imperfect or a postbaking process is employed the etching is arbitrarily delayed. The etching of the SiO_2 film is isotropic resulting in widening of the etched patterns. The adhesion of the resist influences this process.

Figure 2.12 shows the dependence of this relative widening of the etched patterns as a function of the prebaking temperature. The better adhesion of the PMMA film on the SiO_2 surface reduces the widening during the etching. In the case of as-deposited PMMA the relative widening of the etched patterns is as large as 2.8 times. If a prebaking temperature higher than 125°C is employed the relative widening of the etched patterns decreased under 2.0.

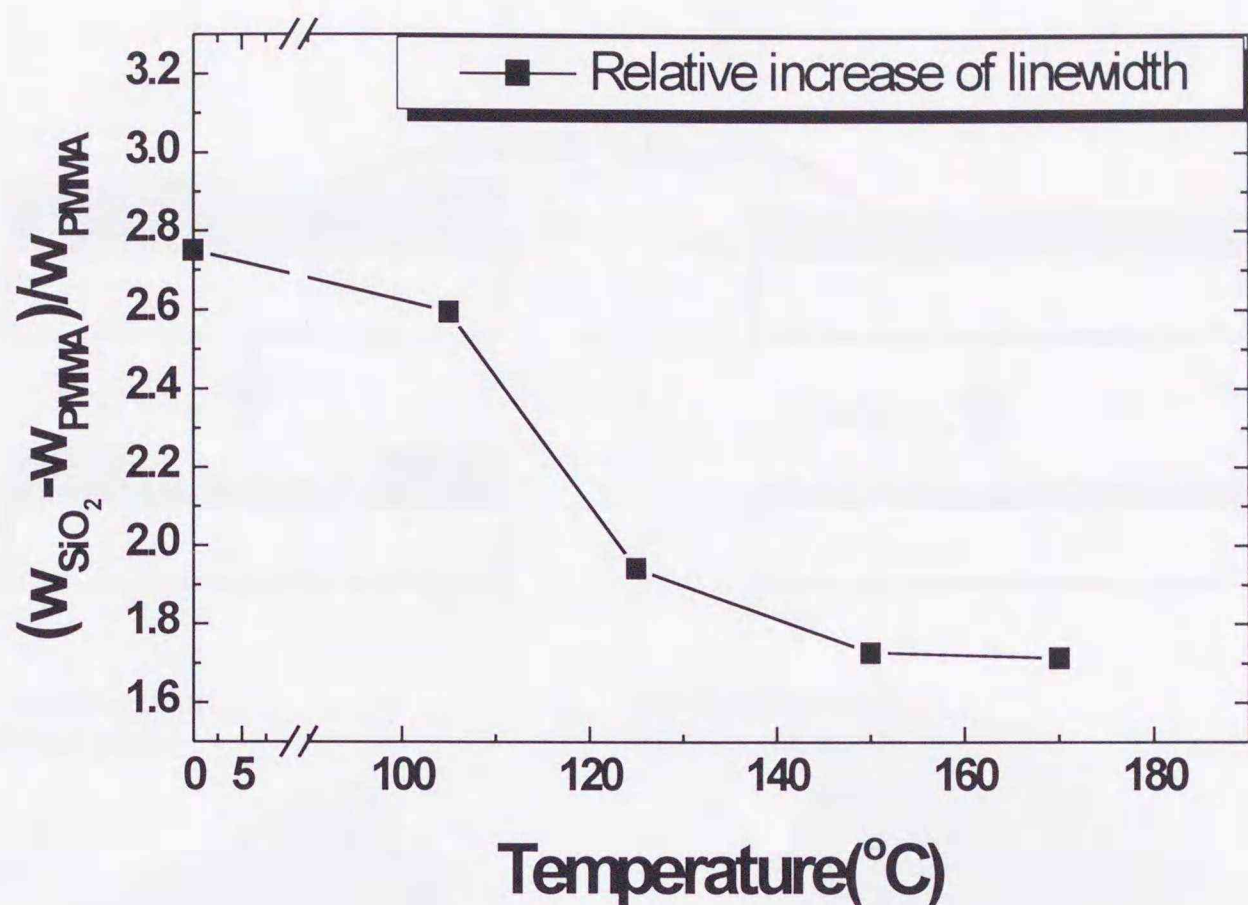


Fig.2.12. The relative increase in linewidth after etching as a function of the prebaking temperature.

In order to reduce further the lateral etching, the SiO_2 thickness was reduced to a minimum of ~ 5 nm and thus the total etching time was also reduced to about 5 s. A schematic of the sample section shown in Fig. 2.13 (a) emphasizes the differences between the 5-nm-thick and 35-nm-thick SiO_2 films. The thinner SiO_2 mask led to higher resolution and also to a more step-like profile at the edge of the etched patterns. The AFM images of wire-like and dot-like patterns etched into the 5-nm-thick and 35-nm-thick SiO_2 films are shown in Fig. 2.13 (b) and (c), respectively. A short etching time produced clear improvement of the etched wire-like pattern in comparison with the etched dot-like pattern. We attribute this behavior to the increased probability to reduce the PMMA film adhesion to the SiO_2 surface in the pattern region, during the mechanic patterning of the wire-like patterns.

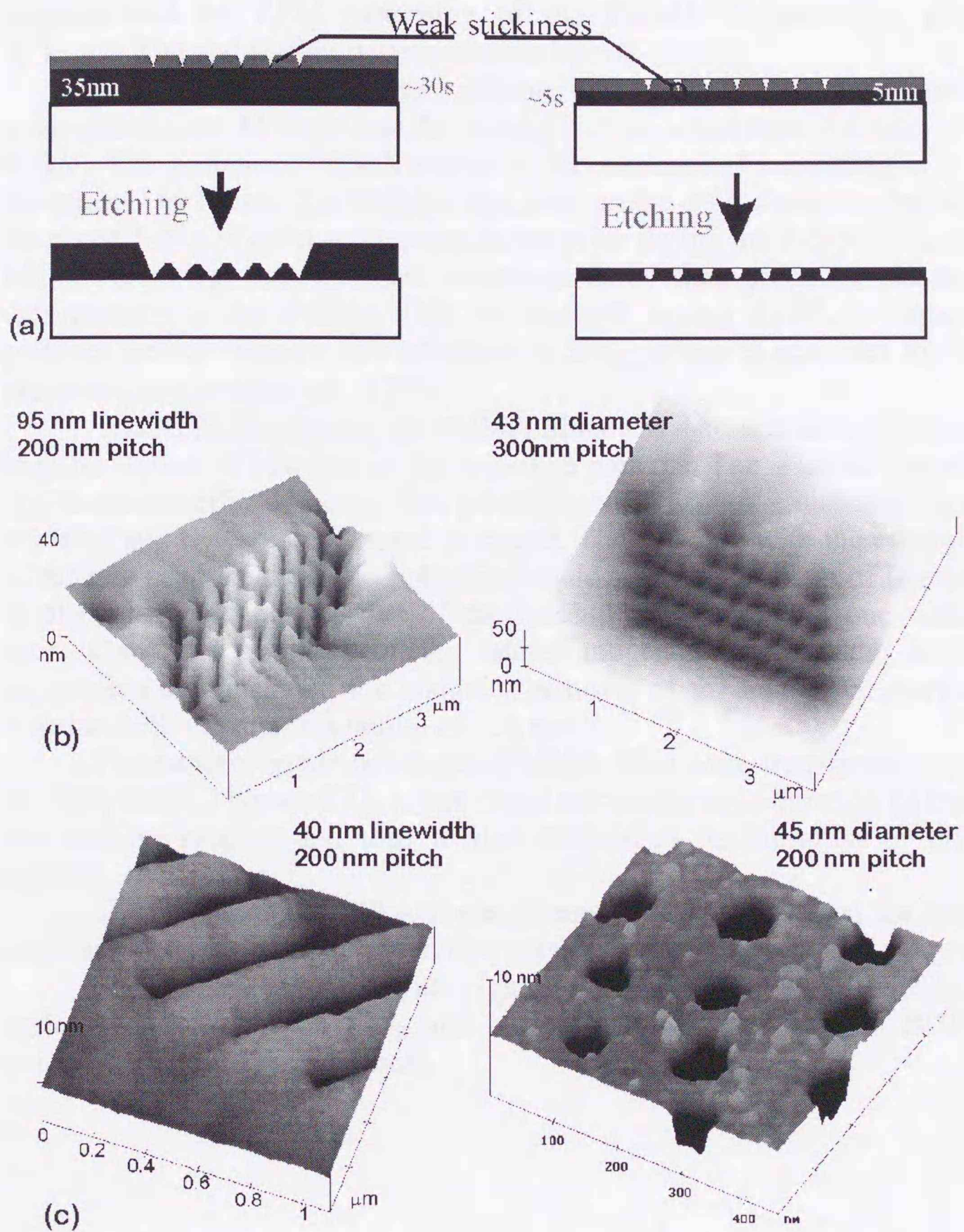


Fig. 2.13. (a) Schematic of the section pointing the differences between thin and thick SiO_2 films. (b) patterns made in the 35-nm-thick oxide (c) patterns made in the 5-nm-thick oxide

2.3.5 Summary

The fabrication of thin SiO_2 masks on GaAs substrates was demonstrated by AFM patterning of the PMMA deposited on the dielectric film and further pattern transfer by wet etching.

The sputter conditions for optimum GaAs surface smoothness and a deposition rate 43 nm/h are: Ar plasma and an accelerating voltage of 0.9kV. The optimum PMMA thickness for mechanical patterning is in the range 7 to 10 nm. The PMMA film spun on the SiO_2 should be baked for about 5 min in order to improve its behavior during the wet etching in BHF. Prebaking increases the minimum force that produces plastic deformation of the PMMA film. A tradeoff among threshold force, pinholes defects density, and adhesion to SiO_2 surface is achieved for a prebaking temperature of $\sim 125^\circ\text{C}$.

The AFM lithography on PMMA films was demonstrated with the high resolution of ~ 20 nm for the wire-like patterns. The issue of lateral displacement effects during the patterning of dot-like structures was revealed and two solutions were proposed. The first one with the control of the rate used for the load application could clear the problem of lateral displacements at the expense of the resolution. The second one with more elaborately control of the lateral movement during the load application demonstrated the complete removal of the additional marks together with the high resolution of ~ 36 nm.

The patterns made in the thin PMMA films were transferred into the SiO_2 films. Thinner SiO_2 layers could reduce the time duration of the wet etching process and thus it also diminished deterioration of the patterns.

The resolutions of 40 nm and 45 nm were demonstrated for the wire- and dot-like patterns in the SiO_2 masks, respectively.

Sharper tips would provide higher resolution. Also, a softer resist, with better adhesion to SiO_2 and better chemical resistance to BHF would give further improvement.

2.4 AFM/SEM Combined Lithography on GaAs Surfaces

2.4.1 Introduction

Scanning probe lithography has demonstrated itself to be capable of patterning different surfaces with high resolution. It demonstrated not only patterning of some simple features but also more complex ones leading to prototypes of unique devices. Among these devices we can find a $0.1\text{ }\mu\text{m}$ n-metal-oxide-semiconductor field-effect-transistor [12], a side-gated transistor on a silicon-on-insulator wafer [13], and a single electron transistor [2]. However, the most cited drawback of the SPM lithography is the slow patterning speed originated from the serial type of patterning and its reduced accessible area for patterning (in photolithography words: a reduced depth of focus). One successful trial to overcome the above mentioned limitation was the use of large array of 144 tips that will provide simultaneous patterning [14].

In order to relax the limitation of large area accessibility, our group proposed the use of a standard SEM in combination with an AFM. The former will “roughly” pattern the wafer and the latter will only be used for the high-resolution patterning [15]. While both instruments have imaging capabilities, their characteristics are in a complementary relation. The SEM usually can scan areas up to several hundreds of microns while the highest practical resolution is limited to around one hundred of nanometers. On the other hand, the AFM can scan areas up to one hundred microns with the minimum feature size at around 1 nanometer.

Another finding relevant to our research was the observation of the “masking” capabilities of carbonaceous contaminations deposited during SEM observation. Figure 2.14 shows the AFM image of a SiO_2 surface where a part of the surface containing a few wire-like patterns was observed with the SEM and subsequently employed for selectively area growth of ZnS by MOMBE at 400°C . The patterns were observed for several minutes with the SEM under high magnification so we could suppose that the deposited contamination have prevented the local growth of the ZnS in contrast to the area that was not under SEM observation for a long time and high magnification.

We proposed the use of a local masking technology based on carbonaceous films that have the capabilities for high-resolution patterning. The carbonaceous film will be deposited by electron-beam irradiation with submicron resolution using a SEM and the high-

resolution patterning of the film will be realized by AFM anodization of the carbonaceous films [15].

The carbonaceous film was demonstrated to have very good mechanical resistance, so that the most suitable approach would be the chemical modification of the film. The anodization of the carbonaceous film under intense local electric fields would ideally give volatile carbon-oxygen related byproducts, making the patterning straightforward.

In the next subchapters, deposition and characterization of the carbonaceous films will be discussed in detail followed by a full analysis of the electric-field induced patterning processes of these films.

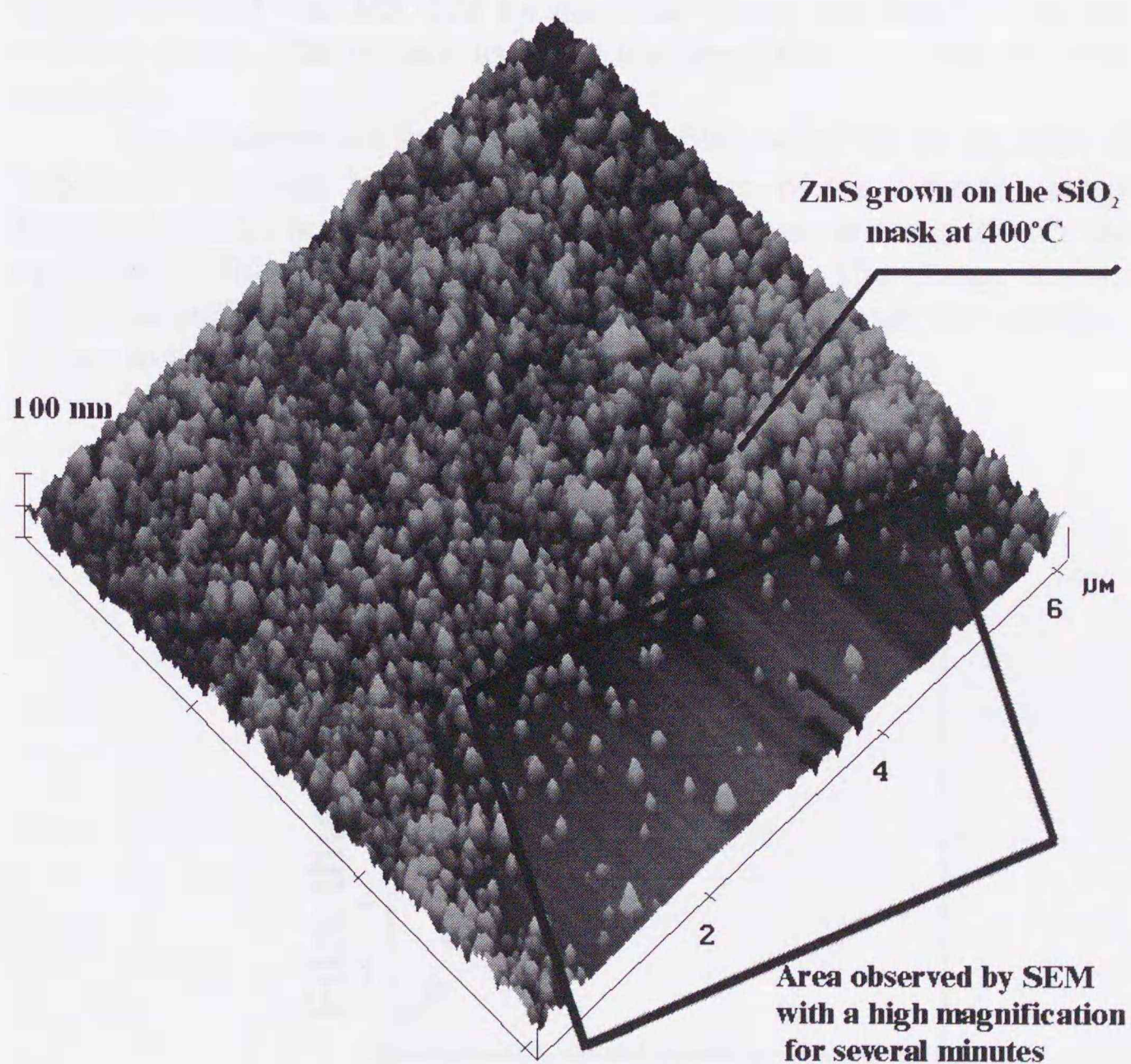


Fig. 2.14. Local selectivity "induced" by the SEM observation.

2.4.2 SEM deposition of carbonaceous films

In a scanning electron microscope, the electron beam is commonly scanned in order to image the surface but it can be also employed to deposit so-called "contamination materials" on the surface under the observation. This contamination material was previously identified as resulting from the electron-beam decomposition of the residual organic molecules such as vacuum pump oil molecules that are adsorbed on the surface [16]. The carbonaceous film was reported as being composed from a fine network of polymer-like materials and amorphous carbon [17].

The SEM employed in our experiments was a JEOL JSM-T300 and the oil used was MR-200 for the rotary pump and LION-S for the diffusion pump. The surface used for the deposition was that of GaAs substrates.

The thickness of the carbonaceous film deposited on an area of $20 \times 20 \mu\text{m}^2$ is given in Fig. 2.15 as a function of the electron charge density. The film is uniformly deposited as the beam is scanned over the square area. The thickness was measured by AFM. The charge density was calculated by measuring the current flowing through the substrate surface to the SEM stage and the time for deposition.

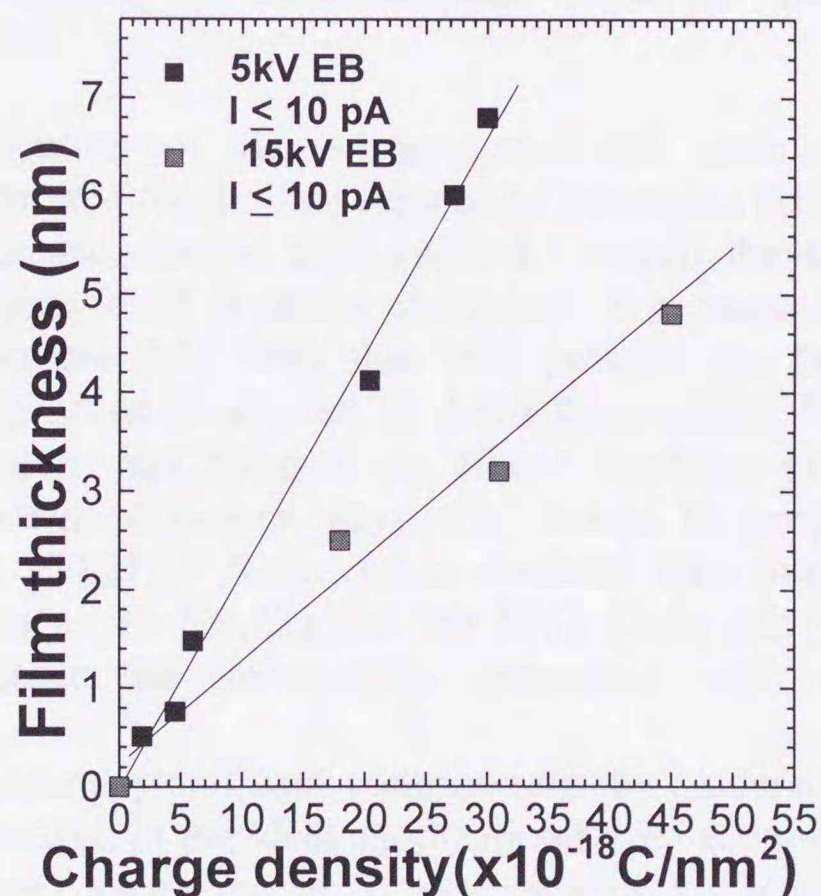


Fig. 2.15. Thickness of the carbonaceous film deposited under different acceleration voltages as a function of the charge density.

The film thickness increases linearly proportional to the time-accumulated total charge density irradiated on the surface. This linear dependence allows controlling the thickness of the carbonaceous film with sub-nanometer precision.

The efficiency of the deposition process is higher at the lower accelerating voltage as compared to the higher accelerating voltage possibly due to the electron-beam induced desorption of the hydrocarbon molecules once deposited on the surface. With the higher accelerating voltage a better adhesion of the carbonaceous film to the substrate as compared with the 5kV case was observed.

The usual linewidth of the wire-like carbonaceous patterns was around 200 nm with a 15 kV acceleration voltage for the electron beam. The beam could be scanned over the surface in a desired pattern when a beam control unit programmed by a computer was used.

The carbonaceous film was usually deposited with the thickness of 2~3 nm with an accelerating voltage of 15kV. This is because the lower deposition rate allows a better control of the thickness. The GaAs substrate covered with the carbonaceous film which thickness is in this range did not show any degradation of the film even it was immersed in HCl (conc.) or BHF (10 %) for several minutes.

2.4.3 AFM lithography of carbonaceous films by electric-field induced anodization

The modification of the surface chemical nature by local anodization was reported for the first time on Si substrates [18]. This was done under the intense electric field applied between the tip and the surface in the presence of a water meniscus. The water molecules ionization will produce OH^- ions that will provide the Oxygen for anodization. This process is referred as AFM anodization. Up to date, most of the research was focused on silicon surfaces [19], whose relatively well-known properties gave the chance to propose some analytical models [20,21]. Some other surfaces like those of thin metallic films such as Ti [22,23] and Nb [24], GaAs [25] and other semiconductors could be successfully processed with the same technique.

Recently, several significant contributions for understanding the basic processes involved in the local anodization have been made. The *in situ* electric force characterization by scanning Maxwell-stress microscopy (SMM) gave some insight into the distribution and temporal evolution of the ionic species involved in the anodization and pointed out the possibility of charge accumulation in the oxide region [26]. Based on

these findings it was suggested that a bias alternating its polarity during the patterning would remove some limiting factors of the oxide growth rate in the direction normal to the surface.

Another contribution in this field was given by the use of non-contact mode for patterning [21,27]. This approach opened the way for higher reliability during the patterning process and also gave additional information about the role played by the water meniscus [27].

It is commonly accepted that the anodization rate is directly dependent on two main factors: the effective electric field intensity together with the concentration of the OH^- ions at the surface-oxide interface.

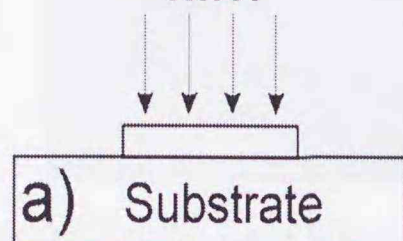
Our interest in patterning thin carbonaceous masks for selective area growth motivated our research in the area of AFM anodization of the carbonaceous films. Most of the fundamental studies discussed below such as the resolution-limiting factors and the methods to overcome them will be easily extended to the more general field of patterning by anodization.

2.4.3.1 Experimental procedure

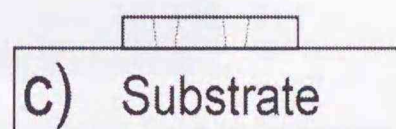
The main steps in the mask processing are illustrated in Fig. 2.16 and are discussed in detail in the following. The p-type or semi-insulating GaAs (001) wafers were chemically cleaned following a standard procedure and then loaded in the SEM (JEOL T 300) for deposition of the carbonaceous film. The SEM employed in our experiments has an additional electron-beam control system, which gives the possibility to achieve the desired design of the pattern. The carbonaceous films are deposited on the semiconductor surfaces by the electron-beam induced decomposition of the residual organic molecules adsorbed on the semiconductor surface in the SEM chamber at a pressure of $\sim 1 \times 10^{-5}$ Torr. The accelerating voltage was 15 kV and the electron-beam current was 8 pA. The area deposited with the carbonaceous film was $30 \times 30 \mu\text{m}^2$ or $20 \times 20 \mu\text{m}^2$ and the thickness was in the range of 2 to 4 nm for a total deposition time of 25 min. 2~2.5 nm is the minimum thickness required to achieve the complete selectivity during the semiconductor growth [28]. The high-resolution patterning was performed using the AFM (DI, Nanoscope III) running for this purpose in contact mode. The relative humidity (RH) and the temperature were controlled around the AFM head. The RH was controlled between 40% and 60%, while the ambient temperature was stabilized at 25°C. The electric bias for anodization was applied using a Source-Measure Unit

(Keithley, SMU 236), which can work either in current or voltage constant mode with the possibility for measuring the complementary unit and of limiting the maximum value.

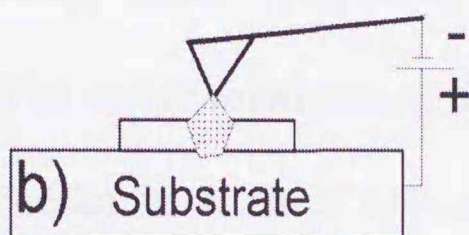
EB deposition of carbonaceous film



Etching in HCl



AFM anodization



Selective epitaxial growth

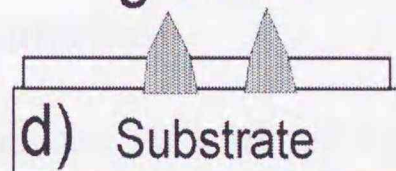


Fig.2.16. The diagram of SEM/AFM fabrication of high-resolution carbonaceous masks.

Because the AFM patterning of carbonaceous films requires biases as high as 18 V, a very stable conductive coating on the tip is necessary. Simple metal coatings such as Cr, Cr-Ni, Ti, were not stable enough because of the anodization of the metal coatings during the patterning and/or because of its peeling off due to the shear force during the patterning as is shown in Fig. 2.17. For preventing this kind of damage, the Si_3N_4 cantilevers were coated with TiN_x films of approximately 10 nm thickness. The deposition was made by radio-frequency magnetron sputtering of a Ti target in an Ar (80%)/ N_2 (20%) gas mixture with the total pressure of 1×10^{-2} Torr. The accelerating voltage was set to 2kV and the total sputtering time was 4 min. The TiN_x films have good adhesion to the cantilevers and are conductive. The TiN_x -coated cantilevers did not show any degradation after patterning of several thousands of dot-like features at 18-V-bias. These stable cantilevers made possible the comparison between patterning results

discussed below, such as the constant bias mode, the constant current mode and the pulsed bias mode.

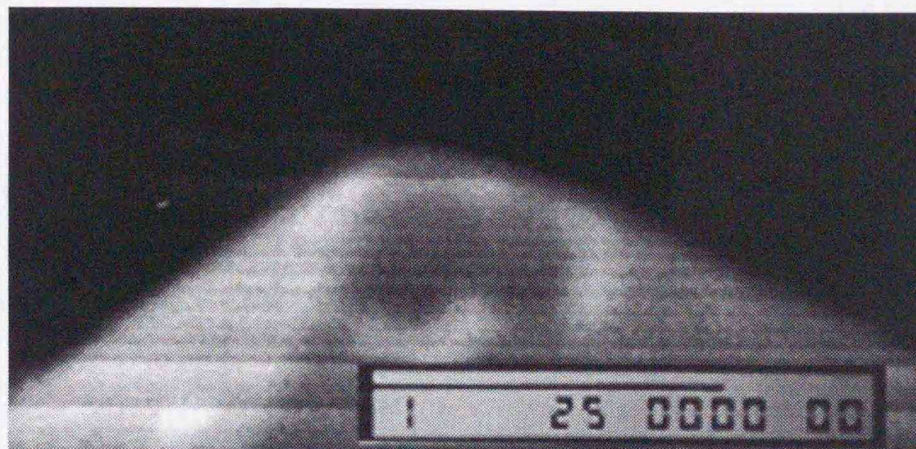


Fig. 2.17. A Cr coated SiN_x tip damaged by the intense electric field and/or wear.

The etching of the oxidized volume was performed in concentrated hydrochloric acid (HCl). After anodization and etching, the patterns were measured by AFM working in the tapping mode.

2.4.3.2 The water meniscus at the tip-surface interface

The anodization of the carbonaceous film can be initiated under electric field only in the presence of a very thin layer of water adsorbed on the film surface. This water layer is present if the AFM is placed in an ambient with relative humidity more than 40 %.

The geometry of the water meniscus formed at the tip-surface interface is approximated as is shown in the inset of Fig. 2.18. The tip was assumed to have a tip radius R_t of 20 nm and was approximated with a truncated cone with the halfangle of 35°. The water meniscus geometry as a function of relative humidity could be estimated using the equation of capillary [29]:

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{\Delta P}{\gamma}, \quad (2.7)$$

where R_1 and R_2 are the meniscus radii as shown in the inset of Fig. 2.18, γ is the water superficial tension, and ΔP is the pressure variation through the water meniscus. Neglecting the gravitational effects, ΔP is approximated by:

$$\Delta P = \frac{RT \log(RH/100\%)}{V}, \quad (2.8)$$

where RH is the relative humidity given by %, T is the temperature, R is the universal gas constant, V is the volume, ($\gamma V/RT=0.54$ nm at room

temperature) [30]. The geometrical relation at the tip-surface-water interface gives the second equation:

$$\tan\left(\frac{90-\theta_t}{2}\right) = \frac{R_1}{R_1 + R_2 - R_t \tan\left(\frac{90-\theta_t}{2}\right)}, \quad (2.9)$$

where θ_t and R_t are the tip halfangle and the radius of the tip, respectively. The wetting angle of water was assumed to be 0° at the interfaces between the water and the cantilever cone and respectively, the carbonaceous film.

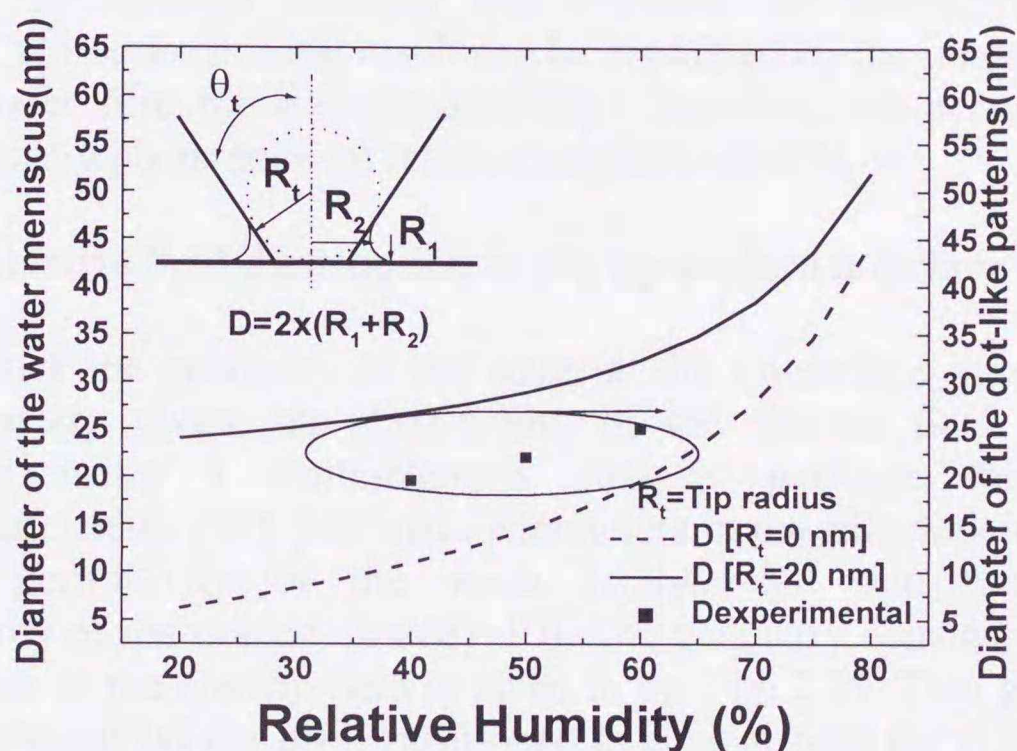


Fig. 2.18 Diameter of the water meniscus as a function of the relative humidity. The inset shows the geometry of the tip-surface-water considered for this calculation.

The diameter of the water meniscus on the carbonaceous film, $D=2.0 \times (R_1 + R_2)$, was calculated and is plotted in Fig. 2.18. The Mathematica code that was employed for this calculation is annexed in Appendix 2. The solid line gives the diameter of the water meniscus for a tip with a radius of 20 nm. The diameter calculated for the case of an ideal sharp tip, $R_t=0$, would give an estimation of the minimum pattern size achievable in the contact-mode SPM anodization lithography and is plotted as a dashed line. The experimental diameters of the anodized dot-like patterns obtained at the threshold voltage and with the minimum time duration are also plotted in Fig. 2.18. These data are most likely to reflect the size of the water meniscus. The reasonable agreement between these two sets of calculated data with the measurements gives some

evidence that the calculated water meniscus can be used as a first approximation in the calculation of the electric-field distribution inside the water. However, the formation of the oxide film on the sample surface during the anodization process and the intense electric field [29] will modify the geometry of the water meniscus with the time. One can speculate that the radius of the water meniscus will increase by the formation of the oxide that should be much hydrophilic in comparison with the carbonaceous film.

If the relative humidity increases from 40% to a value of 60%, the calculated diameter of the water meniscus and the experimental diameter are not drastically enlarged. However, in the case of patterning wire-like features the reduced humidity will decrease the uniformity of the patterns. This experimental result can be explained by the inhomogeneity of the water film for a lower humidity. Therefore, we performed our experiments with an ambient relative humidity of 60%.

2.4.3.3 Electric field distribution at the tip-surface interface

Since the geometry of the water at the tip-surface interface was approximately given, the distribution of the electric field could be estimated using a finite-element analysis package for solving electrostatic fields [31]. The main parameters in the calculation were the relative permittivity of the water ($\epsilon(\text{H}_2\text{O})=80$) and the relative permittivity of the oxide ($\epsilon(\text{oxide})=10$). The geometry considered for the calculation of the electric field is given in the Fig. 2.19. Two geometries are considered: (a) the tip is positioned in contact with the 0.5-nm-thick oxide and (b) the tip is positioned above the oxide surface since a 0.5-nm-thick H_2O layer is sandwiched in between.

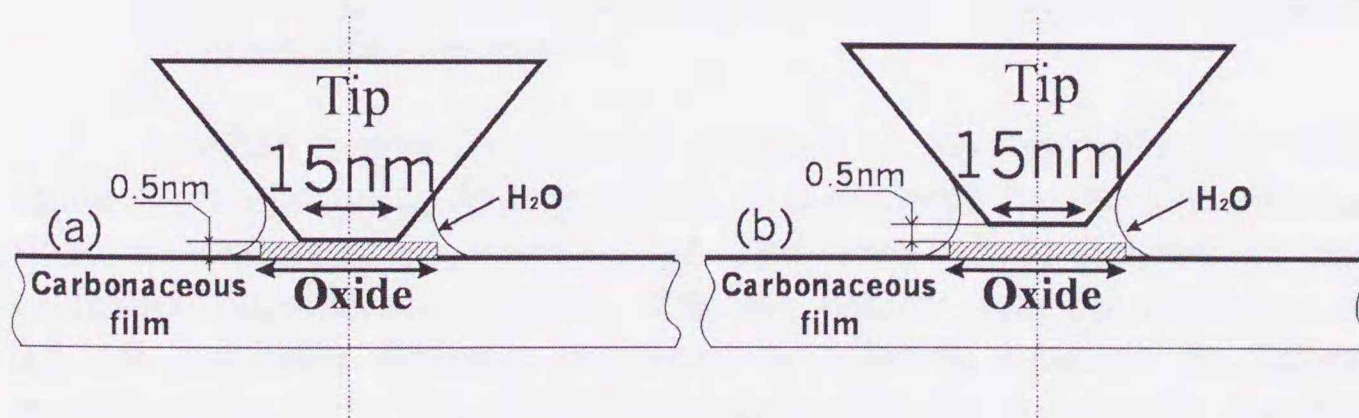


Fig. 2.19 Schematics of the tip-surface-water interface for the electric field calculation. Tip was assumed to have a radius of 20 nm and approximated with a truncated cone with the halfangle of 35° and the top diameter of 15 nm. The oxide that is formed beneath the tip was approximated with a 0.5-nm-thick disk of variable radius. (a) The tip is in contact with the oxide. (b) The 0.5-nm-thick layer of H_2O is sandwiched between oxide and tip.

Figures 2.20 (a) and (b) shows the electric field values that are computed for two geometries that were described in Fig. 2.19 (a) and (b), respectively but without including the oxide disk. The electric potential was taken zero for the metallic tip and +10 V for the substrate, which was considered metallic. The data shown in Fig.2.20 are calculated as a function of the radial position on the sample surface in two cases: with the water meniscus and without the water meniscus. Based on these graphs, one can conclude that the electric field is not essentially modified by the presence of the water meniscus for the short tip-surface separation of 0.5 nm. For the larger tip-surface distance of 1 nm, the electric field tends to be focused by the water meniscus.

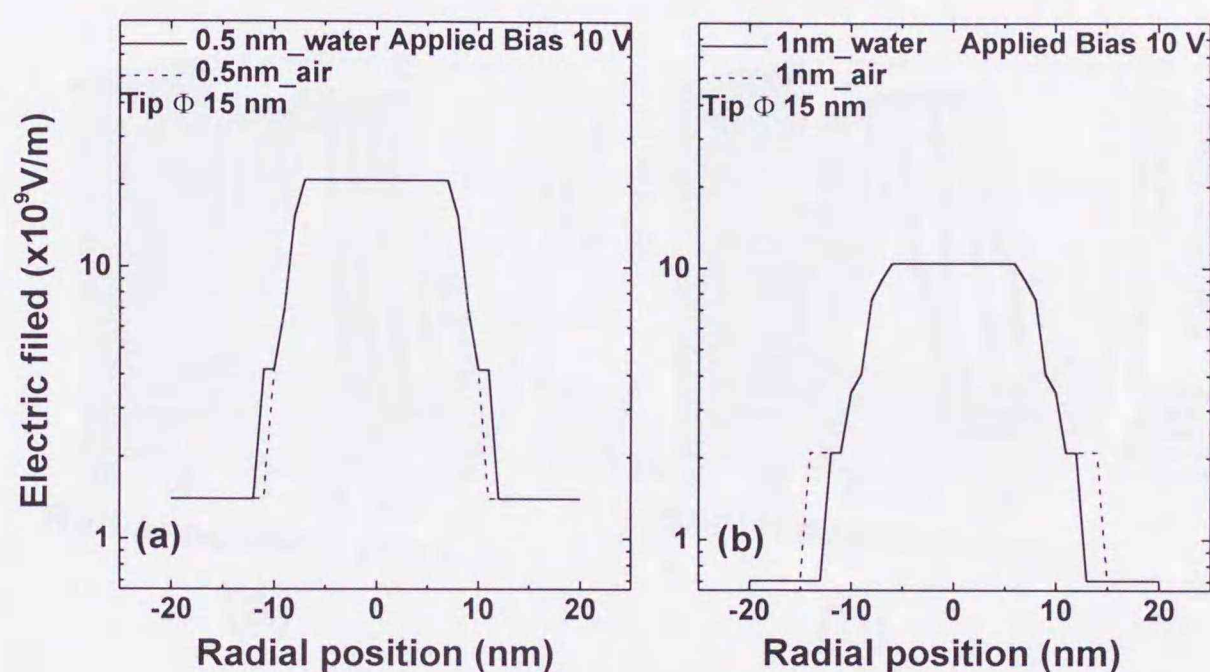


Fig. 2.20 Calculated electric field as a function of the radial position on the carbonaceous film surface for two different tip-surface separations, in the presence of the water meniscus and without it.

Another important result is obtained in the case of a very thin oxide formation under the tip, which is considered for the first time in such calculation of the electric field. The electric-field distribution was calculated considering an oxide disk-like pattern with the thickness of 0.5 nm and with different diameters in order to simulate the lateral growth of the oxide. The electric potential was taken zero for the metallic tip and +10 V for the substrate, which was considered metallic. The electric field was calculated for the two cases illustrated in Fig. 2.19 (a) and (b) and its distribution is illustrated in Fig. 2.21 (a) and (b), respectively. The thin oxide proved to defocus the electric field toward the oxide edge due to the high contrast between permittivity of the water

($\epsilon(\text{H}_2\text{O})=80$) and of the oxide ($\epsilon(\text{oxide})=10$). This effectively results in the enhancement of the electrical field at the oxide pattern edge as compared with the field distribution calculated without considering the oxide pattern. The value of the electric field at the oxide edge for the large diameter patterns is increased as compared with the case of the narrow oxide pattern at the same radial position. In contrast the value of the electric field at the center of the pattern is not very much increased as the oxide diameter increases.

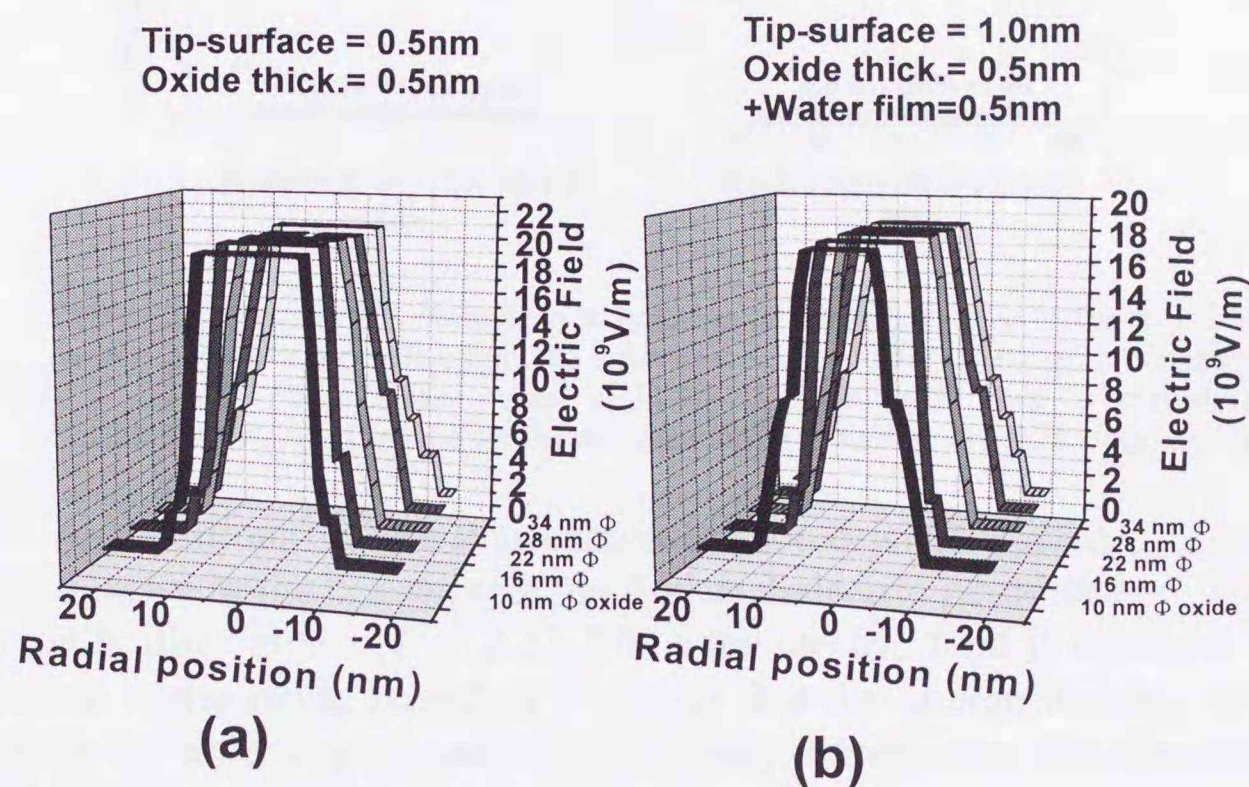


Fig. 2.21. The electric field calculated on the carbonaceous film surface in the case an oxide disk is considered at the tip-surface interface. The oxide disk thickness is 0.5 nm and the diameters considered are 10, 16, 22, 28, 34 nm, from the front to the back.

This phenomenon is better illustrated in the next figures. Figures 2.22 (a) and (b) show the computed electric field for two situations: 1) in the case when the oxide disk has a 34-nm-diameter and 2) in the case when only the water meniscus is considered. In the case when the oxide layer is included, the electric field strength is clearly higher than in the case without the oxide layer. As the radial position increases out from the center of the tip the difference is accentuated. The data resulted from the electric field strength calculation will be quoted in the following sections when a model for the oxide growth will be proposed.

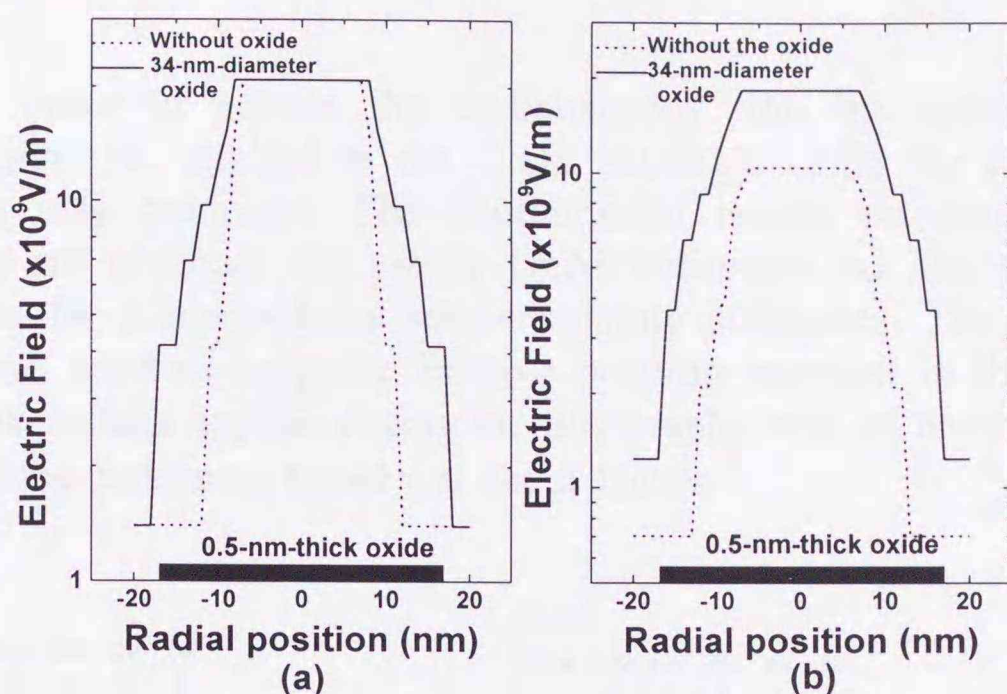


Fig. 2.22. Electric field strength as a function of the radial position for two cases: dashed-line is the case when only the water meniscus, without the oxide, is considered and solid-line is the case when a 34-nm-diameter oxide disk is considered. Calculations were performed for the two geometries described in Fig. 2.19 (a) and (b).

An additional effect that should be noted is the increase of the charge density in the region with the higher dielectric permittivity. This situation is illustrated in Fig. 2.23. Since the electric field is common at the lateral water-oxide boundary it results that the charge density, σ is higher in the water region and will eventually increase the concentration of OH⁻ ions for anodization at the carbonaceous surface:

$$\sigma(H_2O) = \epsilon(H_2O) \times E > \sigma(oxide) = \epsilon(oxide) \times E, \quad (2.9)$$

where E is the electric field and ϵ is the dielectric permittivity. This will enhance the lateral spread of the anodized region.

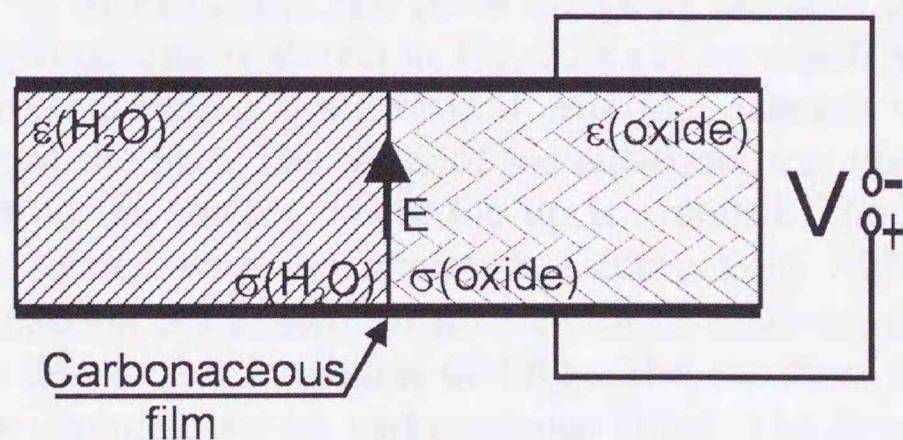


Fig. 2.23 The schematic of the surface charge and the electric field at the water-oxide boundary

2.4.3.4 Constant bias and current anodization of the carbonaceous films

In order to pattern the carbonaceous film by anodization, a positive bias was applied to the GaAs substrate while the conductive cantilever was grounded. The experimental results presented in the following are obtained for p-type GaAs substrates but the patterning could also be performed on semi-insulating substrates. The feedback control was used to keep the relative position constant in the contact mode. The voltage applied during the lithography was set between 3 and 15 V, and the patterning speed was set at $1\mu\text{m/s}$.

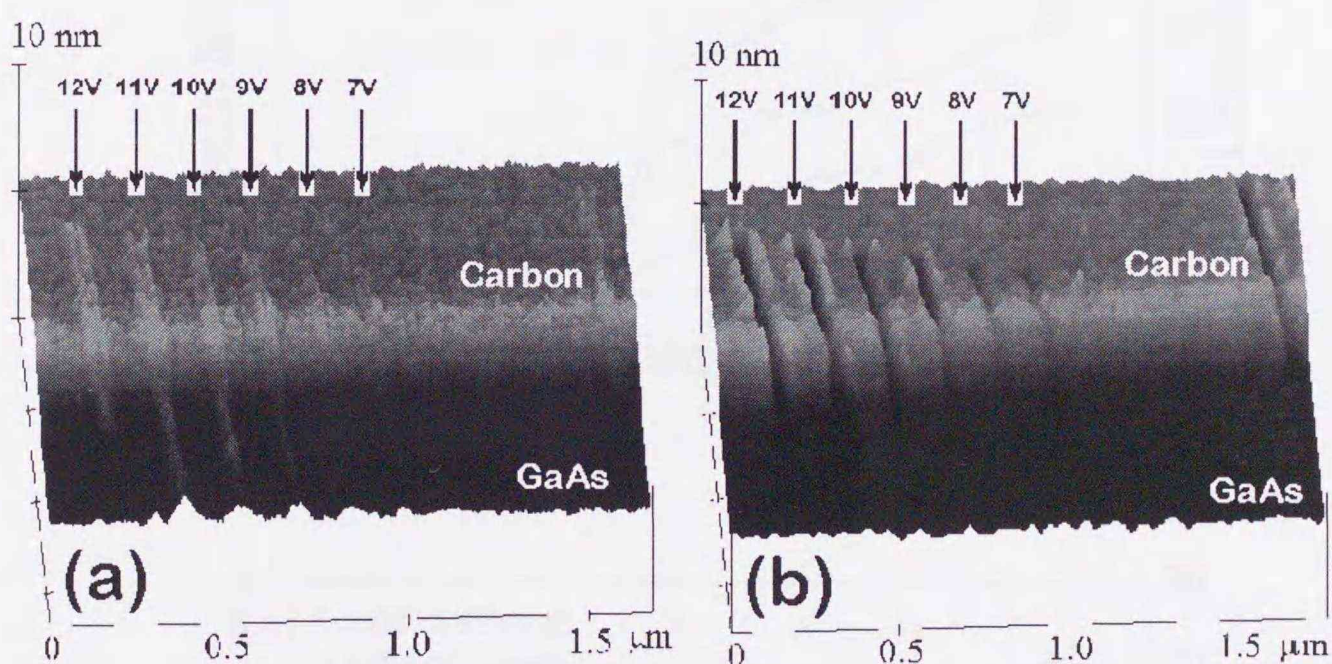
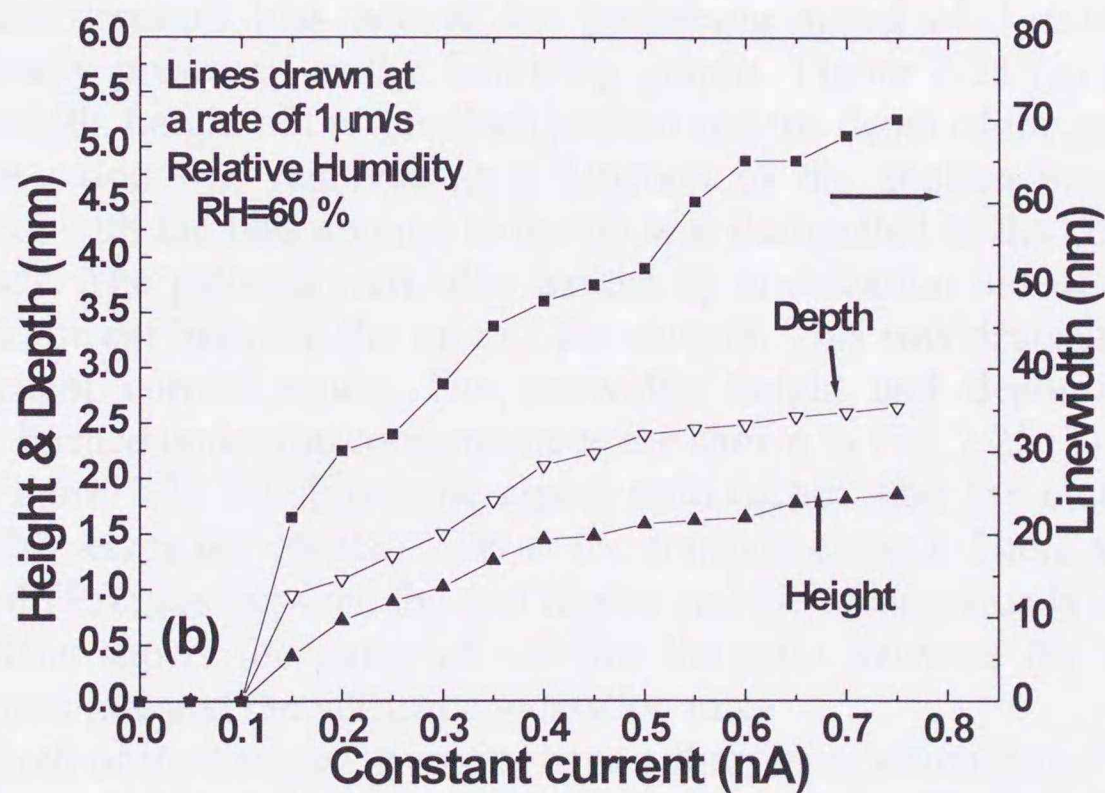
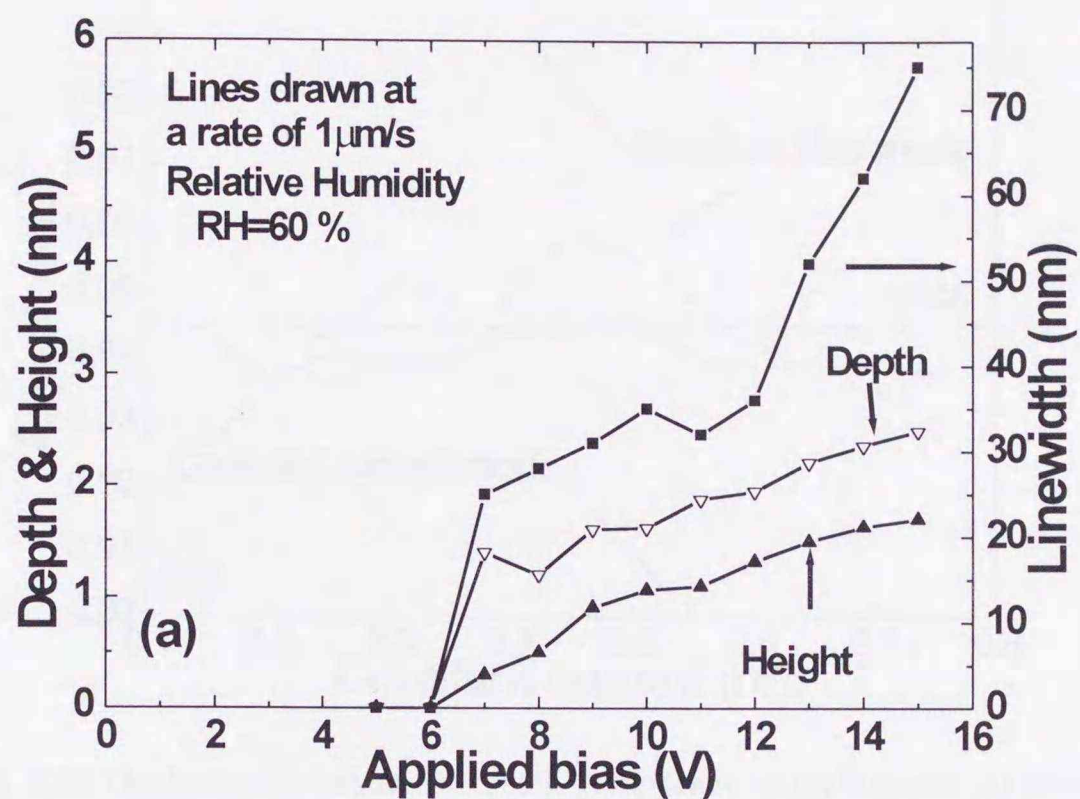


Fig. 2.24. (a) Anodization at the edge of the carbonaceous film under different applied biases. (b) The anodized volume was chemically removed by etching in the HCl.

In the first set of experiments the minimum bias necessary for the anodization was investigated. The AFM image of the edge of the 4-nm-thick carbonaceous film is shown in Fig. 2.24 (a) on which the AFM tip was moved for patterning along several wire-like patterns with a step-wise increase of the bias. The onset of the anodization is noticed by the raised pattern on the surface where the tip is scanned. The anodization onset can be related with the minimum electric field with which the anodization reaction is initiated. In the case of Si surfaces, this increase in volume is due to the formation of SiO_x . The situation seems to be slightly more complex on the carbonaceous films. The increase of the volume after the electric-field writing suggests that Oxygen is incorporated into the film. Since the carbonaceous film is amorphous and will contain hydrocarbon compounds, resulting compounds cannot be

clearly identified. As can be seen in Fig. 2.24 (b), the byproduct of anodization will have a different chemical composition since it is easily dissolved by HCl. Herein it will be simply called “oxide”.



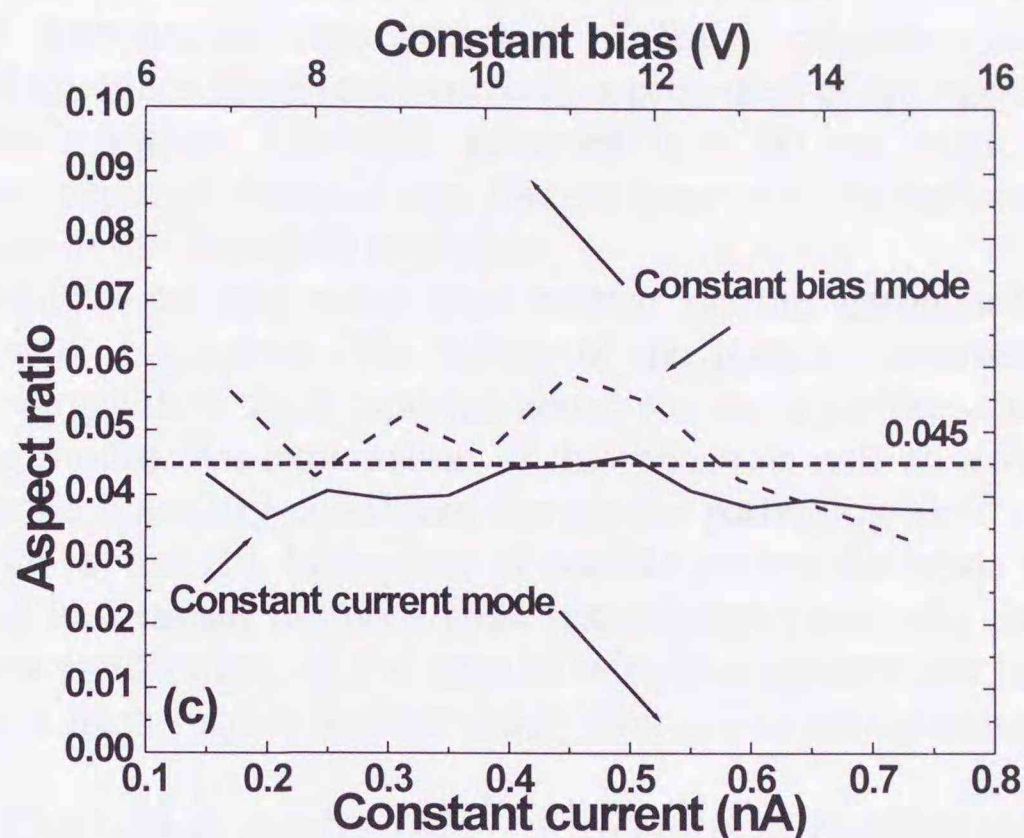


Fig. 2.25 The linewidth, height, and depth dependence on (a) bias and (b) current. The aspect ratio (depth/linewidth) for the constant bias and current mode (c).

The data measured on the wire-like patterns made by anodization under the constant bias and at the patterning speed of 1 $\mu\text{m/s}$ are synthetically presented in the following graphs. Figure 2.25 (a) shows the linewidth, height of the anodized pattern and the depth of the patterns after the oxide was removed as a function of the applied bias. The patterning with the bias applied to the tip was designated as the constant bias mode. The patterns were also written by anodization induced by a constant current between the tip and the sample. This was designated as the constant current mode. The linewidth, height and depth of the patterns formed under the constant mode are shown in Fig. 2.25 (b).

Figure 2.25 (c) shows the aspect ratio (depth after the etch over linewidth) versus the constant bias or the constant current. There are not distinct differences between the two modes and the mean value is around 0.045. This shows the value of ~ 23 for the ratio between the lateral anodization rate and the vertical anodization rate.

Both of the patterning modes have a threshold, which is 6~7 V for the constant bias and 0.15 nA for the constant current. The presence of threshold and the increase of the vertical anodization rate with the applied bias demonstrate that the anodization of the carbonaceous films has a similar mechanism with that of Si [18]. The anodization rate is

determined by the strength of the effective electric field and the presence of the water molecules. In the case of the constant current mode the threshold demonstrates the presence of leaky currents. The set-up employed to reduce these leaky currents is presented in the Appendix 4.

The minimum linewidth achieved is ~ 20 nm with an oxide penetration depth of around 1 nm. Deeper lines could be patterned but at the expense of the linewidth resolution.

Dot-like patterns were also written on the carbonaceous film surfaces with 1 s pulses. The values of the patterns parameters were 15~20 % larger than those reported above for the wire-like ones in both patterning modes. An explanation of this behavior will be given if one considers the boundary conditions during the patterning as is illustrated in Fig. 2.26 (a) and (b). In the case of dot-like pattern the oxide layer will be formed underneath the tip almost instantaneous and will perturb the subsequent anodization. In the case of wire-like patterns the tip will be always on a fresh surface without oxide layer due to the tip movement.

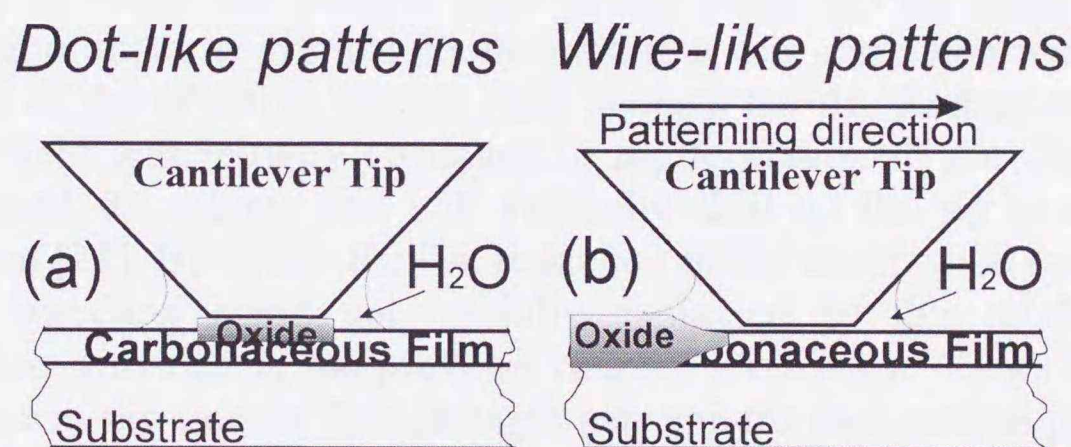


Fig.2.26. Schematics of the boundary conditions during the patterning of (a) dot- and (b) wire-like patterns.

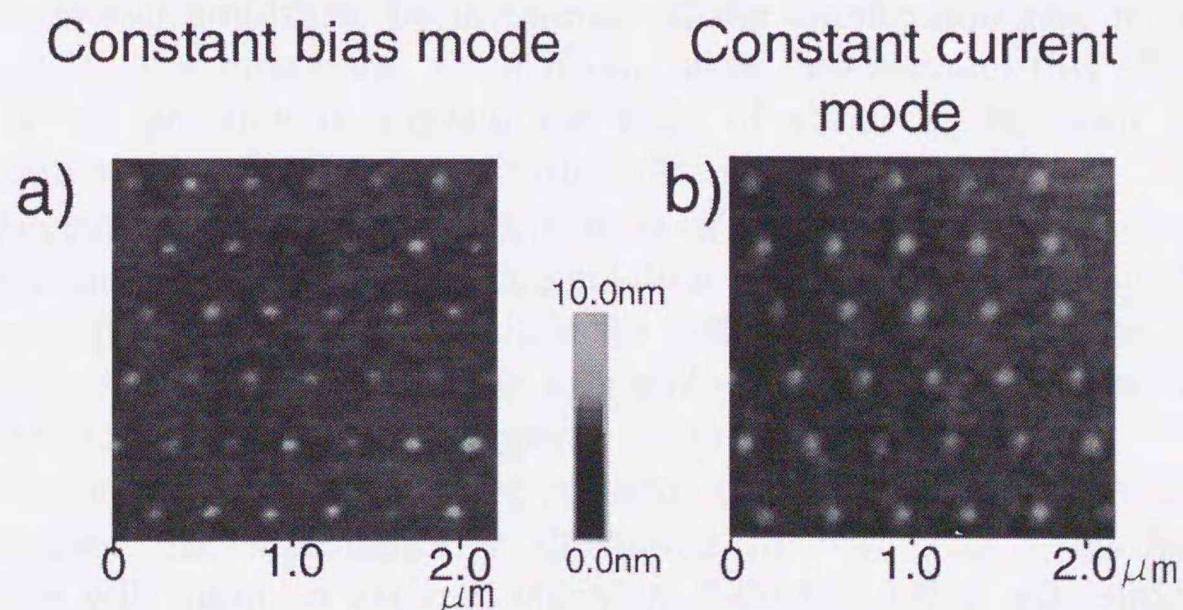


Fig. 2.27 Dot-like patterns fabricated with (a) 15V for 1s and (b) 0.75 nA for 1s.

Although the difference is not clearly seen in Fig. 2.25 for the wire-like patterning, it will be worth noting that the patterning under the constant current mode yielded more uniform and tall dot-like patterns as can be seen in the Fig. 2.27 (a) and (b). A possible explanation for this behavior is the control of the charge variation at the contact between the tip and the carbonaceous film in the former case instead of the applied bias in the latter case. The constant bias mode patterning favors the lateral size fluctuations because the applied electric field is higher than the minimum field for anodization on a larger area.

2.4.3.5 Pulsed bias mode anodization of the carbonaceous films

The constant bias mode or constant current mode could provide high-resolution patterns but the mean aspect ratio was very small value of 0.045. The small aspect ratio was also reported in the anodization of Si [20,21]. Since the electric field is the main driving force in the anodization, this low vertical anodization rate was correlated with a fast decrease of the effective electric field beneath the tip. Reduction of the electric field was initially attributed to the formation of the oxide that will expand its volume and will vertically shift up the tip to a larger separation [21]. However, the fast reduction of the anodization rate in the vertical direction could not be fully explained by this model. The calculation provided in the previous chapter 2.4.3.3 also shows that the difference in the electric field strength between the two vertical positions is not large enough to explain the observed small aspect ratio.

On the other hand from the electric field calculation, we learned about the self-defocusing effect of the oxide growth in the lateral direction, which amplifies the difference of the anodization rate in the two perpendicular directions. Even if one takes into account this effect still it is not possible to explain the ratio of about 23 between the anodization rate in the lateral and vertical directions.

Recently, the SMM characterization of anodized silicon provided some evidence that net charge accumulation is building up during the anodization process. This will reduce the effective electric field at the anodization interface [26], which in turn will reduce the anodization rate in the vertical direction or even suppress the further anodization.

The processes that will most probably take place at the tip-oxide-film interface are schematically illustrated in Fig. 2.28. The bias application will build an external electrical field (E_{ext}) that will initiate the anodization of the carbonaceous film. The OH^- ions are responsible for the anodization, as is well known in the anodization of Si. These ions

will be subject to diffusion and drift under the applied field and will start to accumulate in the newly created oxide. These accumulated ions will induce a local electric (E_{loc}) field of reverse orientation that will reduce the effective electric field at the film-oxide interface as can be seen in Fig. 2.28(a).

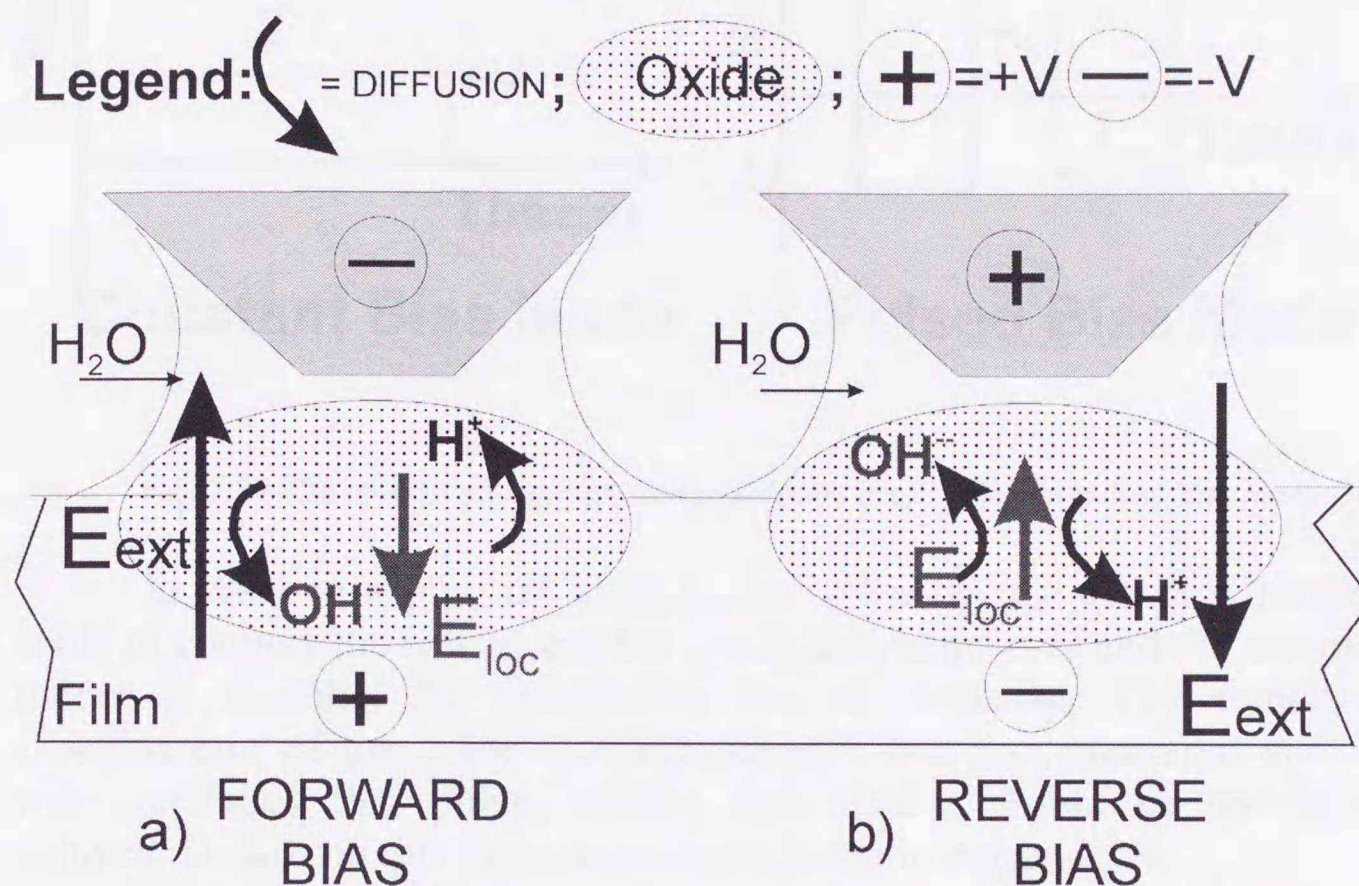


Fig. 2.28 Schematics of the ions and electric fields at the tip-oxide-film interfaces.

If the charge accumulation is considered as the main factor to decrease the oxide growth rate, then a reversed bias will be effective to neutralize the accumulated charges. The reverse bias will reset the E_{loc} to a lower value or eventually in the opposite direction. A pulsed mode anodization composed of forward bias pulses and of reverse bias pulses was shown to be effective in lifting the limitation on the oxide growth rate in the direction perpendicular to the surface for the Si [27,32].

Considering these two limiting processes on the patterning resolution, i.e. the lateral defocusing and the charge accumulation, the pulsed mode operation was investigated as a possible solution [33].

The notation for the parameters of the pulsed mode operation is as follows: the forward bias +V, the reverse bias -U, the forward pulse time duration T_+ , the reverse pulse time duration T_- . These are shown in Fig. 2.29. The pulsed bias mode is composed of successive bias pulses with inverted polarities that are applied to the tip. In the forward bias pulse, a potential +V is applied to the carbonaceous film through the substrate

and the tip is grounded. In the reverse bias pulse $-U$ is applied to the substrate while the tip is grounded as can be seen in Fig. 2.29 (b).

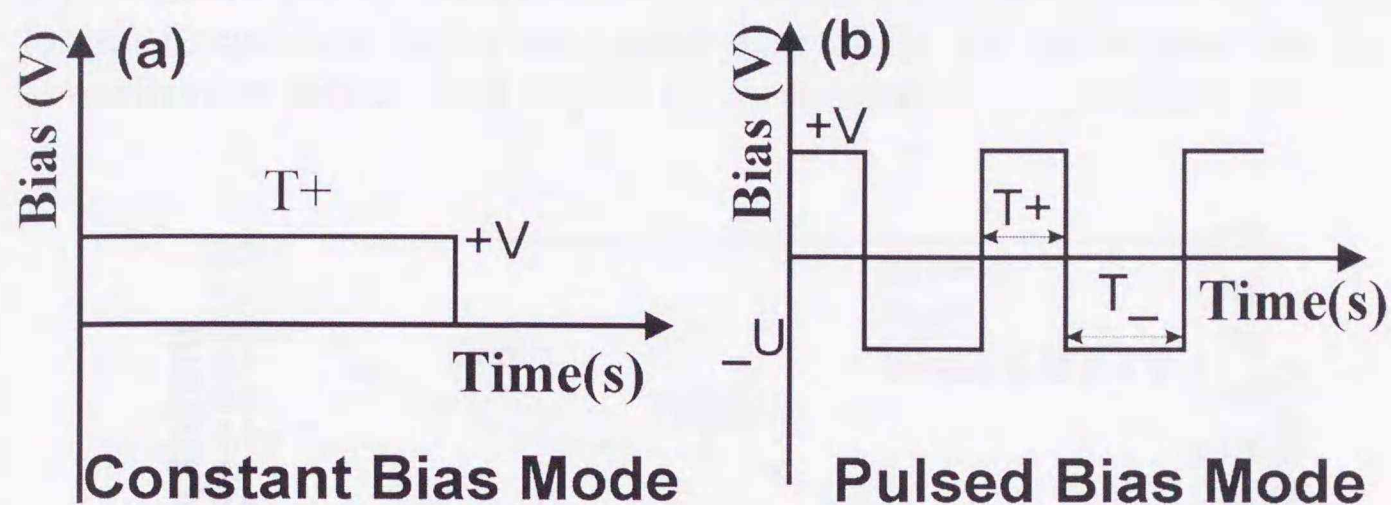


Fig. 2.29 The specific parameters for the constant bias mode and pulsed bias mode.

In order to apply very short pulses to the tip, the use of a triaxial cable to connect the source and the conductive cantilever and the sample holder is essential for minimizing the RC constant. The transient characteristic of the cable-cantilever-sample line was measured and it was concluded that pulses shorter than 0.02 s would be seriously delayed. Details on this measurement are given in Appendix 4.

The pulsed mode experiments were focused on the lithography of dot-like patterns. Nevertheless, the results obtained in this case will be directly extended to the wire-like patterns or other arbitrary shape. The patterns were characterized by their diameter, height and depth. The depth of the patterns was measured after the oxidized volume was removed by etching in HCl.

In the first set of experiments, dot-like patterns were written with the forward and the reverse bias pulses set to have a pulse duty ratio of 50 % and the pulse repetition was varied from 2 Hz to 50 Hz. The total time for the forward bias was set to the constant value of 1 s. The pulse amplitudes were set to 25 V for the forward pulse and to -7 V for the reverse one. The smaller reverse bias is used to prevent eventual oxidization of the TiN_x coating on the tip. The higher forward bias was set to test the upper limits for the anodization depth.

The dependence on the pulse repetition rate is summarized in Fig. 2.30. In the lower pulse repetition range the height and the depth of the patterns were greatly enhanced compared with the values of ~ 3.1 nm and 3.5 nm, respectively, under the constant bias at 25 V.* This enhancement

* High bias voltage under the CW mode tends to cause destructive sparks during lithography

should be attributed to the processes activated during the reverse bias. We assumed that the charge neutralization process is responsible for this enhancement during the reverse bias. Since the enhancement is very high for pulse repetition frequencies lower than 10 Hz one can assume that the neutralization process will require the time duration longer than 0.1 s.

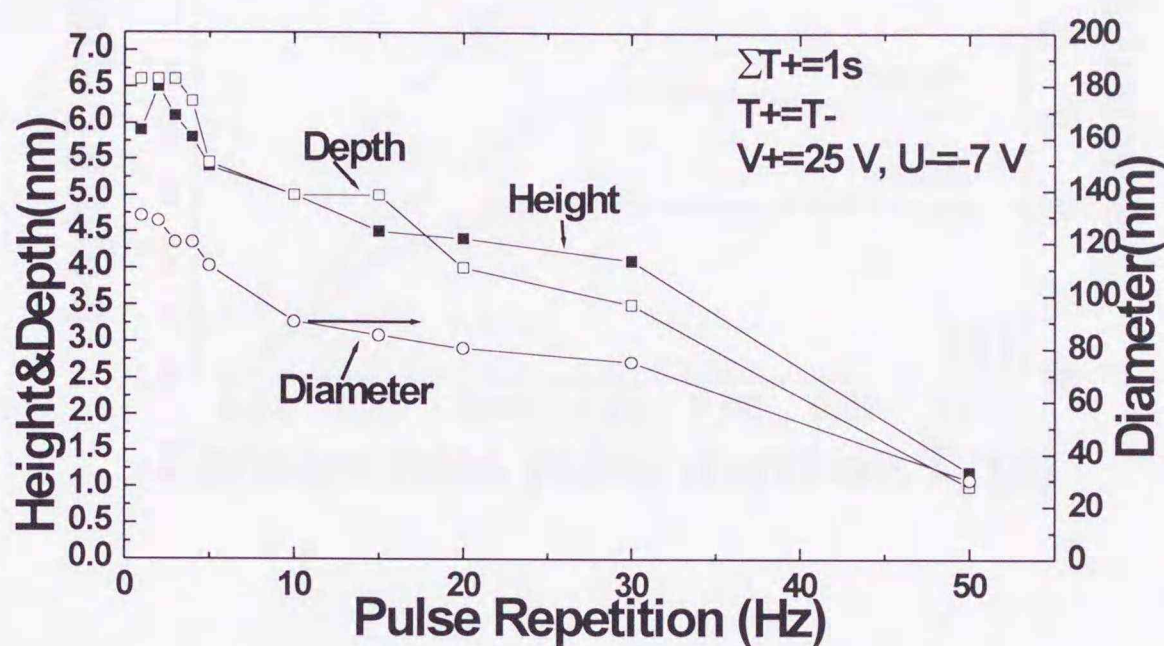


Fig. 2.30 Dot-like patterns characteristics as a function of the pulse repetition frequency.

In order to clearly assign the contribution of each of the forward and reverse pulses, the characteristics of the dot-like patterns as a function of the duration of the forward bias pulse were investigated. The reverse pulse had the constant time duration of 0.2 s and the amplitude of $-7V$, and the forward bias had the amplitude of 15 V. A lower voltage was preferred since the depth of the patterns made at 25 V far exceeded the thickness of the mask (~ 4 nm). The results are shown in Fig. 2.31(a). The depth and height of the patterns increase with the forward bias pulse duration. This increase saturates at around 0.05 s. The increase in the range of the short duration will be explained by the feed-in line delay of which influence gradually decreases as the pulse duration increases up to 0.05 s. The plateau and the small reduction in the value of the pattern depth should be attributed to the charge accumulation at the anodization interface, and the longer forward bias will increase the charge accumulation.

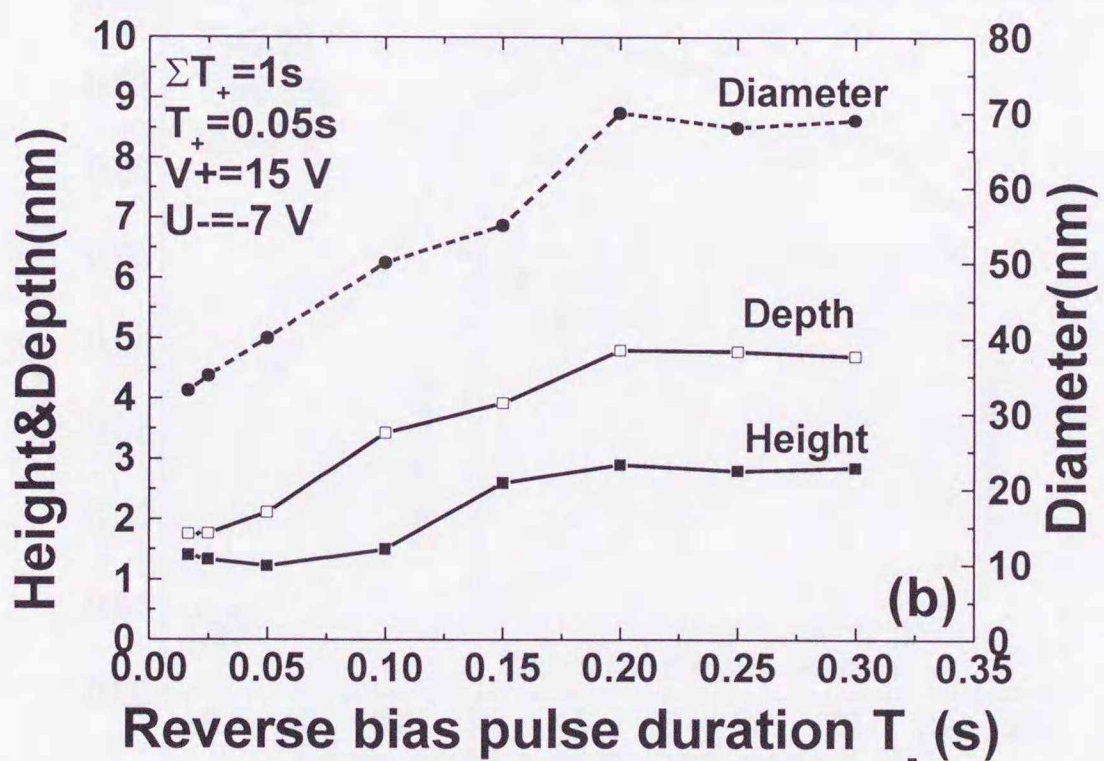
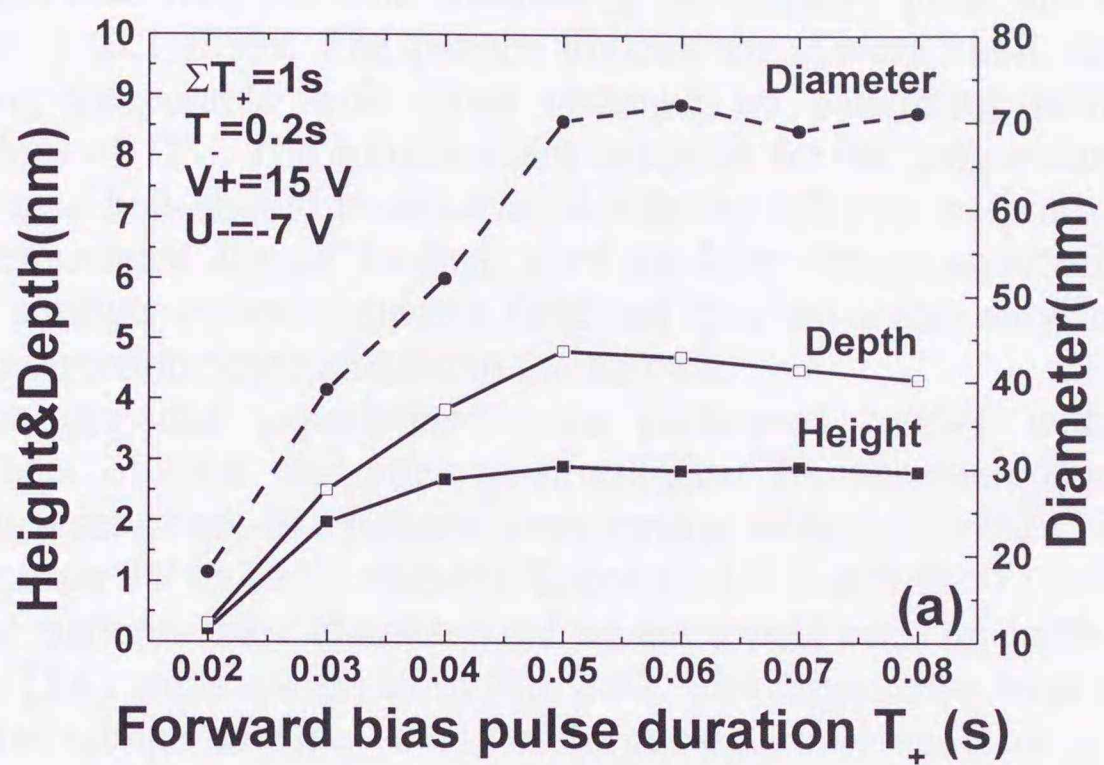


Fig. 2.31 The dot-like pattern characteristics as a function of the (a) forward bias pulse duration and (b) reverse bias pulse duration. The other parameters were kept constant during the patterning and are indicated in the figure.

Also, a set of dot-like patterns were made using the same pulse time duration of $T_+ = 0.05s$ and varying the reverse pulse time duration. The forward bias was 15 V and the reverse bias was -7 V. The results are

shown in Fig. 2.31(b). The height and respectively the depth of the patterns increase with the time duration of the negative pulse and starts to saturate at 0.2~0.25s. The pattern dimensions at very short reverse pulses are comparable with those obtained by patterning with the constant bias of 15V. The enhancement observed for the longer duration of the reverse bias should be associated with the efficient neutralization of the accumulated charge. Reduction of the local charge accumulation gives the stronger effective electric field and thus the higher anodization rate in the direction perpendicular to the surface.

The previous experiments were performed mostly with the forward bias of 15V. In order to investigate the optimum bias for patterning, a set of dot-like patterns were written with the forward bias in the range from 9V to 25 V, with the T_- pulse of 0.2s and the T_+ pulse of 0.05s. The patterns were characterized by the aspect ratio of depth over diameter. The results are given in Fig. 2.32. The aspect ratio was much improved as compared with ~ 0.045 of the constant bias mode.

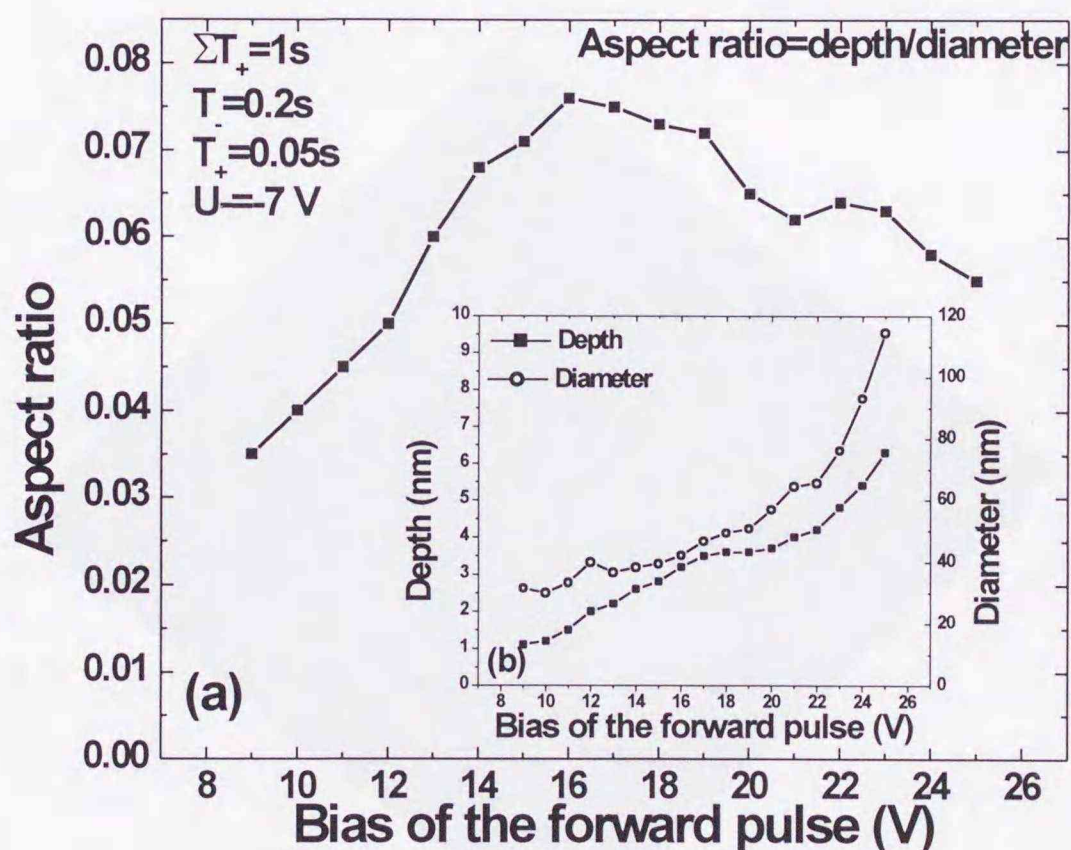


Fig. 2.32 (a) The aspect ratio of the dot-like patterns and (b) the depth and the diameter as a function of the bias of the forward pulse. The other parameters were kept constant and are given in the figure.

In contrast to the constant mode, the depth of the patterns is not saturated and a substantial improvement is obtained in the central range of biases. The following explanation is proposed for this characteristic. For the lower bias the anodization in the vertical direction will be almost

suppressed by the building up of the charge accumulation as could be seen in the constant mode anodization (Fig. 2.24(a)). For the high forward biases the electric field at the film surface will be high enough to promote the high lateral anodization rate from the first pulse. This will initially create a wide pattern and will further defocus the electric field toward the periphery of the pattern. This will result once more in the lower aspect ratio. The highest aspect ratio is obtained in the range from 16 V to 18 V.

Based on the data presented up to this point one can derive the optimum parameters for the lithography on the carbonaceous masks with a 2~3 nm thickness as will be necessary for the intended selective area growth. A combination of these parameters, optimized also for the respective mask thickness yielded a high-resolution mask as can be seen in Fig. 2.33. The lithography was performed in the following conditions: $V_+=16\text{V}$, $V_-=-7\text{V}$, $T_+=0.05\text{s}$, $T_-=0.2\text{s}$, $\Sigma T_+=1.15\text{s}$, $\text{RH}=60\%$, TiN_x coated SiN_x cantilever. The diameter of the patterns is 45 nm and the depth is 3 nm while the thickness of the carbonaceous film is 2.8 nm.

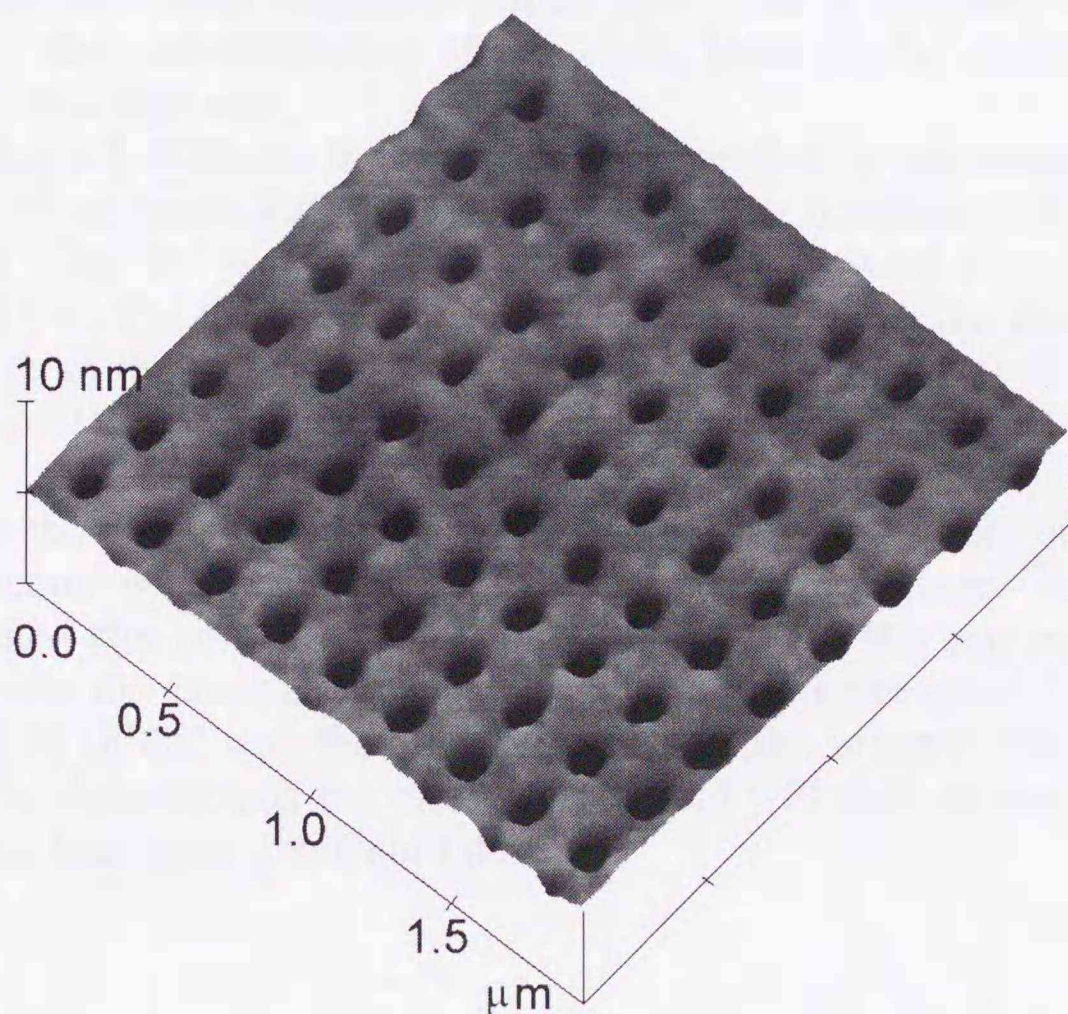


Fig. 2.33 An array of dot-like patterns anodized in a 2.8-nm-thick carbonaceous film. The anodized volume was removed by etching in conc. HCl. The mean diameter is 45 nm and the depth is ~3 nm.

Summing up the above results, one can conclude that the better results for the pulsed mode anodization are explained by the enhancement of the vertical anodization rate as a result of the stronger effective electric field induced by the charge neutralization in the oxide region during the reverse bias.

2.4.3.6 Modulated-amplitude pulsed bias mode anodization of the carbonaceous films

As a further step in the challenge for the higher resolution, the modulated-amplitude pulsed bias mode is proposed for the first time [34]. The pulsed mode itself tries to increase the anodization rate in the direction perpendicular to the surface but does not have any direct contribution toward the reduction of the lateral anodization rate.

The modulated amplitude pulsed bias mode is proposed in order to reduce the self-defocusing effect which leads to the oxide lateral growth with a high rate.

Figure 2.34 shows the calculated electric field at the center and at the edge of an oxide disk underneath the tip as a function of the oxide thickness. The field was calculated for an applied forward bias of 7, 10, 12, and 14 V. The threshold field was approximated with the field value at the edge of the pattern, extrapolated for an oxide thickness of 0.2 nm at a bias of 7V, values given from the experiment. Its value is $\sim 3.2 \times 10^9$ V/m.

At the center of the pattern the situation is a little more complex. At the center we consider a “quasi-threshold at the center” since the accumulated charge will build a local field (E_{local}) in this region, which will increase the external threshold. Therefore the center quasi-threshold level will be shifted with the time, depending on the accumulated charge. During the forward bias the external threshold will shift up and during the reverse bias pulse it will shift down.

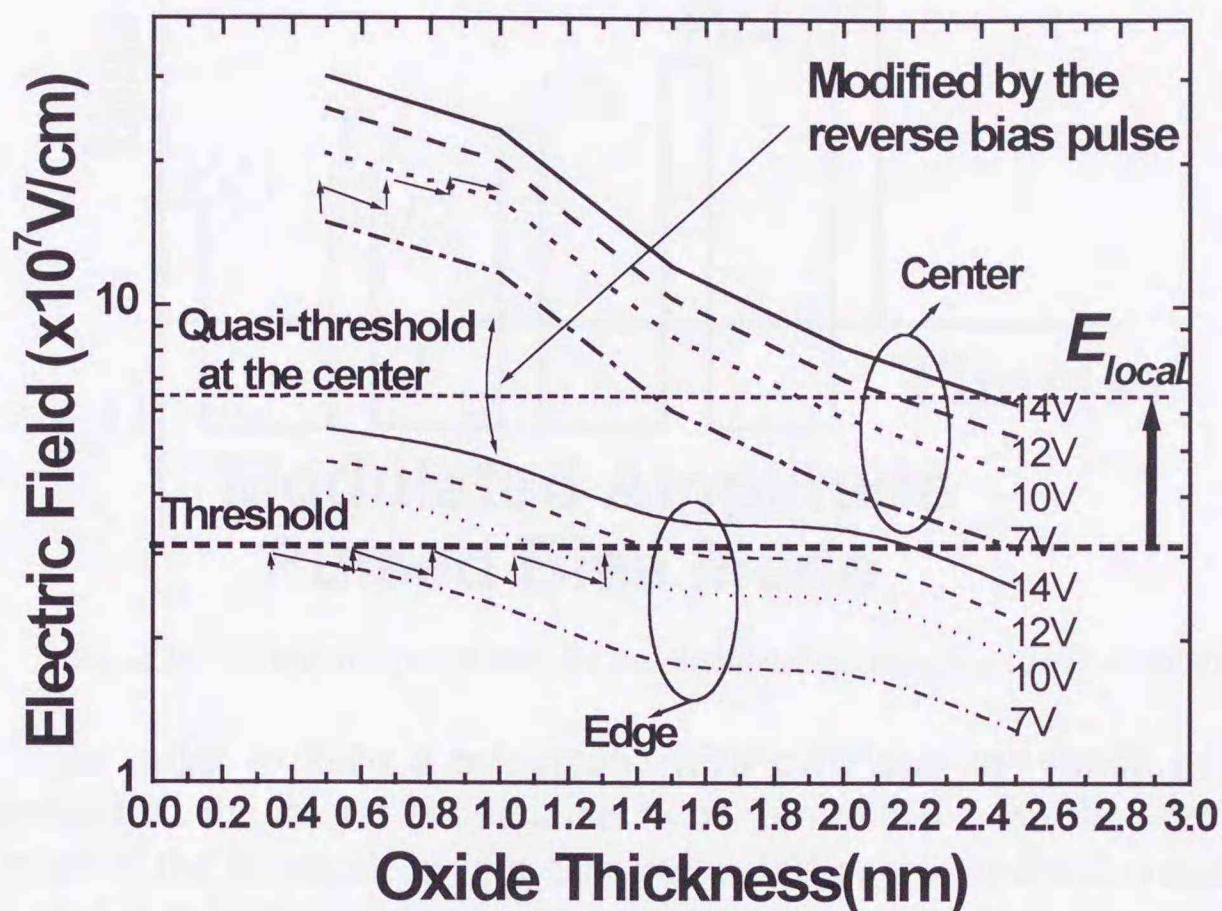


Fig. 2.34 Calculated electric field at the center and at the edge of a 20-nm-diameter oxide disk underneath the tip as a function of the oxide thickness. The field was calculated for an applied forward bias of 7, 10, 12, and 14 V

The larger accumulation of the charge at the center of the pattern reduces the electric field with the higher rate than the field at the edge of the pattern. For an oxide thickness larger than ~ 2 nm the field is drastically decreased. In order to assure the field above the threshold in the central region, the forward bias pulse should be increased to more than 14 V. The “zigzag” of arrows indicates the forward bias variation that will be ideal. In this case the field at the edge of the oxide pattern would be always under the electric field threshold that is indicated by the short-dotted line. As a result, the lateral anodization would be inhibited.

The modulated amplitude pulsed mode is proposed to limit the electric field at the edge of the oxide pattern down to a minimum value. The time sequence for the modulation of the bias amplitude is illustrated in Fig. 2.35. The amplitude of the forward pulse is gradually increased from the threshold value of the anodization to the final value of 16 V to 18 V.

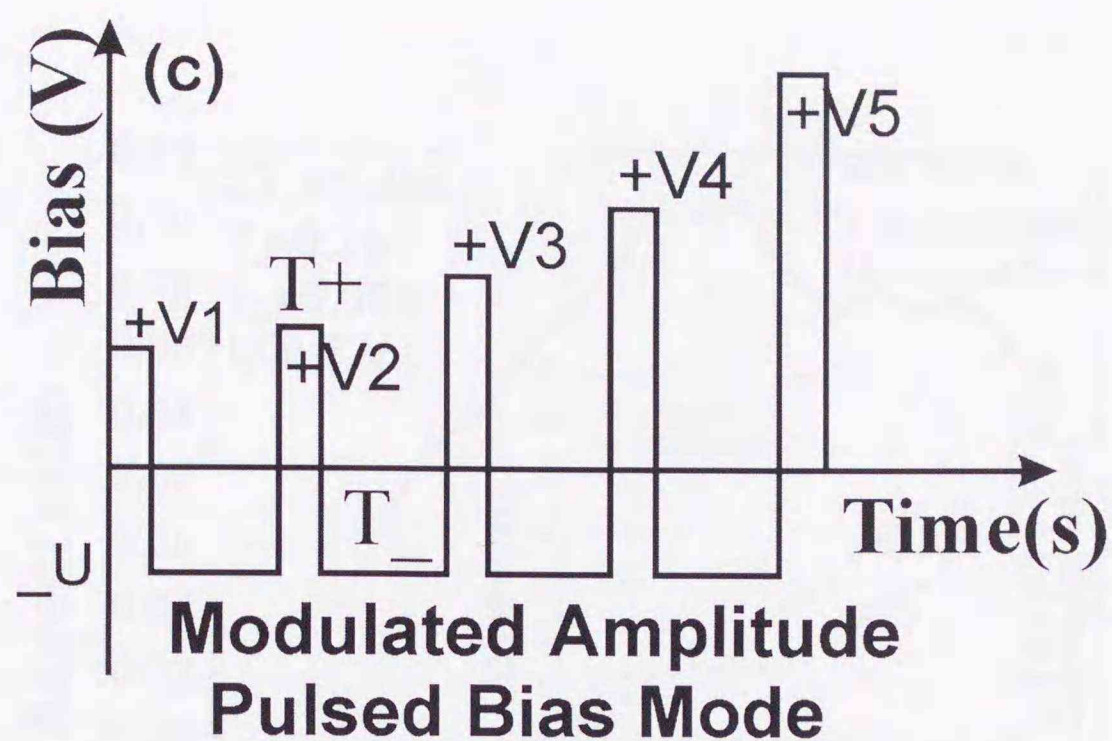


Fig. 2.35 The specific parameters for the modulated-amplitude pulsed bias mode

In order to keep a minimum electric field at the oxide edge is essential that the lateral anodization to be minimized from the very first moment of the anodization. The first pulse will be just as the threshold so will give a minimum lateral size of the pattern. The next forward bias short pulse will find the vertical distance between the tip and the carbonaceous film surface increased by the thickness of the oxide so a higher value will be necessary to proceed. The forward bias is gradually increased to the final value.

A smooth control of the forward bias increase would eventually provide perfect control on the lateral growth rate as is shown in Fig. 2.35. The voltage source used in our experiments can provide linearly increasing stair-like pulses or logarithmically increasing stair-like pulses. In this case only a rough control of the pulse amplitude can be achieved. The logarithmic increase was selected in this work because it gives the smaller rate of bias increase during the very first several pulses. This prevents excess lateral anodization in the initial stage.

The aspect ratio for a set of dot-like patterns prepared in this way is given in Fig. 2.36 as a function of the final pulse bias. The patterning parameters were the following: reverse bias of -7 V, the T_- pulse of 0.2 s, the T_+ pulse of 0.05 s, and the total patterning time of 1.25 s.

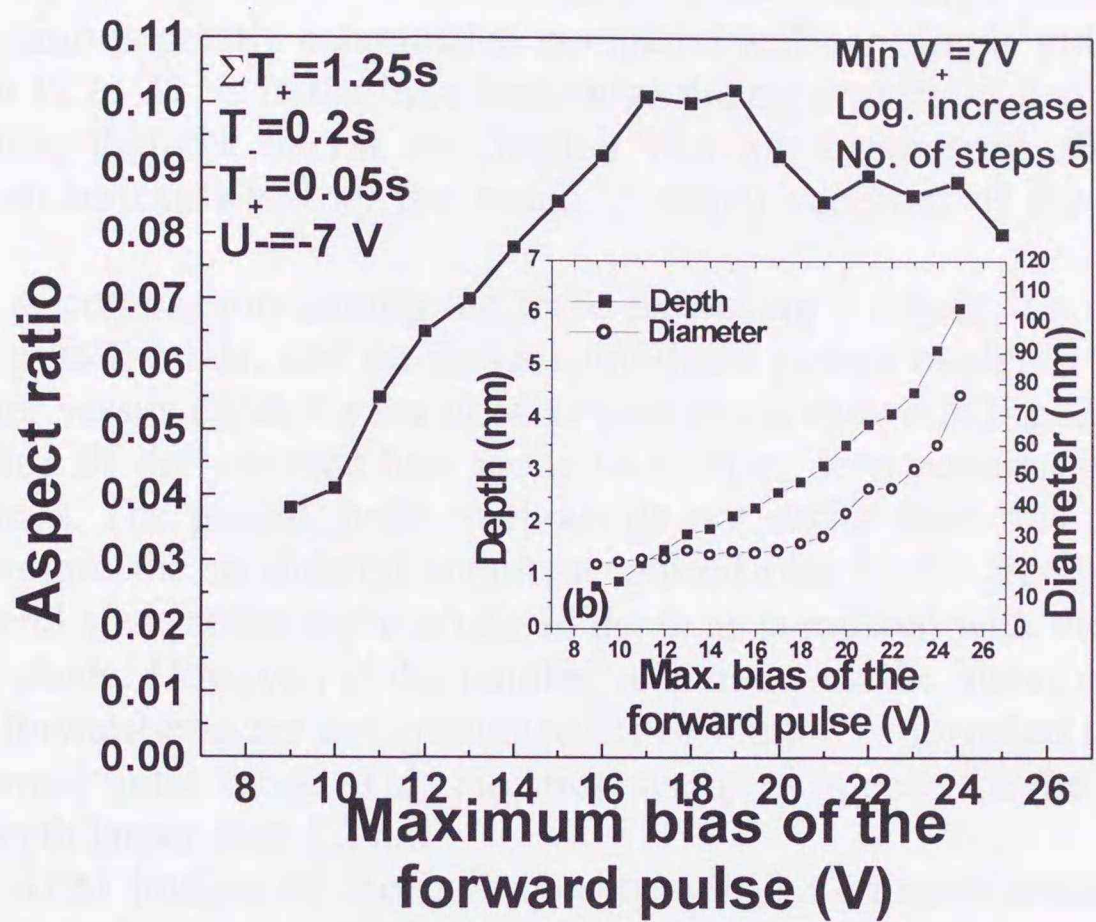


Fig. 2.36 (a) The aspect ratio and (b) the depth and the diameter as a function of the maximum bias of the forward pulse.

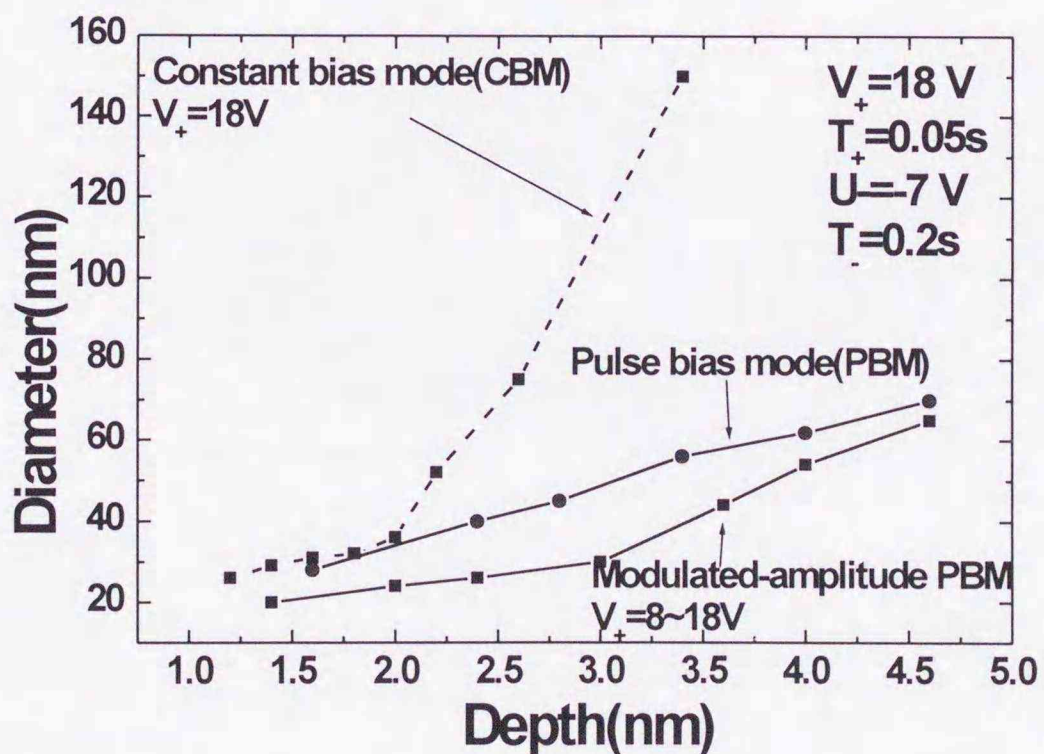


Fig. 2.37 Diameter of the dot-like patterns made with similar anodization parameters. The different depths were accessed by gradually increasing the total patterning time.

The aspect ratio of the pattern depth over the diameter is greatly improved and reaches a value as high as 0.102. The range in which the aspect ratio is greatly enhanced as compared with the simple pulse mode is from 12 to 25 V. In the high bias range the aspect ratio is less than 0.1 indicating that the lateral anodization was not suppressed efficiently. This can be explained by the rough (5 steps) variation of the forward bias.

A comparison among the three patterning methods, i.e. constant mode, pulsed mode, and modulated-amplitude pulsed mode, in terms of diameter versus depth for the dot-like patterns is shown in Fig. 2.37. The limitation of the constant bias mode to anodize deep patterns is clearly evidenced. The pulsed mode methods do not suffer from this problem. Furthermore the modulated-amplitude pulsed bias mode greatly reduce the lateral size for the same accessed depth as compared with the normal pulsed mode. However, if the number of pulses and the increasing steps of the forward bias are not optimized the resolution is degraded to that of the normal pulse mode. This situation seems to appear for the patterns with depth larger than 3.2 nm.

AFM images of the high-density dot-like patterns made by the three methods are presented in Fig. 2.38. The parameters employed are as follows: total patterning time 1.25 s, minimum forward bias 7 V, maximum forward bias 18 V with duration of 0.05 s, reverse bias -7V with duration of 0.2 s, logarithmic increase for the amplitude modulation.

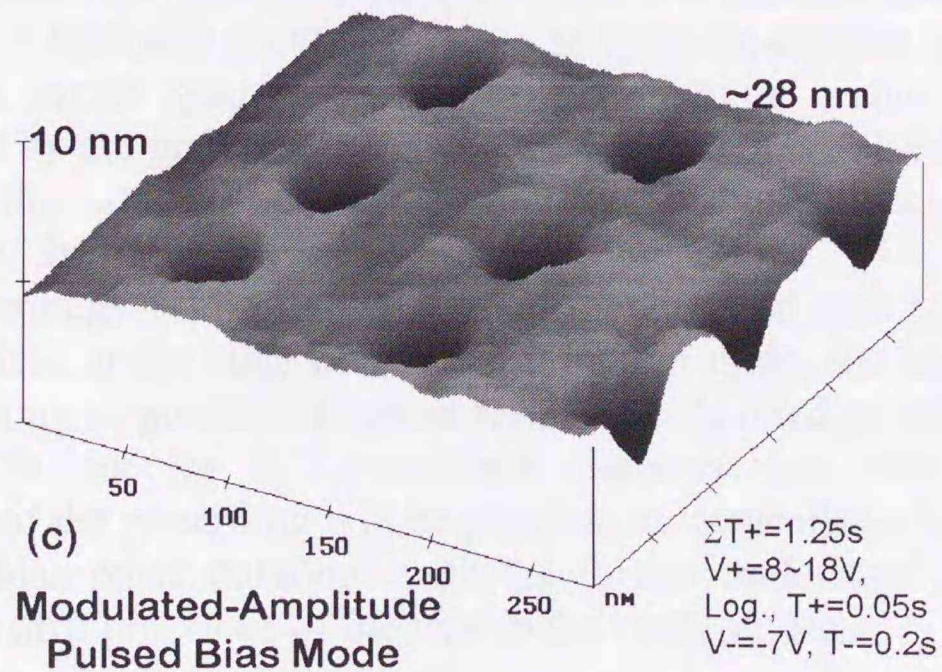
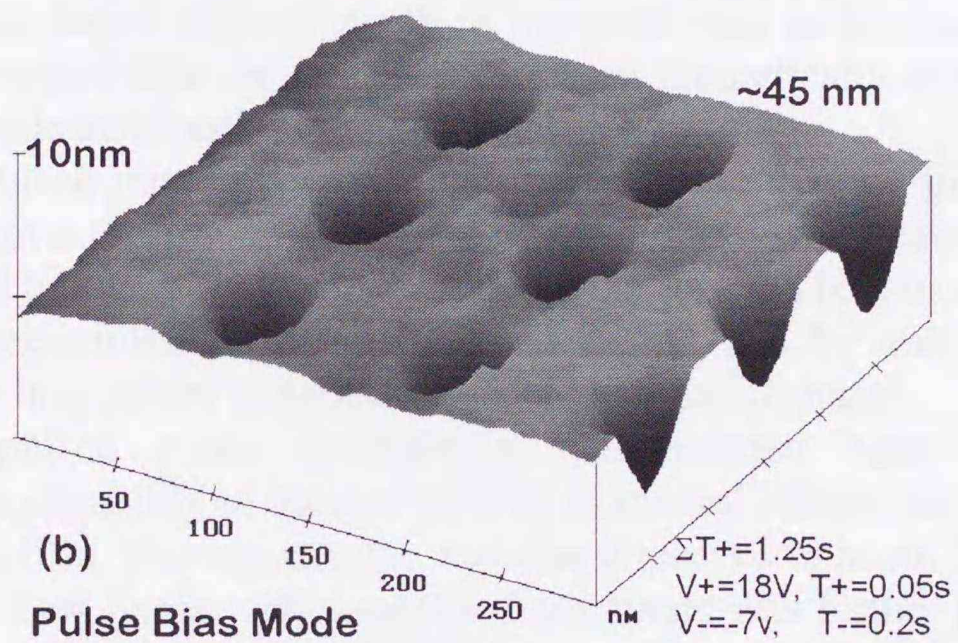
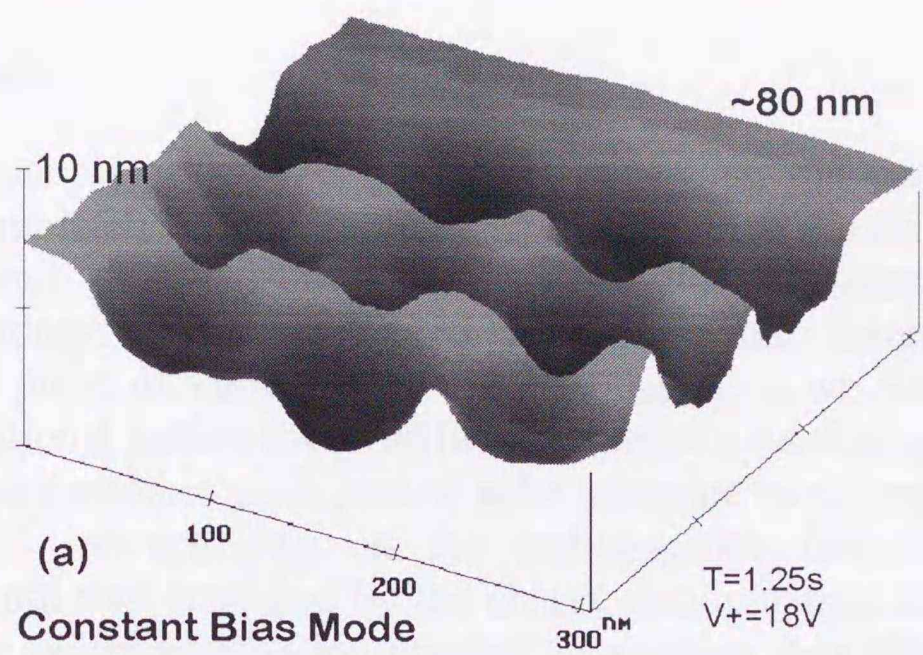


Fig. 2.38 Comparison among the three lithography methods based on electric-field induced anodization. The pitch of the patterns is 100 nm. The thickness of the carbonaceous mask is 2.6 nm.

2.4.4 Summary

The main target of the AFM lithography on the carbonaceous films is to completely oxidize through the film down to the GaAs surface and to achieve simultaneously the high-resolution patterning. The patterning process was investigated both from the theoretical and experimental point of view. Based on the calculation we were able to point the additional factors involved in the patterning resolution.

The constant bias mode proved to be adequate to pattern with high resolution only superficially on the carbonaceous film mask. The patterning depth was saturated by the charge accumulation in the oxide layer and the longer anodization resulted in a severe degradation of the linewidth. The aspect ratio of depth to linewidth was as low as ~ 0.045 . The factors responsible for this situation were theoretically studied and the pulsed-mode anodization was proposed as a solution.

The pulsed mode operation with forward and reverse biases will partially remove the limitation on the vertical anodization rate. This is accomplished by using only short pulses for the forward bias to minimize the charge accumulation in the oxidized region and by subsequently using reverse bias pulses to neutralize the accumulated charge.

The pulsed mode anodization demonstrated better results, especially the capability to oxidize as deep as several nanometers into the carbonaceous film. The aspect ratio was also improved to about 0.07.

The pulsed mode with modulated amplitude was further proposed in order to reduce the lateral anodization rate. The modulated-amplitude pulsed mode is basically providing means to limit the electric field at the edge of the oxide pattern down to a minimum value. This is accomplished by the gradual increase of the forward bias pulse amplitude starting with the value around the anodization threshold to accommodate the increase of the oxide thickness.

This strategy minimized the lateral anodization rate by keeping the electric field at the edge of the oxide pattern under the anodization threshold as long as possible. Highest resolution obtained by this method was about 28 nm for a 2.6-nm-thick carbonaceous film. Further optimization of the patterning will be possible by controlling the forward and reverse bias pulse durations with the further understanding of the diffusion and drift processes of the ions in the oxide region.

2.5 Comparison Between the Mechanical and Electrical-Field Based AFM Patterning Techniques

The mechanical lithography of the PMMA resists coated on SiO_2 films and the electric-field induced anodization of carbonaceous films on GaAs were investigated in detail. Both techniques demonstrated high-resolution patterning capabilities in the scale of several tens of nanometers. Both of the techniques have some unique features. Former one can pattern widely used SiO_2 masks while the latter one in combination with the SEM deposited carbonaceous films can be applied locally.

Table 2.2 summarizes the main differences between the two techniques.

PROPERTY	MECHANICAL LITHOGRAPHY	ELECTRIC-FIELD INDUCED ANODIZATION LITHOGRAPHY
Area	The resist and the mask cover all the wafer surfaces	The mask can be deposited locally, on a limited area
Nature of the wafer	Any	The wafer should have minimal conductive properties
Processing steps	7	5
Patterning speed of lines	0.05~0.1 $\mu\text{m/s}$	1~2 $\mu\text{m/s}$
Patterning speed of a dot	12~14 s	0.5~1.5 s
Ambient	Any	Temperature and humidity well controlled
Final mask resolution	40~45 nm in SiO_2 20~35 nm in PMMA	26~28 nm in carbonaceous film
Further improvements	By sharper tips and resists with better adhesion and etch resistance	By sharper tips, tapping mode, and control of the applied bias parameters

Table 2.2 Main parameters of the two AFM patterning methods

2.6 Summary

The high-resolution lithography with an atomic force microscope was demonstrated. Two different approaches were investigated: the lithography by mechanical modification of soft polymer surfaces and the lithography by chemical modification of carbonaceous films under an intense electric field.

The AFM lithography on PMMA films was demonstrated with high resolution of ~ 20 nm for the wire-like patterns. The issue of lateral forces and the additional marking during the patterning of dot-like structures were revealed and two solutions were proposed. The first one, which is the control of the rate used for the load application, could partially correct the problem at the expense of the resolution. The second one, which consisted in the correction of the lateral motion during the force application, is the more elaborate solution. It demonstrated the complete removal of the additional marks together with the high resolution of ~ 36 nm.

The patterns made in the thin PMMA film were transferred into the SiO_2 film by wet etching. In this process the patterns resolution was reduced. A thinner SiO_2 layer could minimize some of the patterns deformations created during the wet etching process. The minimum feature of 40–45 nm was demonstrated in the SiO_2 mask.

The newly proposed combination of SEM and AFM to locally fabricate high-resolution masks in a simple process would relax some of the limitations inherent to scanning probe lithography. SEM is employed to pattern with the carbonaceous films on a large area and the AFM is used to pattern the carbonaceous films with high resolution.

The AFM patterning by application of an electric field was investigated both from theoretical and experimental point of view. Based on the calculation we were able to point out major factors disregarded in previous works in the anodization patterning.

The electric-field induced oxidization of thin carbonaceous films was demonstrated. The patterning by constant bias application suffered from the low aspect ratio of the patterns. The factors responsible for this situation were identified and the pulsed mode anodization was proposed as a solution. The pulsed bias mode will partially remove the limitation on the vertical anodization rate. This is accomplished by using only short pulses for the forward bias to minimize the charge accumulation in the oxide region, together with the use of the reverse bias pulses that will neutralize the accumulated charge. Pulsed mode anodization demonstrated several-nanometers-deep patterns into the carbonaceous

films. The aspect ratio was improved to about 0.07 and the minimum feature was ~ 45 nm.

The modulated-amplitude pulsed bias mode was further proposed in order to reduce the lateral anodization rate. The electric field at the edge of the oxide pattern was minimized when the forward bias was gradually increased from the anodization threshold of 7 V at the center of the pattern to the higher values, so that the internal electric field is kept just above the threshold during the anodization. The highest resolution obtained by this method was ~ 28 nm for a 2.6-nm-thick carbonaceous film.

These results demonstrated that the AFM lithography has the resolution that makes it possible to obtain nanostructures that show up quantum effects.

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Chapter 3

Design of II-VI materials for bandgap engineering and low-temperature selective area growth

3.1 Introduction

Integration of optoelectronic devices with very fast electronics is currently a field of major interest. High-speed electronics are usually based on III-V compound semiconductors on GaAs substrates and will require appropriate compounds for the integrated optoelectronics, depending on the applications. The most direct approach for the integration of these semiconductor devices will be the selective area growth (SAG). The SAG is necessary to be performed at low temperature for a minimum influence on the electronics already fabricated on the substrate.

A promising application of the SAG is the nanostructures fabrication when this technique is employed with high-resolution masks, such as those described in the second chapter. This will produce high quality nanostructures with lateral size defined by the mask and the vertical size controlled by the growth parameters.

The growth techniques that proved to be the most suitable for SAG were metalorganic vapor phase epitaxy (MOVPE) and metalorganic molecular beam epitaxy (MOMBE). The latter, in special, is very attractive since the growth conditions to achieve selective area growth will cover a wider range due to the lower background pressure. The most representative semiconductor alloys that were grown selectively using a dielectric mask (usually SiO_2 or SiN_x) are the following: GaAs [1], InP [2,3], GaInAs [4,5], and ZnSe [6,7].

II-VI based compound semiconductors will offer some unique characteristics such as emitting blue to yellow wavelengths that are essential in applications such as display panels, high-density optical recording and high-speed optical interconnections. The II-VI compounds require growth temperatures in the range of 250° to 500°C that are lower than those for GaAs [1] or GaN [8].

After the first selective area growth of ZnSe by MOVPE reported back in 1988 [6,7] there was not so much focus on selective area growth of II-VI compounds. Our group reported selective area growth of ZnS and ZnSe by metalorganic molecular beam epitaxy (MOMBE) using SiO_2 masks [9] and the low-temperature SAG of the same compounds

using carbonaceous films [10]. Up to date, only the simple binary alloys were investigated for SAG.

The bandgap requirements for optoelectronic devices are complex and it will be difficult to be fulfilled by using simple binary alloys. Further research is necessary in the SAG of II-VI ternary and quaternary alloys.

This chapter is focused on the design of II-VI compound semiconductors suitable for bandgap engineering and low-temperature selective area growth. A new alloy system of ZnMgCdS/ZnCdS that can be grown lattice-matched to GaAs is introduced. Structural, morphological and optical properties of the grown alloys and control of the Mg composition are discussed for different growth conditions. The influence of the nucleation and initial growth processes on the structural and optical properties of the alloys is emphasized.

3.2 Growth Method

The growth technique employed in the selective area growth of the investigated II-VI compounds was the metalorganic molecular beam epitaxy (MOMBE). The MOMBE is a growth technique that can be included in the broad family of the molecular beam epitaxy (MBE). MBE employs elemental sources to create the molecular beams that will be irradiated on a substrate surface in an ultra-high vacuum environment. Epitaxy takes place by the surface migration of adsorbed species. The growth process of the metalorganic vapor phase epitaxy (MOVPE) involves more complex combinations of gas phase and surface reactions.

MOMBE is basically a MBE technique that introduced the use of metalorganic precursors from the MOVPE. In MOMBE the transport of the precursors is characterized by a molecular flow regime and not by a viscous flow. The metalorganic precursors will be decomposed by the catalytic reactions at the heated substrate surface. There is no boundary layer near the substrate-gas interface, in contrast to MOVPE. The MOMBE, similar to MOVPE, will be capable of selective area growth.

A schematic of the MOMBE system employed in our experiments is drawn in Fig. 3.1. The chamber is equipped with a reflection high-energy electron diffraction (RHEED) apparatus, a quadrupole mass spectroscopy (QMS) system, and a thickness monitor system consisting in a laser diode (LD) emitting at 670 nm and a Si photodetector (PD).

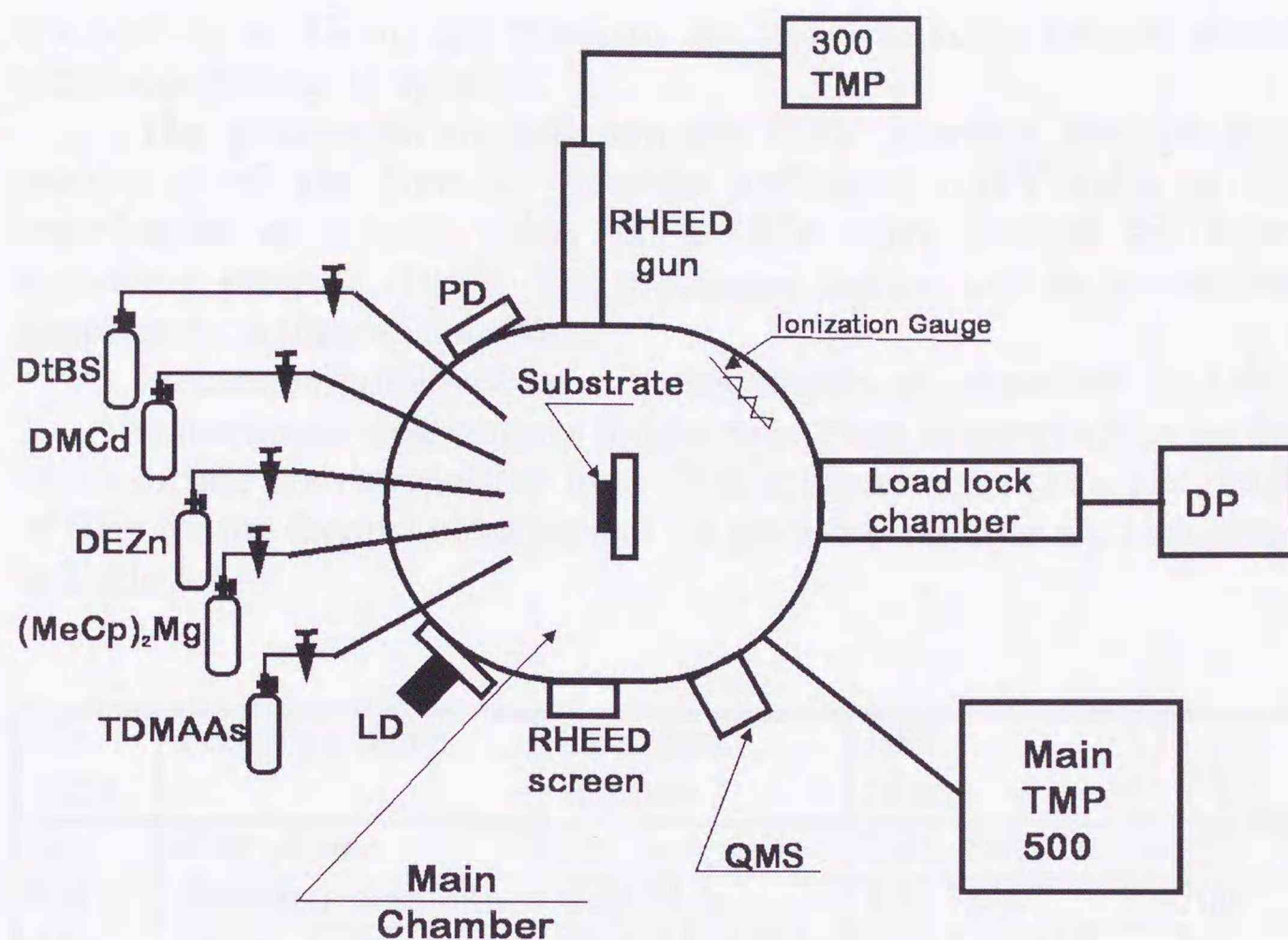


Fig. 3.1 MOMBE reactor schematic draw.

The chamber has a background pressure of $\sim 6.0 \times 10^{-8}$ Torr when it is evacuated with the main turbo-molecular pump (TMP) with the evacuation speed of 500 l/s. During the growth the chamber is evacuated with the diffusion pump (DP) with the rate of 900 l/min.

The sample is mounted on a molybdenum (Mo) substrate holder using indium solder to ensure good temperature uniformity. The sample is introduced into the chamber through an exchange load-lock chamber in order to maintain the UHV in the main chamber. A tantalum heater sandwiched between two ceramic plates heats the substrate holder. The sample temperature can be measured through one of the chamber windows with a pyrometer. The substrate temperature is a very important parameter in the MOMBE growth and should be well stabilized. To maintain a stable temperature, a temperature sensor mounted on the back of the sample holder provides the feedback necessary for the temperature controller to regulate the input power to the substrate heater.

The thickness monitoring system is measuring the intensity of the red laser beam that is reflected from the substrate surface. The refractive index of the II-VI compounds is mostly in the range of 2.2~2.4 and is smaller than ~ 3.4 , which is the refractive index of the GaAs substrate. Therefore the laser light experiences multiple interferences in the grown

epitaxial layer. Using this property the layer thickness can be *in-situ* monitored during the epitaxy.

The precursors are fed into the UHV chamber through pipe nozzles at ~ 5 cm from the substrate surface. A UHV valve or the combination of a leak- valve and a UHV valve controls the beam equivalent pressure (BEP). The precursors bottles kept at a constant temperature in thermostatic bath.

Precursors employed in our experiments are described in Table 3.1. The minimum temperatures for the precursors decomposition on the GaAs surface are extrapolated from QMS measurements [11]. The range of BEP for the thermal cleaning and the growth conditions are also given in Table 3.1.

Element	Precursor name	Chemical formula	BEP (Torr)	$T_{\text{dec.}}$ ($^{\circ}\text{C}$)
Zn	diethyl zinc	$\text{Zn}(\text{C}_2\text{H}_5)_2$	$0.95 \sim 5 \times 10^{-4}$	~ 200
Cd	dimethyl cadmium	$\text{Cd}(\text{CH}_3)_2$	$1.1 \sim 5 \times 10^{-4}$	~ 200
Mg	bis-methyl-cyclopentadienyl magnesium	$\text{Mg}(\text{CH}_3\text{C}_5\text{H}_4)_2$	$1.2 \sim 1.4 \times 10^{-4}$	~ 70
S	ditertiarybutyl sulfide	$\text{S}(\text{t-C}_4\text{H}_9)_2$	$5 \sim 10 \times 10^{-3}$	~ 250
As	trisdimethylamino-arsenic	$\text{As}(\text{N}(\text{CH}_3)_2)_3$	1.0×10^{-5}	~ 375

Table 3.1 MOMBE precursors employed in our experiments. $T_{\text{dec.}}$ indicates the temperature with which the precursors start to decompose on GaAs surface.

Prior to growth, GaAs (001) substrates were chemically cleaned following a standard procedure. The substrates were mounted on Teflon holders and sonically cleaned for 2 minutes in acetone followed by another 5 minutes in boiling acetone. The sample was then sonically cleaned in methanol and water for 2 minutes, respectively. This procedure was used for removing the organic contaminants on the sample surface. The sample was then immersed in concentrated H_2SO_4 for 3 minutes and another 3 minutes in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (4:1:1) at 25°C for mirror etch. After rinsing in pure water a final etch was performed in conc. HCl . After 2-minutes pure water rinse the substrate was dried under nitrogen gas blow.

After loading in the MOMBE system, the GaAs substrates were *in situ* thermally cleaned at 550°C under the TDMAAs beam pressure of 1×10^{-5} Torr. The temperature was increased at a rate of 10°C/min until it reached 550°C and was kept at this value for 10 minutes. The TDMAAs supply was started at 450°C. The temperature was then decreased at a rate of 10°C/min and the TDMAAs supply was cut off at 425°C. This cleaning procedure also provides us with means to control the GaAs surface prior to growth. The GaAs surface can be structured as an As or Ga stabilized one by dosing the TDMAAs beam pressure and controlling the substrate temperature [12].

The RHEED observation provides a very sensitive way to observe changes in the structure of the surface. RHEED was used to monitor the GaAs surface during the thermal cleaning process. The surface structure thus prepared was As-stabilized and characterized by a (2x4) RHEED pattern as shown in Fig. 3.2(a). By the change of the cooling process to a rate of 5°C/min and cut off of the TDMAAs supply at 450°C, the obtained surface structure was changed to Ga-stabilized one and was characterized by a (4x2) RHEED pattern as shown in Fig. 3.2(b).

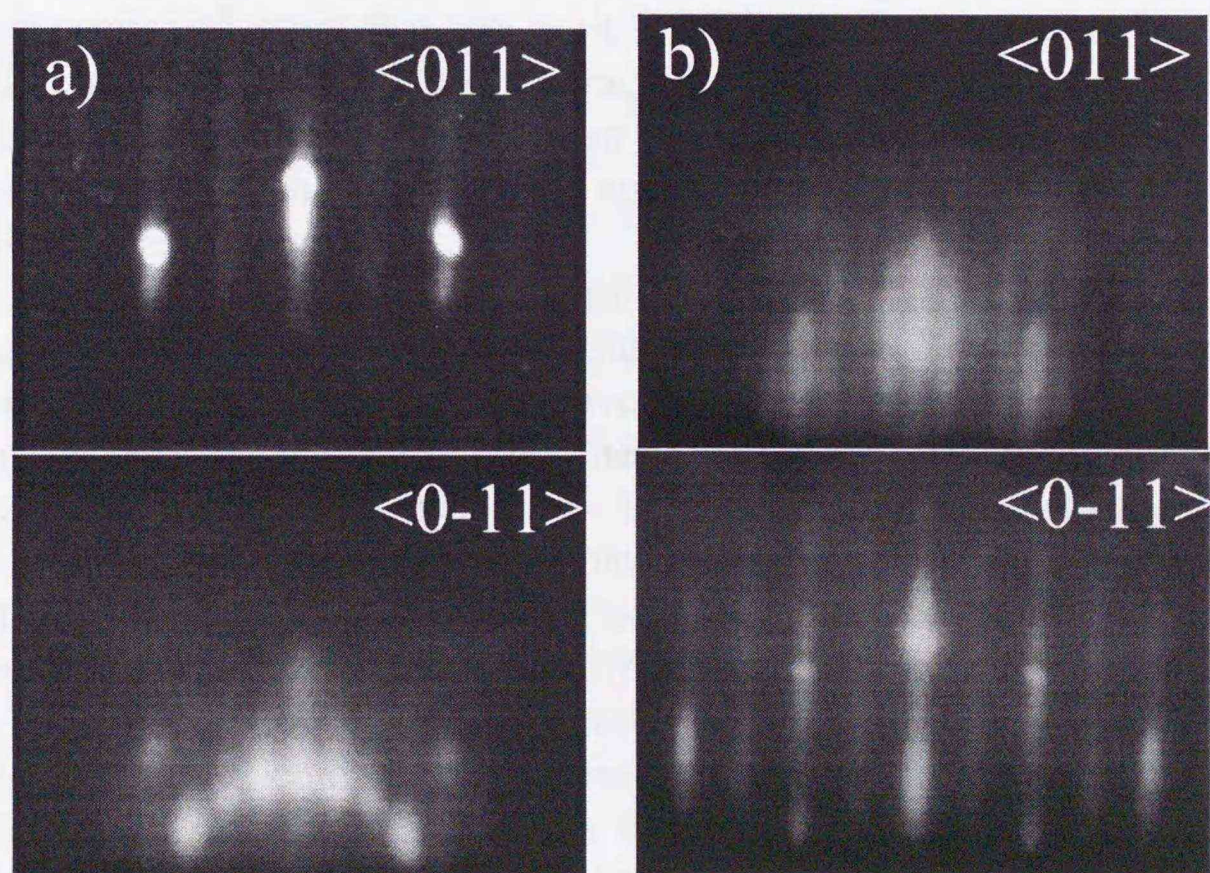


Fig. 3.2 a) RHEED patterns of (2x4) As stabilized GaAs surface b) RHEED patterns of the (4x2) Ga stabilized GaAs surface

The effect of the thermal cleaning in the openings of the patterns made in SiO₂ films and carbonaceous films was investigated. In the case

of carbonaceous films the thermal cleaning produced a 2~4-nm-deep etch inside the patterns with less than 100 nm width. In the case of SiO_x film with patterns defined with the comparable diameter the etched depth reached to 25~35 nm. The shallower etched depth in the carbonaceous mask case may suggest the lower yield for the decomposition and migration of the metalorganic molecules on the mask surface. Alternatively, it may be due to the faster etch of the GaAs surface as a consequence of the surface defects induced by the strain related to the SiO_2 film.

The growth of both ternary and quaternary alloys was initiated at a low temperature of 300°C using the sequence discussed later. The growth of the II-VI was performed in the range 310°C to 425°C.

3.3 Why II-VI Compound Semiconductors

The main features of the II-VI compound semiconductors will be reviewed in order to point out the reasons why this system was selected for fabricating nanostructures by selective area growth. The wide bandgap semiconductors that can emit light from ultra violet region to the visible region such as red have attracted a major interest. The interest was fuelled by the target of 400 nm that was decided for the next generation of DVDs and also by other applications such as panel displays that will require visible light.

The II-VI compounds are based on the group II cations such as Be, Mg, Zn, Cd and group VI anions such as O, S, Se, Te. The chemical bond in these compounds will have a large ionic component in comparison with III-V compounds. The large ionicity will put a special fingerprint on the physical properties. Bulk properties such as bandgap energy and its alignment at the heterointerfaces or surface and interface properties such as surface reconstruction and interface with the III-V compounds will be greatly influenced by the large ionicity.

The first semiconductor laser diode in the blue-green region was reported in the II-VI compound semiconductor system, ZnCdSe/Zn(S)Se , by Haase et al. in 1991 [13]. A laser diode with more than 100 hours lifetime operation at room temperature was reported in 1996 by Taniguchi et al. [14]. This laser diode was based on the system $\text{Zn}_{1-x}\text{Mg}_x\text{S}_y\text{Se}_{1-y}/\text{ZnS}_y\text{Se}_{1-y}/\text{Zn}_{1-x}\text{Cd}_x\text{Se}$.

But not only the blue-green region, the II-VI compound semiconductors can cover a wide range of emitting wavelength. As a demonstration of this capability, red-green-blue photopumped lasing was

reported from ZnCdMgSe/ZnCdSe quantum well laser structures grown on InP [15].

In Fig. 3.3 the bandgap energies and the corresponding wavelengths are given as a function of the lattice constant. In this figure the narrow band gap II-VI alloys based on Hg were not included. The II-VI compound semiconductors can be grown in a zinc-blende crystallographic structure. This property makes it possible to grow on already developed substrates such as GaAs, InP, or GaP provided that the lattice mismatch is not very large.

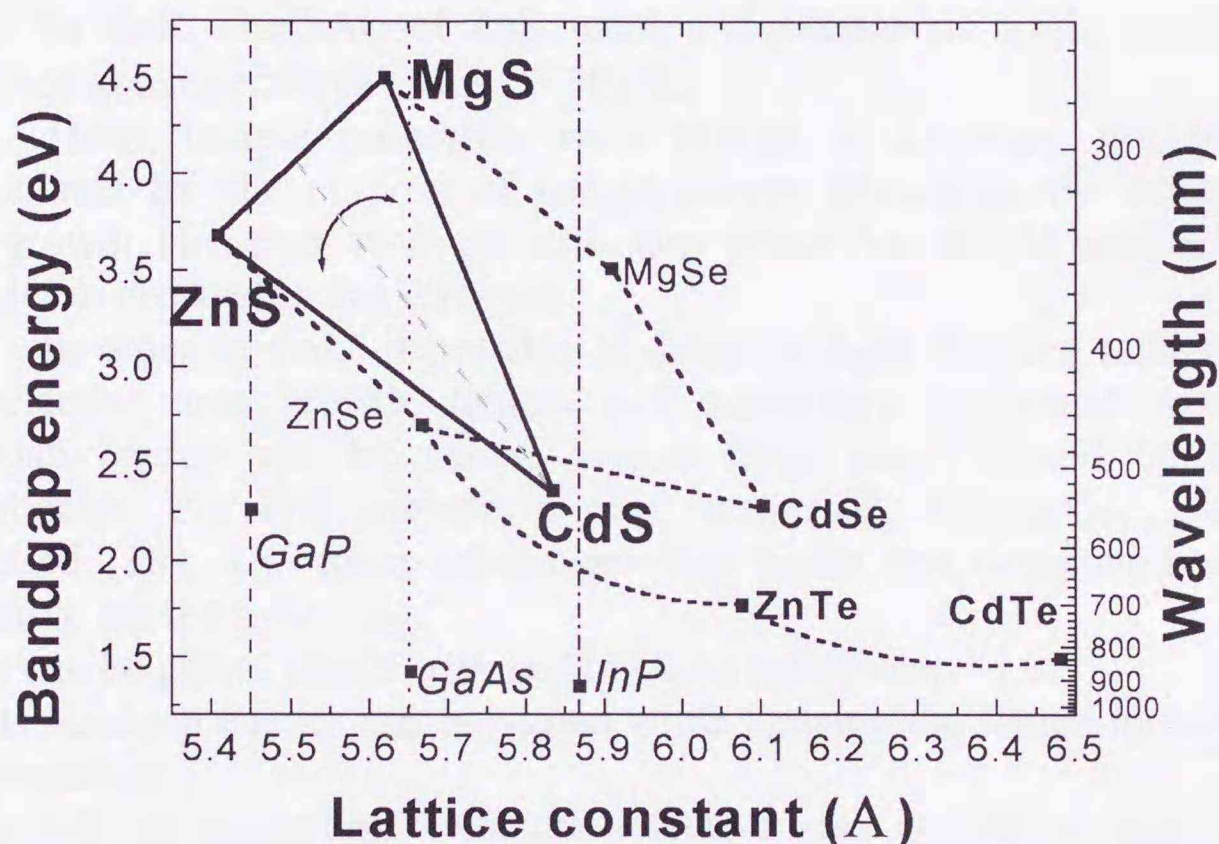


Fig. 3.3 Bandgap energy versus lattice constant for the II-VI compounds. Three possible choices for III-V based substrates are also showed: GaP, GaAs, InP.

The range of energies covered by the II-VI system is quite broad. This extends from 1.49 eV for CdTe up to 4.5 eV [16] or 5.15 eV [17] that are the reported bandgap energy of the MgS in zinc-blende structure.

Another promising feature of the wide gap II-VI compound semiconductors is the large exciton binding energies of 30.2 meV for CdS or of 35.7 meV for ZnS. This large value makes the observation of excitonic phenomena possible up to room temperature.

From the point of view of crystal growth the II-VI materials can be grown at lower temperatures than the III-V compounds. The II-VI alloys have been grown by MBE, MOMBE, low-pressure and

atmospheric pressure MOCVD. Depending on the growth method the growth temperatures were situated in the range from 250 to 500°C. This low temperature makes these alloys promising candidates for monolithic optoelectronic integration.

Moreover the selective area growth (SAG) of II-VI alloys by MOVPE was reported in combination with SiO₂ masks [6,7]. A further development came with the report of the selective area growth of ZnS and ZnSe by MOMBE, which decreased the growth temperature to around 500°C [9]. A further reduction of the growth temperature came with the use of carbonaceous films as a mask [10]. However, the Se compound, ZnSe, could be selectively grown only for temperatures higher than 390°C and the reproducibility of the selective growth was better for ZnS. The SAG of ZnS, using a carbonaceous mask, could be achieved at temperatures as low as 300°C.

These unique properties were crucial in choosing the II-VI compounds for the purpose of nanostructures fabrication by selective area growth. However, there are still many points that should be clarified in order to proceed in this direction.

In order to make it possible to fabricate light emitting structures by selective area growth, ternary and quaternary compounds whose bandgap energy can be varied over a large range should be also investigated. For this purpose, a new compound, Zn_xMg_yCd_{1-x-y}S, is proposed [18]. The main advantages that make this compound very attractive are the following:

- 1) it can be grown lattice-matched to GaAs substrates;
- 2) its bandgap energy can be varied while keeping the lattice-matching conditions;
- 3) it will be compatible with the selective area growth at very low temperature.

The Zn_xCd_{1-x}S alloy, which can be also grown lattice-matched to GaAs [19] and is also Se-free, will be the natural choice for the active layer in a heterostructure fabricated by SAG. As can be seen in Fig. 3.3 the dashed line indicates the possible variation in the bandgap energy of the Zn_xMg_yCd_{1-x-y}S quaternary alloy. Starting with the Zn_xCd_{1-x}S ternary alloy the quaternary bandgap energy will increase with the Mg composition and will reach the maximum value of the Mg_xCd_{1-x}S ternary alloy.

We can also speculate that the Se-free compounds will have larger defect formation energy since the chemical bond of the group II cations with S is stronger than that with Se. For example, ZnS's melting temperature is 1720°C as compared with 1526°C for the ZnSe. The

properties of the $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ quaternary alloys and the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ternary alloys will be discussed in the next subsection.

3.4 New S-based II-VI Compounds for Selective Area Growth

3.4.1 Bandgap energy estimations

The Zn and Mg contents for the $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ alloy that is lattice-matched to GaAs and the theoretical estimation of the bandgap energy at these compositions are presented in Fig.3.4. For this estimation the following parameters were employed.

Compound	Lattice constant (Å)	Bandgap energy at 300K (eV)	Reference
MgS	5.62	4.5*	20
ZnS	5.409	3.684	20,21
CdS	5.835	2.42	20

Table 3.2 The parameters considered for the bandgap estimation of the $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ alloy, and composition estimation for the lattice-matching to GaAs (5.6533).

The lattice constant of the $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ alloy was calculated using the Vegard law as follows:

$$a_{\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}} = x a_{\text{ZnS}} + y a_{\text{MgS}} + (1-x-y) a_{\text{CdS}}, \quad (3.1)$$

where a_{ZnS} , a_{MgS} , a_{CdS} are the lattice constants of the respective binary compounds. The Mg composition, y , for the lattice matched condition to GaAs is given by the following equation as a function of the Zn composition, x :

$$y = 0.8451 - 1.9813x. \quad (3.2)$$

The energy gap of the corresponding alloy is calculated with the expression:

$$E_{\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}} = xE_{\text{ZnS}} + yE_{\text{MgS}} + (1-x-y)E_{\text{CdS}}, \quad (3.3)$$

* 4.5 eV was initially reported. Recently, several groups (Sony, NEC, included ours [17]) have been considering that the bandgap of MgS in ZB structure is much wider.

where the E_{ZnS} , E_{MgS} , E_{CdS} are the bandgap energies of the binaries. In this estimation the bandgap bowing was neglected.

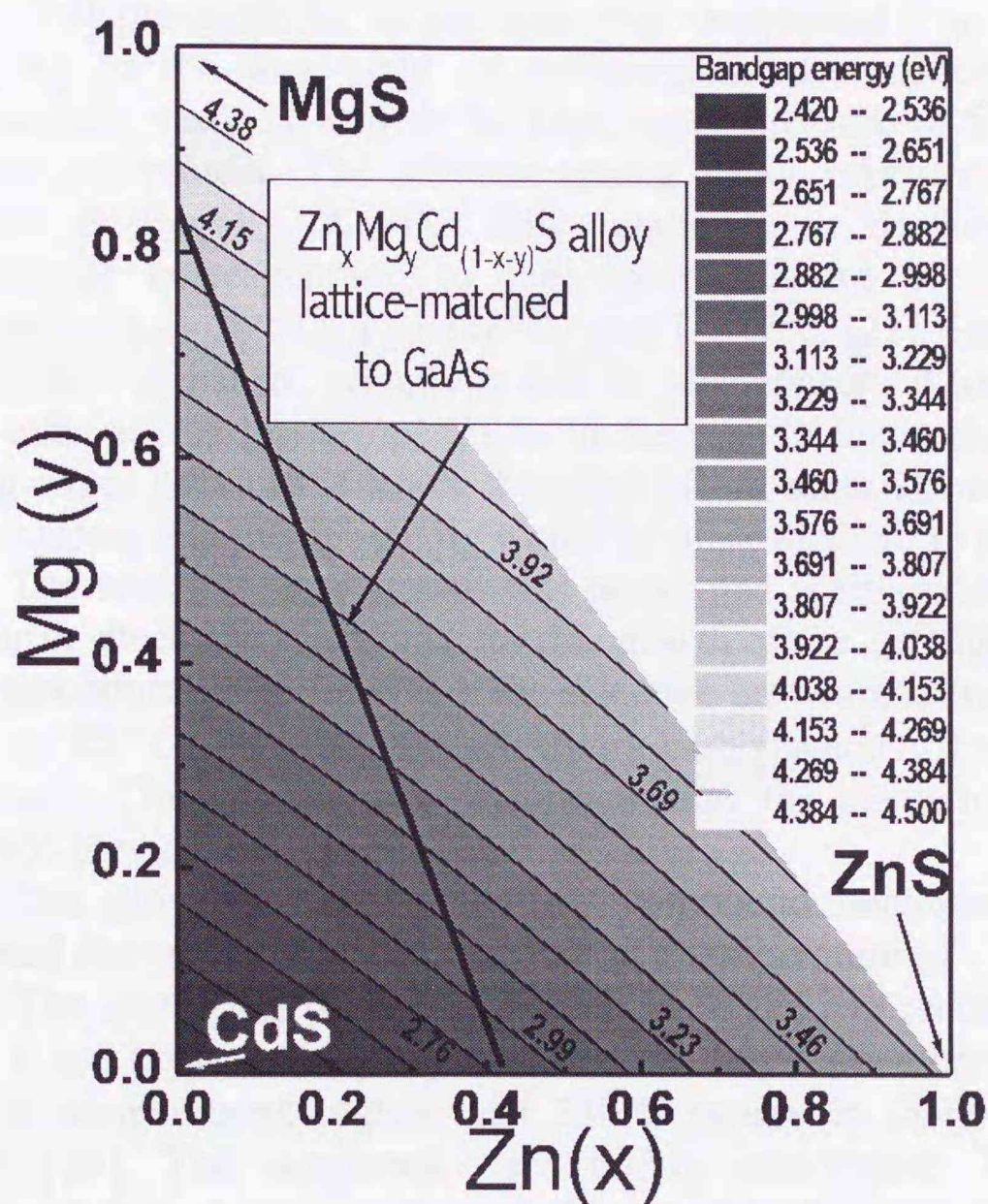


Fig. 3.3 The Zn and Mg compositions for the $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ alloy that is lattice-matched to GaAs and the theoretical estimation of the bandgap energy at room temperature.

From Fig. 3.3 one will note the wide range in which the band gap can be controlled under the lattice-matching condition. Considering the ZnCdS alloy as the active layer, the heterostructure band offsets will be mainly given by the Mg incorporation and will have a large value even for a modest Mg incorporation. The ZnCdS/ZnMgCdS heterostructure will assure enough carrier confinement even at room temperature since

its bandgap difference can be as high as ~ 600 (800) meV for the Mg incorporation of $x \sim 0.5$.

3.4.2 Selective area growth of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ and $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ alloys

The previous results on the ZnS selective area growth down to 300°C [10] prompted us to attribute this exceptional low temperature selectivity to the low yield of metalorganic decomposition on the carbonaceous mask as well as the high vapor pressure of S, the alloy's chemical constituent. The relation among vapor pressure of the four elements is $P_{\text{Mg}} < P_{\text{Zn}} < P_{\text{Cd}} < P_{\text{S}}$. This relation was derived from the temperatures corresponding to the vapor pressure of 1×10^{-5} Torr: $T_{\text{Mg}} = 282^\circ\text{C}$, $T_{\text{Zn}} = 209^\circ\text{C}$, $T_{\text{Cd}} = 146^\circ\text{C}$, and $T_{\text{S}} = 37^\circ\text{C}$ [22]. Based on this, one can expect that the selectivity will be also conserved for the ZnCdS alloys even at this low temperature. In the case of the quaternary alloy, the Mg vapor pressure is lower than that of the other elements and one would suspect that the selectivity would be more difficult to accomplish.

The selective area growth was performed at several temperatures in order to check the selectivity for the growth of the Zn(Mg)CdS alloys. The temperature range for which the selective growth was tried was from 310°C to 425°C . To check the selectivity carbonaceous films were used as a mask. The growth was performed after the cleaning procedures described previously.

The growth of the quaternary compound containing Mg was attempted directly on the GaAs surface at a temperature of $\sim 350^\circ\text{C}$ but it failed. The reason for this is considered to be the Mg reaction with the GaAs. It has been recently reported that the Mg deposition on GaAs by MBE at temperatures higher than 230°C results in three-dimensional growth [23]. The structures were highly anisotropic. The authors considered that these are formed due to the chemical reaction that produces the Mg_3As_2 compound in a face-centered-cubic phase. The formation of such a phase will explain the growth inhibition in the case of direct quaternary growth on GaAs.

Therefore, the growth of the quaternary was performed on a ZnCdS buffer layer. The ~ 10 -nm-thick buffer layer will prevent Mg to interact with the GaAs substrate. The similar behavior was reported for the ZnMgCdSe growth on InP by MBE [24]. A ZnCdSe ternary buffer layer demonstrated a large improvement in the crystalline properties of the epilayers.

If the loss of selectivity in the case of ZnMgCdS would be considered as due to the small imperfections in the 2-nm-thick

carbonaceous mask, the reaction of Mg with GaAs underneath the mask will prevent the growth. The selectivity for the growth of the Zn(Mg)CdS alloys with carbonaceous masks was confirmed experimentally for temperatures as low as 310°C. Figure 3.4 shows the AFM image of the $\text{Zn}_{0.26}\text{Mg}_{0.15}\text{Cd}_{0.59}\text{S}$ -based structures selectively grown at 360°C with a carbonaceous mask. The quaternary alloy composition was measured by electron probe microanalysis (EPMA).

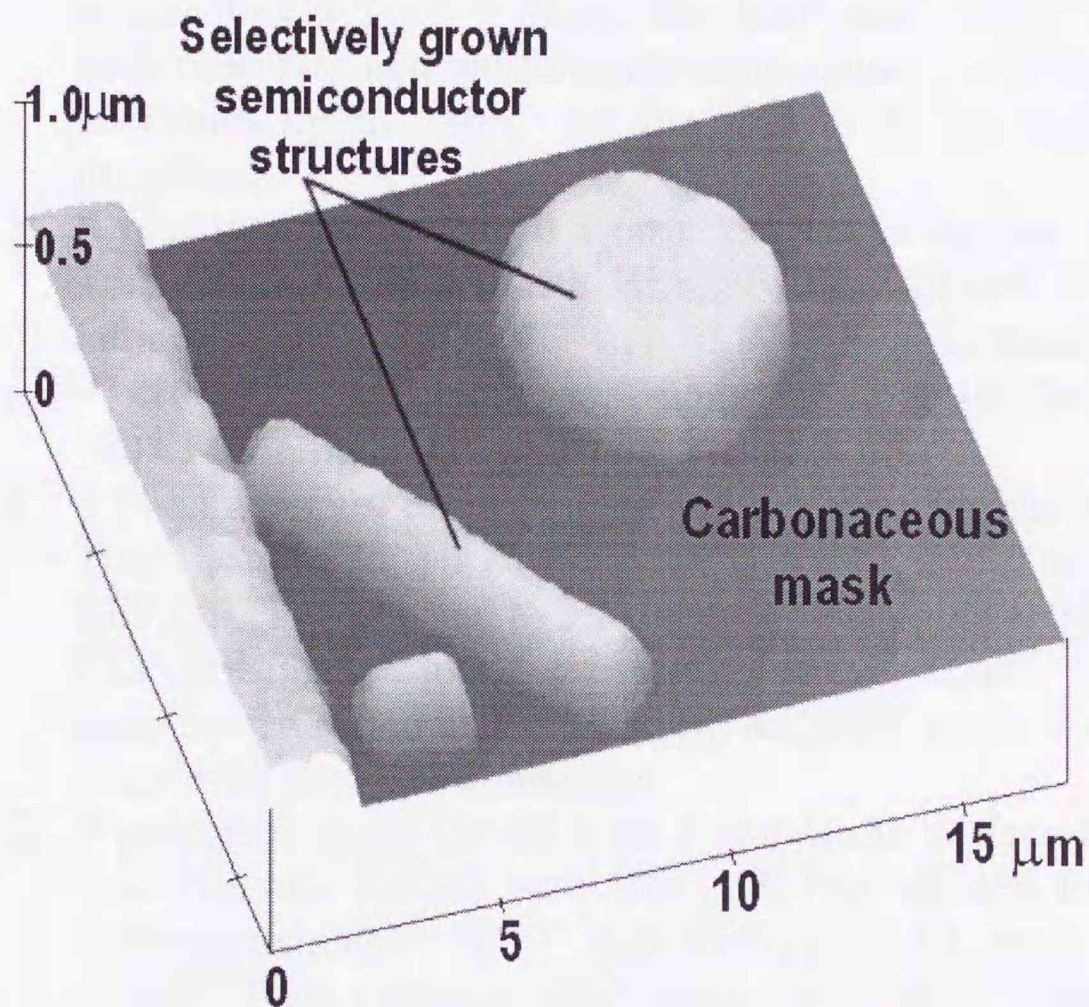


Fig. 3.4 The $\text{Zn}_{0.26}\text{Mg}_{0.15}\text{Cd}_{0.59}\text{S}$ -based structures selectively grown at 360°C with a 2.5-nm-thick carbonaceous mask. The thickness of the epilayer in the maskless area was about 500 nm.

The selective growth of the Zn(Mg)CdS ternary and quaternary alloys were confirmed regardless of the VI/II ratio employed during the growth. This characteristic assures that the crystalline and optical properties of the alloys will be optimized without any restrictions to achieve selective growth with the carbonaceous masks.

3.4.3 Nucleation and initial growth effect on the alloys crystalline properties

The growth of the Zn(Mg)CdS alloys was performed after a low-temperature nucleation step at 300°C. For this purpose four different nucleation initiations and initial growth processes were investigated. These are described in the following.

- A. The following irradiation sequence: [Zn 5s/ Pause 30s/ S 5s/ Pause 30s/Cd 5s] x 5 times. The BEP was $\sim 1 \times 10^{-5}$ Torr for each precursor and the substrate temperature rise at the rate of 10°C/min up to 380°C for the growth at the higher total pressure.
- B. S precursor purge for 10 s on a 2x4 GaAs surface at 1×10^{-5} Torr /10 min ZnCdS with $\text{BEP}_{\text{Zn}}/\text{BEP}_{\text{Cd}}$ adjusted to 2.1 for lattice-matching at 300°C and $\text{BEP}_{\text{VI}}/\text{BEP}_{\text{II}}=1$, total pressure $\sim 3 \times 10^{-5}$ Torr/ substrate temperature raised at 10°C/min up to 380°C for growth at higher total pressure.
- C. S precursor purge for 10 s on a 2x4 GaAs surface at 1×10^{-5} Torr/10 min Zn purge at 1×10^{-5} Torr/10 min ZnCdS with $\text{BEP}_{\text{Zn}}/\text{BEP}_{\text{Cd}}$ adjusted to 2.1 for lattice-matching at 300°C and $\text{BEP}_{\text{VI}}/\text{BEP}_{\text{II}}=1$, total pressure $\sim 3 \times 10^{-5}$ Torr/ substrate temperature raised at 10°C/min up to 380°C under Zn and Cd purge with the same conditions.
- D. S precursor purge for 60 s on a 2x4 GaAs surface at 1×10^{-5} Torr /10 min ZnCdS with $\text{BEP}_{\text{Zn}}/\text{BEP}_{\text{Cd}}$ adjusted to 2.1 for lattice-matching at 300°C and $\text{BEP}_{\text{VI}}/\text{BEP}_{\text{II}}=1$, total pressure $\sim 3 \times 10^{-5}$ Torr/ substrate temperature raised at 10°C/min up to 380° under Zn and Cd purge with the same conditions.

The smoothness of the nucleation-layer surface grown at 300°C under the conditions described in B, C, D was checked by atomic force microscopy (AFM) and was found to have a root mean square (RMS) value of 0.156 nm. The RHEED pattern after the substrate temperature has reached the growth temperature (mainly 380°C) was streaky (1x1) configuration.

The growth was performed at a higher total pressure with the chamber being evacuated with the diffusion pump changing from the turbomolecular pump for the above nucleation process. In the case of the quaternary, the Mg precursor started to be supplied after the ternary buffer layer reached a thickness of ~ 10 nm.

The influence of the nucleation layer was best examined in the case of the quaternary alloy. A set of samples were grown with the 4 different initial conditions described above and were brought up to 380°C. After the 10 nm of buffer layer, ~420-nm-thick quaternary layers were grown with similar growth conditions. The crystalline properties were measured by X-ray diffraction. The rocking curve and the θ -2 θ measurements are given in Table 3.3.

Initial process	A	B	C	D
θ -2 θ (002)FWHM (sec.)	690	656	438	360
Rocking curve (002)FWHM (sec.)	1325	1253	751	549

Table 3.3 The FWHM of the (002) θ -2 θ XRD peak and of the rocking curve θ for the A, B, C, D initial growth processes.

Better results were obtained in the case of process D. This can be explained by the longer purging time of the S on the initial surface that increases the nucleation probability. Additional explanations will be given in the next chapter. The exact contribution of each step in these four processes is not understood at this time, but these results can be the starting point for further investigations.

3.4.4 Structural and optical properties of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ alloys

The crystalline properties of the epilayers were investigated by X-ray diffraction in two diffraction geometries (004) and (002). The XRD apparatus is equipped with 4-crystals monochromator and is suitable for the analysis of thin epitaxial layers. From the XRD measurements of the epilayers, lattice constants and ternary alloy compositions were derived. The surface morphology was characterized by AFM observations in the tapping mode.

The optical properties were investigated by micro photoluminescence under the excitation provided by a 10 mW He-Cd laser and by micro-reflection measurements with Halogen or Xe lamp. The size of the laser spot focused with an objective lens with a magnification of 80 was approximately 2 μm . The incoherent light from the lamp was focused to a spot with a diameter of about 5 μm . The measurements were performed at room temperature under vacuum conditions.

The growth of ZnCdS was performed by MOMBE. The GaAs (001) wafer were chemically cleaned and *in situ* thermally cleaned as described in section 3.2. A growth initiation was performed at low temperature as described in the previous section.

In order to achieve the lattice-matched conditions several experiments were performed first on the ternary system. The first set of experiments was conducted in order to understand the growth temperature dependence of the alloy compositions and of the optical properties. Figure 3.5 shows the dependence of the alloys composition and the linear function that it will approximate this dependence in the temperature range under investigation. The Cd is more volatile than the Zn and therefore it will be less included in the ZnCdS alloy as the growth temperature is increased. Figure 3.6 shows the dependence of the photoluminescence (PL) intensity on the growth temperature. One can conclude that the samples grown in the range of 380°C to 405°C will show the best optical properties. Figure 3.7 shows the dependence of the alloys growth rate on the growth temperature. The growth temperatures in the range from 370°C to 400°C will give the highest growth rates. Based on these dependences we decide to focus the growth experiments on the growth temperature of 380°C.

Figure 3.8 shows the dependence of Zn composition on the ratio of the equivalent beam pressures of the Zn to Cd precursors and on the relative Zn composition of the irradiated beams. The growth was performed at the temperature of 380°C with the VI/II ratio of 30. The dependence of the Zn composition on the ratio of BEP(Zn) to BEP(Cd) was very well approximated with a linear function that is given in the figure. The Zn composition in the solid phase (x) is correlated with the relative Zn composition of the irradiated beams ($\text{BEP}_{\text{Zn}}/(\text{BEP}_{\text{Zn}}+\text{BEP}_{\text{Cd}})$) by a second order polynomial function that is also given in the figure. The non-linearity is introduced by the large difference in the vapor pressure of the Zn and Cd constituents. The continuous dependence diminishes the possibility for existence of any immiscibility gap in the epitaxial ZnCdS alloy grown at 380°C.

These three continuous dependences make it easy to control the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ composition for any growth temperature. The first application was the control of the BEP of the Zn and Cd precursors during the growth initialization at 300°C. The main target was to obtain the pseudo-morphological growth of the ZnCdS alloy on the GaAs substrate. This could be easily accomplished using the dependences that were derived above.

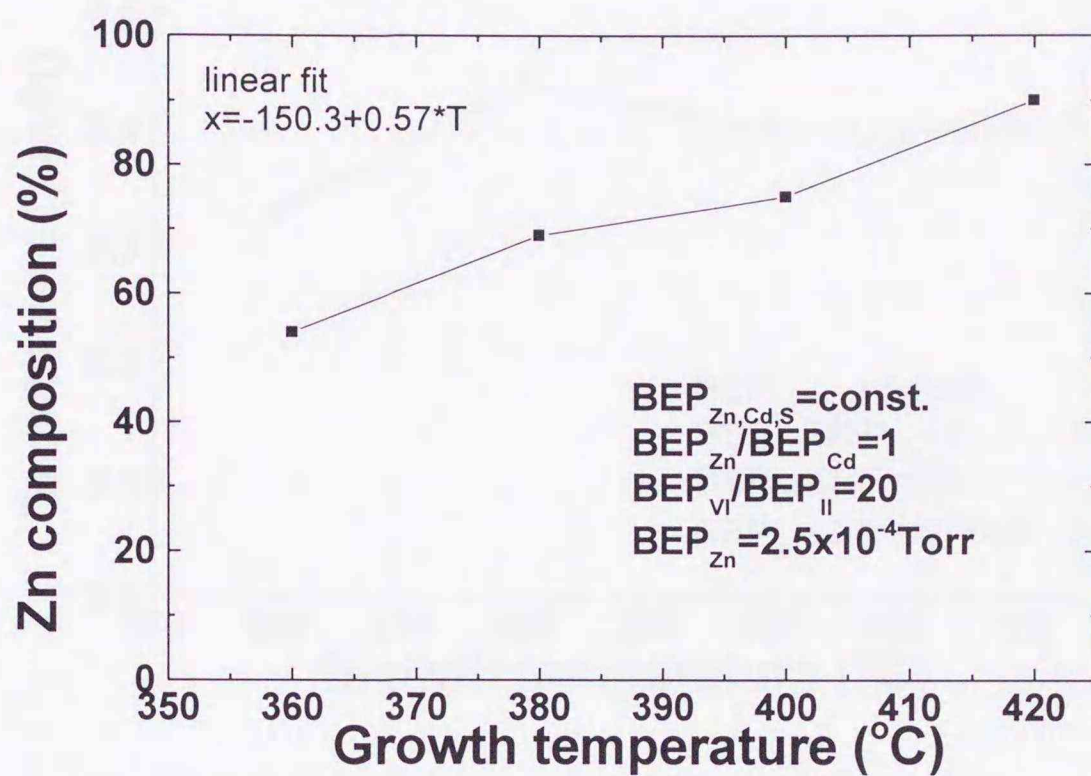


Fig. 3.5 growth temperature dependence of the Zn composition in ZnCdS. The growth conditions are indicated in the figure. A linear fit of this variation provided the equation $x(T)$.

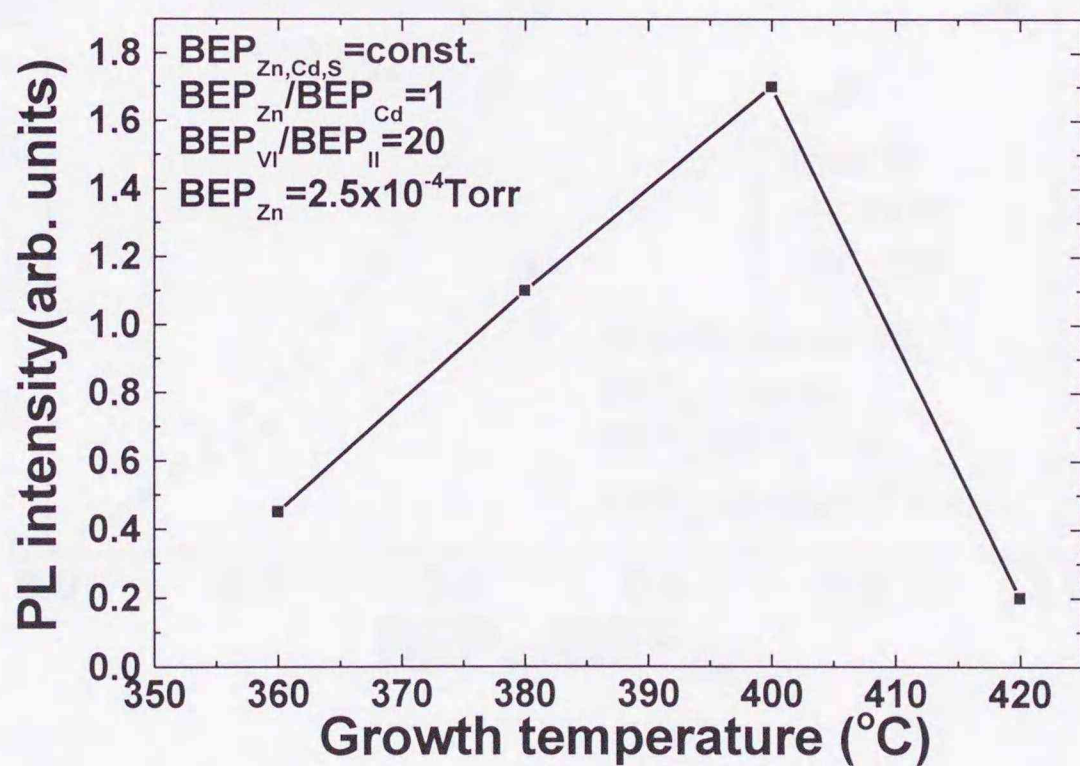


Fig. 3.6 The PL intensity dependence on the growth temperature.

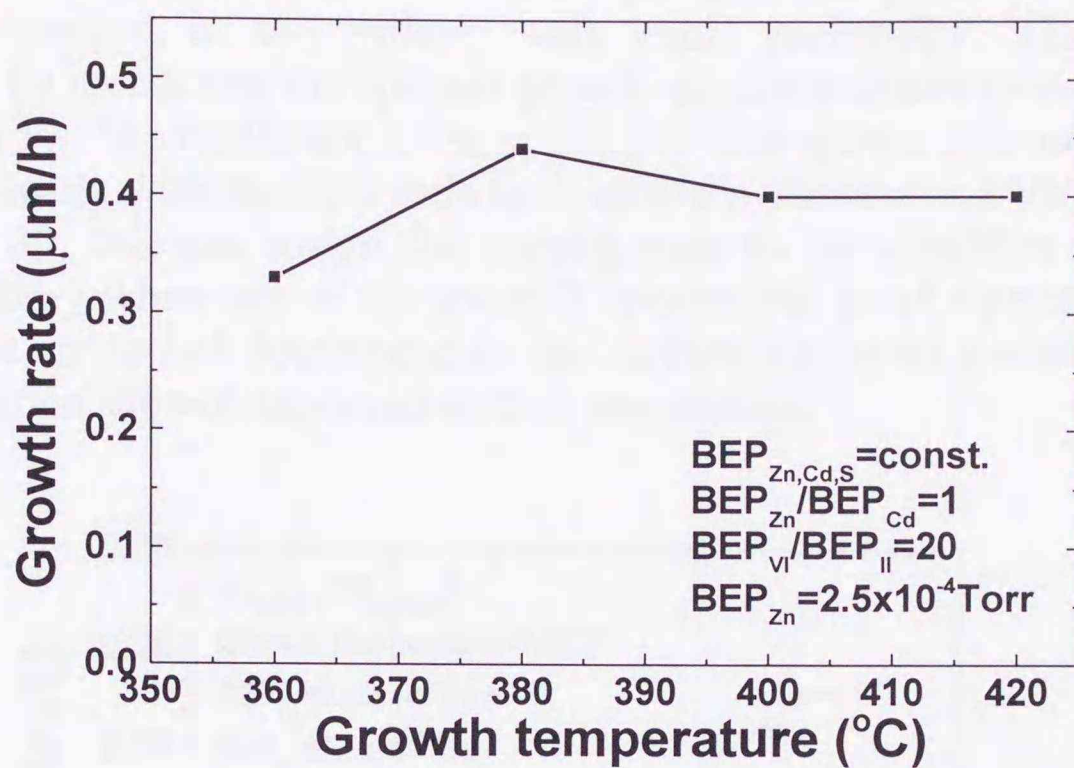


Fig. 3.7 Growth rate dependence on the growth temperature.

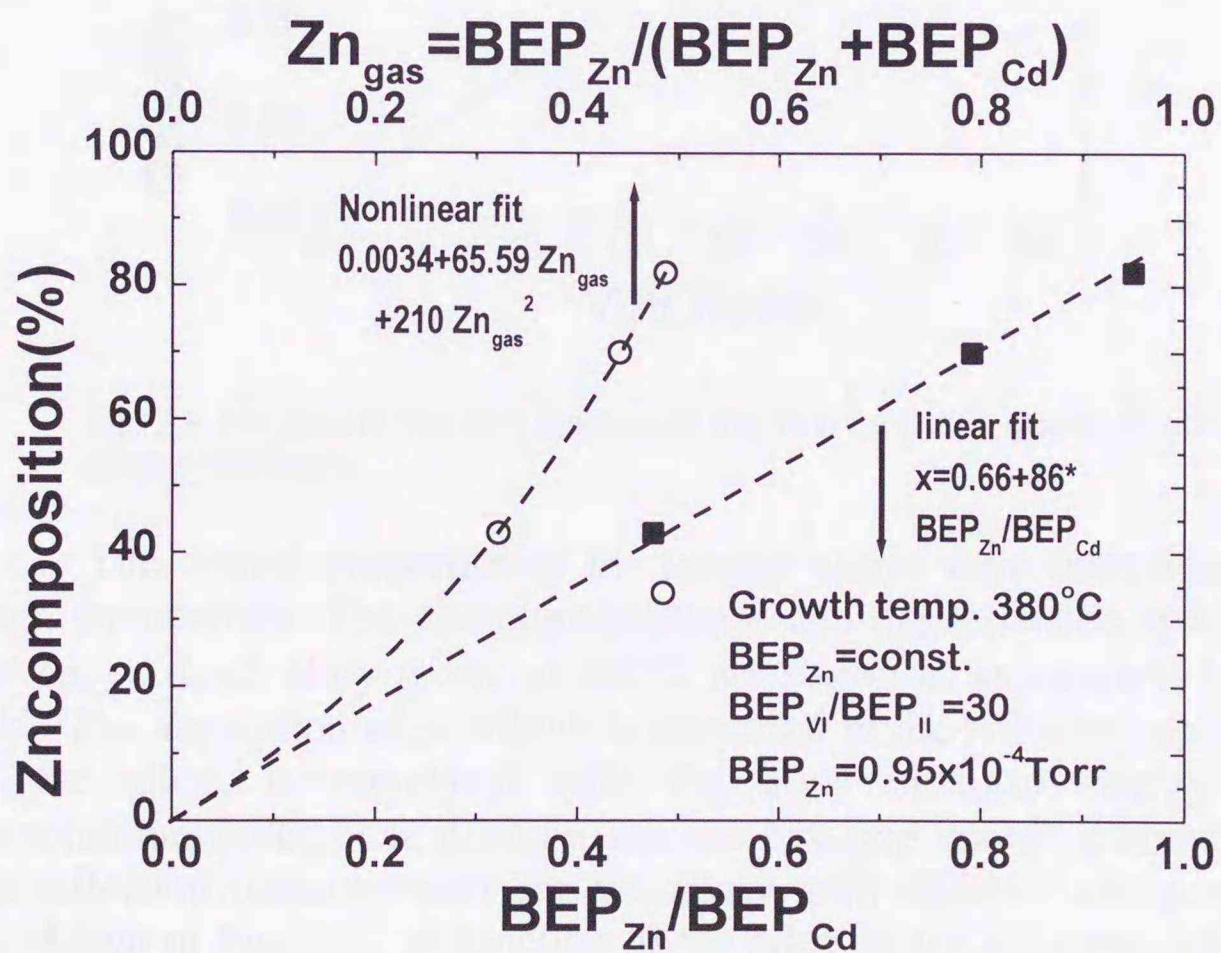


Fig. 3.8 The Zn composition dependence on the Zn over Cd equivalent beam pressures and the dependence of the Zn composition in the solid phase as a function of the Zn composition in the gas phase are plotted. The growth conditions are given in the figure.

In order to obtain high-quality ZnCdS epilayers, it should be determined the BEP ratio, for which the group II and group VI species are incorporated in the epilayer with equal probability. This was achieved by monitoring the epilayer growth rate for different ratios of the $\text{BEP}_{\text{VI}}/\text{BEP}_{\text{II}}$. The results are given in Fig. 3.9. The growth rate increased almost linearly with the VI/II ratio and reached a plateau for a VI/II ratio of about 30. One can assign this turning point to the condition for the stoichiometry when any of the group II species will bond with the S as soon as it arrive and decompose on the surface. Epilayers grown under this condition showed improved surface smoothness.

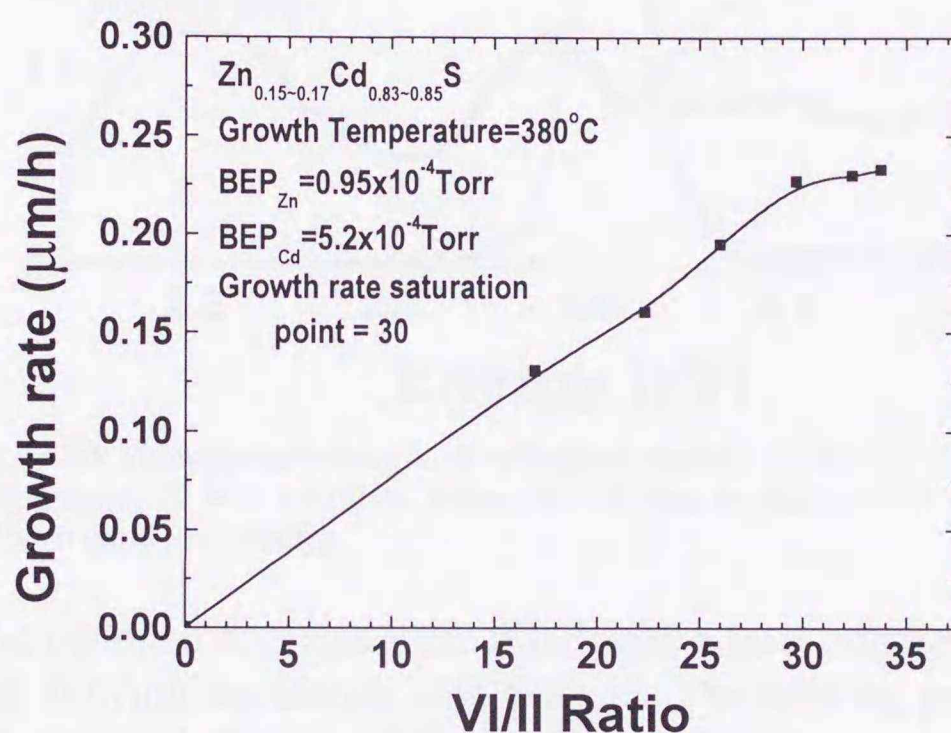


Fig. 3.9 The growth rate as a function of the VI/II ratio. The growth conditions are given in the figure.

The optical properties of the ternary alloys were investigated at room temperature. The photoluminescence and the reflection spectra of the $\text{Zn}_{0.27}\text{Cd}_{0.73}\text{S}$ alloy grown at 380°C are shown as an example in Fig. 3.10. The absorption edge, which is identified in the reflection spectrum of the alloy, is correlated with the alloy bandgap energy. The photoluminescence peak position and the bandgap energy derived from the reflection measurements for the alloys with different compositions are shown in Fig. 3.11 as function of the alloy lattice constant. Near the lattice-match condition, the alloy lattice constant was determined from the XRD (002) diffraction since the GaAs substrate peak is very sharp and it reduces the background of the alloy XRD peak.

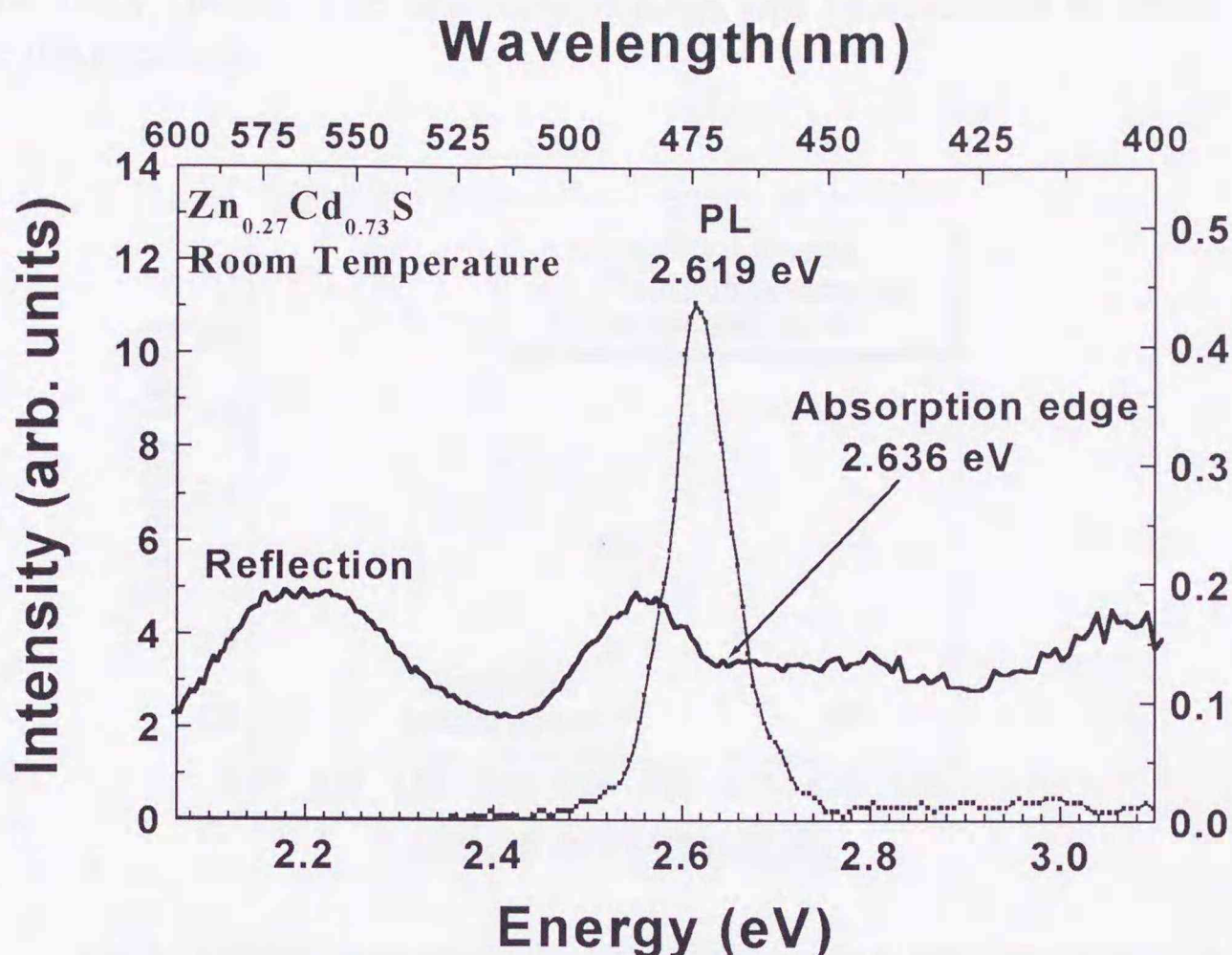


Fig. 3.10 Photoluminescence and reflection spectra of the $\text{Zn}_{0.27}\text{Cd}_{0.73}\text{S}$ at room temperature. PL was measured under He-Cd laser excitation and reflectance under halogen lamp illumination

The bandgap energies were fitted with a least-squares method and a bandgap bowing parameter was derived. The bowing parameter was estimated to be 0.773 eV. The $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ bandgap energy at room temperature is expressed by the following formula:

$$E_{\text{Zn}_x\text{Cd}_{1-x}\text{S}} = 2.42(1-x) + 3.684x - 0.773x(1-x) \text{ [eV]}, \quad (3.4)$$

where x is the Zn content of the alloy. The dashed line in Fig. 3.11 shows this dependence.

As stressed previously the main target is to obtain the lattice-matched conditions. This will further improve the crystalline properties by eliminating the stress-induced defects in the epilayer. Figure 3.12 shows the FWHM of the PL and XRD peaks. In the near lattice-match conditions, these FWHM are much reduced demonstrating an improvement of the epilayers quality. The surface morphology will be also improved in these conditions. The good understanding of the properties of the ternary alloy made easier the investigation of the

quaternary system. The Mg incorporation will be discussed in detail in the next section.

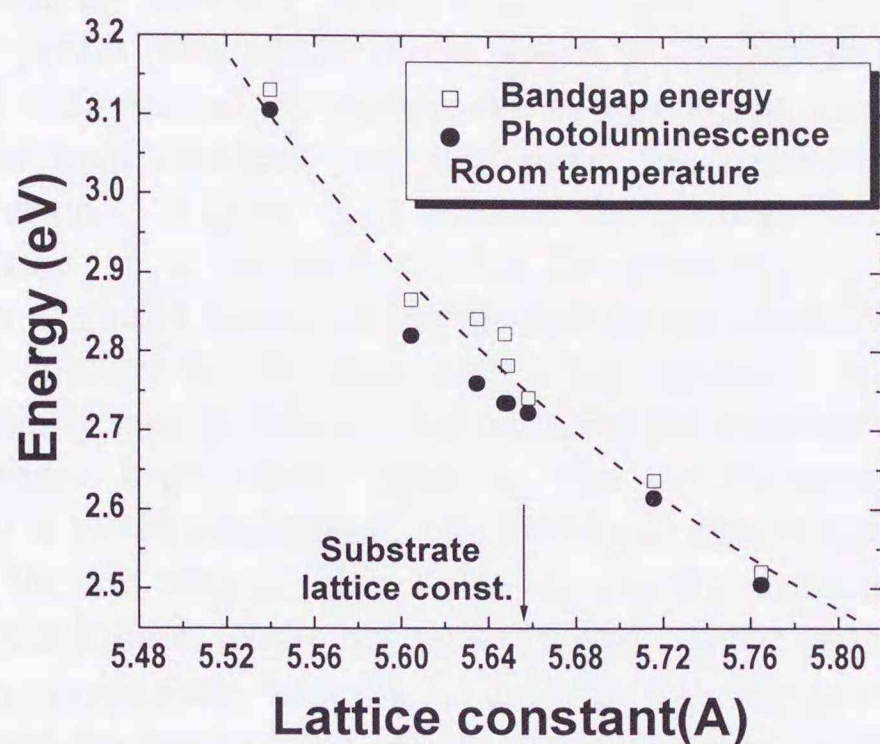


Fig. 3.11 Optical properties for the ZnCdS alloys grown at 380°C with a thickness of about 450 nm. The dashed-line indicates the fitting of the ZnCdS bandgap energy that is given in Eq.3.4.

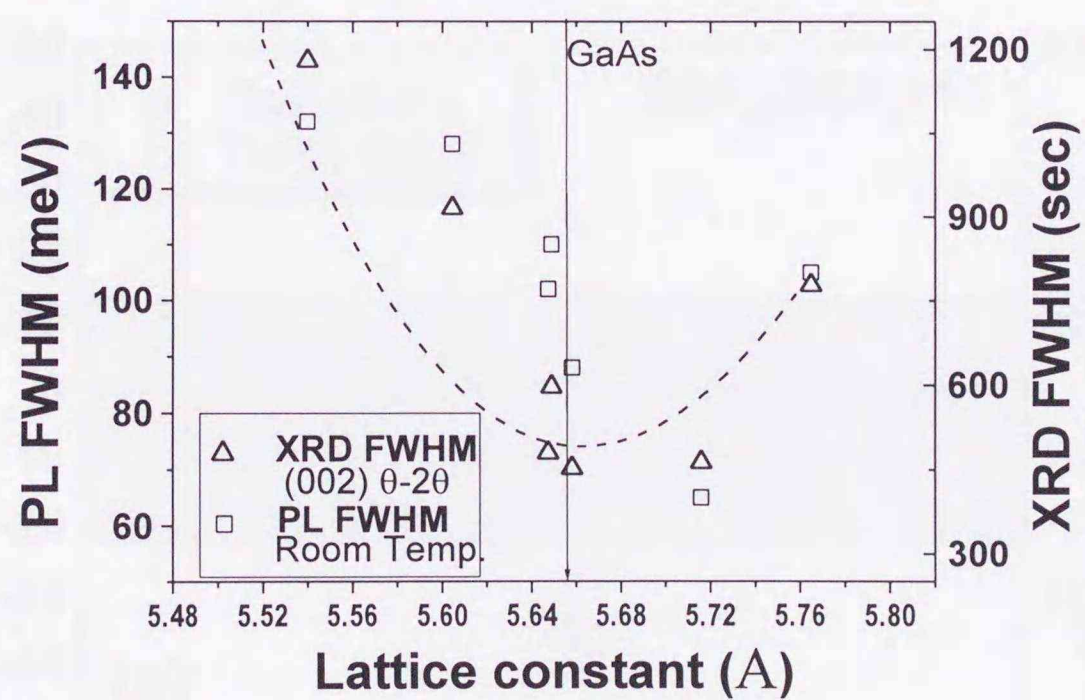
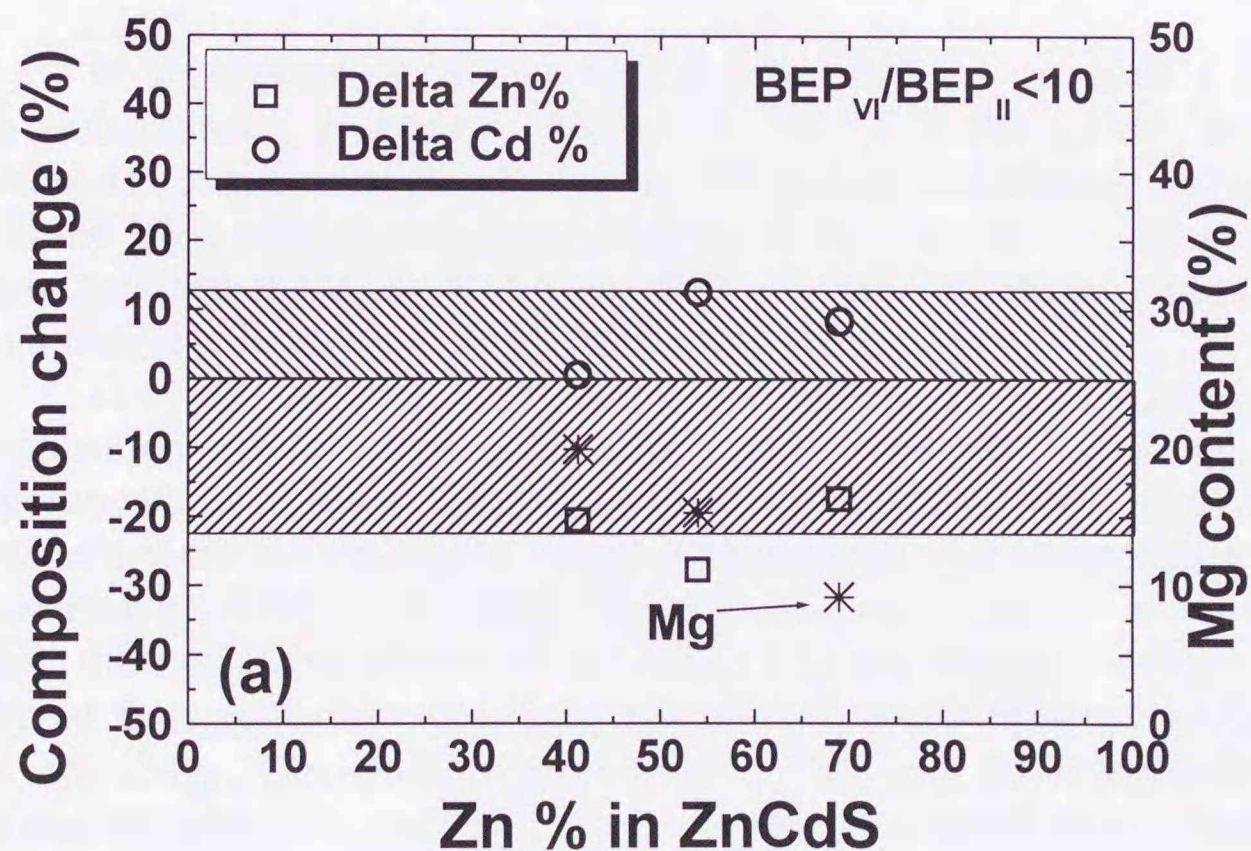


Fig. 3.12 The photoluminescence FWHM and the X-ray diffraction FWHM for the ZnCdS alloys as a function of the constant lattice.

3.4.5 Mg incorporation in $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ alloys

The compositions of the ZnMgCdS quaternary alloys were determined by electron probe microanalysis (EPMA). Details on the electron probe microanalysis are given in Appendix 5. The Zn to Cd supplied ratio varied the quaternary compositions in epilayers. The Mg BEP was kept constant and this gave the possibility to estimate its incorporation. Figure 3.13 shows the change in the Zn and Cd composition as a function of the Zn composition. The investigated epilayers were not grown under stoichiometric conditions but with group II rich conditions. In this case, Mg showed a tendency to be preferentially incorporated in the crystal at the expense of the Zn.

Under high ratios close to the stoichiometry condition, this tendency is much diminished, and the Mg is almost equally replacing the Zn and the Cd atoms. This behavior can be explained by the higher sticking coefficient of the Mg on the surface at the growth temperature of 380°C in comparison with the Zn and Cd. The higher sticking coefficient is assumed because of the lower vapor pressure of the Mg and of the higher bonding energy with S. This gives a better controllability over the alloy composition and facilitates the achievement of lattice-matching to GaAs.



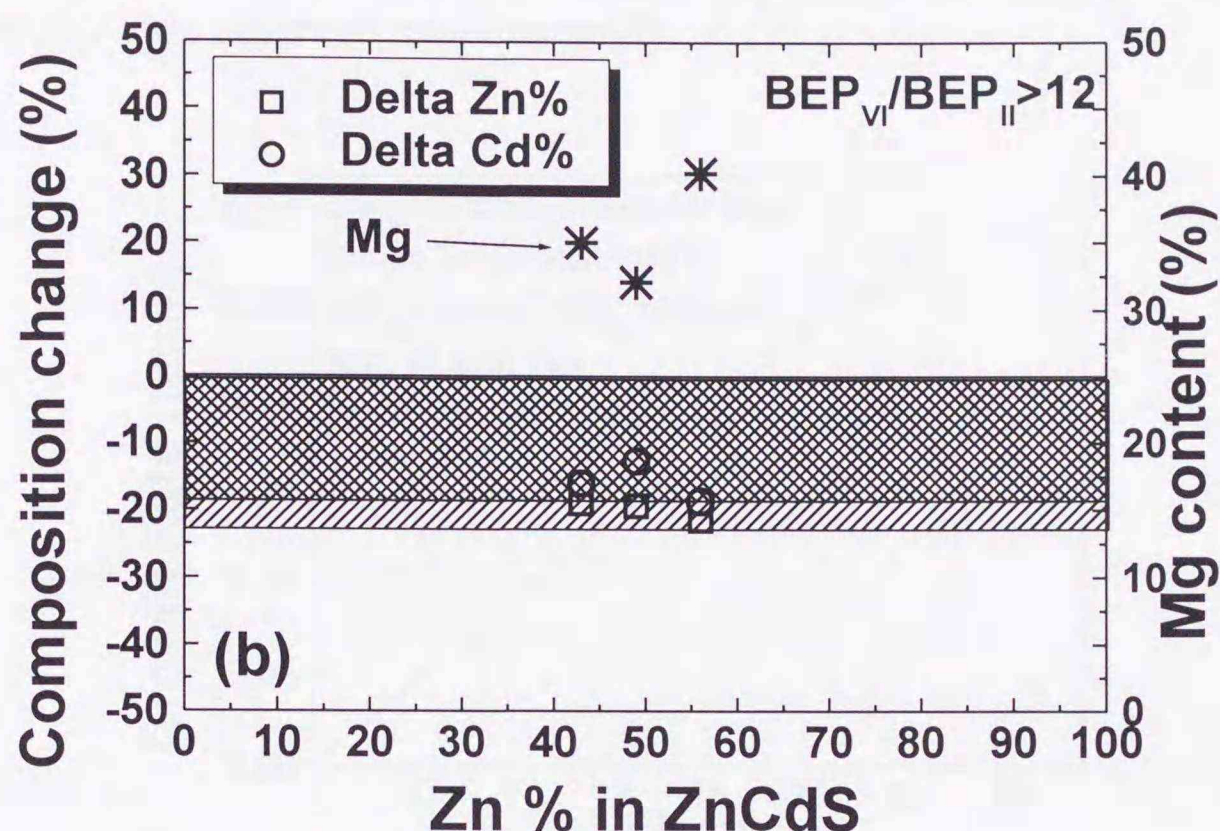


Fig. 3.13 Mg incorporation for (a) VI/II ratio below 10, (b) VI/II ratio above 12

3.4.6 Structural and optical properties of the $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ alloys

In an experiment similar to that performed for the ternary alloy the stoichiometry point was derived. In Fig. 3.14 the growth rate is plotted as a function of the VI/II ratio. The growth rate linearly increased with the VI/II ratio and reached a plateau at the ratio of ~ 25 . The lower vapor pressure of the Mg may cause the lower ratio for the stoichiometry point than that in the case of ZnCdS ternary alloy.

The Zn to Cd BEP ratio controlled the $\text{Zn}_x\text{Mg}_y\text{Cd}_{1-x-y}\text{S}$ composition while keeping the Mg's BEP constant. Two sets of experiments, at different Mg pressures were performed. The alloys lattice constants were determined by XRD measurements, the composition was measured by EPMA. The photoluminescence spectra gave information about the optical properties of the alloys and the bandgap energy was derived from reflection measurements. The PL and reflection spectra of the $\text{Zn}_{0.34}\text{Mg}_{0.40}\text{Cd}_{0.26}\text{S}$ alloy are shown in Fig. 3.15 as an example. In several samples, the quaternary alloy PL spectra showed small intensity deep level emission at room temperature. The PL peak positions and the bandgap energies are given as a function of the alloy lattice constant in Fig. 3.16. The change of the Zn to Cd ratio modified the alloy

composition and the lattice-matching condition could be achieved. For the near lattice-matched conditions bandgap energy difference as large as 470meV was observed experimentally.

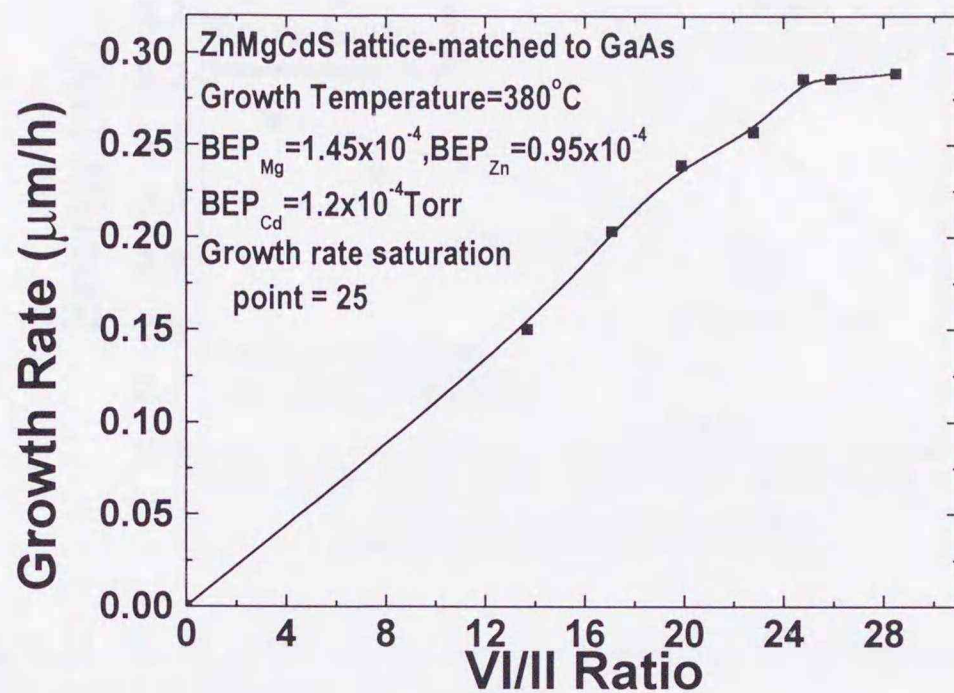


Fig. 3.14 The growth rate as a function of the VI/II ratio.

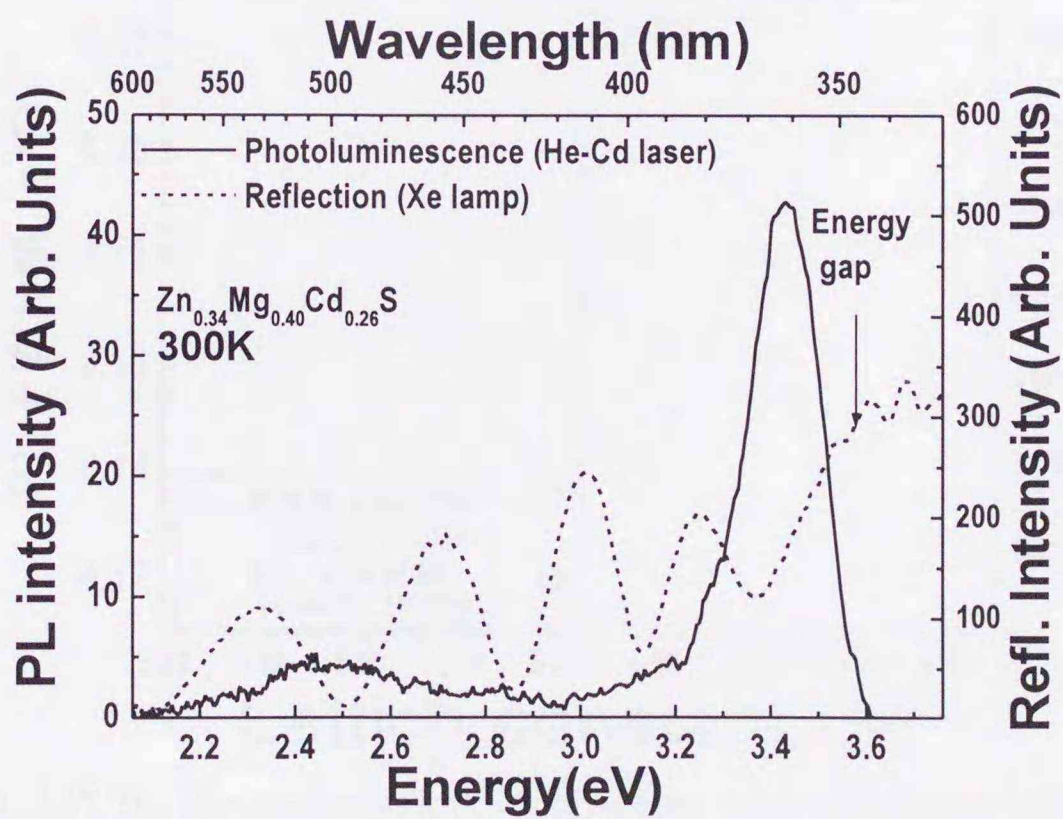


Fig. 3.15 The PL and reflection spectra of the $\text{Zn}_{0.34}\text{Mg}_{0.40}\text{Cd}_{0.26}\text{S}$ alloy at room temperature.

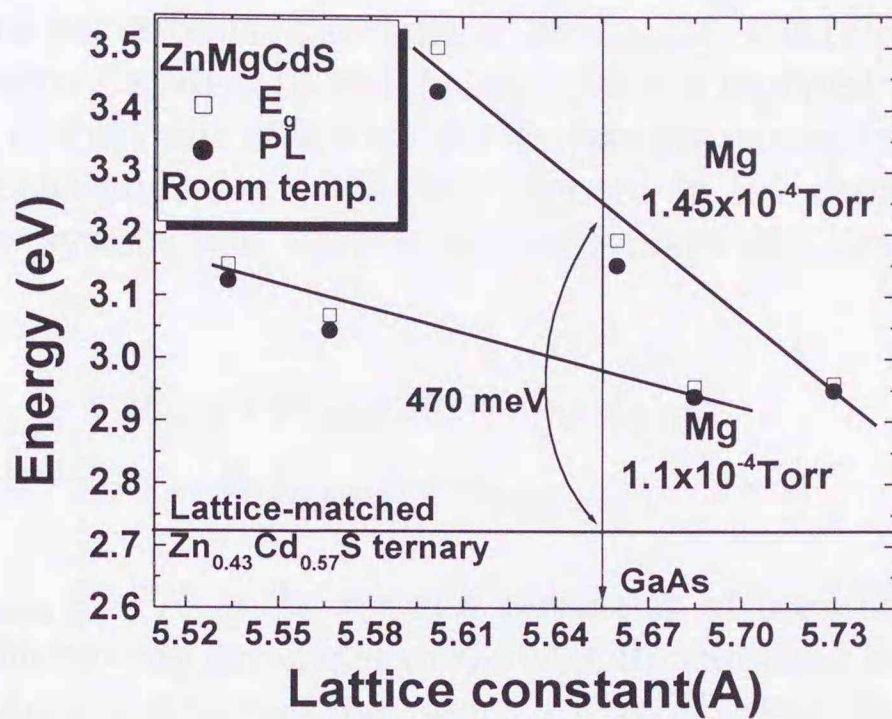


Fig. 3.16 The PL peaks and the bandgap energies of the quaternary alloys grown at 380°C with a thickness of 300~450 nm.

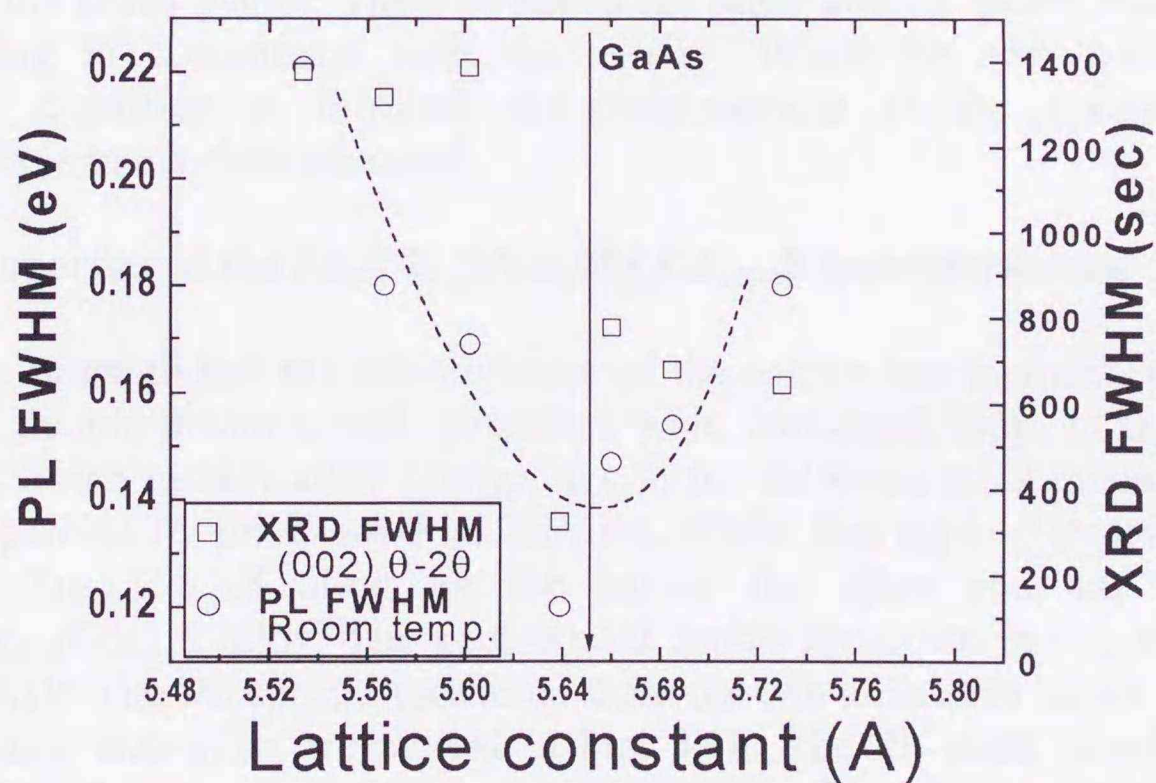


Fig. 3.17 The photoluminescence FWHM and the X-ray diffraction FWHM for the ZnMgCdS alloys as a function of the constant lattice.

From reflection data the bandgap energy was estimated. A least-square fit of the bandgap energy was performed in order to yield the bowing parameter of the quaternary and an estimation of the bandgap

energy of the zinc-blende MgS. The Mathematica code and the result of the fitting are provided in Appendix 6. We consider that the ZnMgS alloy system has a bowing parameter of $E_{bZnMgS} \sim 0.1\text{eV}$. Since in the similar systems $Zn_xMg_{1-x}Te$ and $Zn_xMg_{1-x}Se$ it is reported the absence of the bowing or the value of 0.16eV for the bowing parameter, respectively [25], our assumption has additional support. In the case of the three-cation alloy system will have a an energy bandgap described by the equation:

$$E_{Zn_xMg_yCd_{1-x-y}S} = xE_{ZnS} + yE_{MgS} + (1-x-y)E_{CdS} - E_{bZnCdS}x(1-x-y) - E_{bZnMgS}xy - E_{bMgCdS}y(1-x-y), \quad (3.4)$$

where $E_{bZnCdS}=0.773$ is the bowing parameter of the ZnCdS alloy and E_{bMgCdS} is the bowing parameter of the MgCdS alloy and E_{ZnS} , E_{MgS} , E_{CdS} are the bandgap energies of the binary alloys. The best fit was given by the following values $E_{MgS}=4.6\text{ eV}$ and $E_{bMgCdS}=0.751\text{ eV}$. The bowing in the MgCdS alloy appears to be in the same range as that of the ZnCdS ternary alloy.

Figure 3.17 shows the FWHM of the photoluminescence peak measured at room temperature and the FWHM of the X-ray diffraction peak of the (002) planes. The FWHM of the XRD and PL peaks shows broadening in comparison with the ternary. When the near lattice-matched condition is fulfilled, the improvement of the epilayers properties is much clear observed.

3.4.7 Properties of the $Zn_xCd_{1-x}S/Zn_xMg_yCd_{1-x-y}S$ heterostructure

In order to test the effectiveness of the carrier confinement, two types of double quantum well structures were fabricated. Both of them have a Cd-rich ternary alloy ($Zn_{0.29}Cd_{0.71}S$) for the 6-nm-thick quantum wells separated by the 8-nm-thick barriers. While first type of structure has the $Zn_{0.44}Cd_{0.56}S$ alloy for the barrier the other one has the $Zn_{0.24}Mg_{0.35}Cd_{0.41}S$ alloy. The geometrical details are given in the inset of Fig. 3.18. The PL spectra measured from the two structures under the He-Cd laser excitation are plotted in Fig. 3.18. The PL peak intensity observed in the structure with the quaternary alloy barrier is roughly 18 times higher than that of the structure with the ternary alloy barrier. This demonstrates the good carrier confinements in the double quantum well structure when the barrier is the quaternary alloy with the relatively high content of Mg.

The band alignment of the heterostructure is of type I since the energy of the observed luminescence agrees with the calculated optical transitions. The band offsets were estimated by two methods and the details are given in Appendix 7.

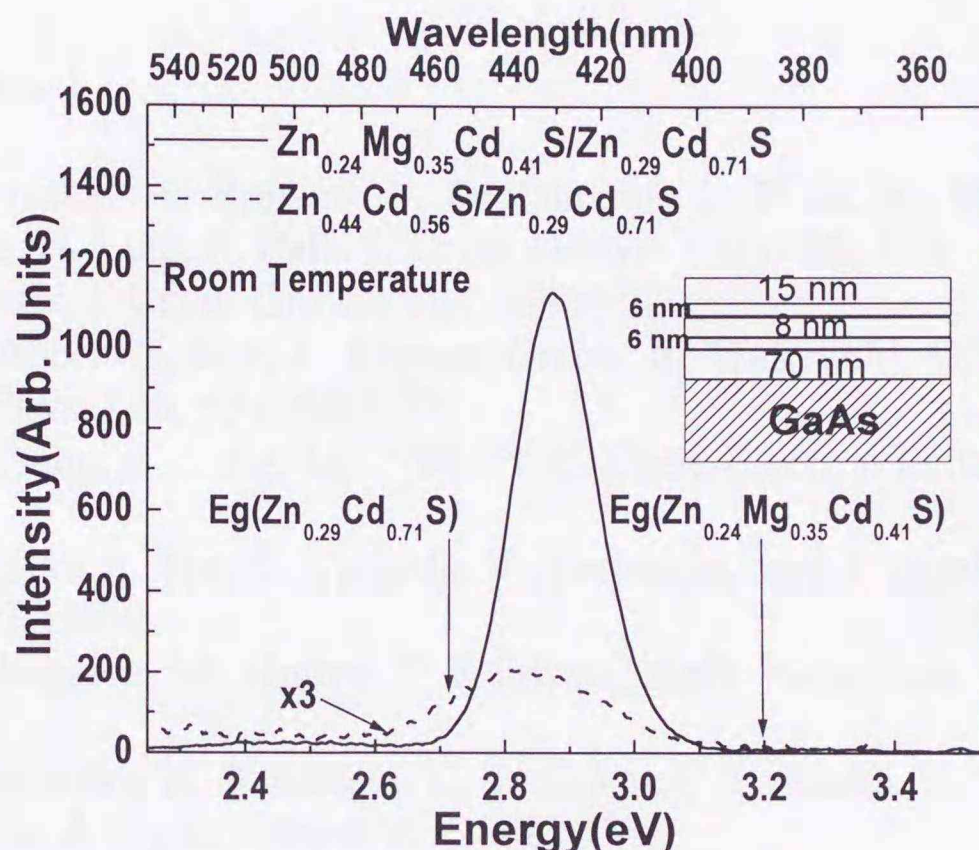


Fig. 3.18 The comparison between two heterostructures with a similar geometry and a similar well alloy. The barrier is in one case a ternary lattice matched to the GaAs and in the second case a quaternary lattice-matched to the GaAs.

3.5 Summary

In this chapter the growth and characterization of a new class of II-VI compound semiconductors were investigated. The ZnMgCdS alloys were grown for the first time. These alloys could be grown selectively with a carbonaceous mask at low-temperatures of 310°C. This alloy could be grown lattice matched to GaAs substrates. In these conditions a bandgap difference of 470 meV was obtained in combination with the ternary ZnCdS when is grown lattice matched to GaAs. The bandgap energies of the ternary and quaternary alloys were fitted and a bowing parameter of 0.773 eV was derived for the ZnCdS alloy. The band gap energy of the zincblende MgS was estimated to be 4.6 eV from the same fitting, if the bowing parameters for the ZnMgS and MgCdS alloys are considered to be 0.1 eV and 0.751 eV, respectively.

The $\text{Zn}_{0.24}\text{Mg}_{0.35}\text{Cd}_{0.41}\text{S}/\text{Zn}_{0.29}\text{Cd}_{0.71}\text{S}$ heterostructure showed a good carrier confinement and has PL efficiency 18 times higher than the heterostructure based only on the ternary alloy.

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Chapter 4

Nanoscale Selective Area Growth of II-VI Compounds

4.1 Introduction

Nanoscale selective area growth is a specific area of the selective area growth. The main characteristic of the nanoscale selective area growth is that the pattern size is much smaller than the diffusion length of the species on the surface at the growth temperature. The pattern size is in the sub-100-nm range.

Research in this area is recent and the semiconductors that were grown using patterns well below 100 nm are the following: GaAs [1], Si [2], GaN [3], ZnS, ZnSe [4].

The motivation for studying this topic is given by the possibility to fabricate semiconductor nanostructure of high quality by the selective area epitaxy if very high-resolution masks are available.

As reported in Chapter 2, these kind of masks with resolution as small as ~20 nm could be fabricated in ultra-thin carbonaceous films. In Chapter 3 it was introduced a new system of II-VI compound semiconductors that can be employed for selective area growth at low temperatures and also leaves room for bandgap engineering.

In this Chapter the nanoscale area growth using the already described masks and materials will be considered. In the first section the growth of simple binaries such as ZnS and ZnSe will be treated and the nucleation issue will be described together with solutions to relax it.

In the third section the nanoscale selective area growth is applied to demonstrate record high density of ordered dot-like structures.

4.2 Nucleation Issue in the Nanoscale Area Selective Growth of II-VI Compounds on GaAs Substrates

Nanometer-scale selective area growth of ZnS and ZnSe was investigated. The growth was performed by metalorganic molecular-beam epitaxy (MOMBE) on a carbonaceous-film masked GaAs substrate at temperatures ranging from 350°C to 390°C. For pattern sizes larger than several hundred nanometers, a good selectivity and uniformity of the grown structures were observed as shown in Fig. 4.1 (a), but for mask opening sizes less than ~100 nm, uniformity of the grown structures was

inhomogeneous as shown in Fig. 4.1(b). In the unmasked area on the same sample surface, ZnS could uniformly grow to a 40 nm thickness in about 15 min while in the patterned area, grown structures were highly inhomogeneous.

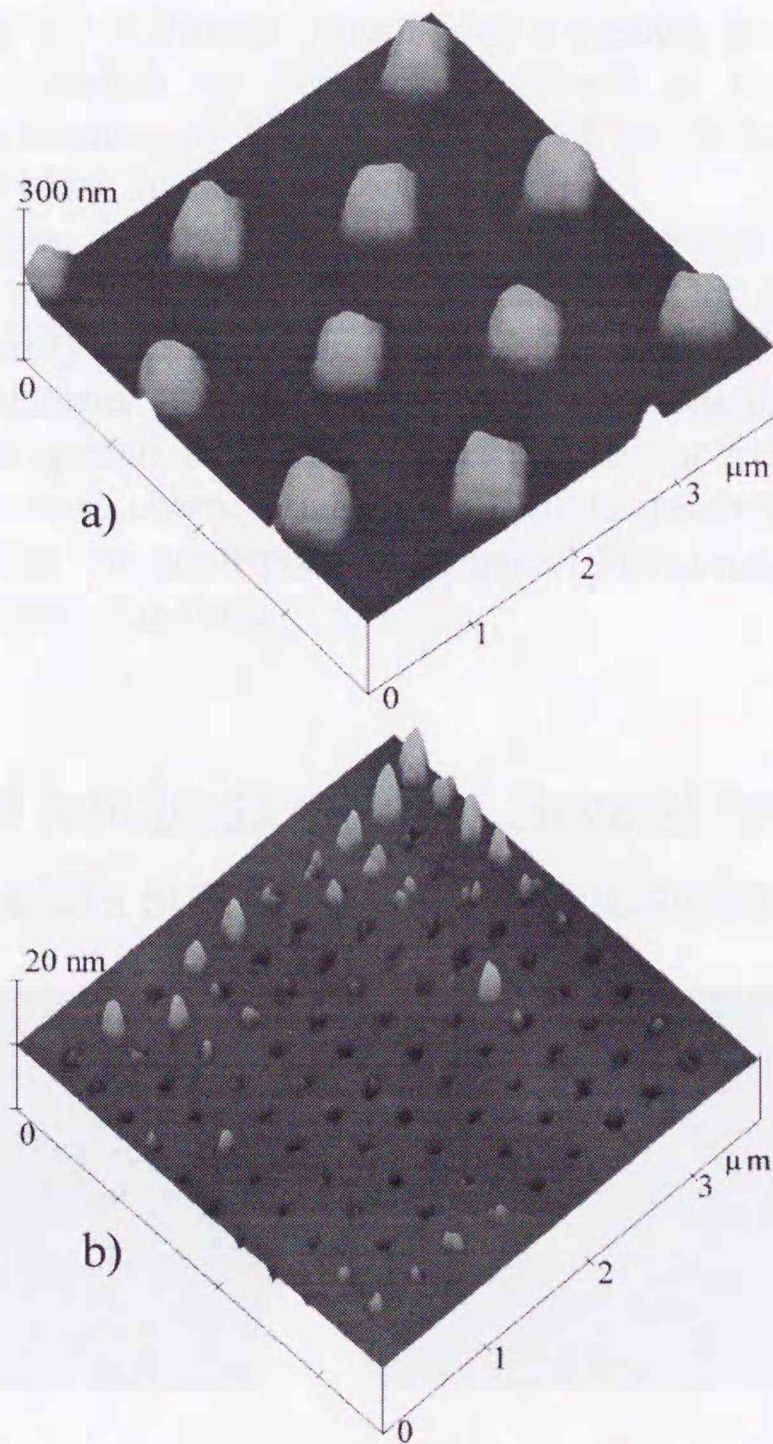


Fig. 4.1 ZnS structures grown at 350°C on a (2x4)As stabilized GaAs surface after a 2 min. Zn precursor purge. Lateral size of the patterns is a) ~700 nm and b) ~80 nm.

A longer growth period of up to 1 h did not change this situation, indicating that the inhomogeneity originates from the poor nucleation. The growth of ZnS and ZnSe gave similar results for the sub-100-nm patterns.

Sub-100-nm scale inhomogeneous nucleation was also reported in the case of GaAs growth and the authors performed some Monte Carlo numerical simulations on this issue [5]. These simulations take into account the Ga adatom diffusion on the GaAs and mask surfaces. Based on these results they pointed out that uniform nucleation will be possible by decreasing the diffusion length of the species on the surface. This reduction is possible by performing growth at lower temperatures. However, application of this approach will be difficult because some growth on the mask surface will occur.

One more general approach for the improvement of nucleation uniformity in small sized patterns is considered. This is the enhancement of the probability of nucleation in the mask opening. The case of very small sized patterns (in the range of adatom diffusion length) may be regarded as a special case of confined space nucleation [6]. Confined space nucleation is characterized by a limited number (N) of species in the unit area that can contribute to the nuclei formation. Figure 4.2 shows schematics of this situation.

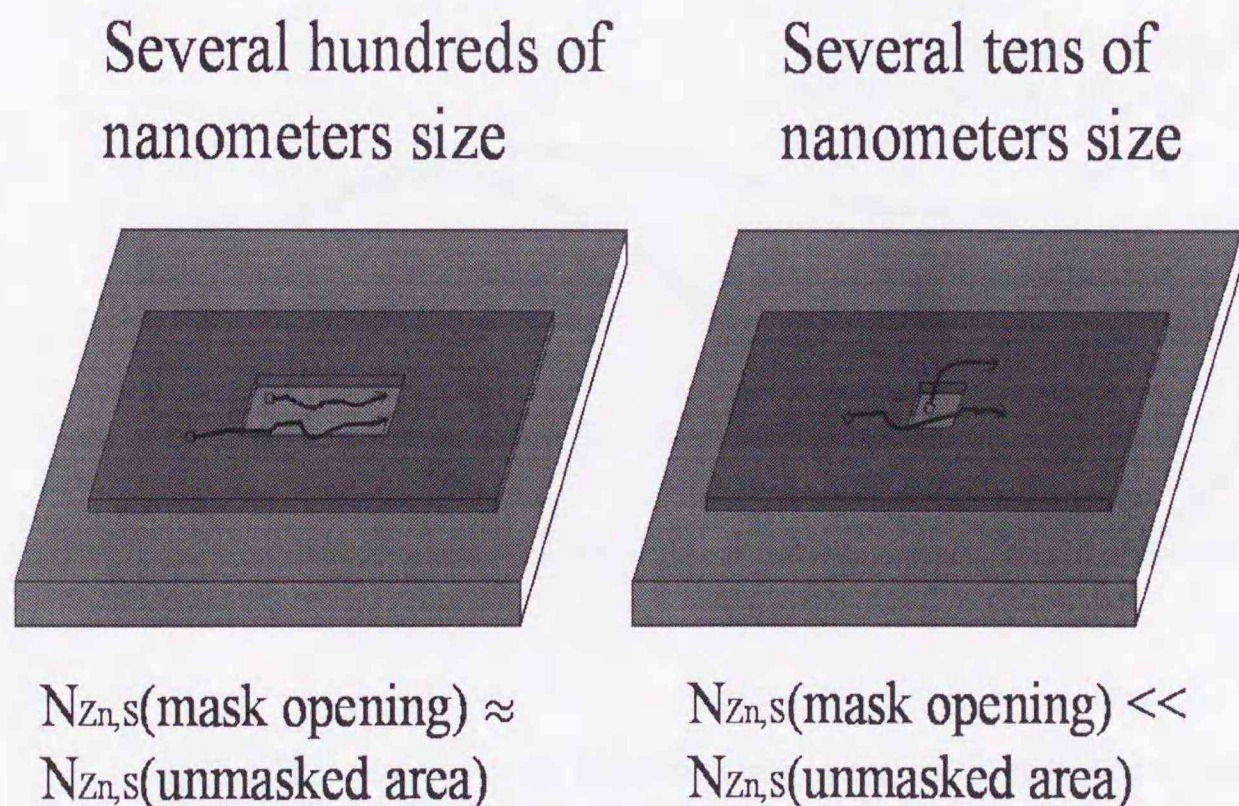


Fig. 4.2 Differences between several hundreds of nm size mask opening and several tens of nm size opening mask. The atoms migrating on the mask surface did not "see" the opening and/or the adatoms created in the mask opening will migrate outside and will be desorbed. $N_{Zn,s}$ denotes the area density of the respective species.

This particularity can be expressed by an additional term in the expression of Helmholtz free energy (under constant volume) variation in the nucleation process as compared with the normal case when the species for nucleation are supplied from an unlimited reservoir ($N \rightarrow \infty$):

$$\Delta F = \Delta F_{\infty} + k_B T \frac{i^2}{N} \quad (4.1)$$

where i is the number of species that take part in the nucleation ($i \ll N$) and ΔF_{∞} is the Helmholtz free energy in the normal case. The additional term may be also derived as configurational entropy corresponding to the number of ways the N molecules can be distributed in the confined space. The additional term is positive and tends to suppress nucleation. This additional barrier for nucleation may induce the observed inhomogeneity in the growth process.

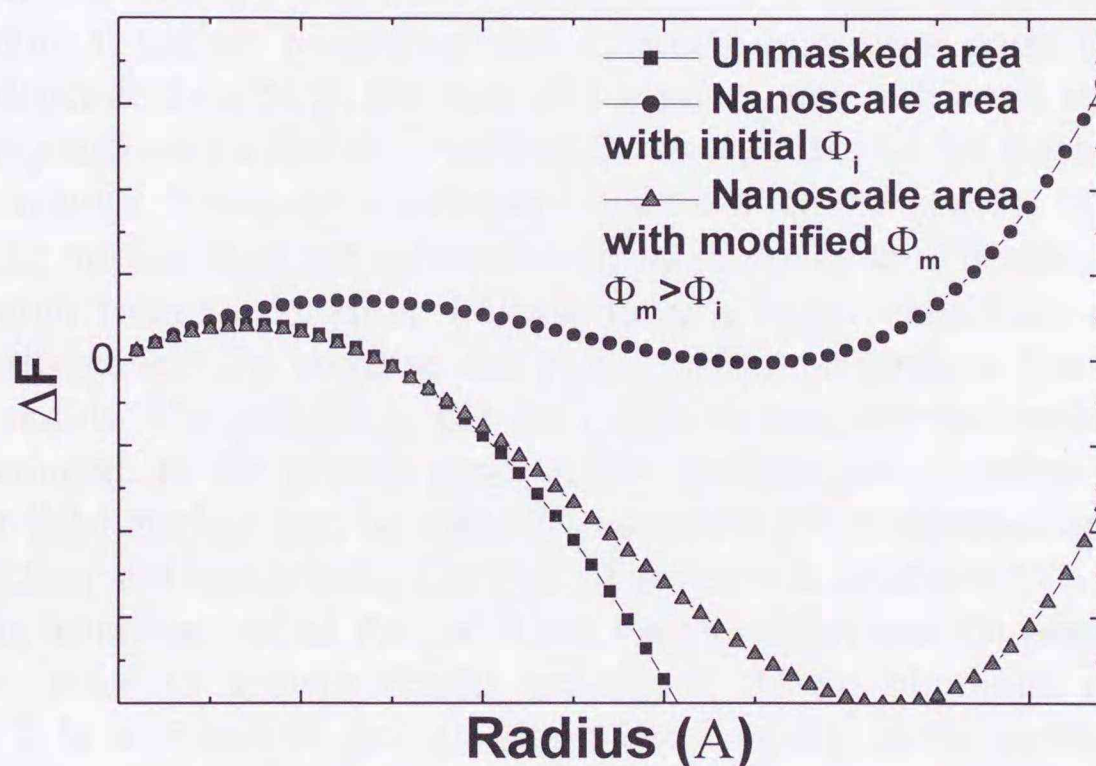


Fig. 4.3 The reduction of the Helmholtz free energy by the reduction of the ΔF_{∞} . The initial weak bonding at the heterointerface characterized by Φ_i is modified to a stronger one characterized by Φ_m .

The Helmholtz free energy ΔF_{∞} is largely dependent on the interface and more precisely on its chemical nature. From a microscopic viewpoint and considering growth of a nucleus with a shape of 2D disk one can assume that:

$$\Delta F_{\infty} = \gamma \frac{2\pi r}{a} - (\mu^g - \mu^c) \frac{\pi r^2}{a^2} \quad (4.2)$$

$$\mu^c = -\Phi - k_B T \ln\left(\frac{k_B T}{h\nu_0}\right)^3 \quad (4.3)$$

where γ is the ledge free energy of the step surrounding the 2D disk, a is the lattice constant, $\mu^{c,g}$ are the chemical potential for crystal and gas phase, respectively, r is the radius of the growing nucleus, ν_0 is the adsorbed atom vibration frequency, and Φ is the work spent for desorption of one atom from the surface and that is directly related to the bond strength between the surface and adatom. The variation of Helmholtz free energy ΔF will be then written as:

$$\Delta F = \gamma \frac{2\pi r}{a} - [\mu^g + \Phi + k_B T \ln\left(\frac{k_B T}{h\nu_0}\right)^3] \frac{\pi r^2}{a^2} + k_B \frac{\pi^2 r^4}{Na^4} \quad (4.4)$$

The variation of Helmholtz free energy as a function of the nucleus radius is given in Fig. 4.3. The additional term due to the configurational entropy increases the activation energy for nucleation and the critical radius. Moreover, this creates a minimum point that is strongly dependent on N . In the case of a small N , this minimum and the maximum joints into a saddle point and the energy barrier for nucleation becomes infinite. However, a stronger bond between the species that are forming the nucleus and the substrate will increase the Φ . Therefore, the negative-sign term in equation 4.4 will have a larger contribution and will partially cancel the increase due to the additional term, in the range of small radius. Consequently, the activation energy for the nucleation will be reduced. In the growth process, the predominant chemical bond present at the interface can be tuned by controlling the substrate surface reconstruction and by choosing the type of pregrowth irradiation.

The usual case of an As-stabilized GaAs surface and Zn-precursor irradiation prior to growth results mainly in As-Zn bondings at the interface. It is well-known that Zn atoms bond weakly to the surface As dimmer atoms [7] so the decrease in the energy barrier for nucleation will be moderate. A rough estimation of the bond strength may be retrieved from the temperature at which Zn starts to desorb from the GaAs surface: 287°C for the Ga-stabilized surface and 312°C for the As-stabilized one [8]. In order to increase the nucleation probability, a stronger bond at the interface will be necessary.

The S passivation of the GaAs surface was widely investigated primarily to reduce the surface states density [9]. The stability and chemical nature of the S passivated GaAs surface were also investigated, and it was concluded that Ga-S bond formation is more probable than

As-S bond formation at temperatures above 200°C [9]. Desorption of S from the GaAs (001) surface starts above 500°C. One can conclude that a Ga-stabilized GaAs surface would increase the ZnS nucleation probability by the increased chances for Ga-S bonds formation.

The GaAs surface was controlled to a Ga-stabilized structure, as is shown in Fig. 3.2(b), followed by the S precursor purge at the BEP of 7.5×10^{-4} Torr for 30 s. The result of the growth of ZnS is shown in Fig. 4.4. The uniformity of the grown structures was significantly improved. ZnS structures were also grown after S purge on the As-stabilized surface, but inhomogeneity similar to the case of Zn purge was observed. These results strongly suggest that only the combination of the Ga-stabilized surface with the initial Ga-S bonding condition enhanced the nucleation in the reduced-size area of the mask openings.

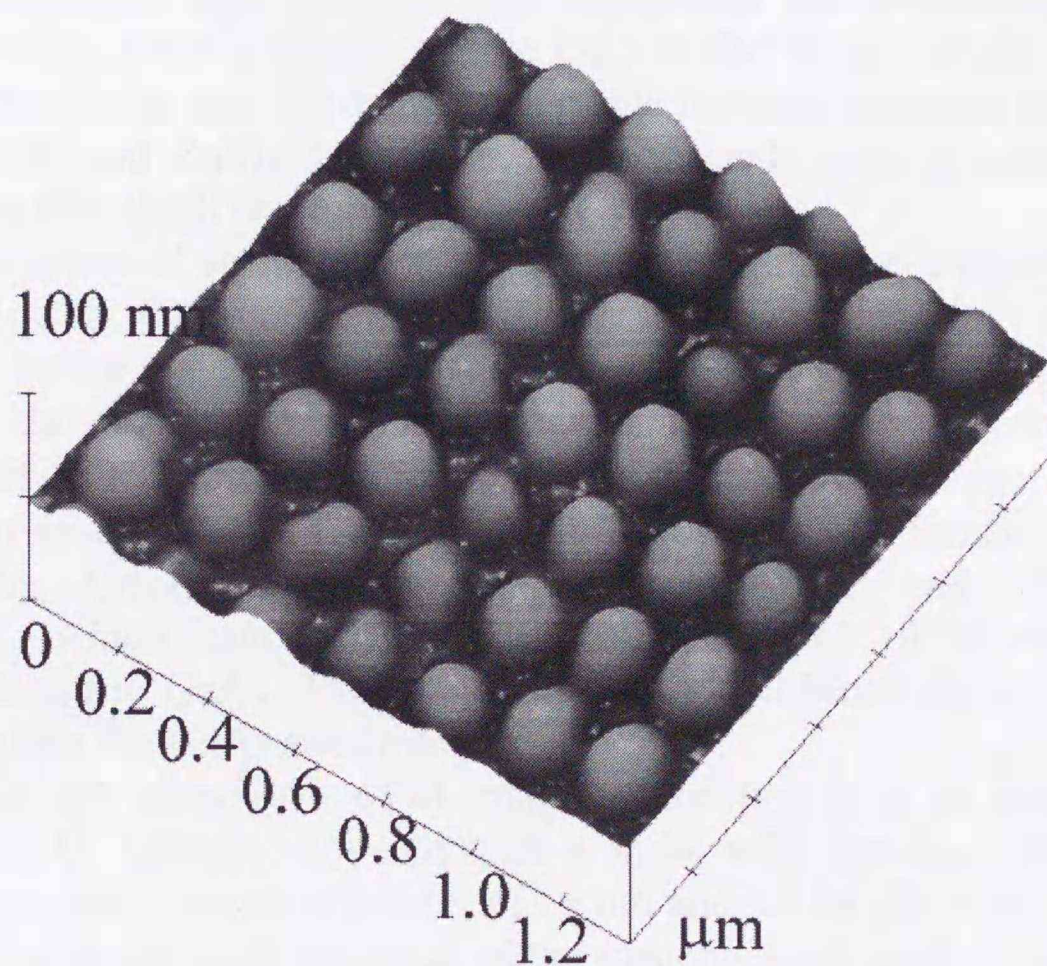


Fig. 4.4 Uniform ZnS dot-like structures grown at 390°C with a VI/II ratio of 12 and BEP_{Zn} of 2.5×10^{-4} Torr on a (4x2) Ga stabilized GaAs surface after S precursor purge at the BEP of 7.5×10^{-4} Torr for 30s. The original pattern size was ~ 80 nm and pitch of 200 nm. After growth the mean diameter at the halfheight of the structures was ~ 80 nm.

The height of the structures grown in the patterns is reduced to about 40 nm as compared with the ~ 80 nm thickness of the ZnS epilayer simultaneously grown in the unmasked area and originates mainly from

the faceting and not from the initial nucleation delay. The 80-nm-thick epilayer in the unmasked area was grown in about 18 min on the Ga-stabilized surface as compared to the 30 min required using the conventional growth parameters (As-stabilized surface and Zn purge).

This difference is mainly related to the faster initiation of the growth on the Ga-stabilized surface even in the unmasked area. Better uniformity was also observed in the growth of ZnSe structures when the growth was performed on the Ga-stabilized GaAs surface in combination with Se-precursor initiation.

4.3 Applications of the Nanoscale Selective Area Growth

The initial growth conditions play an important role in the nanoscale selective area growth. The conditions for enhancing the nucleation were derived for the simple case of the binary compounds. With this knowledge and the experience of the macroscopic area growth of the ZnCdS and ZnMgCdS alloys, the nanoscale area growth was attempted on ultra-high resolution carbonaceous masks.

Two types of structures were grown. The first one consisted of only the ZnCdS ternary compound under the condition that would provide the lattice matching to the substrate. The thickness of the grown epilayer in the unpatterned area was about 10 nm. The growth was performed at 380°C after the growth initiation sequence of type D, as described in section 3.4.3. The second type was a similar ternary alloy layer of $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$ but with the thickness of 10 and 65 nm, respectively, which sandwich the 10-nm-thick layer of ZnMgCdS latticed matched to GaAs. This quaternary layer will block the eventual carrier flow into the GaAs substrate.

Figure 4.5 shows the AFM image of the first type of structure grown on GaAs substrate covered with a mask with dot-like patterns. The structures have a mean diameter of 28 nm and the height of 4~5 nm. The dots grew in the small openings of the carbonaceous mask. In one of the openings the growth did not take place probably due to some contamination. This gives the possibility to observe the original size of the opening that is 35 nm. The distance between the dots is ~225 nm.

The measurement of the PL properties was attempted on this sample but the signal was very weak. One can speculate that the photogenerated carriers easily flew into the GaAs substrate with the narrower bandgap.

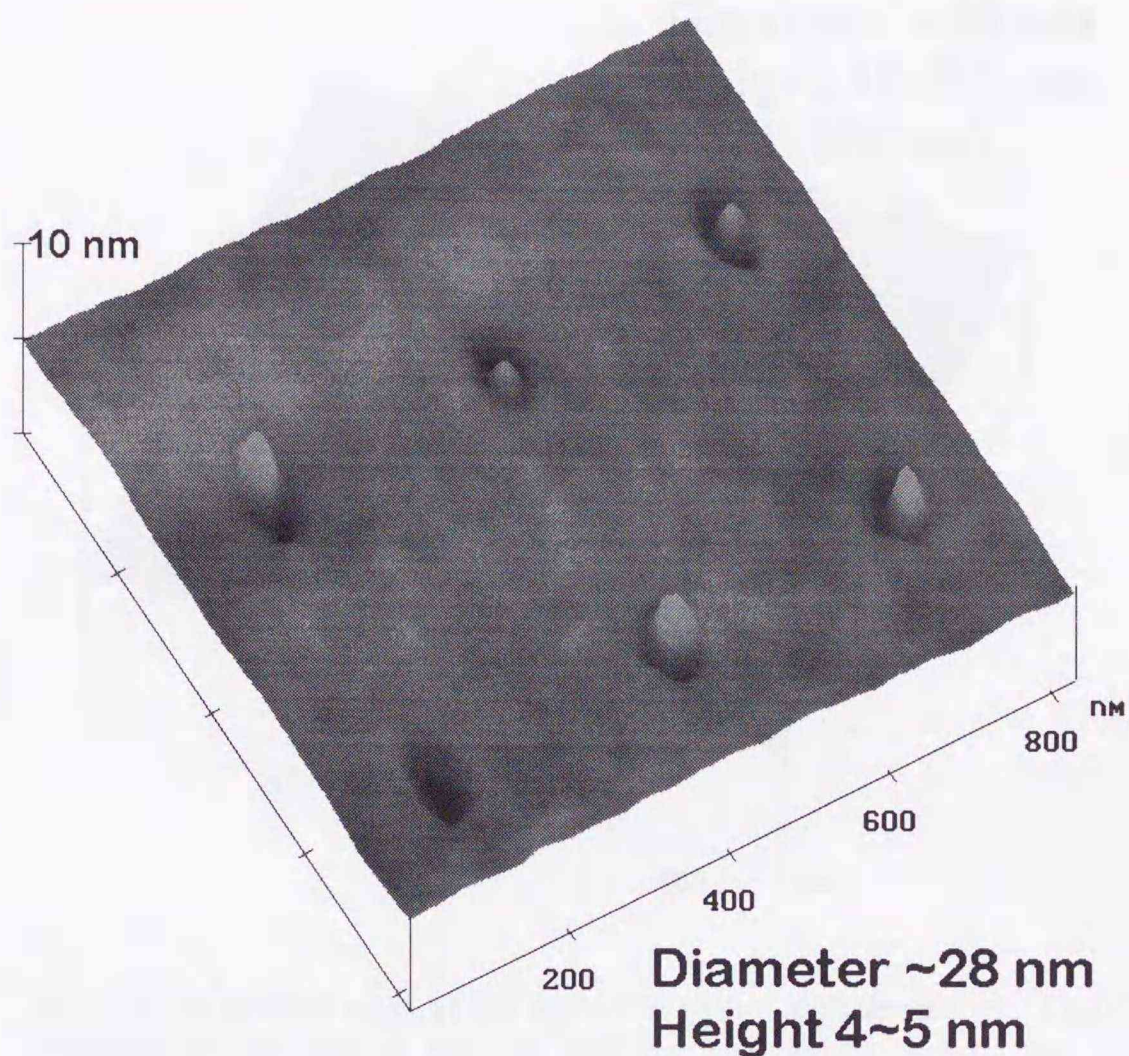


Fig. 4.5 Dot structures based on the $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$ alloy. The growth was performed at 380°C with the thickness of the unpatterned layer of 10 nm. Growth time was ~ 3 min with the Zn BEP of 6.7×10^{-4} Torr, Cd BEP of 0.45×10^{-4} Torr S BEP of 8×10^{-3} Torr.

In the second case, the AFM image of an array the higher density is shown in Fig. 4.6. The mean diameter of the dots at half-heights is ~ 26 nm and the height is 15 to 20 nm.

The patterns used for the selective area growth of dots have the pitch of 100 nm and gives a density of $1 \times 10^{10} \text{ cm}^{-2}$. This is a record high density for uniformly arranged dots. The photoluminescence at 30K was measured and it is displayed in Fig. 4.7. The PL spectrum recorded from the dot area is blue shifted as compared with the PL spectrum measured from the unpatterned area. The shift is 6 meV. The size of the dots will not be small enough to provide a better confinement.

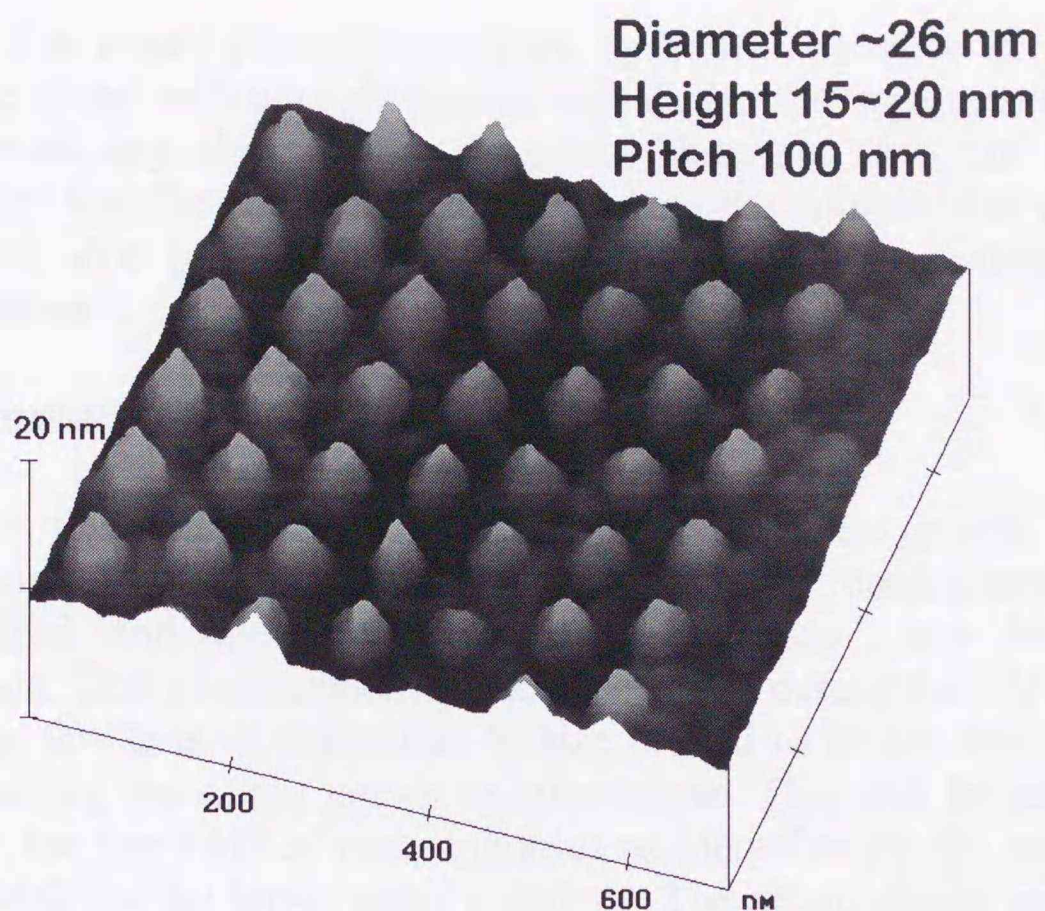


Fig. 4.6 An ordered array of dot structures with a high density of $1 \times 10^{10} \text{ cm}^{-2}$. The diameter of the dots is ~26 nm and the total height ~15-20 nm. The growth temperature was 380°C. The layer in the unpatterned area has the following structure 10 nm $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$ /10nm $\text{Zn}_{0.33}\text{Mg}_{0.18}\text{Cd}_{0.49}\text{S}$ /55nm $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$.

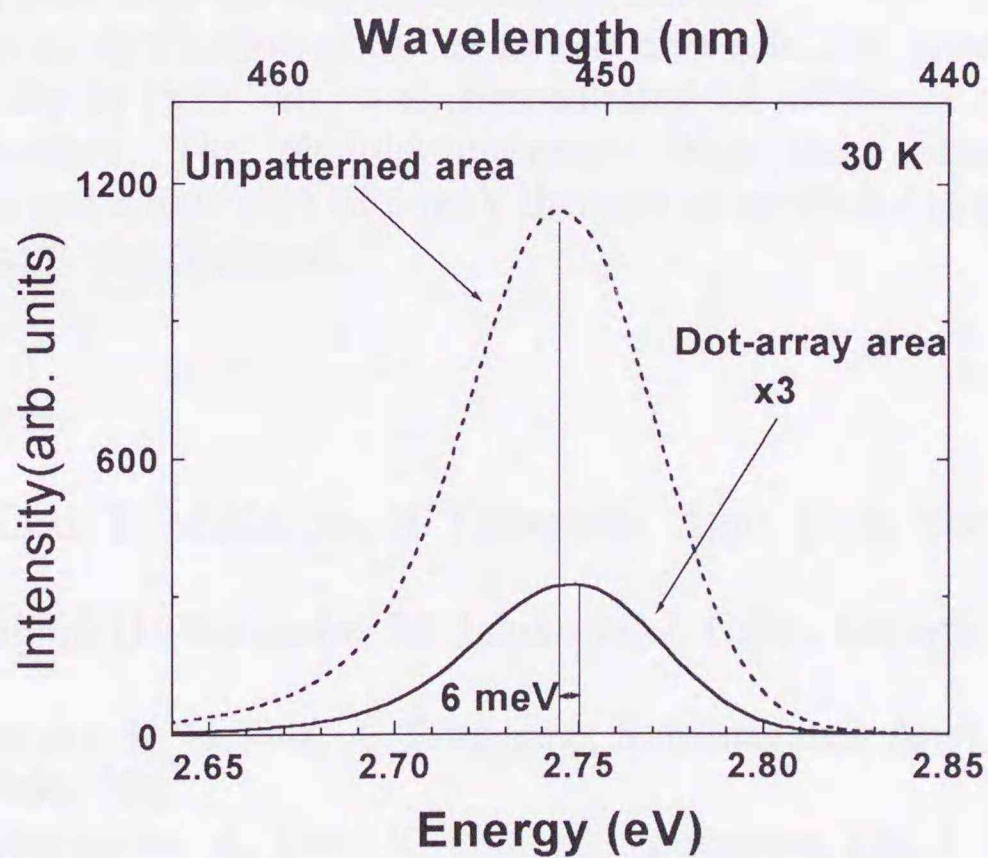


Fig. 4.7 PL spectra recorded at 30 K from the dot-array area and from unpatterned are. The peak of the spectrum recorded in the dot-array area is 6-meV-blue shifted from the peak of the spectrum measured in the unpatterned area..

The micro-photoluminescence spectrum measured from a 400 nm wide stripe, with a height similar with that of the unpatterned area did not showed any shift of the PL peak. Therefore, one can relax the possibility that the small blue shift is due to the composition change in the small dot pattern and should assign it to the carrier spatial confinement.

4.4 Summary

In this chapter the nanoscale selective area growth of II-VI compounds was discussed. The nanoscale-area particularities were emphasized and the so-called "nucleation issue" was brought in discussion. This phenomenon of poor nucleation during the SAG in mask openings few tens of nanometer in size proved to be the main obstacle for obtaining uniformly grown nanostructures. This will be an intrinsic problem for the SAG of nanostructures as identified by the comparison to the SAG for the larger mask openings. The enhancement of ZnS and ZnSe nucleation could be obtained by controlling the initial GaAs surface reconstruction structures together with the pregrowth irradiation with S or Se precursors. This showed that the control of the initial heterointerface bondings, *i.e.* replacement of the As-Zn bonding with the Ga-S or Ga-Se one, is effective for solving the nucleation issue in the selective growth of ZnS and ZnSe nanostructures.

As an application of the nanoscale area selective growth a record high density of $1 \times 10^{10} \text{ cm}^{-2}$ was demonstrated for uniformly ordered dot-like structures. The photoluminescence from these structures was measured and a blue shift of 6 meV that can be attributed to the quantum confinement was observed.

References:

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Chapter 5

Summary and conclusions

5.1 Summary

In this thesis we investigated the fabrication by atomic force microscope (AFM) of a mask with resolution down to a couple of tens of nanometers, which is suitable for selective area growth of II-VI compounds. We introduced a new II-VI alloy system that is easy to be selectively grown at low temperature by MOMBE and to be engineered with different bandgap energies while being lattice-matched to the GaAs substrate. Based on these two ingredients we demonstrated II-VI compound nanostructures obtained by selective area growth.

High-resolution patterning is one of the key points for this approach. In this work high resolution patterning of SiO_2 mask on semiconductor wafers was demonstrated. Patterning was done mechanically on a soft PMMA resist. These patterns were transferred by wet etching in the SiO_2 films with a minimum linewidth of ~ 40 nm.

The second patterning method was based on the combined SEM/AFM lithography. For this purpose a very thin carbonaceous mask deposited on the GaAs substrate was patterned by AFM. The carbonaceous film with a thickness of ~ 3 nm was locally deposited by electron-beam irradiation in a scanning electron microscope (SEM). The carbonaceous film was patterned by oxidation activated by the electric field applied between the tip and the substrate. The highest resolution that was obtained is about 20 nm. This two-instruments combination provides unmatched advantages for the patterning because it gives the means for the continuous monitoring of the patterning status and removes limitations on patterning on wide surfaces with a high resolution, as would appear if only one is employed.

For the selective area growth, the II-VI compound semiconductors are chosen because they grow at low temperature and this system can cover a wide range of bandgap energies from UV to Green. In this direction, we proposed for the first time the quaternary alloy ZnMgCdS and we demonstrated selective area growth of high-quality $\text{ZnCdS}/\text{ZnMgCdS}$ heterostructures that are lattice-matched to GaAs substrates.

Using the highest resolution patterning and the newly developed alloys, arrays of quantum dots uniformly sized ($\sim 26\text{nm}$) and aligned ($\sim 100\text{ nm pitch}$) providing densities as high as 10^{10}cm^{-2} were demonstrated.

5.2 Future applications

As a future application of this research a new design for ultra-small cavity light emitting devices in the blue region that are ready for monolithic integration is proposed. As stressed in the introduction, more efficient light emitters can be obtained by the incorporation of the emitting dipole in a small cavity. The simple inclusion of the emitting dipoles in the cavity is not enough and the exact positioning of these dipoles at the antinodes of the resonant optical field is essential.

Here, the nanostructure selective area growth can show its main advantages. In this kind of application the AFM lithography can demonstrate it is a powerful technique. We propose a ring structure with a very small volume, which supports a few resonance modes. In this cavity the active nanostructures will be placed only at the antinodes of the cavity optical field. If the semiconductor nanostructures can be placed at the exact positions of these resonances then the coupling to the optical field will be enhanced.

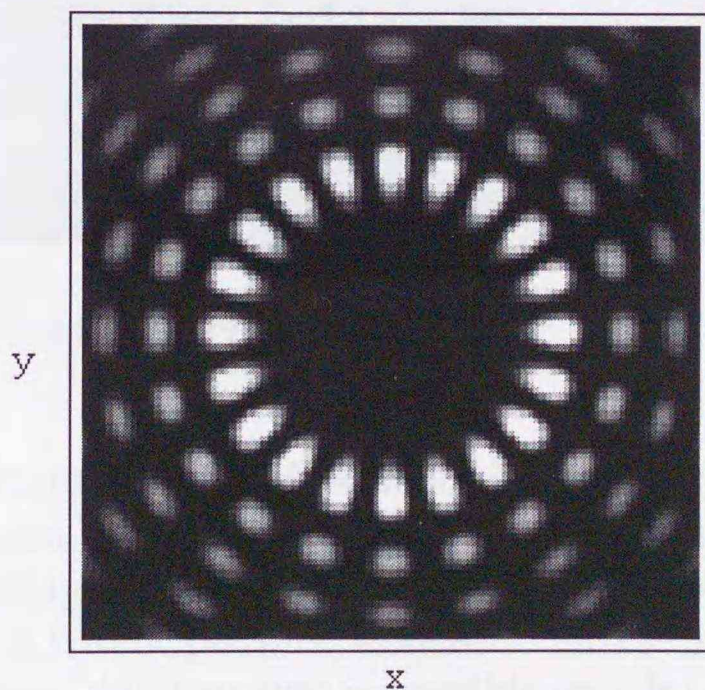


Fig. 5.1 Calculated optical resonances of ring structure. The radius of the ring is 700 nm . The resonance mode is characterized by the azimuthal resonance number, $m=10$ and radial resonance number, $l=1$.

The 2D calculation of the resonance mode in such a ring cavity was performed by a conformal transformation method and the

approximation of optical field intensity for the mode ($m=10$, $l=1$) is shown in Fig. 5.1.

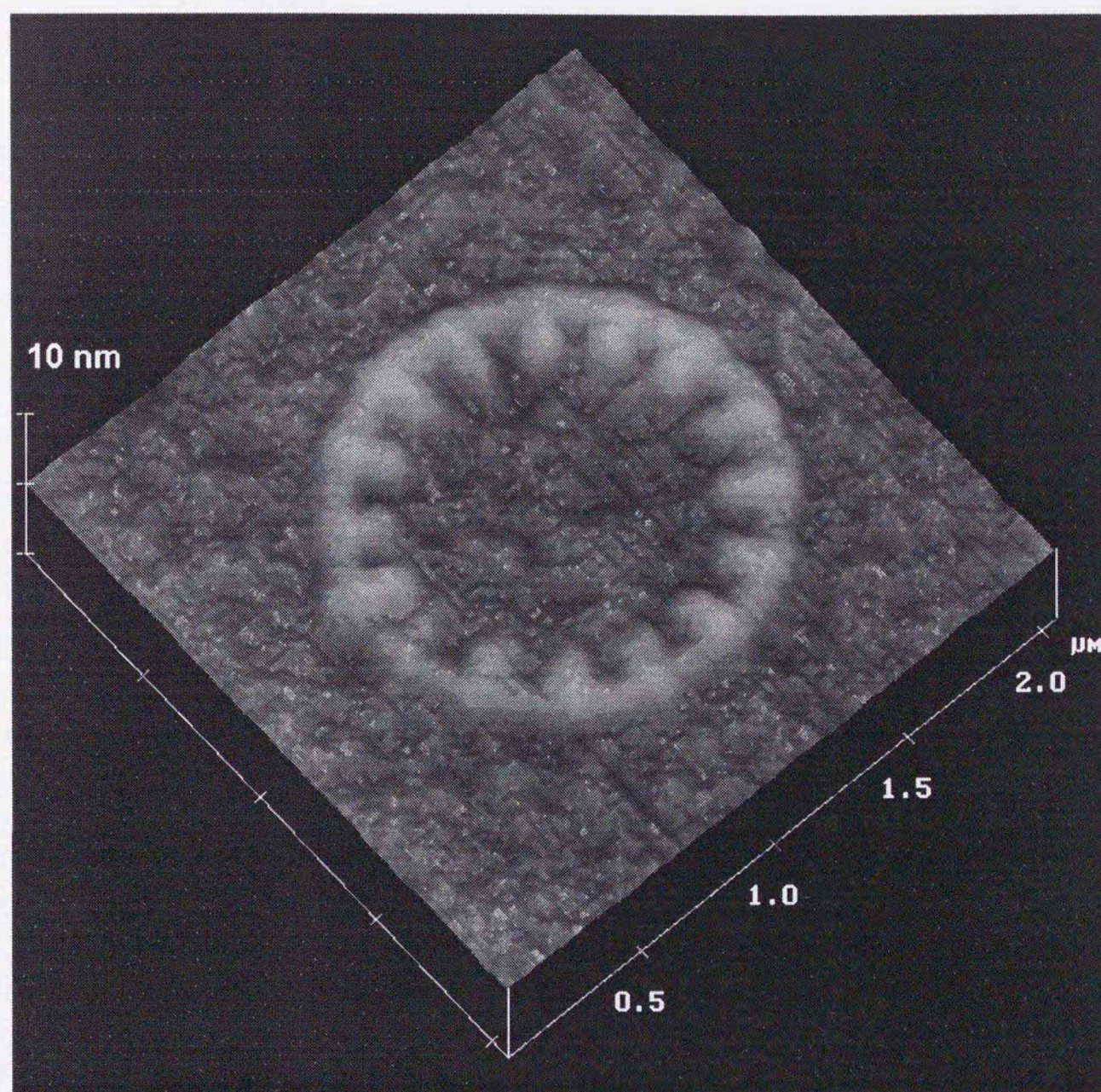


Fig. 5.2 Ring structure patterned by AFM on a carbonaceous film.

The fabrication of such a small ring structure is possible by AFM patterning as can be seen in Fig. 5.2. If this ring structure can be placed on a waveguiding structure and the II-VI nanostructures are grown with this geometry it will be possible to achieve the cavity described above.

This small ring structure is possible only by AFM lithography and selective area growth since the geometrical and the structural quality requirements are very tight in order to minimize the light diffraction.

5.3 Conclusions

The AFM lithography proved to be a powerful technique for patterning SiO_2 and carbonaceous mask with very high resolution. Moreover the newly introduced combination of AFM and SEM proved to be easy to employ and to give high resolution patterning on large areas. This method can be used with success to prototype minute devices that cannot be obtained by other means.

In order to improve the resolution and the aspect ratio of the AFM patterning by electric-field induced oxidation was introduced a new method. The modulated amplitude pulsed bias mode keeps the advantages of the pulse bias mode in removing the charge accumulation in the oxide layer and in addition controls the lateral oxidation rate for a better resolution.

On the other hand, the newly proposed alloys of $\text{ZnMgCdS}/\text{ZnCdS}$ show promising properties for the low temperature selective area growth. These compounds were grown selectively with a carbonaceous mask at growth temperatures as low as 310°C .

In addition to this capability, the ZnMgCdS alloy was grown for the first time lattice-matched to GaAs. In the lattice-matched conditions this alloy demonstrated a bandgap energy difference as large as 470 meV, when compared with the lattice-matched ZnCdS alloy.

The possibility of fabricating II-VI nanostructures by selective area growth was demonstrated based on carbonaceous mask patterned with high-resolution by the AFM. The array of ordered dot-like structures that was demonstrated has high-density of $1 \times 10^{10} \text{cm}^{-2}$.

By embedding an ordered array of nanostructures in a cavity the enhancement of the spontaneous emission will be easy to be achieved since the nanostructures can be positioned at the antinodes of the cavity optical resonance. This positioning will give a strong electron-photon coupling.

As a future application, a ring structure with a small volume, that will embed a few nanostructures positioned at the antinodes of the optical field was proposed. Its patterning was demonstrated but a suitable waveguiding layer to be grown need to be developed.

Another possible application of the AFM patterning and the II-VI compound selective area growth is to fabricate photonic band-gap structures for very short wavelengths, which has not been yet demonstrated.

Appendix 1

#Program for drawing a set of parallel lines

#Translate(x,y,rate)

#Fixz(z,rate)

*Nanolitho

\Program:Si960026

Scale(0.001)

Translate(-4000,4000,0.1)

Fixz(-2.3,0.1)

translate(10000,0,0.1) #1

fixz(2.3,0.3)

releasez

translate(-10000,-200,0.1)

fixz(-2.3,0.1)

translate(10000,0,0.1) #2

fixz(2.3,0.3)

releasez

translate(-10000,-200,0.1)

fixz(-2.3,0.1)

translate(10000,0,0.1) #3

fixz(2.3,0.3)

releasez

translate(-10000,-200,0.1)

fixz(-2.3,0.1)

releasez

Appendix 2

(* Mathematica code for calculating the water meniscus radius *)

```
ClearAll
konst=0.54
ThetaTp=35*Pi/180
Rtip=20.0
a=Rtip*Tan[ThetaTp]*(1/Sin[ThetaTp]-1)
Rk[h_]=Abs[konst/Log[10,h/100]]
SolutionsR1R2=
  Solve[{1/R1+1/R2==1/Rk[h], Tan[(Pi/2-ThetaTp)/2]==R1/(R1+R2-
a)}, {R1,R2}]
SolR1[h_]=R1/.SolutionsR1R2[[2]]
SolR2[h_]=R2/.SolutionsR1R2[[2]]
Plot[{Rk[x],SolR1[x],SolR2[x]}, {x,20,80}]
SolRw[h_]=Abs[SolR1[h]+SolR2[h]];
Plot[SolRw[x], {x,20,80}]
N[SolRw[50]]
datenum=Table[SolRw[x], {x,20,80,5}]
```


Appendix 3

**// Program for writing a set of parallel lines at different scan rates by
// electric-filed AFM patterning**

```
#include <litho.h>
void main()
{
LITHO_BEGIN
double left=-1.3;
double up=1.3;
double left_return=-3;
double rate=1;
double rate1=0.1;
double rate2=0.2;
double rate3=0.4;
double rate4=0.8;
double p_t=0.01;
double x_length=3;
double y_pitch=-0.5;
double puls=-4.95;
LithoTranslate(left,up,rate);
LithoPulseOutput(aoAna2,puls,p_t);
LithoTranslate(x_length,0,rate1);
LithoPause(1);
LithoTranslate(left_return,y_pitch,rate);
LithoPulseOutput(aoAna2,puls,p_t);
LithoTranslate(x_length,0,rate2);
LithoPause(16);
LithoTranslate(left_return,y_pitch,rate);
LithoPulseOutput(aoAna2,puls,p_t);
LithoTranslate(x_length,0,rate3);
LithoPause(23);
LithoTranslate(left_return,y_pitch,rate);
LithoPulseOutput(aoAna2,puls,p_t);
LithoTranslate(x_length,0,rate4);
LithoMoveZ(0.01,0.001);
LITHO_END
}
```


Appendix 4

The properties of the connection to the AFM tip for bias application between the tip and the sample

In order to apply very short pulses to the tip the use of a triaxial cable to connect the source, the conductive cantilever, and the sample holder is essential for minimizing the RC constant. The connection diagram is shown in Fig. A.1. The triaxial cable has three layers: the core for the bias application, the guard layer with a bias equal to that of the core, and the exterior layer that is grounded. The length of the core line unprotected by the guard layer that is connected to the sample holder must be kept as short as possible.

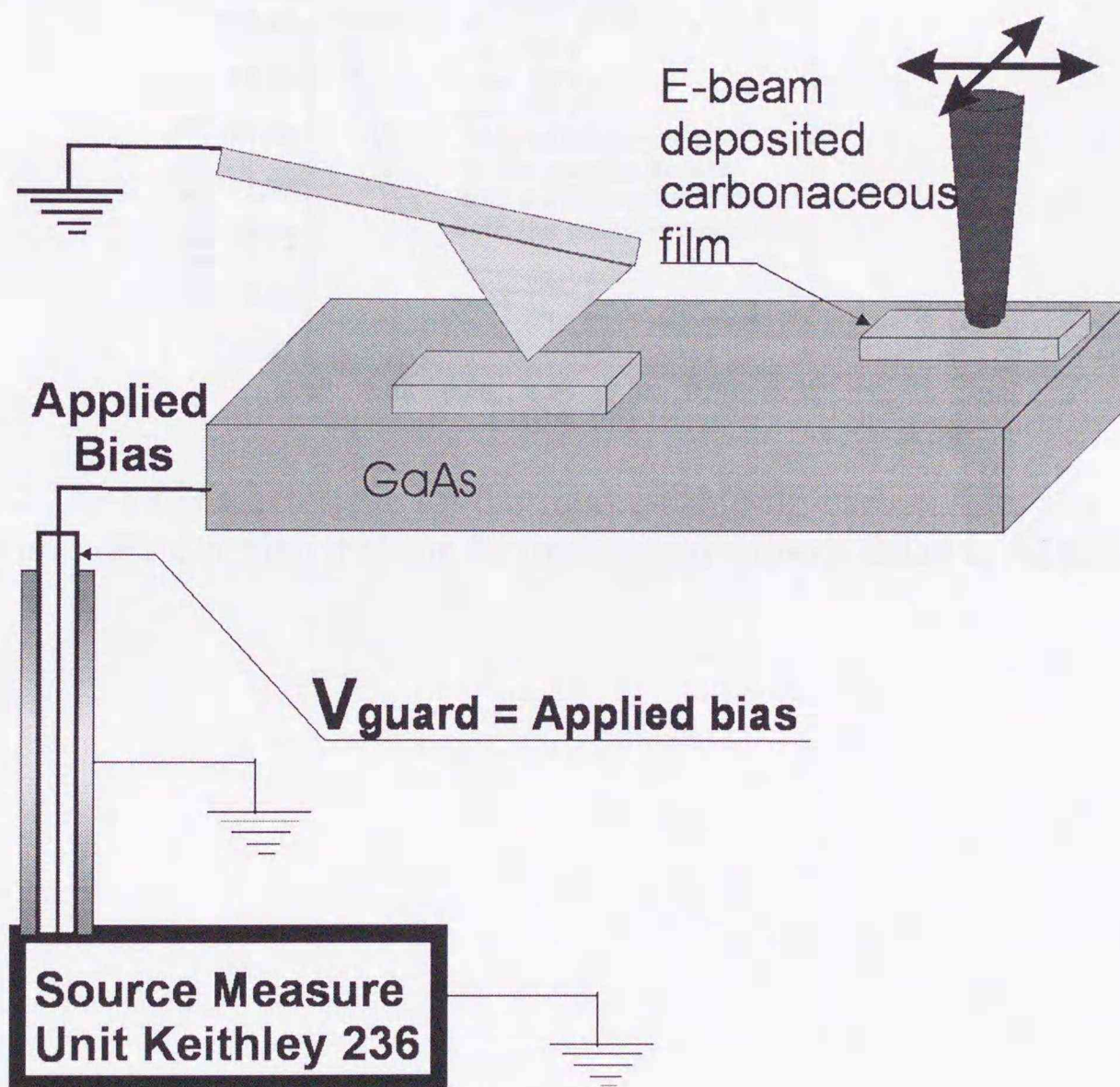


Fig. A.1 Connection diagram.

The transient characteristic of the current in the cable-cantilever-sample circuit for two configurations was measured as a function of the time passed from the application of the constant bias. The two I-t characteristics are shown in Fig. A.2. Pulses shorter than 0.02 s will be seriously delayed.

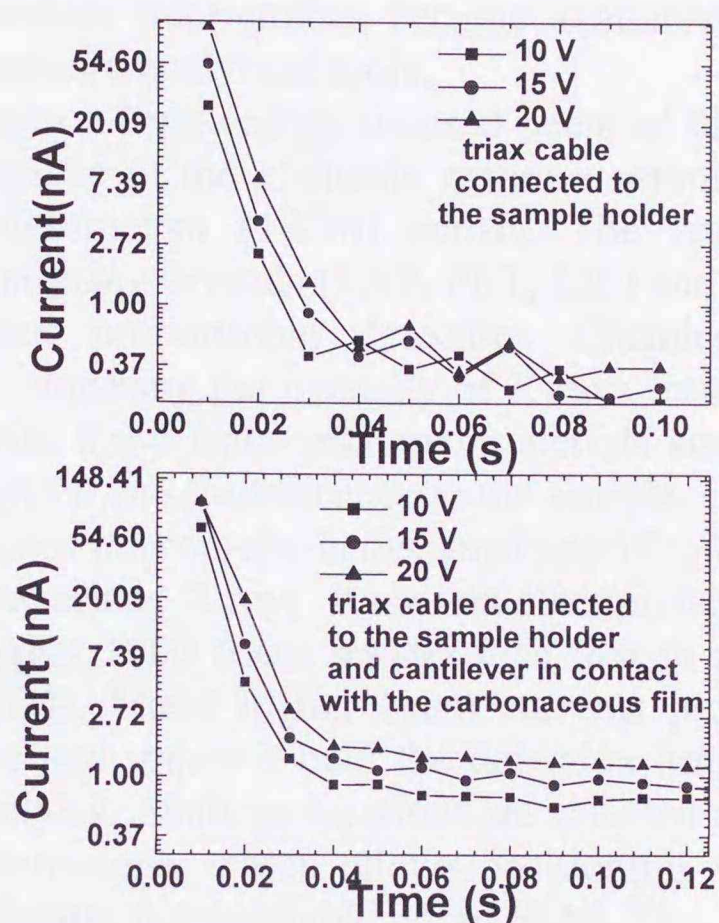


Fig. A.2 The I-t characteristic for the source-cable-tip-carbon line. The minimum pulse duration that can be transmitted without delay is ~ 0.02 s.

Appendix 5

Electron microprobe analysis

Electron microprobe analysis (EMPA) is a non-destructive method for determining the chemical composition of solid materials. Commercial electron microprobes became available in the 1960s, and have become standard analytical tools.

EMPA uses a high-energy focused beam of electrons to generate X-rays characteristic of the elements within a sample from volumes as small as 3 micrometers (10^{-6}m) across. The resulting X-rays are diffracted by analyzing crystals (TAP, PET, LIF) and counted using gas-flow and sealed proportional detectors. Chemical composition is determined by comparing the intensity of X-rays from standards (known composition) with those from unknown materials and correcting for the effects of absorption and fluorescence in the sample.

The electron microprobe is designed specifically for detecting and measuring characteristic X-rays. It uses an electron beam current from 10 to 200 nA, roughly 1000 times greater than that in a scanning-electron microscope (SEM). These higher beam currents produce more X-rays from the sample and improve both the detection limits and accuracy of the resulting analysis. Analysis locations are selected using a transmitted-light optical microscope, which allows positioning accurate to about 1 micrometer, a feature not available on an SEM. The resulting data yield *quantitative* chemical information in a textural context.

The electron microprobe can quantitatively analyze elements from sodium ($Z=11$) to uranium ($Z=92$) at routine levels as low as 100 ppm.

Data sheet example

Group : Adrian Sample : m99097
 UNK No. : 1 Comment :
 Stage : X= 12.8108 Y= 58.4268 Z= 11.3953
 Acc. Voltage : 9.0 (kV) Probe Dia. : 10 Scan : On Mag : 300000
 Dated on Aug 20 11:03 1999
 WDS only No. of accumulation : 1

Curr.(A) : 1.497E-07

Element	Peak(mm)	Net(cps)	Bg-(cps)	Bg+(cps)	S.D.(%)	D.L.(ppm)
1 Zn	133.259	1336.7	124.2	81.6	0.93	150
2 S	171.970	17680.6	114.0	102.2	0.24	77
3 Cd	126.727	10034.9	115.2	94.6	0.32	233
4 Mg	107.503	7057.2	269.9	158.2	0.39	45

ZAF Metal

Element	Wt.(%)	Atom(%)	K(%)	ZAF	Z	A	F
Zn	6.512	5.7729	4.429	1.4704	1.0018	1.4677	1.0000
S	27.168	49.1063	29.268	0.9282	0.9256	1.0089	0.9940
Cd	59.367	30.6071	51.026	1.1635	1.1358	1.0243	1.0000
Mg	6.089	14.5137	4.863	1.2519	0.8410	1.4898	0.9992

 Total 99.136 100.0000 89.587 Iteration = 5

Intensity & Wt. % Group : Adrian Sample : m99097

Unknown Specimen

Group : Adrian Sample : m99097
 UNK No. : 2 Comment :
 Stage : X= 12.5180 Y= 58.4278 Z= 11.3930
 Acc. Voltage : 9.0 (kV) Probe Dia. : 10 Scan : On Mag : 300000
 Dated on Aug 20 11:06 1999
 WDS only No. of accumulation : 1

Curr.(A) : 1.496E-07

Element	Peak(mm)	Net(cps)	Bg-(cps)	Bg+(cps)	S.D.(%)	D.L.(ppm)
1 Zn	133.238	1358.9	118.0	84.8	0.92	149
2 S	171.961	17757.3	117.0	103.4	0.24	78
3 Cd	126.713	10098.5	123.6	95.8	0.32	238
4 Mg	107.518	7040.2	274.7	162.8	0.39	46

ZAF Metal

Element	Wt.(%)	Atom(%)	K(%)	ZAF	Z	A	F
Zn	6.624	5.8416	4.506	1.4702	1.0016	1.4679	1.0000
S	27.301	49.0872	29.415	0.9281	0.9254	1.0089	0.9940
Cd	59.769	30.6530	51.384	1.1632	1.1356	1.0243	1.0000
Mg	6.080	14.4183	4.855	1.2524	0.8408	1.4907	0.9992

 Total 99.774 100.0000 90.160 Iteration = 5

Appendix 6

(* Mathematica code for fitting the bandgap energy of the ZnMgCdS alloy *)

```
ClearAll;
<<Statistics`NonlinearFit`
data={{0.203,0.199,3.01},{0.262,0.153,2.955},{0.515,0.091,3.068},{0.3
59,0.199,3.15},{0.388,0.068,2.9},{0.454,0.163,3.18},{0.466,0.186,3.28}
,{0.114,0.284,2.96},{0.24,0.35,3.19},{0.537,0.0,2.86}}
data1={{0.114,0.284,2.96},{0.24,0.35,3.19},{0.345,0.402,3.51}}
EgZnS300K:=3.6842
EgZnS4K:=3.84
EgCdS300K:=2.42
EgCdS300Ka:=2.36 (* JJAP 28 no.6 1989,L898-L900 *)
EgCdS4K:=2.56
(* EgMgS300K:= to be fitted *)
Ebowx=0.773 (* EbZnCdS from the ZnCdS ternary bandgap fitting *)
Ebowz=0.1 (* EbZnMgS approximated from Phys. Rev. B 57 (1998)
2257*)
(* Ebowy= EbMgCdS to be fitted *)
NonlinearFit[data1,f*EgZnS300K+g*EgMgS300K+(1-f-
g)*EgCdS300K-(Ebowx*f+Ebowy*g)*(1-f-g)-Ebowz*f*g,
{f,g},{EgMgS300K,6.0,3.0,6.0},{Ebowy,3.0,-1.0,3.0}},
ShowProgress-> True]
(* first fit to get an estimation of the Ebowy *)
Egfittedall[f_,g_]=NonlinearFit[data,
f*EgZnS300K+g*EgMgS300K+(1-f-g)*EgCdS300K-
(Ebowx*f+Ebowy*g)*(1-f-g)-Ebowz*f*g,
{f,g},{EgMgS300K,6.0,3.0,6.0},ShowProgress-> True]
points=Point /@data;
pointsgraph=Graphics3D[{PointSize[0.03],RGBColor[1,0,0],points}];
fitting:=Plot3D[Egfittedall[i,j],{i,0,1},{j,0,1},PlotPoints->20,
DisplayFunction->Identity];
Show[fitting,pointsgraph,PlotRange->{{0,1},{0,1},{2.2,4.85}},Shading-
>False,
AxesLabel->{"x","y","Eg"},ViewPoint->{-2.310,-1.170,0.300},
DisplayFunction->$DisplayFunction]
```

>output

$$3.6842 f + 2.42 (1-f-g) - (1-f-g) (0.773 f + 0.75162 g) + 4.60008 g - 0.1 f g$$

>

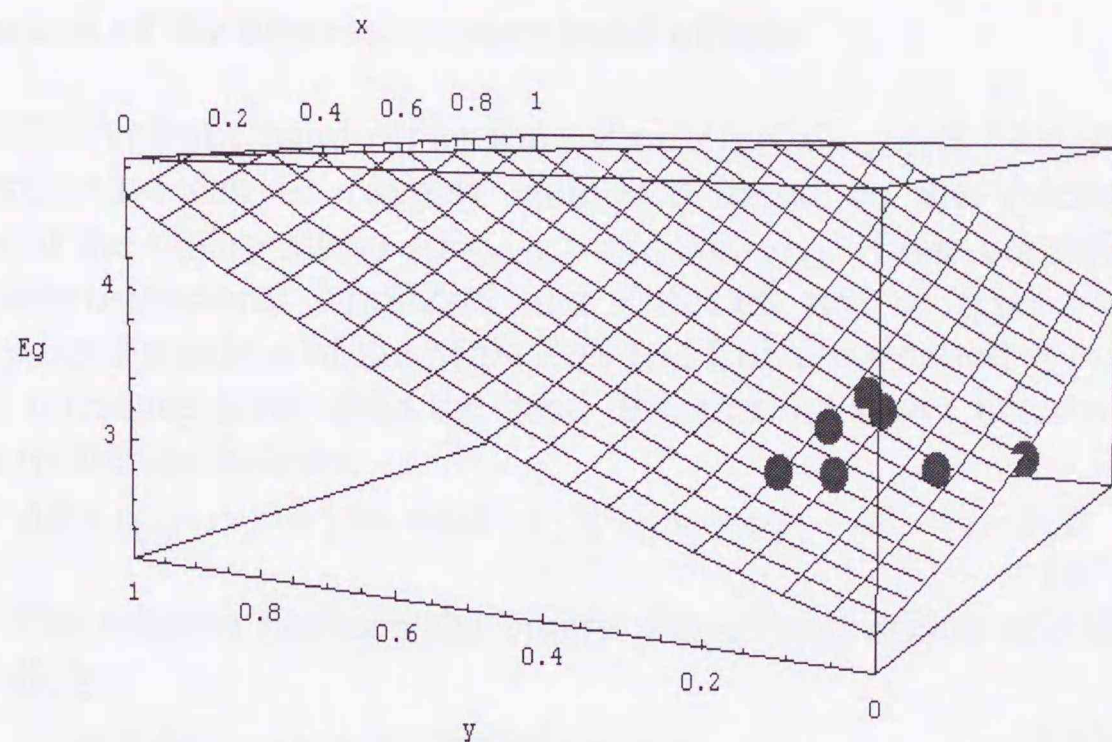


Fig. A3. The fit of the bandgap energy of the $Zn_xMg_yCd_{1-x-y}S$ alloy. The full circles are the experimental data. Some of the experimental data are situated behind the fitted surface.

Appendix 7

Estimation of the heterostructure band offsets

The valence band offset for a $\text{Zn}_{x_1}\text{Mg}_{y_1}\text{Cd}_{(1-x_1-y_1)}\text{S} / \text{Zn}_{x_2}\text{Cd}_{(1-x_2)}\text{S}$ heterostructure can be roughly estimated based on the valence band offsets of the binary alloys $\Delta E_{\text{ZnS/MgS}}$ and $\Delta E_{\text{Cd/ZnS}}$. If one considers that both heterostructures MgS/ZnS and ZnS/CdS are of type I and the valence band maxima of the MgS , ZnS and CdS are situated at m , z , c eV from a reference level then the band offset of the above heterostructure can be written as follows:

$$\Delta E_v(x_1, y_1, x_2) = [zx_2 + c(1 - x_2)] - [zx_1 + my_1 + c(1 - x_1 - y_1)] \quad (\text{A7.1})$$

The relation between the binary alloys band offsets and the m, z, c is as follows:

$$z - m = \Delta E_{\text{ZnS/MgS}}; c - z = \Delta E_{\text{CdS/ZnS}} \quad (\text{A7.2})$$

By developing the equation A7.1, regrouping and replacing c, z, m based on the eqs. A7.2, the band offset of the alloy results to be:

$$\Delta E_v(x_1, y_1, x_2) = \Delta E_{\text{ZnS/MgS}} \times y_1 + \Delta E_{\text{CdS/ZnS}} \times (x_1 + y_1 - x_2), \quad (\text{A7.3})$$

where $\Delta E_{\text{Zn/MgS}} = 0.3 \text{ eV}$ [1], $\Delta E_{\text{Cd/ZnS}} = 0.18 \text{ eV}$ [2]. In the case of the $\text{Zn}_{0.335}\text{Mg}_{0.18}\text{Cd}_{0.485}\text{S} / \text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$ heterostructure, ΔE_v is 0.069 eV , ΔE_c is 0.191 eV and results in ratio of the band offsets of $\Delta E_c / \Delta E_v = 73\% / 27\%$.

A second method for the estimation of the band offsets it is to calculate the energy of the optical transitions for a series of single QW with different thickness and then to compare these with the experimental data.

For this purpose, a series of samples containing a heterostructure lattice-matched to GaAs were grown. The epilayers grown by MOMBE were: 100-nm-thick $\text{Zn}_{0.335}\text{Mg}_{0.18}\text{Cd}_{0.485}\text{S}$ barrier followed by 2,4,6-nm-thick single quantum well of $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{S}$, respectively, and a 100-nm-thick $\text{Zn}_{0.335}\text{Mg}_{0.18}\text{Cd}_{0.485}\text{S}$ layer.

After growth initiation of type D at 300°C , the epilayers were grown at 380°C with the following BEPs: $\text{DEZn} - 0.95 \times 10^{-4} \text{ Torr}$, $(\text{MCp})_2\text{Mg} - 1.3 \times 10^{-4} \text{ Torr}$, $\text{DMCd} - 1.6 \times 10^{-4} \text{ Torr}$, $\text{DtBS} - 10 \times 10^{-3} \text{ Torr}$. The quantum wells thickness was estimated from the growth time and the growth rate of a thick epilayer with similar composition and growth conditions. This may introduce some uncertainty in the estimation of the QW thickness, especially when this is in the range of a few monolayers (MLs).

At room temperature, the bandgap energies of the bulk alloys with similar compositions as the well and the barrier regions were considered to be 2.77 eV and 3.03 eV, respectively. At low temperature, the bandgap energy difference was considered to be the same but the contribution of the exciton binding energy was included (~ 30 meV) [3].

The energy levels of the quantum well were calculated considering a linear approximation for the effective mass of the carriers in alloy. The conduction band effective mass in the well region was approximated with a linear relation $0.34x + (1-x)0.14$, where x is the Zn composition and the conduction band effective masses of ZnS and CdS were taken from published data [4]. The effective mass in the barrier region was considered to have the same value (data on MgS are not available in the literature). The valence band effective mass in the well region was approximated using the effective masses of the binary alloys, which are $m_{\text{ZnS}}^{\text{hh}} = 1.76m_0$ and $m_{\text{CdS}}^{\text{hh}} = 1.432m_0$ [4]. The alloy valence band effective mass was calculated to have value of $1.515m_0$ by using a linear dependence. However, these values are relatively large so a second calculation of the energy levels was performed for the case when the valence band effective mass was calculated based on Luttinger parameters [5]. In this case the alloy valence band effective mass has a value of $0.75m_0$. The photoluminescence spectra were measured at room temperature and at 30 K under He-Cd laser excitation.

Figures A4(5) (a) and (b) show the peak energies of the measured photoluminescence spectra at room temperature and 30 K, respectively. In the same A4 and A5 figures the calculated energies for the single quantum wells optical transitions are plotted as a function of the well thickness for different band offsets in the case of the two valence band effective masses considered. The line connecting the closed-square symbols gives the closest match to the experimental data. In the case $m_{\text{ZnCdS}}^{\text{hh}} = 1.515m_0$, the band offsets are the following: ΔE_v is 0.04 eV, ΔE_c is 0.22 eV and results in a ratio of the band offsets of $\Delta E_c/\Delta E_v = 84\%/16\%$ (Fig. A4). In the case $m_{\text{ZnCdS}}^{\text{hh}} = 0.75m_0$, the band offsets are the following: ΔE_v is 0.06 eV, ΔE_c is 0.2 eV and results in a ratio of the band offsets of $\Delta E_c/\Delta E_v = 77\%/23\%$ (Fig. A5).

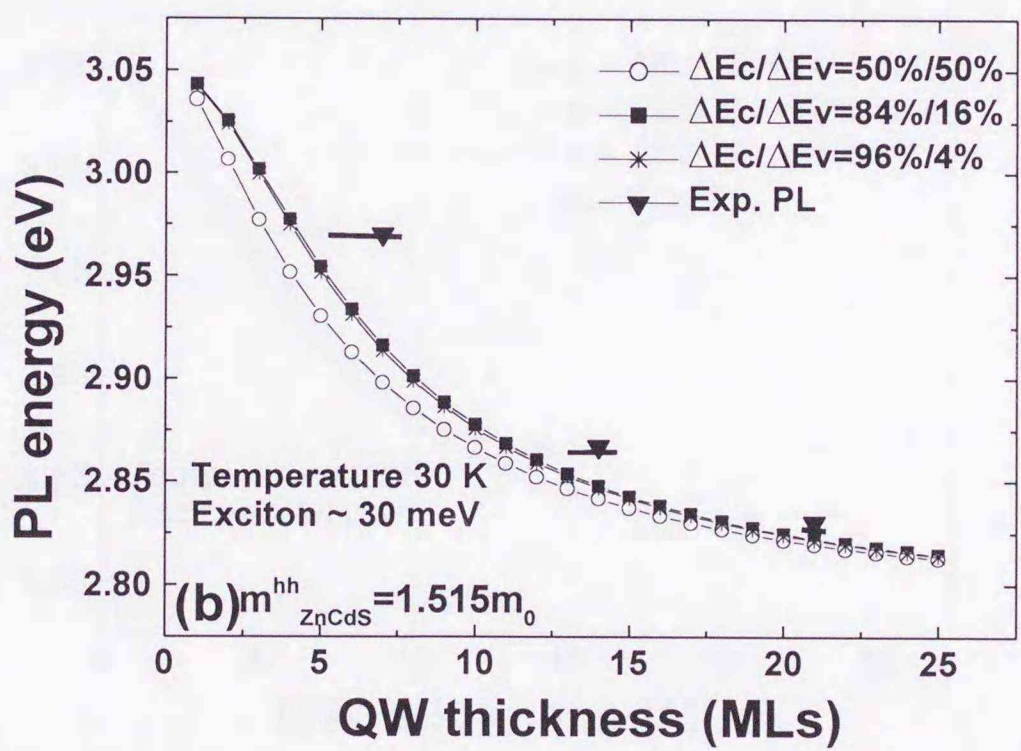
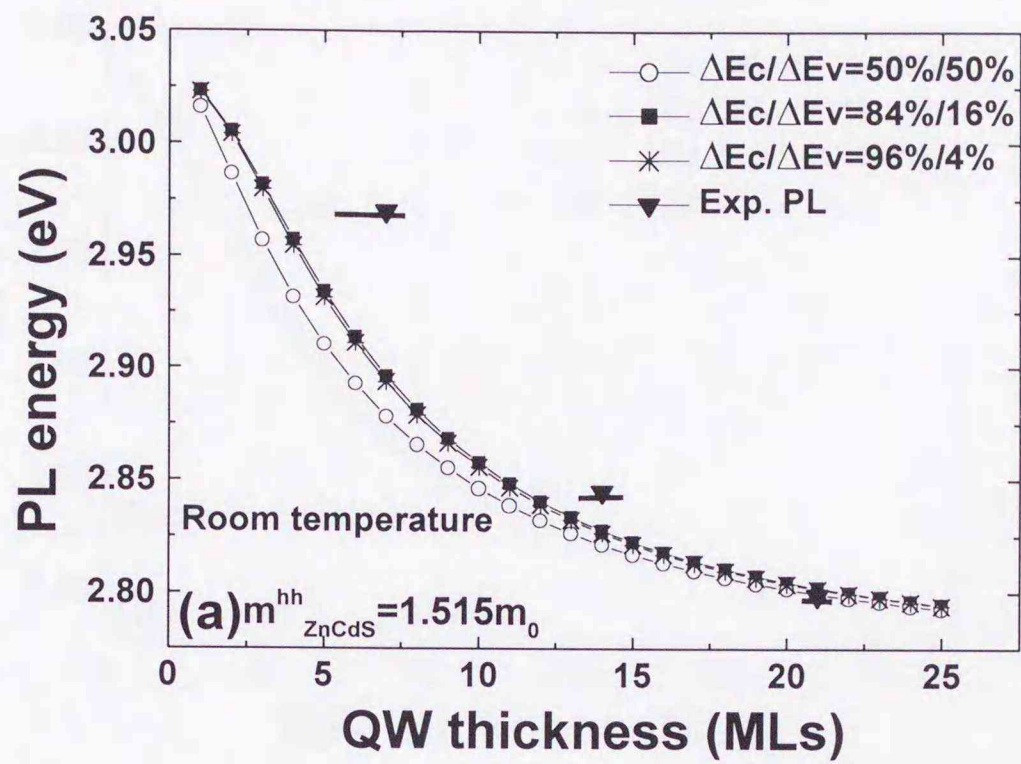


Fig. A4 (a) Room temperature (b) 30 K. The horizontal lines crossing the experimental data (solid triangles) give the error in calculation of the QW thickness. The exciton contribution was considered only at low temperature.

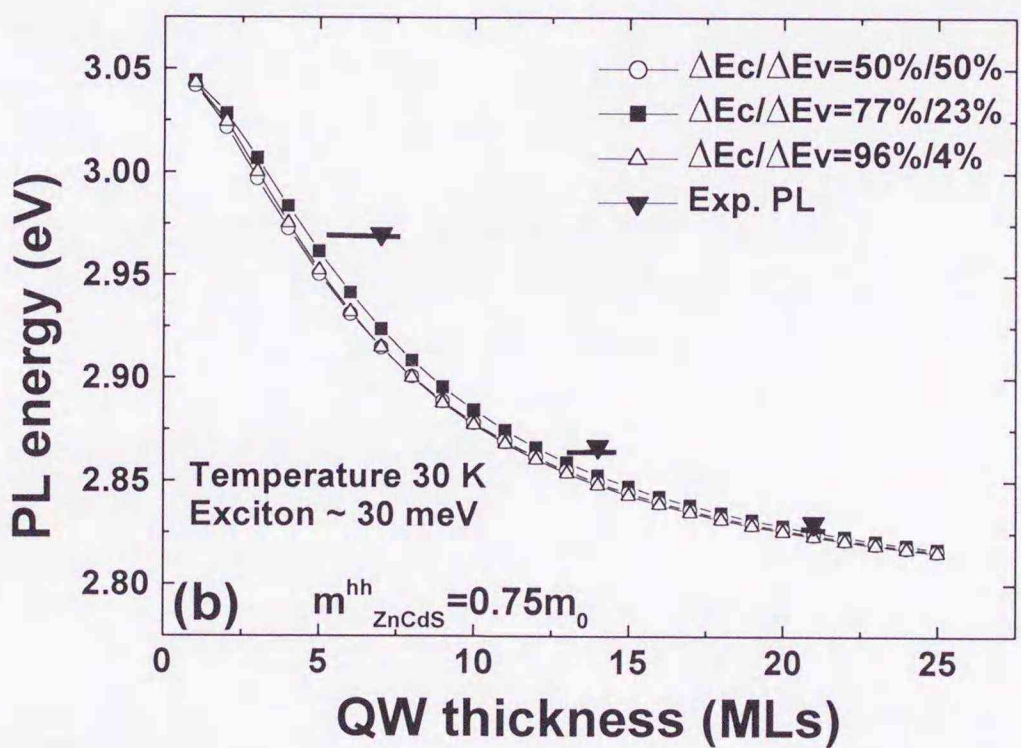
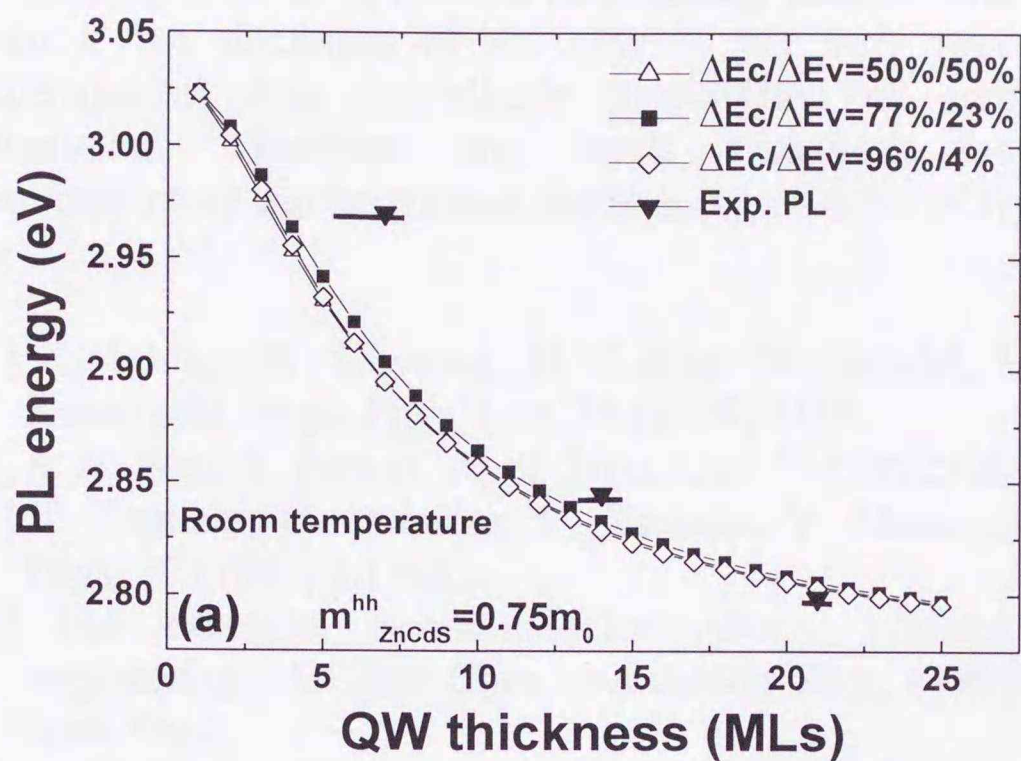


Fig. A5 (a) Room temperature (b) 30 K. The horizontal lines crossing the experimental data (solid triangles) give the error in calculation of the QW thickness. The exciton contribution was considered only at low temperature.

In the case of the lighter valence band effective mass, the band offsets distribution between the conduction band edge and the valence band edge does not influence very much the energy of the optical transitions in the QW.

This method will give more accurate results only in the case when the thickness of the QWs will be precisely known. One should note that even if the thickness of the QW is not very precisely known, the experimental data are clearly blue-shifted as compared with the calculation. Therefore, the bands alignment for this type of heterostructure can be without doubt assigned to be of type I.

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