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Formation of Size- and Position-Controlled Nanometer Size Pt Dots on GaAs and InP Substrates by Pulsed Electrochemical Deposition

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Abstract

Attempts were made to form regular arrays of size- and position-controlled Pt-dots on GaAs and InP by combining an in situ electrochemical process with the electron beam (EB) lithography. This utilizes the precipitation of Pt nano-particles at the initial stage of electrodeposition. First, electrochemical conditions were optimized in the mode of self-assembled dot array formation on unpatterned substrates. Minimum in-plane dot diameters of 22 nm and 26 nm on GaAs and InP, respectively, were obtained under the optimal pulsed mode. Then, Pt dots were selectively formed on patterned substrates with open circular windows formed by EB lithography, thereby realizing dot-position control. The Pt dot was found to have been deposited at the center of each open window, and the in-plane diameter of the dot could be controlled by the number, width and period of the pulse-waveform applied to substrates. A minimum diameter of 20 nm was realized in windows with a diameter of 100 nm, using a single pulse. Current-voltage (I-V) measurements using an atomic force microscopy (AFM) system with a conductive probe indicated that each Pt dot/n-GaAs contact possessed a high Schottky barrier height of about 1 eV.

KEYWORDS: metal dot array, Schottky contact, electrochemical process, electron-beam lithography, Pt, InP, GaAs, SEM, AFM, conductive probe

1. Introduction

In view of their applications to next-generation electronic devices, studies on the single-electron transistors and memories are being carried out extensively. The unique feature of these single-electron devices is that they possess quantum dots for the confinement of electrons. Therefore, in order to realize high-density logic and memory circuits, it is necessary to fabricate arrays of size- and position-controlled dots in the nanometer size range.

With this background, various fabrication techniques for the formation of arrays of quantum dot structures have been investigated thus far, for example, selective growth techniques, self-organized formation techniques and nano-processing techniques based on scanning probe microscopy (SPM). The selective growth technique is one of the promising methods for the fabrication of quantum dot structures. On the other hand, the self-organized formation technique has an advantage of a high-density dot formation as compared to the selective growth technique, though, it is difficult to control the dot position precisely.

The purpose of this paper is to show that nanometer-size Pt dots can be formed in a size- and position-controlled fashion on GaAs and InP substrates by combining our novel in-situ electrochemical process with the electron beam (EB) lithography. This is an extension of our recent work¹⁻⁶⁾ where nanometer-sized metal particles were formed on III-V semiconductor substrates in self-organized fashion using the in situ electrochemical process. This process is capable of producing well-behaved Schottky contacts with high Schottky barrier heights of 1.1 eV and 0.9 eV for n-GaAs¹⁾ and n-InP²⁾, respectively.

In this study, Pt particles were first deposited in a self-assembled fashion on the unpatterned n-GaAs and n-InP substrates in order to optimize the electrochemical condition for

the formation of small Pt particles with uniform size distribution. Then, attempts were made to form regular arrays of size- and position- controlled Pt dots by depositing Pt onto the patterned substrates having open circular windows as defined by EB lithography. Finally, current-voltage (I-V) measurements of each nano-Schottky dot was carried out, using an atomic force microscopy (AFM) system with a conductive probe.

2. Experimental

The in situ electrochemical process consisted of controlled anodic etching of the semiconductor surface followed by metal deposition in the same electrolyte. In this study, an HCl-based electrolyte containing Pt ions was used for Pt deposition.

The electrolyte bath contained three electrodes, i.e., a semiconductor electrode, a Pt counter electrode and a reference saturated calomel electrode (SCE). N-type (100) InP wafers with a donor concentration of $5 \times 10^{16} \text{ cm}^{-3}$ and n-type (100) GaAs wafers with a donor concentration of $2 \times 10^{16} \text{ cm}^{-3}$ were used as the semiconductor electrodes. For the current supply, GeAu/Ni ohmic back contacts were formed by vacuum deposition and subsequent annealing in N_2 atmosphere. Just before immersing the semiconductors into the electrolyte, the native oxide of the samples was chemically etched by a H_2SO_4 -based solution for a minute. The potential of the semiconductor electrode was controlled with respect to the SCE reference by a potentiostat with a pulsed mode capability.

It was found that the selective etching and metal deposition could be performed on the semiconductor electrodes by mask patterning the electrode surface with the photo resist film (OFPR8600, Tokyo Ohka Kogyo CO., Ltd.) or the EB resist film (OEPR1000, Tokyo Ohka Kogyo CO., Ltd.) using standard lithography techniques. Such organic films are not attacked by an electrolyte, and the electrochemical reactions occur only at the conductive area of the electrolyte/semiconductor interface.

Figures 1(a) and 1(b) show the pulse waveforms applied to the substrate for the anodic etching of the surface and metal deposition, respectively. In the pulsed mode, the waveforms were adjusted so that the electrochemical reactions occurred only in the pulse-on time. Therefore, the electrochemical process could control both the etching thickness and the deposition thickness by the number of pulses applied.

An avalanche pulse was first applied to the substrate for the anodic etching. Compared with the chemical etching, the anodic pulse etching produced smooth surfaces by repeated production of anodic products of the semiconductor through oxidation reaction in pulse-on time and its removal from the surface vicinity in the pulse-off time.

After the etching, the plating pulse was immediately applied to the substrate in situ in the same electrolyte. In this way, exposure of the semiconductor surface to the air could be avoided. In order to obtain the reducing reaction of the metal ions only in the pulse-on time, the negative offset bias (V_{rd}) was set at around 0.4 V, where the cathodic current started to flow. Typical values of the pulse width (t_{wd}), the pulse period (t_{pd}) and the pulse height (V_{hd}) were 10 ms, 400 ms and 1.0 V, respectively.

Use of the pulsed mode instead of the dc mode was found to result in an additional advantage of improving the current efficiency for metal plating. This largely avoided the problem of H_2 -evolution on the semiconductor electrode.³⁾ Other researchers also reported that Pt-film formation could be affected by the H_2 -adsorption onto the working electrode.^{7,8)}

The experimental procedure used in this study is schematically shown in Figs. 2(a) and 2(b). First, using the mode of self-assembled dot array formation on unpatterned substrates as shown in Fig. 2(a), the electrochemical conditions were optimized for the formation of small and uniform Pt particles. Then, the patterned substrates were employed for the selective formation of Pt dot arrays as shown in Fig. 2(b). For the selective deposition of Pt dots at desired positions, open windows were patterned on the top of the semiconductor surface with periods of 200 nm -

300 nm by standard EB lithography using JBX-5000LS (JEOL). An electron beam with an accelerating voltage of 50 kV and a beam diameter of 50 nm was used.

The scanning electron microscopy (SEM) and AFM observations of the surface morphology of Pt deposited substrate were carried out using a Hitachi S-4100 and a Nanoscope II (Digital Instruments, Inc.), respectively. Furthermore, the electrical measurements of the Pt dots were performed using an AFM system with a Si conductive probe.

3. Results and Discussion

3-1. Pt deposition on unpatterned substrates

Figures 3(a) and 3(b) show the typical SEM images of Pt-deposited surfaces of unpatterned n-GaAs and n-InP after the pulsed electrochemical process, where the measured diameter distributions of the Pt particles are also indicated. The conditions of the waveforms were $V_{hd} = 1.0$ V, $V_{rd} = 0.35$ V, $t_{wd} = 10$ ms, $t_{pd} = 400$ ms and deposition time = 10 s for GaAs and $V_{hd} = 1.0$ V, $V_{rd} = 0.4$ V, $t_{wd} = 10$ ms, $t_{pd} = 400$ ms and deposition time = 3 min for InP. In the initial stages of deposition, nanometer-sized Pt particles were formed on the substrates in a self-organized fashion. Further deposition increased the number of size-saturated particles, eventually leading to full surface coverage by Pt nano-particles.

As seen in Figs. 3(a) and 3(b), the particle formation process proceeded in almost the same fashion for n-GaAs and n-InP. The size distribution of such Pt particles can be represented in terms of the average in-plane diameter, the average vertical height and their standard deviations. As for the in-plane size, it was found that the average in-plane diameter of the particle and its uniformity strongly depended on the electrochemical conditions. Compared with the dc mode, the pulsed mode produced smaller, more uniform Pt particles on the III-V substrates. For example, the average diameter and a rms size deviation of Pt particles on InP formed by the dc mode were 29 nm and 10 nm, respectively. On the other hand, the pulsed mode produced smaller, more uniform Pt particles on InP with an average diameter of 26 nm and a rms deviation of 3 nm under an optimum condition.

Furthermore, in the pulsed mode, the diameter distributions were strongly dependent on the pulse conditions. For example, Fig. 4 shows the observed average particle diameter and the standard deviation vs the ratio of the applied pulse width (t_{wd}) to the pulse period (t_{pd}) of the pulse for Pt particles on InP. As seen in Fig. 4, both the particle diameter and the width of the diameter distribution decreased with smaller t_{wd} and longer t_{pd} . This result shows that the size distribution is basically determined by the supply of metal-ion species at the semiconductor/electrolyte interface. Furthermore, this result suggests that it is important to quickly deposit the metal in a short pulse-on time and to recover the reduced metal-ion density to a sufficient level in a long pulse-off time.

The vertical height of the particle was generally smaller than the in-plane diameter of each particle, and it was also observed that it had a tendency to vary with the in-plane diameter, roughly keeping the ratio of the height to the diameter within the range of 0.5 to 0.8. However the correlation of the particle height and the electrochemical conditions were less clear as compared to the relationship between the particle diameter and the electrochemical conditions.

3-2. Fabrication of Pt dot array on patterned substrates

In order to selectively deposit Pt dots at desired positions, windows with a diameter of 100 nm were patterned on n-GaAs and n-InP substrates by standard EB lithography, as shown in Fig. 2(b), before the electrochemical Pt deposition. Figures 5(a) and 5(b) show the SEM images of the Pt dot array formed on n-GaAs and n-InP patterned substrates, respectively. Pt dots were selectively formed within the open windows, as shown in Fig. 5. This result indicates that the electrochemical reaction occurred only within the conductive area at the semiconductor/electrolyte interface and not through the EB resist film.

Furthermore, the shape of the Pt dot arrays formed by changing the number of pulses applied was investigated in detail by AFM observation. The AFM image of a Pt dot array formed

on n-GaAs by applying five pulses and one pulse are shown in Figs. 6(a) and 6(b), respectively, with a surface profile. As seen in Fig. 6(a), the Pt dots with a diameter of 100 nm and a period of 300 nm were selectively fabricated on the open window formed by the EB lithography applying five pulses. Furthermore, it was also observed that each Pt dot with a diameter of 100 nm consisted of several Pt particles with diameters of 20 - 30 nm. This particle diameter was almost consistent with the particle diameter observed at the initial stage of Pt deposition on the unmasked substrates. This result suggests that smaller Pt dots corresponding to one particle size can be obtained by reducing the number of the pulses applied, hence reducing the total electric charge passing through the electrolyte/semiconductor interface.

With the application of one pulse, as shown in Fig. 6(b), Pt dots were selectively formed only within the open windows with a period of 200 nm, thereby realizing precise dot-position control. Furthermore, it was also observed that Pt dots were formed at the center of each open window without initially touching the window periphery. From the AFM observation, the diameter of a Pt dot was estimated to be about 20 nm which was much smaller than the size of the open window formed by EB lithography. The reason why the Pt dot formation starts at the center of the window is not yet clear. One possible reason could be that the center of the window provides a minimum electrochemical potential for Pt deposition due to its symmetry, whereas the pulse fields near the periphery cannot increase due to the presence of the thick insulating resist film. However, the possibility of the local modification of the surface energy caused by electron-beam irradiation cannot be ruled out.

The measured relationship between the dot diameter and the applied pulse numbers is shown in Fig. 7. The solid line in Fig. 7 provides visual reference. In this case, the diameter of the Pt dots increased in proportion to the number of the applied pulses, and the smallest particles with diameters of 20 nm were obtained by application of one pulse. Further size reduction appears possible by a further optimization of the applied pulse waveform so as to reduce the charge supply per pulse.

3-3. *I-V characteristics of a single Pt dot/n-GaAs contact*

Current-voltage (I-V) characteristics of a single Pt dot/n-GaAs contact were measured by an AFM system equipped with a conductive probe. The schematic diagram of the conductive AFM system and the typical I-V curve of Pt dot/n-GaAs contact are shown in Figs. 8(a) and 8(b), respectively. This conductive AFM system can provide the normal AFM observation by the optical lever method and the I-V measurements between the sample surface and back surface using a HP4156A parameter analyzer. The conductive probe is fabricated from highly doped Si with a radius of curvature of about 10 nm. During the electrical measurements, the laser light was turned off in order to avoid the photovoltaic effect.

As shown in Fig. 8(b), the current-voltage (I-V) characteristics of a single Pt dot/n-GaAs contact clearly show rectifying behavior. This result indicates that each Pt dot formed a well-behaved Schottky barrier with a high Schottky barrier height (SBH) (1.0 eV) and very low leakage currents on the n-GaAs surfaces. Thus, this electrochemical process is expected to be used for the fabrication of metal Schottky dot arrays with high electron confinement.

4. Conclusions

Nanometer-scale Pt dots were successfully formed on n-InP and n-GaAs substrates by an electrochemical process in a self-organized fashion. The results can be summarized as follows.

- (1) The electrochemical process in pulsed mode can produce uniform Pt particles. The size distribution of the particles strongly depends on pulse conditions, and their uniformity is improved with shorter pulse widths and longer pulse periods.
- (2) Regular arrays of Pt particles can be selectively formed within the open areas defined by EB lithography, thereby realizing precise dot-position control. The size of Pt dots decrease with pulse number. The smallest Pt particles with the diameter of 20 nm were formed within the open windows with a diameter of 100 nm.

(3) According to I-V measurements obtained by a conductive AFM probe, each Pt dot/n-GaAs contact forms a nanometer-sized Schottky barrier with a high barrier height.

From these results, we believe that our in situ electrochemical process is promising for the fabrication of size- and position-controlled quantum dot arrays.

Acknowledgement

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References

- 1) N-J. Wu, T. Hashizume and H. Hasegawa: Jpn. J. Appl. Phys. 33 (1994) 936.
- 2) T. Sato, S. Uno, T. Hashizume and H. Hasegawa: Jpn. J. Appl. Phys. 36 (1997) 1811.
- 3) N. J. Wu, T. Hashizume, H. Hasegawa and Y. Amemiya: Jpn. J. Appl. Phys. 34 (1995) 1162.
- 4) S. Uno, T. Hashizume, S. Kasai, N. J. Wu and H. Hasegawa: Jpn. J. Appl. Phys. 35 (1996) 1258.
- 5) T. Sato and H. Hasegawa: Proc. 9th Int. Conf. Indium Phosphide and Related Materials ,Cape Cod, 1997 (IEEE Cat. #97CH36085, 1997) p.517.
- 6) C. Kaneshiro, T. Sato and H. Hasegawa: Proc. 10th Int. Conf. Indium Phosphide and Related Materials, Tsukuba, 1998 (IEEE Cat. #98H36129, 1998) p.191.
- 7) P. Allongue and E. Souteyrand: J. Vac. Sci. Technol. B 5 (1987) 1644.
- 8) R. Reineke and R. Memming: Surf. Sci. 192 (1987) 66.

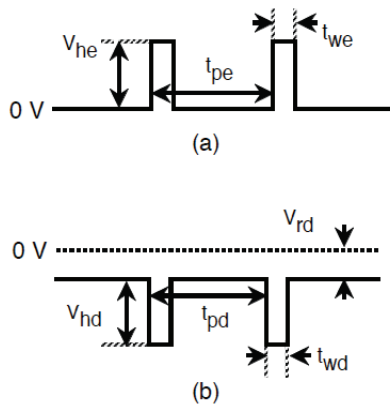


Fig. 1. Applied potential waveforms for (a) anodic etching of semiconductor surfaces and (b) cathodic metal deposition in in situ electrochemical process.

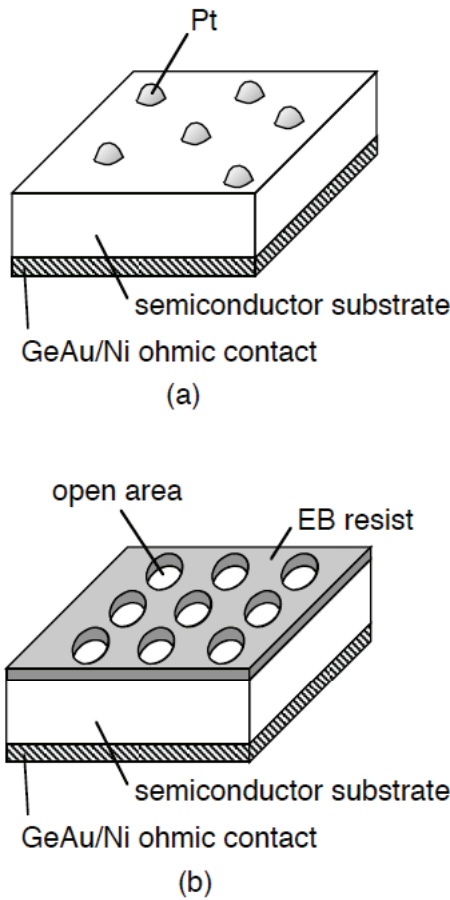


Fig. 2. Schematic of sample preparation: (a) for self-organized formation of Pt particles on unpatterned substrate and (b) for selective fabrication of Pt dot array on patterned substrate.

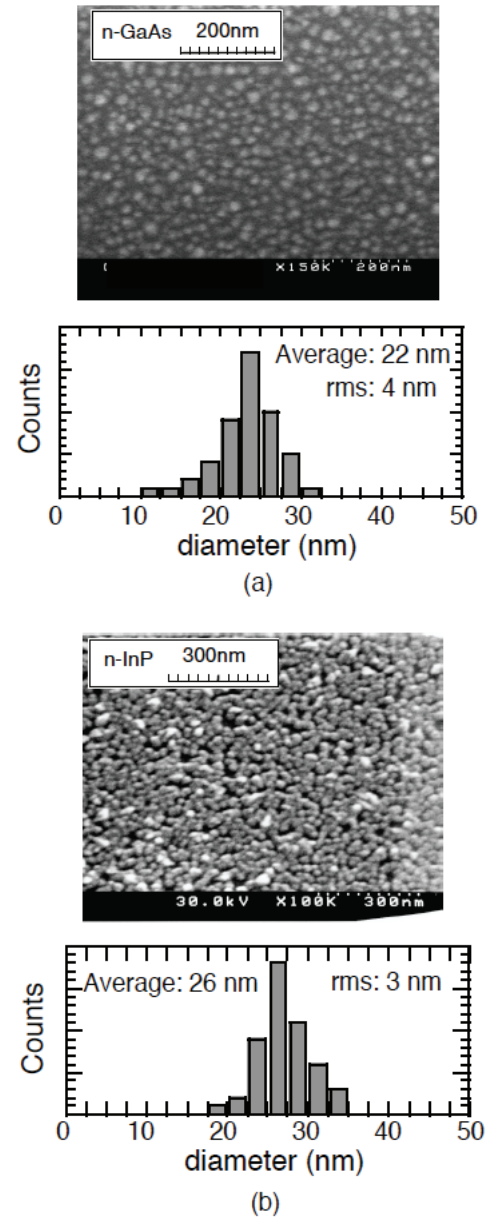


Fig. 3. Typical SEM images of Pt-deposited surface and diameter distributions of Pt nano-particles formed on (a) n-GaAs and (b) n-InP in pulsed mode.

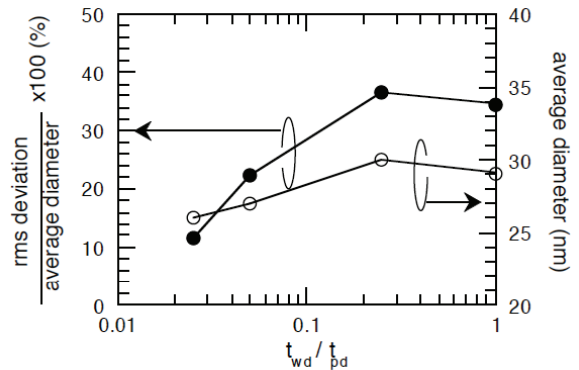


Fig. 4. Plot of average diameter and diameter distribution of Pt particles vs ratio of pulse width to pulse period in pulsed mode.

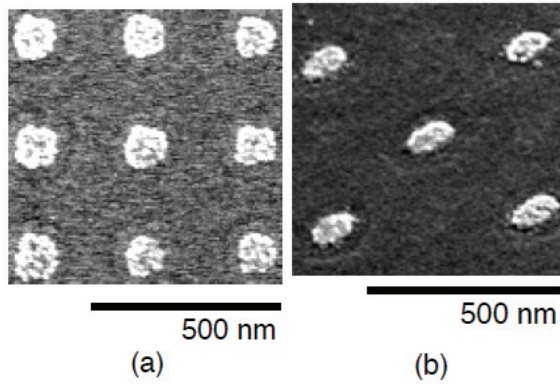


Fig. 5. SEM images of Pt dot array fabricated on (a) n-GaAs and (b) n-InP.

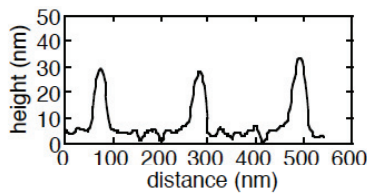
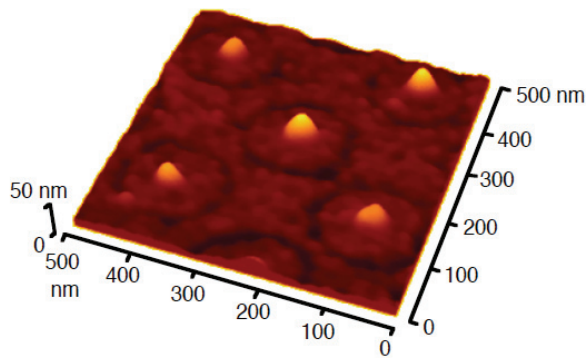
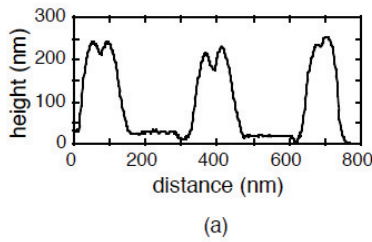
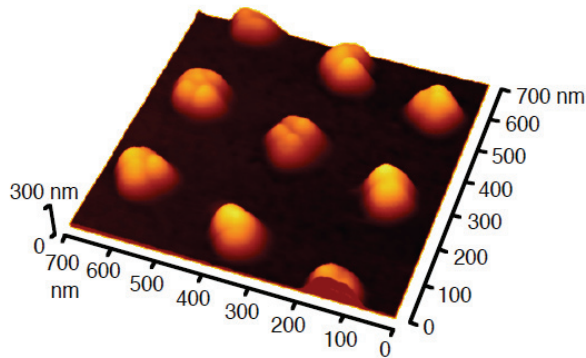


Fig. 6. AFM image and surface profile of Pt dot array formed on n-GaAs (a) applying five pulses and (b) applying one pulse.

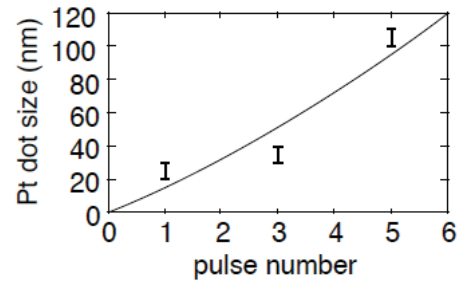


Fig. 7. Correlation between Pt dot diameter and applied plating-pulse number. The solid line provides visual reference.

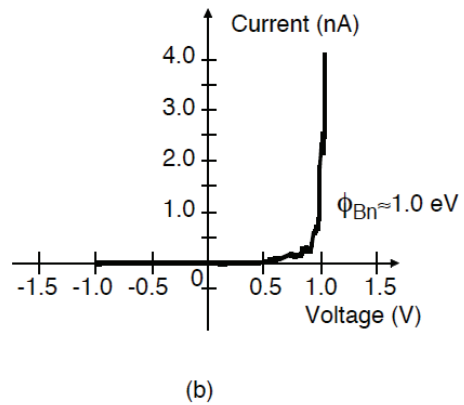
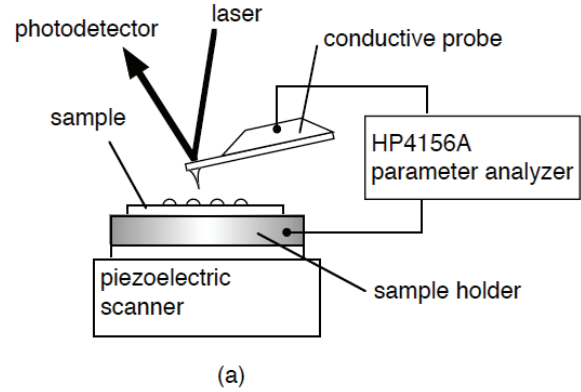


Fig. 8. (a) Schematic of AFM system with Si conductive probe and (b) typical I-V curve measured at Pt dot/n-GaAs contacts.