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In situ observation of anodic dissolution process of *n*-GaAs in HCl solution by electrochemical atomic force microscope

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Anodic dissolution of a GaAs(100) face was investigated by *in situ* electrochemical atomic force microscope (AFM). While no surface structure change was observed at -0.6 V (vs Ag/AgCl) where no current flowed, dome structure on surface was removed, and flat surface was obtained after keeping the potential at 0 V (vs Ag/AgCl) where anodic current of $\sim 150 \mu\text{A cm}^{-2}$ flowed. An atomically resolved AFM image was obtained in the flat region and shows the surface is dominated by a (111) face after the anodic dissolution.

I. INTRODUCTION

Control of electrochemical and photoelectrochemical dissolution reactions of semiconductor electrodes is very important in establishing electrochemical/photoelectrochemical etching process and stable photoelectrochemical cells.^{1,2} GaAs is one of the most attractive semiconductor materials to be used in various electronic devices and dry/wet solar cells. Thus many papers on electrochemical behaviors of GaAs in dark and under illumination have been published.³⁻⁹

Scanning tunneling microscope (STM) is now recognized as one of the most useful techniques to investigate the surface structure of electrodes *in situ* with very high resolution.¹⁰⁻¹³ We have applied STM to monitor the surface structure change of *n*-GaAs during anodic photocorrosion.^{14,15} Unfortunately, however, STM can be applied only to observe the surface of conductive samples. The existence of anodic oxide films as well as the space charge layer in the depletion condition makes the STM measurement of semiconductor electrode relatively difficult¹⁶ and atomic image of semiconductor surface in contact with electrolyte have been obtained only on H-terminated silicon and germanium in H_2SO_4 ,¹⁷ HF,¹⁸ and NaOH solutions.¹⁹ On the other hand, atomic force microscope (AFM) can image even nonconducting surfaces. Furthermore, electrochemical process on tip which may be a serious problem in the STM measurements in electrolyte solutions can be avoided in the AFM measurements. Thus AFM may be more useful technique than STM in electrochemistry, at least for the imaging of semiconductor electrode surfaces. Recently, Gewirth *et al.* demonstrated that electrochemical AFM has an atomic resolution and is a useful technique to observe electrode surfaces *in situ*.²⁰⁻²² We also have successfully employed AFM to monitor the surface structure change of InSe during electrochemical potential cycling with atomic resolution.²³

In this paper, we investigate the surface structure change during anodic dissolution of a GaAs(100) face in HCl solution using *in situ* electrochemical AFM and report that prolonged oxidation removes dome structure and give relatively flat surface. An atomically resolved AFM image of GaAs was obtained *in situ* for the first time and shows that the

surface is dominated by a (111) face after the anodic dissolution in HCl.

II. EXPERIMENT

A (100) face of *n*-GaAs single crystal wafers doped with Si ($8 \times 10^{17} \text{ cm}^{-3}$) was used as an electrode in this study. The sample was etched by dip treatment in HCl-HNO₃ (1:1) solution for 30 s then rinsed with Milli-Q water.^{24,25} This procedure was repeated three times. After these treatments, the surface roughness of the sample was decreased quite significantly. Ohmic contact was secured using In.

The electrochemical AFM measurements were carried out by using a NanoScope II with electrochemical AFM unit (Digital Instruments, CA) operating in the constant force mode. Microfabricated Si₃N₄ cantilevers of 100 μm long with integrated Si₃N₄ pyramidal tips (length: 4 μm , nominal radii: 40 nm) were used. The spring constant of the cantilevers was 0.58 N/m and the typical force during the measurements was ~ 1 nN.^{26,27} A glass fluid cell supplied by Digital Instruments (volume: 0.2 ml) was used for the electrochemical AFM measurements. A Pt wire and a Ag/AgCl (3.3 M KCl) electrode were used as a counter and a reference electrode, respectively. An exposed electrode area in contact with solution was about 0.32 cm².

All measurements were carried out in 10 mM HCl solution which was prepared by using reagent grade chemicals

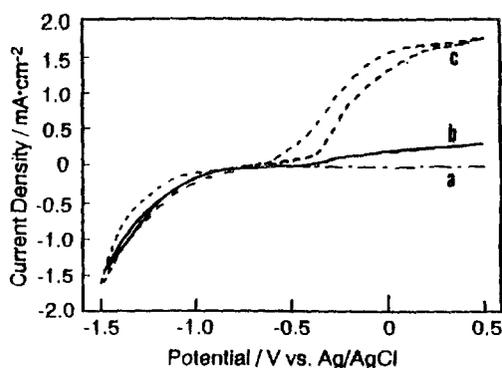


FIG. 1. Current-potential relation of *n*-GaAs in 10 mM HCl. (a) in dark, (b) during AFM measurement, and (c) under white light illumination.

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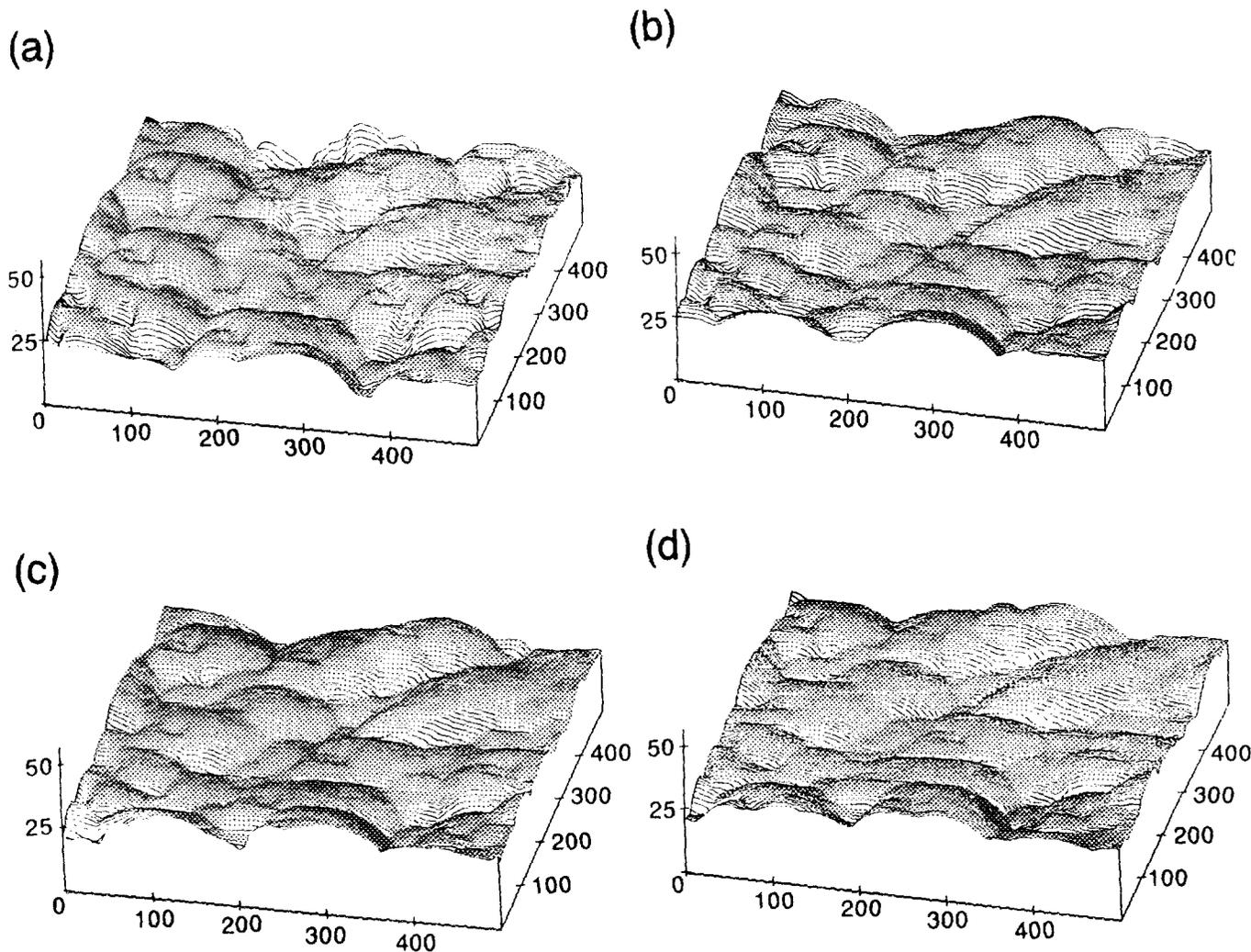


FIG. 2. Sequentially obtained AFM images of *n*-GaAs in 10 mM HCl while potential was held at -0.6 V where no anodic current flowed. Time after application of the potential at -0.6 V was (a) 0.5 min, (b) 7 min, (c) 13.5 min, and (d) 20 min.

(Wako Pure Chemicals) and Milli-Q water and was deaerated by passing high purity nitrogen gas for 20 min.

III. RESULTS AND DISCUSSION

Figure 1 shows current-potential relations of *n*-GaAs in (a) 10 mM in dark, (b) during AFM measurement, and (c) under white light illumination by 30 W halogen lamp. As expected for the *n*-type semiconductor electrode, large cathodic current was observed, but no anodic current flowed in dark and anodic current was strongly enhanced by illumination.¹ The anodic current was also observed during AFM measurement, although small compared with that under white light illumination. This current should also be photocurrent as some portions of laser light which was used for sensing the deflection of the cantilever hits the electrode surface. Cathodic and anodic current should be due to hydrogen evolution and GaAs dissolution, respectively.

Figure 2 shows AFM images obtained sequentially after -0.6 V was applied. At this potential almost no current

flowed (cf. open circuit potential = -0.58 V) and no structure change was observed even after 20 min. Similar results were obtained by STM in NaOH solution.¹⁴

Figure 3(a) is an AFM image obtained at -0.6 V after the images of Fig. 2 were collected, i.e., 35 min after the application of the potential. Still no surface change was observed. However, as soon as the potential was pulsed to 0 V where anodic current of $\sim 150 \mu\text{A cm}^{-2}$ flowed, surface structure started to change as shown in Figs. 3(b)–3(f). The change was significant. Dome structures were removed, the structure became flat and only large structure remained. Since similar structure was observed at places where the contact AFM imaging was not carried out, the effect of the tip on the dissolution reaction of the surface can not be important. Our previous studies on photochemical anodic dissolution of *n*-GaAs by STM showed that electrolyte solutions have strong influence on the surface morphology.^{14,15} Photoelectrochemical etching leads to a flat surface in HClO_4 solutions,¹⁴ but generated rougher surface in NaOH solution.¹⁵ Preliminary investigation using electrochemical AFM in various electrolyte solutions also suggests the important role of electrolyte so-

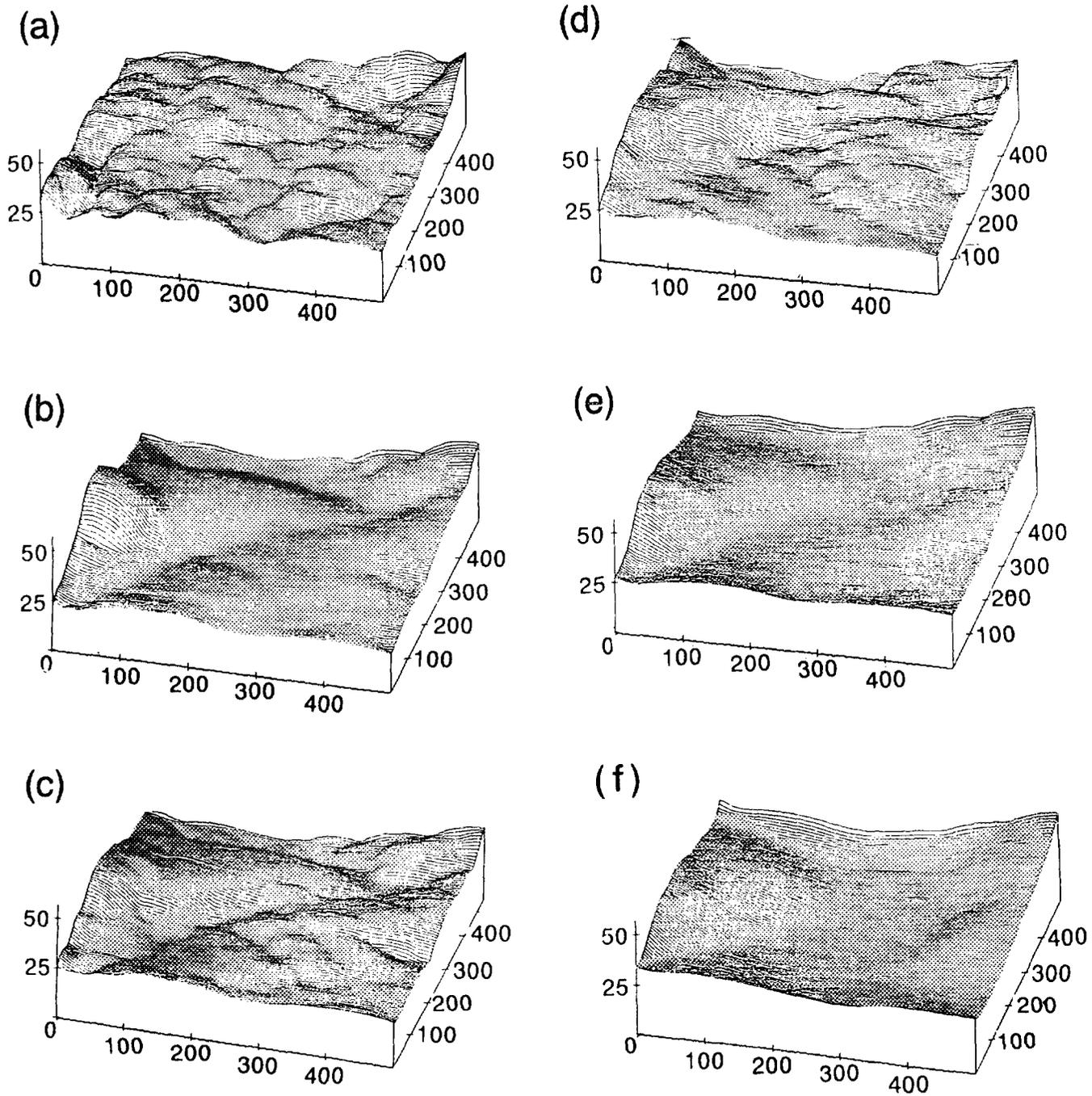


FIG. 3. AFM images of *n*-GaAs in 10 mM HCl obtained (a) after the potential was held at -0.6 V for 35 min and (b)–(f) after the potential was pulsed from -0.6 to 0 V where anodic photocurrent of $\sim 150 \mu\text{A cm}^{-2}$ flowed. Time after the application of 0 V was (b) 3.5 min, (c) 6.5 min, (d) 10 min, (e) 17.5 min, and (f) 25 min.

lution in determining the morphology of electrochemically etched surface. Detailed investigation is now under way.

Although some portions of the surface became atomically flat after prolonged oxidation [Fig. 3(f)], an atomically resolved structure was not observed at 0 V. An atomically resolved AFM image was, however, obtained if potential was pulsed to -0.6 V where no current flowed. Structure became clear with time and several minutes after -0.6 V was applied an atomically resolved AFM image, as shown in Fig. 4, was obtained at some portion of the surface. The reason why the

atomic image was obtained at -0.6 V and not at 0 V is that the dissolution process is actively taking place at 0 V and/or the oxide covers the surface.⁷ This image suggests the (111) arrangement with atom–atom distance of 0.4 nm which agrees with atom–atom distance of a GaAs(111) face.²⁸ It is reasonable as it was reported that chemical etching of a (001) face of GaAs in HCl solution selectively gives a (111) face.^{24,25} One must, however, note that 0.4 nm atomic separation can be observed also at a (100) face. The difference between the two is the crossing angle of atom rows, i.e., 60°

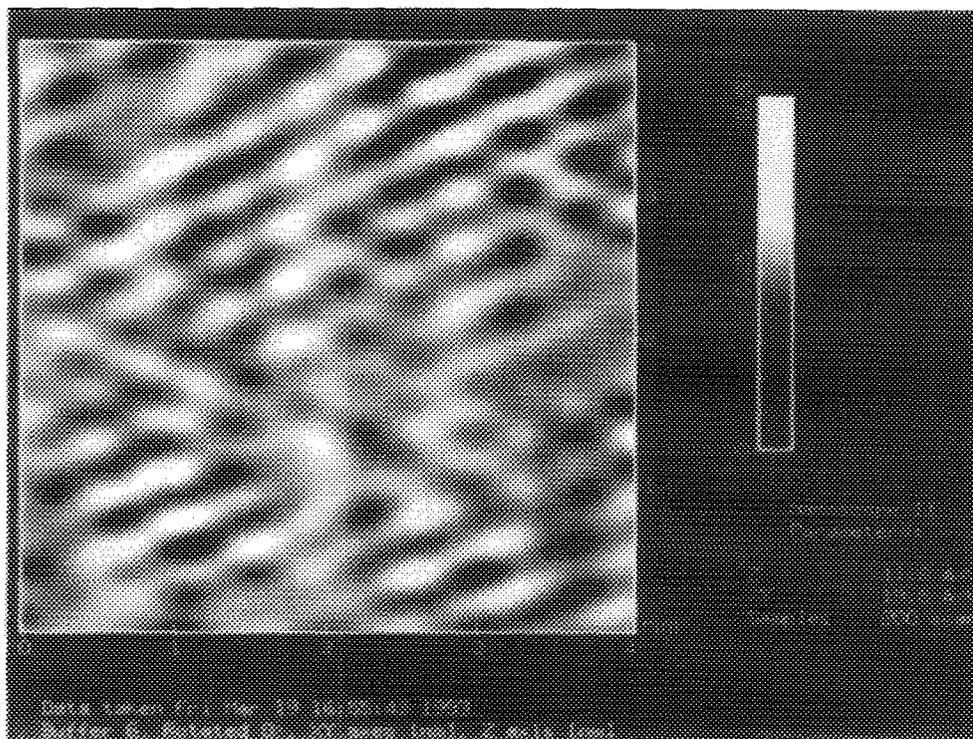


Fig. 4. An atomically resolved AFM imaged of *n*-GaAs electrode surface in 10 mM HCl obtained at -0.6 V vs Ag/AgCl after potential was held at 0 V for 25 min [Fig. 3(f)]. The structure shows the (111) arrangement. The image was FFT filtered.

for (111) and 90° for (100). Thus the possibility that the imaged surface is the (100) face cannot be totally rejected, because of a relatively unclear image. More detailed investigation is now under way.

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