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In situ scanning tunneling microscopy of GaAs(001), (111)A, and (111)B surfaces in sulfuric acid solution

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In situ electrochemical scanning tunneling microscopy (STM) was used to examine *n*-type GaAs(001), (111)A, and (111)B surfaces in 0.05 M sulfuric acid. Cathodic polarization of the GaAs electrodes effectively inhibited the oxidation of the surface, making it possible to acquire STM images with atomic resolution. Atomically-flat terrace-step structures were consistently observed on all surfaces prepared by the chemical etching method. Steps observed on these surfaces are composed of double layers with step heights of 0.28 and 0.33 nm for the (001) and (111) surfaces, respectively. *In situ* STM atomic images revealed that those surfaces have (1×1) structures with the square and hexagonal lattices, respectively. © *1996 American Institute of Physics.* [S0003-6951(96)03410-2]

Scanning tunneling microscopy (STM) has been extensively applied to investigate surface atomic structures of GaAs, a III–V compound semiconductor, in ultrahigh vacuum (UHV). It is well-known that GaAs exhibits various surface-reconstructed structures such as (4×2), (2×4), and *c*(4×4) on the (001) surface[1–3] and (2×2) on the (111)A surface.[4] A large number of investigations have been carried out in UHV on the GaAs surfaces, whereas not much *in situ* STM work has been performed on semiconductor electrodes in electrolyte solutions. Surface topographic images of semiconductors such as *n*-TiO_2,[5] *n*-ZnO,[6] Si,[7–11] and GaAs[12–16] have been obtained in aqueous solutions usually without atomic resolution, mainly because of the difficulty in preparing well-defined surfaces. It is, however, becoming more urgent for the semiconductor technology to understand wet chemical etching processes, particularly those of Si and GaAs, with atomic resolution.

In situ STM has recently demonstrated its capability of imaging atomic structures of Si(111) and Si(001) in solutions and elucidating etching processes with atomic resolution.[7–11] Although it was more recently reported that atomic force microscopy (AFM) can also reveal atomic structures of GaAs surfaces in solution,[12,13] no atomic resolution has been achieved, to our knowledge, in previous *in situ* STM investigations.[14–16] Here we report the first atomic STM images acquired in a 0.05 M H_2SO_4 solution on GaAs(001), (111)A, and (111)B surfaces treated with 1 M HCl or a mixed solution of $1H_2SO_4:8H_2O_2:1H_2O$. The results clearly demonstrate that the ideal GaAs(001)–(1×1) and (111)–(1×1) structures exist in a pure H_2SO_4 solution in a cathodic potential region.

The samples were *n*-type Si-doped GaAs (001), (111)A, and (111)B wafers (Sumitomo Electric Industries Ltd., Japan), grown by the horizontal Bridgman method. The carrier concentration of the GaAs samples was $1–3\times10^{18}$ cm^{-3}, and the misorientation of the wafers was within ±0.2°. A sample was mounted in an electrochemical cell made of Teflon with a reversible hydrogen electrode (RHE) in 0.05 M H_2SO_4 and a Pt counter electrode.

The GaAs(001) and (111)B samples were treated with 1 M HC1 for 10 min at room temperature. The GaAs(111)A sample was etched with a selective etching solution ($1H_2SO_4:8H_2O_2:1H_2O$ by volume). The etching rate of (111)A surface has been reported to be the slowest among all low-index planes in this mixed solution.[17] Therefore, we expected that the (111)A surface should possess a well-ordered structure after the selective etching. After the etching, each solution was completely replaced with 0.05 M H_2SO_4. The replacement of the etching solution was repeatedly carried out to exclude HCl and H_2O_2 in the solution. All STM experiments were carried out in the dark using a Nanoscope-III (Digital Instrument Inc., CA). The STM tips were prepared by electrochemical polishing of a tungsten wire followed by electrically insulating it with colorless nail polish.

Figure 1 shows cyclic voltammograms (CV) for the freshly etched GaAs (001), (111)A, and (111)B electrodes in 0.05 M H_2SO_4 in the dark. Proton discharge with hydrogen evolution was observed at the cathodic end of each CV. The hydrogen evolution reaction was previously investigated on GaAs electrodes.[18–20] However, it was found in this study that the current-potential profiles for the hydrogen evolution reaction are slightly different from each other, suggesting that the surfaces might be terminated by different kinds of atoms depending on their crystallographic orientations. The hydrogen evolution reaction seems to begin at less negative potentials, approximately −0.6 V, on the (111)A surface than on the (001) and (111)B surfaces. This result suggests that the hydrogen discharge takes place more favorably on the hexagonal (111) surface terminated by Ga as pointed out previously.[18] On the other hand, it is more significant to note in Fig. 1 that the anodic current for the oxidation of GaAs strongly depends on the crystallographic orientation. The oxidation of the GaAs(111)A surface occurs only at potentials more positive than 1.1 V. The oxidation current commences at substantially less positive potentials on the other

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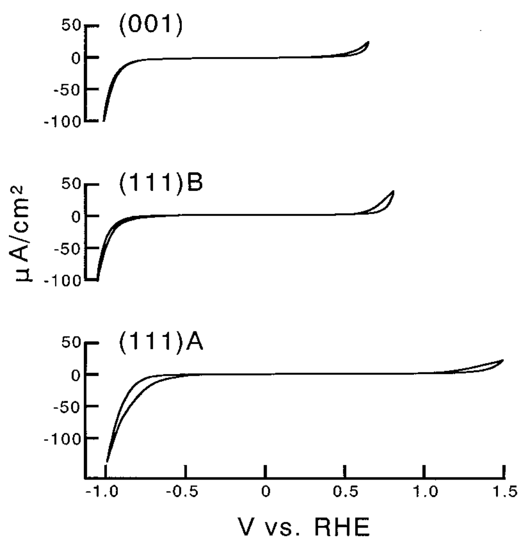

FIG. 1. Current-potential curves of *n*-GaAs(001), *n*-GaAs(111)A, and *n*-GaAs(111)B in 0.05 M H_2SO_4 in the dark. The scan rate of the electrode potential was 50 mV/s.

surfaces. These results are consistent with the fact that the (111)A surface is most stable, giving the lowest etching rate in the selective etching solution as described above.

Figure 2(a) shows a typical surface topography of a chemically etched GaAs(001) surface acquired in an area of 50×50 nm^2. It can be clearly seen that the surface of the (001) exhibits a well-defined step-terrace structure extending over a large area. Wider terraces are seen to extend over 30 nm. The rather uniform appearance of the terraces strongly suggests that the (001) surface has a structure well-defined on an atomic scale. It is also clear that the steps intersect each other to form an angle of 90°, as expected for a surface with fourfold symmetry. These steps appearing as straight lines were confirmed as double layer steps on the (001) surface based on the observed height of 0.28 nm obtained by a cross-section analysis. This unique height of 0.28 nm for the steps straightforwardly indicates that the (001) surface prepared by etching in HCl must be either Ga or As terminated (see Fig. 4). According to the crystallographic orientation of the GaAs(001) electrode, these steps were found to be parallel to either $[110]$ or $[\bar{1}10]$ directions.

Figure 2(b) shows our first atomic STM image acquired on the atomically flat terraces. It is clear that the ideal square arrangement expected for the (001) surface with fourfold symmetry is discerned by *in situ* STM. The observed nearest interatomic distances in the $[110]$ and $[\bar{1}10]$ directions were found to be 0.4 ± 0.02 nm. The atomic image shown in Fig. 2(b) clearly demonstrates that the ideal, nonreconstructed GaAs(001)–(1×1) structure, as shown in Figs. 4(a) or 4(b), is exposed in H_2SO_4 solution under the cathodic polarization. Note that the ideal (1×1) structure seemed to be extended over the entire region of the terrace, because pits or even single atomic defects were rarely observed.

The (111)A surface etched in the mixed solution containing H_2O_2 was also found to have an atomically flat terrace-step structure in H_2SO_4 solution as shown in Fig. 3(a). All steps observed were double layer steps with a height of 0.33 nm. The double layer steps in local areas were straight and

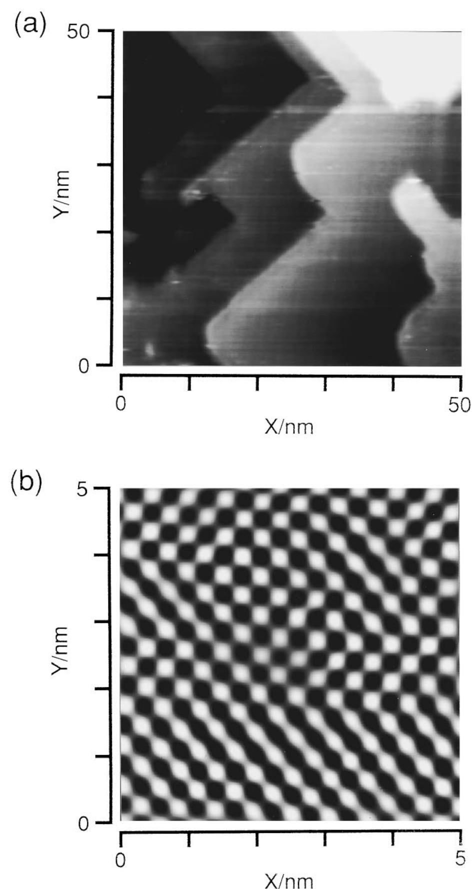

FIG. 2. STM top views of areas of (a) 50×50 nm^2 and (b) 5×5 nm^2 on *n*-GaAs(001) obtained in 0.05 M H_2SO_4. The electrode potentials of GaAs and the tip were set at -0.7 and 0.3 V vs RHE, respectively. The tunneling current was 10 nA. Scan speed was 25 ms/line.

parallel to one of the three $\langle 1\bar{1}0\rangle$ directions, the close packed atomic row direction of (111) surface. In contrast with the step direction observed on the (001) surface, these steps now intersect each other with an angle of 60°, as expected for a surface with threefold symmetry. Figure 3(b) shows a typical atomic STM image, revealing an interatomic distance of 0.4 nm with an almost perfect hexagonal arrangement. This result clearly demonstrates that the ideal GaAs(111)A–(1×1) structure, as shown in Fig. 4(c), is exposed in H_2SO_4 solution. It is reasonably expected that the uppermost layer on the (111)A surface consists of Ga atoms in solution even after etching. Note that Figs. 2(b) and 3(b) are the atomic images obtained in a constant current mode. The corrugation height was found to be $\sim$0.02 nm in both images. The atomic resolution images of GaAs could be observed in the potential range between -1.0 and -0.45 V. At potentials more positive than -0.45 V, the tip electrode seemed to be plunged into the GaAs electrode because of the formation of the space-charge layer. It was described in previous papers that the electron tunneling from the conduction band in *n*-type semiconductors to the tip is inhibited when the electrode potential of the semiconductor is more positive than the flat band potential.[5,6,16]

We tentatively assume that the GaAs(001)–(1×1) and GaAs(111)A–(1×1) surfaces are terminated by hydrogen at least under cathodic polarization. Although the adsorption of

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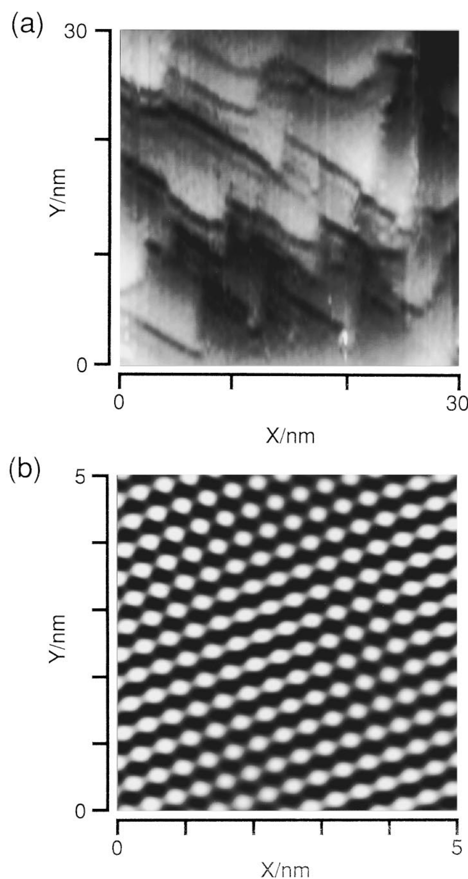

FIG. 3. STM top views of areas of (a) 30×30 nm^2 and (b) 5×5 nm^2 on *n*-GaAs(111)A obtained in 0.05 M H_2SO_4. The tunneling current was 10 nA. Scan speed was 25 ms/line.

Cl^- might be expected to occur on the GaAs(001) surface etched in HCl, the cathodic potential control in pure H_2SO_4 in the absence of Cl^- should release the adsorbed Cl^- from the surface and replace it with hydrogen. This hypothesis seems to be consistent with the model proposed previously based on an electrochemical study,[19] in which the adsorption of hydrogen on the GaAs electrode was thought to be a precursory step for the hydrogen evolution reaction.

Finally, it is noteworthy that the GaAs(111)B surface prepared by etching in 1 M HCl also showed an atomically flat terrace-step structure in H_2SO_4 with a step height identical to that observed on the (111)A surface. Although the average terrace width was typically 5–10 nm, obviously smaller than that found on the A surface, an atomic STM image revealed a hexagonal arrangement of As atoms with the interatomic distance of 0.4 nm. The above results indicate that the GaAs(111)B surface also has the ideal (1×1) structure shown in Fig. 4(d). A more detailed study is now in progress.

In summary, it was demonstrated that the well-defined GaAs(001), (111)A, and (111)B surfaces can be prepared by chemical etching in solutions. We successfully obtained the first atomic STM images which showed that the ideal GaAs(001)–(1×1), GaAs(111)A–(1×1), and GaAs(111)B–(1×1) structures are exposed and persist in H_2SO_4 solution.

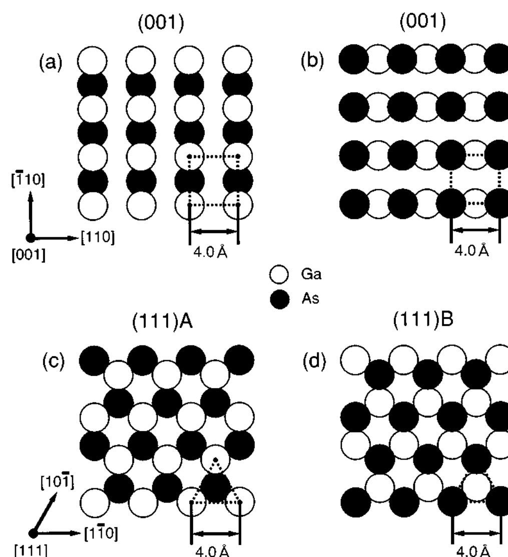

FIG. 4. Top views of ball models for ideal Ga-terminated GaAs(001) (a), As-terminated GaAs(001) (b), GaAs(111)A (c), and GaAs(111)B (d) surfaces. The open and black circles represent Ga and As atoms, respectively.

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