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ADSORPTION OF ATOMIC-HYDROGEN ON THE Si(100)-(2×1)-Sb SURFACE STUDIED BY TOF-ICISS/LEED

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ABSTRACT

We have investigated a structural change of Si(100)-(2×1)-Sb surface caused by atomic hydrogen adsorption at room temperature using time-of-flight impact collision ion scattering spectroscopy (TOF-ICISS) and low energy electron diffraction (LEED). We found that when atomic hydrogen adsorbs on the Si(100)-(2×1)-Sb surface, (1) the partial desorption of Sb atoms from the Si(100) surface occurs even at room temperature, (2) the rest Sb atoms are displaced from their original positions and form an almost two-dimensional layer with dispersive distribution of Sb atoms, and (3) the structural transformation into the Si(100)-(1×1)-H periodicity is induced by the formation of the 1×1-H dihydride phase on the Si substrate.

INTRODUCTION

In semiconductor physics, hydrogen has long been used as inert gas for crystal growth, or as a component in gases for the various forms of chemical vapor deposition (SiH₄, GeH₄, Ge₂H₆, etc.). It is well known that hydrogen coverage on the growth front during epitaxy has a considerable effect on growth kinetics of films. Therefore, influence of adsorbed hydrogen on structures and morphologies of adsorbates on semiconductor substrates has attracted much attention from both fundamental and practical viewpoints.

Recently, Oura et al.¹⁻³⁾ discovered an interesting behavior of hydrogen atoms on a Si(111) surface using ion scattering spectroscopy, low energy electron diffraction, and scanning tunneling microscopy. They report-

ed that the growth mode of Ag film is drastically changed by the hydrogen termination of the Si(111)7×7 surface and that the epitaxial growth of A-type films with the orientation of Ag(111)[11-2]//Si(111)[11-2] is promoted by the atomic-hydrogen residing at the film/substrate interface. They also reported that adsorption of atomic hydrogen on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface induces structural transformation from the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface into the Si(111)-(1×1)-H one, and Ag atoms form very small three-dimensional Ag clusters grown epitaxially on the Si(111) substrate. These phenomena were also observed for Si(111)- $\sqrt{3} \times \sqrt{3}$ surface phases of different metals such as Pb⁴⁾, In⁵⁾. These observations have disclosed an interesting process of exchange adsorption of hydrogen and metal

atoms followed by the rearrangement involving substrate Si atoms. However, in order to obtain more insight on H-induced structural changes of metal-adsorbed Si surfaces, a more schematic study on other metal adsorbates is necessary. In particular, the investigation of an interaction of H with Si surfaces terminated by group-elements has never been examined. Among adsorbates of group-elements on Si surfaces, Sb terminated Si surfaces have recently received considerable attention in connection with two technologically important phenomena: surfactant-mediated epitaxy (SME)⁶ and construction of delta-doping layers⁷. Thus, it would be of importance to study an interaction of H with Sb terminated Si surfaces from the technological and fundamental points of view.

In this work, we have studied a structural change of the Si(100)-(2×1)-Sb surface caused by atomic-hydrogen (H) adsorption at room temperature (RT) using time-of-flight impact collision ion scattering spectroscopy (TOF-ICISS) and low energy electron diffraction (LEED). TOF-ICISS^{8,9} is a useful technique for investigation of thin film growth on solid surfaces in real time as well as for monitoring the structural change of the sample surface. We found that the H adsorption on the Si(100)-(2×1)-Sb surface induces the partial desorption of Sb atoms from the Si(100) surface as a result of the break of Si-Sb bonds caused by the formation of 1×1-H dihydrides, and that the rest Sb atoms are displaced from their original positions and form an almost two-dimensional layer with dispersive distribution of Sb atoms. These results for the Sb/Si(100) system are different from those for other metal adsorbates/Si systems reported before.

EXPERIMENTAL

Experiments were carried out in an ultra-high vacuum (UHV) system. The UHV system is equipped with TOF-ICISS, and LEED facilities. Since the apparatus of TOF-ICISS is described in detail elsewhere¹⁰, only an outline is given in this paper. The energy of the ions ranges from 0.5 to 5 keV. The beam current and diameter are 20~30 nA and 3mm at the sample surface, respectively. Scattered ions and neutrals from the sample at a scattering angle of $\theta=180$ (actually $179^\circ \sim 179.6^\circ$) can be detected by an annular type micro-channel plate (MCP) placed coaxially along the primary ion beam at a flight path of 60cm from the sample. Energy analysis of scattered particles is done by measuring the time of flight between the sample and the detector by the use of an 8-stop time-to-digital converter.

A P-type, 6~8 Ω ·cm, 10×30×0.5mm³ Si(100) wafer was cleaned in situ by annealing for about 5 hours at 600 followed by a flash heating at 1200°C under a base pressure of $\sim 10^{-10}$ Torr. The temperature of the sample surface was measured with an infra-red pyrometer and alumel-chromel thermocouple fixed at the rear part of the sample. After the cleaning, a sharp (2×1) LEED pattern was observed. Sb of 99.999% purity was deposited from a Knudsen-cell at a deposition rate of 0.1ML/min, where 1ML is defined to be 6.8×10^{14} atoms/cm², the ideal Si surface atomic density in the (100) plane.

A 1800°C tungsten filament, positioned 10 cm from the Si surface, was used to dissociate molecular hydrogen. The exposure of the surface to atomic hydrogen was made with the specimen facing the hot filament and by

backfilling the chamber with H₂ at 110⁻⁶ Torr. Since the flux of atomic hydrogen was not measured, the exposure (L) is expressed in terms of the pressure of molecular hydrogen recorded by the Bayard-Alpert (BA) gauge (1L=1×10⁻⁸Torr·s).

RESULTS AND DISCUSSION

The Si(100)-(2×1)-Sb structure was made of the Sb atoms deposited on the Si(100)2×1 surface at substrate temperature of 500°C for 30min. In order to obtain an ordered Sb overlayer, this sample was annealed at 500°C for 10min. The experimental results are shown in the Fig. 1(a) and (b). The primary ion beam of 2.0 keV He⁺ was used in these experiments. The direction of primary ion beam is fixed at =90°, i.e., Si(100)[-100] direction. Fig. 1(a) shows the Sb signal intensity as a function of the Sb coverage. The signal intensity increases in proportion to the Sb coverage until about 0.8 ML. However, after that, the signal intensity saturates at 0.8 ML of the Sb coverage. Although the deposition of Sb atoms was stopped, the signal intensity due to Sb atoms did not decrease. This result suggests that desorption of Sb atoms forming two-dimensional (2D) layer on the Si(100) surface do not occur by annealing at 500°C. Fig. 1(b) shows a typical TOF-ICISS spectrum of the Si(100)-(2×1)-Sb surface formed by the process as Fig. 1(a). One can see two sharp signals (surface peaks) at 5.6 and 6.2 sec due to Sb and Si, as well as a broad signal originating from multiple scattering in the Si substrate. At this time, the specimen exhibited a (2×1) LEED pattern with slightly diffused half-order

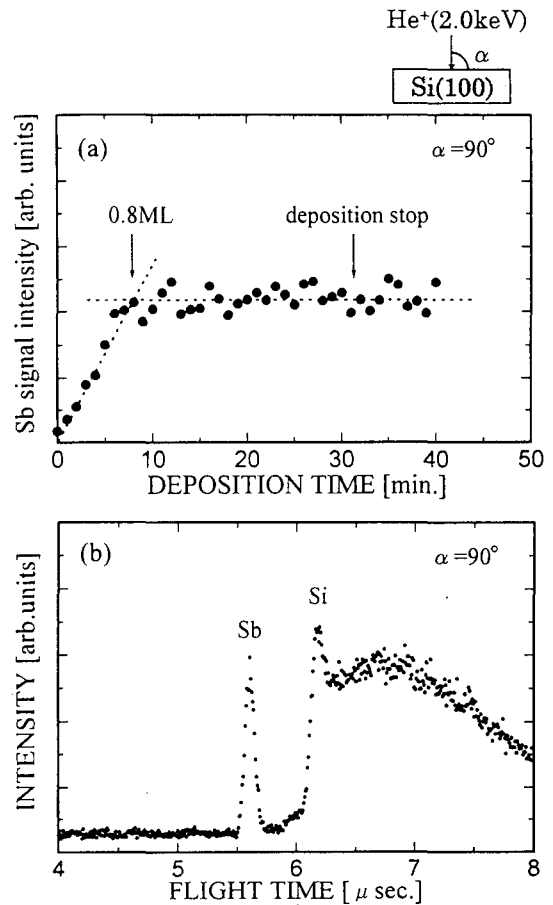


Fig. 1 (a) The variation of the Sb signal intensities with increasing of the Sb coverage. (b) TOF-ICISS spectrum taken from the Si(100)-(2×1)-Sb surface. The primary ion used a He⁺ of 2.0keV. The incident angle of He⁺ ions is fixed at $\alpha = 90^\circ$

sports. The intensity of the surface peak due to Sb strongly depends on the impact angle (α) and on the structure of surfaces, so that we can obtain an information on a structural change of this surface caused by H adsorption by measuring angular variations of the Sb signal intensity.

Fig. 2 shows the intensity of the surface peak due to Sb as a function of the impact angle, α (measured from the surface plane), along the l^{-10} azimuth, measured for two kind

of specimens; curve (a) : the Si(100)-(2×1)-Sb surface with no H adsorption, curve (b) : taken after H adsorption of 1000L exposure on the specimen of the curve (a) at RT. The specimen of the curve (b) exhibited a (1×1) LEED pattern, indicative of the H-induced structural change of the surface. As we can see, there are two dominant peaks in the α -scan of the (2×1)-Sb surface at $\alpha=16^\circ$ and 164° , as the curve (a) in Fig. 2. These peaks can be explained in terms of the focusing effects of Sb atoms which are dimerized on the surface: these peaks are composed of three kind of focusing peaks corresponding to an intradimer bond length and Sb-Sb spacings between dimers (along both perpendicular and parallel directions to dimer rows). Upon adsorption of H onto this surface, an interesting result was observed as the curve (b) in Fig. 2. After H adsorption,

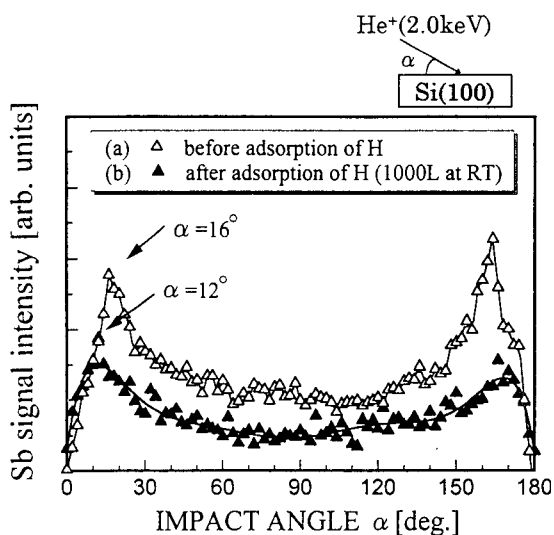


Fig. 2. Sb signal intensities as a function of the impact angle, α (measured from the surface plane), along the [1-10] azimuth, measured for two kind of the specimens; (a) the Si(100)-(2×1)-Sb surface with no H adsorption and (b) taken after H adsorption of 1000L exposure at RT.

the-scan did not drastically change: the curve (b) has only two dominant peaks at grazing incident angles and no peaks at larger incident angles, which is similar to the curve (a). On the other hand, as compared with the case of no H adsorption, one can see different features in the curve (b) as follows: (1) the scattering intensities due to Sb were reduced over most incident angles, (2) the positions of the two dominant peaks were shifted toward grazing incident angles, i.e. from $\alpha=16^\circ$ and 164° to 12° and 168° , respectively, and (3) the peak became more broad. These features can be interpreted as discussed below.

First, the reduction of the scattering intensities after H adsorption suggests that a part of Sb atoms desorbs from the Si(100) surface caused by H adsorption. More direct evidence for the H-induced partial desorption of Sb will be shown later. Secondly, the presence of only two dominant peaks at a grazing incident angles and the absence of peaks at large incident angles indicate that the rest Sb atoms which survive from the desorption form not three-dimensional (3D) crystalline clusters but an almost two-dimensional (2D) layer: if Sb atoms would form crystalline clusters grown epitaxially on the Si(100) substrate, several focusing peaks corresponding to crystalline structure should appear at larger incident angles. Although we can not discard a possibility of the formation of amorphous Sb clusters induced by H adsorption, it can be suggested at least that even if a part of rest Sb atoms would form amorphous clusters, the amount of Sb atoms incorporated in the formation of the clusters should be much smaller than that incorporated in the formation of the 2D layer. Thirdly, the shift of the

position of the two dominant peaks to grazing incident angle of $\alpha=12$ and 168° implies that the nearest-neighbor Sb-Sb distance becomes to expand from the original intradimer distance after H adsorption, indicating that Sb-Sb dimer bonds are broken as a result of H adsorption and that the rest Sb atoms are displaced from their original positions. Fourthly, the broadening of the peak suggests that the rest Sb atoms are dispersively distributed on the surface, because various focusing effects corresponding to different Sb-Sb distances contribute to intensity enhancement at different incident angles in the case of the dispersive distribution of Sb atoms, resulting in broadening of the peak. If the rest Sb atoms would form long-range ordered (1×1) -Sb domains, the peaks should appear sharply at $\alpha=14^\circ$ and 166° , due to the focusing effect of Sb atoms corresponding to the interatomic distance, 3.84 \AA , in the (1×1) periodicity. Therefore, the appearance of the (1×1) LEED pattern is found to be attributable not to the formation of (1×1) -Sb domains but to the formation of the (1×1) -H dihydride phase on the Si(100) surface.

Figs. 3(a) and 3(b) show TOF spectra taken after H adsorption 1000L and 5000L exposures onto the Si(100)- (2×1) -Sb surface at RT, respectively. TOF spectra taken before H adsorption are also shown in Fig. 3. In both cases of Fig. 3(a) and 3(b), the scattering intensity due to Sb was reduced after H adsorption. In contrast, intensities of the surface peak and multiple scattering due to Si were increased after H adsorption. From the following experiment, it is found that the reduction of the Sb scattering intensity is attributable not to a shadowing effect

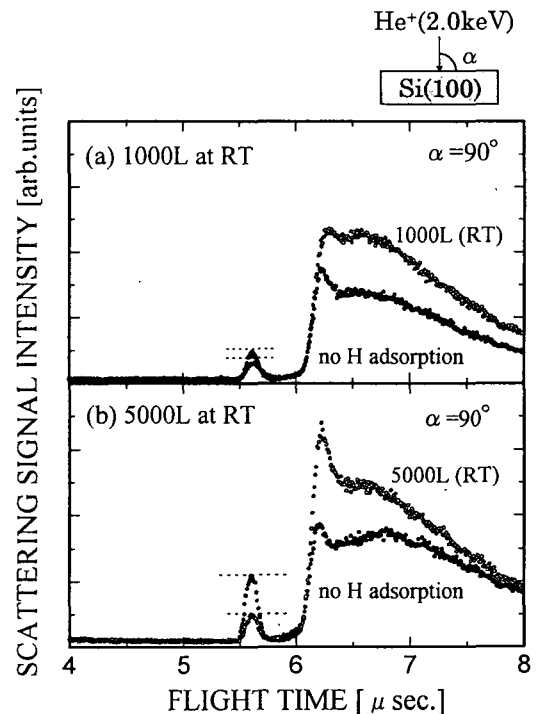


Fig. 3. TOF spectra taken after H adsorption of (a) 1000L and (b) 5000L exposures onto the Si(100)- (2×1) -Sb surface at RT. TOF spectra taken before H adsorption are also shown.

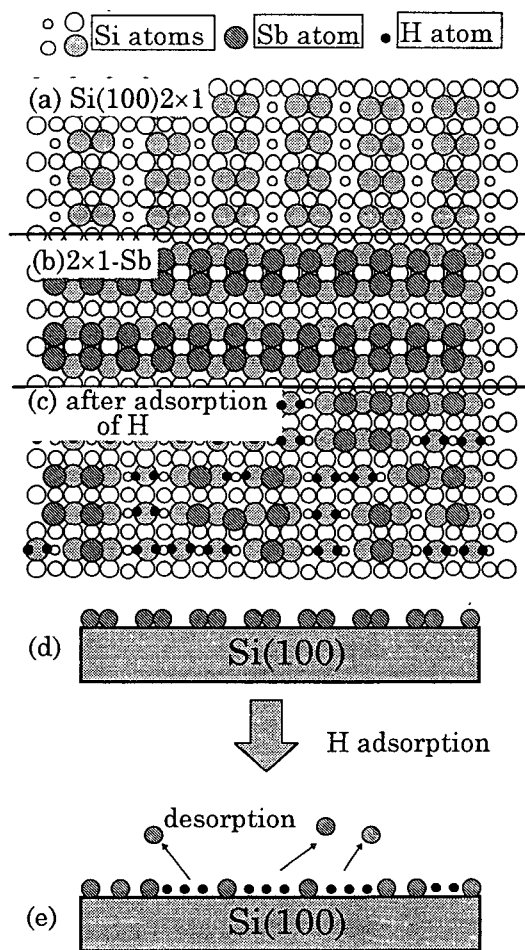
of adsorbed H atoms on Sb atoms but to a partial desorption of Sb atoms. We measured a TOF spectrum of the sample annealed at 500°C for 10 min after H adsorption of 1000L on the Si(100)- (2×1) -Sb surface at RT. It is well known that H atoms existing on the Si(100) surface desorb at the temperature of 500°C , while desorption of Sb atoms forming a 2D layer from the Si(100) surface is negligible at this temperature¹²⁾ as shown in Fig. 1(a). If Sb atoms would be shadowed by adsorbed H atoms, the scattering intensity due to Sb should recover to that for the Si(100)- (2×1) -Sb surface after annealing at 500°C because of desorption of H atoms. How-

ever, the result showed that the scattering intensity due to Sb did not recovered but unchanged by the annealing. This result clearly indicates that H adsorption induces the partial desorption of Sb atoms from the Si(100) surface. The increase of scattering intensities due to Si after H adsorption observed in Fig. 3 is found to be due to ion scattering from Si third and fourth layers partly exposed to vacuum as a result of desorption of Sb atoms, which are shadowed by Sb atoms before H adsorption. In Fig. 3, one can see that the desorption of Sb atoms induced by H adsorption becomes remarkable with increasing coverage of hydrogen. Namely, the scattering intensity due to Sb was reduced by about one-third after H adsorption of 1000L exposure, while it was reduced by about two-third after H adsorption of 5000L exposure. As we can see, the Sb surface peak does not have a shoulder on the low-energy side after H adsorption. This also supports that the rest Sb atoms form an almost 2D layer: if the rest Sb atoms would form 3D clusters with considerable sizes, a shoulder should be accompanied with the Sb surface peak on the low-energy side due to multiple scattering from a deeper region in Sb cluster.

Next, we will briefly discuss about the possible mechanism for the H-induced desorption of Sb atoms even at RT as observed in this study. Murakami et al.^[13] reported that the sticking probability for Sb is significantly reduced even at RT when Sb is deposited onto the H terminated Si(100) surface. Moreover, Nakagawa et al.^[14] found that the reduction of the sticking probability for Sb on the H terminated Si surface is due to thermal desorption of Sb with a relatively small activation

energy of 0.14 eV, which corresponds to the energy of the van der Waals bond between the Sb atoms and the H terminated Si surface. Hence, it is presumably suggested that H adsorption on the (2×1)-Sb surface results in the break of Si-Sb bonds in part accompanied by the formation of Si-H bonds, and then expelled Sb atoms migrates over the H-terminated Si surface and partly desorbs from the Si(100) surface because of a weak interaction between the Sb atoms and the H-terminated Si surface.

Fig. 4 shows a schematic illustration of the structural change of the Si(100)-(2×1)-Sb



surface induced by the H adsorption, based on the above-mentioned TOF-ICISS and LEED results. It is suggested that Sb-Sb dimer bonds are broken by H adsorption, and then the partial desorption of Sb atoms occurs from the Si(100) surface with breaking of Sb-Si bonds due to bonding of Si-H.

CONCLUSIONS

We have investigated a structural change of the Si(100)-(2×1)-Sb surface caused by H adsorption at RT on the basis of TOF-ICISS and LEED analysis. We found that the H adsorption on the Si(100)-(2×1)-Sb surface induces the partial desorption of Sb atoms from the Si(100) surface as a result of the break of Si-Sb bonds caused by the formation of (1×1)-H dihydrides, and that the rest Sb atoms are displaced from their original positions and form not three-dimensional crystalline clusters but an almost two-dimensional layer with dispersive distribution of Sb atoms. These results for the Sb/Si(100) system are different from those for other metal adsorbates/Si systems reported before.

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