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Hydrogen analysis of silicon surfaces by low-energy ion beams

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Abstract

For the analysis of hydrogen adsorption on silicon surfaces, low-energy recoil ion spectroscopy (LE-RIS) is one of the most powerful methods because it directly provides information over 'real-space' interatomic distance and the adsorbed coordinates. Observing both the surface recoils and the direct recoils which are created by He ion beams, we investigate the structure of Si(100)-1 × 1:2H dihydride and Si(100)-2 × 1:H monohydride surfaces. Comparing our experimental results with computer simulations, we conclude that the H–Si bond angle in the Si(100)-2 × 1:H monohydride surface is 65–70° and that in the Si(100)-1 × 1:2H dihydride surface is 55–60°. For this dihydride surface, a canted dihydride structure is suggested rather than a symmetric dihydride structure. © 1997 Elsevier Science B.V.

1. Introduction

Recently, hydrogen on solid surfaces has been attracting considerable interest and many investigations have been made from the scientific point of view. Since the adsorption of hydrogen on Si and other semiconductors is the most fundamental system, the structural, thermal and dynamical properties have been studied in detail. Another motivation of the recent research is the important and expected role of hydrogen in future Si LSI process techniques and other industrial applications.

Various surface analytical techniques have been used in these studies, such as infrared spectroscopy (IR) [1], high resolution electron energy loss spectroscopy (HREELS) [2], thermal desorption (TD) [3], scanning tunneling microscopy (STM) [4], and electron stimulated desorption (ESD) [5]. However, one of the difficulties is the detection of surface hydrogen by conventional analytical methods, and therefor these studies usually lack absolute coverage information. In addition the structural analysis of adsorbed hydrogen atoms has never been made.

In this paper, we will demonstrate that low-energy recoil ion spectroscopy (LE-RIS) is a very powerful technique to analyze the surface hydrogen, by applying this technique to Si(100)-2 × 1:H monohydride and Si(100)-1 × 1:2H dihydride surfaces.

2. Experimental procedures

Experiments were carried out in an ultrahigh vacuum low-energy ion scattering system equipped with low energy electron diffraction (LEED) for sample characterization [6]. The sample, consisting of a 0.5 mm thick, chemically polished Si(100) wafer, was cut of the size of 5 × 25 mm^2, which was cleaned by an ordinary method of flash and annealing under an ultrahigh vacuum condition. The cleaned surface was hydrogenated with atomic hydrogen produced by a method using a hot tungsten filament at a hydrogen gas partial pressure of 10^{-6} Torr. To prepare the Si(100)-2 × 1:H monohydride surface, hydrogenation was done at a surface temperature of about 400°C, and this surface condition was maintained during the LE-RIS experiments. At 400°C, a sharp 2 × 1 LEED pattern showing that the surface consisted of two domains was observed. On the other hand, the Si(100)-1 × 1:2H dihydride surface was prepared by the atomic hydrogen exposure at room temperature.

The beam current at the sample surface was reduced to 10–20 nA/cm^2 in order to minimize the surface damage. The ion beam incidence was adjusted to coincidence with the ⟨110⟩ azimuth of the surface by observing the LEED

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pattern. The recoil hydrogen ions were measured with a hemispherical electrostatic energy analyzer having a full width at half maximum (FWHM) resolution of 100 $(E/\Delta E)$.

3. Results

3.1. Sensitivity for surface hydrogen

The reconstructed Si(100)-2 × 1 surface was used as the start surface. For this cleaned surface, hydrogenation was performed according to the above-mentioned procedures. Fig. 1 shows the H^+ recoil intensity change recorded as a function of the hydrogen exposure at room temperature. From the figure, it is found that atomic hydrogen adsorption precedes abruptly on the clean surface. Moreover, we can see that there is a turning point after which the intensity gradually increases toward a saturation value. Referring to the LEED observations, we found that the atomic hydrogen adsorption at a lower coverage proceeded in such a manner that the reconstructed (2 × 1) structure was preserved on the surface, and at higher coverage, the adsorption proceeded such that the (2 × 1) structure was changed and the (1 × 1) structure was formed on the surface. We succeeded repeatedly in producing this behavior for the cleaned Si(100)-2 × 1 surface by preparing it with mild annealing for 30 s at 800°C in a hydrogen gas partial pressure of 1×10^{-6} Torr.

Comparing with our previous results [7] by means of ERDA (elastic recoil detection analysis) enabled us to perform the quantitative analysis, we can scale the vertical line as shown in Fig. 1. Considering the statistical fluctuation of the incident beam intensity and the detection efficiency of the whole system, the hydrogen detection sensitivity was estimated to be about 0.03 ML in our LE-RIS case using an Ne^+ ion beam.

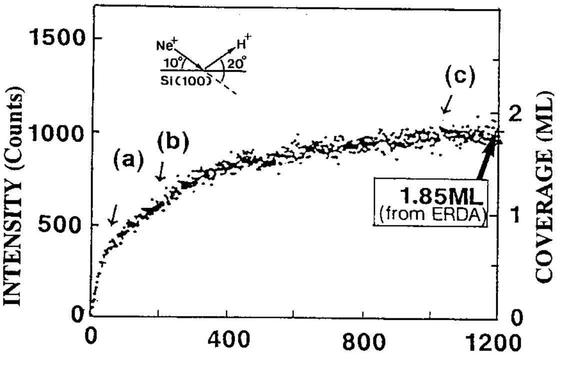

Fig. 1. Hydrogen-recoil ion intensity as a function of hydrogen gas exposure. A Ne ion beam with energy of 1000 eV is used. The beam incident angle is 10° and the recoil angle is 20°. Absolute scale for coverage is derived from ERDA data. (a) and (b) show (2×1) LEED patterns, and (c) shows (1×1) LEED patterns.

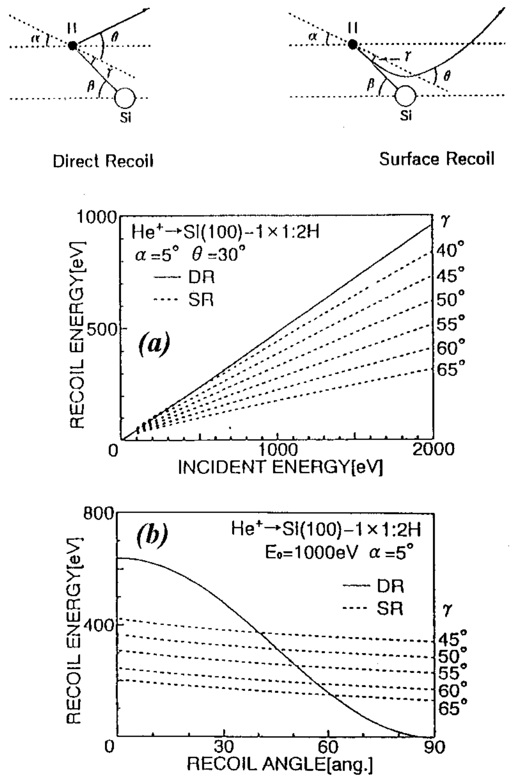

Fig. 2. Computer simulations for direct-recoil and surface-recoil ions performed for a H–Si bond shown in the figure. γ means a parameter to decide the H–Si bond angle β $(=\gamma+\alpha)$. (a) Recoil-ion energies as a function of the ion incident energy. (b) Recoil-ion energy as a function of the recoil angle.

3.2. Structure analysis

3.2.1. Computer simulation

Hydrogen-recoil ion spectra reflect the local positions of the adsorbed hydrogen atom, since the hydrogen can be recoiled as 'direct recoil (DR)' ions and/or 'surface recoil (SR)' ions depending on the geometries of the ion impact, and the energy of the SR ions strongly depends on the bonding angle to the surface silicon atom. For the specific surface such as Si(100)-2 × 1:H monohydride or Si(100)-1 × 1:2H dihydride, DR and SR processes are easily simulated by assuming the surface structure and the geometrical parameters of the incident ion beam for the surface. Changing the incident ion energy E_0, recoil angle Θ_L, and impact angle α under various H–Si bond angle β $(=\gamma+\alpha)$, we simulated the recoil hydrogen–ion energies. In brief, a mono-energetic ion was assumed to bombard a bonding pair of H–Si. It was also assumed that elastic events by the incident ion gave rise to the individual recoil

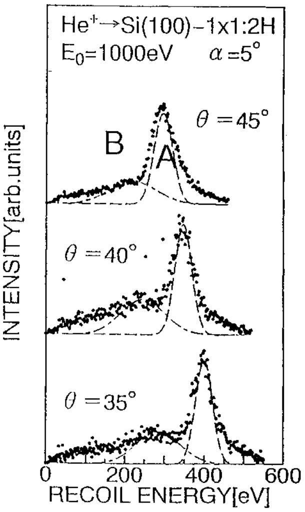

Fig. 3. Hydrogen-recoiling energy spectra observed for the Si(100)-1 × 1:2H dihydride surface. The ion incidence is adjusted to a coincidence with ⟨110⟩ azimuth of the surface. Labels, A and B, indicate the high energy peak and the low energy peak, respectively.

trajectory of the hydrogen atoms. Recoil atom–recoil atom interaction and thermal vibrations of atoms were neglected. On the ion–atom interaction of He–H, the Thomas–Fermi–Moliere potential (TMF) was used under a certain scaling factor of 0.8. The results of the simulation are shown in Fig. 2, where both the DR ion-energy and the SR ion-energy are demonstrated as functions of the incident ion-energy (Fig. 2a) and the recoil angle (Fig. 2b). From these figures, it is found that energies of the SR ions strongly depends on the bond angle β ($= \gamma + \alpha$), while energies of the DR ions are independent of bond angle β.

3.2.2. Si(100)-1 × 1:2H surface

Fig. 3 shows the spectra of recoil hydrogen ions taken at the ion beam incidence which is adjusted to coincidence with the ⟨110⟩ azimuth of the surface by observing LEED patterns. For two peaks observed in the spectra, the peak appearing at higher energies was labeled A and the peak appearing at lower energies was labeled B, respectively. From Fig. 3 it is noticed that the energies of peak A and peak B decrease with increasing recoil angle. On the other hand, it was found that no energy shift was observed for both peak A and peak B even if the impact angle was changed under the conditions that the incident ion energy and the recoil angle are fixed. Thus, the observed spectra of hydrogen recoil-ions are found to consist of two peaks, A and B. Comparing the energies of peak A and peak B with the results of the above-mentioned simulation, we

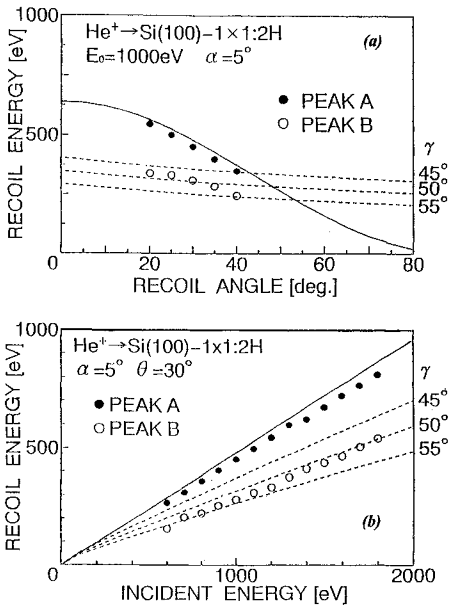

Fig. 4. (a) Plots of the peak energies observed for the Si(100)-1 × 1:2H dihydride surface as a function of the recoil angle. The solid line and dotted line indicate the calculated values for the various H–Si bond angles under the same ion incident condition. (b) Plots of the peak energies observed for the Si(100)-1 × 1:2H dihydride surface as a function of the incident energy. The solid line and dotted line indicate the calculated values for the various H–Si bond angles under the same ion incident condition.

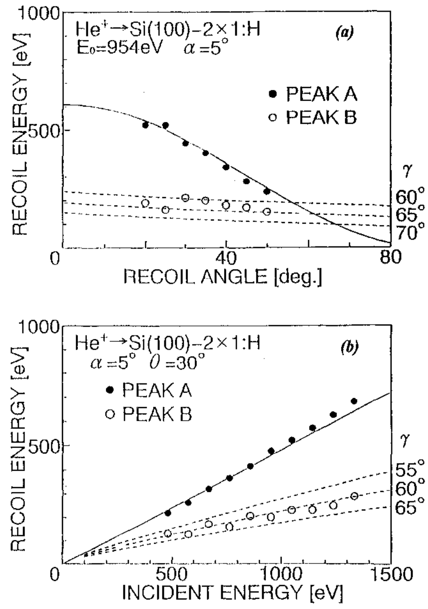

Fig. 5. (a) Plots of the peak energies observed for the Si(100)-2 × 1:H monohydride surface as a function of the recoil angle. The solid line and dotted line indicate the calculated values for the various H–Si bond angles under the same ion incident condition. (b) Plots of the peak energies observed for the Si(100)-2 × 1:H monohydride surface as a function of the incident energy. The solid line and dotted line indicate the calculated values for the various H–Si bond angles under the same ion incident condition.

discussed the H–Si bond angle β of the surface hydrogen. Fig. 4(a) shows the plots of energies of peak A and peak B as a function of the recoil angle, and Fig. 4(b) shows the results as a function of the incident ion energy. In both figures, the results of the simulation are shown for some bond angles of H–Si. Comparing the experimental results with the simulation, the H–Si bond angle β $(= \gamma + \alpha)$ is found to be of a value between 55° and 60°.

3.2.3. Si(100)-2 × 1:H surface

For this surface, we also observed two peak features. Fig. 5 shows the plots of the peak energies together with the results of simulation. As seen from the figures, the H–Si bond angle β $(= \gamma + \alpha)$ is found to be a value in the range from 65° to 70°.

4. Discussion

For the Si(100)-1 × 1:2H dihydride surface, two different models shown in Fig. 6 are proposed from experimental and theoretical approaches. In the symmetric dihydride, hydrogen symmetrically adsorb on silicon atoms. On the other model, canted dihydride, hydrogen asymmetrically adsorb on silicon atoms. From the theoretical approach, Northrup [8] reported that the H–Si bond angle β is 39° for the symmetric dihydride and 70° for the canted dihydride, and Zheng and Smith [9] reported that is β 44.9 for the symmetric dihydride and 76.6° for the canted dihydride. On the other hand, Shi et al. [10] proposed that β is 34 ± 4° from experimental approaches. Comparing the values of β in these previous reports with our presented result, we notice that our value of 55–60° is not of the symmetric dihydride, and may be of the canted dihydride.

For the Si(100)-2 × 1:H monohydride surface, a structure model shown in Fig. 7 is well accepted, in which hydrogen adsorb on dimerized silicon atoms. On the H–Si bond angle β, numerous approaches are carried out from theoretical view points, and 70.5 [11], 69.8 [12], 70.6 [13], 71.0 [14], 65.3 [15] and 70.0° [16] are reported. From experimental approaches, Wang et al. [15] and Wampler [16] reported 47 and 74 ± 6°, respectively. Recently, our group reported a value of near 70° by means of LE-RIS using Ne ion beams [17]. Comparing these values with our value of 65–70°, we notice that our experimental value is in good agreement with the theoretically obtained values and the experimental value by LE-RIS using Ne ion beams.

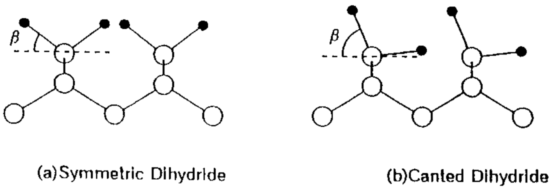

Fig. 6. Models of the Si(100)-1×1:2H dihydride structure, (a) symmetric dihydride, (b) canted dihydride. Solid circles denote H atoms.

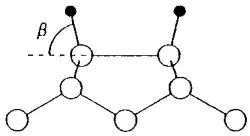

Fig. 7. Model for the Si(100)-2×1:H monohydride structure. Solid circles denote H atoms.

It should be noted that there exists inelastic effects in hydrogen recoil processes by Ne ion beams [18]. Therefore, He ion beams without inelastic effects are preferable probes for surface hydrogen analysis. However, in this He ion beam the shadow cone is clearly formed behind the hydrogen atom compared with the case of Ne ion beams. For a more precise determination of the H–Si bond angle, further investigation on this shadowing effects may be necessary. Furthermore, the scaling factor used in the simulation is important for the bond angle determination because it affects the shadow cone radius.

5. Summary

Low-energy He, and Ne ion beams enable us to analyze the hydrogen adsorbed on Si(100) surface. Using He ion beams, we obtained information on the bonding geometries of hydrogen atoms of both the Si(100)-2 × 1:H monohydride surface and the Si(100)1 × 1:2H dihydride surface. On the monohydride surface, the estimated bonding angle of 65–70° agrees with the theoretically proposed values. On the dihydride surface, the canted dihydride structure is preferred over the symmetric dihydride structure.

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