

Hydrogen at the surface and interface of metals on Si(111)

K. Fukutani*

Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8558, Japan

H. Iwai

Department of Chemistry, Utsunomiya University, Mine, Utsunomiya 321-8505, Japan

Y. Murata

Physics Department, Division of Natural Sciences, The University of Electro-Communications, Chofugaoka, Chofu, Tokyo 182-8585, Japan

H. Yamashita

Research Center for Nuclear Science and Technology, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113, Japan

(Received 18 November 1998)

The depth-resolved measurement of hydrogen using the resonant nuclear reaction of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ in the formation of (Pb, Ag, and Cu)/Si(111) interfaces is reported. It was found that Pb deposition on Si(111)1×1-H at 110 and 360 K leads to the formation of the Pb/H/Si(111) interface. Upon deposition of Ag at 110 K, however, it was found that a quarter of the monolayer of H migrates to the surface of Ag with the rest of H remaining at the Ag/Si(111) interface. The preadsorbed H atom was desorbed from the surface by deposition of Ag and Cu at 360 K, suggesting that (Ag, Cu)/H/Si(111) is a metastable structure. The relative stability of the interface H is discussed. [S0163-1829(99)03619-X]

I. INTRODUCTION

Hydrogen at solid surfaces and interfaces has received much attention in recent years from the viewpoint of technological application as well as fundamental physics and chemistry.¹ Hydrogen adsorption at solid surfaces is the initial step for a variety of surface and bulk phenomena such as hydrogen storage in materials and hydrogenation reactions. From a fundamental point of view, many concepts of adsorption and diffusion are embodied in the system of H at solid surfaces. Furthermore, hydrogen at semiconductor surfaces and interfaces is of practical interest and importance because hydrogen atoms frequently passivate semiconductor surfaces and also reduce the density of the interface states by saturating the dangling bond. According to the work by Mönch and co-workers, hydrogen at the metal-semiconductor interface, depending on the kind of metals, significantly influences the Schottky-barrier height thereby offering an opportunity to modify and control the barrier height by dosing H atoms before formation of metal-silicon contacts.²⁻⁴ In recent years, it has been found that hydrogen atoms sometimes modify the growth mode of the metal⁵⁻¹⁰ and semiconductors¹¹⁻¹⁵ acting as a surfactant. However, little is known about the real role of H and the H concentration in the resulting epitaxial film and the interface.

A difficulty for the study of H at surfaces and interfaces is that H is visible to quite limited techniques, because of the small scattering factor due to light mass and limited availability of electron spectroscopic techniques. High-energy ion beams offer a way to detect hydrogen atoms. Stability of H at the Au-Si interface was investigated by the measurement of D coverage using nuclear reaction analysis,¹⁶ and the system of Au deposition on H-terminated Si was recently investigated by core-level spectroscopy.¹⁷ Application of a resonant nuclear reaction instead of a nonresonant reaction

enables us to directly detect H with depth resolution, which is well suited to the study of metal on H-terminated surfaces. It is demonstrated that the nuclear reaction of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ has detection limit for H adsorbed on a solid surface less than 1/10th of a monolayer.^{18,19} This reaction was applied to the investigation of the H trapping at the Al-Si interface.²⁰ In our previous papers, we reported that the use of resonant nuclear reaction analysis (RNRA) enables us to distinguish surface and interface hydrogen. When Si is evaporated on H-terminated Si(001) at a low temperature, H atoms are present at the interface between the substrate and the deposited Si layer.²¹ In the case of metal deposition on the Si(111)-H surface at room temperature, Ag induces H desorption from the surface²² while Pb forms interface hydrogen.²³

In this paper, we report a RNRA investigation of H upon metal (Pb, Ag, and Cu) deposition on a hydrogen-terminated Si(111) surface at 360 and 110 K. Depending on the kind of deposited metals and the substrate temperature, the behavior of hydrogen upon metal deposition and also the growth mode of the metal reveals dramatic changes.

II. EXPERIMENT

The experiments were performed in an UHV chamber (base pressure: 1×10^{-10} mbar) which was attached through two-stage differential pumping to the 2C beam line of the tandem-type Van de Graaff accelerator at the Research Center for Nuclear Science and Technology at the University of Tokyo. The $^{15}\text{N}^{2+}$ ion beam was accelerated to an energy of 6.385 MeV and introduced into the UHV chamber, inducing the $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ nuclear reaction with H atoms adsorbed at the surface. Detection of γ rays with an energy of 4.43 MeV emitted as a result of the nuclear reaction by a $\text{Bi}_4\text{Ge}_4\text{O}_{12}$ scintillator enables us to measure the H concentration. Since

the reaction at this energy has a resonance width of 1.8 keV (Ref. 24) and the stopping power of a solid for the incident N beam is the same order of magnitude,^{25,26} variation of the ion energy gives us the depth information about H atoms in a solid. The energy width of the incident ion beam was 10 keV, which was achieved by monochromatization with the energy analyzer (orbital radius: 1270 mm) at a slit width of 4 mm and with the help of a slit feedback system. The typical beam current and beam size at the sample were 30 nA and 2 mm in diameter, respectively. The measurement time was 100–200 s per data point and one monolayer of H for Si(111) yields 51 counts/ μC at the resonance energy. Since the γ -ray yield gradually decreases after a prolonged measurement with a time constant of about one hour probably due to ion-induced desorption, estimation of H coverage was carried out after correcting the effect of the decay. The ion source at this accelerator is a Cs-sputtering type with a solid cathode of $\text{Ti}^{15}\text{N}+\text{C}$, which produces a CN^- ion of around $1 \mu\text{A}$.

The sample used in the present study is $\text{Si}(111)1\times 1\text{-H}$, which was prepared by dosing atomic H at a sample temperature of 820 K until the H coverage was saturated. Before dosing H, the Si(111) sample was cleaned by flashing at 1470 K. Atomic hydrogen was produced by passing hydrogen molecules through a tungsten tube (2 mm in diameter, 0.1 mm thick, 30 mm long) heated at 1900 K. The sample prepared in this way exhibited a clear 1×1 low-energy electron diffraction (LEED) pattern indicating the formation of H-terminated Si(111). A previous scanning tunnel microscope (STM) study²⁷ reports that this $\text{Si}(111)1\times 1\text{-H}$ is the ideal 1×1 structure with one H atom at a dangling bond and H coverage of one monolayer (ML) ($7.83\times 10^{14}/\text{cm}^2$). The sample temperature of lower than 400 K was measured by a Pt-PtRh thermocouple attached to the Ta electrode supporting the Si sample, while the temperature of higher than 700 K was measured with an optical pyrometer. The sample temperature from 400 to 700 K was determined by extrapolating the relation between the sample current and temperature in the range of 700–1100 K.²⁸ The evaporation of metal (Cu, Pb, and Ag) was performed by using tungsten filaments and the thickness was measured by a quartz oscillator placed below the sample. The typical evaporation rate was $0.4 \text{ \AA}/\text{s}$. The sample temperature during metal evaporation and measurements was kept at 360 or 110 K, which was achieved by liquid-nitrogen cooling.

III. RESULTS AND DISCUSSION

A. Pb/Si(111)1×1-H

Figure 1(a) shows the γ -ray intensity profile as a function of the incident ^{15}N beam energy taken for the $\text{Si}(111)1\times 1\text{-H}$ at a sample temperature of 360 K. The profile reveals a peak at the resonance energy²⁹ which is assumed to correspond to the H of $7.83\times 10^{14}/\text{cm}^2$. The solid curve fits to a Gaussian function of the form of $A \exp[-\{(E-E_R)-E_0\}^2/\sigma^2]$, where E is the ion energy, E_R is the resonance energy of 6.385 MeV, and A , E_0 , and σ are fit parameters. The spectral width [full width at half maximum (FWHM)] obtained from the fit is $12.7\pm 0.4 \text{ keV}$, which is much broader than the resonance width of 1.8 keV because of the Doppler effect caused by the zero-point vibration of adsorbed H at the surface.²⁴ Consid-

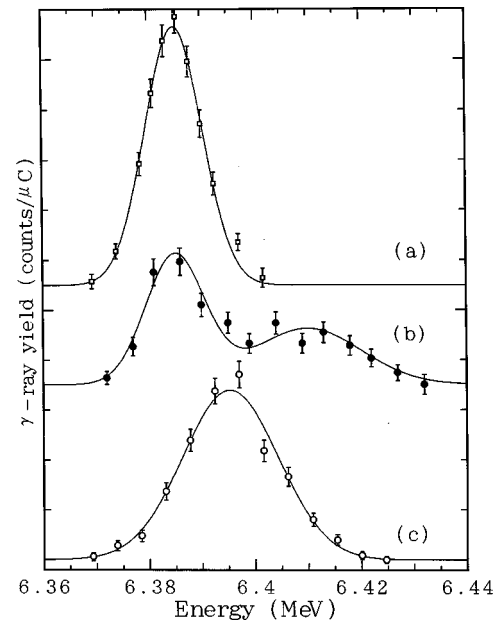


FIG. 1. Intensity profiles of the γ ray from the $^1\text{H}(^{15}\text{N},\alpha)^{12}\text{C}$ nuclear reaction as a function of the incident ^{15}N beam energy taken for the sample of Pb deposition on $\text{Si}(111)1\times 1\text{-H}$. (a) $\text{Si}(111)1\times 1\text{-H}$ before Pb deposition, (b) Pb deposition of 45 \AA at 360 K, and (c) Pb deposition of 45 \AA at 110 K. Solid curves are fits to a Gaussian form [a sum of two Gaussian forms for (b)].

ering the instrumental width of 10 keV that is estimated from the slit width of the ion energy analyzer, the observed width is roughly consistent with the vibrational energy of H at $\text{Si}(111)$.³⁰

Figures 1(b) and 1(c) show the γ -ray intensity profiles as a function of the incident ion energy after Pb deposition of 45 \AA on $\text{Si}(111)1\times 1\text{-H}$ at sample temperatures of 360 and 110 K, respectively. Figure 1(b) reveals the presence of two components, one centered at 6.385 MeV and the other centered at a higher energy, while Fig. 1(c) exhibits one component at an energy higher than the resonance energy. The presence of the higher-energy component clearly indicates that appreciable amounts of hydrogen atoms are present below the surface after deposition of Pb atoms. The profile (b) is fitted to a sum of two Gaussian functions, which is shown by the solid curve in Fig. 1. The parameters E_0 and FWHM ($=2\sqrt{\ln 2}\sigma$) obtained from the fit are $23.5\pm 3.5 \text{ keV}$ and $24.0\pm 8.5 \text{ keV}$ for the higher-energy component. A fit of the data in Fig. 1(c) to a Gaussian form, on the other hand, gives us E_0 and FWHM values of $10.3\pm 0.4 \text{ keV}$ and $21.3\pm 1.2 \text{ keV}$, respectively. Furthermore, the H concentration estimated from the integrated intensity of the spectrum (c) is $1.10\pm 0.08 \text{ ML}$. At a sample temperature of 360 K, the H concentrations for the surface and higher-energy components in Fig. 1(b) are estimated to be 0.63 ± 0.1 and $0.41\pm 0.17 \text{ ML}$, respectively. The total amount of H is preserved during the Pb deposition at 360 K as well as at 110 K. Since the E_0 value represents the shift of the distribution with respect to the resonance energy due to the energy loss of the incident beam, one can know the mean depth of H from the stopping power. With the stopping power of Pb for N at 6.385 MeV, 0.232 keV/\AA ,²⁶ the depth of the H correspond-

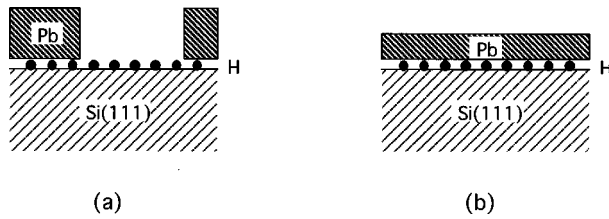


FIG. 2. Schematic figures of Pb growth on Si(111)1×1-H at substrate temperatures of (a) 360 K and (b) 110 K. Black dots denote H atoms.

ing to the higher-energy components in Figs. 1(b) and 1(c) is calculated to be 101 and 44.4 Å, respectively.

The mean depth of the higher-energy component observed at 360 K is twice as much as the deposited amount of Pb, hence it is considered that the Pb atoms form islands on this surface, covering about 40% of the surface with a height of 101 Å and that 0.63 ML of H is present at the Si surface, giving rise to the surface peak, while the rest of H remains at the interface between the Si substrate and Pb layer as schematically shown in Fig. 2(a). Since the amount of deposited Pb on the surface (45 Å) is in remarkable agreement with the depth of H in Fig. 1(c) (44.4 Å), on the other hand, it is concluded that all the H atoms preadsorbed on the surface remain at the interface between the substrate and the Pb layer at a sample temperature of 110 K with a Pb layer of uniform thickness as schematically shown in Fig. 2(b). It should be noted that the effect of the Pb-Si interdiffusion may be neglected at these deposition temperatures.

According to previous studies, the Schottky-barrier height for the Pb contact formed on Si(111)1×1-H is reported to be higher than that formed on the bare Si(111) surface by 0.08 eV.^{3,31} It is claimed that a H-induced dipole layer is present at the interface and that H atoms remain at the Pb-Si interface,³ which is strongly supported by the present study.

It is worth noting that the spectral width corresponding to the interface component is substantially broadened compared with the profile for Si(111)1×1-H. Although this broadening may suggest the H atoms corresponding to the interface components are distributed within some layers around the interface, the main cause for this broadening is considered to be the energy straggling of the incident ion traveling in the Pb layer. According to the work by Rud, Böttiger, and Jensen, the energy straggling of the N ion at an energy of 6.385 MeV is reported to be proportional to the square root of the ion-transmitting thickness of the solid and the atomic number to the 0.39th power.³² By using the curve reported in this paper, FWHM of the energy straggling in the Pb layer is described as $1.8\sqrt{t}$ keV where t is the thickness of the Pb layer in the unit of Å. From this formula, the energy straggling for thicknesses of 101 and 44.4 Å are calculated to be 18.1 and 12.0 keV, respectively. Assuming that both energy straggling and vibrational widths are described in a Gaussian form, convolution of these two terms leads to total widths of 22.1 and 17.5 keV, which are roughly in agreement with the experimental values of 24.0 and 21.3 keV, respectively. The remaining difference might be caused by the following reasons: (1) uncertainty in the energy straggling, (2) inhomogeneity of the Pb layer thickness, (3) H migration into the Si substrate and/or the Pb layer, and (4) hardening of the H vibration at the interface.

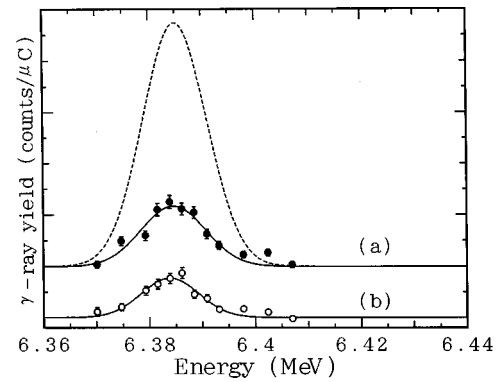


FIG. 3. Intensity profiles of the γ ray from the ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$ nuclear reaction as a function of the incident ${}^{15}\text{N}$ beam energy taken for Ag deposition on the Si(111)1×1-H with coverages of (a) 39 Å and (b) 70 Å at a sample temperature of 360 K. Solid curves are fits to a Gaussian form and the broken curve denotes the curve for Si(111)1×1-H.

B. Ag/Si(111)1×1-H

Intensity profiles taken after Ag deposition on Si(111)1×1-H at 360 and 110 K are shown in Figs. 3 and 4, respectively. The Ag deposition at 360 K brings about a substantial decrease in the γ -ray intensity corresponding to the surface H, suggesting that adsorption of Ag atoms causes H desorption from the surface at this temperature. The H coverage is estimated to be 0.25 ± 0.03 and 0.15 ± 0.02 ML at Ag coverages of 39 and 70 Å, respectively. Since the reduction rate of H is small, the deposited Ag is concluded to form islands without H atoms at the Ag-Si interface and that the H atoms remain at the uncovered surface, which is similar to the case of Ag deposition on Si(111)7×7-H (Ref. 22) as schematically shown in Fig. 5(a). Although the possibility for H atoms to be present at the surface of Ag islands cannot be ruled out, this is unlikely to occur because the thermal desorption temperature of H at Ag(111) is known to be 190 K (Ref. 33) and H is expected to desorb at 360 K. From the relation between the Ag coverage and the area covered by

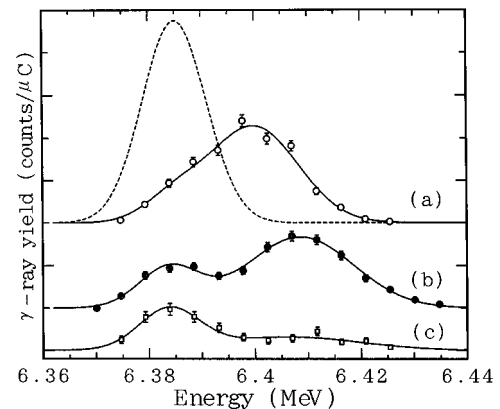


FIG. 4. Intensity profiles of the γ ray from the ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$ nuclear reaction as a function of the incident ${}^{15}\text{N}$ beam energy taken for Ag deposition on Si(111)1×1-H with coverages of (a) 33 Å and (b) 67 Å at a sample temperature of 110 K. (c) Intensity profile taken after annealing at 300 K of the sample corresponding to (b). Solid curves are fits to a sum of two Gaussian forms and the broken curve denotes the curve for Si(111)1×1-H.

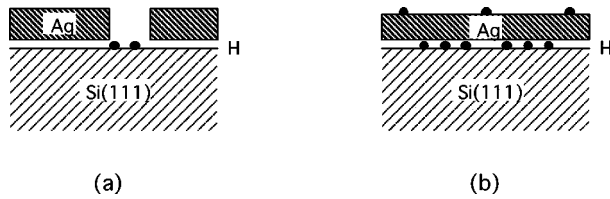


FIG. 5. Schematic figures of Ag growth on Si(111)1 \times 1-H at substrate temperatures of (a) 360 K and (b) 110 K. Black dots denote H atoms.

Ag islands, the height of Ag islands is estimated to be 52 and 82 Å at Ag coverages of 39 and 70 Å, respectively. Island formation on the H-terminated Si surface is supported by a previous study using scanning-electron microscopy where Ag atoms are observed to form islands with a height of 30 Å and a coverage of 13.4 Å.³⁴ This result is in good agreement with the present study. It is worth noting that Ag atoms induce desorption of H only after islanding, not while diffusing on the surface, because Ag atoms arrive at the surface randomly and migrate on the surface, leaving H atoms on Si before island formation. The previous study on the Ag contact with Si(111) shows that the Schottky-barrier height formed on the H-terminated Si(111)1 \times 1 surface is identical with that formed on Si(111)1 \times 1 without H, suggesting that preadsorbed H atoms are replaced by deposited Ag atoms.⁴ This conclusion is strongly supported by the present result.

Figures 4(a) and 4(b) show intensity profiles taken after Ag deposition of 33 and 67 Å, respectively, on Si(111)1 \times 1-H at 110 K. Upon Ag deposition at 110 K, in contrast to the deposition at 360 K, a single peak observed for Si(111)1 \times 1-H before the deposition splits into two peaks with increasing Ag coverage. This result suggests that both surface and interface components are present after Ag deposition at 110 K. The spectra are well fitted to a sum of two Gaussian forms, which are displayed by solid curves in Fig. 4. The obtained result for the coverage of 67 Å shows that one is centered at E_R (6.385 MeV) with a coverage of 0.28 ± 0.03 ML and the other is centered at $E_R + (23.7 \pm 0.38)$ keV with a FWHM of 23.7 ± 0.8 keV with a coverage of 0.58 ± 0.05 ML. It seems that the total amount of H is almost preserved during Ag deposition at 110 K. With the stopping power of 0.335 keV/Å, the mean depth of the bulk H is calculated to be 70.7 Å, which coincides with the amount of Ag deposited onto the surface. Therefore, it is concluded that Ag atoms form a uniform layer at 110 K, in contrast to the growth at 360 K. It is noted that the effect of the Ag-Si interdiffusion can be neglected because of the low substrate temperature. Furthermore, since there exists a surface component of H, it is considered that about a quarter monolayer of H segregates to the surface, occupying the surface site of the Ag layer while the rest of H remains at the Si-Ag interface as schematically shown in Fig. 5(b).

Figure 4(c) shows the γ -ray intensity profile taken after annealing at 300 K the sample corresponding to Fig. 4(b). It is noticed that the intensity of the interface component is dramatically reduced while the surface component seems to remain intact. The interface H is either desorbed from the surface or diffused into the bulk. It seems that the presence of H at the surface of Ag even after annealing at 300 K contradicts the previous discussion that H is desorbed from

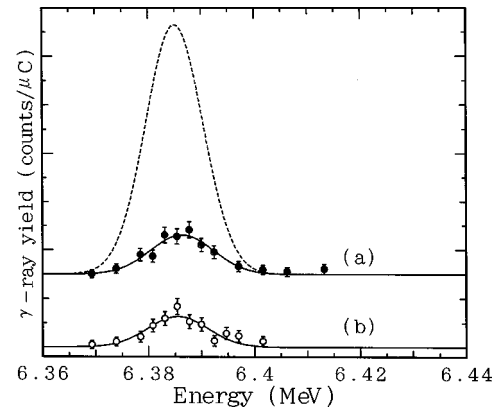


FIG. 6. Intensity profiles of the γ ray from the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction as a function of the incident ^{15}N beam energy taken for Cu deposition on Si(111)1 \times 1-H with coverages of (a) 19 Å and (b) 31 Å at a sample temperature of 360 K. Solid curves are fits to a Gaussian form and the broken curve denotes the curve for Si(111)1 \times 1-H.

the Ag surface at 300 K. A possible interpretation is that annealing brings about islanding of Ag atoms with a part of the Si surface exposed to the vacuum. Although we cannot definitely identify the adsorption site of the surface H between Ag and Si from the spectrum, we suggest another possibility, that the H atom corresponding to the surface component exists at the subsurface site of Ag with a higher activation barrier for desorption.

As in the case of Pb deposition, it should be noted that the spectral width corresponding to the interface H is broadened compared with that of the surface component. The width obtained from the fit is 23.7 keV. The energy straggling in Ag is described as $1.94\sqrt{t}$ keV following the formula mentioned above, which gives us the energy width (FWHM) of 16.3 keV. By convoluting with the vibrational width, a total width of 21.6 keV was obtained, which is in good agreement with the experimental value of 23.7 keV.

C. Cu/Si(111)1 \times 1-H

Figures 6 and 7 show the γ -ray intensity profiles in the case of Cu deposition on Si(111)1 \times 1-H at 360 and 110 K, respectively. Upon deposition of Cu at 360 K, the γ -ray intensity corresponding to the surface H is dramatically decreased to 0.13 ML [Fig. 6(b)], which is similar to the case of Ag deposition. Since no substantial intensity is observed in the region higher than the resonance energy, most of the H atoms preadsorbed on the Si surface are concluded to be desorbed from the surface by Cu deposition. The small amount of surface H observed even after Cu deposition of 31 Å suggests that Cu atoms form islands with H remaining at the uncovered region of the surface. However, the possibility of 0.13 ML H remaining at the surface of Cu deposited onto the Si surface cannot be ruled out at this stage, because the thermal desorption temperature is higher than 350 K at a low coverage.³⁵ At 110 K, on the other hand, while the γ -ray intensity corresponding to the surface component is reduced with increasing Cu coverage, a small intensity corresponding to the bulk component is appreciably observed with Cu deposition of as much as 60 Å. After subtraction of the surface component, a fit of the subtracted spectrum to a Gauss-

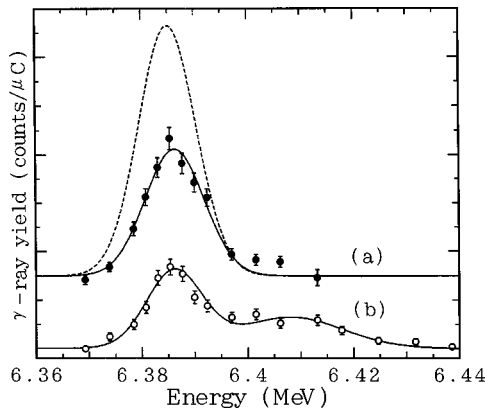


FIG. 7. Intensity profiles of the γ ray from the ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$ nuclear reaction as a function of the incident ${}^{15}\text{N}$ beam energy taken for Cu deposition on the $\text{Si}(111)1\times 1\text{-H}$ with coverages of (a) 19 \AA and (b) 60 \AA at a sample temperature of 110 K. Solid curves are fits to a Gaussian and a sum of two Gaussian forms for (b) and (c), respectively, and the broken curve denotes the curve for $\text{Si}(111)1\times 1\text{-H}$.

ian form gives the E_0 and FWHM values of 23.1 ± 1.1 keV and 23.2 ± 2.7 keV, respectively, which is demonstrated by a solid curve in the figure. Although the fit parameters obtained include large uncertainty due to the small intensity of this bulk component, the mean depth of H is calculated to be 68.3 \AA with the stopping power of 0.338 keV/ \AA for Cu, which is in rough agreement with the amount of Cu deposited on the surface. Since the H coverages of the surface and interface components are 0.29 ± 0.04 and 0.19 ± 0.04 ML, respectively, it is concluded that as in the case of Ag deposition at 110 K Cu atoms form a uniform layer with 0.29 and 0.19 ML of H at the surface of Cu and the Cu-Si interface, respectively. Different from the Ag deposition, about 0.5 ML of H is desorbed from the surface by Cu deposition.

The growth of Cu on the H-terminated $\text{Si}(111)$ surface has been investigated by medium-energy ion scattering.¹⁰ It is reported that the preadsorbed H hardly affects the growth of Cu on $\text{Si}(111)$ at a substrate temperature of 300 K although H adsorption is effective at higher temperatures. It is suggested that H adsorbed on $\text{Si}(111)$ is replaced by Cu atoms impinging on the surface at 300 K, which is in good agreement with the present work.

D. Chemical trend

The present results for Pb, Ag, and Cu deposition on $\text{Si}(111)1\times 1\text{-H}$ show a chemical trend for the formation of interface hydrogen. Comparing the experimental data at a sample temperature of 110 K, one monolayer of interface H is found to be formed at the Pb-Si interface, while a part of the predosed H occupies the surface site of the metal layer upon deposition of Ag and Cu. Furthermore, the coverage of the interface H for Ag is higher than that at the Cu-Si interface. We can qualitatively understand this trend from the difference of the bonding energy between Si-H and Si-metal. To the first approximation, the bonding strength may be described by the thermal desorption temperature of adsorbates at a surface, although the thermal desorption reflects not only the bonding energy but also a combination of various pro-

cesses such as diffusion and recombination. The thermal desorption spectrum of H_2 from the 1×1 phase of $\text{Si}(111)$ is reported to have a maximum at 840 K.³⁶ To compare with the isothermal desorption data for Pb, Ag, and Cu, we tentatively assign the desorption temperature of H_2 to the onset of the spectrum (temperature with a desorption rate of 10% of the maximum in the spectrum), 720 K. On the other hand, isothermal desorption data are presented at substrate temperatures as low as 420, 550, and 600 $^\circ\text{C}$ for Pb,³⁷ Ag,^{38,39} and Cu (Ref. 40) on $\text{Si}(111)$, respectively. Therefore, the bonding strength of Si-H is stronger than that of Si-Pb but weaker than those of Si-Ag and Si-Cu, provided that the thermal desorption temperature is determined by the bond strength. H atoms tend to remain at the interface upon Pb deposition while they are likely to be replaced by Ag and Cu atoms arriving at the surface. As described above, the exchange process between H and metal atoms is temperature dependent and most of the H atoms seem to be replaced by Ag and Cu at 360 K. Hence, the exchange process is activated with a higher barrier for Ag than Cu. The H atom replaced by a metal atom is considered to be desorbed from the surface at a deposition temperature of 360 K because of weak binding of H at Cu and Ag surfaces, as discussed above. It should be noted that about half of the monolayer H is desorbed by Cu deposition at 110 K even though the H-Cu bond is stronger than that of H-Ag. This could be because Cu readily forms silicide at the interface.^{10,41} The dynamics of H-metal exchange should be discussed in terms of the relative stability between the structures of metal/H/ $\text{Si}(111)$, H/metal/ $\text{Si}(111)$, and H/silicide/ $\text{Si}(111)$ along with the competing process of desorption from the surface. We also note that H might occupy the subsurface site of metal during the exchange process, as suggested in Sec. III B. To elucidate the bonding mechanism of metal atoms at the H-terminated Si surface as well as the exchange process, further experimental and theoretical investigations are required.

IV. CONCLUSION

We have investigated the behavior of H at $\text{Si}(111)$ upon formation of metal-Si interfaces. By applying a resonant nuclear reaction of ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$, we showed that H residing at the metal/Si interface is well resolved from that at the surface. We found that H atoms stably occupy the interface site of Pb/ $\text{Si}(111)$, the growth mode of Pb being dependent on the substrate temperature. Low-temperature deposition of Ag and Cu leads to separation of the preadsorbed H layer into surface and interface H, while room-temperature deposition causes desorption of H.

ACKNOWLEDGMENTS

The authors are grateful to K. Kobayashi, S. Hatori, C. Nakano, and Y. Sunohara for their valuable advice and assistance in operating the accelerator. This work was supported by a Grant-in-Aid for Creative Basic Research, Scientific Research, and Scientific Research on Priority Areas from the Ministry of Education, Science, Sports and Culture of Japan, and by the Iron and Steel Institute of Japan.

- * Author to whom correspondence should be addressed. Electronic address: fukutani@iis.u-tokyo.ac.jp
- ¹K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).
- ²W. Mönch, J. Vac. Sci. Technol. B **14**, 2985 (1996).
- ³T. U. Kampen and W. Mönch, Surf. Sci. **331-333**, 490 (1995).
- ⁴T. U. Kampen, R. F. Schmitsdorf, and W. Mönch, Appl. Phys. A: Mater. Sci. Process. A **60**, 391 (1995).
- ⁵W. F. Egelhoff, Jr. and D. A. Steigerwald, J. Vac. Sci. Technol. A **7**, 2167 (1989).
- ⁶K. Sumitomo, T. Kobayashi, F. Shoji, and K. Oura, Phys. Rev. Lett. **66**, 1193 (1991).
- ⁷M. Naitoh, F. Shoji, and K. Oura, Jpn. J. Appl. Phys., Part 1 **31**, 4018 (1992).
- ⁸K. Murano and K. Ueda, Surf. Sci. **357-358**, 910 (1996).
- ⁹A. Nishiyama, G. ter Horst, P. M. Zagwijn, G. N. van den Hoven, J. W. M. Frenken, F. Garten, A. R. Schlatmann, and J. Vrijmoeth, Surf. Sci. **350**, 229 (1996).
- ¹⁰T. Yasue and T. Koshikawa, Surf. Sci. **377-379**, 923 (1997).
- ¹¹M. Copel and R. M. Tromp, Phys. Rev. Lett. **72**, 1236 (1994).
- ¹²A. Sakai and T. Tatsumi, Appl. Phys. Lett. **64**, 52 (1994).
- ¹³J. E. Vasek, Z. Zhang, C. T. Salling, and M. G. Lagally, Phys. Rev. B **51**, 17207 (1995).
- ¹⁴M. H. Hoegen and A. Golla, Phys. Rev. Lett. **76**, 2953 (1996).
- ¹⁵S.-J. Kahng, Y. H. Ha, J.-Y. Park, S. Kim, D. W. Moon, and Y. Kuk, Phys. Rev. Lett. **80**, 4931 (1998).
- ¹⁶Z. H. Lu, K. Griffiths, P. R. Norton, and T. K. Sham, Phys. Rev. B **44**, 5648 (1991).
- ¹⁷C. Grupp and A. Taleb-Ibrahimi, Phys. Rev. B **57**, 6258 (1998).
- ¹⁸B. Maurel and G. Amsel, Nucl. Instrum. Methods Phys. Res. **218**, 159 (1983).
- ¹⁹Y. Iwata, F. Fujimoto, E. Vilalta, A. Ootuka, K. Komaki, K. Kobayashi, H. Yamashita, and Y. Murata, Jpn. J. Appl. Phys., Part 2 **26**, L1026 (1987).
- ²⁰J. C. Liu, A. D. Marwick, and F. K. LeGoues, Phys. Rev. B **44**, 1861 (1991).
- ²¹K. Fukutani, M. Tsunoda, Y. Murata, H. Yamashita, K. Komaki, and K. Kobayashi, Surf. Sci. **283**, 447 (1993).
- ²²M. Tsunoda, K. Fukutani, Y. Murata, H. Yamashita, K. Komaki, and K. Kobayashi, in *Formation of Semiconductor Interfaces*, edited by B. Lengler, H. Lüth, W. Mönch, and J. Pollmann (World Scientific, Singapore, 1994), p. 162.
- ²³K. Fukutani, H. Iwai, H. Yamashita, Y. Murata, S. Hatori, and K. Kobayashi, Surf. Sci. **377-379**, 1010 (1997).
- ²⁴M. Zinke-Allmang, S. Kalbitzer, and M. Weiser, Z. Phys. A **323**, 183 (1986).
- ²⁵T. F. Ziegler, *Handbook of Stopping Cross-Sections for Energetic Ions in All Elements* (Pergamon, New York, 1980).
- ²⁶*Handbook of Modern Ion Beam Materials Analysis*, edited by J. R. Tesmer and M. Nastasi (Materials Research Society, Pittsburgh, 1995).
- ²⁷F. Owman and P. Mårtensson, Surf. Sci. **303**, L367 (1994).
- ²⁸T. Ichikawa and S. Ino, Surf. Sci. **105**, 395 (1981).
- ²⁹Since the energy analyzer for the incident ion needs a calibration for determining the absolute ion energy, the peak position of this curve is set to be the resonance energy of 6.385 MeV for the ¹⁵N beam.
- ³⁰G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, Appl. Phys. Lett. **56**, 656 (1990).
- ³¹D. R. Heslinga, H. H. Weitering, D. P. van der Werf, T. M. Klapwijk, and T. Hibma, Phys. Rev. Lett. **64**, 1589 (1990).
- ³²N. Rud, J. Bøttiger, and P. S. Jensen, Nucl. Instrum. Methods **151**, 247 (1978).
- ³³G. Lee, P. T. Sprunger, M. Okada, D. B. Poker, D. M. Zehner, and E. W. Plummer, J. Vac. Sci. Technol. A **12**, 2119 (1994).
- ³⁴M. Naitoh, F. Shoji, and K. Oura, Surf. Sci. **242**, 152 (1991).
- ³⁵G. Anger, A. Winkler, and K. D. Rendulic, Surf. Sci. **220**, 1 (1989).
- ³⁶R. Imbihl, J. E. Demuth, S. M. Gates, and B. A. Scott, Phys. Rev. B **39**, 5222 (1989).
- ³⁷J. A. Carlisle, T. Miller, and T.-C. Chiang, Phys. Rev. B **45**, 3400 (1992).
- ³⁸G. Lelay, M. Manneville, and R. Kern, Surf. Sci. **72**, 405 (1978).
- ³⁹S. Hasegawa, H. Daimon, and S. Ino, Surf. Sci. **186**, 138 (1987).
- ⁴⁰Z. H. Zhang, S. Hasegawa, and S. Ino, in *Proceedings of the 4th International Conference on the Structure of Surfaces*, edited by X. Xie, S. Y. Tong, and M. A. Van Hove (World Scientific, Singapore, 1994), p. 371.
- ⁴¹T. Yasue, C. Park, T. Koshikawa, and Y. Kido, Appl. Surf. Sci. **70/71**, 428 (1993).