(BL4B)

Synchrotron-radiation stimulated desorption of SiO_2 thin films on Si(111) surfaces observed by scanning tunneling microscopy

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Synchrotron radiation (SR), which involves wavelengths ranging from infrared to x-ray, is thought to be a suitable light source in photo-excitation. Recently, scanning tunneling microscopy (STM) is a powerful tool to obtain the information about the surface morphology and the local electronic structures. STM should give us various information about the SR-irradiated surfaces with atomic scale resolution. On the other hand, silicon dioxide films are also known to be removed during SR-irradiation at elevated temperatures in an ultrahigh vacuum (UHV).[1] Therefore, SR-stimulated desorption of SiO_2 films have been the target of intense research in the field of surface science and the semiconductor devices.

A STM system was constructed at BL4B of UVSOR. During STM measurement, the STM chamber was covered by a soundproof mat because of the elimination of the acoustic noise from the rotary pumps, turbomolecular pumps, and compressors of other beamlines in the UVSOR.

The sample (3×8 mm^2) was an *n*-doped Si(111) wafer with a thickness of 0.5 mm and a resistivity of about 1 Ω/cm. The thickness of the native oxide layer treated by the above method was about 1 nm. Mechanically ground Pt/Ir tips were used without any special cleaning for the STM measurements.

Figure 1 (a) shows the LEED pattern observed after 2 h SR-irradiation, which gave a 19200 mA·min dose, to the sample at a surface temperature of 700°C. At a sample temperature of 700°C, the 7×7 spots were observed, even for the 0.5 h SR-irradiation, although the intensities of the 1/7-order diffraction were fairly weak compared with those of the thermally cleaned Si surface. Notice that the SR non-irradiated region, LEED spots were not observed, and meaningful changes were not observed in the Auger spectra before and after the SR-irradiation at this temperature.

In Fig. 2, we show a topograph of the occupied states of the Si(111) surface after 2 h SR-irradiation to the samples at a temperature of 700°C. The morphology of the SR-irradiated surface seems to be rather inhomogeneous, and quite different from that in the usual thermal desorption process.[2-4] The bright grains in Fig. 2 (a) indicate areas of residual oxide and the dark regions correspond to the exposed Si surfaces. The grain height is uncertain since we have not determined the barrier height difference for the clean and oxide covered surfaces. Figure 2 (b) shows a magnified topograph of the dark region in Fig. 3 (a). Atomic image of Si(111)-7×7 surface was clearly observed and several bright sites were found in the STM topograph of the Si surface. The most important result in the present study is that the nanometer-size void structures, which are observed in the thermal desorption process, are not formed on SR-stimulated surfaces. In the case of the thermal desorption of thin SiO_2 films, the nanometer-size holes (voids) were created.[3,4] These void formations can be explained by Si atoms, which are supplied from the substrate lattice, migrating to the edge of the residual oxide. Such voids were not found in the SR-stimulated surface, indicating that the desorption mechanism is completely different from that associated with the thermal desorption processes of the SiO_2 films.

Next we consider the mechanism of SR-stimulated desorption of SiO_2. When a SR beam is irradiated to a SiO_2 film, the valence and core electrons of both Si and O atoms are excited.[1] SR induces Si-O bond breaking [5] and the photo-stimulated oxygen atom or ion desorption takes place on the oxide surface. High Si-content regions are formed as a result of oxygen desorption from the oxide surface. In the SiO_2, SR also forms numbers of defects such as non-bonding oxygen (Si-O), peroxyl bridges (Si-O-O-Si), peroxyl radicals (Si-O-O), and Si dangling bonds in the SiO_2 film.[6] By heating the sample, these defects dissociates and desorbs the oxygen, and volatile SiO, which can be thermally desorbed, is formed over the whole SR-irradiated area. Consequently, an atomically flat surface is obtained. From this model, it is predicted that the desorption of oxide film by SR-irradiation proceeds preferentially at the defect rich regions such as grain boundaries. This is consistent with the observation of inhomogeneous STM images shown in Fig. 2 (a). The model is also consistent with the observation of atomically flat SR-irradiated surfaces.

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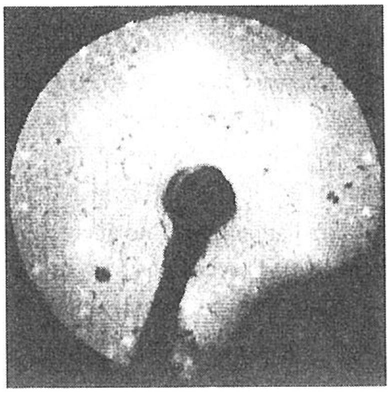

Fig. 1. (a) The LEED pattern for the SR-irradiated native oxide film on Si(111) surface. The primary electron energy is set at 50 eV. The SR-irradiation was made for 2 h at a sample temperature of 700°C.

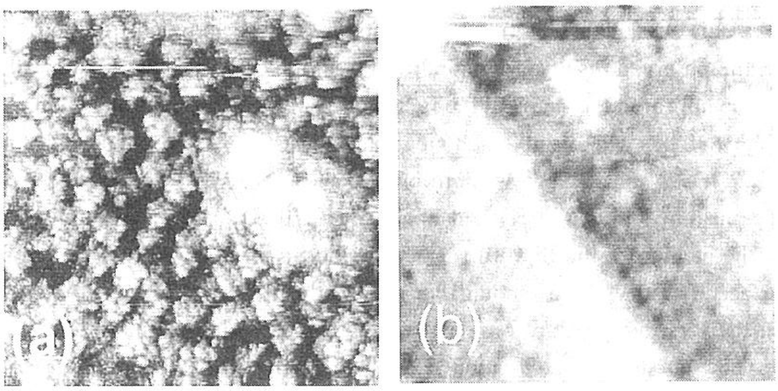

Fig. 2. (a) STM image of the SR-irradiated sample surface. The SR-irradiation was made for 2 h at a temperature of 700°C. The image is 250 × 500 nm. (b) Magnification of topograph in (a). The image is 20 × 20 nm.

(BL-4B)

Annealing and Synchrotron Radiation Irradiation Effect on Hydrogen Terminated Si(100) Surfaces Investigated by Infrared Reflection Absorption Spectroscopy

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We are considering the application of synchrotron radiation (SR) stimulated processes, which have characteristics of high spatial resolution and low damage, to nano structure fabrications on semiconductor surfaces. From this viewpoint, the understanding and the control of the chemical nature of chemisorbed hydrogen on Si(100) surfaces are extremely important research subjects in SR processes as they are commonly occurring processes. In this work, the structure of the D-Si(100) 1x1 surface formed at 400 K and its change by annealing and SR irradiation have been investigated by measuring the high resolution IR spectrum by the BML-IRRAS method using a $CoSi_2$ BML Si(100) substrate, and reflective high-energy electron diffraction (RHEED).

The SiD stretching vibration band[1)] and its change by annealing observed by BML-IRRAS are shown in Fig. 1. The observed change of the SiD stretching vibration band due to the annealing plus SR irradiation is shown in Fig. 2. The change of the integrated absorbance (IA) and the peak position of the SiD stretching vibration band, with increasing annealing temperature are shown in Figs. 3(A) and 3(B), respectively.

The rapid decrease of the IA at around 700 K (Figs. 1 and 3(A)) and the corresponding peak shift to the lower frequency side (Fig. 3(B)) is explained by the decrease of the dipole-dipole coupling interaction.[1)] It is known that monohydride phase desorption occures through preparing mechanism, i.e., desorbs through the precursor form of H-Si-Si-H (D-Si-Si-D). Therefore, it is concluded that the surface after the annealing at 650 K or higher is covered only by D-Si-Si-D, if there exist no defects on the surface, and the sharp SiD stretching vibration band observed in Fig. 1 (spectrum D and E) is assigned to the D-Si-Si-D symmetric stretching vibration. On the other hand, the increase of the IA with annealing temperature increase from 570 to 650 K is explained by the thermal decomposition of $2SiD_2$ to D-Si-Si-D. It is reported that the SR irradiation decomposes di- and trihydrides but not the monohydride.[1)] In the present case, a slight increase of the IA of the SiD stretching vibration band is observed upon 570 K annealing plus SR irradiation (Fig. 3(A)▲). This increase is explained by the decomposition of dideuteride to monodeuteride by the SR irradiation, since no increase is observed only upon 570 K annealing (Fig. 3(A)○). Concerning this dideuteride decomposition by SR irradiation, not only desorption of deuterium atom by breaking the Si-D bond, but also the possibility of the etching (desorption of SiD or SiD_2) must be considered. By comparing Figs. 1 and 2, we can discuss this etching effects from a different viewpoint. By annealing at 650 K or higher, if there is no defect on the Si(100) surface, the existing surface deuteride species become only D-Si-Si-D (preparing mechanism) as experimentally verified by STM.[2)] Therefore, the IRRAS SiD stretching vibration band shape becomes sharp and symmetric as observed in Fig. 1 (D and E). However, the observed results are quite different in the case of SR irradiation plus annealing. The SR irradiation effects clearly appear in the shape of the IRRAS SiD stretching vibration band i.e., at the annealing temperature higher than 650 K, where only monodeuteride exists, the band shape becomes broad and asymmetric as shown in Fig. 2 (D, E and F), and as more clearly shown in Fig. 4, where the band shapes are compared for the cases of annealing only (670 K) and annealing (670 K) + SR irradiation. This asymmetric shape can be explained by the etching of the Si(100) surface by the SR irradiation. If there are no defects on the Si(100) surface, the surface hydride species should be, as already mentioned, only D-Si-Si-D, which are thermodynamically stable in the high temperature region where the surface migration of deuterium atoms frequently occurs. But, the observed SiD stretching vibration band shape shows that the surface species are not just D-Si-Si-D. Therefore, it is concluded that some defects are generated by SR irradiation on D-Si(100)1x1 surface which consists of D-Si-Si-D and D-Si-D, and it is concluded that the defects are generated by SR stimulated desorption (etching) of D-Si-D, since monodeuteride is not decomposed by SR irradiation. Since only monodeuteride exists on the surface after 650 K annealing, the component of the low frequency side tail of the SiD stretching vibration band in the high temperature region above 650 K in Figs. 2 or 4 is assigned to the stretching vibration of Si-D at the defect site generated by the etching. This means that the SR irradiation induces not only the desorption of D by breaking the Si-D bond, but also the desorption of SiD and/or SiD_2 by breaking the backbonds of D-Si-D.

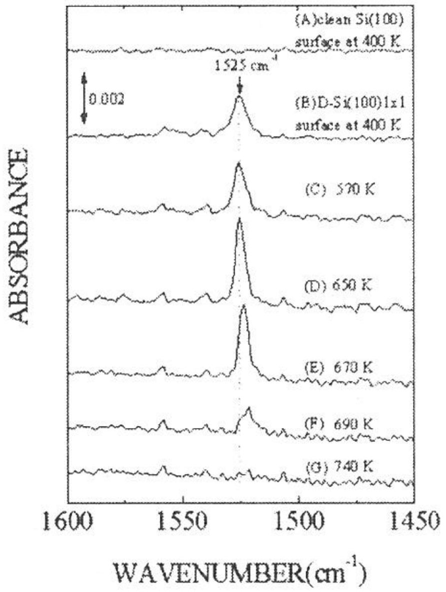

Figure 1. The change of the IRRAS spectrum of the SiD stretching vibration band with increase in annealing temperature.

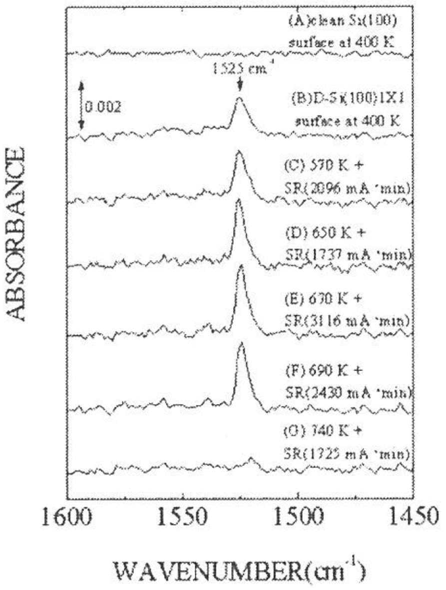

Figure 2. The change of the IRRAS spectrum of the SiD stretching vibration band annealing plus SR irradiation.

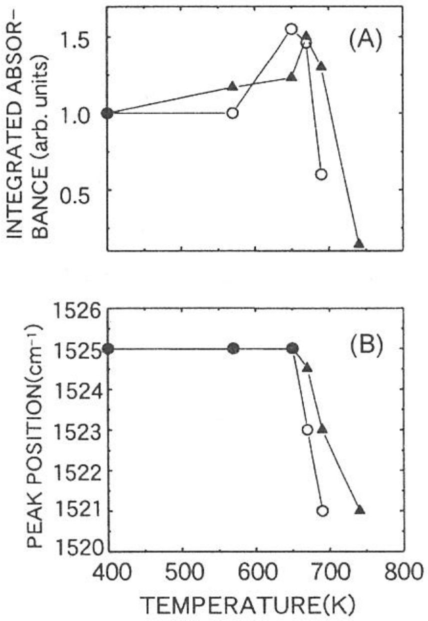

Figure 3. The change of the IA (A) and peak position (B) of SiD stretching vibration band upon annealing (○) and upon annealing plus SR irradiation (▲).

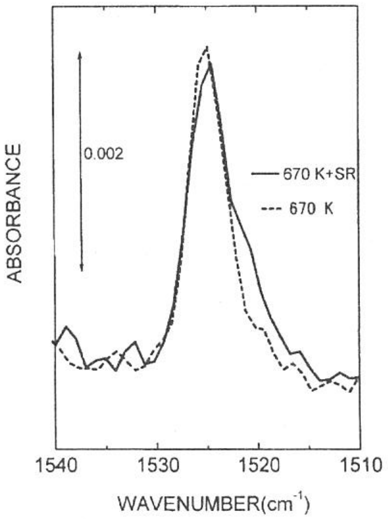

Figure 4. The band shapes of the SiD stretching vibration are compared for 670 K annealing only and the annealing + SR irradiation. Here, peak positions coincide between the two data sets.

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(BL-4B)

Fabrication of $CoSi_2$ buried metal layer substrates of IRRAS for *in situ* monitoring of synchrotron stimulated surface reactions

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The $Si/CoSi_2/Si$ structure which consisted of a semiconductor–metal–semiconductor is very useful for such high-speed devices as the metal base transistor and the permeable base transistor. Furthermore, this buried metal layer (BML) structure can be applied to the substrate for the high sensitive infrared reflection absorption spectroscopy (IRRAS) on Si surfaces. BML-IRRAS is a well-established technique for monitoring submonolayer amount adsorbates on Si surface and excellent in the point of no limitation with applicable wavelength by the substrate material. It is especially suitable for in situ monitoring of the surface reactions induced by synchrotron radiation (SR) irradiation.[1)] In comparison with conventional IR techniques using bulk Si, however, it is more important to control the surface and interface structure of the Si epitaxial layer on the BML. Typical techniques of $CoSi_2$ layer formations are ion beam synthesis (IBS), solid phase epitaxy (SPE) and codeposition of Si and metal using molecular beam epitaxy (MBE). The way of silicides growth by IBS and SPE are compared schematically in Figure 1. The IBS technique employs high–dose ion implantation into heated substrates and subsequent annealing to produce buried epitaxial $CoSi_2$ layers under a single–crystal Si overlayer (about 50～100 nm). In SPE, on the other hand, cobalt is deposited on the Si wafer by sputtering and a subsequent anneal forms the silicide. In this work, we used a Si_2H_6 gas source MBE (GSMBE) to grow epitaxial Si(100) layer on samples synthesized by IBS and SPE methods. Surfaces and interfaces of BML-Si(100) were evaluated by reflection high energy electron diffraction (RHEED) and scanning electron microscopy (SEM).

The surface cleaning of the substrates was achieved by the conventional wet method, followed by annealing to remove the surface oxide. Figure 2 shows RHEED patterns of IBS and SPE samples after surface cleaning, removal of the surface oxide and after epitaxial growth. The RHEED patterns changed from spotty to clear 2x1 by the epitaxial growth, as shown in photographs (Fig. 2(a) → (b) / Fig. 2(c) → (d)). Change from 2(a) to 2(b) indicates reconstructions of surface by homoepitaxial Si(100) growth. The 2x1 streak pattern of Fig. 2(d) indicates that heteroepitaxial Si(100) was successfully grown on a $CoSi_2$ layer. As compared to 2(b), however, the RHEED pattern 2(d) had a slightly weak 2x1 pattern, together with ring patterns. It is considered that this ring patterns of weak intensity indicates the growth of polycrystalline Si. Figure 3 shows the cross sectional SEM photographs obtained before and after Si(100) epitaxial growth. The buried $CoSi_2$ layer formed IBS method was continuous and had a nearly uniform thickness (Fig. 3(a)). And also, interfaces and surfaces of $Si/CoSi_2/Si$ structure were maintained smooth and continuous after epitaxial growth, as shown in Fig. 3(b). On the other hand, in the case of SPE, structures of Si epitaxial layer and interfaces of $Si/CoSi_2/Si$ were rough as shown in Fig. 3(d).

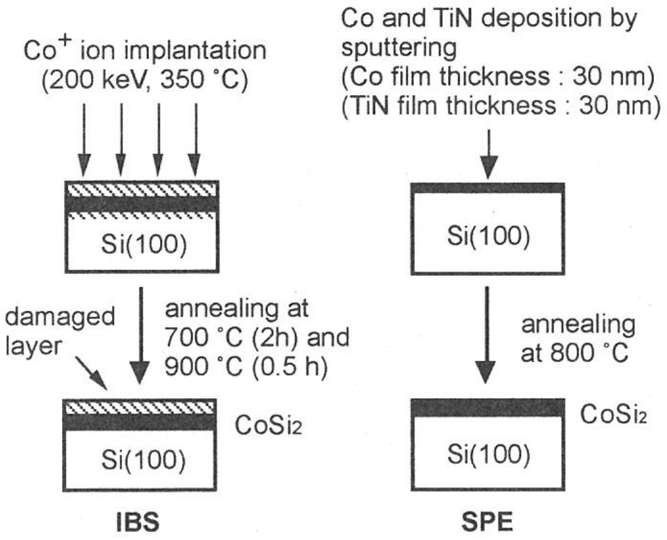
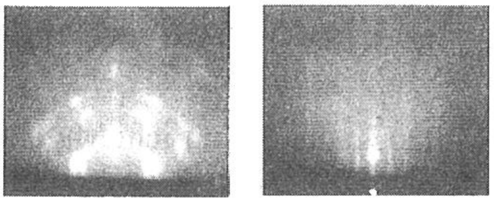
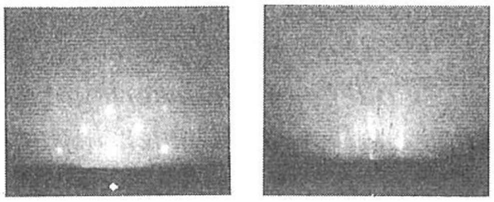


Fig. 1. The fabrication processes of CoSi$_2$ layer. Comparison of IBS and SPE.



(a) annealing (950 °C) (b) GS-MBE (750 °C)



(c) annealing (850 °C) (d) GS-MBE (750 °C)

Fig. 2. RHEED patterns of IBS (a and b) and SPE (c and d) sumples : after removal of the surface oxide (a and c), after Si epitaxial growth (b and d).

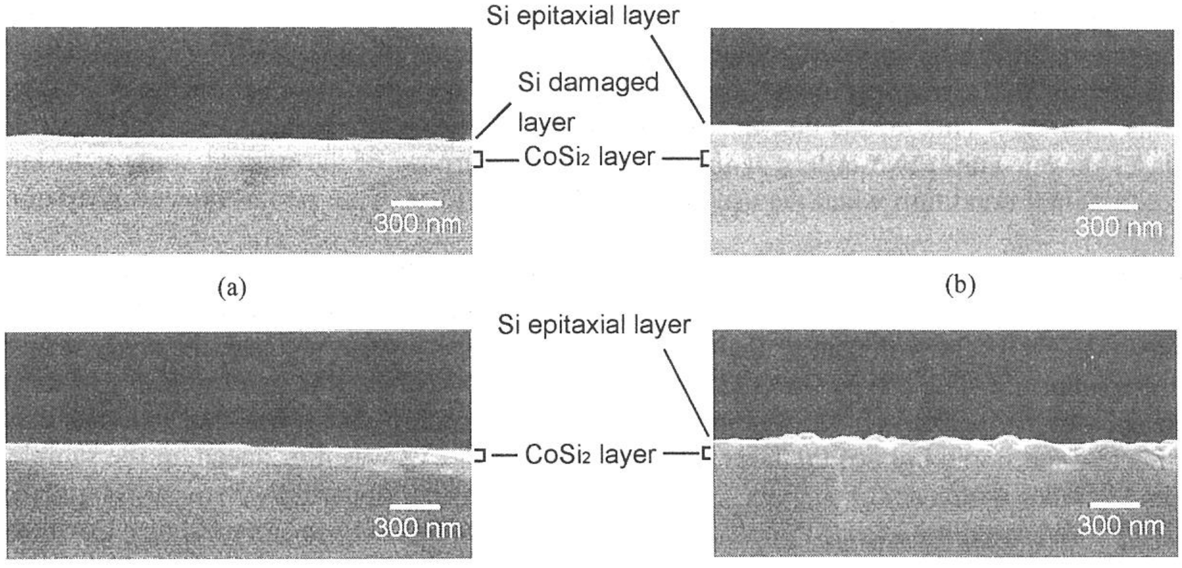


Fig. 3. Cross sectional SEM photographs of IBS (a and b) and SPE (c and d) samples : before (a and c), after (b and d) Si epitaxial growth.

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