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Surface Hydrogen and Growth Mechanisms of Synchrotron Radiation-assisted Silicon Gas Source Molecular Beam Epitaxy using Disilane

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Surface hydrogen and growth mechanisms are investigated for synchrotron radiation (SR)-assisted gas source molecular beam epitaxy (SR-GSMBE) using Si_2H_6 on the Si(100) surface in the low-temperature region. The surface silicon hydrides (deuterides) are monitored *in situ* during the epitaxial growth by means of infrared reflection absorption spectroscopy with a Si(100) substrate and a $CoSi_2$ buried metal layer. It is concluded that the chemisorption of gas-phase reactive species such as SiH_n and H generated by SR irradiation and the subsequent hydrogen desorption are the key mechanisms of SR-GSMBE at low substrate temperatures. © 1998 John Wiley & Sons, Ltd.

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1 INTRODUCTION

Synchrotron radiation (SR)-assisted semiconductor processing, such as etching and chemical vapor deposition (CVD) including epitaxial growth, has been widely investigated from the viewpoint of application to a fabrication technology of large-scale integrated circuits (LSIs) and future devices. SR-assisted silicon gas source molecular beam epitaxy (SR-GSMBE) has the following characteristics.[1,2] At high substrate temperatures, where the growth rate is limited by the thermal desorption rate of the surface hydrogen, it depends strongly on the substrate temperature, i.e. it decreases rapidly with a decrease of substrate temperature. At low substrate temperatures, where hydrogen desorption proceeds purely by photo-excitation, the growth rate is almost independent of the substrate temperature. The turning point between these two temperature regions exists at about 500 °C when Si_2H_6 gas at 1.0×10^{-3} Torr is used. In the low-temperature region, the growth rate is significantly enhanced by photo-excitation, but the crystallinity is rapidly degraded with a decrease of the substrate temperature. It should be pointed out that hydrogen incorporation into the deposited film causes degradation of film crystallinity in the low-temperature range.[3] Concerning the growth mechanisms at this low temperature region, both surface and gas-phase excitation mechanisms are reported to contribute almost equally to the film deposition, and SR irradiation on the surface has the effect of improving the crystallinity.[2] These results were obtained only from the deposited film profile measurements; details of the surface chemical reactions are completely unknown.

In the present work to elucidate the deposition mechanisms based on the chemical reaction of silicon hydrides during SR-GSMBE at low substrate temperatures, the changes in the surface silicon hydrides (deuterides) during SR-GSMBE with Si_2H_6 gas was monitored *in situ* by means of infrared reflection absorption spectroscopy using a buried metal layer substrate (BML-IRRAS).[4] To observe clearly changes in the surface during the deposition without interference from the background hydrogen, the Si(100) surface of the BML

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substrate was first terminated by saturation adsorption of deuterium atoms instead of hydrogen atoms.

2 EXPERIMENTAL

Experiments were conducted by using the BL-4B beamline of the 0.75 GeV SR storage ring (UVSOR) at the Institute for Molecular Science. The calculated photon flux was 2.3×10^{16} photons s^{-1} (0.7 W) for the 100 mA ring current on the $14 \times 14\,mm^2$ sample surface and the spectrum was distributed from about 1000 eV to less than 10 eV with a peak at about 100 eV. Details of our apparatus are described elsewhere.[4] An ultrahigh-vacuum (UHV) reaction chamber evacuated by a $500\,l\,s^{-1}$ turbo-molecular pump with a base pressure of 2.0×10^{-10} Torr was equipped with a reflection high-energy electron diffraction (RHEED) and an IRRAS optical system. The sample was set in the reaction chamber at an 45° angle of incidence to the SR beam and was heated by a pyrolytic graphite/pyrolytic boron nitride heater (Advanced Ceramics International Corp.). The temperature of the sample was monitored by a tungsten–rhenium thermocouple which was attached to the rear of the substrate with thickness of 500 µm. The temperature of the substrate surface was found to be a few tens of degrees lower than the values measured by the thermocouple when an optical pyrometer was used for the calibration. The Si_2H_6 gas (99.999%) and the D_2 gas (99.99%) were fed into the reaction chamber through a variable-leak valve.

The optical system for IRRAS consisted of a Fourier-transformed infrared spectrometer (JEOL model JIR7000), reflection and focusing mirrors, and a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector. The spectrum was taken with a $4\,cm^{-1}$ resolution and an accumulation of 1000 scans. A p-polarized IR beam selected by a wire-grid polarizer was introduced into the UHV reaction chamber through the ZnSe viewing port at an incident angle of 85°. The optical path was purged by dry N_2 gas.

IRRAS is used conventionally to detect adsorbates on metal surfaces.[5] However, it is difficult to apply IRRAS to the detection of adsorbates on the semiconductor or the insulator substrates which are transparent to IR. To overcome this problem in applying IRRAS to semiconductor substrates, BML-IRRAS has been examined by several researchers.[4–6] The Si(100) BML substrate with a $CoSi_2$ buried metal layer formed by ion implantation was purchased from Toray Research Center Inc. The BML substrate was cleaned by the standard wet method[7] and subsequent thermal desorption of the thin layer of surface silicon oxide at about 1100 °C in the UHV reaction chamber. After these wet and thermal cleaning processes for the as-purchased BML substrate, an silicon epitaxial layer about 10 nm thick was grown on the substrate by conventional gas source molecular beam epitaxy using Si_2H_6 (1.0×10^{-3} Torr) at 700 °C. By this epitaxial growth the RHEED pattern, which was initially spotty due to an ion implantation damage, was changed to a sharp 2 × l. After this silicon epitaxial growth, the substrate surface was exposed to the atomic deuterium generated by a hot tungsten filament up to 10^4 L, which gives saturation coverage. Here, the exposure ($1\,L = 1.0 \times 10^{-6}\,Torr \times 1\,s$) is expressed as the deuterium molecule pressure measured by an uncorrected ionization gauge reading.

3 RESULTS AND DISCUSSION

First, the adsorption of deuterium atoms on the Si(100) surface and the SR irradiation effects on the deuterium-adsorbed surface were investigated by IRRAS and RHEED. Figure 1 shows the change in the IRRAS spectrum as a function of the deuterium exposure. At low exposure (12 L, 100 L), a broad IRRAS spectrum with a peak at $1525\,cm^{-1}$ was

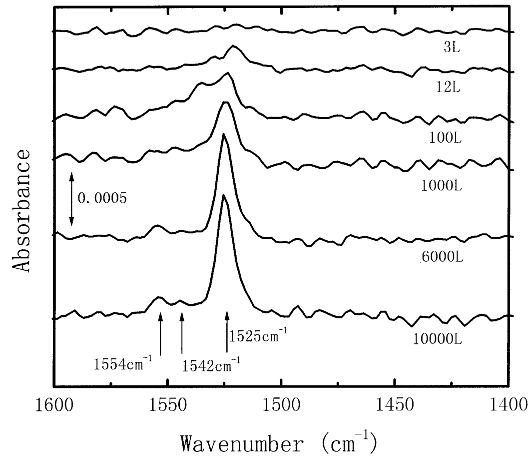

Figure 1 IRRAS spectra for the Si(100) surface exposed to atomic deuterium are given as a function of the exposure at 140 °C. Atomic deuterium was generated by the decomposition of deuterium molecules using a hot tungsten filament.

observed. At these exposures the RHEED pattern was 2 × 1. With an increase in the deuterium exposure, additional peaks at around 1542 and 1554 cm^{-1} appeared and the RHEED pattern changed to 1 × 1. According to the previous reports concerning the adsorption of hydrogen atoms on the Si(100) surface,[8] it is considered that this 1 × 1 phase consists of a mixture of SiH, SiH_2 and SiH_3 species. Chabal *et al.* reported that the SiD symmetric stretching vibration is observed at 1527.8 cm^{-1} [9] or 1530.2 cm^{-1},[10] and the asymmetric one at 1519 cm^{-1} [9] or 1521.6 cm^{-1} [10] on the Si(100) surface. The symmetric and the asymmetric stretching vibrations of SiD_2 are observed at 1517.5 cm^{-1} and 1539 cm^{-1}, respectively.[10]

In the present case, only the symmetric stretching vibration should be observed for both SiD and SiD_2 species according to the surface selection rule[5] of IRRAS. Therefore, the observed 1525 cm^{-1} peak in Fig. 1 is assigned to the SiD symmetric stretching vibration. An SiD_2 symmetric stretching vibration is not clearly observed in the present case. However, this does not mean that SiD_2 species does not exist on the surface; rather, it may not be observed because the dynamic dipole moment of SiD_2 is small. In fact, the SiD_2 symmetric stretching vibration is only weakly observed (at about 1/7 of the SiD symmetric stretching peak intensity) even in the 3 × 1 phase where about 50% of deuterium atoms are in the form of SiD_2.[10] The intensities of the 1554 and 1542 cm^{-1} peaks decreased and disappeared when the substrate temperature was increased to 300 °C for 15 min. The data of temperature-programmed desorption (TPD) experiments show that desorption peaks relating to SiH_2 and SiH_3 are observed at 190–200 and 370 °C, respectively.[8] Therefore, the peaks observed at 1554 and 1542 cm^{-1} should most probably be assigned to the SiD_3 stretching vibrations.

Figure 2 shows the SR irradiation effects on the Si(100) surface saturation-adsorbed by deuterium atoms. It is known that SiD_3 is decomposed to SiD, but SiD is not decomposed by the SR irradiation, agreeing with our previous results with SiH_n.[4]

Furthermore, it is notable that no change in the spectrum was observed after exposure to Si_2H_6 gas, not only for the deuterium-saturated surface corresponding to spectrum A, in Fig. 2 but also for the SiD surface after SR irradiation corresponding to spectrum B. This means that both the deuterium-saturated and the SiD surface after SR irradiation are non-reactive to Si_2H_6 gas, while IRRAS peaks of SiH_n appear due to dissociative adsorption in the case of Si_2H_6 exposure of the

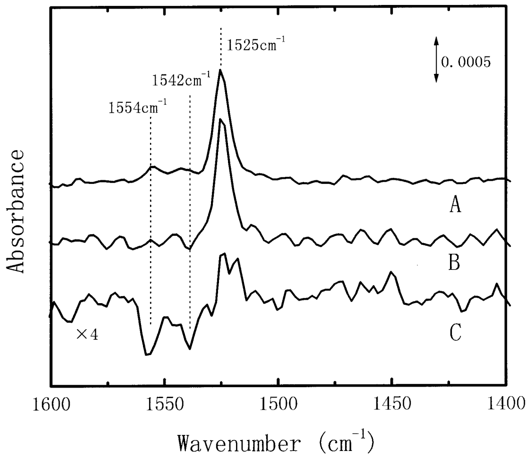

Figure 2 SR irradiation effects on SiD_n adsorbed on an Si(100) surface at 140 °C: BML-IRRAS spectra for (A) a deuterium-saturated Si(100) surface; (B) after SR irradiation (2.0 × 10^4 mA min) of the surface (A). (C) Difference between spectra A and B.

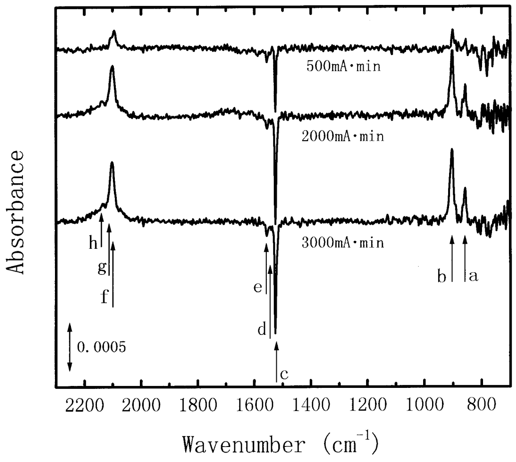

Figure 3 Change in the IRRAS spectrum during SR-GSMBE with increasing SR dose (mA min) at 140 °C. The spectrum of the deuterium-saturated Si(100) surface (Fig. 2, spectrum A), which was as the initial surface, has been subtracted from each spectrum, i.e. the upward and downward peaks indicate increases and decreases in the species, respectively. The assignments of peaks are: a, SiH_3 symmetric deformation (860 cm^{-1}); b, SiH_2 bending scissors (908 cm^{-1}); c, SiD symmetric stretching (1525 cm^{-1}); d and e, SiD_3 stretching (1542 and 1554 cm^{-1}); f, SiH symmetric stretching (2100 cm^{-1}); g, SiH_2 symmetric stretching (2113 cm^{-1}); h, SiH_3 stretching (2140 cm^{-1}).

clean Si(100) surface. These facts mean that repetition of the dissociative adsorption of Si_2H_6 gas followed by SR-stimulated hydrogen desorption does not operate as a deposition mechanism during SR-GSMBE at low temperatures.

The observed change in the spectra for the deuterium-saturated Si(100) surface as SR-GSMBE progresses is shown in Fig. 3 as a function of the SR dose. The SiH_n peaks are assigned in our previous work.[4] Figure 3 shows that surface SiD_n is gradually replaced by SiH_n and finally completed as film deposition progresses. As already mentioned, no spectrum change was observed for the deuterium-saturated Si(100) surface by only exposing it to Si_2H_6 gases without the SR irradiation. These results indicate that chemisorption of the gas-phase reactive species such as SiH_n and H, including their ions, on the SiH_n (SiD_n)-adsorbed surface is a principal mechanism of deposition in the low-temperature region. Hydrogen desorption from the surface is a necessary process for continuous deposition to occur. In the high-temperature region (> 400 °C), surface hydrogen can be desorbed thermally;[1] In the low-temperature region (< 400 °C), however, the thermal desorption rate becomes extremely low;[1]. Moreover, as already mentioned, SR irradiation cannot decompose SiH (SiD). Therefore, from the above arguments, it is concluded that the necessary energy for the surface desorption of hydrogen in low-temperature SR-GSMBE is supplied by the chemisorption of the gas-phase reactive species generated by the SR irradiation. For example, the activation energy of H_2 desorption from the monohydride phase is reported to be 57–58 kcal mol^{-1} (238–243 kJ mol^{-1} and that from the dihydride phase is 46.3–47 kcal mol^{-1}. (194–197 kJ mol^{-1}).[11] These requirements can be supplied by the energy, 75 kcal mol^{-1} (314 kJ mol^{-1} of the Si– Si σ-bond which is formed by the chemisorption of SiH_n. These results indicate that the gas-phase excitation mechanism plays an important role in low-temperature SR-GSMBE. On the other hand, however, it is also known that not only the gas-phase excitation mechanism but also the surface excitation mechanism, which can be confirmed by the deposition rate enhancement observed in the SR-irradiated area, operates in SR-GSMBE.[2] From the present experimental results and those reported elsewhere[2] it is also concluded that the area where higher hydrides (SiH_2, SiH_3) are decomposed by SR is more reactive for the chemisorption of gas-phase reactive species than the non-irradiated area. Furthermore, since the existence of higher hydrides during the deposition possibly enhance the inclusion of hydrogen atoms into crystals, causing the degradation of crystallinity, the decomposition of SiH_n on the surface by SR irradiation during deposition may be operated effectively to improve crystallinity at low temperatures, as reported in Ref. 2.

4 CONCLUSIONS

We conclude that the chemisorption of the gas-phase reactive species generated by SR irradiation and the successive desorption of hydrogen on the surface covered by SiH_n is a key mechanism of deposition in the low-temperature region of SR-GSMBE. The SR irradiation decomposes adsorbed SiH_2 and SiH_3 on the Si(100) surface, and this makes the surface more reactive for the chemisorption of the gas-phase reactive species, and the decomposition of these higher hydrides also possibly causes an improvement in the crystallinity.

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