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Citation: Applied Physics Letters **58**, 2776 (1991); doi: 10.1063/1.104783
View online: http://dx.doi.org/10.1063/1.104783
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/58/24?ver=pdfcov
Published by the AIP Publishing

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(Received 21 January 1991; accepted for publication 21 March 1991)

Silicon photoepitaxy excited by synchrotron radiation (SR) has been observed for the first time. The epitaxial growth is observed even at lower than a 400 °C substrate temperature. The surface of the as-grown film exhibits a 2×1 reconstruction reflection high-energy electron diffraction pattern, indicating two-dimensional growth. At lower than 600 °C, the SR-irradiation growth rate is larger than that of thermal growth. This result suggests that SR irradiation enhances the dynamic surface reactions, such as desorption of hydrogen and surface migration of adsorbed species.

Silicon photoepitaxy[1–4] has been widely investigated in attempts to realize key technologies for future semiconductor fabrication, such as low-temperature selective growth and highly efficient selective doping. Light sources generally used in these attempts are ultraviolet (UV) discharge lamps[1–3] or excimer laser.[4] The photon energies of these light sources lie below the ionization potential (IP) of most epitaxial gases, e.g., monosilane (IP 12.36 eV) and disilane (IP 10.53 eV). This means that possible photoinduced reactions are restricted at most to the energy region of molecular binding electronic or vibrational and rotational excitations.

Synchrotron radiation (SR) has recently been utilized as a continuum light source in the vacuum ultraviolet (VUV) region for the purpose of photoexcited chemical vapor deposition.[5,6] Photons contained in the SR beam have enough energy for excitation of epitaxial gas molecules to core electronic excitation levels. The strong interaction of photons with gas molecules or adsorbed species leads to direct photolysis into SiH_n radicals, atoms, and their ions. In addition to photon energy value, the energy continuity of the SR source has high potentiality for the aritificial control of dynamic surface reactions, such as surface migration and photostimulated desorption, through the use of insertion devices in storage rings or monochromators in beam lines. Furthermore, the excellent directivity of the SR beam is expected to realize area-selective excitation. From this standpoint, investigation of SR irradiation effects during silicon epitaxy has a great deal of significance.

As for the actual apparatus, SR beam lines essentially consist of ultrahigh-vacuum systems. Surface analyzing systems, as well as x-ray photoelectron and Auger electron spectroscopy, but also molecular beam epitaxy (MBE) systems, match well with SR beam lines and facilities. For this reason, we have chosen silicon MBE using silane or disilane gas as a silicon source (gas source MBE) for the purpose of investigating SR irradiation effects on silicon epitaxy. Silicon gas source MBE has many practical advantages over the conventional solid source system. These include low-surface defect density[7,8] and no requirement for vacuum break when the source replenishment.

Figure 1 shows a schematic view of our experimental system. The SR beam line was constructed in the Photon Factory at the National Laboratory of High Energy Physics (KEK-PF).[9] The gas source MBE system was positioned downstream of the beam line. The epitaxial chamber can be evacuated by a turbomolecular pump to the background pressure of about 10^{-10} Torr. The reaction gas was fed into the chamber by the gas supply system through a variable leak valve. The beam line and the reaction chamber were directly connected with a stainless-steel duct of 5×10 mm^2 rectangle cross section. The differential vacuum pumping system prevents reaction gas from flowing in the storage ring and the chamber containing optical components. The photon beam from the 2.5 GeV storage ring was bent 8° and focused at the sample surface by using a Pt-coated toroidal mirror. The incident SR beam, ranging from 10 to 1000 Å in wavelength, radiated the sample surface perpendicularly; the effective beam diameter on the sample surface being about 4×6 mm^2. A sample holder with a carbon heater was mounted in the reaction chamber with a manipulator. Surface temperature of samples was monitored using a thermocouple calibrated with a radiation thermometer. For the purpose of observing the cleanliness of substrate surface and the crystallinity of grown films, the reflective high-energy electron diffraction (RHEED) system was utilized.

Substrates were 2 in. Si(100) and Ge(100) just oriented wafers. The substrates were cleaned and oxidized for surface protection with conventional chemical treatment. Heating for 10 min at 950 °C (for Si) or 500 °C (for Ge)

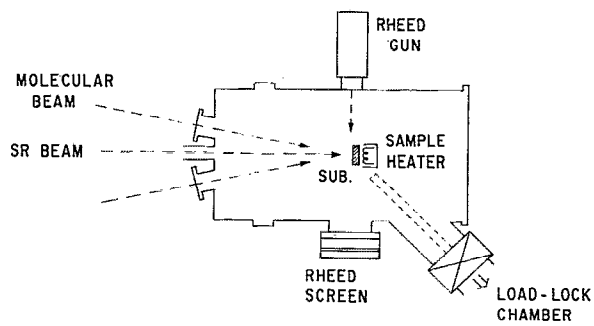

FIG. 1. SR-excited gas source MBE system.

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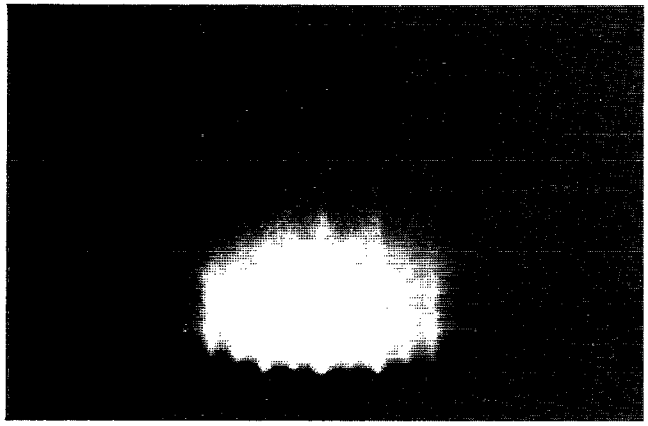

FIG. 2. RHEED pattern of as-grown film deposited on Si(100) surface at 520 °C ([110] incidence). Si_2H_6 pressure was 1.5×10^{-4} Torr.

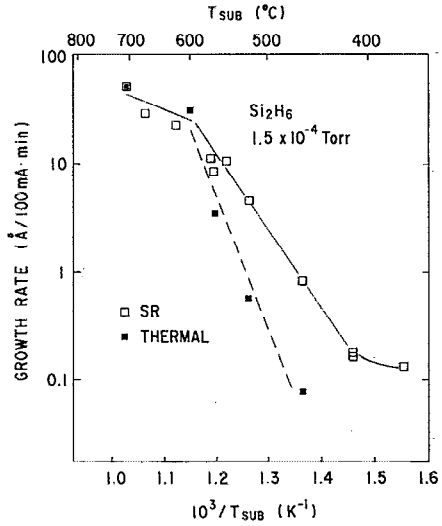

FIG. 3. Substrate temperature dependence of epitaxial growth. Si_2H_6 pressure was 1.5×10^{-4} Torr. Opened squares correspond to SR-irradiated growth and closed ones to thermal growth.

just before film growth evaporated surface oxide. The elimination of the surface oxide was ascertained by observing 2×1 RHEED patterns. The reaction gas was pure disilane and the pressure was 1.5×10^{-4} Torr during the SR irradiation.

The RHEED patterns of the film grown on the SR-irradiated area exhibited a 2×1 reconstruction surface for substrate temperature ranging from 380 to 700 °C. An example of the RHEED pattern is shown in Fig. 2. This means that two-dimensional growth was realized on the SR-irradiated area. The crystallinity of the films were evaluated also by using Raman scattering measurements. The LO phonon peak position (520.5 cm^{-1}) and peak width were the same as crystalline Si over the entire temperature range. These results indicate the perfection of the grown film crystallinity. Secondary-ion mass spectroscopy (SIMS) measurements revealed no incorporation of carbon and oxygen in the grown films. The detection limits of the SIMS measurement for carbon and oxygen were 5×10^{17} and 1×10^{19} cm^{-3}, respectively.

The growth rates of the epitaxial films are shown in Fig. 3 as a function of the substrate temperature, corresponding to the disilane pressure 1.5×10^{-4} Torr. In this figure, thermal growth rates (i.e., growth without SR irradiation) are also shown for comparison. The growth rates were calculated based on the profile of film thickness obtained by optical reflectance and SIMS measurements. Figure 4 shows the thickness profile of the grown film across the substrate for lower than 550 °C. In this figure, profiles of SR-excited and thermal growths at 1.5×10^{-4} Torr disilane pressure are presented. As shown in the figure, the profile of the SR-excited growth consists of two components: (1) thermal growth which reflects the uniformity of the substrate heater, and (2) SR-enhanced growth due to pure SR excitation. The ratio of enhanced thickness (i.e., the thickness difference between the SR excited growth and thermal growth) to total thickness increased with decreasing substrate temperature. At 500 °C, the ratio exceeds 90%. The growth rate in Fig. 3 was determined as the peak thickness per dose [storage ring current (mA) × growth time (min)]. In Fig. 3, the substrate temperature range can be separated into two regions at about 600 °C. In the higher temperature region, the difference in the growth rate between SR-excited growth and thermal growth was negligible. Activation energy of the growth in this region is 9.1 kcal/mol. On the other hand, in the lower temperature region SR-excited growth rate was enhanced. Activation energies in the low-temperature region for SR-excited growth rate and thermal growth rate are 32 and 54 kcal/mol, respectively.

Temperature dependence for the two temperature regions in the case of silane gas source MBE or ultrahigh-vacuum chemical vapor deposition (UHVCVD) has already been demonstrated.[8,10] In the higher temperature region, surface adsorption of the reaction gas is a rate-limiting process, and in the lower one, surface reaction, particularly hydrogen desorption, is rate-limiting. The activation energies of the thermal growth rate in our exper-

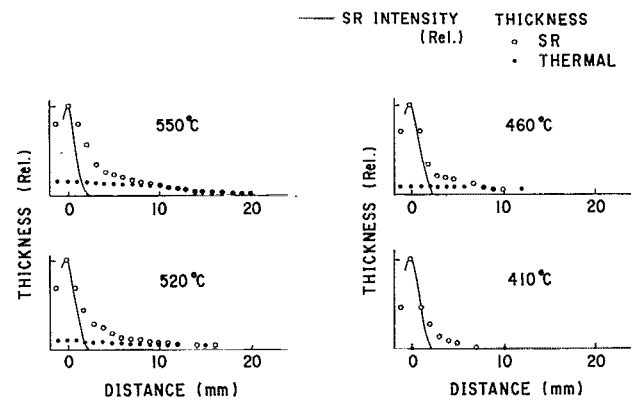

FIG. 4. Thickness profiles of the epitaxial film in the lower temperature region (surface reaction is rate-limiting). Opened circles correspond to SR-irradiated growth and closed ones to thermal growth. The thickness is normalized with the maximum thickness value of SR-irradiated growth at each temperature. Distribution of SR intensity is also presented as a solid curve.

iment are close to those in these experiments using silane.

The growth rate enhancement due to SR irradiation in the surface reaction-limiting region can be assumed to be caused by the reasons below: (1) direct photoexcitation, such as photolysis of gas phase or adsorbed molecules and direct dissociation of surface terminating Si—H bonds followed by H desorption, and (2) rate enhancement of surface reaction, such as surface mmigration of adsorbed SiH_n and reassociation of surface-terminated Si—H bonds followed by H_2 desorption. (1) is accompanied with electronic excitation and independent of temperature. On the other hand, (2) requires activation energy. It is supposed that the origin of the activation energy reduction due to SR irradiation is energy barrier lowering of (2), which is caused by (1).

Suemitsu *et al.* have reported that 8.4 eV photon irradiation during silane gas source MBE can enhance the growth rate in the higher temperature (adsorption-limited) region.[11] They considered that this enhancement was due to the adsorption of radicals on the surface. In our SR-excitation case, on the other hand, the growth rate in lower temperature region was enhanced. This result suggests that SR beam photons have enough energy to desorb surface hydrogen and to migrate adsorbed species. It is supposed that the flattening of the growth rate curve at about 400 °C (Fig. 3) is due to other surface reaction mechanisms peculiar to the low-temperature region.

The profile of the SR-enhanced growth can be separated into two parts. One is that which is proportional to the SR intensity and the other is that which spreads out of the SR-irradiated region. It is naturally considered that the former is due to SR-induced surface reaction. It is supposed that the deposited area, which spreads out of the SR-irradiated region, is due to gas phase reaction, e.g., hydrogen extraction due to gas phase SiH_3 radicals, adsorption enhancement of photoexcited molecules, and so on.

In conclusion, it is confirmed that SR irradiation during Si gas source MBE growth enhances growth rate, especially in the low-temperature region where the surface reaction is rate-limiting. Excellent epitaxial films were obtained with this method even at 380 °C. This result indicates that SR-excited epitaxy can be applied to low-temperature film formation with high controllability which, in turn, yields excellent crystal quality.

The authors would like to thank Tetsushi Sakai for his continuous encouragement and support through this work. The authors also thank the staff of the Photon Factory for thier collaboration.

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