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Radical Beam Deposition — A New Approach of Thin-Film Growth

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Silicon thin-films on crystalline silicon substrates have been deposited at temperatures between 300 and 600 °C by using radical beam deposition technique, in which the radical beam is created in a separate chamber by the glow discharge decomposition of pure silane gas. The radicals effused from the discharge chamber into the UHV deposition chamber have been verified by mass spectrometry. The crystallinity of Si thin-films is evaluated through the Raman scattering and the reflection high energy electron diffraction measurements. The result has revealed that the Si epitaxial films can be grown at a temperature of 600 °C.

§1. Introduction

Low temperature growth of device quality thin-films has become very important, in particular, for the purpose of fabrication of submicron electron devices such as multiple quantum well (MQW) structures and very large scale integrated (VLSI) circuits. Wide varieties of low temperature deposition techniques have been developed so far by using thermally-vaporized ground state atoms or molecules (molecular beam deposition[1~5]), ionized particles or clusters (ion beam deposition[6], ionized cluster beam deposition[7]), or the mixture of ions and neutrals including the excited species (plasma enhanced chemical vapor deposition[8,9], plasma assisted deposition[10]). Recently we have proposed a new category of deposition technique named "radical beam deposition (RBD)", in which chemically reactive and electrically neutral radicals produced by the glow discharge decomposition of a material gas have been used as film precursors[11].

The RBD technique appears to have prospective feasibility to largely decrease the growth temperature of crystalline thin-films, because radical species transported onto the substrate are expected to possess higher surface mobilities as well as higher chemical energies than those created by thermal activation processes. This method enables us to grow both semiconductors and insulators by means of exchanging source gases.

In this work, novelty of RBD method has been demonstrated by growing silicon thin-films on crystalline Si substrate from a SiH_4 gas source. The epitaxial growth of silicon has also been verified at 600 °C.

§2. Experimental

Figure 1 shows a schematic diagram of radical beam deposition (RBD) apparatus. The RBD system is constructed from the following three major parts: (I) The discharge chamber in which the radicals are created by the glow discharge decomposition of a material gas and the glow discharge is generated between the anode electrode and grounded wall having the first orifice. (II) The differentially-pumped transport tube, in which the radicals effused from the first orifice are transported to the deposition chamber through the second orifice. (III) The ultra-high vacuum deposition chamber where the heated substrate are placed together with quadrupole mass spectrometer. The transport tube and the deposition chamber are pumped out using oil diffusion pumps fitted with liq. N_2 traps, since a continuous steam of highly reactive gas has to be pumped during the deposition. The discharge chamber is pumped by a mechanical booster pump.

As a first step the intensity and uniformity of the radical beam reaching the substrate surface were estimated for the present apparatus geometry

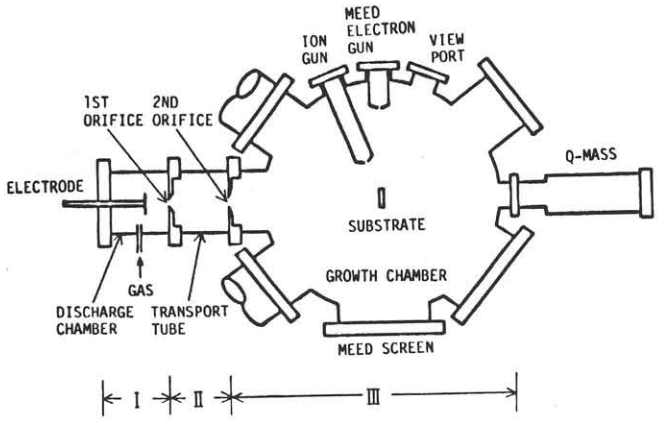

Fig. 1. Schematic diagram of RBD system.

based on a simple model[11], where the radicals passing through an orifice were approximated as molecular fluid[12]. The growth conditions appropriate for silicon deposition were determined by the result of model calculations and by taking into account the pumping capability of the present apparatus. The radicals were produced by the glow discharge decomposition of pure silane gas in the discharge chamber maintained at ∿ 0.3 Torr. The transport tube was pumped down to a pressure of 10^{-8} Torr and held at ∿ 10^{-4} Torr when the radical beam was effused. The radical beam passing through the two orifices was incident to the heated substrate being placed in the deposition chamber, whose base pressure was lower than 3×10^{-9} Torr. N-type Si(100) (3 ∿ 6 Ωcm) or Si(111) (50 ∿ 60 Ωcm) wafers were used as substrates. The Si substrate was chemically cleaned in conventional etching solutions and subsequently boiled in an H_2O:HCl: H_2O_2 = 6:1:1 solution to form a protective oxide on the substrate surface. Further surface cleaning was carried out by heating the silicon substrate up to ∿ 800 °C for 10 min at a pressure of ∿ 10^{-8} Torr, and the appearance of the clean surface was confirmed by MEED. In order to confirm the existence of radicals effused into the deposition chamber, mass spectra were taken by using the quadrupole mass spectrometer. Structural properties of resulting Si films were studied by employing the Raman scattering with 514.5 nm light from an Ar^+ ion laser, the reflection high energy (80 keV) electron diffraction (RHEED) and scanning electron microscopy (SEM).

§3. Results and Discussion

The beam flux density on the substrate surface in the present apparatus is calculated as a function of pressure of the transport tube as shown in Fig. 2, in which the pressure of the discharge chamber is kept at 0.3 Torr. The terms I_a+I_b are composed of directly impinging flux on the substrate surface along a collision-free path, I_a, and the subsidiary beam formed at the second orifice through collisions between the main beam and the background gas in the transport tube, I_b. The flux I_c is the subsidiary beam formed by effusion of background gas in the transport tube through the second orifice. In the figure, the terms I_a+I_b are more important than I_c for the film growth because the beam components I_a+I_b are more reactive than I_c. Therefore, the result of Fig. 2 indicates that the pressure in the transport tube P_1 should keep a value below which the mean free path length λ is sufficiently larger than the transport tube length (d_1-d_2). Figure 3 represents the calculated beam intensity distribution on the substrate surface for the same conditions as listed in Fig. 2, together with the measured thickness distribution of a silicon thin-film deposited at a substrate temperature of 400 °C. This indicates satisfactory agreement between the result of model calculation and the deposited film thickness

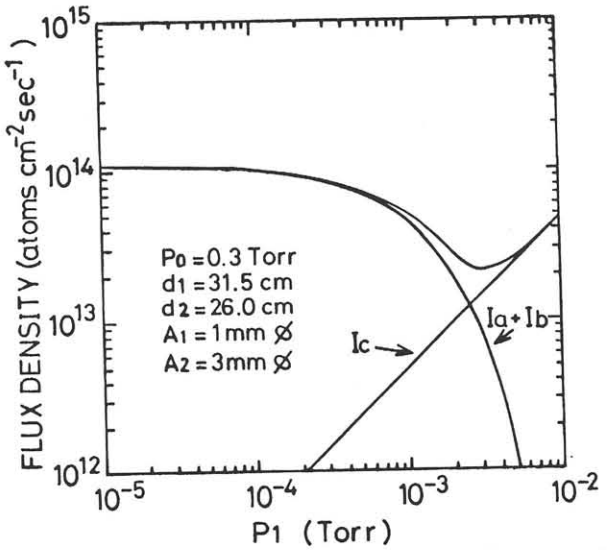

Fig. 2. Flux density as a function of the pressure in the transport tube P_1. d_1 and d_2 are the distance from the first orifice and from the second orifice to the substrate, respectively. A_1 and A_2 are the area of the first orifice and the second orifice, respectively. P_0 is the pressure in the discharge chamber.

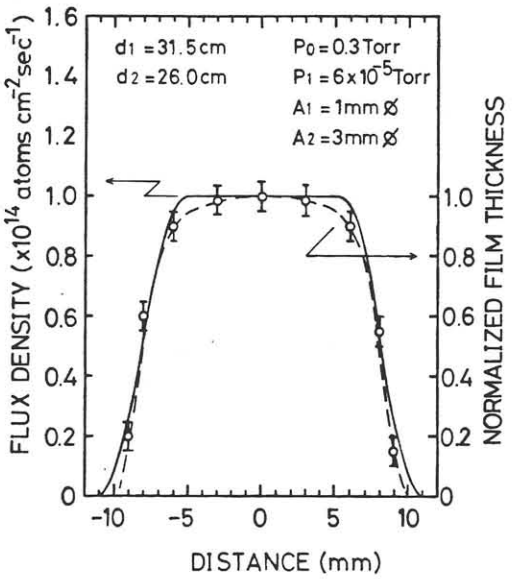

Fig. 3. Calculated beam intensity as a function of the distance from the center of the substrate (solid line) and the measured distribution of the film thickness normalized by maximum film thickness at the center is shown by dashed line.

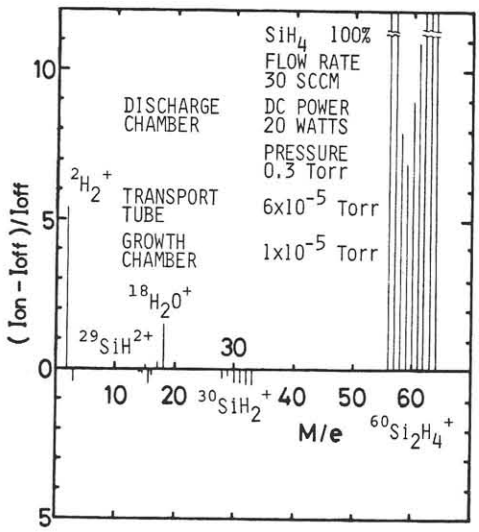

Fig. 4. The $(I_{on}-I_{off})/I_{off}$ ratio calculated from the mass spectra. I_{on} and I_{off} are the ion current with and without discharge, respectively.

distribution. The maximum flux density ($\sim 1\times10^{14}$ atoms $cm^{-2}sec^{-1}$) shown in Fig. 3 correspond to 0.1 monolayer growth per second for a sticking probability of 1.0. In the present deposition conditions, the measured deposition rate is about 0.1 μm/h, and hence the average sticking probability of the SiH_x (x=0∿3) radicals estimated to be more than 0.2 by comparing the silicon growth rate with the calculated beam intensity. This value is extremely large as compared to the sticking probability of SiH_4 on Si being equal to 10^{-4} [12]. As shown in Fig. 4, when the glow discharge of SiH_4 is turned on in the discharge chamber, the signal intensities of $Si_2H_x^+$ (x=0∿8) and H_2^+ measured in the deposition chamber are dramatically enhanced and those of SiH_x^+ (x= 0∿5) are slightly lowered. This implies that the SiH_x radicals created by the glow discharge reach the substrate surface, because the increase in the $Si_2H_x^+$ (x=0∿8) intensity could be ascribed to the radical-ion reactions in the ionization chamber of the mass spectrometer. The fragments of H_2O also increase during the discharge. This might arise from insufficient baking of the discharge chamber and the transport tube, and must be eliminated by changing the discharge chamber and the transport tube to a completely bakable system. Oxygen contamination of the deposition surface might interupt the epitaxial growth.

The surface morphologies of Si films strongly depend on both the pressure P_1 and the transport tube length (d_1-d_2). When the mean free path length of the radicals λ is shorter than (d_1-d_2), the deposited film is composed of stacked fine-particles, because the gas-phase collisional reactions among radicals occur near the first orifice and/or in the transport tube. While (d_1-d_2) is sufficiently shorter than λ, the mirror-like film is obtained as a result of the surface reactions of adsorbed radicals on the heated substrate. Raman spectra for the former type silicon film having an average grain size of ∿ 2000 Å in diameter exhibit a broad peak at 480 cm^{-1} which arises from the TO mode of silicon [11]. The interesting feature of this film is that the microcrystallization proceeds at an extremely low power density of Ar^+ ion laser irradiation. The threshold power density of the microcrystallization (< 6.3 W/cm^2) is at least one or two orders of magnitude smaller than that of the conventional laser annealing of amorphous silicon [13]. This could be explained in terms of the high surface energy being built in the stacked fine particles in the film.

In contrast to this, the latter film with a smooth surface exhibits a spectrum with a main peak at 520 cm^{-1} and with a very little trace of the 480 cm^{-1} peak for a specimen grown at 300 °C (Fig. 5). The yield at 480 cm^{-1} might originate in the highly disordered region existing near the

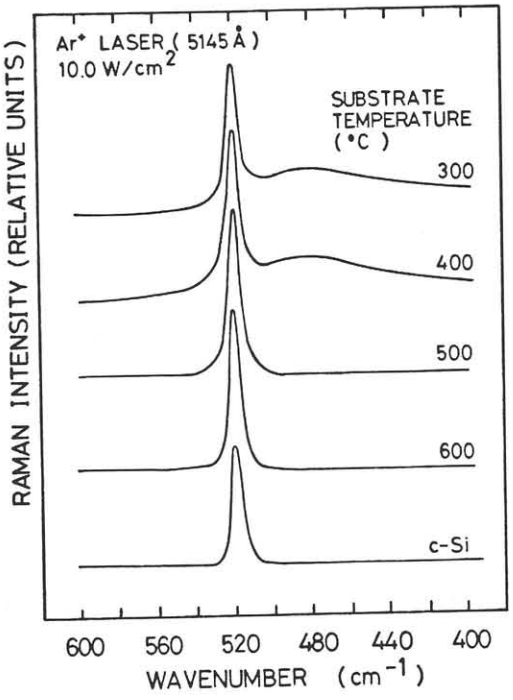

Fig. 5. Raman spectra for films grown at 300, 400, 500 and 600 °C with mirror-like morphologies and that for c-Si substrate as a reference.

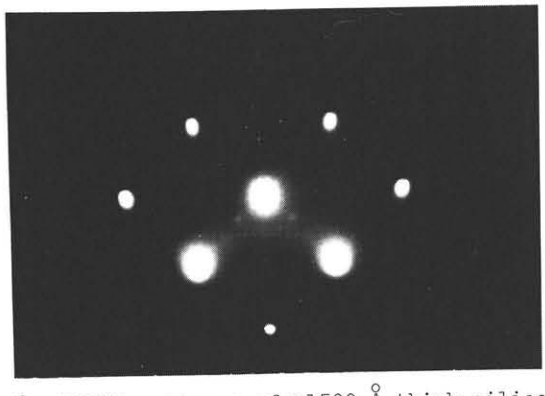

Fig. 6. RHEED patterns of ∿1500 Å thick silicon film deposited on Si(100) substrate at 600 °C. The direction of the incident electron beam is <100>.

interface between the deposition layer and substrate as a consequence of incomplete cleaning of the substrate prior to the deposition and some oxygen contamination involved in the radical beam. The whole spectrum is kept unchanged even with laser irradiation at a power density of 28 W/cm^2. Polarization effect of the Raman intensity at 520 cm^{-1} for the specimen grown on a Si(100) substrate even at temperatures of 300, 400 and 500 °C indicated that the film is preferentially oriented to the same direction as the substrate[11]. As shown in Fig. 5, the Raman spectra of the films grown at substrate temperatures above 500 °C is essentially identical to that of a crystalline Si substrate and the 480 cm^{-1} peak due to disordered regions in the films is not observed. Figure 6 shows the RHEED pattern of a film grown on a Si(100) substrate at a temperature of 600 °C. The photograph indicates that the silicon epitaxial growth occurs at 600 °C by the use of SiH_x radical beam. Further decrease of the epitaxial temperature would be possible when the oxygen contamination in the beam is eliminated.

§4. Conclusions

Silicon thin-films on crystalline Si substrate have been grown in the temperature range from 300 °C to 600 °C by using radical beam deposition technique. The films grown at temperatures below 500 °C are preferentially oriented to the same direction as the substrate, while at a temperature of 600 °C the epitaxial growth occurs on Si(100) surface.

Acknowledgments

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