

Selective Growth of Polycrystalline Silicon by Laser-Induced Cryogenic CVD

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Polycrystalline silicon has been selectively grown at -74°C in an $\text{Si}_2\text{H}_6+\text{He}$ gas mixture by irradiating an ArF excimer laser light through a stencil mask. It is shown that the photodissociation reactions of Si_2H_6 condensed on a cooled substrate results in the film formation. It is likely that a thin polymerized Si layer is first produced and subsequent photoexcitation of the metastable matrix leads to laser induced crystallization.

1. INTRODUCTION

Thin film formation by laser induced CVD generally proceeds through the photodissociation of reactive gas molecules. The activated species isotropically diffuses in the system, so that spatially selective deposition of thin films in the area irradiated with laser is not readily achieved. When gas molecules are condensed or adsorbed on a cooled substrate, the effective molecular concentration on the surface is dramatically increased, and the optical absorption coefficient of the adsorbates becomes significantly large compared to the gas phase condition because it exhibits a red shift with respect to the molecular spectrum¹⁾. Therefore, the adsorbed molecules are efficiently photodecomposed by a pulsed UV laser without any serious temperature rise in the irradiated region, and the pattern projection CVD becomes possible. Even at room temperature, selective laser CVD at 248 nm (KrF excimer laser) has been achieved by using triisobutylaluminum (TIBA) because TIBA has

no significant optical absorption in the gas phase while adsorbed TIBA on glass is photodecomposed²⁾. The authors have carried out the selective silicon deposition in Si_2H_6 at room temperature under ArF excimer laser (193 nm) irradiation although the growth rate was extremely low³⁾. Concerning chemical vapor deposition at temperatures below -20°C , SiO_2 films have been grown by using liquefaction reaction of hexamethyldisiloxane (HMDS) produced by gas phase reaction between tetramethylsilane and microwave excited oxygen⁴⁾.

In this study, the adsorbed layer of Si_2H_6 on a cooled substrate was photochemically decomposed by an ArF excimer laser light to promote spatially activated surface reactions and pattern projection CVD of polycrystalline Si was achieved.

2. EXPERIMENTAL

The detailed system of the experimental setup of Si laser CVD has been described elsewhere³⁾. An ArF excimer laser was used for the direct photolysis of Si_2H_6 . Silicon

or quartz substrates were cooled down to -74°C . The reaction pressure, the laser power and the repetition rate were 1 - 10 Torr, 11 - $42\text{ mJ}\cdot\text{cm}^{-2}$ /shot and 10 Hz, respectively. Disilane gas was diluted with He.

3. RESULTS AND DISCUSSION

A typical example of pattern projection CVD of silicon at a temperature of -69°C

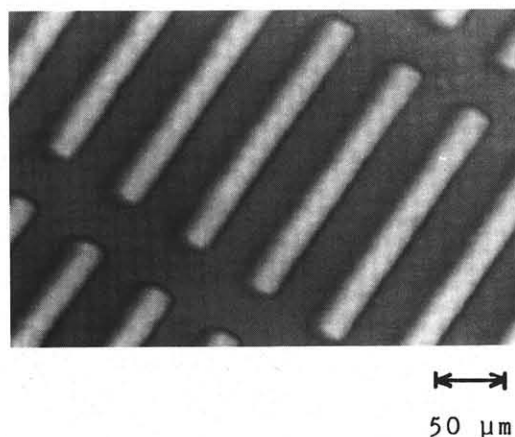


Fig. 1 Microscope image of a selectively deposited Si pattern.

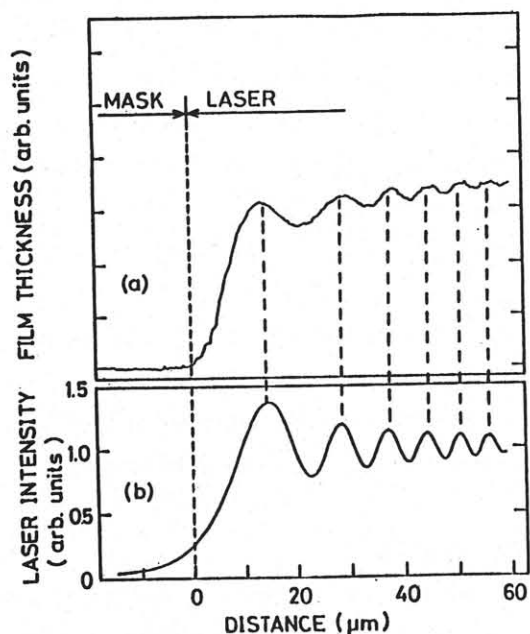


Fig. 2 Silicon pattern edge profile for a $130\text{ }\mu\text{m}$ slit width (a) and calculated laser intensity profile (b).

is shown in Fig. 1, where the laser beam was incident perpendicularly to a quartz substrate through a stencil mask located at $30\text{ }\mu\text{m}$ away from the substrate. The detailed shape of the Si pattern edge was examined by using a high precision surface roughness meter as shown in Fig. 2. The film thickness maxima correspond to the local maxima of the laser light intensity at the surface calculated by assuming Fresnel diffraction. The distance between the thickness maxima is about $10\text{ }\mu\text{m}$, being significantly short compared with the mean free path length of photodecomposed species in the gas phase. Also, the Si growth rate expected for the photodissociation reaction rate of Si_2H_6 in the gas phase is only $12\text{ }\text{\AA}/\text{min}$ at an Si_2H_6 partial pressure of 0.05 Torr. Whereas, the observed growth rate in the present experiment is considerably high and strongly temperature dependent as indicated in Fig. 3. Note that the growth rate

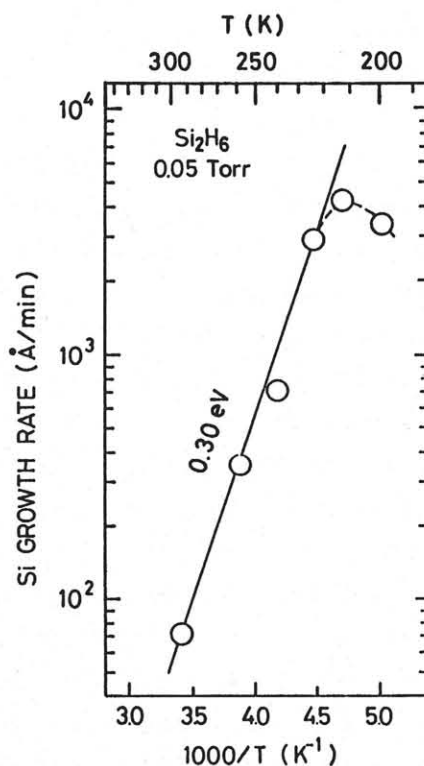


Fig. 3 Silicon growth rate plotted against substrate temperature.

increases with decreasing the substrate temperature. This implies that adsorbed Si_2H_6 molecules are photodecomposed by laser irradiation to produce a silicon deposit. The activation energy of the growth rate, 0.30 eV, could be related to the heat of adsorption for Si_2H_6 , because the heat of desorption for Si_2H_6 is 0.22 eV⁶⁾ and because the heat of adsorption is in general close to the heat of desorption. The multilayer adsorption of disilane must take place at low temperatures and hence the growth rate becomes high. At temperatures below -49°C the growth rate first saturates and subsequently starts to decrease. This is probably due to increase in the laser induced desorption of multilayer Si_2H_6 adsorbates from the top surface and due to the resulting decrease in the light intensity near the bottom layer of adsorbed Si_2H_6 . The hydrogen desorption from the growing surface is also interrupted by such Si_2H_6 adsorbates, leading to decrease of the growth

rate. The disilane partial pressure dependence of growth rate is consistent with the growth model described above. As shown in Fig. 4, near room temperature or at low Si_2H_6 partial pressure, the surface coverage of Si_2H_6 is rather low and the film growth is controlled by Langmuir-Hinshelwood mechanism in which the growth rate is proportional to the square root of the reaction pressure under the surface equilibrium reaction condition such as $\text{Si}_2\text{H}_6 \rightleftharpoons \text{Si}_2\text{H}_5 + \text{H}$ ³⁾ and/or $\text{Si}_2\text{H}_6 \rightleftharpoons \text{SiH}_4 + \text{SiH}_2$ ⁵⁾.

At low temperatures, the quantity of Si_2H_6 molecules on the surface N becomes significantly large because N is given by:

$$N = K \times G \times \tau. \quad (1)$$

Here, K is the condensation coefficient of Si_2H_6 , G is the incident Si_2H_6 flux intensity per unit time and τ is the residence time of adsorbate. In eq. (1) G is proportional to Si_2H_6 partial pressure, while K and τ are strongly temperature dependent, so that N becomes large at low temperatures. The growth rate is basically determined by the decomposition rate of adsorbates and enhanced with the secondary surface reactions caused by hydrogen radicals and silyl radicals (Si_xH_y). Namely, atomic hydrogen created by photodissociation of adsorbates and by laser excitation of SiH bonds on the growing Si surface can react with adsorbed Si_2H_6 to produce Si_2H_5 radical through abstraction reaction. Also, the insertion reaction of SiH_2 created by Si_2H_6 photodissociation might occur to promote the polymerization⁷⁾. Hence, the growth rate is dependent upon the 3rd to 4th power of the partial pressure as shown in Fig. 4.

The existence of the secondary reaction pathways in the film growth is also confirmed by the fact that the growth rate is

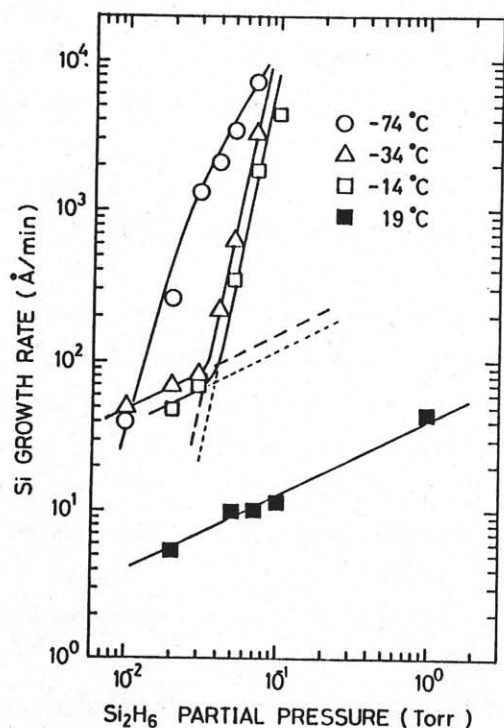


Fig. 4 Silicon growth rate versus Si_2H_6 partial pressure.

proportional to the 2nd power of laser intensity. Consequently, the growth rate is controlled by the photodissociation rate of Si_2H_6 adsorbates as well as by the rate of the secondary reactions.

From these discussion we may conclude that the selective silicon film formation in the area irradiated with laser beam proceeds through the photochemical decomposition of adsorbed Si_2H_6 and subsequent polymerization followed by photoexcited crystallization. Very small amount of activated species created in the gas phase can not directly react with the substrate surface because it is covered with Si_2H_6 adsorbates, and hence silicon thin film is not formed in an unirradiated area. This explains the reason why the selective growth of silicon films can be achieved on a cooled substrate.

The structural characterization of as grown silicon films was carried out by Raman scattering. A single peak at 518 cm^{-1} arising from the T0 mode of crystalline Si phase is observed as shown in Fig. 5. The grain size estimated by the full width at half maximum of the spectrum is about 500 Å in consistence with the x-ray diffraction

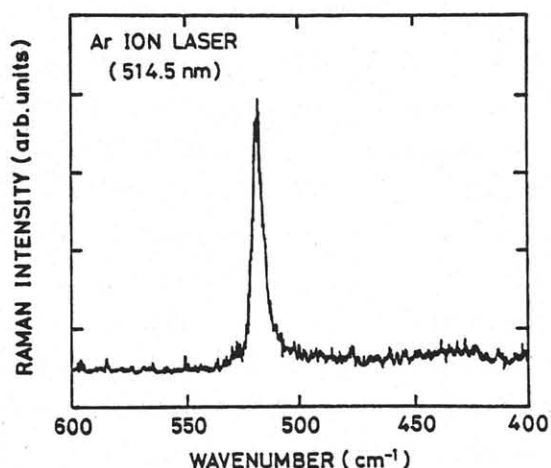


Fig. 5 Raman spectrum taken with 514.5 nm light excitation from an Ar ion laser. The peak at 518 cm^{-1} refers to the T0 mode of crystalline silicon.

data. The infrared spectra of the films exhibited the presence of incorporated Si-H bonds whose content is $0.5 \sim 4.5\text{ at.}\%$. The bonded hydrogen might be incorporated mainly in the grain boundary region⁸⁾. Conductivity of as grown poly-Si is Arrhenius type and the activation energy is in the range of $0.35 \sim 0.57\text{ eV}$ depending on the content of incorporated hydrogen⁹⁾.

In conclusion pattern projection cryogenic laser CVD has been done for the first time and a possible mechanism of the selective growth is discussed.

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