

## Low Temperature CVD Technique for Crystalline Si Deposition

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The CVD technique which utilizes microwave discharge and KrF excimer laser irradiation was studied. The crystalline Si was deposited at the deposition rate of 30-70nm/min below 400°C. The nonlinear increase of the (110) crystalline component was observed around deposition rate of 50nm/min and laser fluence of 40mj/cm<sup>2</sup>. This effect can be explained by the laser enhanced crystallization. The formation of (110) component is determined by the thermal process, and its activation energy was estimated to 0.44eV. The increase of the grain size of the (111) crystalline was observed at lower substrate temperature. Also, the effect of the laser irradiation on crystalline growth was investigated.

### 1. INTRODUCTION

There are increasing needs to lower process temperature to fabricate ICs of higher speed and higher packing density. In particular, the Si crystalline deposition at low temperature is very useful for ULSI devices and solar cell fabrication. Therefore, there have been several attempts to realize low temperature crystalline Si deposition by UV irradiation<sup>1),2)</sup> or discharge<sup>3)</sup>. Although the source gas can be decomposed at low substrate temperature, the deposited film is not efficiently crystallized by these single excitation method.

In this paper, the deposition characteristics of the CVD technique which utilizes microwave discharge and excimer laser irradiation is reported. The effect of the laser irradiation on Si crystallization was studied by the x-ray diffraction method.

### 2. EXPERIMENTAL

A diagram of the CVD system used in the experiments is illustrated in Fig.1. The 100Hz amplitude modulated microwave was

supplied to the reaction chamber through the quartz window. The microwave power was set 200W constant during the experiments. The KrF excimer laser was operated at 100Hz and its beam was introduced into the reaction chamber through the synthetic quartz window after converged by the synthetic quartz lens. The laser beam was incident at 19.5° on the substrate.

The CORNING 7059 glass was used as a substrate. The deposition was carried out at 0.2Torr after evacuated below  $5 \times 10^{-6}$  Torr. The total reaction gas flow rate was 10sccm. SiH<sub>4</sub> gas was diluted by Ar gas or H<sub>2</sub> gas to change the SiH<sub>4</sub> partial pressure. The deposition time was 20min.

Aluminum electrodes were evaporated on the substrate for the conductivity measurement. Also, x-ray diffraction pattern of the deposited film was measured to evaluate the texture and amount of the crystalline component. The grain size of the Si crystal was estimated by Debye-Scherrer's formula.

### 3. RESULTS AND DISCUSSION

#### 3.1 DEPOSITION CHARACTERISTICS

Fig.2 shows the relation between  $\text{SiH}_4$  partial pressure and deposition rate. The deposition rate of the Si crystalline increases proportional to the  $\text{SiH}_4$  pressure. The deposition rate is 30-65nm/min with  $\text{H}_2$  dilution and 15-45nm/min with Ar dilution.

The relation between x-ray diffraction intensity of the deposited film and deposition rate is shown in Fig.3. The (110) crystalline component appear as (220) peak at the diffraction pattern. As can be seen in Fig.3, both the (111) and the (110) crystalline component increases proportional to the deposition rate below 40nm/min(linear region), but the (110) crystalline component shows nonlinear increase around 50nm/min(nonlinear region). The film was deposited at linear region with Ar dilution and nonlinear region with  $\text{H}_2$  dilution to investigate the difference of their dependence on the laser fluence and substrate temperature. The laser fluence dependence (Fig.4) shows that the crystalline component of the film deposited with Ar dilution increases linearly as laser fluence becomes higher, however the (110) component of  $\text{H}_2$  dilution case shows an abrupt increase between 35 and 40  $\text{mj}/\text{cm}^2$ .

The substrate temperature dependence (Fig.5) shows that (111) crystalline component have weak dependence on substrate temperature, but (110) crystalline component gradually increases as raising substrate temperature. The same data is plotted in Fig.6 to elucidate the relation between the logarithm of the amount of the (110) crystalline component and the reciprocal of substrate temperature. The amount of the (110) crystalline shows Arrhenius type dependence with temperature. Therefore, the formation of the (110) crystalline is

determined by the thermal process and its activation energy is estimated to be 0.44eV. Fig.7 shows the substrate temperature dependence of grain size of crystal deposited with Ar dilution. The grain size of (111) crystalline component become larger as the substrate temperature is decreased. The grain size of (111) Si crystal deposited at 200°C is about 70nm. This grain size is much larger than reported value of the  $\mu\text{-SiH}_4$ .

The difference of the laser induced temperature rise between 35 and 40  $\text{mj}/\text{cm}^2$  is estimated to be less than 100°C, and then, the abrupt increase of (110) component can not be explained only by the change of the temperature. The increase of the (110) component seems to be due to some kind of laser enhanced crystallization effect. And, this laser enhanced crystallization may be obstructed by the contamination from the surrounding at the low deposition rate region.

The fact that the (110) crystalline component increases at higher substrate temperature can be explained by the H content of the film deposited at the interval between the laser pulses. The film deposited at the interval of the laser pulse seems to contain much H at low temperature, and the extraction of this excess H drops the efficiency of the transition from amorphous to (110) crystalline. From this assumption, the activation energy of 0.44 eV corresponds to the activation energy of H extraction process. On the other hand, the large H concentration on surface at low temperature seems to enhance the surface migration that result in large grain growth of the (111) crystal.

#### 3.2 THE EFFECT OF LASER IRRADIATION

To elucidate the effect of the laser irradiation, the film was deposited with

the two different laser irradiation schemes. Fig.8 and 9 shows the x-ray diffraction intensity of the film deposited at these different laser irradiation scheme as a function of the time without laser irradiation. The (110) component decreases as the deposition time without laser irradiation become longer.

These result suggest two meaning. First, laser irradiation on thin film nucleate crystals more efficiently, and these nucleation at the thin film state determines the crystalline growth of upper layer. Next, the continuous laser irradiation is necessary to grow crystals after the nucleation.

#### 4.SUMMARY

The deposition characteristics of the CVD system using microwave discharge and excimer laser irradiation was studied. The crystalline Si was obtained at the depositon rate of 30-70nm/min below 400°C. The amount of (110) component and the grain size of (111) component depend on the deposition rate, laser fluence, and substrate temperature. These dependences are explained by the laser enhanced crystallization effect and H content of the film. From the result of the deposition partly without laser irradiation, the continuous laser irradiation from the thin film state is necessary to form crystalline component. This CVD technique seems to be promising to fabricate future high performance LSI and high efficiency solar cells.

#### 5.REFERENCES

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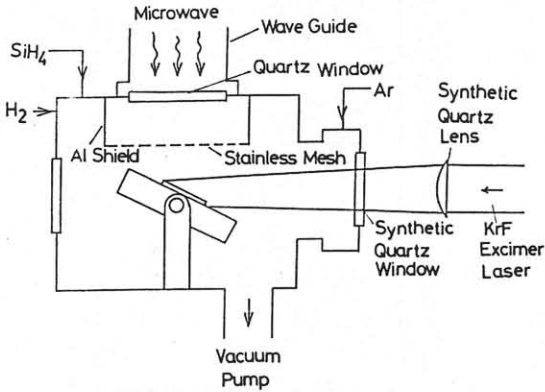


Fig.1 Schematic diagram of the experimantal apparatus.

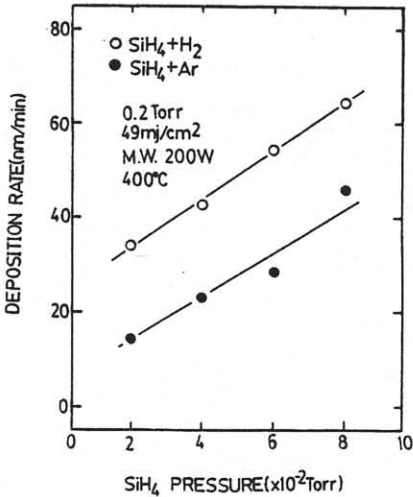


Fig.2 The relation of the SiH4 partial pressure and deposition rate.

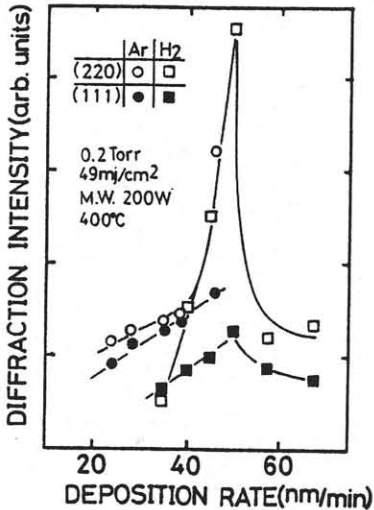


Fig.3 The x-ray diffraction intensity of the deposited film as a function of deposition rate.

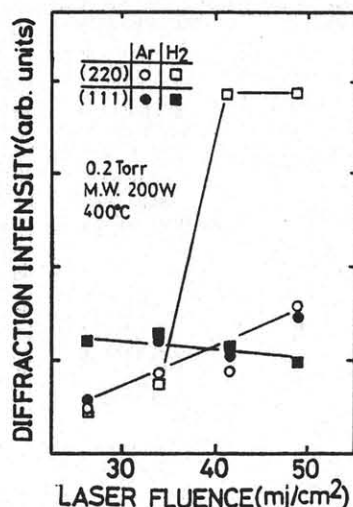


Fig.4 The relation of x-ray diffraction intensity and the laser fluence. The difference of the film thickness is corrected to compare the Ar dilution case and H2 dilution case.

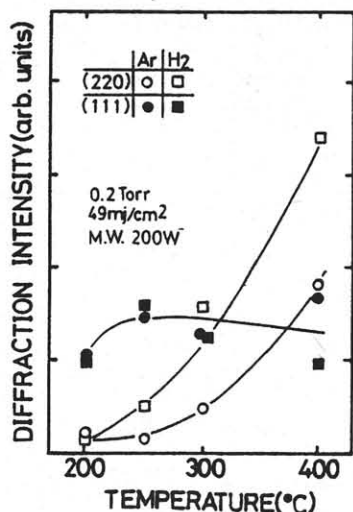


Fig.5 The x-ray diffraction intensity as a function of the substrate temperature. The difference of the film thickness is corrected.

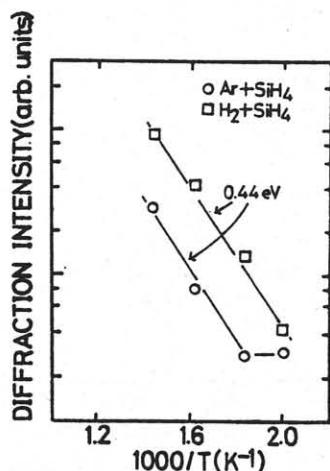


Fig.6 The Arrhenius plot of the (110) crystalline component against the substrate temperature.

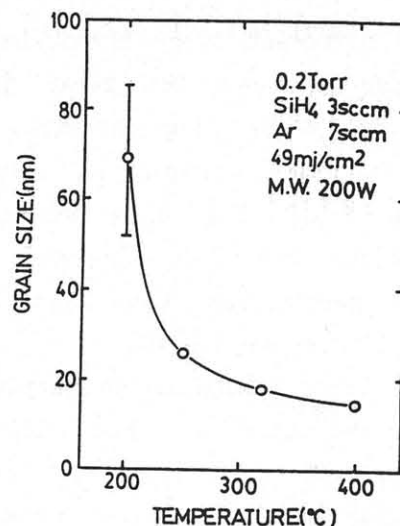


Fig.7 The relation of the grain size of (111) crystalline component and substrate temperature.

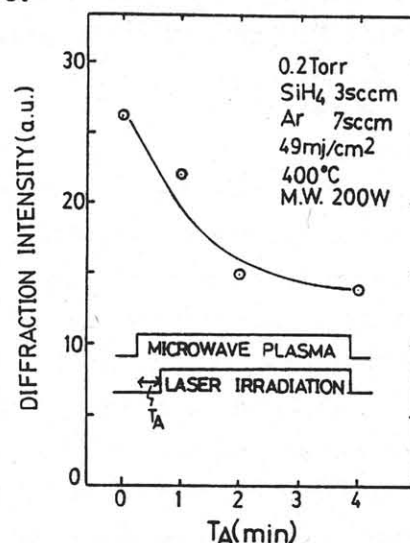


Fig.8 The x-ray diffraction intensity of Ar dilution case as a function of the deposition time without the laser irradiation.

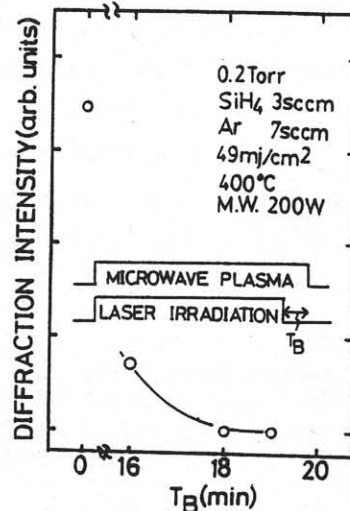


Fig.9 The relation of x-ray diffraction intensity of Ar dilution case and the deposition time without the laser irradiation.