Photo-CVD of a-Si Films Using Unified Reactor with Lamp

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A novel photo-CVD method using a unified reaction chamber with a lamp is described. This photo-CVD system without the lamp wall and chamber window makes the short wavelength lights irradiation available. Using the unified reactor a-Si films are deposited from SiH₄ without mercury sensitizer. Emission spectrum from the unified reactor is measured. It has the strong peaks of Si and the weak peaks of SiH, H₂, Ar etc., in contrast with that of the RF plasma. The electron temperature derived from the spectra is 4600-6100 K of the unified reactor.

§1. Introduction

Photo-chemical vapor deposition is a low temperature process which attracts attention for its possible capability of depositing high quality films without charged-particle damages. In 1967 Nishizawa et al. reported that the epitaxial temperature of silicon is lowered by light irradiation. Afterwards photo-CVD has been undertaken using monosilane or disilane gas for depositing a-Si films, or mixing those gases with oxygen or ammonia gas for SiO₂ and Si₃N₄ films. We demonstrated high deposition rate of 1 nm/sec in monosilane and 1.6 nm/sec in disilane utilizing a newly developed low pressure mercury lamp (λ=185nm) and a mercury sensitizer. However, a conventional photo-CVD system involves some difficulties which arise from the necessity of a window to introduce photon energy. That is, the light of short wavelength is absorbed by the window material, and the film growth on the inside wall of the window gradually reduces light intensity and deposition rate.

This paper reports on the first trial of a-Si film deposition without the window using an unified reactor and spectroscopic analysis of the system.

§2. Experiment

2.1 Apparatus

A schematic diagram of an unified photo-CVD reactor with lamp and a top-view photograph thereof are shown in Fig.1 and 2 respectively. The unified reactor comprises two parts: the upper half is the lamp and the lower half is a deposition region. The lamp part includes two outlets of gases for discharge, for example pure argon or argon containing mercury vapor, and two electrodes between which the light is generated by the collision of electrons and gases. The light irradiates the substrate in the lower half of the reactor directly. The short wavelength lights are available to deposit films, because of no walls which absorb them between the lamp part and the substrate.

Fig.1 A schematic diagram of a unified reactor with a lamp.

Fig.2 A top-view of the unified reactor with the lamp in the operation.
The film-deposition part contains a temperature-controlled susceptor (R.T.~400°C), and a raw gas outlet which faces toward the susceptor to supply the raw gas efficiently and to prevent the diffusion of the gas toward the lamp part.

A Baratron gauge measures the pressure of the reactor. The gas flow rates are kept constant by mass flow controllers and the pressure of the reactor is controlled by varying the conductance of the exhaust valve. Mercury atoms are transported by the argon gas passing through the Hg-saturator. The temperature of the Hg-saturator is controlled at a range from -40°C to +70°C by an electric thermo-controller.

2.2 Film Deposition

One of the advantages of using the unified reactor is that a-Si films are deposited from SiH₄ gas without a mercury sensitizer. As shown in Fig.1, the distance from the outlet of the raw gas to the susceptor (i.e., substrate) is denoted by "L". Figure 3 shows the thickness distribution of a-Si films produced from SiH₄ gas for L = 5 mm and 33 mm. The deposition conditions are as follows: the substrate temperature is 250°C, the reactor pressure is 2 Torr, and the flow rates of SiH₄ and Ar gas are 5 SCCM and 100 SCCM, respectively. The a-Si film thickness is rather uniform for L = 33 mm, while it is varied steeply for L = 5 mm.

![Graph showing thickness distribution of a-Si film](image)

Fig.3 A thickness distribution of a-Si film produced from SiH₄ gas. The distances from the outlet of the raw gas to the substrate are (a) L = 5 mm, and (b) L = 33 mm.

The a-Si film deposition using mercury sensitizer is carried out. Compared with the direct dissociation, the thickness variation is reduced, which would be attributed to the mercury sensitizer. The deposition rate is slightly higher than that without mercury sensitizer. This may be caused by that the increase in the deposition rate with adding mercury sensitizer is cancelled to some extent by the decrease in the Ar line intensities (to which the direct dissociation is proportional).

2.3 Emission Spectrum

A quartz optical fiber is used as an optical guide from the reactor to a spectrometer, which has a PMT detector and measures the emission spectra in the range of UV-visible light. In the unified reactor the emission spectra are measured at three points, namely at the top of the reactor (PO-1 in Fig.1), at the side of the reactor almost at the center of the discharge region (PO-2), and at a point just above the susceptor (PO-3). The distinctive features of the spectra shown in Fig.4 are as follows:

1) An emission spectrum of Hg-added Ar is almost similar to that of a 185 nm low pressure mercury lamp. The 254 nm line intensity is 1/2~1/8 of the 185 nm lamp.

2) A pure argon's emission from the plasma in the unified reactor has a different intensity profile from the RF plasma. (The dissimilarity indicates a difference in the electron temperature of the two kinds of the plasma.)

3) Ar + SiH₄ gas has higher line peaks of S1 but has lower peaks of Ar, SiH etc. than the RF plasma.

4) The peaks of Ar and Hg become weaker in the presence of SiH₄ gas.

5) Adding Hg atoms to Ar gas makes the Ar peaks lower.

6) The spectra measured at the three different points of the unified reactor are quite similar each other.

3. Discussion

3.1 Deposition of a-Si

Direct photo-CVD from SiH₄ by the mercury lamp is usually difficult since light of shorter wavelength than 150 nm which can excite SiH₄ can be hardly transmitted through a lamp tube and/or a reactor window. It is very interesting that a-Si films are deposited from SiH₄ without mercury sensitizer in the case of unified reactor. This fact suggests that in this reactor the UV light...
from Argon discharge can contribute to the direct photochemical reaction of \text{SiH}_4 effectively.

A theoretical model for the profile of the a-Si film thickness is proposed. By fitting the theory with the data on a \text{Si}_2\text{H}_6 case similar to Fig.3(a), the lifetime of the excited carrier is determined to be about 0.02 sec\(^{14}\).

### 3.2 Electron Temperature

The fact that the lamp electrode have a filament suggests the electron temperature of the plasma produced by the discharge between the two electrodes in the lamp part will be lower than that of the RF-plasma which discharges without filaments. The electron temperature is derived from the emission spectra\(^{15,18}\). A radiation intensity of a spectral line is given by

\[ I_{nm} = j_{nm} \nu = \frac{1}{4\pi} \cdot A_{nm} \hbar \nu N_n, \]  

where \(A_{nm}\) and \(\nu\) are the transition probability and frequency of the line, \(\hbar\) is the Planck's constant and \(N_n\) is the density of the particles in the \(n\)th state. Assuming the local thermodynamic equilibrium (LTE), the Boltzmann equation holds

\[ N_n = \frac{N}{U} s_n \exp\left( -\frac{E_n}{kT} \right), \]  

where \(N\) is the particle density, \(s_n\) and \(E_n\) are the statistical weight and excitation energy of the \(n\)th state, and \(U\) is the partition function. Equations (1) and (2) yield

\[ \ln \left( \frac{\lambda^2}{g_{nm}} \right) = -\frac{E_n}{kT} + \text{const}. \]  

where \(\lambda\) is the wavelength of the line, \(g_{nm}\) is the absorption oscillator strength related to the transition probability \(A_{nm}\), namely

\[ f_{nm} = \frac{mc^3}{8\pi^2e^2} \frac{g_m}{g_n} A_{nm}. \]  

Plotting \(\ln(\lambda^2\nu/g_{mf})\) vs \(E_n\) gives a straight line. An example of the plottings is shown in Fig. 5. An electron temperature \(T_e\) is obtained from a gradient of the line drawn by a least square method.

Various kinds of electron temperatures are calculated by using several values of \(A_{nm}\) reported\(^{16-18}\). The obtained temperatures are listed in Table 1 and 2. As shown in Table 1, the electron temperature \(T_e\) of the plasma in the unified reactor and
the RF plasma are $5 \sim 6 \times 10^3$ K and $7.5 \sim 11 \times 10^3$ K, respectively. The former is confirmed to be lower than the latter, as expected. And the former is almost equal to the $T_e$ of the independent 185 nm low pressure mercury lamp. In addition $T_e$ is independent of a variety of the gas mixtures. But the value of the RF plasma is more or less smaller than that obtained by the electro-probe method.

$$\text{Fig.5 A plotting for obtaining an electron temperature } T_e \text{ of the plasma in the unified reactor.}$$

Table 1. Electron temperature of various plasma calculated by using several values of $A_{nm}$ reported in A) Ref.16, B-D) Ref.17 and E) Ref.18.

<table>
<thead>
<tr>
<th>PLASMA</th>
<th>Unified Reactor</th>
<th>RF Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5400</td>
<td>7600</td>
</tr>
<tr>
<td>B</td>
<td>5200</td>
<td>8200</td>
</tr>
<tr>
<td>C</td>
<td>5500</td>
<td>10000</td>
</tr>
<tr>
<td>D</td>
<td>6100</td>
<td>11000</td>
</tr>
<tr>
<td>E</td>
<td>5100</td>
<td>7900</td>
</tr>
</tbody>
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Table 2. Electron temperature of various gas mixtures using $A_{nm}$ reported in Ref.17.

<table>
<thead>
<tr>
<th>GAS</th>
<th>Unified Reactor</th>
<th>RF Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>5500</td>
<td>10000</td>
</tr>
<tr>
<td>Ar-Hg</td>
<td>5500</td>
<td>10000</td>
</tr>
<tr>
<td>Ar-SiH$_4$</td>
<td>5700</td>
<td>7900</td>
</tr>
</tbody>
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§4. Conclusion

An unified reactor with a lamp is constructed. a-$Si$ film from SiH$_4$ is possible to be deposited without a mercury sensitizer. The system is distinguished from a conventional plasma-CVD apparatus in respect to a separation of the substrate from the discharge region, and an electron temperature of the discharge region is lower than that of the RF plasma. A deposition of a-$Si$ films using unified reactor is demonstrated. For further improvement, an analysis of the deposition mechanism, an optimization of the filament material and structure to emit an uniform and strong light, and etc. are necessary.

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References

14. to be presented elsewhere