Extended Abstracts of the 18th (1986 International) Conference on Solid State Devices and Materials, Tokyo, 1986, pp. 221-224

A-5-3

Thin Film Formation by Radical Jet Generated by UV Laser-Induced Multi-Photon Dissociation

Y.Ichikawa, N,Itoh, H.Sakai and Y.Uchida

Fuji Electric Co. Research and Development, Ltd.

2-2-1 Nagasaka, Yokosuka, Kanagawa 240-01, Japan

Radical Jet Type Laser-Induced CVD (RJ-LCVD) has been developed. In the conventional LCVD, the combination of reactant gases and lasers is restricted because there is a threshold photon energy to decompose a reactant gas. In the RJ-LCVD, the multi-photon absorption process induced by a focused high intensity beam is applied to the decomposition of the reactant gas. Therefore, various gases become usable for the film depositon. The apparatus of RJ-LCVD and the properties of thin film Si deposited by this method have been discussed.

1.Introduction

Photo-chemical vapor deposition (photo-CVD) has been studied as a new thin film formation method. In photo-CVD, various kinds of ultraviolet (UV) light sources are used to decompose reactant gases. Mercury discharge lampes are commonly used in the conventional photo-CVD. However, UV lasers such as various excimer lasers are also expected to be a powerful UV source because the light intensity of the laser beam is much higher than that of discharge lamps. Therefore, a number of studies on laser-induced CVD (LCVD) have been reported in recent years.[1,2)]

In LCVD, two incident directions of laser beams are commonly employed; one is parallel beam irradiation to a subatrate, and the other is perpendicular irradiation to it. To study photo-dissociation process and to avoid pyrolitic decomposition of reactant gases, the parallel-incident laser beam is more advantageous. In the perpendicular beam irradiation, it is difficult to discriminate the gas phase reaction from the surface reaction on the substrate and to avoid the influence of laser irradiation damage on the film characteristics.

In the parallel-incident beam method, however, the reactant gas utilized for film deposition is restricted by the wavelength of the laser beam employed because there is a threshold energy to make direct photo-dissociation of the gas. For instance, only higher order silanes such as Si_2H_6 and Si_3H_8 are available even when ArF excimer laser having a wavelength of 193nm is utilized. Another problem is film deposition on the window used for the laser beam incidence to the reactor. In the conventional method, however, we cannot avoid the film deposition on the window, and the thickness of the film deposited on the substrate is restricted by the blur of the window. To avoid this, several methods such as blowing nonreactive gases and painting the oil for vacuum pumps on the window have been attempted. However, these methods cannot be a fundamental solution.

To solve these problems, we have developed a new LCVD technique named Radical Jet Type LCVD (RJ-LCVD). The principle of the RJ-LCVD bases on the multi-photon process induced by a focused high intensity laser beam. In the following sections, we present the configuration of the apparatus and preliminary experimental results of the film deposition.

2.Experimental Apparatus

Figure 1 shows the schematic diagram of the apparatus developed for the RJ-LCVD. The apparatus consists of a chamber and an excimer laser. The chamber is equipped with gas injecting nozzles, a susceptor having heaters and a vacuum

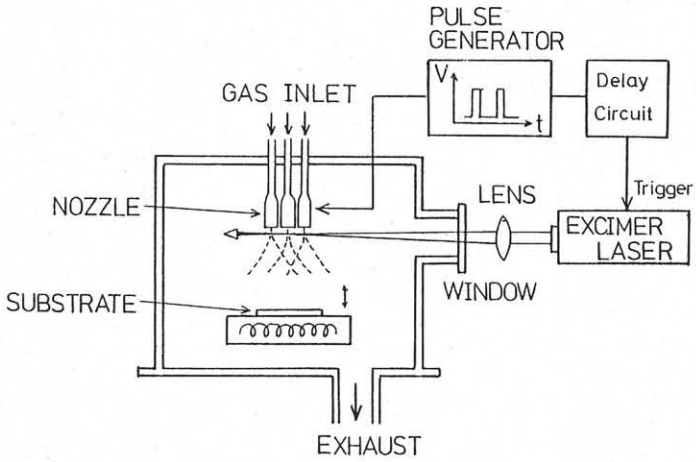

Fig.1 Schematic diagram of Radical Jet Type Laser CVD apparatus.

pump system consisting of a mechanical booster pump and a rotary pump. The chamber is also equipped with a window made of quartz, through which the laser beam is introduced.

Reactant gases are injected into the chamber through a 0.5 mm diameter orifice of the nozzle. The nozzle is opened and closed by a needle valve activated by a electromagnet, and the opening of the nozzle is made by applying a voltage pulse to the electromagnet. The minimum opening duration of the nozzle , which is controlled by the pulse width, is 1 ms in the present apparatus. The voltage pulse genetated by a pulse generator is also connected to the excimer laser through a delay circuit to trigger it. Thus, the excimer laser is fired to synchronize with the injection of the reactant gas.

The gas injected from the nozzle forms a supersonic jet because the gas pressure inside the nozzle is kept to be at an atmospheric pressure or higher and that inside the chamber is kept at below 10Pa. The laser beam is focused near the orifice by a quartz lens, and is crossed to the supersonic jet. At the crossing point, the interaction between the UV laser beam and the gas jet occurs to generate free radicals.

Since substrates on the susceptor are placed perpendicular to the jet, the generated free radicals are transported along the jet flow and form the film on the substrates. Namely, the film deposition is made by a radical jet flow. The distance between the orifice and the substrate can be changed from 5 mm to 25 mm in the present apparatus. Therefore, the deposition condition in RJ-LCVD is adjustable by the duration and the repetition rate of the nozzle opening, gas pressure and the distance between the nozzle and the substrate as well as the intensity of the laser pulse.

3.Experimental results

In this study, we used SiH_4 and Si_2H_6 as a reactant gas, and these gases were injected through one of the nozzles. These gases were decomposed by a excimer laser. The excimer laser used was Lumonics HE-460, and was operated as ArF laser (193 nm) and KrF laser (248 nm). Typical experimental conditions are shown in Table 1.

In the conventional LCVD, Si_2H_6 irradiated by ArF laser beam is only a combination to deposit thin film Si. In other combinations, the photon energy is smaller than the threshold energy for the photo-dissociation of reactant gases. However, in the RJ-LCVD, film deposition was observed in all combinations as shown in Table 2. This implies that the dissociation of reactant gases by the multi-photon absorption process is induced at the crossing point where the laser beam is focused. Moreover, when the gas was dissociated by the multi-photon absorption process, no film deposition was observed on the window. It is considered that the intensity of laser beam is not strong enough to induce

Table 1 Experimental Conditions

Laser	ArF 15 - 20 mJ/shot krF 60 - 70 mJ/shot
Gas	100% SiH_4, 100% Si_2H_6
Gas Injection	Gas Injection Time 2 - 5 ms Repetition rate 0.2 - 5 shot/s
Gas Pressure	Inside Nozzle 0.5 - 3 kg/cm^2 Avarage Operation Pressure 0.01 - 0.2 Torr
Distance between Orifice and Substrate	5 - 25 mm
Substrate Temperature	Room Temperature - 250°C

Table 2 Comparison of usable combination of gases and laser beams for Si film deposition in conventional LCVD and in RJ-LCVD.

Gas	Wave Length of Laser Light	Film Formation	
		Conventional Laser CVD	Radical Jet Laser CVD
SiH_4	193nm	No	Yes
	248nm	No	Yes
Si_2H_6	193nm	Yes	Yes
	248nm	No	Yes

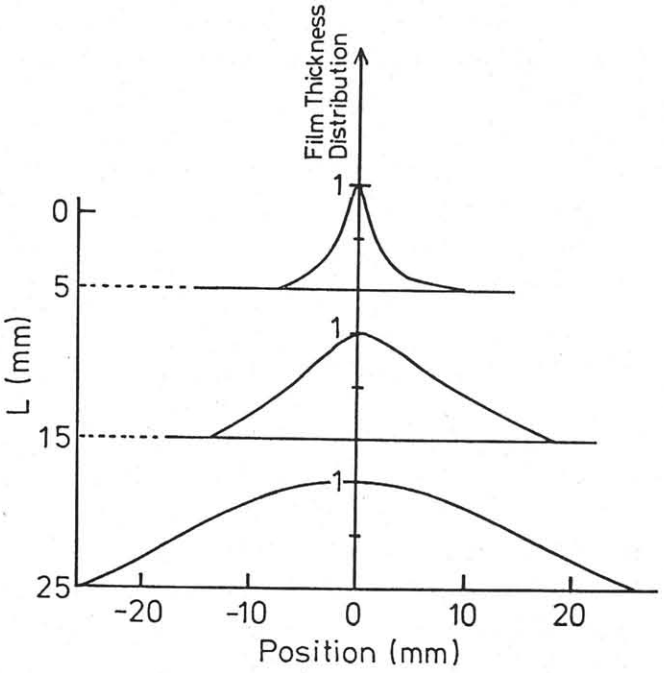

Fig.2 Normalized film thickness distribution for normal distance from orifice L = 5, 15 and 25 mm.

the multi-photon process near the window.

The pattern of the deposited film on the substrate was a disk-like shape, and its diameter increases linearly with increasing the distance between the orifice and the substrate. Figure 2 shows the normalized thickness distribution of the Si film deposited with SiH_4 decomposed by KrF laser for L=5, 15 and 25 mm, where L is the normal distance from the orifice. From this figure, it is deduced that the radical jet generated is a conical flow. Thus, uniformity in film thickness is expected to be improved according as L increases.

The deposition rate strongly depends on the focusing position and the intensity of laser beam. When the beam is focused very close to the orifice (within 1 mm), we obtained a deposition rate of about 2 Å/shot for Si_2H_6 (KrF laser) and 1 Å/shot for SiH_4 (KrF laser) at L=25 mm. These values correspond to 10 Å/s and 5 Å/s, respectively, for repetition rate=5 shots/s. The repetition rate in the present apparatus is mainly restricted by the performances of the gas injecting valve and the vacuum pump system, since the interaction time of the laser beam and the reactant gas is negligibly short (~10 ns). Therefore, if we reduce the opening duration of the valve and increase the pumping speed, a deposition rate of more than 100 Å/s, which corresponds to a repetition rate of 100 shots/s, could be easily attained without any problem.

4.Optical and Electrical Properties of Film

To study the physical properties of the deposited films, we carried out optical and electrical measurements for samples deposited with SiH_4 decomposed by KrF laser.

The optical absorption spectra for a-Si films deposited with SiH_4 for Ts=25°C, 130°C and 200°C are shown in Figure 4, where Ts is the substrate temperature. These films were deposited on Corning 7059 glass. The optical energy bandgap Egopt for L=25 mm is about 1.65 eV, and these films were comfirmed to be an amorphous silicon (a-Si) from both Raman scattering and X-ray diffraction measurements. It tends to decrease with decreasing L. For L=5 mm, Egopt becomes less than 1.5 eV. On the other hand, Egopt is almost independent of Ts. In the present arrangement of the RJ-LCVD, therefore, it is expected that

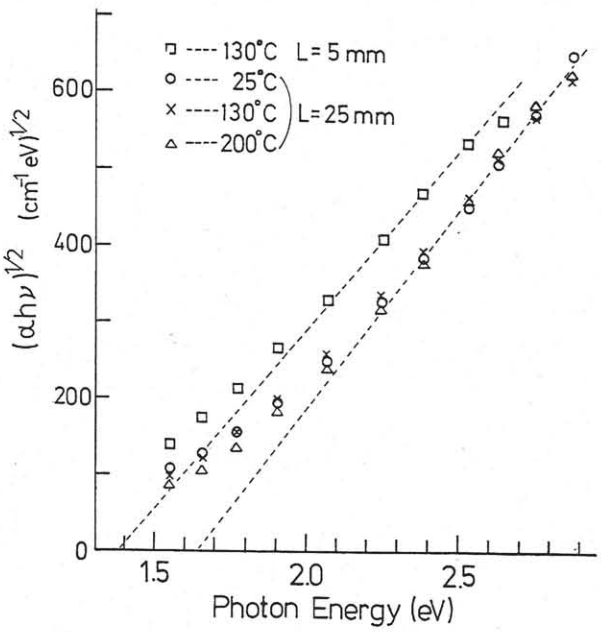

Fig.3 Absorption spctra ($\alpha h\nu$ vs. $h\nu$ plot) for L=5 and 25 mm, where α is the absorption coefficient.

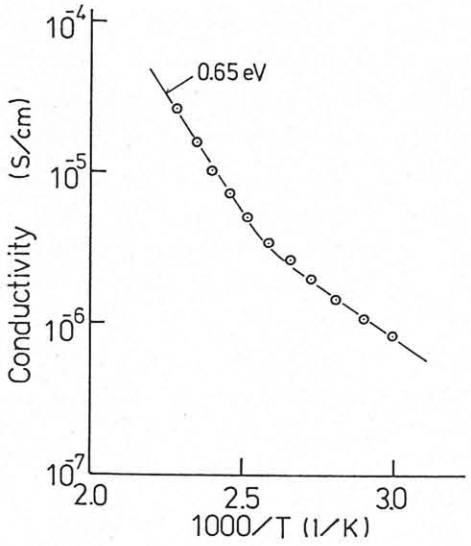

Fig.4 Conductivity of RJ-LCVD film as a function of reciprocal temperature.

surface reactions on the substrate is not so important and the properties of the film is mainly determined by gas phase reactions. The absorption tail below Egopt is larger than that in glow discharge a-Si:H films. This indicates that the localized states in the gap are not sufficiently compensated with hydrogen in the present RJ-LCVD films.

Figure 4 shows the conductivity of an RJ-LCVD film as a function of reciprocal temperature. Though the activation energy Ea is estimated to be 0.65 eV, there exists a bend point at T~125° C, and the slope below the point is 0.27 eV. This behavior in conductivity can be explained by the hopping conduction.[3] It is supposed that the hopping conduction through the defect levels dominates the conduction below this point.

5.Discussion

It was demonstrated that thin film Si can be deposited by the supersonic flow of free radicals generated by the laser-induced multi-photon absorption process. The obtained film has similar properties to that of Si film deposited by CVD. According to the IR absorption measurement, the hydrogen content was found to be several atm.% or less. These results are consistent with narrow optical bandbap and relatively high density of gap-states in the RJ-LCVD Si film.

Though only SiH_4 and Si_2H_6 were studied in this work, other reactant gases are also usable. For instance, silicon-nitride and silicon-oxide films could be formed by using gas mixtures such as SiH_4-NH_3 and SiH_4-N_2O. These films could be useful for the passivation layer or insulator of semiconductor devices because films can be deposited at even room temperature in the RJ-LCVD. Moreover, if two or three nozzles placed along the laser beam path were used, we could deposit multi-layered films and alloys by supplying different gases and controlling the opening of each nozzle independently.

In the material for amorphous semiconductor devices, it is very important to compensate the dangling bonds in the film. For this purpose, supplying the hydrogen radicals during the film deposition could be useful. This is made by, for instance, providing a nozzle for the hydrogen radical jet.

In conclusion, we have developed Radical Jet Type LCVD having following features:

1. By applying multi-photon process, it becomes possible to decompose the gases that cannot be used in the conventional LCVD.
2. As a result, the film deposition on the window can be avoided.
3. Increasing the distance between the substrate and the nozzle, this method can be, in principle, used for large-area film deposition.
4. As discussed above, this method is potentially applicable to insulator and poly-crystalline film formations as well as amorphous semiconductor film formations.

Acknowledgement

The authors are grateful to Dr. H. Haruki for his advice and to Mr. H. Sato for his assistance.

This work was partly supported by the New Energy Development Organization as a part of the Sunshine Project.

References

1) D.J.Ehrlich and J.Y.Tsao, J. Vac. Sci. Tech. B, 1 (1983) 969.
2) Y.Rytz-Froidevaux et al., Appl. Phys. A, 37 (1985) 121.
3) W.Beyer and H.Overhof "Hydrogenated Amorphous Silicon" Part C, ed. J.I.Pankov (Academic Press 1984) Chap. 8.