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Deposition of large area amorphous silicon films by ECR plasma CVD*

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The deposition of hydrogenated amorphous silicon (a-Si:H) films over a large area were performed using an electron cyclotron resonance (ECR) plasma with a multi-slot antenna. The uniformity of the ECR plasma was within 5% over 200 mm in diameter, and the density and temperature of electrons in front of a substrate were 7×10^{16} m^{-3} and 6 eV, respectively. Hydrogenated amorphous silicon films were deposited from flowing SiH_4(10%)/He gas. The deposited films were almost 200 mm in diameter, corresponding to that of the plasma. The deposition rate, optical band gap, and infrared (IR) absorption of the films were investigated to find whether the multi-slot antenna was effective for chemical vapor deposition (CVD); as the substrate temperature was increased, the optical band gap decreased.

Introduction

Hydrogenated amorphous silicon (a-Si:H) films for solar cells have been prepared mainly by a radio frequency (RF) glow discharge of silane (SiH_4). The properties of these a-Si:H films have gradually been understood, such as the dependence of the defect density on the deposition rate, and this suggests the possibility of obtaining better-quality films using a higher density plasma than that of the RF plasma. There has been considerable interest in electron cyclotron resonance (ECR) plasma[1] for plasma processing such as CVD, etching. The main reasons are as follows: (i) high electron density and acceptable high electron temperature, (ii) low ion energy, (iii) electrodeless plasma production, and (iv) high deposition and etching rates of thin films. High efficiency of deposition or etching using ECR plasmas have been reported[1–6] for plasma processing but, to our knowledge, preparation of thin films over a large area by ECR plasma CVD has not been described for the following reasons. Firstly, it is hard to produce a large diameter ECR plasma and secondly, the physics of the ECR plasma CVD has not been completely understood compared with that of a two parallel electrode reactor using RF plasma (13.56 MHz). On the other hand, the recent trend of making devices by plasma processing is becoming a more precise and larger area in industry, which raises many new problems. Specifically, it is most important to generate a uniform and large diameter ECR plasma suitable for a wafer of 200 mm in diameter. An ECR plasma is usually produced by the microwave of the principal mode of the waveguide, TE_{10} or TE_{11}, so it is hard to realize a uniform and large diameter ECR plasma. There are very few reports[6] on the production of such ECR plasmas using electromagnetic coils, although a lot of attempts have been made, so far. We succeeded in the production of a large diameter ECR plasma using a multi-slot antenna (MSA)[7–9] which has an advantage that the plasma diameter does not depend on the frequency of the incident microwave.

In this paper, we report the experimental results on the deposition of a-Si:H films with a large area by the ECR plasma produced with MSA. In the next section, the experimental apparatus is presented, and the subsequent section is the experimental results and discussion. In this section, it is described that the uniformity of the ECR plasma within 5% over 200 mm in diameter, suitable for plasma processing, was obtained under optimum conditions. Furthermore, a-Si:H films were deposited using SiH_4/He plasma with a large diameter. The deposition rate (DR), the optical band gap (E_g), and infrared absorption of the films were investigated in order to prove the usefulness of MSA for CVD.

Experimental apparatus

The schematic diagram of the experimental apparatus is shown in Figure 1. The vacuum chamber was made of stainless steel with an inner diameter of 290 mm, and a length of 1200 mm. The magnetic coil assembly consisted of six coils; four to make uniform magnetic fields, and two to form the mirror. The frequency of the microwaves was 2.45 GHz, and the power could be varied up to 1000 W. A matching between the microwave circuit and the plasma was adjusted with three stub tuners in such a way that reflected microwave powers are as low as possible.

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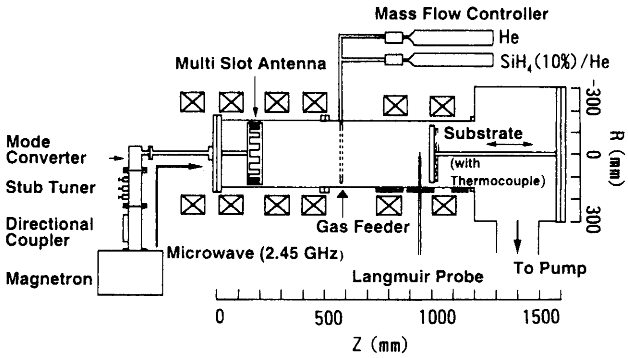

Figure 1. Schematic diagram of the experimental apparatus.

An ECR plasma was produced with MSA which was made of stainless steel of 280 mm in diameter. As seen in Figure 2, the length and width of slots were 70 mm and 2 mm, respectively.

In discussing a large diameter plasma, it is important to specify whether or not a substrate is placed in the chamber, because the plasma may be disturbed by the substrate. Here we examined the uniformity and parameters of the ECR plasma in the presence of a substrate. Plasma parameters were the best fit curve for the Langmuir probe characteristics. The electron density Ne was determined from Te and the ion saturation current density (I_{is}), the accuracy of which was confirmed with a microwave interferometer of 8 mm in our previous experiment. The introduced gas was He with a typical pressure of 2.7×10^{-2} Pa when measuring plasma parameters. Hydrogenated amorphous silicon films were deposited onto Corning #7059 glass substrates or c-Si wafers in varying deposition conditions by flowing SiH_4(10%) gas diluted in He gas. The flow rate was a constant 50 sccm. As is well known, the uniformity of deposited films is influenced by the uniformity of the gas stream. Hence, we used a circular tube along the wall of the chamber as a gas feeder. The gas spouted from several holes in the tube to the center.

In this experiment, the substrate was placed 800 mm from MSA ($Z = 1000$ mm). The diameter of the substrate holder was 270 mm, which enabled a wafer of 250 mm in diameter to be held. The substrate holder was heated in the range from 50 to 430°C over 250 mm in diameter with the uniformity of 5%, and the temperature was monitored with a spectrophotometer. The values of DR and E_g were determined by the interference method and well-known formula by Tauc,[10] respectively. The deposition rate was estimated by dividing the thickness of films by the deposition time. Infrared absorption in the range 4000–30000 mm^{-1} was examined to identify the type of silicon–hydrogen bonds.

Results and discussion

Production of large diameter and uniform ECR plasmas using MSA. In order to search an optimum condition for a uniform plasma, the radial profile of the ion saturation current density (I_{is}) was measured under the various conditions of input microwave power, gas pressure, and magnetic field configuration. It was found that uniform plasmas were obtained using MSA under the limited experimental conditions. Figure 3 shows the radial profile of I_{is} when the incident microwave power and the gas pressure were 300 and 470 W and 2.7×10^{-2} Pa, respectively. (He gas was used.) This figure shows that the uniformity of the radial profile of I_{is} is within 5% over 200 mm in diameter. The electron density and electron temperature which were measured 50 mm from the substrate were 7×10^{16} m^{-3} and 6 eV, respectively. Thus, in this experiment, the ionization degree is estimated to be 1%, which means that MSA is an efficient antenna for ECR plasma production. The uniformity of floating potential (V_f) was ± 0.75 V over 200 mm in diameter. The value V_f is slightly positive, although V_f in the cases where the radial profiles of I_{is} was not uniform was in the range from -5 to -20 V, which means that there were little high energy electrons in the uniform plasma.[5] Thus, the results of Figure 3 demonstrates that the large diameter uniform ECR plasma suitable for plasma processing was generated.

Since magnetic fields generally play an important role in the behavior of plasmas, two dimensional axial field lines were calculated. The ECR plasma was damped at the positions, $R = \pm 120$ mm, as seen in Figure 3, which is explained by the fact that the plasma using MSA flowed along the magnetic field lines in Figure 4. The magnetic field is stronger near the wall of the chamber, and the plasma outside the peaks dies out because the recombination occurs at the points where the magnetic field lines cross the wall of the chamber. Thus, it is expected that uniform ECR plasma with a diameter larger than 200 mm will be obtained with MSA if the chamber is enlarged.

Deposition of a-Si:H films using ECR plasmas. Hydrogenated

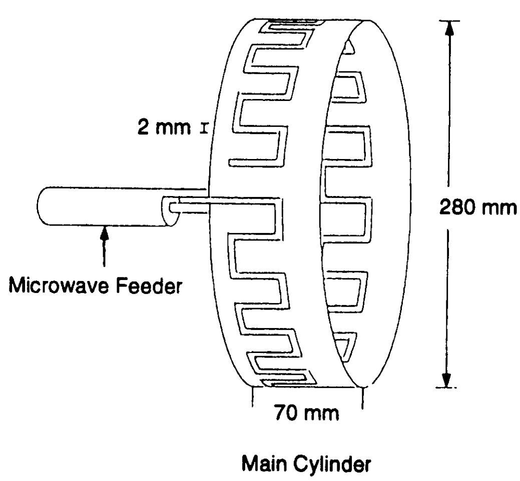

Figure 2. Schematic view of the multi-slot antenna.

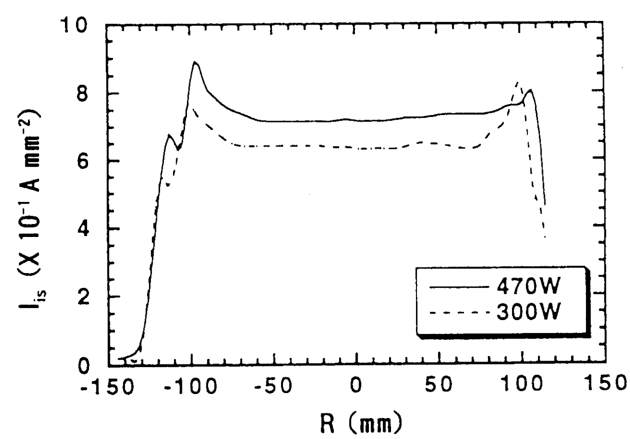

Figure 3. Radial profiles of I_{is} (the ion saturation current density) for the uniform case.

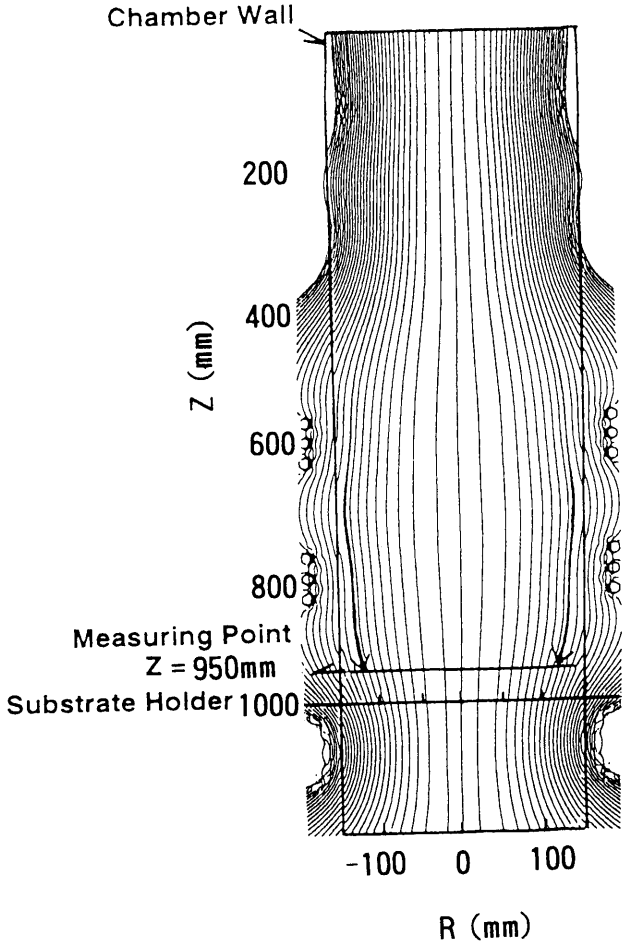

Figure 4. Two dimensional magnetic field lines corresponding to the magnetic field configuration of Figure 3.

amorphous silicon firms were deposited by flowing SiH_4(10%) gas diluted in He gas. Figure 5 shows a typical radial profile of DR of a-Si:H films deposited under the conduction where the uniform He plasma was obtained as described above. The incident microwave power was 300 W, and the substrate was not heated intentionally. The films were deposited over about 200 mm in diameter, and the diameter of the films is almost the same as that of the plasma, as seen in Figure 3. Figure 5 shows that the radial profile of DR is not uniform. The uniformity did not change when the substrate was heated. As the reason for the non-uniform profile of DR, it is considered that the flow or the mean free paths of radicals strongly influenced the radial profile of DR, because the substrate was set far from the gas feeder in this experiment. The uniformity of the films would be improved by controlling a shape or a position of the gas feeder, which will be published elsewhere.

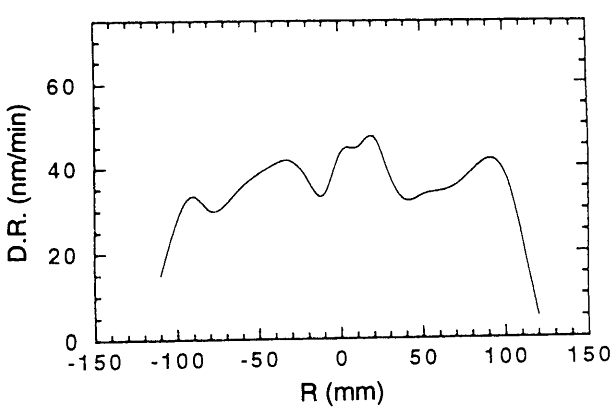

Figure 5. The radial profile of the deposition rate produced under the same condition as 300 W in Figure 3.

The dependence of E_g and DR on the temperature of a surface of the substrate (T_s) are shown in Figures 6(a) and (b), respectively. The films were deposited under the same conditions except T_s. The value E_g decreased as T_s was increased. The ratio of photo-to dark-conductivity of the film deposited under $T_s = 200°C$ was measured, and it was found to be more than 10^6, which indicated that the deposited film by the ECR plasma using MSA was suitable for use in a solar cell. When the substrate was not heated intentionally (T_0), the substrate temperature was about 50°C, so there is no difference between this case and the case where the substrate was heated at 50°C. As seen in Figure 6(b), DR decreases when T_s is increased. The reason for this was considered as follows. The increasing of T_s heated the gas adjust to the substrate, and the radical density in the plasma sheath decreased due to the constant gas pressure.

Infrared absorption in the range from 4000 to 30000 mm^{-1} was examined to identify the type of silicon–hydrogen bonds. Figure 7 shows a typical spectra of transmission of the deposited films. The dependencies of the absorption of Si–H (20000 mm^{-1}), Si–H_2 (8800 mm^{-1}), and $(Si–H_2)_n$ (8900 mm^{-1}) normalized by

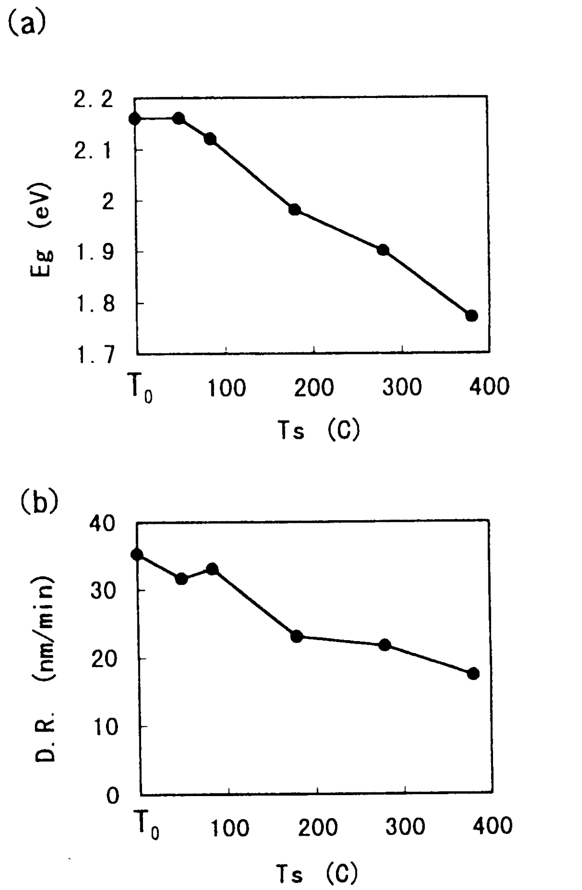

Figure 6. Dependence of (a) the optical band gap and (b) the deposition rate on T_s. T_0 corresponds to the temperature of the substrate is not heated.

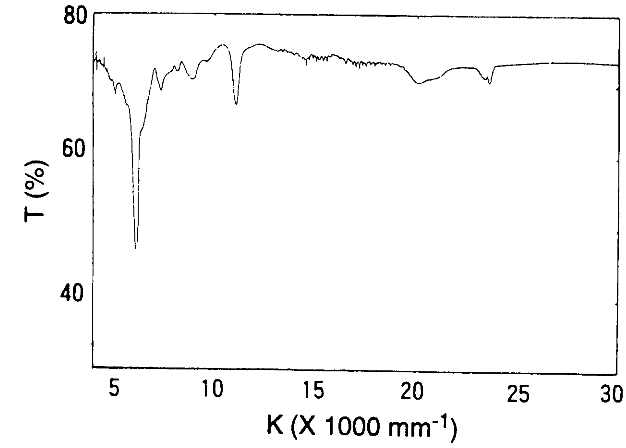

Figure 7. Typical transmission spectra of the.deposited a-Si:H films.

that of Si–H_2 (20900 mm^{-1}) on T_s were measured. The dependencies of the rates of absorption, Si-H/Si-H_2 and $(Si–H_2)_n$/Si–H_2 on T_s are shown in Figure 8. The value of Si-H/Si-H_2 increases as T_s is decreased, and the other rates do not change appreciably.

Hydrogenated amorphous silicon films were deposited for different incident microwave powers, 300, 470, and 500 W. The substrate was not heated intentionally. The dependences of E_g and DR on the incident microwave power are shown in Figures 9(a) and (b), respectively. The value of DR is almost same at the incident power of 300 W and 470 W, and increases at 500 W. The dependence of DR on the incident microwave power was similar to that of the electron density.

Conclusion

A large diameter uniform ECR plasma was produced with MSA, and the uniformity was within 5% over 200 mm in diameter. Hydrogenated amorphous silicon films with a large area were deposited using ECR plasmas. The average deposition rate was 35 nm/min at the silane flow rate of 10 sccm. The energy band gap decreased to 1.75 eV as the substrate temperature was increased. It is concluded from the results described above that MSA is suitable for the deposition of thin films with a large area. The films were deposited over about 200 mm in diameter, and the diameter of the films was almost the same as that of the plasma. In order to obtain the more uniform thin films, it will be necessary to control a shape or a position of a gas feeder.

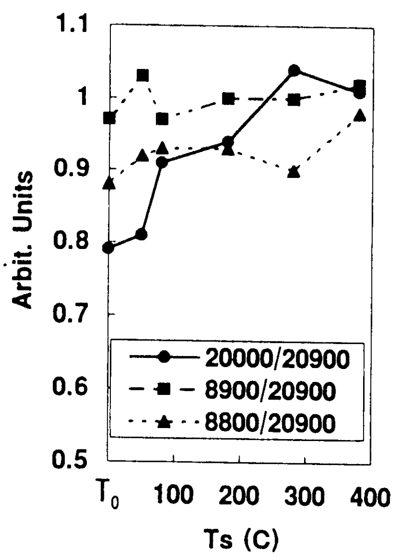

Figure 8. Dependence of the normalized absorption constants for Si–H vibrational modes on T_s (the temperature of the substrate): Si–H stretch (20000 mm^{-1}), Si–H_2 scissors (8800 mm^{-1}) and $(Si–H_2)_n$ wagging mode (8900 mm^{-1}) normalized to Si–H_2 (20900 mm^{-1}) stretch.

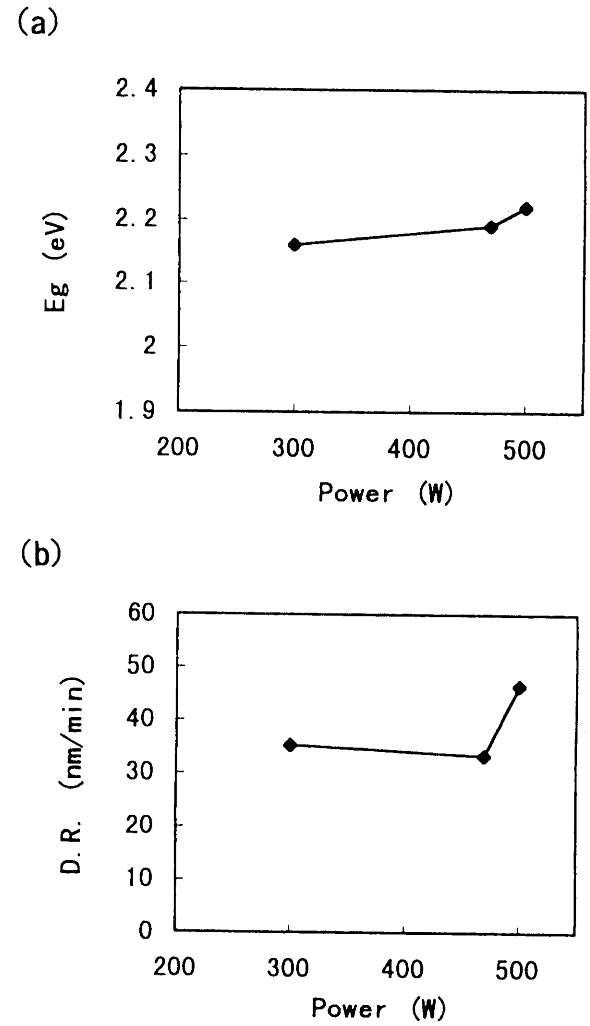

Figure 9. Dependence of (a) the optical band gap and (b) the deposition rate on the incident microwave power.

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