Effect of Multi-Polar Magnetic Field on the Properties of Nanocrystalline Silicon Thin Film Deposited by Internal-Type Inductively Coupled Plasma

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An internal linear-type inductively coupled plasma (ICP) source with multi-polar permanent magnets was used to deposit nanocrystalline silicon thin films on a large-area substrate (470 mm × 370 mm), and the effects of a magnetic field on the characteristics of the plasma and deposited film were investigated. By applying the magnetic field, it was possible to obtain a high-density plasma of 2.8 × 10^{11} cm^{-3} at 15 mTorr Ar and 4000 W of RF power, which is about 50% higher than was obtained for the source without the magnetic field. The application of the multi-polar magnet field to the ICP source during the deposition of silicon film using SiH4/H2 also increased the deposition rates of the silicon thin films and the ratio H2/\text{SiH}^+, which transformed the structure of the silicon films deposited on the glass substrates from amorphous to nanocrystalline. Furthermore, the use of the magnetic field increased crystalline volume fraction and dark conductivity while decreasing the absorption coefficient. The improved characteristics were related to the increase in the ionization rate and the dissociation rate of SiH4/H2, which confined the plasma to the chamber volume and avoided losses to the chamber wall. The decrease in the absorption coefficient of the nanocrystalline silicon thin films deposited with a higher H2 percentage and with the magnetic field present is also related to the increase in the crystallization volume fraction. At 70% H2 with the magnetic field present, the nanocrystalline silicon thin films had a high crystalline volume fraction (68%), a dark conductivity of 3.4 E−7 Ωcm^{−1}, a deposition rate of 10 Å/s, and grain sizes of approximately 15 nm.

Keywords: Plasma Enhanced-Chemical Vapor Deposition, Nanocrystalline Silicon Thin Film, Magnet, Internal-Type Antenna, OES, Inductively Coupled Plasma.

1. INTRODUCTION

Nanocrystalline silicon thin films have been studied intensively for application to large-area thin film electronics, such as photovoltaic devices and thin film transistors (TFTs) for flat panel displays (FPDs). These thin films are usually grown with plasma enhanced chemical vapor deposition (PECVD) using silicon-containing gas mixtures such as SiH4 and H2. To increase the photovoltaic conversion efficiency and to improve the mobility of TFT devices, it is necessary to produce nanocrystalline silicon films with higher crystallization percentages, but an increase in the crystallization percentage is generally accompanied by a lower deposition rate and, especially at lower substrate temperatures, lower crystallization percentage is obtained at the same deposition rate. Therefore, to increase the crystallization percentage or to obtain higher deposition rates at lower substrate temperatures when depositing nanocrystalline silicon thin films, researchers have investigated a variety of high-density plasma sources, such as electron cyclotron resonance (ECR) plasma, helicon wave plasma, and inductively coupled plasma (ICP), for the PECVD of silicon films. Of these sources, ICP sources in particular have been studied extensively because of their simple physics and the fact that they can easily be scaled to a large size. One internal linear-type ICP source, the “double comb-type ICP source,” has been investigated for the production of especially large thin films, up to 2,750 mm × 2,350 mm, for application in large-area FPDs.
Magnetic fields have been used with various plasma sources to improve the properties of the plasma.9–11 Even though an internal linear-type ICP source can generate high-density plasmas by itself, the addition of a multi-polar type magnetic field to the internal-type ICP source can further increase the plasma density and the dissociation rate by increasing the path length of energetic electrons and by confining the plasmas in the chamber. In fact, when an internal linear-type ICP was employed for silicon etching using reactive gases, the addition of a magnetic field to the internal linear-type ICP not only increased the etch rate but also improved the etch uniformity on the substrate.12

In this study, we used a double comb-type internal ICP source with a multi-polar magnetic field for the deposition of nanocrystalline silicon and investigated the effects of the magnetic field on the characteristics of SiH$_4$-based plasma. Besides investigating such deposition characteristics as the deposition rate and uniformity, we studied the effects of the multi-polar magnetic field on the properties of nanocrystalline silicon thin films. It is believed that a magnetic-field-enhanced ICP source can increase plasma density and plasma uniformity, which implies that the use of our plasma source for the deposition of nanocrystalline silicon should increase the uniformity of the deposited nanocrystalline silicon as well as the crystallization percentage of the deposited silicon at low temperatures.

2. EXPERIMENTAL DETAILS

Figure 1 shows a schematic diagram of the experimental apparatus used in the experiment. To deposit the nanocrystalline silicon thin films we designed a rectangular plasma processing chamber with inner dimensions of 1,020 mm × 830 mm that held substrate with dimensions 470 mm × 370 mm. Samples were loaded onto the substrate holder in vacuum through a loadlock chamber. The antenna for the internal linear-type ICP was made of 10 mm-diameter copper tubing inside quartz tubing that was 15 mm in diameter and 2 mm in thickness. A series of five linear antennas was embedded in the process chamber, with the antennas connected to an RF power supply (13.56 MHz) through a matching network in an alternating fashion in order to form a “double comb-type antenna.” A multi-polar magnetic field was applied by inserting permanent magnets, each with 3000 G on the magnet surface, in the quartz tubing located above and parallel to the linear internal antennas, as shown in Figure 1. The plasma characteristics with and without the magnetic field were measured using a Langmuir probe (Hiden Analytical, UK, ESP) for Ar.

Corning 1737 glass was used for the substrate, and, to grow nanocrystalline silicon thin films, SiH$_4$ diluted by H$_2$ was fed into the chamber with the operating pressure maintained at 20 mTorr. RF power to the ICP source was fixed at 4000 W while the substrate temperature was maintained at 180 °C. While deposition process was proceeding, an OES (PCM 420 SC-Technology) was used to measure the dissociated species in the SiH$_4$/H$_2$ plasma. To evaluate the crystalline volume fraction of the films at the deposition thickness of 4000 Å (±200 Å), we used Raman spectroscopy (Kaiser Optical System Inc.). The absorption coefficient and the dark conductivity of the 4000 Å thick films deposited were investigated as a function of the H$_2$ percentage in SiH$_4$/H$_2$ by an ultraviolet-visible (UV-Vis) spectrometer (Scinco S-1000) and by a semiconductor characterization system (Keithley 4200), respectively, after the formation of Al coplanar electrodes on the deposited nanocrystalline silicon. The activation energy ($E_a$) of charge carriers was calculated from the temperature-dependent dark conductivity measurements. The nanostructure of the deposited hydrogenated silicon thin film was observed using high resolution transmission electron microscopy (HRTEM, JEOL JEM 3000F).

3. RESULTS AND DISCUSSION

The plasma density from the internal linear-type ICP was measured as a function of RF power from 1000 W to 4000 W for 15 mTorr Ar, either with or without the application of the magnetic field, as shown in Figure 1. The magnetic field was measured using a Langmuir probe located 4 cm below the ICP antenna. The results of the measurements are shown in Figure 2, and, as can be seen in the figure, the plasma density increased almost linearly with increasing RF power both with and without the multi-polar magnetic field. However, for the same RF power, the ICP with the magnetic field had a plasma density that was almost 50% higher than the density without the magnetic field. At 4000 W of RF power, the ICP with the magnetic field produced a plasma density of approximately 2.8 × 10$^{11}$ cm$^{-3}$. The presence of a magnetic field results in a higher plasma density because of the increased confinement of the plasma within the chamber as well as the
increased path lengths of the energetic electrons. The magnetic field at each magnet’s surface was about 3000 G, while the magnetic field measured near the antenna line was approximately 10 G. The electron cyclotron frequency near the antenna line was calculated to be about $f_{ce} = 28$ MHz, while the ion cyclotron frequency was about $f_{ci} = 0.38$ KHz. Because of the gyromotion of the energetic electrons formed in the plasma, the ions travel a longer path length before they are collected at the chamber wall, which results in an increase in the plasma density. Furthermore, the magnetic field formed between the chamber wall and the antenna by the multi-polar magnets causes the mobility of electrons moving perpendicular to the antenna line and, especially, those moving toward the chamber wall located close to the antenna line to be significantly decreased, which in turn causes the plasma to be confined effectively in the chamber without losing charged particles to the chamber wall near the antenna.

Using 4000 W of RF power, which was the level that produced the highest plasma density, we investigated the degree of dissociation of the SiH$_4$/H$_2$ gas mixture using OES. The total flow rate of SiH$_4$/H$_2$ was maintained at 200 sccm, and the working pressure was maintained at 20 mTorr. Figure 3 shows the OES data for H$_2^*/$SiH$_2^*$ measured as a function of H$_2$ dilution from 10% to 70%. The optical emission peaks of SiH$_2^*$ and H$_2^*$ were measured to be at 413 nm and 656 nm, respectively. As shown in the figure, as the H$_2$ percentage in the gas mixture increased, the ratio H$_2^*/$SiH$_2^*$ increased almost linearly both with and without the magnetic field. For each fixed H$_2$ percentage, the ratio of H$_2^*/$SiH$_2^*$ was higher for the ICP with the magnetic field; at 70% H$_2$, for example, the ratio was about 3.7 for the ICP without the magnetic field and about 4.4 with the magnetic field. Thus the addition of the multi-polar magnetic field enhanced the dissociation of the gas mixture while increasing the percentage of hydrogen radicals in the plasma. It has been reported that the amount of hydrogen radicals in the SiH$_4$-based plasma plays an important role in determining the structure of the deposited silicon thin film, with an increase in the percentage of hydrogen radicals in the plasma leading to an increased crystallization percentage for the silicon thin film being deposited.

To investigate the effect that the amount of hydrogen radicals in the SiH$_4$/H$_2$ plasma has on the crystal structure, we investigated the material properties, such as dark conductivity, crystallization percentage, and the absorption coefficient of photon energy, for the silicon deposited by the ICP with and without the magnetic field. Figure 4(a) shows the dark conductivity and crystalline volume fraction of the silicon film as a function of H$_2$ percentage in SiH$_4$/H$_2$ for the ICP with and without the magnetic field. A 4000 Å (±200 Å) thick silicon film was deposited with 4000 W of RF power, 200 sccm of total flow rate, and 20 mTorr of working pressure at a substrate temperature of 180 °C. The crystalline volume fraction ($X_c$) was estimated by deconvoluting the peak obtained from Raman spectroscopy to the amorphous peak (480 cm$^{-1}$) and the crystalline peak (510 cm$^{-1}$ and 520 cm$^{-1}$). As shown in the figure, when the multi-polar magnetic field was turned off, the deposited film showed the characteristics of nanocrystalline silicon when the H$_2$ dilution percentage was higher than 50%, and increasing the H$_2$ percentage to 70% increased $X_c$ to about 63%. On the other hand, when the magnetic field was applied, the deposited film showed the characteristics of nanocrystalline silicon one the H$_2$ percentage reached 30%, and, when the H$_2$ percentage was increased to 70%, the crystalline volume fraction reached 68%. In short, the silicon deposited by the ICP with the magnetic field present showed a higher crystallization volume fraction at the same H$_2$ percentages compared with the silicon deposited by the ICP without the magnetic field. The role of the magnetic field in producing a higher crystallization volume fraction is thought to be related to the higher H$_2^*/$SiH$_2^*$ ratio observed when the magnetic field was present (Fig. 3), that is, related to the
larger number of hydrogen radicals in the plasma caused by the enhanced dissociation of the gas mixture.

The dark conductivity of the deposited silicon thin films in Figure 4(a) showed a trend similar to the one observed for the crystalline volume fraction of the deposited silicon film. As shown in the figure, higher H2 percentages led to deposited silicon films with a higher dark conductivity, and, at a given H2 percentage, the silicon film deposited with the magnetic field present showed higher dark conductivity than the silicon film deposited without the magnetic field. Since the electrical properties of nanocrystalline silicon are known to be related to the degree of crystallization, the increased dark conductivity of the deposited film is believed to be related to the decrease of the number of crystal defects in the deposited silicon.

Figure 4(b) shows the absorption coefficient measured as a function of photon energy for the silicon thin films. Generally speaking, the absorption coefficient increased with increasing photon energy up to 3.0 eV; however, silicon films deposited with higher H2 percentage and with magnetic field present displayed a lower absorption coefficient at a given photon energy. As with dark conductivity, the decreased absorption coefficient in silicon films deposited with higher H2 percentage and with the magnetic field present is related to the increase in the crystallization volume fraction. Because of the indirect energy band gap of crystalline silicon, increased crystallization in the deposited film decreases the absorption coefficient.

Figure 5 shows how the temperature dependence of dark conductivity for silicon thin film deposited with a multi-polar magnetic field varies as a function of H2 percentage during deposition. The dark conductivity was measured for temperatures between room temperature and 573 K, and the charge carrier activation energy was calculated from the equation

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The activation energy can be calculated from the slope of the Arrhenius plot. The activation energy measured as a function of H2 percentage decreased from 0.57 eV to 0.29 eV as the H2 percentage increased. Defects in nanocrystalline silicon thin film lead to a decrease in activation energy because of the increased presence of trapping states. This behavior in the silicon thin films explains the increase in the crystalline volume fraction with increasing H2 percentage.

Figure 6 shows the deposition rate of silicon measured as a function of the percentage of H2 in SiH4/H2 for the ICP both with and without the magnetic field. The deposition condition was the same as for Figure 4. As can be seen from the figure, an increase in the hydrogen percentage in the gas mixture led to a decrease in the deposition rate from 22 Å/s at 10% H2 to 8 Å/s at 70% H2 for the ICP without the magnetic field; thus the increase in the crystallization volume fraction was accompanied by a decrease in the deposition rate. In the case of the ICP with the magnetic field present, the deposition rate also decreased, in this case from 26 Å/s at 10% H2 to 10 Å/sec at 70% H2, which was similar to the pattern seen for the
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Fig. 6. Deposition rate of nanocrystalline silicon thin films as a function of \( \text{H}_2 \) percentage with and without a multi-polar magnetic field present.

ICP without the magnetic field. However, at a given \( \text{H}_2 \) percentage, the deposition rate for the ICP with the magnetic field present was higher than with magnetic field not present. The higher rate of deposition with the magnetic field present is related to the increased dissociation of \( \text{SiH}_4 \) by the gyromotion of the energetic electrons in the plasma.\(^{19-20} \)

Fig. 7. Non-uniformity of nanocrystalline silicon thin films deposited on a glass substrate with an area of 470 mm \( \times \) 370 mm, measured at 4000 W of rf power, 70\% of \( \text{H}_2 \) in \( \text{SiH}_4/\text{H}_2 \), and 20 mTorr of working pressure (a) with a multi-polar magnetic field present and (b) without a multi-polar magnetic field. (\( \square \) 3500–3800, \( \blacksquare \) 3800–4100, \( \blacksquare \) 4100–4400, units: Å).

The deposition uniformity along the substrate area of 370 mm \( \times \) 470 mm was measured at 70\% \( \text{H}_2 \), while keeping the other deposition parameters same as those for Figure 4, and the results are shown in Figure 7(a) for the ICP with the magnetic field present and (b) for the ICP without the magnetic field. The deposition uniformity of the ICP without the magnetic field was approximately 11\%, while that with the magnetic field present was about 9\%, implying that a more uniform deposition can be obtained for the ICP with the magnetic field present. The improvement of the deposition uniformity appears to be related to the plasma confinement effect obtained with the multi-polar field configuration. In Figure 8, grain sizes ranging from 5 to 15 nm can be identified, and the crystallization percent was around 70\%. The multi-polar magnet configuration used in this study decreases the electron mobility in the vertical direction from the antenna line. Thus the increase of deposition uniformity in the presence of the magnetic field is believed to be related to a decrease in charged particle loss near the chamber wall caused by a decrease in electron mobility towards that wall, along with an increase in the plasma density.\(^{13} \)

4. CONCLUSIONS

We investigated the effects of applying a multi-polar magnetic field to a particular type of internal linear ICP (the “double comb-type ICP”) on the device’s plasma characteristics and also on the characteristics of the nanocrystalline silicon thin films deposited using \( \text{SiH}_4/\text{H}_2 \). The applications of such thin films include FPDs and silicon photovoltaic devices. Using the multi-polar magnetic field with the internal-type ICP not only increased the plasma density but also increased the dissociation rate. Furthermore, the use of the magnetic field with the ICP improved the quality of the deposited silicon thin film by increasing the crystallization volume fraction and the dark conductivity and decreasing the absorption coefficient of photon
energy. The improvement of the plasma characteristics and the material characteristics in the presence of the magnetic field is believed to be due to plasma confinement in the chamber volume, which decreases the mobility of electrons moving in a vertical direction from the antenna line and increases the path lengths of energetic electrons by causing a gyromotion. The plasma confinement created by the magnetic field also leads to a higher deposition uniformity. Using the double comb-type ICP with the magnetic field present, we were able to deposit nanocrystalline silicon thin films having a crystallization volume fraction of 68% at a deposition rate of 10 Å/s when using 4000 W of RF power at 20 mTorr of SiH4/H2 (70% H2) and a substrate temperature 180 °C. Most of the grain sizes in the film ranged from 5 to 15 nm.

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References and Notes