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Characteristics of hydrogenated silicon thin film deposited by RF-PECVD using He–SiH_4 mixture

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ABSTRACT

Nanocrystalline silicon thin films (nc-Si:H) were deposited using He as the dilution gas instead of H_2 and the effect of the operating pressure and rf power on their characteristics was investigated. Especially, operating pressures higher than 4 Torr and a low SiH_4 containing gas mixture, that is, SiH_4(3 sccm)/He(500 sccm) were used to induce high pressure depletion (HPD) conditions. Increasing the operating pressure decreased the deposition rate, however at pressures higher than 6 Torr, crystallized silicon thin films could be obtained at an rf power of 100 W. The deposition of highly crystallized nc-Si:H thin film was related to the HPD conditions, where the damage is decreased through the decrease in the bombardment energy at the high pressure and the crystallization of the deposited silicon thin film is increased through the increased hydrogen content in the plasma caused by the depletion of SiH_4. When the rf power was set at a fixed operating pressure of 6 Torr, HPD conditions were obtained in the rf power range from 80 to 100 W, which was high enough to dissociate SiH_4 fully, but meantime low enough not to damage the surface by ion bombardment. At 6 Torr of operating pressure and 100 W of rf power, the nc-Si:H having the crystallization volume fraction of 67% could be obtained with the deposition rate of 0.28 nm/s.

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1. Introduction

Hydrogenated nanocrystalline silicon (nc-Si:H) thin film has been considerably studied during the last two decades, due to its electrical and optical properties and stability against light-induced degradation (LID). Although there are many processes that can be used to deposit nanocrystalline silicon thin films, plasma enhanced chemical vapor deposition (PECVD) has generally been used.

To obtain nc-Si:H during PECVD, the processing parameters, such as the H_2 dilution, substrate temperature, power density, operating frequency, pressure, etc., need to be optimized [1–3]. Increasing the percentage of hydrogen increases the percentage crystallization of the deposited Si:H, however it also decreases the deposition rate significantly. This decrease in the deposition rate can be partially compensated by using a higher rf power, however it is known that this also tends to decrease the percentage crystallization, as well as decreasing the grain size of the nanocrystalline structure [4]. One of the well-known methods of increasing both the deposition rate and percentage crystallization of nc-Si:H is to use very high frequency (VHF) rf power. By using VHF instead of a conventional 13.56 MHz rf frequency, even though the distance of energy delivery in the plasma is decreased, the electrons are trapped in the VHF electric field and high density plasmas with low electron temperatures are obtained by the trapping effect [5].

nc-Si:H films deposited by VHF PECVD are also known to have few crystalline defects possibly, due to the decreased ion bombardment effect, in addition to the increased deposition rate and percentage crystallization [6]. However, due to the standing wave effect caused by the short wavelength, it is difficult to achieve a uniform plasma using a large area plasma source. Even though various methods such as split electrodes or split power, etc. are investigated to improve the plasma uniformity over a large area, it remains to be a major problem [7,8] and, consequently, various deposition processing techniques have also been investigated using conventional 13.56 MHz rf power in an attempt to obtain high percentage crystallization in addition to a low electron temperature, one of which is to use high pressure depletion (HPD) conditions. The HPD condition uses a high pressure and a low SiH_4 gas concentration in the feed gas, as a result of which the electron temperature is decreased by using an operating pressure higher than a few Torr and SiH_4 is depleted during the deposition due to its low concentration [9]. Even though the HPD condition has been extended to function with VHF, the deposition mechanism in this

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case is not well understood [10,11]. The deposition of nc-Si:H using various inert gases as the additive gas instead of H_2 has also been investigated, in an attempt to obtain high quality nc-Si:H thin films [12,13]. Among the various inert gases, He has the lowest mass, similar to that of hydrogen, and because of this and due to its non-reactivity with the deposited silicon thin film, metastable He* and He^+ ions are known to activate the thin film surface during their bombardment without severely damaging the surface.

The deposition of silicon thin film with SiH_4/He instead of SiH_4/H_2 has been investigated by other researchers previously [14,15], but the operation of SiH_4/He under HPD conditions and the properties of the resulting nc-Si:H thin film deposited with SiH_4/He have never been investigated. Therefore, in this study, nc-Si:H was deposited by a capacitively coupled rf (13.56 MHz) plasma source under HPD conditions using He as the dilution gas instead of H_2 and the effect of the operating conditions, such as the operating pressure and rf power, on the structural and optical characteristics of nc-Si:H was investigated.

2. Experiment

Hydrogenated silicon thin films were deposited on 1737 corning glasses and p-type Si substrates using a conventional parallel plate type capacitively coupled PECVD system operated at 13.56 MHz with SiH_4/He gases. Prior to the deposition, the reaction chamber was evacuated by a dry pump while maintaining the substrate temperature at 200 °C. The effect of various dilution gases, viz. Ar, H_2, and He, added to SiH_4 on the deposition rate and degree of crystallization was investigated at a constant dilution gas flow rate of 500 sccm added to 3 sccm of SiH_4 while keeping the operating pressure at 2.5 Torr and the rf power at 100 W. Each gas mixture was fed into the chamber by introducing Ar, H_2, He and SiH_4 through separate gas lines. The gas flow rates were controlled by mass flow controllers (MFC) and the chamber pressure was maintained at a predetermined value using a throttle valve. After comparison with other gas species, the characteristics of the helium condition were determined. The total flow rate of the gas composed of SiH_4 (3 sccm) and He (500 sccm) was kept constant, while the applied rf power was varied from 25 to 140 W and the processing pressure in the reaction chamber was varied from 4 to 7 Torr.

The optical emission intensities afforded by the dissociated species in the SiH_4/He plasmas were observed using optical emission spectroscopy (Avaspec-3648) and the plasma potentials of the SiH_4/He plasmas were measured using a Langmuir probe (Hiden Co. ESP) to estimate the ion bombardment energy onto the substrate during the deposition. The deposition rate was estimated by a step profilometer (Alpha step; Tencor 500). For material characterization, X-ray diffraction (XRD, Bruker D8 Discover) was carried out for the estimation of the crystallization orientation and the crystalline size. Raman spectroscopy (Kaiser Optics RXN 1) was also carried out by means of a laser Raman spectrometer using the 633 nm line of a He–Ne laser for the estimation of percentage crystallization of the deposited thin film. The laser light was focused on the sample through a Leica DMLP microscope. Fourier transform-Infrared spectroscopy (FTIR, bruker IFS-66/S) was used for the estimation of the hydrogen content in the deposited thin film by measuring the peak intensity near a wave number of 640 cm^{-1}. UV–vis spectroscopy (Shimadzu UV-3600) was used for the measurement of the optical band gap energy of the deposited thin film.

3. Results and discussion

The effect of the various dilution gases, viz. Ar, H_2, and He, added to SiH_4 on the deposition rate and degree of crystallization was investigated for a constant dilution gas flow rate of 500 sccm added to 3 sccm of SiH_4 while keeping the operating pressure at 2.5 Torr and the rf power at 100 W, and the results are shown in Fig. 1. The crystallization volume fraction (Xc) was estimated using Raman spectroscopy by the deconvolution of the peak intensity into the amorphous ($I_{480cm-1}$) and crystalline ($I_{510cm-1}$ and $I_{520cm-1}$) components. As shown in Fig. 1, for the deposition of silicon thin film, the use of He as the dilution gas resulted in deposition rates as high as 0.48 nm/s, while the use of Ar and H_2 as the dilution gas gave rise to deposition rates of less than 0.15 nm/s, even though it led to an Xc of about 50%. Therefore, the use of He as the dilution gas resulted in a much higher deposition rate compared to Ar and H_2 even though amorphous silicon was deposited. The increased deposition rate obtained with He instead of Ar and H_2 appears to be related to the enhanced dissociation of SiH_4 caused by the collision of SiH_4 with the metastable He* (20 eV) abundant in the plasma in addition to He^+ ions (24_eV). Therefore, to investigate the deposition conditions required to produce silicon thin films with a highly crystallized phase at a high deposition rate, the deposition characteristics with SiH_4/He were further studied.

The deposition of hydrogenated silicon thin films using a SiH_4/He mixture was investigated as a function of the operating pressure to obtain the HPD condition and the deposition rate and Xc were measured as a function of the operating pressure in the range from 4 to 7 Torr are shown in Fig. 2. The gas flow rates of SiH_4 and He were kept fixed at 3 sccm and 500 sccm, respectively. The rf power was kept at 100 W and the substrate temperature was also maintained at 200 °C. As shown in Fig. 3, with increasing operating pressure from 4 to 7 Torr, the deposition rate decreased monotonically from about 0.36 to 0.2 nm/s, while Xc increased from 0 (amorphous up to 5 Torr) to 67.1% at 6 Torr and further to 77.8% at 7 Torr.

The optical emission intensities from He*(586 nm) and H_α (656 nm) in the SiH_4/He plasmas for the operating conditions in Fig. 2 were measured using optical emission spectroscopy as a function of the operating pressure and the results are shown in Fig. 3. Due to the small percentage of SiH_4 in the gas mixture, the optical emission peaks from SiHx could not be measured precisely. As shown in the figure, increasing the operating pressure decreased the optical emission intensity from He*. However, the optical emission intensity from H_α showed a minimum at around 5 Torr in the range of operating pressure from 4 to 7 Torr. In Fig. 3, the plasma potential measured as a function of the operating pressure with a Langmuir probe is also shown to estimate the ion

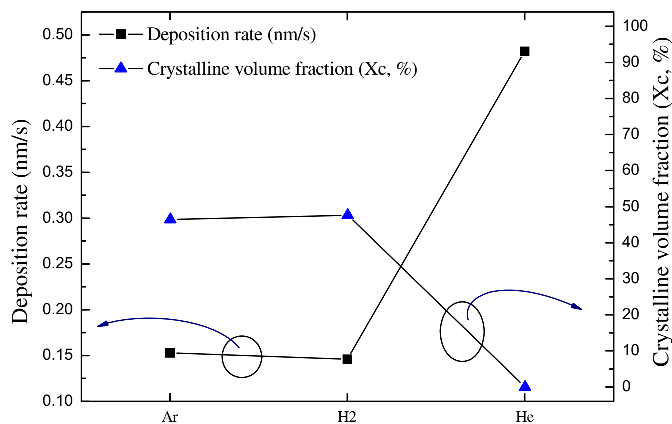


Fig. 1. Deposition rate and crystalline volume fraction of the deposited silicon thin film for the different dilution gases of Ar, H_2, and He at the same gas dilution ratio of SiH_4 (3sccm)/dilution gas (500 sccm), operating pressure of 2.5 Torr, rf power of 100 W, and substrate temperature of 200 °C.

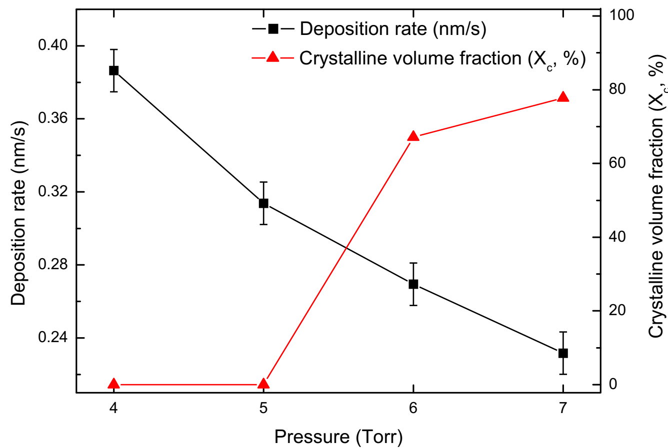
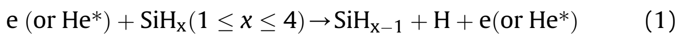


Fig. 2. Deposition rate and crystalline volume fraction measured as a function of operating pressure from 4 to 7 Torr. SiH_4 (3 sccm) and He (500 sccm) were used as the gas mixture, the rf power was kept at 100W, and the substrate temperature was maintained at 200 °C.

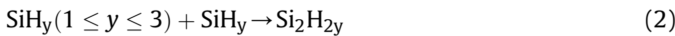
bombardment energy on the substrate. As shown in the figure, increasing the operating pressure from 4 to 7 Torr decreased the plasma potential from about 40 to about 30 V, indicating that the ion bombardment energy decreased with increasing operating pressure.

The decrease of the silicon thin film deposition rate with increasing operating pressure in Fig. 2 is believed to be related to the decreased electron energy and/or decreased density of metastable He* in the plasma, as shown in Fig. 3, which can be used to dissociate the SiH_4 through the following reaction.;



$$e\ (\text{or He}^*) + SiH_x(1 \le x \le 4) \rightarrow SiH_{x-1} + H + e(\text{or He}^*) \quad (1)$$

In addition, as the operating pressure is increased, the recombination between the dissociated species, such as through the following reaction, is increased.



$$SiH_y(1 \le y \le 3) + SiH_y \rightarrow Si_2H_{2y} \quad (2)$$

The recombined species such as Si_2H_{2y} in addition to H_2 and SiH_4 tend not to get involved in the formation of the thin film, due to their volatility and structural stability. Therefore, due to the decreased dissociation of SiH_4 and increased recombination with increasing operating pressure, the silicon deposition rate decreased with increasing operating pressure. However, the formation of a crystallized structure and the increase of Xc with increasing operating pressure at pressures higher than 5 Torr appear to be related to the formation of the HPD condition at such pressures. As shown in Fig. 2, at pressures up to 5 Torr, the optical emission intensity from H_α decreases, due to the decrease in the extent of the reaction (1). However, when the operating pressure is higher than 5 Torr, the optical emission intensity from H_α increases with increasing operating pressure, possibly due to the depletion of SiH_4 at the high pressure. In fact, it is well-known that atomic hydrogen, H, can easily dissociate SiH_4 through the following reaction to form H_2 [9].

$$H + SiH_4 \rightarrow SiH_3 + H_2 \quad (3)$$

Therefore, the depletion of SiH_4 at a high operating pressure will suppress reaction (3) and thereby increase the amount of atomic hydrogen in the plasma, even though the decrease in reaction (2) at the high operating pressure tends to decrease the amount of atomic hydrogen. The presence of atomic hydrogen can contribute to the increased crystallization of the film by removing the lose silicon atoms on the growing silicon surface. It is believed that, even though the amount of dissociated hydrogen may be small due to the small percentage of SiH_4 in the SiH_4/He gas mixture used in the experiment, the increased number of hydrogen atoms in the plasma can also help to increase the crystallization of the silicon film. Increasing the operating pressure also decreases the bombardment energy by ions such as He^+, H^+, etc., as shown by the decrease of the plasma potential with increasing operating pressure in Fig. 3. Therefore, the surface damage caused by the plasma decreases with increasing operating pressure. Consequently, the formation of a crystallized structure at pressures higher than 6 Torr appears to be related to the increased amount of atomic hydrogen in the plasma and the decreased surface damage caused by the decreased ion energy on the growing silicon film, which are believed to be related to the HPD condition.

Fig. 4 shows the effect of the operating pressure on the hydrogen content (C_H) and optical band gap energy (E_{opt}) of the deposited silicon thin film for the deposition conditions in Fig. 2. As shown in the figure, increasing the operating pressure from 4 to 7 Torr decreased the percentage of hydrogen in the film from 13.7% to about 5%, indicating that the crystallinity in the deposited film

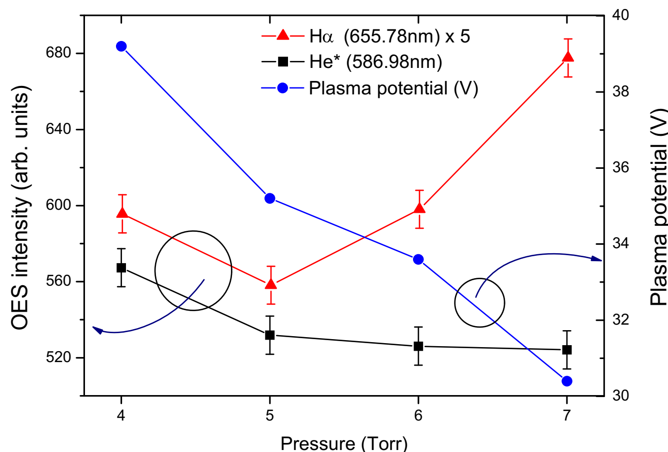


Fig. 3. Optical emission intensities from He* and H_α in the SiH_4/He plasmas for the operating conditions indicated in Fig. 2. The plasma potential measured as a function of the operating pressure with a Langmuir probe is also shown to estimate the ion bombardment energy on the substrate.

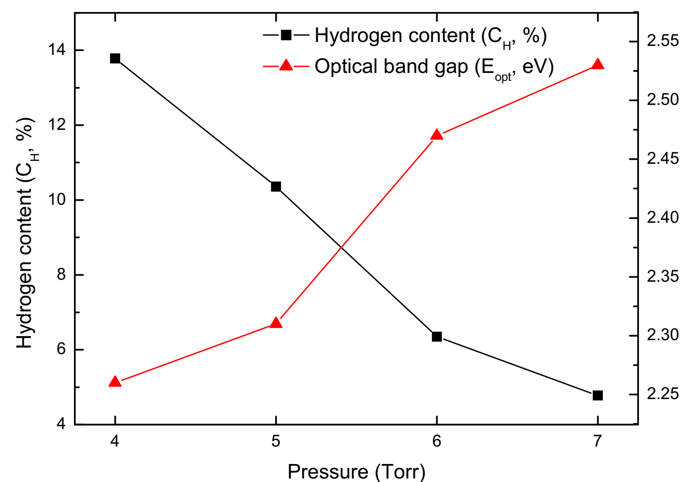


Fig. 4. Hydrogen content and optical band gap of the deposited silicon thin film measured as a function of the operating pressure for the deposition conditions in Fig. 2.

increased with increasing operating pressure. Also, the observed increase of E_{opt} from 2.26 to 2.53 eV with increasing operating pressure from 4 to 7 Torr also appears to indicate that the crystallinity in the deposited silicon thin film was increased. The value of E_{opt} obtained in our experiment was higher than that of amorphous silicon (1.7 eV) and is believed to be related to the formation of nanosize crystal particles in the deposited thin film. The formation of nanosize crystal particles in the deposited silicon thin film increases the optical scattering and, as the crystallinity of the deposited silicon thin film increases, the number of nanosize crystal particles is increased and this increases the optical absorption significantly, resulting in a higher E_{opt}, which is known as the quantum size effect [16].

The HPD condition obtained at a given operating pressure in Fig. 2 can be varied by adjusting the rf power to the plasma, because the depletion condition of SiH_4 is also dependent on the electron energy and electron density in the plasma. Therefore, while keeping the operating pressure at 6 Torr with SiH_4(3 sccm)/He(500 sccm) and a substrate temperature at 200 °C, the rf power was varied from 25 to 140 W to investigate the effect of the rf power on the silicon deposition characteristics near the HPD condition.Fig. 5 shows the effect of the rf power on the deposition rate and Xc. As shown in the figure, increasing the rf power initially increased the deposition rate up to 50 W from 0.18 to 0.28 nm/s, however, further increasing the rf power to 140 W did not increase the deposition rate (in fact, a slight decrease of the deposition rate was observed). Crystallization was observed when the rf power exceeded 50 W and showed a maximum of 67% at 100 W, while further increasing the rf power to 140 W decreased the Xc value to 51%.

Fig. 6 shows the optical emission intensities from He* and H_α in the SiH_4/He plasmas measured using OES and the plasma potentials of the SiH_4/He plasmas measured using the Langmuir probe for the conditions indicated in Fig. 5. As shown in the figure, the optical emission intensities from He* and H_α increased with increasing rf power, indicating that the electron energy/electron density in the plasma and dissociation of SiH_4 in SiH_4/He were both increased. The observed increase of the plasma potential from 25 to 45 V with increasing rf power from 25 to 140 W indicates that the ion bombardment energy increased with increasing rf power.

The increase of the deposition rate while retaining an amorphous structure at an rf power lower than 50 W in Fig. 5 is therefore believed to be related to the non-HPD condition due to the lesser dissociation of SiH_4 at the low rf power. As the rf power is increased

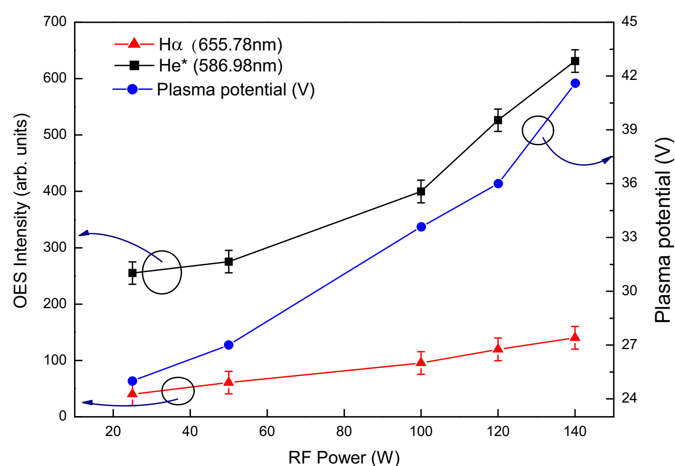


Fig. 6. Optical emission intensities from He* and H_α observed using OES and the plasma potential measured using a Langmuir probe in the SiH_4/He plasmas as a function of the rf power for the operating conditions in Fig. 5.

to 80 W and above, the HPD condition is reached due to the complete dissociation of SiH_4 caused by the enhanced electron energy/electron concentration and the deposition rate is nearly saturated due to the complete dissociation of SiH_4, while a crystallized structure is obtained by hydrogen assisted crystallization. However, when the rf power is higher than 100 W, due to the increase of the ion bombardment energy/flux, as shown by the increase of the plasma potential with increasing rf power, the Xc value is decreased, due to the increased damage caused by the ion bombardment. In addition, the slight decrease of the deposition rate at rf powers higher than 100 W appears to be related to the sputtering of the deposited silicon thin film.

Fig. 7 shows the hydrogen content and E_{opt} measured as a function of the rf power for the conditions in Fig. 5. The hydrogen content decreased from 10.3 to 6.4% with increasing rf power from 25 to 140 W, while E_{opt} increased from 2.33 to 2.49 eV with increasing rf power from 25 to 100 W and further increasing the rf power to 140W decreased E_{opt} to 2.34 eV. The initial decrease of the hydrogen content and increase of E_{opt} with increasing rf power is believed to be related to the crystallization of the deposited silicon afforded by obtaining the HPD condition. However, the decrease of E_{opt} as the rf power is further increased above 100W is believed to

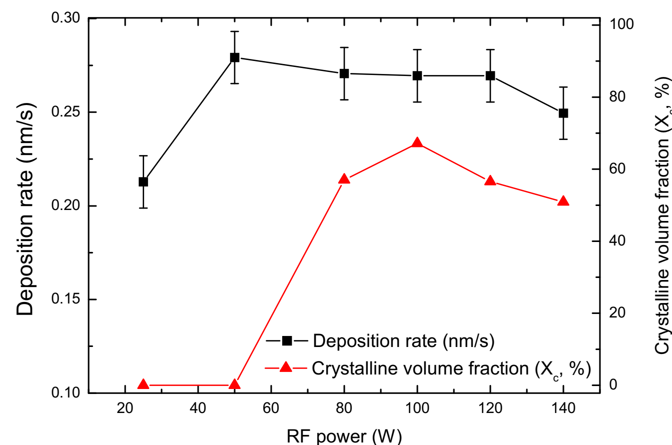


Fig. 5. Deposition rate and crystalline volume fraction measured as a function of rf power. SiH_4 (3 sccm) and He (500 sccm) were used as the gas mixture at an operating pressure of 6 Torr and substrate temperature of 200 °C.

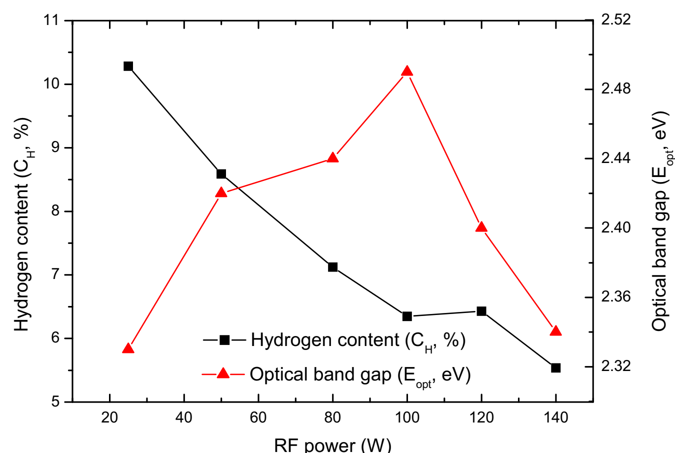


Fig. 7. Hydrogen content and optical band gap of the deposited silicon thin film measured as a function of the rf power for the deposition conditions in Fig. 5.

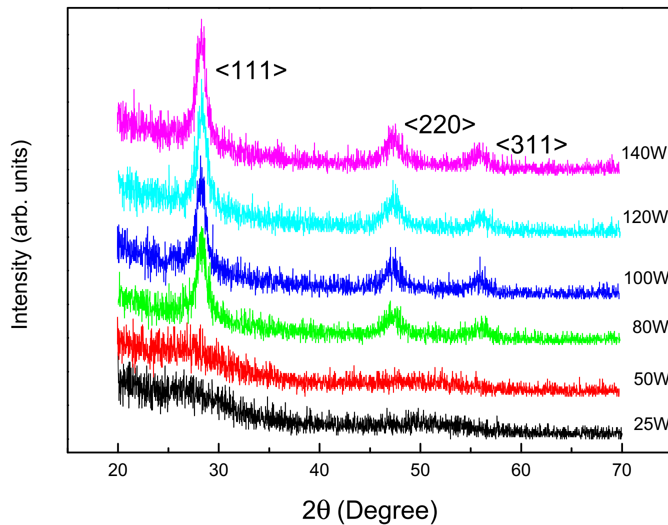


Fig. 8. XRD patterns for the silicon thin films deposited as a function of the rf power with the conditions in Fig. 5.

be related to the decreased crystallization or increased damage of the deposited silicon thin film caused by the increased ion bombardment.

Fig. 8 shows the XRD patterns for the silicon thin films deposited with the conditions indicated in Fig. 5. As shown in the figure, crystallization was observed from an rf power of 80W, with diffraction peaks being observed at 2θ values of ~28°, ~47° and ~56°, which correspond to the <111>, <220>, and <311 > crystallographic planes, respectively, and the peak was saturated at an rf power of 100–120 W. Therefore, the XRD data indicate the initiation of crystallization at an rf power of 80 W and that the highest percentage crystallization is obtained at an rf power of 100–120 W, which are similar to the results shown in Fig. 5 for the Xc value. When the crystal size was calculated from the full width at half maximum of the <111 > diffraction pattern peaks using Scherrer's formula, it was found that nanosize grains in the range of 10–15 nm could be obtained for rf powers in the range of 80–140 W.

4. Conclusions

SiH_4/He was used to deposit nc-Si:H at a high deposition rate utilizing the HPD condition by varying the operating pressure and 13.56 MHz rf power at a fixed SiH_4/He gas flow rate using a conventional capacitively coupled plasma system. The use of SiH_4/He resulted in a higher silicon deposition rate compared to SiH_4/H_2 or SiH_4/Ar, possibly due to the increased dissociation of SiH_4 caused by the metastable He* atoms in the plasma. By increasing the operating pressure to 7 Torr at a fixed SiH_4(3 sccm)/He(500 sccm) gas flow rate and a fixed rf power of 100 W, the increase of the crystallization of the deposited thin film to 77.8% at a relatively high deposition rate of 0.2 nm/s could be obtained, due to the increased hydrogen atom assisted crystallization and the decreased damage to the substrate at the higher operating pressure afforded by the HPD condition. To obtain the HPD condition, the rf power was also required to be chosen carefully because, at rf powers equal to and lower than 50 W, the HPD condition is not achieved, due to the lower dissociation of SiH_4, whereas at rf powers equal to and higher than 120 W, the surface is damaged and the crystallization is decreased, due to the increased ion bombardment onto the surface. It is believed that the use of SiH_4/He with carefully chosen HPD conditions is beneficial in obtaining highly crystallized nc-Si:H with a uniform and relatively high deposition rate using a conventional 13.56 MHz capacitively coupled plasma system, which is beneficial for depositing the film uniformly on a large area substrate without having a standing wave problem.

Acknowledgments

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