Better control over the onset of microcrystallinity in fast-growing silicon network

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In view of obtaining a Si:H network at the onset of microcrystallinity at a high deposition rate, we have adopted an intelligent approach to find out a tricky plasma condition in radio frequency (rf) plasma-enhanced chemical vapor deposition that provides a better control on growth introducing retarded microcrystallization. The deposition parameter includes a combination of high electrical power applied to the (SiH_4+H_2)-plasma and high gas pressure in the reaction chamber. High rf power increases the number density of film-forming precursors as well as atomic H density in the plasma, which helps to increase the film deposition rate and to promote microcrystallinity, respectively. In addition, high pressure helps not only to increase the film-growth rate by producing a dense plasma but also retards the microcrystallization process by increasing significantly the gas phase collision frequency and consequently reducing the effective reactivity of atomic H on the surface of a fast-growing Si:H network. A combination of high-power and high-pressure plasma conditions provides a reasonably wide range of H_2 dilution to work with and better control in producing a Si:H network at the onset of microcrystallinity, while increasing the film-growth rate.

I. INTRODUCTION

Hydrogenated silicon (Si:H) films, both in amorphous and microcrystalline form, are very useful in thin film technologies, e.g., in the fabrication of devices like solar cells and thin film transistors. The μc-Si:H is a mixed phase material with a composition of crystalline grains embedded in an amorphous matrix and the degree of microcrystallization is determined by the crystalline volume fraction of the network. Because of the favorable combination of high carrier mobility and high doping efficiency μc-Si:H thin films are in significant use as component layers in solar cells. However, when used as intrinsic absorber layer in solar cell, it is required in large thickness of about 2–3 μm because of its low absorption of solar radiation. Moreover, the stringent condition required for the fabrication of μc-Si:H films by conventional plasma-enhanced chemical vapor deposition (PECVD) contributes a very low deposition rate, and that stands against the cost-effective throughput of the device using this material. On the contrary, the most stable a-Si:H based solar cells have been reported to be obtained at just before the onset of microcrystallinity,[1,2] and that has initiated a lot of work dealing with the material in the neighborhood of such structural transition.[3–7] Accordingly, in the present work, we concentrate on the development of Si:H network at the onset of microcrystallinity and simultaneous increase in the film deposition rate with a goal of extending the material in the fabrication of cost-effective and stable solar cells.

II. EXPERIMENTAL

The hydrogenated silicon films were prepared by plasma enhanced chemical vapor deposition using 13.56 MHz radio frequency (rf) power at a substrate temperature of 200 °C. SiH_4 was used as the source gas and H_2 as a diluent to the SiH_4-plasma. The gas pressure in the reaction chamber was kept constant at a relatively high magnitude of 2.0 Torr and the Si:H films were deposited by varying either the H_2 dilution [$Y = H_2/(SiH_4 + H_2)$] or the rf power density (P_{rf}) applied to the glow discharge plasma.

For electrical, optical, and structural studies, samples 7000–8000 Å in thickness were deposited on 7059 Corning glass substrates. Carbon coated copper grids were used for transmission electron microscope (TEM) study. The optical absorption coefficient spectra were obtained from the transmission and reflection measurements by an

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ultraviolet-visible-near infrared (UV-VIS-NIR) double-beam spectrophotometer. The electrical conductivities were measured in a cryostat after annealing the samples at 150 °C under vacuum (~10^{-6} Torr) using Al electrodes in a gap cell configauration. X-ray diffraction pattern was taken using Cu K_α radiation (λ = 1.5418 Å). The Raman spectra of the films were obtained at room temperature using 632.8 nm light from a He–Ne laser in a micro-Raman spectrophotometer, in a back scattering geometry.

III. RESULTS AND DISCUSSION

In view of obtaining a high deposition rate, a set of films were prepared at a rather high rf power of 310 $mWcm^{-2}$ and varying the hydrogen dilution from 93% to 98%, while maintaining a high pressure of 2.0 Torr. Figure 1 shows the variation of the film deposition rate (R_d) with the hydrogen dilution in the plasma. The deposition rate decreased monotonically from 185 to 90 Å min^{-1} due to continuous lowering in the density of film forming precursors on increasing hydrogen dilution, as usual. However, we compare the deposition rates to a series of samples prepared at a relatively low-power (35 mW cm^{-2}) and low-pressure (0.5 Torr) condition as reported earlier.[8] A definite step down in the deposition rate corresponding to a sharp transition of the network from amorphous to microcrystalline structure was demonstrated (as shown by curve 2 in Fig. 1) and that happens to be absent (in curve 1) for the present set of samples identifying a rather gradual network transformation towards crystallinity. In addition, we have attained at least one order of magnitude higher deposition rate at the present parametric condition with a combination of relatively high gas pressure and high electric power applied to the plasma.

Figure 2 represents the variation of dark conductivity (σ_d) and its activation energy (ΔE) as a function of hydrogen dilution (Y). At a low dilution of 93% the film exhibited a low value of $\sigma_d \sim 6.4 \times 10^{-10}$ Scm^{-1} along with a rather high magnitude of $\Delta E \sim 770$ meV, which altogether indicates an amorphous-like network structure. With the increase in Y, σ_d increased gradually along with the simultaneous reduction in ΔE. Up to Y = 94.5% an amorphous dominated network was identified. For Y > 94.5%, a rather fast increase in σ_d along with similar decrease in ΔE was identified, and that indicated a gradual development of crystallinity. However, σ_d attained a peak value of 1.1×10^{-5} Scm^{-1} corresponding to the lowest ΔE = 270 meV at Y = 96%, and on further increase in Y, σ_d reduced gradually to 1.6×10^{-7} Scm^{-1} along with similar increase in ΔE to 630 meV at Y = 98%. When hydrogen dilution to the SiH_4 plasma is increased, although it promotes microcrystallization to the Si network, very high hydrogen dilution adversely affects the microcrystallization process probably by defect creation through atomic hydrogen induced etching of the network.

The optical absorption coefficient (α) spectra of the films have been presented in Fig. 3. The amorphous-like film prepared at Y = 94% contributed rather high optical absorption. On increase in Y, the entire optical absorption coefficient spectrum reduced in intensity and the lowest magnitude of α-spectrum was obtained at Y = 96%.

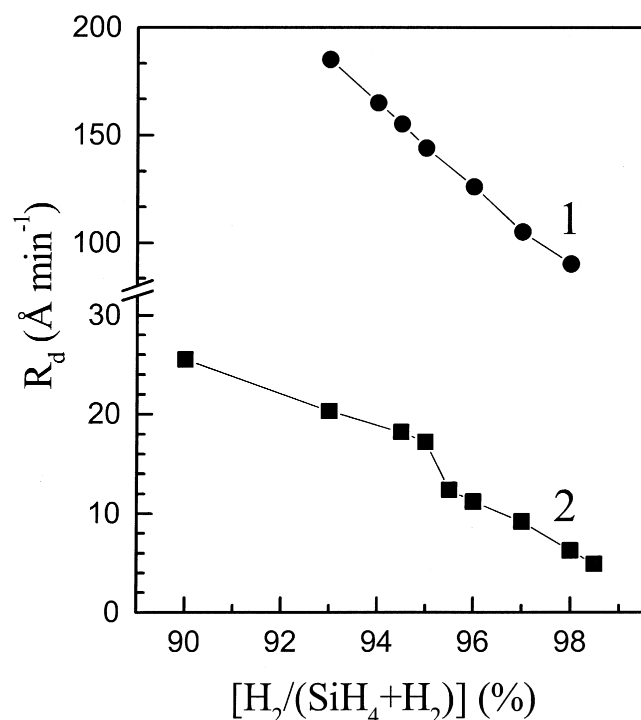

FIG. 1. Variation of film deposition rate with hydrogen dilution at two different power-pressure combinations in the plasma (curve 1 for P_{rf} = 310 mW cm^{-2}, p = 2.0 Torr; curve 2 for P_{rf} = 35 mW cm^{-2}, p = 0.5 Torr).

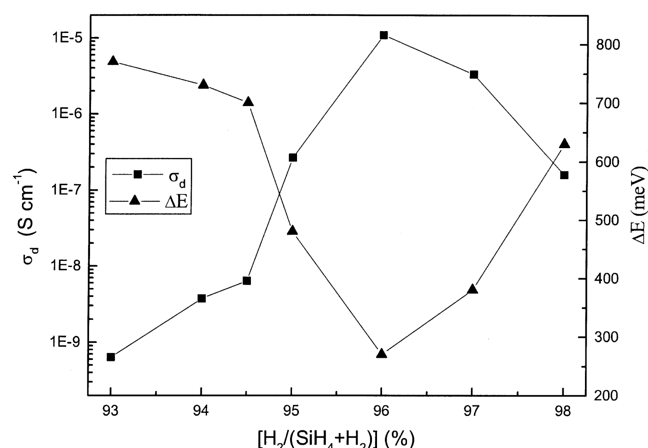

FIG. 2. Variation of dark conductivity (σ_D) and activation energy (ΔE) of the Si:H films deposited at different hydrogen dilution.

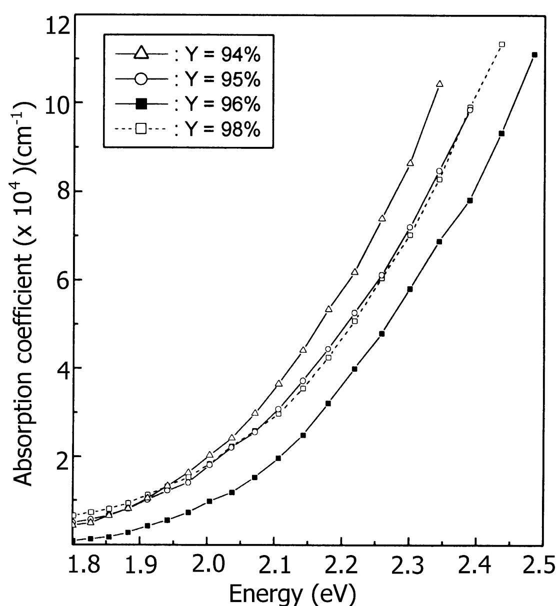

FIG. 3. Optical absorption co-efficient spectra of Si:H films prepared at different hydrogen dilution (Y).

However, on further increase in Y to 98% the α-spectrum again increased in intensity. The gradual reduction in the magnitude of α as Y changed from 94% to 96% might be correlated to the gradual transformation of the Si:H network from an amorphous-like to a microcrystalline-like structure, and further increase in Y to 98% may lead to a deviation from microcrystallinity and/or significant defect creation induced by excess atomic H collision of the growing network in a high-power and high-pressure plasma condition. The variation of optical absorption identified similar nature of changes in the Si:H network structure as indicated by the variations of electrical properties on continuous increase in H_2 dilution to the SiH_4 plasma.

Raman backscattering studies have been performed to estimate the degree of crystallinity as well as the ordering of the network structure. Figure 4 shows the Raman spectra of the films deposited at different hydrogen dilution (Y). Each spectrum in the range 400–560 cm^{-1} was deconvoluted into several satellite spectra. The Raman spectrum for Y = 94.5% exhibited an asymmetric distribution. On deconvolution it contributed a relatively flat Gaussian component (a) peaked at approximately 475 cm^{-1}, which was assigned to TO mode vibration of amorphous silicon (a-Si) and another small but sharp Gaussian component (b) at approximately 505 cm^{-1}. In earlier studies, this b-component in the Raman spectrum was associated to the thermodynamically stable micrograins in the range ⩽ 30 Å[9,10] or to the bond dilation at the grain boundary zone.[11] For Y = 95%, in addition to the above mentioned two satellite spectra, a sharp Lorentzian component (c) at ~518 cm^{-1} corresponding to the TO vibrational mode of crystalline silicon (c-Si) was clearly identified in the Raman spectrum. At Y = 96% the c-component exhibited its dominant contribution, thereby changing the overall shape of the Raman spectrum. The deconvoluted satellite spectra (a), (b), and (c) have been pictorially presented in Fig. 5. However, on further increase in Y, the c-component again reduced in intensity. The overall crystalline volume fraction in the network has been estimated from the simplified empirical relation[12]

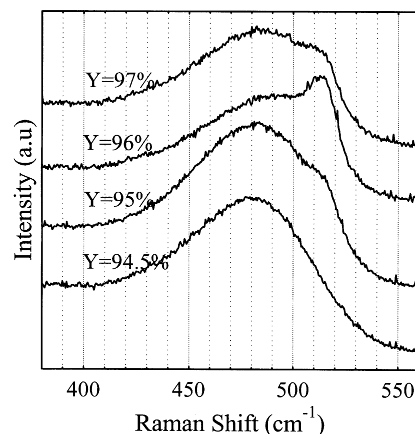

FIG. 4. Raman backscattering spectra of the Si:H films prepared at various hydrogen dilution (Y).

$$f(c) = [I(b) + I(c)]/[I(a) + I(b) + I(c)] \quad ,$$

where I(a), I(b), and I(c) are the integrated intensities corresponding to a, b, and c satellite components in the Raman spectrum, respectively. Figure 6 demonstrates the variation of net crystalline volume fraction in the network while changing the H_2 dilution to the SiH_4 plasma. On increase in H_2 dilution, crystallinity developed in the network, attained a maximum magnitude of <50 % at Y = 96%, and then reduced on further increase in Y.

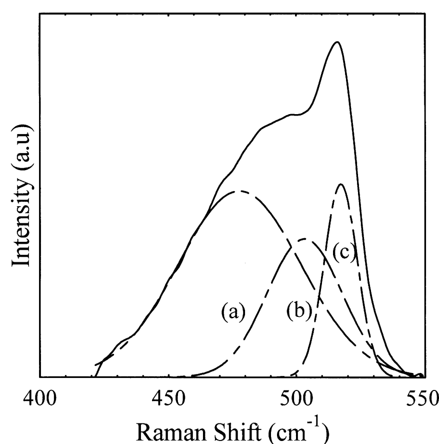

FIG. 5. Deconvoluted Raman spectrum of the film deposited at Y = 96%, where (a), (b), and (c) are the satellite components.

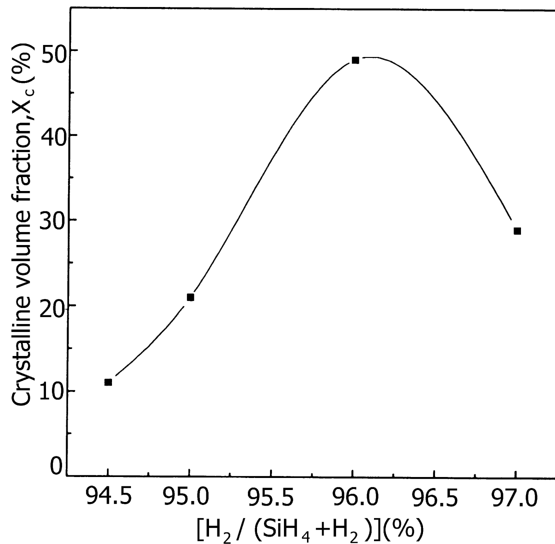

FIG. 6. Variation of crystalline volume fraction of the films prepared at different hydrogen dilution.

The crystallinity in the films has been detected by x-ray diffraction studies. Figure 7 presents the x-ray diffraction pattern for Si:H films prepared at different H_2 dilution. The ⟨220⟩ crystallographic orientation of c-Si has been identified in the diffraction spectra at $2\theta \sim 47°$ for $Y \geqslant 95\%$, and that happens to be absent for lower Y. The crystalline grain size in the films has been estimated from a full width at half-maximum of the ⟨220⟩ diffraction peak, using Scherrer's formula. Figure 8 shows the changes in the grain size with increase in hydrogen dilution. The crystalline grain size increased on H_2 dilution, attained a peak magnitude of 335 Å at $Y = 96\%$ and then reduced on further increase in Y. Chou et al.[13] proposed a model of silicon growth by controlling the

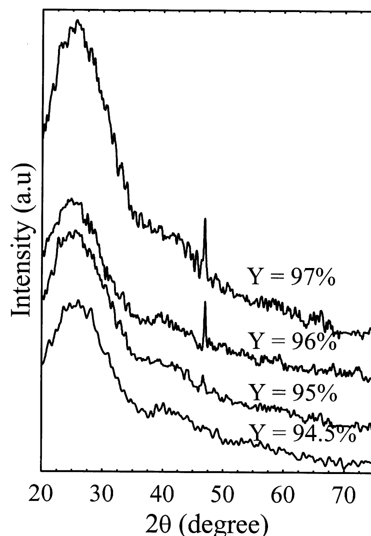

FIG. 7. XRD spectra of the films deposited at different hydrogen dilution (Y).

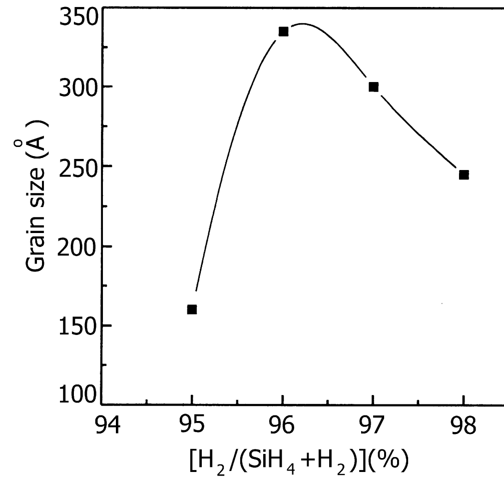

FIG. 8. Variation of grain size (as measured from XRD spectra) of the films deposited at different hydrogen dilution.

surface mean free path of SiH_n and the film-growth rate. On the growing surface, Si-$(SiH_3)_3$ clusters do not have any distorted Si–Si bonds, and they act like seeds. In the case of low hydrogen dilution, a large number of SiH_n radicals arrive at the growth surface per unit time. So the average distance between the clusters becomes much smaller than the mean free path, and the grains are not large enough to detect and the deposited films are amorphous. As the growth rate decreases at higher hydrogen dilution, distance between the clusters tends to increase, and that allows the grains to grow larger. With further increase of hydrogen dilution, the lateral growth rate becomes low, and the average distance between nucleation centers is fixed by mean free path. Then the laterally expanding cluster has a larger probability to form bonds with underlying Si atoms before meeting the neighboring cluster. This results in further reduction in grain size.

The crystallinity of the films has also been identified by transmission electron microscope study. Figures 9(a) and 9(b) represent the transmission electron micrograph of the films prepared at $Y = 96\%$ and 97%. Very small silicon micrograins are homogeneously distributed in amorphous matrix. The diameter of the crystallites are 200 Å for the films deposited at $Y = 96\%$ and it is 150 Å for the films deposited at $Y = 97\%$. In the TEM micrograph, we see that the small dark spots appear as surrounded by dark patches. Dark spots correspond to the silicon micrograins, and dark patches correspond to the grain boundary region that might be correlated to the bond dilation at the grain boundary identified by the intermediate b-component in the Raman spectrum, which appeared in intensity comparable to that of c-Si component.

High hydrogen dilution and high rf power applied to the SiH_4 plasma are two key parameters to attain microcrystallization in Si:H network by PECVD. Both the parameters increase the atomic H density in the plasma,

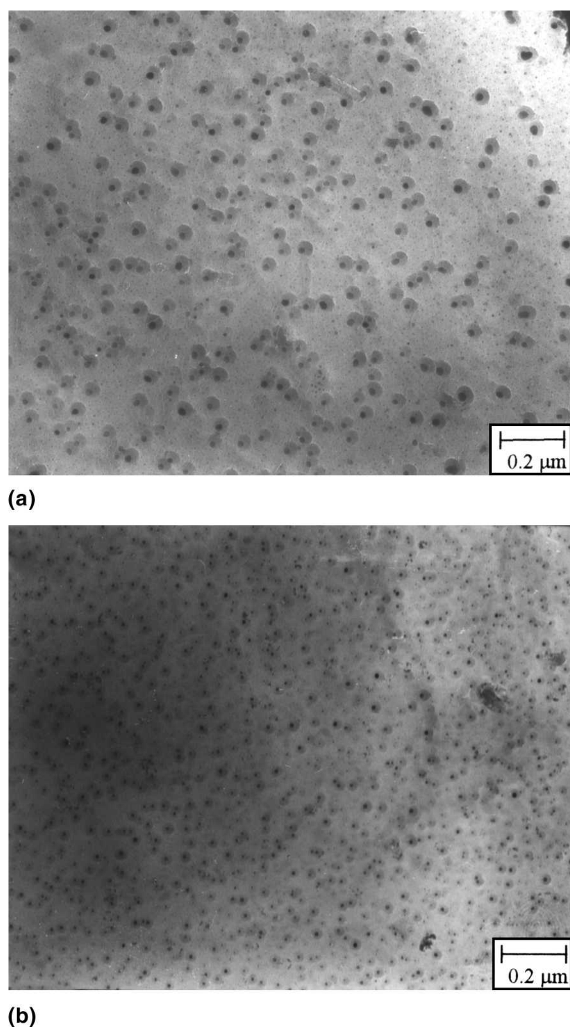

FIG. 9. Transmission electron micrograph of the films deposited at (a) Y = 96% and (b) Y = 97%.

which has been identified as instrumental in promoting microcrystallinity in Si:H films.[14]

In case of a moderately low-power and low-pressure combination at a microcrystalline-like growth condition, it has been generally observed by earlier studies that during increase in H_2 dilution to the SiH_4 plasma, a very sharp transition from amorphous to microcrystalline structure happens to take place and the crystalline volume fraction attains a very high magnitude. Working at rf power density of 35 $mWcm^{-2}$ and gas pressure of 0.5 Torr, our earlier study[8] identified such a sharp transition as H_2 dilution was changed from 95% to 96%, and a maximum crystalline volume fraction of 85% was attained.

In addition to work in favor of improving crystallinity, increasing rf power simultaneously increases the film deposition rate because of supplying higher density of film forming precursors. A combination of high rf power and high gas pressure in the reaction chamber significantly increases the collision frequency of the SiH_n precursors and atomic hydrogen in the plasma. As a result, the effective reactivity of atomic H on the surface of a fast-growing Si:H network happens to reduce drastically and that leads to a retarded crystallization process and a lower degree of ultimate attainable crystallinity.

In the present investigation, a high rf power density of 310 $mWcm^{-2}$, and a relatively high gas pressure of 2.0 Torr has been chosen as the parametric condition. From the experimental results on the variations of deposition rate, electrical conductivity, optical absorption, and the structural studies by Raman spectroscopy, x-ray diffraction (XRD), and TEM, it has been identified that the Si:H network changes quite gradually from amorphous-dominated to a microcrystalline-like structure with increase in H_2 dilution to the SiH_4 plasma. The best crystallinity was attained at a hydrogen dilution of 96% at which a maximum crystalline volume fraction of <50% was obtained. This definitely identifies a retarded crystallization process obtainable at a high-power and high-pressure plasma condition. As the objective of our present investigation is not to find out a very good microcrystalline network rather to obtain Si:H material at the onset of crystallinity and at a high deposition rate, a high-power and high-pressure plasma condition provides a wide H_2 dilution range to work with. Typically, we choose 95% H_2 dilution, which produced a Si:H network contributing $\sigma_d \sim 3 \times 10^{-7}$ Scm^{-1} and ΔE = 460 meV and a crystalline volume fraction f(c) of about 21% with an average grain size of ~160 Å. The material has been obtained at a high growth rate of approximately 144 Å min^{-1} using conventional rf PECVD.

At a H_2 dilution of 95% and gas pressure of 2.0 Torr, another set of films were prepared by increasing the rf power density (P_{rf}) from 310 to 430 $mWcm^{-2}$. Figure 10 shows the variation of electrical properties and that

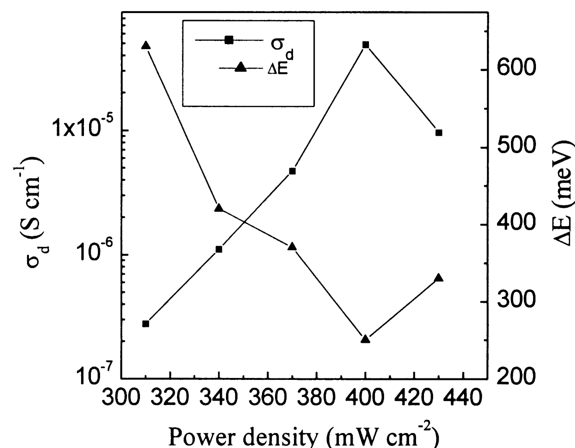

FIG. 10. Variation of dark conductivity (σ_D) and activation energy (ΔE) of Si:H films deposited at different power densities applied to the plasma.

demonstrates gradual increase in σ_d to attain a peak magnitude of approximately 5×10^{-5} Scm^{-1} corresponding to a minimum $\Delta E = 250$ meV at 400 mW cm^{-2} of rf power density, beyond which σ_d reduced and ΔE increased again. The Raman spectra of the films as presented in Fig. 11, demonstrates a gradual increase in the intensity of c-Si component for an increase in P_{rf} up to 370 mW cm^{-2}. At $P_{rf} = 400$ mW cm^{-2}, a sharp rise in the c-Si component introduced a radical change in shape of the corresponding Raman spectrum and identified a significantly microcrystalline dominated network structure. The net crystalline volume fraction increased from 32% to 58% for increase in P_{rf} from 370 to 400 mW cm^{-2} as shown in Fig. 12. On further increase in P_{rf}, however, f(c) reduced to 45%. The film deposition rate increased sharply with increase in P_{rf}. A very high deposition rate of 276 Å min^{-1} was attained at $P_{rf} = 400$ mW cm^{-2}. However on further increase in P_{rf}, the deposition rate reduced and a similar nature of variation of growth rate and the net crystalline volume fraction in the network was obtained as shown in Fig. 12.

The number density of radicals, neutral atoms, and ionic species generated in the (SiH_4 + H_2) plasma increases with the increase in rf power density. Neutral radicals are responsible for the film growth; accordingly, the deposition rate increased with applied rf power. Neutral atoms like hydrogen help to modulate the Si–Si network to attain a rigid structure. Moderate ion bombardment on the growing surface enhances the surface temperature. Such increase in surface temperature helps in crystalline growth in a disorder silicon matrix. Such ion bombardment phenomenon is beneficial up to a certain degree. At higher rf power density excess ion bombardment produces defects in the film. As a consequence crystallinity decreased as rf power was increased beyond 400 mW cm^{-2}. Moreover, significant increase in surface temperature due to much ion bombardment at such high rf power may lead to a lowering in deposition rate. In addition, intense atomic H induced etching of the relatively defective network resulted in a significant reduction in the ultimate growth rate of the deposited film at rf power beyond 400 mW cm^{-2}.

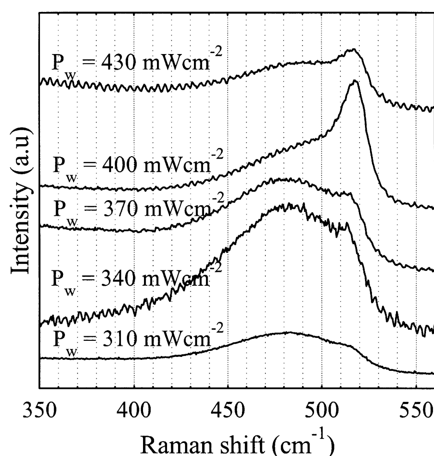

FIG. 11. Raman spectra of the Si:H films deposited at different power densities applied to the plasma.

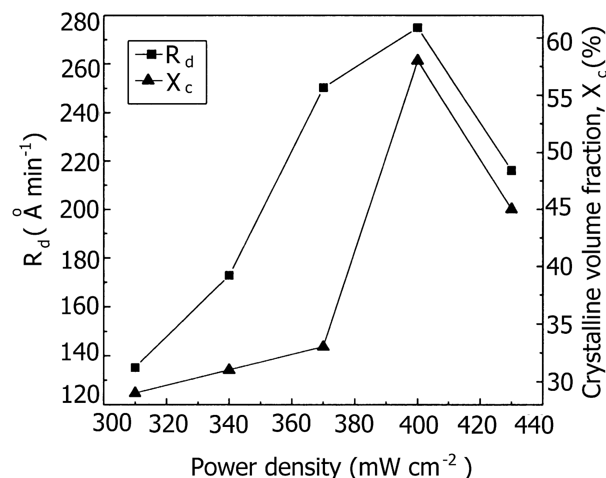

FIG. 12. Variation of film deposition rate and crystalline volume fraction of the films deposited at various power densities applied to the plasma.

With a goal of obtaining Si:H films at the onset of crystallinity at a high deposition rate, a typical parametric condition has been traced out combining a H_2 dilution of 95%, a gas pressure of 2.0 Torr and a rf power density of 370 $mWcm^{-2}$ applied to the plasma; those all together produced a Si:H network contributing $\sigma_d \sim 5 \times 10^{-6}$ Scm^{-1}, $\Delta E = 260$ meV and containing crystalline volume fraction <33% in the network. A high deposition rate of approximately 250 Å min^{-1} for such a desired material seems to be attractive for cost-effective utilization in the fabrication of solar cells by rf PECVD.

IV. CONCLUSIONS

High rf power applied to the SiH_4 plasma, in general, increases the film deposition rate. In addition, high H_2 dilution to SiH_4 is instrumental in promoting microcrystallization in Si:H network. However, increasing H_2 dilution introduces a sharp transition from amorphous to microcrystalline structure at a critical magnitude, and it appears to be very difficult to control the network at the onset of microcrystallinity. In view of obtaining Si:H network at the onset of microcrystallinity at a high deposition rate, we have introduced a tricky plasma condition in rf PECVD that includes a combination of high electrical power applied to the plasma and high gas pressure in the reaction chamber. High pressure helps not only to increase the film-growth rate by producing a dense plasma but also retards the microcrystallization process by increasing significantly the gas phase collision frequency and consequently reducing the effective

reactivity of atomic H on the surface of a fast-growing Si:H network. A combination of high-power and high-pressure plasma condition provides a rather wide range of H_2 dilution to work with and a better control in producing Si:H network at the onset of microcrystallinity, while increasing the film-growth rate.

At a typical parametric condition with H_2 dilution of 95%, a gas pressure of 2.0 Torr and a rf power density of 370 mW cm^{-2} applied to the SiH_4 plasma, Si:H films contributing $\sigma_d \sim 5 \times 10^{-6}$ Scm^{-1}, $\Delta E = 260$ meV and containing <33% crystalline volume fraction in the network have been prepared. A high deposition rate of ~250 Å min^{-1} for such a desired material at the onset of microcrystallinity seems to be attractive for cost-effective utilization in the fabrication of solar cell by rf PECVD.

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