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INFRARED AND RAMAN SPECTROSCOPY STUDIES ON PULSED PECVD a-Si:H FILMS

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ABSTRACT

This work presents a study on the structural properties of hydrogenated amorphous silicon (a-Si:H) prepared by pulsed plasma enhanced chemical vapour deposition (PECVD) technique using Raman and infrared spectroscopy. The bonded hydrogen content and hydrogen bonding configurations in the a-Si:H films were investigated from the Fourier transform infrared (FTIR) spectra of the films. The Raman spectra of the films have been used to obtain evidence of nanocrystallinity in the films. The dependence of silane flow-rates and discharge power on these properties was investigated. Increase in the discharge power resulted in films with lower hydrogen content and increase the dihydride bond concentration. Nanocrystallinity was observed in films prepared at low discharge power at all silane flow-rates but increase in discharge power resulted in films with purely amorphous structure.

INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) films produced by pulsed PECVD technique has been proved to be a respectable material for applications in thin film device technology like in solar cells [1] and thin film transistors (TFTs) [2]. This deposition technique suppresses the dust formation in-a-Si:H films deposited at high deposition rates [3]. This is accomplished by modulating the plasma frequency and varying the ON-time to OFF-time. In such plasma conditions, nanocrystallites are formed in the a-Si:H films structure, improving the stability of the film properties [4]. Besides, by modulating the glow-discharge, the size of the particles generated in the plasma phase and incorporated into the growing film can be monitored [5].
In this work, the structural properties of a-Si:H films obtained by pulsed PECVD techniques are observed using FTIR spectroscopy and Micro-Raman spectroscopy techniques. A comparison between the effects of silane flow-rate and discharge power on the structural properties of the pulsed PECVD a-Si:H films are made and studied.

EXPERIMENTAL DETAILS

The a-Si:H films studied in the work were prepared using a home-built pulsed PECVD system and was deposited on polished c-Si substrates. The pulsed power supply was applied to the PECVD system with the discharge time of 30 seconds and post-discharge time 30 seconds. The 30 seconds discharge time was accomplished using a pulsed

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voltage with a modulation frequency of 10 kHz. Table 1 presents the deposition parameters used in the deposition of the a-Si:H films studied in this work. Samples in Set 1 and Set 2 consist of films prepared at different silane flow-rates and different discharge powers respectively.

Table 1: Preparation condition of pulsed PECVD films.

	Set 1	Set 2
Flow-Rate of Silane (sccm)	5, 10, 20, 30, 40	40
Deposition Pressure (mbar)	0.45	0.60
Deposition Power (W)	14.0	7.0, 9.8, 14.0, 21.0, 32.0
Deposition Time	3hours	3hours
Substrate Temperature (^{o}C)	200	200

The Fourier Transform infrared (FTIR) spectra were performed in transmission mode within the scanning range of 400 to 4000 cm^{-1} using a Perkin-Elmer System 2000 FTIR spectrometer. The hydrogen content and the microstructure parameter were determined from the integrated intensities of the Si-H wagging and Si-H/Si-H_2 stretching bands respectively [6, 7].
In this work, the Renishaw System 2000 Micro-Raman spectrometer was used to obtain the Raman spectra of the samples. The light source used was Ar+ laser, 514.5 nm (25 mW) wavelength with laser spot size of 1mm. The scanning range used for this measurement was from 200 cm^{-1} to 1000 cm^{-1}.

RESULTS AND DISCUSSIONS

The FTIR spectra of a-Si:H films prepared by pulsed PECVD at different silane flow-rates and discharge powers are shown in Figures.1 and 2 respectively. As seen from spectra, all the samples have major infrared absorption bands near 2000 cm^{-1} and 630 cm^{-1} which correspond to the stretching and wagging modes of local vibrations of the Si-H/Si-H_2 bonds respectively. The absorption band at 880 cm^{-1} which corresponds to the bending mode of local vibrations of dihydride (SiH_2) or polyhydride (($SiH_2)_n$ bonds (isolated or clustered) [8] shows significant appearance for the set of films prepared at different discharge powers increasing in intensity with increase in discharge power. This absorption band merely appears as a shoulder in the FTIR spectra of the set of films prepared at different silane flow-rates which were prepared at comparatively low discharge power of 14 W. These results suggest that increase in discharge power results in the increase in SiH_2 and $(SiH_2)_n$ bonds in pulsed PECVD film.

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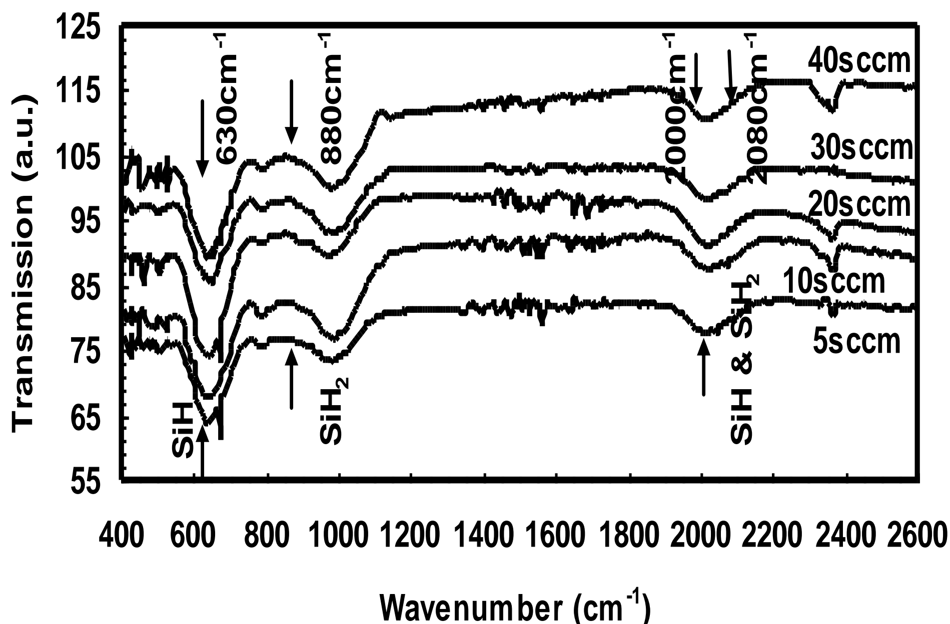

Figure 1: FTIR spectra of pulsed PECVD a-Si:H films at different silane flow-rates

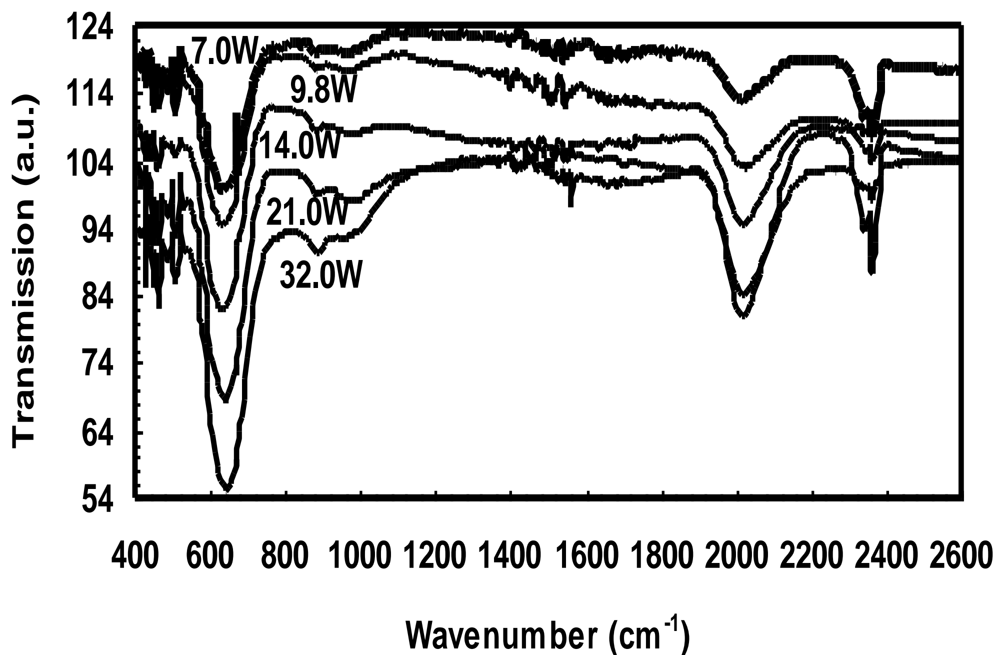

Figure 2: FTIR spectra of pulsed PECVD a-Si:H films at different discharge powers

Figure. 3 shows the variation of the hydrogen content of a-Si:H films prepared by pulsed PECVD with silane flow-rate and discharge power as determined from the FTIR spectrum of the films. The hydrogen content increases significantly to a maximum at

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silane flow-rate of 20 sccm and decreases again with further increase in silane flow-rate. For the samples prepared at different discharge power, the hydrogen content appears to decrease to a saturation value with increase in discharge power from 7.0 to 32.0 W. The decrease in the H content in film structure maybe attributed to the depletion of SiH_4 molecules in the plasma as the rate of dissociation is increased with the increase in the discharge power. As a result of this the concentration of H atoms in the plasma stabilizes. We believe that the H etching effect is active during the OFF-time of the pulsed plasma discharge if the presence of H atoms is sufficient. H etching effect breaks weak Si-Si bonds and incorporates H into the film structure also creates growth sites for strong highly ordered film structure This activity also saturates with increase in discharge power which explains the saturation of H content in the a-Si:H films formed with further increase in discharge power. Increase in the silane flow-rate on the other hand increases the H atoms in the plasma as the number of SiH_4 molecules increases, however the discharge power of 14 W is only able to support the dissociation activity of a certain population of SiH_4 molecules in the plasma. This occurs when the SiH_4 flow-rate is 20 sccm for the films studied in this work. Further increase in SiH_4 flow-rate results in an increase in secondary reactions which also involves H atoms thus depleting the H atoms in the plasma. This results in the slight decrease in the H content in the films with further increase in SiH_4 flow-rate.

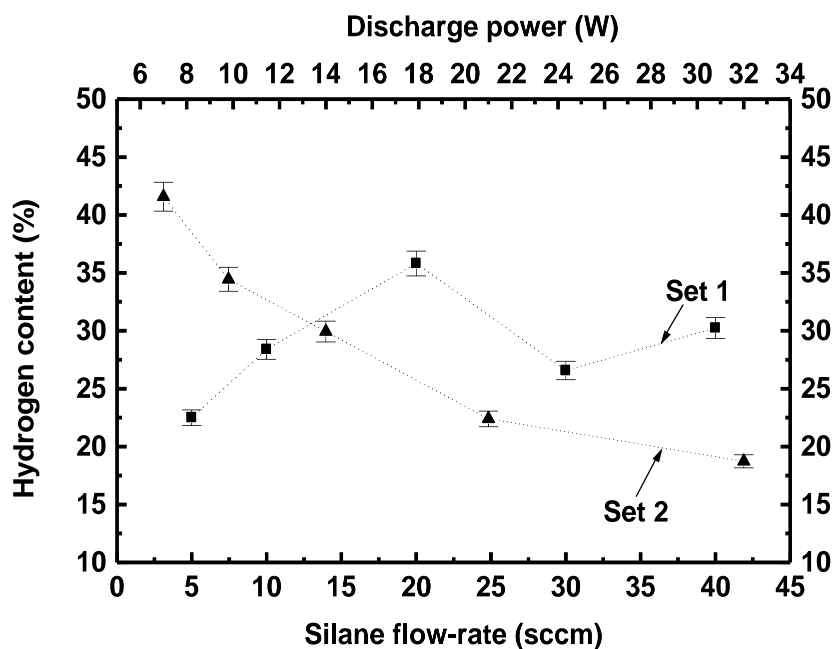

Figure 3: Variation of the hydrogen content of a-Si:H films with silane flow-rate and discharge power by using pulsed PECVD technique

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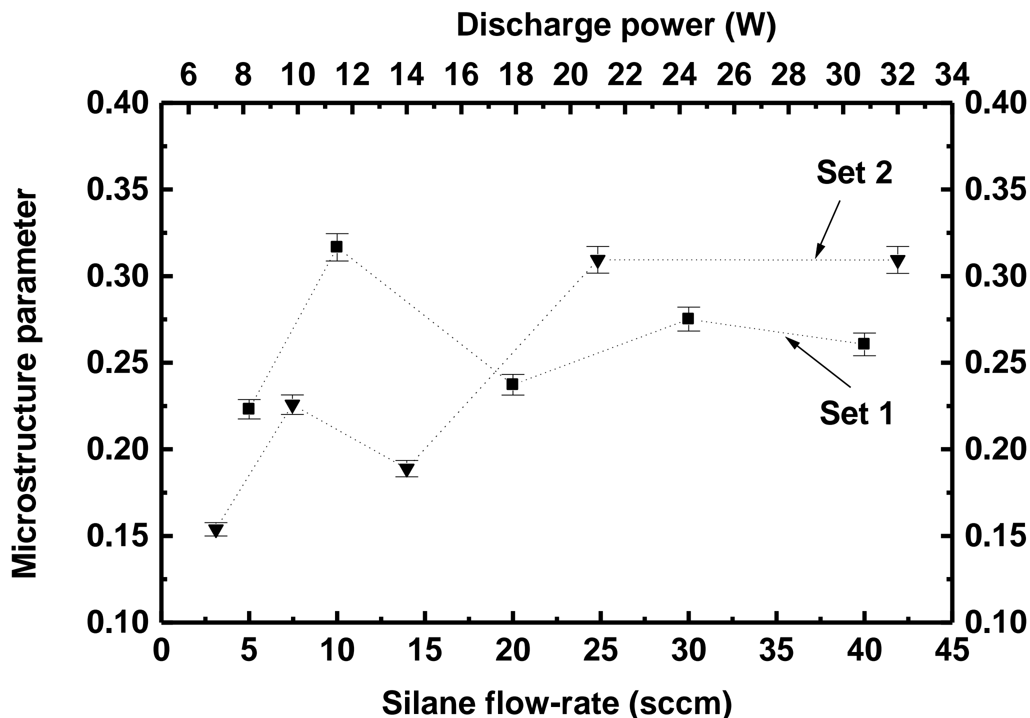

Figure 4: Variation of the microstructure parameter of a-Si:H films with silane flow-rate and discharge power by using pulsed PECVD technique.

Figure. 4 shows the variation of the microstructure parameter, R with SiH_4 flow-rate (Set 1) and discharge power (Set 2). It is observed that R is not dependent on the SiH_4 flow-rate except for the film prepared at 10 sccm which shows a significant increase. This increase maybe the result of the increase in the population of SiH_4 molecules and therefore resulting in the increase in the formation of various radicals in the plasma. Insufficient secondary reaction due to dissociation of most of SiH_4 molecules reduces the number of deposition precursors, SiH_3, in the plasma. The incorporation of many different radicals like SiH and SiH_2 into the film structure results in a highly disordered film structure which is reflected by the high value of the R parameter. With further increase in the SiH_4 flow-rate, the rate of secondary reactions increases. During the OFF-time of the discharge, H etching effects and activity of SiH_3 radicals with Si-H bonds and dangling bonds result in a more ordered film structure as indicated by the decrease in the R parameter value. The R parameter increases with increase in the discharge power indicating a more disordered film structure with higher concentration of microstructures in the film. High dissociation rate of SiH_4 molecules reduces secondary reactions and as in the case of increase in the R parameter for the film prepared at SiH_4 flow-rate of 10 sccm, the films prepared at high discharge powers also show high R values. The low H content in these films creates high density of dangling bonds in the film structure which also contributes to the high R values in these films

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this. This contributes to the formation of vacancies in the film and the clustering of these vacancies forms microstructures in the film.

Figure. 5 presents the Raman spectra of a-Si:H films deposited at different silane

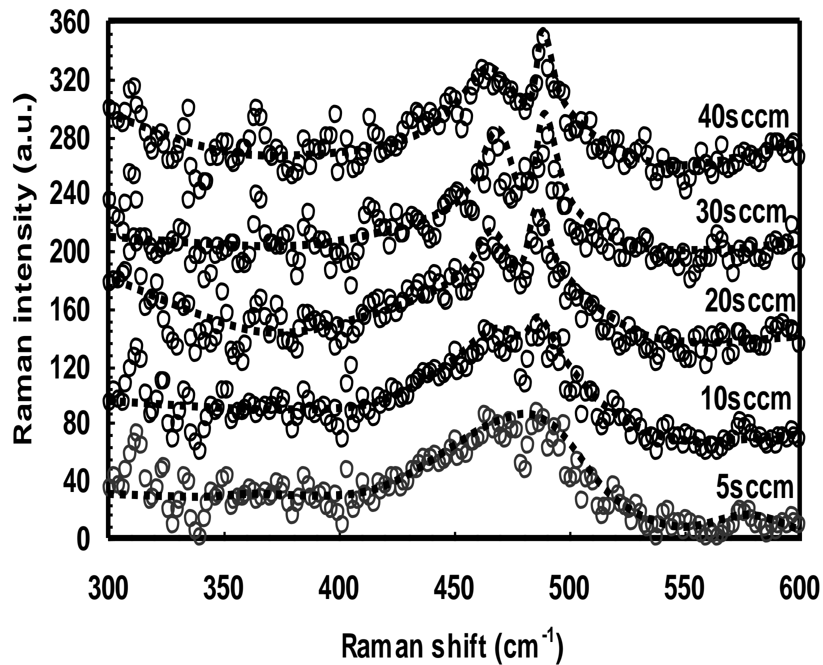

Figure. 5: Raman spectra of a-Si:H films deposited at different silane flow-rates.

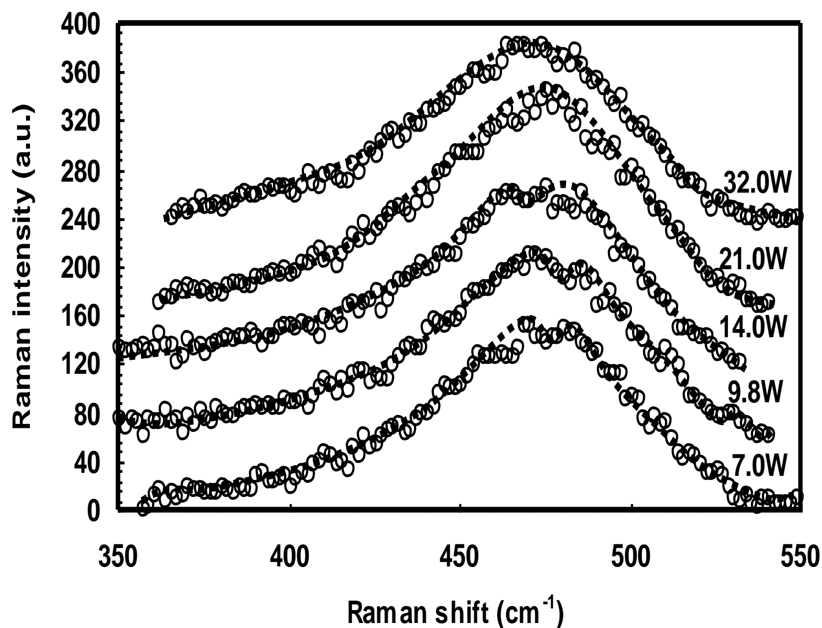

Figure. 6: Raman spectra of a-Si:H films deposited at different discharge powers

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flow-rates. The Raman spectra for all films showed broad peaks near at 480 cm^{-1} indicating amorphous phase in the film. The Raman spectra for the films prepared at silane flow-rate of 40, 30 and 20 sccm showed a sharp protruding peak at 495 cm^{-1} emerging from the broad amorphous peak. The Raman peak at 495 cm^{-1} corresponds to the scatterings from grains boundaries [9]. This indicates that the films consists of nano-sized crystallites embedded in a dominant amorphous matrix and the grain boundary which separates the nanocrystallites from the amorphous structure is more dominant than the nano-sized crystallites.

The Raman spectra for the films prepared at different discharge power is shown in Figure. 6. The peak at 495 cm^{-1} is observed as a small protrusion in the Raman spectra of the films prepared at low discharge power of 7 to 14 W. As in the above case, this indicates that films prepared at high discharge power are purely amorphous and nano-crystallites are formed only in the films prepared at low discharge power. Referring to figure 4, these films are also more ordered with low R parameter values. Therefore formation of nano-crystallites in the film structure results in a more ordered film structure. We believe that these nano-crystallites are formed in the ordered layers formed during the OFF-time of the discharge and at the initial onset of the discharge and these layers are ultra-thin and are less that 1nm thick. During the OFF-time, H etching effects dominates if sufficient H atoms are present. This removes weak Si-Si bonds and creates growth sites for a more ordered film structure in the presence of SiH_3 radicals at the onset of the discharge.

CONCLUSIONS

The infrared and Raman spectroscopy of pulsed PECVD a-Si:H films prepared using our home-built system have been studied. The effects of silane flow-rates and discharge powers on the infrared and Raman spectra of these films have been analyzed. The films prepared at higher SiH_4 flow-rates and low discharge powers have higher H content and indicate a more ordered film structure. The more ordered film structure in these films is due to the presence of nano-crystallites in these films. We believe that the nano-crystallites are formed in ultra-thin layers formed during the OFF-time of the discharge and the initial onset of the discharge which are separated from each other by an amorphous layer formed during the ON-time of the discharge. H etching effects and SiH_3 being the dominant deposition precursors play an important role in the formation of these multi-layers of highly-ordered and amorphous structure.

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