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EFFECTS OF THERMAL ANNEALING ON THE PROPERTIES OF HIGHLY REFLECTIVE nc-Si:H/a-CN_x:H MULTILAYER FILMS PREPARED BY r. f. PECVD TECHNIQUE

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ABSTRACT

The effects of thermal annealing in the range of 100-700°C on highly reflecting multilayer thin film consisting of 7 periods of alternating nc-Si:H/a-CN_x:H layers prepared by radio-frequency plasma enhanced chemical vapour (r.f. PECVD) deposition technique were investigated. The films were deposited on quartz and <111> p-type c-Si substrate and were studied using ultra-violet-visible-near infrared (UV-Vis-NIR) and Fourier transform infrared (FTIR) spectroscopy. The as-deposited multilayered films show high reflectivity and wide stop band width at a wavelength of approximately 650 ± 60 nm and the value starts to reduce as the annealing temperature, T_A increase. Its FTIR spectra showed the formation of Si-H and Si-H_2 bonds in the nc-Si:H layer and C=C, C=N, C≡N, C-H and N-H bonds in a-CN_x:H layer. The films remain thermally stable up to the T_A of 400°C and then begin to degrade above this temperature. The results shows that both a-CN_x:H and nc-Si:H were affected by heat treatment.

Keywords: hydrogenated nanocrystalline silicon; thin film; reflectivity;

INTRODUCTION

Hydrogenated nanocrystalline silicon (nc-Si:H) and hydrogenated amorphous carbon nitride (a-CN_x:H) are both important and interesting materials with great potential in various areas of applications such as solar cells and thin film transistors (TFTs) [1-4]. The high index contrast between these two materials and highly transparent in the visible and infrared regions also makes them suitable for the fabrication as distributed Bragg reflectors (DBR) [5]. Among others, one of the major concerns in the applicability of the fabricated device is the thermal stability and temperature constrains. In this work, the effect of T_A on highly reflective nc-Si:H/a-CN_x:H multilayered thin films is studied in terms of the optical and chemical bonding properties. The results suggest that the nc-Si:H/a-CN_x:H thin film is thermally stable up to 400 ^oC. Above this temperature, a bonding modification occurs and leads to a significant decrease in the peak intensity of the stop band.

EXPERIMENTAL DETAILS

A custom-build radio frequency plasma enhanced chemical vapour deposition system was used in depositing the highly reflective nc-Si:H/a-CN_x:H multilayer films. The film consist of 7 period of alternating nc-Si:H and a-CN_x:H which makes up a total of 14 layers of film. Details of the fabrication and characterization of the multilayered films is reported elsewhere [5]. Sample annealing was carried out in a quartz-tube furnace in the temperature range of 100-700 ^{o}C in a nitrogen-rich environment for 60 minutes.

Optical properties were studied from the transmittance and reflectance spectra of the film using Jasco V570 UV-Vis-NIR spectrometer. The bonding properties of the films were studied by means of infrared spectroscopy using Perkin-Elmer System 2000 Fourier transform infrared (FTIR) spectrometer. The spectra were obtained from wavenumber of 400-4000 cm^{-1} in the transmission mode.

RESULTS AND DISCUSSION

Reflectance spectra of the film grown on quartz substrate as a function of T_A are illustrated in Figure 1. The as-deposited film shows a relatively high reflectivity at 84.5 %. The variation of the optical properties as a function of T_A is studied in terms of the peak position, maximum intensity and the width of the stop-band measured as the full width half maximum (FWHM) of the corresponding peak. These values are obtained by standard Gaussian fittings and are shown in Figure 2. As T_A is increased, the peak position, intensity and FWHM decrease progressively. Moreover, the variation in peak position and its intensity decreases up to T_A of 500 ^{o}C then appears to saturate. The peak intensity degrades from the initial 84.5 % down to 29.4 % at this T_A.

As seen in Figure 1, the edge of the interference fringes, which is indicated by the arrow, shifts to shorter wavelength from 450 to 400 nm as T_A increases. In the same way, with the corresponding decrease in reflectance intensities, the absorption intensities in this region increase. According to Goh et al. [6] in their study of the effects of annealing on a-Si:H films, the shifting indicates an increase in the degree of crystallinity in the nc-Si:H layers in the film.

The corresponding transmission spectra for the different T_A are shown in Figure 3. The presence of the two distinctive layers of nc-Si:H and a-CN_x:H in the as-deposited film could easily be seen in the two distinctive region in the interference fringes. However with the increase in T_A, the regions evolve and finally, above 400^{o}C, form fringes similar to single layered films. This suggests that above this T_A, the distinctive DBR characteristics of the film is suppressed which explains the significant decrease in the peak intensity of the stop-band.

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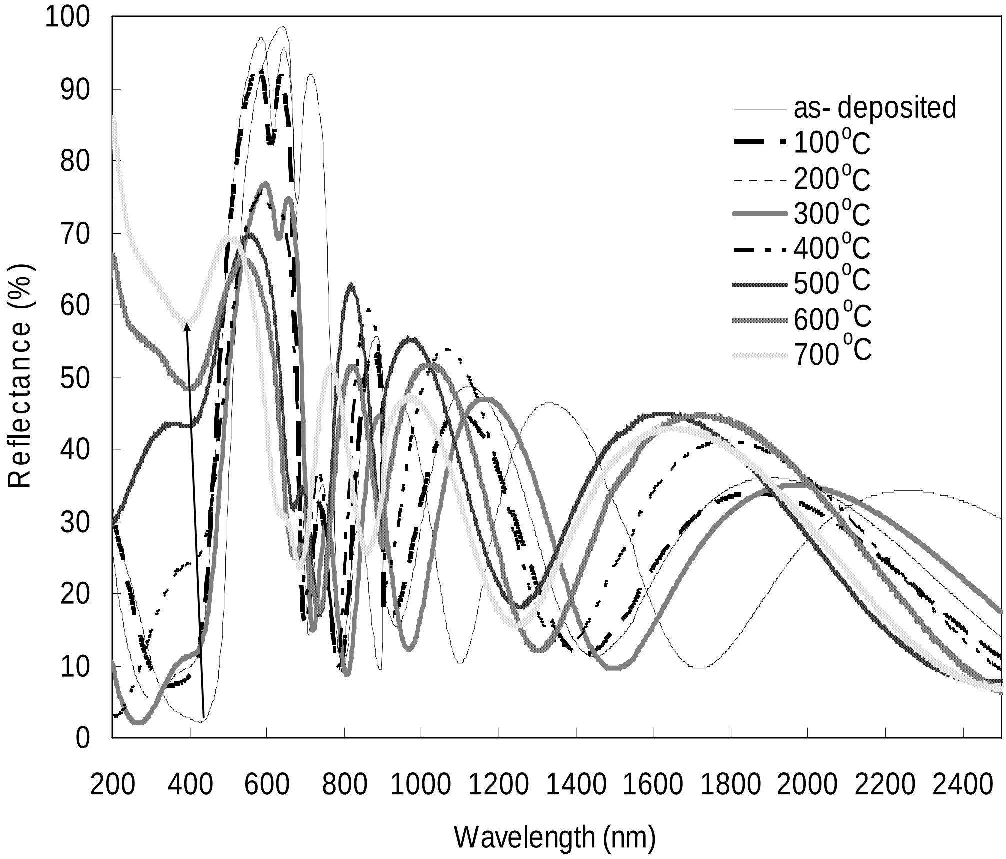

Figure 1: Optical reflectance spectra of 7 periods a-CN_x:H/nc-Si:H layers as a function of annealing temperature

Figure 4 represent the FTIR spectra of the sample as a function of T_A. The spectra show the expected bonding in multilayered film, which includes the peak around 680, 880 and 2000-2100 cm^{-1} correspond to Si-H wagging, $(Si\text{-}H_2)_n$ bending and Si-H/Si-H_2 stretching bands respectively [7,8], for the nc-Si:H and the wide (overlapping) band located between 1000-1800 cm^{-1} associated with sp^2 C-N, C=N and C=C bending modes [9], the small band between 2100-2300 cm^{-1} assigned to the C≡N nitrile groups [10] and the wide band above 2700 cm^{-1} which is correlated to the present of hydrogen that includes the O-H and N-H (3200-3500cm^{-1}) and the C-H (2800-3000cm^{-1}) bands [11], for the a-CN_x:H layer.

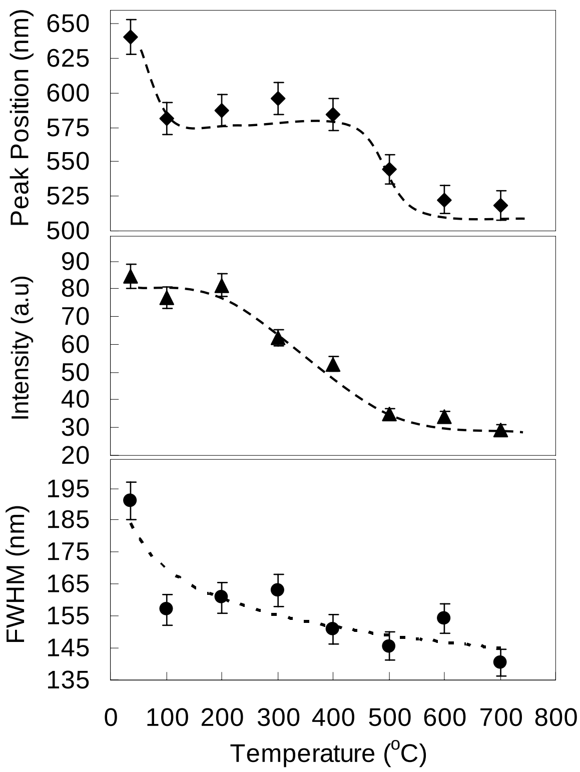

Figure 2: Variation of peak position, peak intensity and full width half maximum (FWHM) as a function of annealing temperature

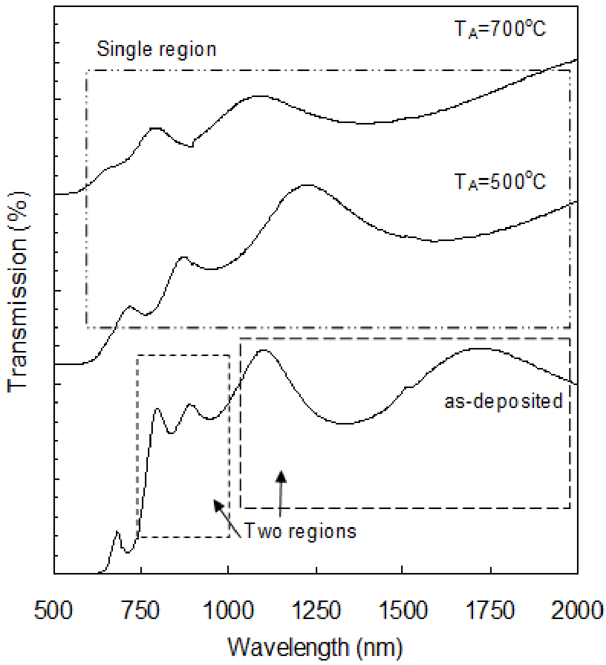

Figure 3: Transmission spectra of 7 periods a-CNx:H/nc-Si:H layers for the as deposited film and after annealing at 500 °C and 700 °C

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The FTIR results indicate that the multilayered film is thermally stable up to T_A of 300 ^oC. At T_A of 400 ^oC, the intensities of the peaks corresponding to SiH wagging modes at approximately 620 nm, SiH/SiH_2 stretching modes at 2000-2100 cm^{-1} and CH_n stretching modes between 2800 and 3000 cm^{-1} begins to decrease and disappears at higher T_A. The disappearances of the SiH, SiH/SiH_2 and CH_n bands suggest the removal of hydrogen from the multilayered film when annealed at these temperatures. Consequently bonding and structural modifications in each layer are expected. In the case of the nc-Si:H layer, this would lead to an increase in crystallinity as suggested in the optical reflectance spectra. The changes brought about by these structural changes would lead to a corresponding change in the refractive indexes of the films and may also lead to a change in the layer thickness. However the studies on the effect of the bonding modifications on each layers is currently being carried out and will be reported elsewhere.

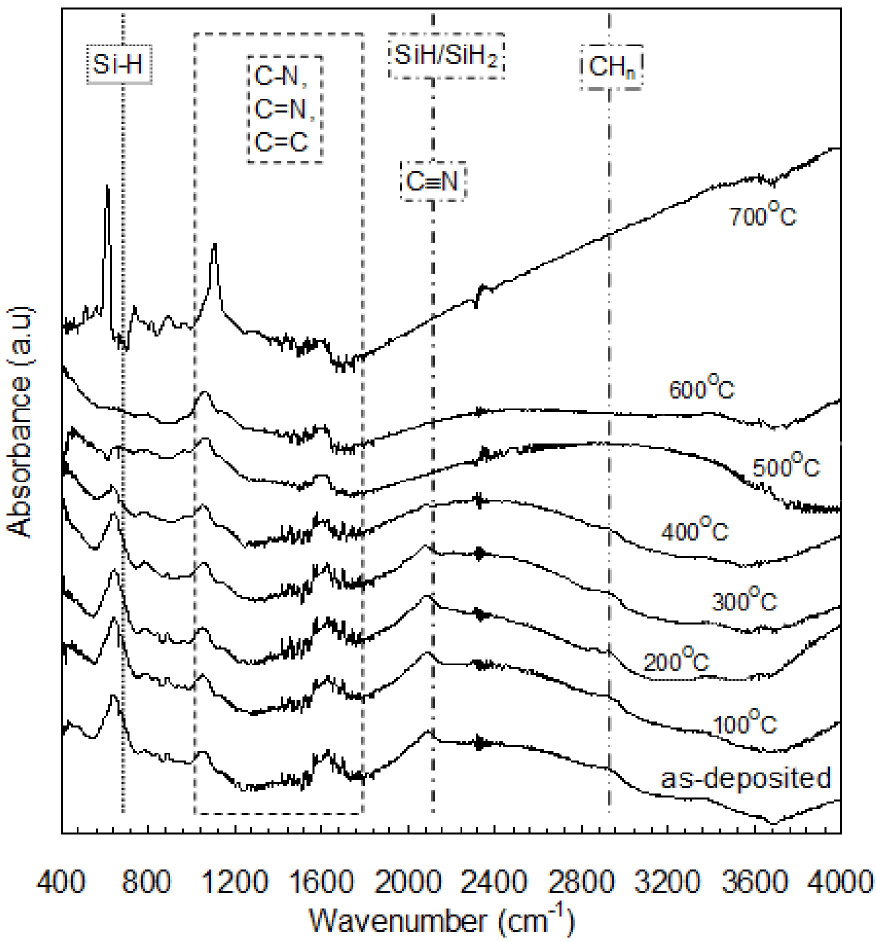

Figure 4: FTIR spectra of 7 periods a-CN_x:H/nc-Si:H layers at as deposited and different annealing temperature

CONCLUSION

The effect of annealing temperature in range of 100-700 ^{o}C on the optical and structural properties of a-CN$_x$:H/nc-Si:H multilayer film was investigated. From all of the results, the conclusions are as followed. The film is thermally stable below the annealing temperature of 400 ^{o}C. Above this temperature bonding modifications occurs in each layer cause by the removal of hydrogen as seen in the disappearance of the SiH and CH$_n$ bonds. In the nc-Si:H layers this leads to a higher degree of crystallinity. The loss of hydrogen and the C≡N in the a-CN$_x$:H layer would also lead to a significant change in the structure. These changes in the film result in a significant decrease in the peak intensity, position and FWHM above 400 ^{o}C.

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