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Thin Solid Films

journal homepage: www.elsevier.com/locate/tsfHighly reflective nc-Si:H/a-CN_x:H multilayer films prepared by r.f. PECVD technique

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ABSTRACT

Multilayer thin films consisting of a-CN_x:H/nc-Si:H layers prepared by radio-frequency plasma enhanced chemical vapour (r.f. PECVD) deposition technique were studied. High optical reflectivity at a specific wavelength is one of major concern for its application. By using this technique, a-CN_x:H/nc-Si:H multilayered thin films (3–11 periods) were deposited on substrates of p-type (111) crystal silicon and quartz. These films were characterized using ultra-violet–visible–near infrared (UV–Vis–NIR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, field effect scanning electron microscopy (FESEM) and AUGER electron spectroscopy (AES). The multilayered films show high reflectivity and wide stop band width at a wavelength of approximately 650 ± 60 nm. The FTIR spectrum of this multilayered structure showed the formation of Si–H and Si–H₂ bonds in the nc-Si:H layer and C=C and N–H bonds in a-CN_x:H layer. SEM image and AES reveal distinct formation of a-CN_x:H and nc-Si:H layers in the cross section image with a decrease in interlayer cross contamination with increasing number of periods.

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1. Introduction

Hydrogenated amorphous carbon nitride a-CN_x:H and nanocrystalline hydrogenated silicon, nc-Si:H have been widely studied this past decade due to their potential application in a wide variety of devices. This is due to the unique properties of these materials, such as unusual mechanical, chemical, optical and electrical properties [1,2] seen in a-CN_x:H and the enhancement brought about by the nanostructures in nc-Si:H which promotes its application in solar cells, thin film transistors and sensors [3–5].

In the quest to explore new area of application for both materials, the unique properties of both films particularly in the high transparency in the visible and near infrared regions, and high index contrast between both materials has motivate the study of their application as distributed Bragg reflectors (DBR) [6,7]. Single layered a-CN_x:H and nc-Si:H thin films deposited for calibration purposes with thickness of approximately 700 nm showed maximum transmittance above 85% in the visible region (~600 nm) for both materials, with refractive indexes of 1.59 and 2.96 respectively. DBR mirrors are useful tools in enhancing and increasing the efficiency of optoelectronic devices such as light emitting devices and photodetectors. There are a number of different techniques commonly employed in the deposition of a-CN_x:H and nc-Si:H thin films. In this study, plasma enhanced chemical vapour deposition (PECVD) technique was employed which offers high deposition rates for both these materials. Furthermore, it is relatively easier to operate and is cost-effective.

In this work, we have grown nc-Si:H/a-CN_x:H multilayer films using radio-frequency (r.f.) PECVD. Relatively low number of alternating periods is required to obtain highly reflecting films. The optical reflectance characteristics, cross section profile and chemical bonding are presented and discussed. To the best of our knowledge, no work similar to this study has been reported.

2. Experimental method

Multilayer of a-CN_x:H/nc-Si:H films were deposited by a home-built plasma enhanced chemical vapour deposition system using a conventional radio-frequency (13.56 MHz), parallel-plate system (133 cm², 5 cm apart) as shown in Fig. 1. The substrates used (quartz and p-type (111) silicon) were placed on the grounded electrode. These substrates were subjected to the standard cleaning procedures, which includes the etching of the silicon substrate in a diluted hydrochloric acid solution. Prior to the film deposition, the substrates were treated in hydrogen plasma for 10 min at r.f. power, hydrogen flow rate and process pressure of 40 W, 20 sccm and 80 Pa, respectively. All gasses used were introduced into the system via a shower head which also act as the powered electrode.

The nc-Si:H layers were deposited using a SiH₄ + H₂ mixture, at flow rates of 1.0 sccm and 20 sccm respectively, at an r.f. power of 20 W. a-CN_x:H were deposited in a mixture of CH₄ + N₂ at a flow rates of 20 sccm and 46.7 sccm respectively giving a [N₂]/[N₂ + CH₄] ratio of 0.7 N₂, at r.f. power of 80 W. The chamber pressure and substrate temperature were maintained at 80 Pa and 100 °C for these depositions. Between each alternating deposition, the chamber was evacuated to remove any residual gases. The thickness of the layers is

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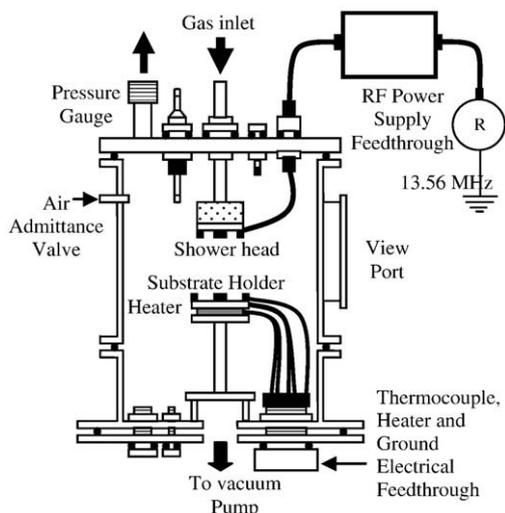


Fig. 1. Schematic diagram of r.f. PECVD deposition system.

controlled by deposition time and is predetermined by using a transfer-matrix method. In general the method is derived from the equation $d = \lambda/4n$, where the d , λ and n refers to the desired film thickness, stop band peak wavelength and refractive index of the film, respectively. The refractive indexes of the a-CN_x:H and nc-S:H films, calculated from the optical transmission of single layer films, were 1.59 and 2.96 respectively. The desired thickness for a stop band peak wavelength at approximately 600 nm were calculated to be approximately 94 nm and 51 nm for a-CN_x:H and nc-S:H films respectively. These values corresponds to a deposition time of 5 min for the a-CN_x:H layers and 2 min for the nc-S:H films. The number of a-CN_x:H/nc-S:H pairs, each pair corresponds to one period, was varied from 3 to 11 periods. For reference, some results of single layered nc-Si:H and a-CN_x:H films are also included. Details of the studies of the single layered nc-Si:H and a-CN_x:H, can be found elsewhere [8,9].

Reflectance spectra for the a-CN_x:H/nc-S:H films were carried out in the wide wavelength range of 190–2500 nm at normal incident using a Jasco V570 UV–Vis–NIR spectrophotometer. The cross section images were obtained from FEI Quanta 200 field emission scanning electron microscope. Auger electron spectroscopy (AES) was employed for the study of the depth profile of these films using Jeol JAMP-9500F Field Emission Auger Microprobe at etching rate of 0.74 nms⁻¹. The chemical bonding of the multilayered films was analyzed by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were performed in transmission mode within the scanning

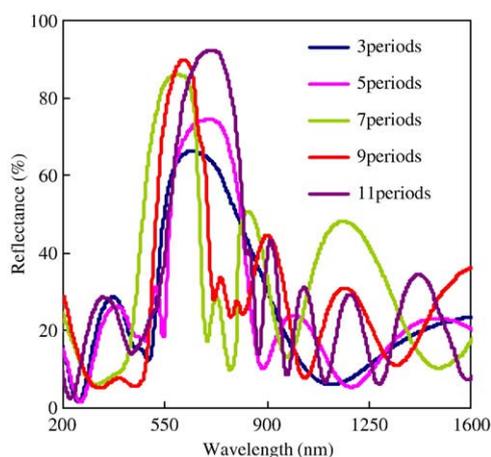


Fig. 2. The reflectance spectra of multilayered a-CN_x:H/nc-Si:H films for varied number of periods.

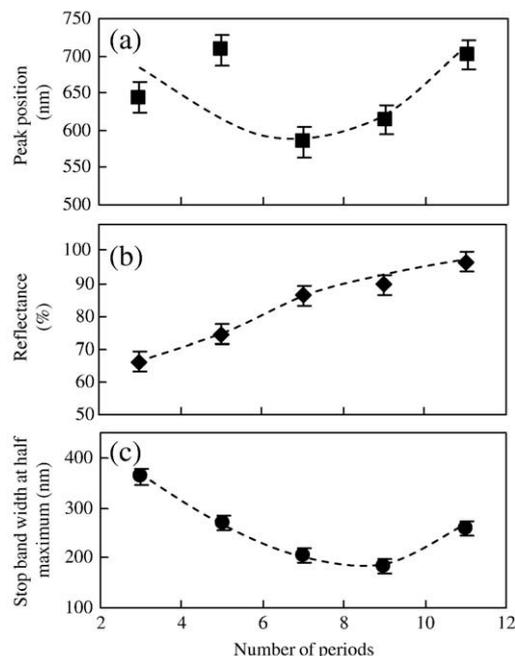


Fig. 3. Variation of (a) peak position, (b) reflectance and (c) stop band-width at half maximum of multilayered a-CN_x:H/nc-Si:H films for varied number of periods. Lines are as guide for the eyes.

range of 400–4000 cm⁻¹ using a Perkin-Elmer System 2000 FTIR spectrometer.

3. Results and discussion

Multilayered a-CN_x:H/nc-Si:H films with different number of stacks varied from 3 to 11 periods were grown. Fig. 2 shows the reflectance spectrum of these films grown on quartz substrates in the range of 200–1600 nm. The corresponding variation in peak position, reflectance and stop band-width at half-maximum of these films are shown in Fig. 3. As shown, the peak of the stop band is located in the range of 650 ± 60 nm. The highest reflectivity is 96.6% corresponding to reflectance spectrum of the 11 periods multilayered a-CN_x:H/nc-Si:H films. It is also noted that, to achieve high reflectivity, relatively few periods are required, owing to the high index contrast between the a-CN_x:H (1.59) and nc-Si:H (2.96) layers. The stop band-width at half-maximum of these films is relatively large and decreases significantly from 362 to 184 nm, with increasing number of periods. However at

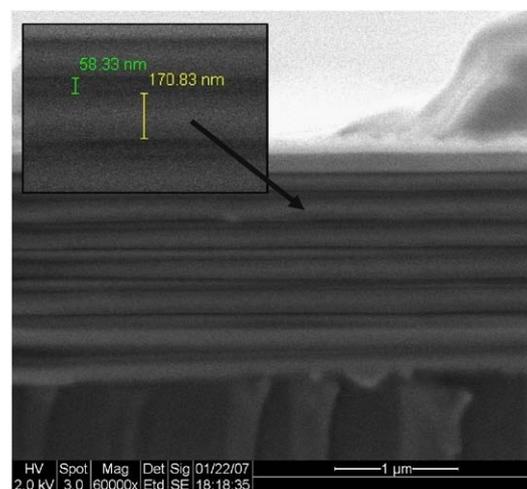


Fig. 4. Cross section FESEM image for 7 periods a-CN_x:H/nc-Si:H multilayered films.

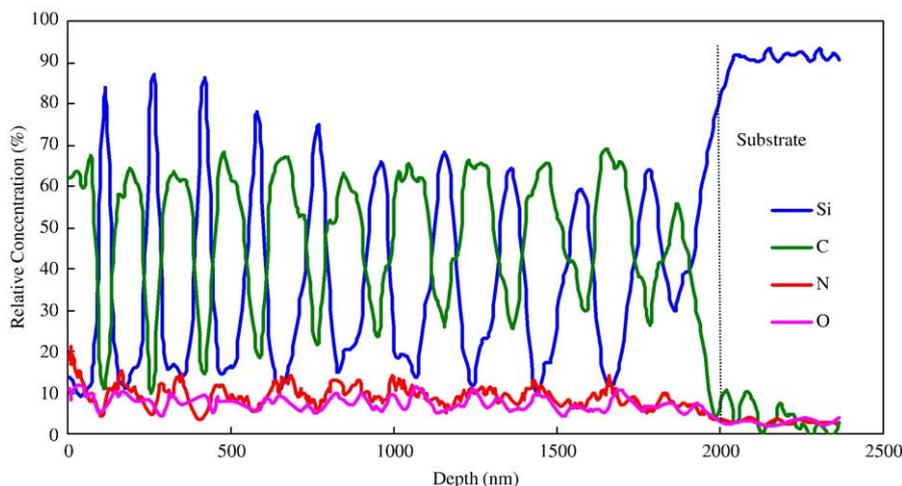


Fig. 5. Depth profile spectrum of the 11 periods multilayered a-CN_x:H/nc-Si:H films.

the current time, the sudden increase in the stop band-width for the 11 period multilayers could not be explained.

The cross section FESEM image of the 7 periods a-CN_x:H/nc-Si:H films (Fig. 4) shows distinct formation of a total of 14 alternating layers. The thickness of the nc-Si:H films deposited for 2 min was measured at approximately 58 nm, while that of a-CN_x:H deposited for 5 min is approximately 121 nm. The thickness of the nc-Si:H layer is close to the designed parameters (50.7 nm), while that of the a-CN_x:H layers differs from the designed thickness set at 94.3 nm. The differences may have come from the plasma processes during the deposition and interlayer interaction during the layer growth. The processes of turning off the plasma and stopping of reactive gas flow at the end of each layer deposition may result in thicker films. Also, coalescence to the surface of different layer material during initial deposition of the layer may result in different film structure at the interface, resulting in a thicker layer.

To further study the multilayered properties, depth profiling of the films were carried out as shown in Fig. 5 for the 11 period stacks. Similar to the SEM cross section image, the profile shows distinct formation of the multilayered film. The presence of nitrogen and oxygen is limited to the carbon containing layer, both with relative concentration of approximately 10–15%. The presence of oxygen is likely due to ambient contamination resulting from the porous nature of a-CN_x:H films which infuses into the film in the form of H₂O.

One of the most interesting features obtained from the depth profile is seen in the relative concentration of both Si and C in the earlier periods formed on the substrates (1–7 periods). This is particularly distinct in the nc-Si:H layers, which shows high concentration of C. The presence of carbon in this layer, either in the form of atoms or molecules, seems to have caused an increase in the thickness observed for the nc-Si:H and portrays the a-CN_x:H layers as being thicker. The infusion of carbon into the nc-Si:H layer may be due to the high r.f. power used in the deposition of the a-CN_x:H layer, which would produce highly energetic ions that bombard and penetrates the nc-Si:H layer. In contrast, the layers above 8 periods, appears more distinct with significantly lower interlayer contamination particularly in the nc-Si:H layers. This results in a significantly thinner and distinct layers of both nc-Si:H and a-CN_x:H. The decrease in carbon diffusion may be caused by the increase in the resistance of the film with the film thickness, due to the high resistivity of both these materials. This could lead to an increase in surface charge effect and thus decreases ion bombardment.

Additionally, the carbon in the nc-Si:H layer does not appear to be bonded to Si as observed from the FTIR spectra depicted in Fig. 6. The

spectra shows the expected bonding in the multilayered film, which includes the peaks around 630, 880 and 2000–2100 cm⁻¹ corresponding to Si–H wagging, (Si–H₂)_n bending and Si–H/Si–H₂ stretching bands respectively [10,11], for the nc-Si:H, and the wide band located between 1000 and 1800 cm⁻¹ associated with C–N (1020–1280 cm⁻¹), C=N (1610–1660 cm⁻¹) and C=C (1300–1500 cm⁻¹) bending modes [2], the small band between 2100 and 2300 cm⁻¹ assigned to the C≡N nitrile groups [1] and the wide band above 2700 cm⁻¹ which is correlated to the presence of hydrogen (C–H, N–H and O–H) [12], for the a-CN_x:H layer. It is also noted that the spectrum of the a-CN_x:H/nc-Si:H film is similar to the single layered films. The FTIR results suggest that the carbon in the nc-Si:H layers remain as solitary clusters rather than as being bonded to the Si network. In addition, the presence of O–H bonds from the band centered at 3400 cm⁻¹ confirms the presence of water in the a-CN_x:H/nc-Si:H films similar to those seen in the single layered a-CN_x:H film.

The average thickness estimated from the depth profile for the 1st to the 7th periods was approximately 62 nm and 128 nm for nc-Si:H and a-CN_x:H layers, respectively which coincides with those measured in the FESEM image. For the layers above 8th period, the thickness were measured at 52 nm and 97 nm for nc-Si:H and a-CN_x:H layers, respectively which appears closer to the designed parameters.

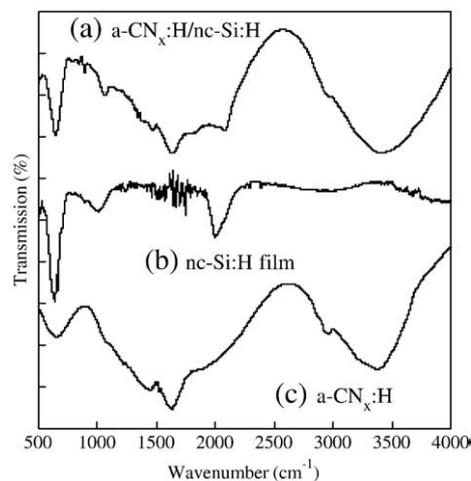


Fig. 6. FTIR spectrum of the single layered a-CN_x:H and nc-Si:H and the multilayered a-CN_x:H/nc-Si:H thin films.

4. Conclusion

Highly reflective (~96%) a-CN_x:H/nc-Si:H multilayered films have been successfully produced, with relatively low period stacking required. The peak reflectance of these films is located at 650 ± 60 nm and a wide stop band-width at half-maximum ranging from 184 to 362 nm. The cross section image and depth profile show distinct formation of alternating a-CN_x:H/nc-Si:H layers, with a decrease in interlayer cross contamination with increasing layer stacking, resulting in an improvement in the layer formation. The results show the potential of these materials in the fabrication of DBR mirrors. However more studies are necessary to improve the film formation in regards to peak location and interlayer cross contamination.

Acknowledgements

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