

## **EFFECT OF SUBSTRATE BIAS ON THE OPTICAL, BONDING AND ELECTRICAL PROPERTIES OF a-CN<sub>x</sub> DEPOSITED BY rf PECVD**

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### **ABSTRACT**

Hydrogenated amorphous carbon nitride (a-CN<sub>x</sub>:H) thin films were deposited using rf PECVD technique. The effects of negative dc substrate biasing on formation of these films were studied. UV-Vis-NIR spectroscopy was used to obtain the deposition rate (D) and optical energy gap (E<sub>04</sub>). Bonding properties were studied by means of FTIR spectroscopy while the I-V characteristics were measured by using two probes I-V. The results show a significant change in deposition at a substrate bias of -120 V with an increase in the deposition rate and E<sub>04</sub>. Effects of the substrate biasing on the optical, bonding and electrical properties are discussed.

### **INTRODUCTION**

Research on carbon nitride (CN<sub>x</sub>) films has received worldwide attention because of the fundamental and applications such as electron emitters, solar cell and electronic material. Many efforts have been made by researchers to synthesize CN<sub>x</sub> by different experimental techniques. However, the most preferable method to prepare carbon nitride is plasma enhanced chemical vapor deposition (PECVD) because of the desirable properties such as uniform large area deposition and easy handling [1]. The relationship between the growth of the carbon nitride films and various deposition parameters such as substrate temperature [2], gas pressure [3], plasma etching [4], and gas flow rate have been studied. This work focuses on the effect of applied negative dc biasing of the substrate in rf PECVD, on the optical, chemical bonding and electrical properties of the films obtained.

### **EXPERIMENTAL DETAILS**

The films were grown in a custom-build radio frequency plasma enhanced chemical vapor deposition (r.f PECVD) system [5] with a parallel plate electrode configuration. Hydrogenated amorphous carbon nitride films (a-CN<sub>x</sub>:H) were grown on quartz, ITO and Si substrates for optical, electrical and chemical bonding characterizations. These substrates were placed on the lower electrode where different negative dc voltage was applied (40-200V). The rf power (80W) was applied to the top electrode which also acts as the gas showerhead. The electrode distance, substrate temperature and the methane to nitrogen (CH<sub>4</sub>/N<sub>2</sub>) flow rate ratio were fixed at 5cm, 100°C and 1:3 respectively. The films were deposited for an hour at a fixed deposition pressure of 0.8 mbar. Prior to the film deposition, nitrogen pre-treatment was carried out for 15 minutes at the N<sub>2</sub> flow

rate of 60sccm and rf power of 50W. This is done to reduce impurities on the substrate surface which would improve the adhesion of a-CN<sub>x</sub>:H layers onto the substrate [6].

The films thickness, deposition rate (D) and optical energy gap (E<sub>04</sub>) were determined from the optical transmission spectra performed in a Jasco V570 UV-VIS-NIR spectrophotometer. Fourier transform infra-red (FTIR) spectroscopy carried out within a scanning range of 1000-4000 cm<sup>-1</sup> was used to analyze the chemical bonding in the films. The optical and FTIR measurements were carried out on the films deposited on quartz and Si, respectively. Current-voltage (I-V) characteristic was measured at room temperature using a two point probes I-V setup. The I-V were measured using a Keithley Source Measure Unit (SMU) Model 236 on the a-CN<sub>x</sub>:H films sandwiched between two electrodes in an aluminum (Al) / a-CN<sub>x</sub>:H / indium tin oxide (ITO) configuration. The ITO acts as the anode while Al acts as the cathode.

## RESULTS AND DISCUSSION

The variations in D and E<sub>04</sub> as a function of bias voltage (V<sub>b</sub>) are shown in Figure 2. The D of the biased deposition is generally lower than that of the grounded deposition, owing to the presence of sputtering effect due to ion bombardment during the growth. This etching effect appears to increase up to the V<sub>b</sub> of -120V and is consistent with the increase in the energies of the bombarding positive ions due to the increase in potential between the electrodes. Above this voltage, the slight increase in D could be attributed to a sufficient potential contributing to the dissociation of the gases thus increases the active species in the plasma. E<sub>04</sub> decreases significantly at V<sub>b</sub> =-120 V. Since it is generally known that the E<sub>04</sub> is associated to the relative ratio of sp<sup>2</sup>/sp<sup>3</sup> [7], the variation of E<sub>04</sub> for these films indicates structural modification at different range of applied voltage potential and an increase in the sp<sup>2</sup>/sp<sup>3</sup> ratio in the sample deposited at V<sub>b</sub> of 120V.

FTIR absorption spectra, normalized to the film thickness, are shown in Figure 3. The spectra show the following three functional regions: the C=C and C=N bending modes (1000-1800 cm<sup>-1</sup>), C≡N nitrile groups (2100-2300 cm<sup>-1</sup>) and C-H, N-H, OH [5] (above 2700 cm<sup>-1</sup>). Within the 1000-1800 cm<sup>-1</sup> region, the absorption bands of interest are the vibration modes of C-N, C=C and C=N in the region of 1000-1800 cm<sup>-1</sup>. This wide band is usually correlated to the overlapping absorption of Raman graphitic and disordered sp<sup>2</sup> bonded carbon. The increase in the intensities of these peaks for the V<sub>b</sub> =-120 V as seen in the variation of the maximum intensities of two prominent peaks shown in Figure 4(a), and the decrease in E<sub>04</sub> support the suggestion of an increase in sp<sup>2</sup> bond in the film.

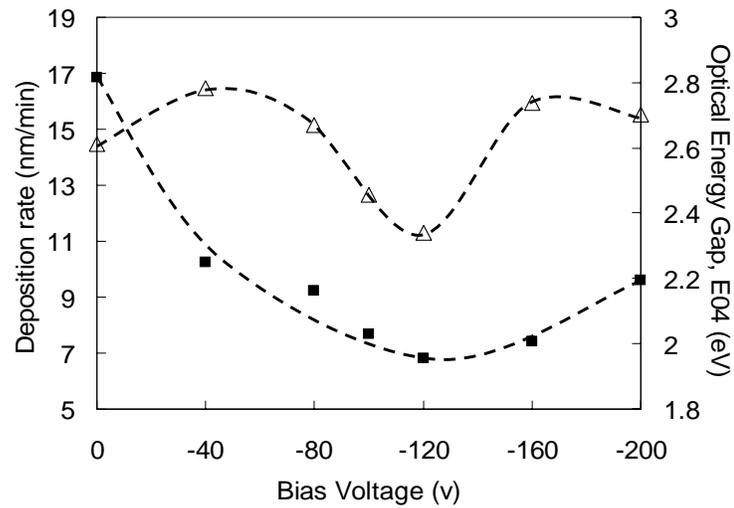


Figure 2 : Variation of deposition rate (■),and optical gap (Δ) as a function of bias voltage. The grounded deposition is plotted out as 0V bias

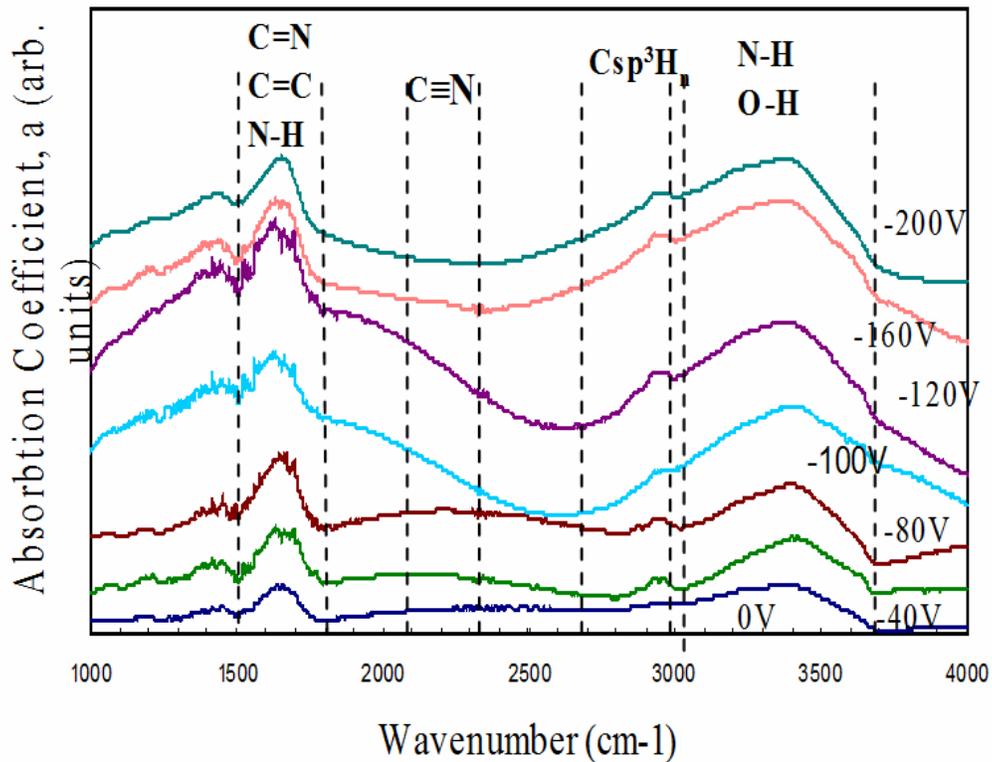


Figure 3: FTIR absorption spectra of the a-CN<sub>x</sub>:H films at varies bias voltage.

Figure 5 shows the I-V characteristics as a function of  $V_b$  for the carbon nitride thin films. With the increase in  $V_b$  a significant change in I-V characteristic occurs. The I-V characteristic which shows rectifying behavior for  $V_b$  of -40V and -80V, changes to Schottky diode behavior above -100V. This behavior is related to the broad band shift of the terminating nitrile  $C\equiv N$  bonds at above -100V as seen in Figure 4(b). Thus, above  $V_b$  of -100V the increase in terminating nitrile bonds results in shorter chains which increase the degree of disorder in the film. This in turn increases the film resistivity and limits the flow of current across the thin films. The result also shows that the electric field threshold decreases with increasing  $V_b$  as shown in Figure 6b.

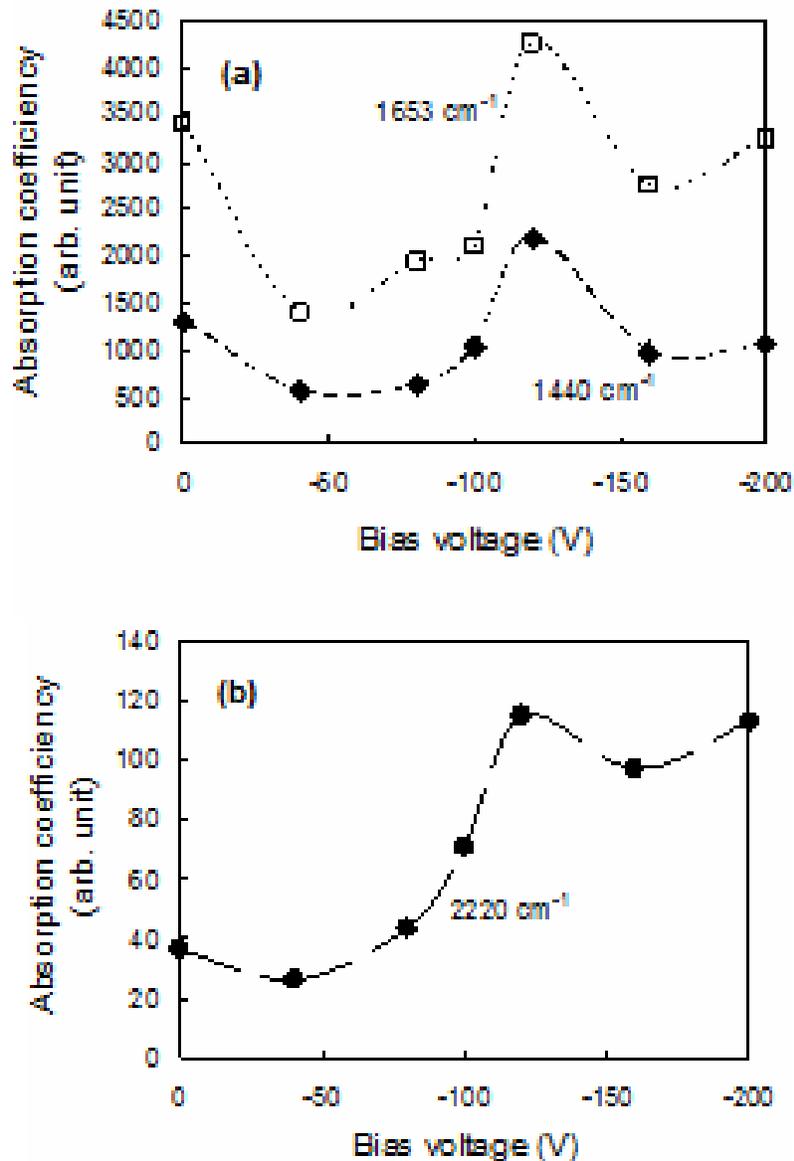


Figure 4: Variation in integrated intensities of prominent peaks in the regions of (a) 1000-1800 cm<sup>-1</sup> corresponding to the sp<sup>2</sup> bonding regions and (b) 1800-2300 cm<sup>-1</sup> for sp<sup>1</sup> bonds

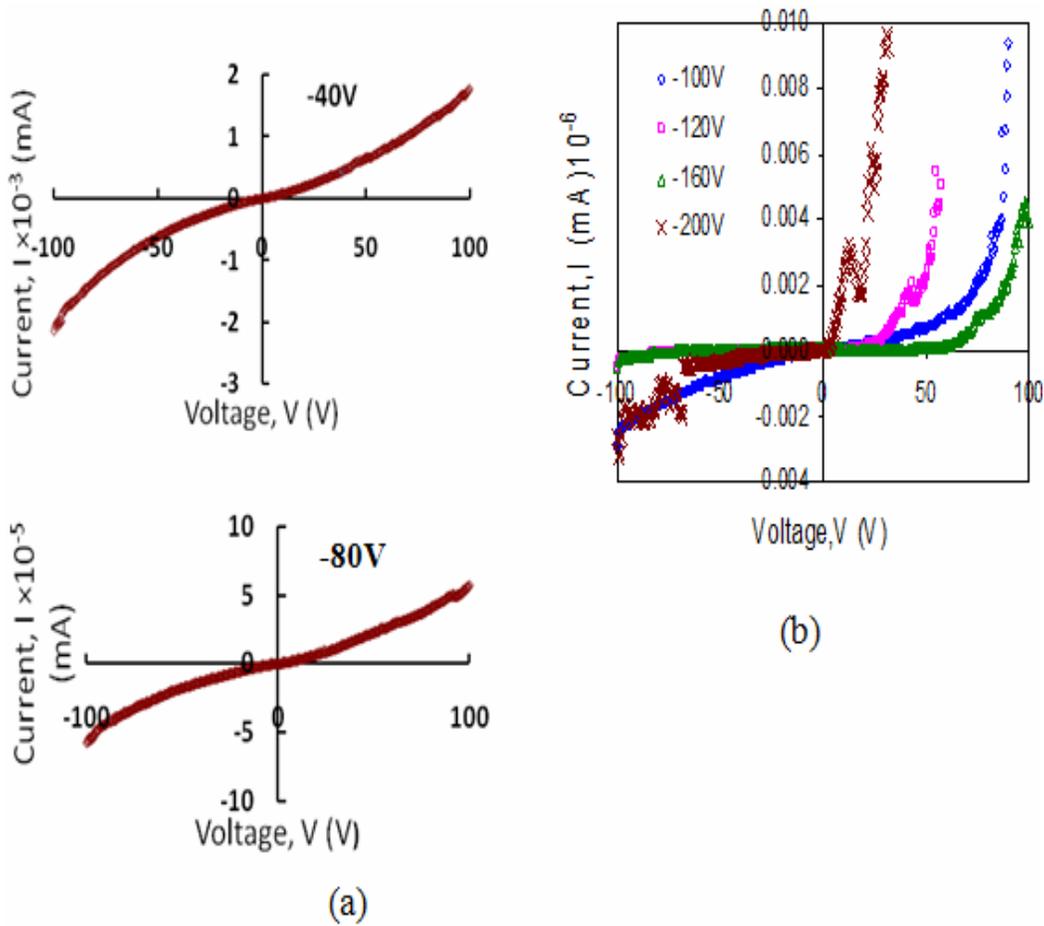


Figure 5: The current versus voltage (I-V) measurement of carbon nitride thin film biasing at (a) -40,-80V and at (b) -100V,-120V,-160V and -200V

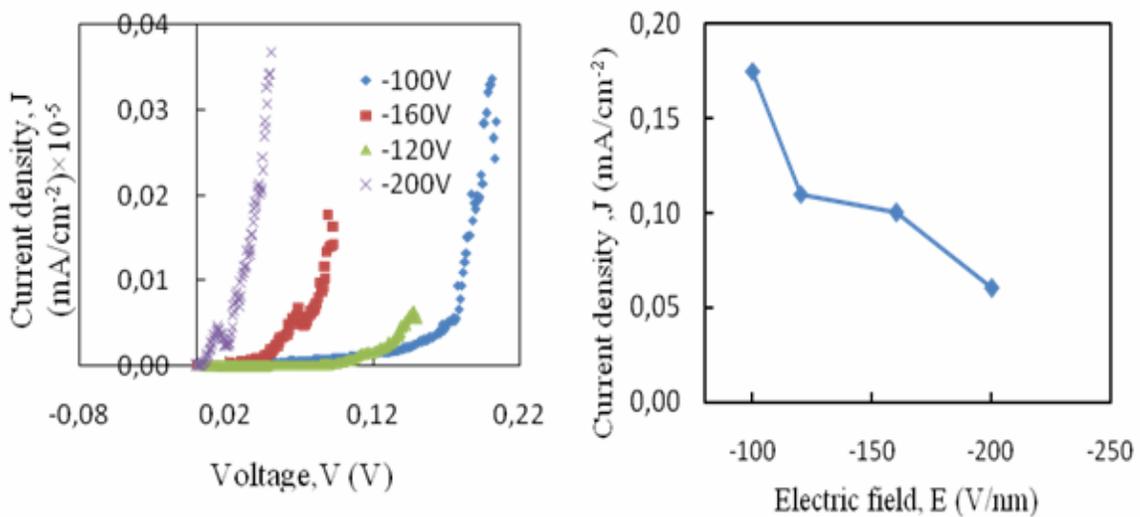


Figure 6: The current density versus Electric field (J-E) measurement of carbon nitride thin film prepared by rf-PECVD negatively bias at 100V to 200V

## CONCLUSIONS

The optical, chemical bonding and electrical properties of Hydrogenated amorphous carbon nitride films deposited at different substrate voltage biasing were studied. The films deposition rate decrease with increasing  $V_b$  up to -120V which may be due to the etching process during deposition. Above this  $V_b$  the increasing deposition rate may be due to the additional dissociation of the gases by the applied biasing potential which increases the active species in the plasma. The I-V characteristic shows Schottky diode characteristic for higher  $V_b$  and rectifying for lower  $V_b$  which is correlated to the broad band shift in terminating nitrile  $C\equiv N$  group as seen from IR spectra.

## ACKNOWLEDGEMENT

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## REFERENCES

- [1] E.F. Motta, I. Pereyra. (2004). *J. Non-Cryst. Solids* **525** 338-340
- [2] A. A. Onoprienko and I. B. Yanchuk.(2006). *Powder Metallurgy and Metal Ceramics* **45**, 190
- [3] M. Rusop, S. Abdullah and J. Podder. (2006).*Surf. Rev. Lett.* **13** 7
- [4] C. L. Cai, D. F. Diao and W. H. Ma. (2006). *Vacuum* **80**, 939
- [5] R. Ritikos, B.T. Goh, R. Awang, S.M.A Gani and S.A. Rahman, (2006) IEEE Xplore, DOI: 10.1109/SMELEC..380743
- [6] L. Valentini, J.M Kenny, Y.Gerbig, A. Savan, H. Haefke, L. Lozzi, S. Santucci. (2001) *Thin Solid Films* **398-399** 124-129
- [7] R.U.A. Khan, A.P burden, S.R.P. Silva, J.M. Shanon and B.J. Sealy. (1999) *Carbon*. **37** 777.