CHARACTERIZATION OF CARBON NITRIDE FILMS PREPARED BY THE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

M. Eliáš, J. Šustek, M. Lorenc and J. Janča

Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

1. Introduction

Several papers have been published about the deposition of carbon-nitride thin films since Cohen and Liu [1,2] predicted the hypothetical compound β-C_3N_4 with properties comparable to diamond. In addition to crystalline form, amorphous carbon nitride have many attractive properties such as extreme hardness, low friction coefficient, chemical inerties, and variable optical band gap. Amorphous carbon nitride films are already currently used as protective coatings on magnetic disk driver. Today, several techniques for the production of hard carbon-nitride films exist (RF and DC sputtering [3,4], ion beam deposition [5], laser ablation [6]). Plasma-enhanced chemical vapour deposition (PECVD) is another promising method for the deposition of these films [7,8]. We used RF plasma in NH_3 and CS_2 mixtures for the CN film syntheses.

In this paper, we study the changes of optical and structural properties of deposited films in the correlation with the deposition parameters (gas flow rate, substrate temperature, total pressure and negative self-bias).

2. Experimental

The drawing of the experimental set-up is given in Fig. 1. The capacitively coupled plasma was generated inside the quartz tube (i.d. 40 mm, length 90 cm) between the internal central and the external electrodes. The RF generator operated at the frequency of 2 MHz with the maximum power output of 70 W. As working gases the mixture of NH_3 and carbon

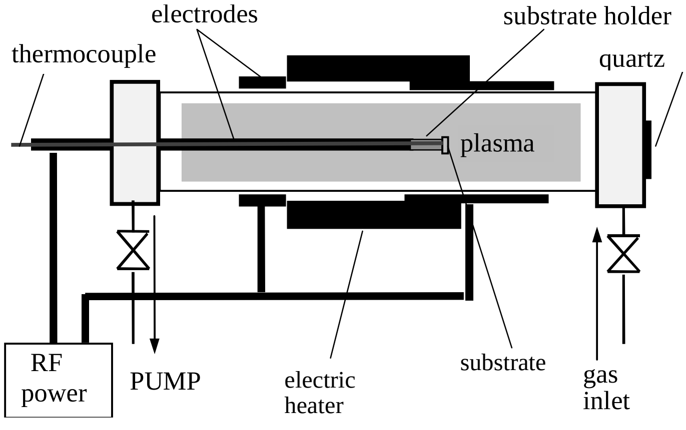

Fig. 1. The schematic drawing of our experimental set-up

sulphur (CS_2) vapours were used. The flow rates were established by the needle valves in the range 0.5-1.5 sccm for CS_2 and 10-15 sccm for NH_3. The total pressure was regulated by a throttle valve from 80 to 150 Pa. The substrate was heated to temperature ranging from 150^0C to 600^0C. The substrate temperature was measured by thermocouple inside the internal electrode. The CN thin films were deposited on Si (111) substrates.

The composition and the chemical structure of deposited films were characterised by the Fourier transform infrared spectroscopy (FTIR). The optical properties of films were determined from ellipsometric parameters measured in the spectral range 400 - 830 nm. The morphology of the deposited films was studied by scanning electron microscopy (SEM).

3. Results and discussion

The infrared transmission spectra were recorded for the films prepared under the variety of the deposition condit-ions. The typical spectrum is shown in Fig. 2. Comparing this spectrum with those of a-CN_x :H films reported in the literature [9], broad absorption band around 2190 cm^{-1} can be identified with the stretching vibration of a C≡N triple (nitrile), and the broad peak around 1000 cm^{-1} corresponds to CN single bond stretching. The absorption peaks at 3300 cm^{-1} are due to N-H stretching modes. This band indicate the presence of hydrogen in films. As we can see from Fig. 2 the ion bombardment has a significant effect on the structure of deposited films. Under the ion bombardment the absorption bands for C≡N triple bond and N-H bond are not present and the peak around 1000 cm^{-1} is sharper. It means hydrogen was desorbed from this layer by the ion bombardment. This change has considerable effect on the optical properties of the deposited films.

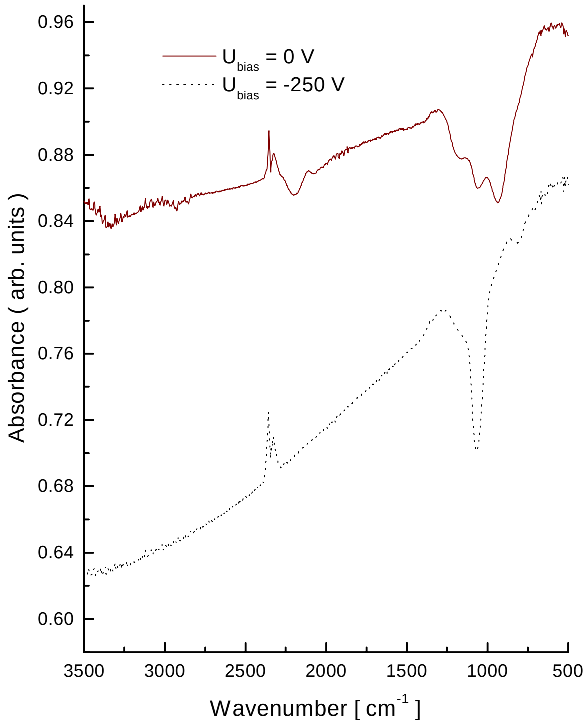

Fig. 2. FTIR spectra of the deposited CN_X thin films for different negative self-bias at substrate

U_{bias} [V]	n (600 nm)	k (600 nm)
0	1.524 ± 0.005	0.0351 ± 0.0025
-300	1.450 ± 0.002	0.0175 ± 0.0043

Table. 1. Optical properties CN films (N = 70 W, Q_{NH3} = 14 sccm, Q_{CS2} = 1.1 sccm, P = 100 Pa, T_s = 200^{0}C) deposited under different negative self-bias on substrate.

The ellipsometric parameters of all deposited films were fitted by the model of one absorbing layer on the silicon substrate in the spectral range 400 - 830 nm. The Cauchy formula of refractive index *n* and the exponential formula of absorption index *k* were applied. The optical parameters changed with the self-bias changes. The layer prepared without self-bias has higher refractive and absorption indices (Table 1). Dispersive influence of the wavelength at *n* and *k* is show in Fig. 3.

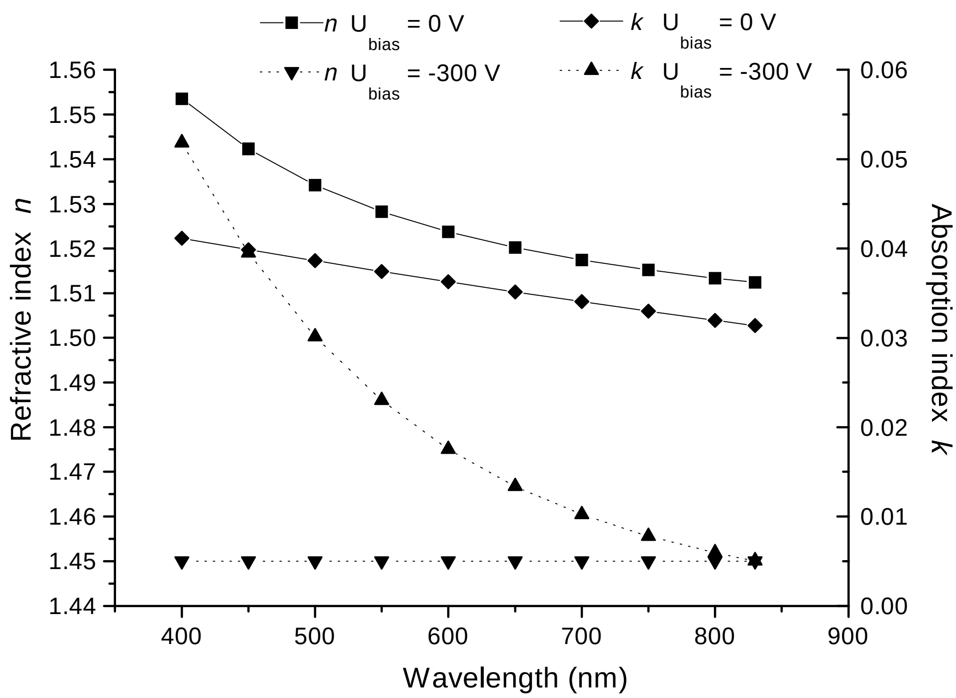

Fig. 3. Influence of negative self-bias at substrate on refractive and absorption indices

The morphology of the films were determined by SEM. The big change of the film surface appeared when the substrate was heated up to 250 ^{0}C (Fig. 4). The layers are smooth for the substrate temperatures below 250 ^{0}C, while the films deposited at the temperature higher than 250 ^{0}C are grey and very porous. However the FTIR spectra did not change on the films deposited at higher temperature. We could not measure the ellipsometric spectra, because the reflected beam has a very small intensity, due to the scattering on the rough surface.

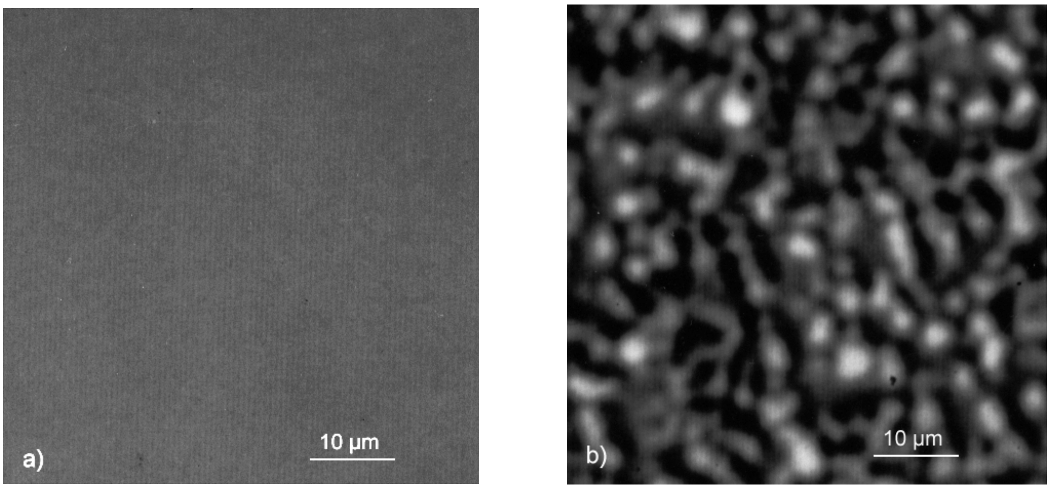

Fig. 4. Scanning electron micrograph of carbon nitride films deposited at substrate temperatures of (a) 150 and (b) 400 ^{0}C.

4. Conclusion

We have studied the structural and optical properties of the amorphous carbon nitride films prepared by PECVD using NH_3 and CS_2 as the source gases. We observed that presence of the self-bias during the deposition has an important influence on the layer properties. These layers have the refraction index independent on wavelength, but the absorption index decreases with increasing wavelength.

Acknowledgement

The present work was supported by the Grant Agency of the Czech Republic, contract 106/96/K245.

References

[1] A.Y. Liu and M. Cohen: Science **245** (1989) 841
[2] A.Y. Liu and M. Cohen: Phys. Rev. B **41** (1990) 10727
[3] H. Gruger, D. Selbmann, E. Wolf, A. Leonhard: Surface and Coatings Technol. **97** (1997) 109
[4] S. Veprek, J. Weidmann and F. Glatz: J. Vac. Technol. A **13** (1995) 2914
[5] F. Fujimoto and K. Ogata: Jpn. J. Appl. Phys. **32** (1993) L420
[6] E. Aldea, A.P. Caricato, G. Dinescu and A. Perrone: Jpn. J. Appl. Phys. **36** (1997) 4686
[7] F.L. Freire Jr.: Jpn. J. Appl. Phys. **36** (1997) 4886
[8] W. Dawei, Fu Dejun,G. Huaixi, Z. Zhihong, M. Xianquan: Phys. Rev. B **56** (1997) 4949
[9] J.H. Kim, D.H. Ahn, Y.H. Kim: J. Appl. Phys. **82** (1997) 658