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OPTICAL CHARACTERISTICS OF CARBON NITRIDE FILMS PREPARED BY HOLLOW CATHODE DISCHARGE*

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Carbon nitride films (CN_x) were deposited on Si (111) wafers by a hollow cathode discharge process. The films were prepared by evaporation of a graphite target in an N_2 atmosphere. The substrate bias voltage was varied in the range 0 - 100 V. Chemical bondings were determined by Fourier transform (FTIR) infrared spectroscopy. There was observed that bias voltage applied to the substrate has a notable influence on the occurrence of various absorption bands associated with CN bonding states. The real and imaginary parts, *n* and *k*, of the complex index of refraction of carbon nitride films have been determined by spectroscopic ellipsometry (ES) in the range 0.3 - 0.8 nm. Both *n* and *k* (refractive index and extinction coefficient) reveal a significant variation with deposition conditions. Optical band gap of the deposited films was situated in the range 0.5 eV - 1.5 eV.

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1. Introduction

Carbon nitride films have received considerable attention recently due to their interesting properties (high hardness, high transparency, and chemical inertness) predicted by early papers of Liu and Cohen [1]. These films have potential applications as hard transparent optical coatings, wear resistant coatings and as a semiconducting material because it has been demonstrated that amorphous semiconducting films can be doped *n* or *p* type [2].

Till now all efforts were directed towards increasing nitrogen content up to the value corresponding to β-C_3N_4 compound and for getting good crystalline carbon nitride films. Most carbon nitride CN_X films reported were amorphous and nitrogen deficient with x less than 1.

We present the results of optical measurements on a series of CN_X samples prepared by a technique based on a hollow cathode discharge. Optical properties such as refractive index, extinction coefficient and optical gap have been determined. The films were also characterized by Fourier transform infrared spectroscopy (FTIR).

2. Experimental

The films were prepared by evaporation of a graphite target in a nitrogen atmosphere. An electron beam generated by the hollow cathode produces the evaporation. Electron beam has also an additional role; namely it generates a high-density plasma in the vicinity of the substrate contributing in this manner at reactive species activation. Experimental setup is described elsewhere [3]. The films

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were deposited on Si (111) wafers cleaned ultrasonically in HF solution and rinsed in deionized water. Some of the deposition parameters were kept constants (total gas pressure: 10^{-2} mbar, graphite evaporation rate 0.035 g/min., discharge power: 3.5 kW, deposition time: 30 min.), whereas substrate bias voltage was varied as shown in Table 1.

Table 1. Deposition parameters AFR - argon flow rate; NFR- nitrogen flow rate; Vs - substrate voltage.

Sample	AFR (cm^3/min)	NFR (cm^3/min)	-Vs (V)
1	30	0	100
2	30	50	0
3	30	50	40
4	30	50	100

3. Results and discussion

3.1. Infrared transmission spectroscopy

A 360 Nicolet FTIR spectrometer was used to obtain the infrared absorption spectra of the films deposited under the conditions described in the Table 1. The IR spectra of the films are presented in the Fig. 1.

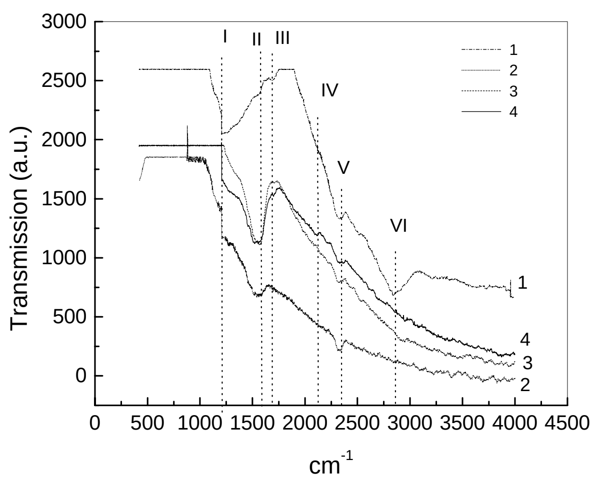

Fig. 1. FTIR spectra of the layers prepared under the conditions described in the Table 1.

Six absorption bands denoted as band (I) to (VI) have been observed. Their possible assignments are given in the Table 2.

The sample no. 1 deposited without nitrogen injection shows four absorption bands (I, III, IV and V). Band (I) raises few questions concerning its assignment. Most authors are inclined to ascribe this region (around 1200 cm^{-1}) to a symmetric tetrahedral CN bond, while work of Zhao [5] ascribe this region to come from vibrational modes of disordered sp^2 bonded C. Band (III) is attributed to C=C stretch. As concerning bands (V) and (VI) associated to CO_2 (2350 cm^{-1}) and CH bonds respectively, they might be the results of contamination with water vapors and/or air originating from chamber walls during deposition or subsequent exposure in air.

Table 2. Infrared absorption bands of hydrogenated carbon nitride films.

Band	Wave number (cm^{-1})	Assignment and wavelength (cm^{-1})	References
I	1228	1297, 1360 disordered sp^2 bonded C 1212 - 1265 sp^3 C-N	[4] [5]
II	1500	1530 - 1725 C=N stretching 1580 - 1650, NH_2 bending 1520, C=N	[6][2] [7] [8]
III	1600	1634, C=C, stretching , sp^2 1600, C=C, stretching , sp^2 1650, C=C olefinic stretch	[9] [7] [8]
IV	2123 - 2202	2143, C≡N 2170, C≡N 2180, C≡N, stretching 2200, C≡N, stretching 2210 - 2260, C≡N, stretching	[5] [5] [8] [6] [6]
V	2350 2325	CO_2 CO_2	[10] [10]
VI	2800	2850 - 2950 C-H, stretching (asym.), sp^3 2875 CH_3, stretching (sym.), sp^3	[11] [7]

When nitrogen is introduced in the discharge a slight shift of the band (I) from 1250 cm^{-1} to 1330 cm^{-1} was observed which indicates a modification of binding geometry. This fact was ascribed by Yap et al. [4], when bias voltage was increased, to a transformation of graphitelike sp^2 C-N bonds into the tetrahedral sp^3 C-N binding state. The double band (II) situated at around 1500 cm^{-1} was attributed to many contributions, as it is indicated in Table 2. When bias voltage is increased a slight shift from 1580 - 1525 cm^{-1} to 1568 - 1501 cm^{-1} was observed. The shifting of band (II) was explained as a result of reduction of graphitization of CN films [4]. When substrate bias voltage has a value of 100 V, a band (IV) corresponding to C≡N binding state appears, probably as a result of increasing the energy of the species reaching the substrate and consequently new bondings can be formed.

3.2. Ellipsometric spectroscopy

Ellipsometric spectroscopy was used to determine the optical constants n-refractive index and k-extinction coefficient. The *semiinfinite model* [12] was adopted to perform this task. In Fig. 2 are illustrated the dependence of optical constants n and k for films prepared under conditions described in Table 1.

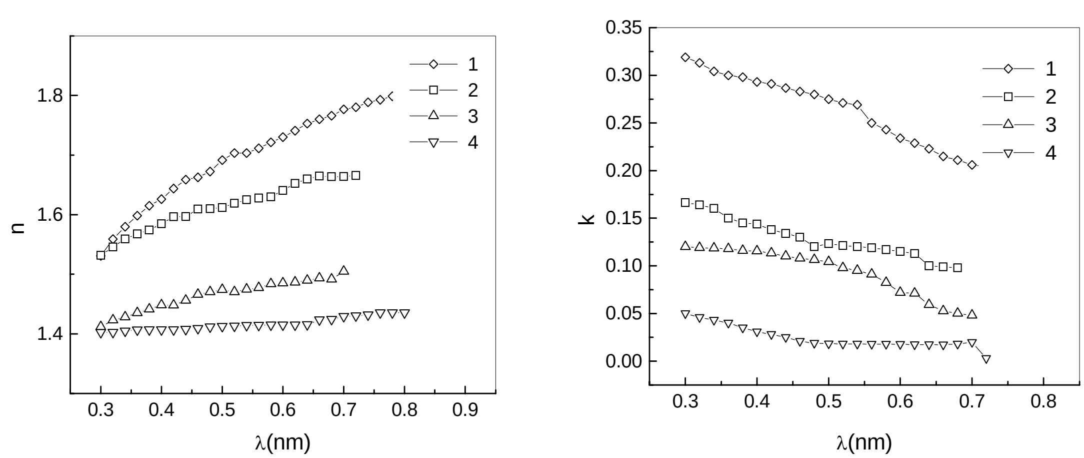

Fig. 2. Spectral dependence of the refractive index (*n*) and extinction coefficient (*k*) for deposition conditions shown in Table 1.

We note a slight increase in refractive index with wavelength. It can be observed the role of nitrogen in the reduction of refractive index and extinction coefficient. Increasing in substrate bias voltage determines reduction of refractive index and extinction coefficient. This low value of n is consistent with the low density of the film.

The electron band gap E_{opt} was determined by using the Tauc equation. According to this E_{opt} of the films are evaluated from the x-intercept for linear segment of the plot $(h\nu\alpha)^{1/2}$ against the photon energy hν. Tauc theory shows that $(h\nu\alpha)^{1/2}$ is proportional to $h\nu\text{-}E_{opt}$ for amorphous semiconductors.

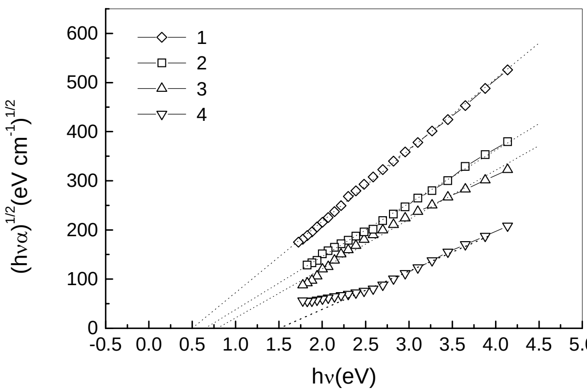

Fig. 3. Optical absorption spectra of the films deposited under conditions given in Table 1.

In Fig. 3 are represented the plots of $(h\nu\alpha)^{1/2}$ against the photon energy for the films deposited under conditions described in Table 1. The curves have been extrapolated on their linear region, as it is shown, in order to determine the optical gap parameter E_{opt}. The film deposited in absence of N_2 has an optical gap of 0.5 eV. When nitrogen is introduced in the discharge the films became more transparent having an optical gap of 0.68 eV. A growth of the bias voltage from 0 to 100 V leads to an increase of the optical gap to a value of 1.5 eV at 100 V, as it can be seen from Fig. 3 (curves 2 - 4).

4. Conclusions

The influence of substrate bias voltage on optical properties of carbon nitride films has been investigated. Films were deposited by evaporation of a graphite target in a nitrogen environment. The optical gap was found to increase (up to 1.5 eV) with substrate bias voltage as a result of various bonding configurations between nitrogen and carbon.

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