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Carbon nitride thin films prepared by a capacitively coupled RF plasma jet

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Abstract

Carbon nitride thin films have been downstream deposited from a nitrogen plasma beam sustained by a capacitively coupled discharge generated between a RF powered carbon electrode and a grounded carbon nozzle. The spectral emission of the plasma jet strongly exhibits the CN radical emission indicating that the deposition takes place via a mechanism involving the CN radical. The deposition process is enhanced by DC biasing the powered electrode. The films have been investigated by X-ray diffraction, infrared absorption spectroscopy and X-ray photoelectron spectroscopy. The results show that the films are amorphous and contain in a large extent carbon nitrogen bonds.

1. Introduction

Low compressibility polymorphs of carbon nitrides have attracted much interest in the last years as their predicted hardness could be higher than that of diamond [1,2]. A large variety of techniques have been used for synthesis of carbon nitride materials: deposition from gaseous precursors assisted by plasma [3] or hot filament [4], evaporation of carbon and condensation under exposure of ionic, atomic, molecular nitrogen species [5–7], nitrogen implantation of carbon thin films [8], sputtering of carbon or carbides in nitrogen ambient [9–12], laser ablation of carbon in a nitrogen atmosphere, nitrogen plasma or nitrogen ionic beams irradiation [13–15], chemical transport of carbon in nitrogen plasma [16], etc.

In this paper the synthesis and deposition of carbon nitride thin films with a new technique, downstream deposition from a RF generated, capacitively coupled nitrogen plasma beam with carbon electrodes is reported. The films obtained at room temperature, are amorphous and contain carbon to nitrogen bonding, as is revealed by XRD, FTIR, XPS investigations.

2. Experimental

The capacitively coupled RF discharge plasma jet and its properties when working in nitrogen have been presented in detail elsewhere [17]. Essentially a capacitively coupled RF discharge (less than 100 W) is generated in flowing nitrogen (at 100 sccm) in a small distance (1–2 mm) gap, at medium pressure (3–25 Torr). The gap is limited by a planar (40 mm diameter) electrode and a nozzle (1.5 mm opening). Plasma expands as a bright excited nitrogen beam in a much larger vessel at low pressure (10^{-1} Torr). The sample holder was placed downstream the nozzle at several centimeters distance, being exposed to the plasma beam. For carbon nitride deposition the RF electrode and the nozzle have been made from graphite. Si (100) polished wafers have been used as substrates. Separate biasing of the discharge electrodes has been used in order to change the deposition conditions. During the deposition no external heating of the substrate was done.

The plasma beam has been investigated by optical emission spectroscopy. Emission spectra have been recorded in the spectral range 250–700 nm with a SPM-2 grating monochromator (1200 lines/mm) equipped with a EMI QB 9558 photomultiplier which is connected to a data acquisition system.

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A chromel–alumel thermocouple has been used to measure the temperature variation of the substrate during the deposition process. The substrate temperature during deposition was around 50°C.

The XRD analyses were conducted with a URD6 apparatus using the $\text{CuK}\alpha$ line ($\lambda = 1.54 \text{ \AA}$). The infrared spectra were obtained with a Brucker IFS 66 Fourier Transform spectrometer. The XPS measurements have been performed with a ESCALAB MK II spectrometer by using the monochromatic $\text{AlK}\alpha$ radiation. The spectra calibration has been done with the $\text{Ag3d } 5/2$ line ($E_b = 368.26 \text{ eV}$) having the Fermi level as reference for energies.

3. Results and discussion

3.1. Deposition rates

The mass loss rate of electrodes measured in the case of discharge sustained only by the RF field was $0.019 \mu\text{g}/(\text{cm}^2 \text{ s})$ for the upper electrode and $0.021 \mu\text{g}/(\text{cm}^2 \text{ s})$ for the nozzle. By DC biasing the upper electrode at -200 V this rate has been increased to $0.080 \mu\text{g}/(\text{cm}^2 \text{ s})$ for the upper electrode and decreased to $0.017 \mu\text{g}/(\text{cm}^2 \text{ s})$ for the nozzle.

In the present experiments the deposited films are nonuniform, the maximum thickness corresponding to the position of the centre of the plasma beam. In case of films deposited during 1 h in the presence of external bias, a thickness of $1.14 \mu\text{m}$ has been measured in a zone adjacent to this position, leading to a deposition rate of 0.3 nm/s . Assuming that the deposition rates are proportional to the mass loss rates of electrodes, a value of 0.1 nm/s

can be estimated for the deposition rate in the absence of the DC bias.

3.2. Emission spectra

In Fig. 1 are shown the emission spectra from nitrogen plasma, in the spectral range 375–425 nm. The recorded spectra exhibit the presence of CN violet bands ($\text{B}^2\Sigma - \text{X}^2\Sigma$, $\Delta v = 0, \pm 1$). This emission is strongly enhanced in case of DC bias of the RF electrode and should be related to the much higher sputtering rate and/or due to the intensification of chemical reaction of solid carbon with atomic nitrogen [16]. The deposition takes place in presence of gas impurities, originating from desorption or in the supplying gas as is shown by some other spectral bands as: γNO bands in UV, NH bands at 336 nm, OH bands (the 3060 Å system).

3.3. Layer composition

3.3.1. X-ray diffraction results

In the XRD spectra of our samples an increase of diffraction level in the zone $2\theta = 20\text{--}30^\circ$ has been observed. The XRD spectra in this zone are very similar to the spectra obtained from carbon nitride films obtained with other techniques [16,18]. In a similar way this increase of diffraction level around 26.5° was attributed in our case to a slightly ordered amorphous carbon structure named as “layered amorphous carbon”.

3.3.2. Infrared absorption spectroscopy

The infrared absorption spectrum of a film deposited in presence of -200 V DC bias is shown in Fig. 2. The

Fig. 1. Emission spectra of the RF plasma jet generated in nitrogen with carbon electrodes (with and without DC bias).

Fig. 2. Infrared absorption spectrum of deposited film (down right corner the detailed deconvolution of absorption in the range 1100–1800 cm^{-1} is presented).

spectrum is similar to those obtained by using other techniques [3,16,18,19].

For the sample under discussion a refractive index $n = 3$ and a thickness $d = 1.14 \mu\text{m}$ have been deduced from the interference pattern at 4000–5000 cm^{-1} . The bands can be assigned to carbon, nitrogen and hydrogen bonding [3,15,19].

The bonding of nitrogen with carbon is proven by the absorption bands associated to CN bonds vibration. There is a general agreement that the peak around 2200 cm^{-1} (in the present spectrum at 2190 cm^{-1}) is due to carbon bond in sp state (triple bonded CN stretching mode [3,15,16,18–20]). The bands due to carbon bonded with N having sp^2 and sp^3 states should appear in the region 1200–1400 cm^{-1} [6,15,20,21] and are present in the spectrum as shoulders of the large double peaked absorption band around 1600 cm^{-1} . This band is caused by the superposition of NH_2 bands at 1550 cm^{-1} and 1660 cm^{-1} (sym-

metric and asymmetric bending modes) and the $\text{C}=\text{C}$ band at 1630 cm^{-1} [3,6]. In order to establish the contribution of different bands to the film absorption in the region 1200–1500 cm^{-1} the deconvolution of absorption for this spectral range has been performed. The deconvoluted absorption spectrum is shown in the inset of Fig. 2. The peaks appearing at 1222 cm^{-1} and 1386 cm^{-1} should be probably associated to carbon nitrogen bonds. The literature is rather conflictual as concerning the actual assignment of absorption peaks in this region. Carbon sp^3 bonded to nitrogen should appear at 1250 cm^{-1} [21]. In Ref. [15] this zone is assigned to C–N vibrations (at 1300 cm^{-1}) and peaks at 1360–1370 cm^{-1} to disordered sp^2 domains. Two peaks situated at 1225 cm^{-1} and 1400 cm^{-1} are assigned as the C–N stretching mode in [6]. In Ref. [18] it is observed as a relative increase of absorption in this region when nitrogen concentration increases but two peaks at 1300 cm^{-1} and 1500 cm^{-1} are found to be independent

Fig. 3. X-ray photoelectron spectra of substrate and deposited sample (C 1s, N 1s and Si 2p lines).

Table 1

The relative amount of atoms involved in the observed bond types as estimated from the fit of the XPS spectra of a deposited sample

Element	Binding energy [eV]	Relative amount [%]	Chemical bond
C	283.2	13.0	C–Si
	284.4	42.9	C–C (carbon phase)
	287.2	14.9	C–N (carbon nitride phases)
N	398.4, 399.9	17.1	N–C (carbon nitride phases)
Si	100.4	12.1	Si–C

of the nitrogen content and are assigned to C–C and C = C bonds.

3.3.3. X-ray photoelectron spectroscopy

Samples deposited without external bias have been analysed using XPS. The chemical state of Si, C, N elements has been investigated. In Fig. 3 the XPS spectra corresponding to substrate and deposited samples are presented.

The XPS spectra of the substrate are interpreted as follows. The peak around 99.5 eV corresponds to the Si–Si bond while the peak around 103 eV corresponds to the native silicon oxides [22]. No signal is detected in the N 1s zone showing the lack of nitrogen. A maximum is exhibited at 284.8 eV. At this bonding energy it corresponds to adventitious carbon (homonuclear C–C bonds [5–8,22–25]) which contaminates the substrate.

In case of deposited samples the interpretation of the spectra is done taking into account that in the present experiments the deposited film is not uniform and the investigated surface covers the film deposited at the center and at the margin of the plasma beam as well. The film deposited at the centre of the plasma beam has a thickness higher than hundreds of Å, while the film deposited at the margin of the plasma beam has tens of Å, being in this last case comparable with the investigation depth. It results that besides the data concerning the chemical content of the deposited film (signal detected from the centre of deposition zone), data concerning the chemical composition in the vicinity of the silicon substrate surface are obtained as well.

In the carbon bonding zone (C 1s core level) the spectra exhibit, at a first sight, at least three carbon bond types. The maximum at 283.2 is attributed to Si–C bonds. The shoulder around 284.8 eV is assigned to carbon phases (C–C bonds) and the shoulder around 287 eV to carbon nitride phases (C–N bonds) [7,8,23].

In the Si 2p zone a single peak situated at 100.1–100.3 eV is present. This bonding energy corresponds again to Si–C bonds [22,25]. The small thickness of the deposited film at the margin of the plasma beam incidence explains the presence of silicon atoms at the level of investigated surface.

In the nitrogen spectrum, two nitrogen bondings at 398.4 and 399.9 eV have been identified. Both are attributed to the bonds with C (as was shown in Refs. [24,26]

these peaks could correspond to two different phases of carbon nitride, a phase with stoichiometry near that of tetrahedrally bonded phase (β -C₃N₄) and another phase containing a variable ratio of [N]/[C].

In Table 1 the results of the XPS quantitative analysis of the investigated film are presented. The results were obtained from the integrated areas of the XPS curves fitted with Gaussian peaks and using sensitivity factors $S_C = 0.25$, $S_N = 0.42$ and $S_{Si} = 0.27$. The investigated layer has an overall composition of 71% C, 17% N and 12% Si. From the total number of the carbon atoms 20% are bonded to nitrogen, the ratio [N]/[C] being 1.21 and 60% are bonded to other carbon atoms. These results show that the deposited material is composed of carbon and carbon nitride phases. This agrees with the XRD and IR results.

The XPS analyses indicate that in the early stages of the deposition a silicon carbide interlayer is favoured to appear at the substrate surface. Such bonds can appear as a result of reaction of plasma beam (containing excited carbon, CN radicals in fundamental and excited states, C₂N₂ molecules, etc.) with the silicon substrate. This intermediate layer could be advantageous for the subsequent growing of carbon nitride phases.

4. Conclusions

A carbon nitride material has been synthesised as thin film with a new technique: downstream deposition from a RF generated, capacitively coupled nitrogen plasma beam with carbon electrodes. The emission spectra of plasma beam indicate that the deposition mechanism is sustained by the CN radicals. The CN radicals are formed in plasma from sputtered carbon atoms and/or chemically transported carbon as results of the electrodes reaction with atomic nitrogen. The material has been investigated as structure and composition by XRD, IR and XPS techniques. It is revealed as being amorphous and containing a mixture of carbon and carbon nitride phases having tetrahedral sp³ and trigonal sp² carbon to carbon and carbon to nitrogen bondings.

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