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Chemical binding and structure of carbonic thin films with advanced properties studied by electron spectroscopy

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There is considerable interest in new materials like the hard C-films, with good mechanical properties such as hardness, elasticity, low friction coefficient and chemical inertness. The properties of the carbonic thin films strongly depend on their chemical binding and microstructure. The ratio of sp^3/sp^2 carbon atoms is one of the most important factors governing the quality of the carbonic films. The ESCA (Electron Spectroscopy for Chemical Analysis) measurements were utilized to study the chemical binding in some carbon nitride thin films deposited using some plasma techniques (LCVD, Capacitively coupled RF plasma jet). A detailed analysis of the problem of assignment of spectral features in ESCA spectra is presented.

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1. Introduction

There is considerable interest in new materials like the hard C-films, with good mechanical properties such as hardness, elasticity, low friction coefficient and chemical inertness. A large number of film deposition methods have been employed to produce films with diamond-like properties [1-7].

The interest in trying to synthesize carbon nitride thin films largely stems from the prediction made by Liu and Cohen in 1989. Their calculations suggested a high bulk modulus of the hypothetical covalent bonded carbon nitride solid, β-C_3N_4, with a structure similar to β-Si_3N_4.

The hardness of such new material would have to exceed that of diamond.

The properties of the carbonic thin films strongly depend on their chemical binding and microstructure.

The ESCA technique (Electron Spectroscopy for Chemical Analysis) can be utilized for precision measurements of binding energies of the core electrons. These energies are not a property solely of the atom but also of its chemical environment. The change in the charge distribution in the valence shell, which occurs when an atom changes its valence state, is relayed to all the core electrons and revealed in the electron spectra. In quoting electron binding energies of an element to within a fraction of an eV, which is possible from ESCA measurements, one therefore has to specify the chemical compound in which the measurements were made.

In this paper we present an analysis of our results obtained by ESCA about the chemical binding in some carbon nitride thin films deposited at National Institute for Laser, Plasma and Radiation Physics, using some plasma techniques (LCVD, Capacitively coupled RF plasma jet).

The experimental data are compared with data from literature.

A detailed analysis of the problem of assignment of spectral features in ESCA spectra is presented.

2. Experimental

ESCA measurements

X-ray Photoelectron Spectroscopy (XPS) investigations of the deposited films have been performed with an ESCALAB MK II (V.G.Scientific) spectrometer. The residual pressure inside the measurement chamber was 10^{-9} Torr.

The X-ray Al K_α (E=1486.6 eV) radiation was used and the calibration of the instrument was obtained taking as reference the silver line Ag $3d_{5/2}$ at 368.2 eV. Spectra were collected in the analyzer constant energy mode, with pass energy Ep of 10. The analyzer resolution was proximately 2% of the pass energy.

The samples with NCx deposited films were produced by LCVD [4] and by a Capacitively coupled RF plasma jet [5].

N_x deposited by LCVD [4] were deposited on the following substrates: Polished alumina ceramics; Laser activated alumina; Pre-deposited Ti films on alumina; Quartz plates (2 mm thick); Single crystal sapphir. The experimental set-up for LCVD has been described elsewhere [4].

It consisted of a cross-shaped glass reaction cell (base pressure: 10^{-3} Torr) in which the gases/ vapors and the substrate were introduced. In order to monitor the gas composition by IR spectrometry, one arm of the reaction cell was provided with ZnSe windows. The UV laser radiation was directed through a quartz window perpendicular to the substrate. The KrF excimer laser

employed had the following characteristics: 40 mJ per pulse, υ_{FWHM} τ 20 ns and 2 Hz repetition frequency.

The deposition of CN_X films was performed by irradiating a mixture of ethylene/nitrous oxide/ammonia (C2H4/N2O/NH3=1/2/8), at a total pressure of about 80 Torr with 5000 laser pulses.

CN_x thin films prepared by a Capacitively coupled RF plasma jet [5] have been deposited on silicon substrates downstream of a nitrogen plasma beam generated in a combined rf (13.56 MHz, 40-50 W) and DC (voltage 200V, power 1-10 W) discharge between a graphite electrode and a graphite nozzle. By combining the rf and DC sources the capability of the rf field to create extended plasmas is used together with the enhanced sputtering and biasing effect of the DC source. The precursors (gaseous carbon species and gaseous carbon compounds) are formed in a combined rf and DC discharge. It is sustained in nitrogen at 10-20 mbar between two circular graphite plates separed by a small distance (1-2 mm). The two graphite plates are exposed to the sputtering and to surface chemical reactions with the nitrogen plasma [5]. The resulting carbon containing species are subsequently transported by the plasma flow towards the deposition region. The application of the DC bias is of paramount importance for the film bombardment during deposition and the electrode that is the main carbon species source. The graphite nozzle, the deposition chamber and the substrate are electrically connected and they form a large electrode, which is grounded.

When the rf electrode is negatively biased, the cathode fall is localized near this electrode and the discharge is supplied with carbon atoms coming mainly from this electrode; the ion flux toward the grounded substrate is small. In contrast, when the rf electrode is positively biased, the cathode fall is localized near the nozzle surface and substrate, which leads to a large ion flux and ion bombardment of the film during deposition.

3. Results and discussion

X-ray photoelectron spectroscopy characterization of carbon nitride thin films

Synthesis of β-C_3N_4 has recently been claimed by Niu, Lu and Lieber [1] on the basis of electron diffraction data but the overall composition of the films was not stoichiometric: the N to C concentration ratio attained in most cases is about [N]/[C] = 0.7.

The reason for this discrepancy can be the fact that for the deposition methods investigated, β-C_3N_4 forms only in very small crystallites that are embedded in amorphous sp^2 bonded C_XN_Y where y/x is typically between 0.2 and 0.5, depending on deposition conditions.

These two carbon nitride phases can be distinguished by their binding energies. Such a distinction provides researchers with a tool to assess quickly the quality of their films not simply on the basis of the overall nitrogen content, but rather based on the nitrogen and carbon that are in proper binding states.

If pure β-C_3N_4 were readily available, it would be a simple routine procedure to establish characteristic binding energies for this purpose.

The problem of the correct assignment of the peaks which correspond with different chemical states of carbon and nitrogen identified in the XPS spectra to the two carbon nitride phases is that the precise knowledge of the binding energies has to precede the production of β-C_3N_4 in a purer form.

XPS analysis of carbon nitride thin films [2,3], typically shows four distinguishable features in the carbon spectrum and three in the nitrogen spectrum.

The carbon peak at the binding energy 284.6 eV is identified as originating from adventitious carbon and surface carbon that may have lost its nitrogen neighbors due to reaction with O_2 and/or CO from the air. The peak at 289.5 eV is identified as originating from CO type bonds. These two peaks are incidental and are excluded from further consideration. The remaining two carbon peaks at 285.9 and 287.7 eV reflect two different binding states between carbon and nitrogen. Correspondingly, there are two nitrogen peaks at 400.0 and 398.3 eV for these two binding states, while the peak at 402.0 eV is identified as originating from N-O or N-N bonds and is not considered further.

In the assumed β-C_3N_4 structure, the carbon atoms are in tetrahedral sites and the nitrogen atoms are in threefold positions. Diamond, the tetrahedral allotrope of carbon, has about the same binding energy as other pure carbon forms and hydrogenated carbons.

The binding energy of the 1s electrons is quite insensitive to the coordination as long as the bonds are nonpolar. Even moderate polarization of carbon bonds leads, however, to significant binding energy changes.

For example, in pyridine (C_5H_5N), which is a π-bonded aromatic ring with only one nitrogen atom, the carbon binding energy is 285.5 eV. In the tetrahedral bonded nitrogen containing compound urotropine (hexamethylene-tetramine: $C_6H_{12}N_4$) the carbon binding energy is 286.9 eV. The shift is probably due to the higher degree of polarization of the urotropine bonds. The nitrogen binding energies in these compounds are 399.8 eV for pyridine and 399.4 eV for urotropine.

Note that the later compound contains the nitrogen and carbon atoms in position closely resembling those in the predicted β-C_3N_4 structure. The difference between this molecule and a subnanometer size crystallite of β-C_3N_4 is mainly that the carbon dangling bonds are hydrogen terminated although the nitrogen atoms in urotropine are in tetrahedral, rather than in trigonal sites. It is then to be expected that in amorphous carbon nitride, the carbon and nitrogen atoms in positions resembling β-C_3N_4 (to be referred to as phase 1, or C^1 and N^1) will have similar binding energies to those in urotropine. However, since the nitrogen atoms are now in trigonal positions, the extra electron pairs will contribute more effectively to screening of the 1s orbitals and this should lead to some decrease of the N 1s binding energy. Atoms in "defective" positions, i.e., in areas with excess carbon (phase 2, or C^2 and N^2), will have binding energies closer to those in pyridine. In

keeping with this analysis, we assign the peaks at 287.7 and 398.3 eV as C1 and N1 peaks, respectively, and the peaks at 285.9 and 400 eV as C2 and N2 peaks, respectively.

XPS analysis of CN_x thin films deposited by LCVD [4]

The irradiation with 5000 laser pulses of the mixture C2H4:N2O:NH3=1:2:8 (P=80 Torr) using different substrates for the film deposition, led to different degrees of gas depletion and acetylene formation as well as changes in film composition and morphology, as revealed by XPS results.

The chemical composition and bonds in the films were studied by XPS. The elemental composition indicates the usual carbon and oxygen contamination in the ambient. In this respect, the film deposited on the Ti substrate exhibited a higher degree of surface oxidation. The highest nitrogen incorporation in film seems to occur on pre-deposited Ti and laser –activated alumina substrates, whereas the N content of a sample deposited on quartz is very poor.

Following the analysis of carbon and nitrogen XPS lines performed by Marton et al. [2], there are four characteristic peaks in the C 1s spectrum and three in the N 1s spectrum. Typical C1s and N1s spectra of films deposited on α-Al_2O_3, on activated alumina and on pre-deposited Ti are shown in Fig. 1.

Peaks at 284.6, 285.9, 287.5 and 289.5 eV of the C1s photoelectrons and 398.4, 399.8, and 402.1 eV for the N1s photoelectrons were chosen in order to deconvolute the spectra considering the best gaussian fits.

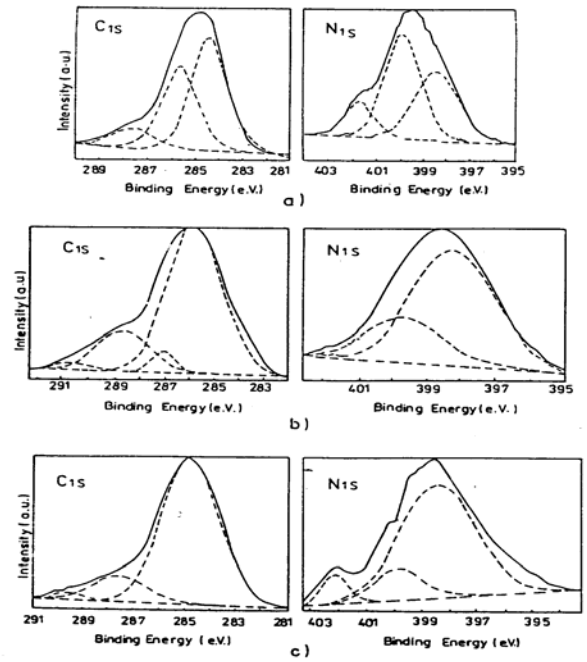

Fig. 1. C1s and N1s photoelectron spectra of films deposited on (a) α-Al2O3, (b) laser - activated alumina and (c) pre-deposited Ti layer.

The results of deconvolution of C1s and N1s suggested the presence of different types of chemical bonds in the films. The C1s peak at 284.6 eV is usually assigned to adventitious carbon but may contain contributions from amorphous carbon, graphite, and surface carbon that have lost their nitrogen due to reactions with O_2. However, this peak was also associated with the N1s peak at 402.1eV and ascribed to a carbon nitride phase with a very low nitrogen incorporation [5]. Also, the nitrogen peak around 402.1 eV was identified as belonging to free nitrogen atoms. Correspondingly, the C 1s peak at 289.5 eV was attributed to CO type bond. The remaining C1s and N1s peaks were selected in two pairs, each reflecting different bonding states between carbon and nitrogen: the pair 287.5 and 398.4 eV was assigned to phase 1 (C^1 and N^1), reflecting a tetrahedral sp^3 bonded carbon phase that should resemble the β-C_3N_4 phase; the pair 285.9 and 399.8 eV was ascribed to phase 2 ($C^2$and N^2) corresponding to sp^2 bonded C and comprising a lower N content.

This composition may vary from C_5N to C_4N_2 and beyond. Based on the relative percentage atomic concentration of C^1, C^2, N^1 and N^2 phases, the N/C composition for phase 1, ($[N^1]/[C^1]$, as well as the fractional concentration of phase 1, $([N^1]+[C^1])/([[N^1]+[N^2]+[C^1]+[C^2])$ may be obtained [4].

The results suggest that on a quartz substrate, the composition and fractional concentration of phase 1 are favored, and the overall composition (of both phase 1 and phase 2, $[N^1+N^2]/[C^1+C^2]$) seems to prevail in CN_X films deposited on a Ti substrate.

The processes through which the substrate could influence nitrogen incorporation in a specific bonding state are not clear, and further investigations are required in order to elucidate them.

XPS analysis of CN_x films prepared by a Capacitively coupled RF plasma jet [5-7]

The film composition was determined from XPS measurements. The information about the nature of carbon and nitrogen chemical bonds was obtained from the profiles of the lines corresponding to the binding energies of the two atoms. In Fig. 2, XPS spectra are shown which are obtained in the region of the binding energy of carbon atoms (around 285 eV) and of the binding energy of the nitrogen atoms (around 399 eV). Spectra of the undeposited substrate (Fig. 2a) show a quite symmetric carbon peak due to the contamination with carbon. No nitrogen peak is observed. The spectra of the deposited films (Fig. 2 b,c) show the incorporation of nitrogen and the appearance of a marked shoulder of the C1s line on the higher energy side.

This shoulder is attributed to the carbon-nitrogen bonds.

Taking into account sensitivity factors of 0.25 for carbon and 0.42 for nitrogen [8], from the area of C1s and N1s peaks a global N/S ratio of 0.28 was obtained in the two cases of supplementary negative and positive DC bias of the upper electrode.

An analysis of the line shapes of the C1s and N1s signals was performed in order to identify the different bond types. In the carbon binding zone (C1s core level), the spectra exhibit three carbon bond types.

The main peak at about 284.5 eV must be assigned to carbon phases (carbon-carbon bonds) as can be concluded from the signal of the undeposited sample. The peaks located at 286.4 eV and 288.1 eV are related to nitrogen incorporation and are assigned to C-N bonds.

In the nitrogen – binding zone the spectra are also a superposition of three peaks. The peaks located at 398.7 and 400.3 eV are assigned again to C-N bonds, probably being associated to sp^2 and sp^3 hybridized C, respectively. The small peak located at 402 eV is assigned to N-O bonds and is probably related to the accidental incorporation of oxygen into the sample during the deposition.

We have tried to treat the data in the frame of the analysis given in Ref. 2, as in the case of films deposited by LCVD**,** and to separate two carbon nitride phases, one with a stoichiometry similar to C_3N_4 and another with N:C variable between 0.2-0.7. We have failed to find such phases in our films. However, following the same methodology, we observed that the N:C ratio associated with the peaks located at 288.1 and 400.3 eV is the same for the two samples within the experimental uncertainty. Consequently, the C1s peak located at 288.1 eV and N1s peak located at 400.3 eV are assigned to a type of C-N bond (referred to as type I). The N:C ratio in this phase is around 0.7, suggesting a stoichiometry corresponding to a compound like C_3N_2.

The remaining peaks located at 286.1eV and 398.6 eV are assigned to another carbon nitride phase, or to a mixture of CN phases (referred to as type II). The N:C ratio is for this mixture of phases 0.43 and 1.52 for negative bias and positive bias, respectively.

The XPS investigations show that the C-N bond type distribution in the films is different for different bias conditions. The so-called type II bond, corresponding to lower binding energies of carbon and nitrogen, is almost absent in the case of the film exposed to ion bombardment during deposition.

These results must be correlated with recent theoretical calculations [9] about the coordination of carbon as a function of nitrogen concentration in energetically deposited carbon nitride: a structural transformation from primarily sp^3 –bonded to sp^2 – bonded carbon was observed as the nitrogen concentration increases. Calculations on nitrogen – substituted carbon clusters indicate that there is a preference to form sp^2 – bonded carbon when the nitrogen concentration is larger than 12%.

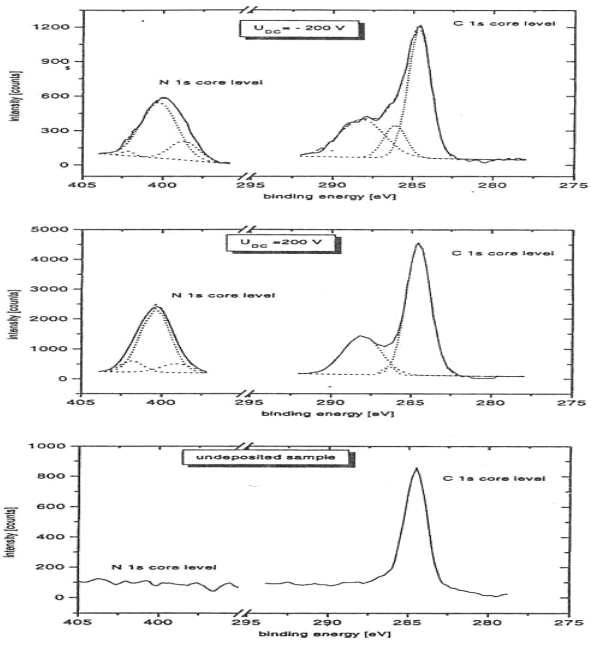

Fig. 2. The C1s and N1s core level XPS spectra for: (a) undeposited substrate, (b) a film deposited at positive bias of the rf electrode (200 V), and (c) a film deposited at negative bias of the rf electrode (-200 V).

4. Conclusions

The principal results of our studies by ESCA (Electron Spectroscopy for Chemical Analysis) for characterization of chemical bonding in carbon nitride thin films, deposited using some plasma techniques (LCVD, Capacitively coupled RF plasma jet) are presented.

A chemically specific technique as XPS is required to determine chemical states of the atoms present in these films.

The peak deconvolutionof C1s and of the nitrogen N1s lines allows identification of at least two carbon-nitrogen bond types.

The C-N bond type is influenced by the substrate nature and by parameters of the deposition process

The results of XPS analysis of CN_x thin films deposited by LCVD show that the substrate could influence nitrogen incorporation in a specific bonding state by processes which are not clear, and further investigations are required in order to elucidate these processes.

The results of XPS analysis of CN_x films prepared by a Capacitively coupled RF plasma jet show that the C-N bond type distribution in the films is different for different bias conditions. The so-called type II bond, corresponding to lower binding energies of carbon and nitrogen, is almost absent in the case of the film exposed to ion bombardment during deposition.

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