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X-Ray photoelectron spectroscopy reference data for identification of the C_3N_4 phase in carbon–nitrogen films

A.P. Dementjev[a,*], A. de Graaf[b], M.C.M. van de Sanden[b], K.I. Maslakov[a], A.V. Naumkin[a], A.A. Serov[a]

[a] *RRC Kurchatov Institute, Kurchatov sq.1, Moscow 123182, Russia*
[b] *Eindhoven University of Technology, Department of Applied Physics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

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Abstract

The β-C_3N_4 phase should have a tetrahedral (sp^3-bonded) structure resulting in C1s and N1s XPS peaks with only one feature at a position defined by the electronegativity of four C–N bonds. In this work we determined the binding energy of the C1s and N1s XPS peaks in melamine ($C_3N_6H_6$). In this compound the carbon atoms have four bonds with nitrogen atoms (double and two single); the nitrogen atoms have two chemical states: C–N=C and C–N=H_2. Since the total number of chemical bonds in this compound is the same as in the hypothetical β-C_3N_4 compound, this compound is more suitable as a C1s XPS reference for the β-C_3N_4 phase. The binding energy of the C1s and N1s XPS peaks in melamine was determined to be equal to 287.9 and 399.1 eV, respectively. The binding energies were determined relative to the C1s XPS peak for carbon contamination (adventitious carbon).

Keywords: X-Ray photoelectron spectroscopy; Melamine; C–N bonds; C_3N_4

1. Introduction

The great interest in carbon nitride materials is mainly driven by the possibility of realizing the superhard β-C_3N_4 compound [1]. To obtain information about the chemical state of the carbon and nitrogen atoms X-ray photoelectron spectroscopy (XPS) is often used. There are many publications devoted to the identification of the chemical C–N bonds by use of the C1s and N1s XPS spectra [2–16]. In those publications the C1s peak has been deconvoluted into from two to five peaks with binding energies at approximately 284.6, 285.9, 287.7 and 288.2 eV. The intensities of these peaks differ very strongly in different cases. In some works the main intensity of the C1s XPS peak is situated close to 284.6 eV [5,12,14–16]. Boyd et al. [12] identified the peak at 284.6 eV as adventitious carbon and used it to charge reference the spectra. The peaks at 285.9 and 287.7 eV were assigned to sp^2 and sp^3 carbon–nitrogen bondings, respectively, and the peak at 288.2 eV was ascribed to C–O bonds. Bhattacharyya et al. [14,15] deconvoluted the C1s XPS peak into five components at approximately 284.7, 285.3, 286.7, 287.7 and 289.6 eV which were assigned to pure carbon, C=N, C≡N, C–N, and C–O bonds, respectively. Diani et al. [4] observed in their CN_x:H films a C1s XPS peak at 287.5 eV, by 3.1 eV above the binding energy of the C–C bonds in graphite.

There are some ambiguities in literature concerning the structure and binding energy of the N1s XPS spectra. Marton et al. [5] and Boyd et al. [12] prepared

* Corresponding author. Tel.: +7-95-196-7286; fax: +7-95-196-4588.
E-mail address: a.dem@g23.relcom.ru (A.P. Dementjev).

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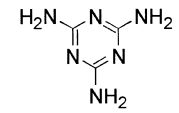
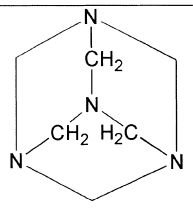
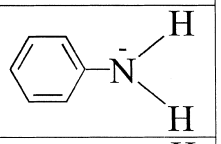
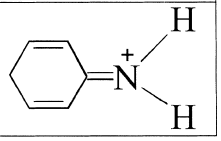
carbon nitride films by means of ion beam deposition. They deconvoluted the N1s XPS spectra into three peaks at 398.3, 400.0 and 402.5 eV the first two of which were assigned to sp^3 and sp^2 bonding, respectively. The peak at 402.5 eV Boyd et al. [12] assigned to N–O surface contamination and/or N_2 trapped within the film during deposition. Since the same N1s spectrum structure was observed for in situ nitrogen ion implantation in graphite without any oxygen contamination [17], the proposed assignment to trapped N_2 in the film [12] seems the most likely. There may be another explanation for the peak at 402.5 eV. When nitrogen atoms form only two bonds with carbon atoms, the nitrogen atoms become in fact N· radicals. According to data for NO radicals [18] the splitting of the N1s XPS peak is equal to 1.5 eV with the component at lower binding energy having a three times higher intensity than the one at higher binding energy. In this perspective the peak at 402 eV could be attributed to the high-energy component of the N· radicals. Accordingly, this N1s XPS peak component should be accompanied by a low-energy peak at 400.5 eV with a three times higher intensity. Rossi et al. [6] found peaks at 398.2 and 400.2 eV which they attributed to N≡C and N=C bonds, respectively. Bhattacharyya et al. [14,15] deconvoluted the N1s peak into four components at 398.3, 398.8, 399.8 and 400.8 eV corresponding to C–N, C≡N, C=N and N–O bonds.

Plenty of data in the literature clearly shows the complexity and non-equilibrium nature of physical and chemical processes involved in the carbon nitride synthesis. Since until now synthesis of the β-C_3N_4 phase has not been realized in practice, the interpretation of C1s and N1s data at present is not unambiguous because of absence of a reliable XPS fingerprint of one-phase carbon nitride compound with four C–N bonds. The β-C_3N_4 phase should have a tetrahedral (sp^3-bonded) structure resulting in C1s and N1s XPS peaks with only one feature at a position defined by the electronegativity of four C–N bonds. As a standard for identification of the carbon sp^3-bonds hexamethylenetetramine is often used [5,12]. The XPS data on hexamethylenetetramine were taken from the paper by Gelius et al. [19]. However, because the carbon atoms in this compound have only two single bonds with nitrogen and two single bonds with hydrogen (see Table 1) the identification may not be completely correct. According to Siegbahn et al. [20] the total number of bonds between atoms of different electronegativity values determines the chemical shift of any XPS peak. In the present work results of measurements of the binding energy of C1s and N1s XPS spectra in melamine ($C_3N_6H_6$) are presented. The carbon atoms in this compound have four C–N bonds (one double and two single ones), nitrogen atoms have three bonds with carbon atoms. Because the total number of chemical bonds is the same as in the hypothetical β-C_3N_4 phase, melamine should be suitable as a reference standard for β-C_3N_4.characterization.

Compound	Chemical formula	Chemical structure
Melamine	$C_3N_6H_6$ **Eb(C1s)=287.9 eV Eb(N1s)=398.5, 399.1 eV this work**	
Hexamethylenetetramine	$C_6H_{12}N_4$ **Eb(C1s)=286.9 eV Eb(N1s)=399.4 eV ref. 19**	
Aniline	Resonance form 1 **ref. 20**	
Aniline	Resonance form 2 **ref. 20**	

2. Experimental

The XPS data were obtained using the MK II VG Scientific spectrometer. Photoelectron processes were excited by an Al Kα X-ray source with photon energy of 1486.6 eV. The vacuum in the analysis chamber was 1.5×10^{-7}–6.5×10^{-8} Pa. The spectra were collected at the analyzer energy mode being constant. The pass energy for XPS was 20 eV. The C1s, N1s and O1s XPS spectra were measured at 0.1 or 0.05 eV step size. Under these conditions the FWHM of the Au4f peak was 1.2 and 1.1 eV, respectively. Melamine films of approximately 5 nm thickness were deposited on Cu by ex situ vacuum evaporation at 5×10^{-6} Pa. The small thickness of the films assures the absence of charging effects during the XPS measurements. After the deposition the oxygen contamination was approximately 2%. This concentration does not show C–O noticeably interaction in C1s XPS peak.

3. Results and discussion

Fig. 1 shows the C1s XPS spectra of a melamine film recorded at normal and grazing angle (75° from the

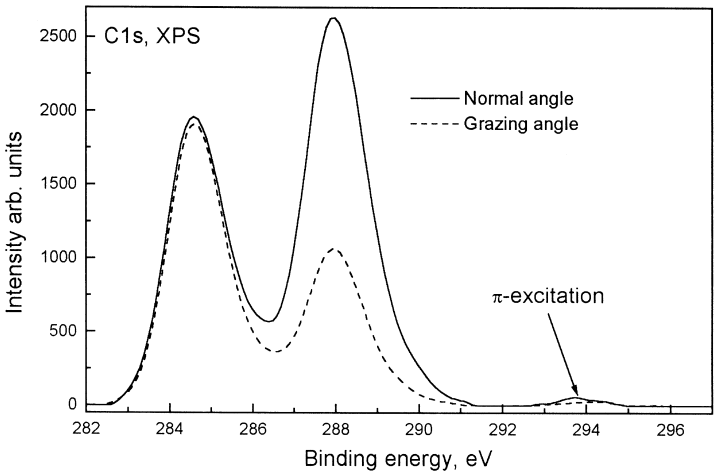


Fig. 1. The C1s XPS spectrum for melamine obtained at the normal and grazing angle.

normal). The C1s spectrum consists of two features of binding energy values realized at 284.6 and 287.9 eV, full width at half maximum (FWHM) was 1.6 eV for both states. One can see an increase of intensity of the left part of the spectrum for the case of the grazing angle. These data allow us to identify the peak at 284.6 eV as originated from a carbon-containing contamination. The melamine has a strong tendency to be carbon-contaminated as it is testified by the 284.6 eV C1s XPS peak of a melamine powder which had a double intensity in comparison with the melamine film. The binding energies of the C1s components in the powder were the same as in Fig. 1.

Therefore, the binding energy at 287.9 eV is the characteristic of the carbon atoms that have one double and two single bonds with the nitrogen atoms (see Table 1). According to Ronning et al. [16] the predicted β-C_3N_4 phase is expected to induce a single line at 400 eV in the N1s spectrum and a single line at high binding energies of approximately 288 eV in the C1s spectrum. In the case of melamine we find a C1s peak at 287.9 eV, which is very close to the predicted value of 288 eV [16]. We suggest that the C1s peak at 287.9 eV is a good indication of the C–4N interaction.

The presence of the double C=N bonds is also testified by the observed π-excitation which appears in all carbon compounds with double bonds. Its position is 7 eV above the basic C1s peak [21]. The peak at 284.6 eV shows no π-excitation, confirming that double bonds are absent in those adventitious carbon.

Fig. 2 shows the N1s XPS spectrum of melamine. The binding energy of this peak is equal to 398.7 eV with FWHM of 2.4 eV. This peak shows an asymmetry in the right part and π-excitation. The N1s XPS spectrum was deconvoluted into three peaks at 398.5, 399.1 and 400.7 eV with FWHM = 1.4 with an intensity ratio

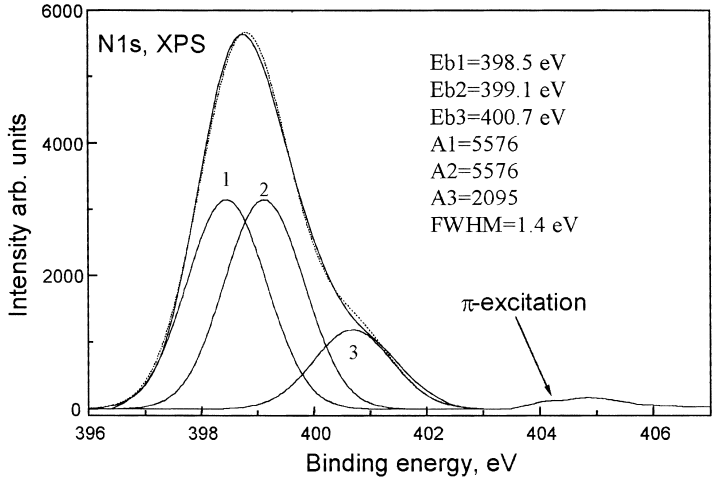


Fig. 2. The N1s XPS spectrum for melamine obtained at a normal angle. The shape of the N1s XPS spectrum is independent of the angle.

of the first and the second peaks of 1:1. The nitrogen atoms have two chemical states in melamine: C=N–C and $C-NH_2$ with state ratio 1:1 (see Table 1). Estimation of the charge on the nitrogen atom for these two groups [22] has shown that in the $C-NH_2$ group nitrogen atoms have more negative charge than the one in the C=N–C group. Therefore, the peaks at 398.5 and 399.1 eV were attributed to $C-NH_2$ and C=N–C bonds, respectively. We cannot identify the peak at 400.7 eV by simple chemical interaction. It is possible one can use two states as in case of aniline [20] (see Table 1). In that case the $-NH_2$ group has two features in N1s XPS peak one of them is at 400.7 eV.

Since in the β-C_3N_4 phase the nitrogen atoms have three bonds with carbon atoms, according to our deconvolution result, the binding energy at approximately 399.1 eV (i.e. that of C=N–C) should be used for the identification of this phase.

The N1s XPS spectrum of polyemeraldine base as recorded in [22,23] showed a similar structure with almost the same individual peak positions as in Fig. 2. The spectrum was deconvoluted into two major components at 399.3 and 398.1 eV with FWHM of 1.65 eV which were attributed to =N– and –NH– chemical interaction. The feature at approximately 400.7 eV was not discussed. The coincidence of our N1s spectrum with that in [22,23] testifies that one should use two states in –NH group for interpretation of N1s XPS peculiarities.

4. Conclusions

The C1s and N1s XPS spectra of melamine were analyzed in order to obtain a more reliable reference data for identification of the C_3N_4 phase in CN_x films. For the carbon atoms having four bonds (double and two single) with nitrogen the measurements gave the C1s binding energy of 287.9 eV. The binding energy of the N1s for nitrogen atoms having three bonds with carbon (C=N–C) should be used the value 399.1 eV. It seems reasonable to say that the melamine is the best up-to-date reference compound for C_3N_4 detection and characterization.

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