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Soft X-ray emission spectroscopy used for the characterization of a-C and CN_x thin films

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ABSTRACT

We present the results of a soft X-ray emission spectroscopy study of a-C and CN_x films on a Si(100) substrate. Also for the characterization of the homogeneity in depth of these films electron energy loss spectroscopy measurements with localization better than 4 nm were carried out. In case of CN_x films the highest diamond-like modification occurs in the region close to the Si(100) substrate. The film density decreases with increasing distance from the substrate and becomes almost constant in range of thicknesses more than ~2 nm.

1. Introduction

Carbon thin films have a highly promising industrial potential as they are characterized by chemical inertness, low friction coefficient, high hardness and elasticity [1]. They found a use in various areas from high temperature electronics to protecting coatings for magnetic carriers (hard discs) [2]. The present work is devoted to the investigation of electronic structure and a number of other properties of amorphous carbon (a-C) and carbon nitride (CN_x) films. The structure and the chemical bonding configurations of these films have been usually examined by using ellipsometry, Raman spectroscopy, Fourier transform infrared spectroscopy, secondary ion mass spectrometry, Auger electron spectroscopy, photoelectron spectroscopy, X-ray absorption spectroscopy, soft X-ray emission spectroscopy and electron energy loss spectroscopy [2–17]. We used the latter two methods to extend and improve the mentioned investigations.

2. Experimental

Thin a-C and CN_x films were prepared by magnetron sputtering of a high purity graphite target in Ar and Ar/N_2 atmosphere, respectively. It is described in details in Refs. [2–4]. Variation of x in CN_x films was done by changing the N_2 concentration in the gas mixture. Thickness of films was several nanometers and the substrate temperature during preparation T was varied from 300 to 530 K. As a substrate we used mostly the (100) surface of silicon (Si), but also the same one covered with a cobalt (Co) film. The preparation of cross-sectional samples for investigations in a transmission electron microscope followed the procedure described in detail in Ref. [18]. Such measurements were performed using a "FEI Tecnai 20 F" microscope (field emission gun, accelerating voltage of 200 kV, lateral resolution 0.14 nm) equipped with a Gatan image energy filter "GIF-100". This allowed obtaining high resolution transmission electron microscopy (HRTEM) images as well as performing electron energy loss spectroscopy (EELS) measurements from areas of 4 nm in diameter. For study of electronic structure features we used X-ray emission spectroscopy. Excitation of the sample was done by an electron beam of energy from 1 to 9 keV, current density of 0.15 mA/mm^2 and angular incidence of the electron beam of 135°. Electron penetration depth and X-ray emission depth depend on the electron beam energy (both are $\leq$2.5 nm at 5 kV). Spectra of the induced X-ray emission were studied in a PCM-500 spectrometer with diffraction grid of 600^{-1} mm period,

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energy resolution was about 0.2 eV. In a number of cases near-edge X-ray absorption fine structure (NEXAFS) measurements were performed.

3. Experimental results and discussion

Transmission electron microscopy was used for sample characterization. Fig. 1 shows a HRTEM image of a CN_x film of 2 nm thickness on a Si(100) substrate. The sample was prepared in such a way that one can see CN_x film boundaries with Si(100) and also the binder. In more detail they are given in the inset in Fig. 1. Here one can see Si planes of (100) type with interplanar spacing of 0.54 nm.

A series of soft X-ray emission spectra of CN_x with thicknesses of $d =$ 1.5 (a), 2.5 (b) and 3.5 nm (c) on Si(100) substrate at bombardment with electrons of 2–7 keV energies is given in Fig. 2a–c. The intensity of C K_α emission band ($2p \rightarrow 1s$ transition) increases with increasing energy of primary electrons. It is more intensive in lower than for higher electron energies. Particularly, for a CN_x film of $d = 1.5$ nm at energy of initial electrons increasing from 2 to 3 keV and from 3 to 4 keV intensity increases by a factor of 1.7 and 1.1, respectively. The same behavior is observed for thicker CN_x films. With increase of excitation energy from 2 to 3 keV for CN_x films of 2.5 and 3.5 nm thicknesses intensity of C K_α band increases by a factor of 1.8 and 2.0, respectively (see Fig. 2b, c).

Comparison of CN_x spectral shape for films of various thicknesses shows substantial differences. Features A and B observed in low-energy region of C K_α emission band are analogous to those of hydrogenated carbon (a-C:H) films [19]. They are strongly pronounced for the CN_x film of $d = 1.5$ nm and weakly visible for $d = 2.5$ and 3.5 nm. For all samples one of the features shows a splitting (double feature is denoted with C and D). The ratio of these two peaks changes with the thickness of the CN_x film. For a sample with $d = 1.5$ nm the feature D is less pronounced than C, independently on the energy of incident electrons. For $d = 2.5$ nm, intensities D and C are equal at primary electron energy of 2 keV, but for higher energy D is already somewhat higher than C. So, the asymmetry of these lines is determined by the electron penetration depth. Completely similar dependences are observed for CN_x films with $d = 3.5$ nm.

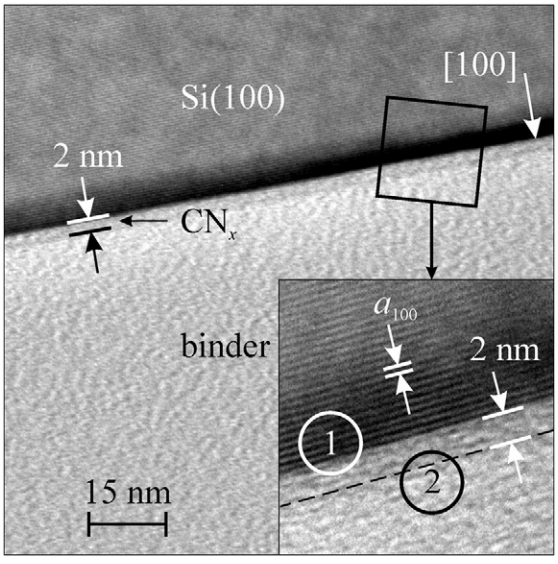

Fig. 1. Cross-sectional micrograph of the 2-nm thick CN_x sample deposited at the substrate temperature of 300 K. The area marked with a square is shown in more detail in the inset. Other explanations are given in text.

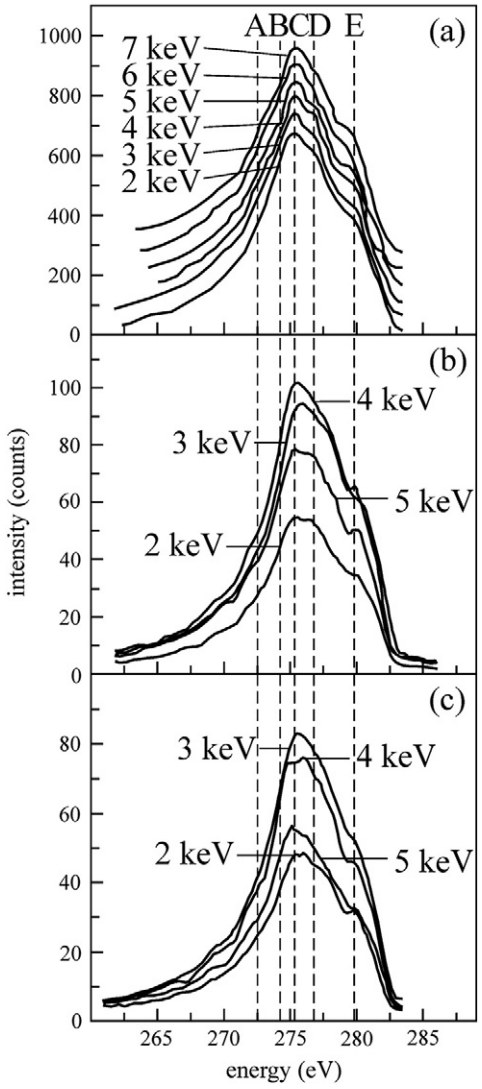

Fig. 2. Electron stimulated soft X-ray emission spectra at the C K_α band of 1.5 (a), 2.5 (b) and 3.5-nm (c) CN_x films prepared at the substrate temperature of 300 K. The spectra obtained using 2–7 keV presented in (a) are scaled by the maximum amplitude to the spectrum obtained at 2 keV and linearly shifted for clarity.

One can conclude that feature D is associated with the appearance of new bonds (for example, due to hydrogenation) which are located in the vicinity of the surface, as this feature is observed at very low energy of only 2 keV. With decrease of the film thickness the intensity of feature D becomes lower, which means a decrease of hydrogenation contribution. Such changes of shape of the C K_α emission bands can be connected with radiation damage effects. Contributions from chemical compounds with other atoms (nitrogen, oxygen) were excluded as these elements were not found in the studied samples. Only at high energies of primary electrons oxygen can come from the substrate (SiO_2 is a native oxide on the Si surface), but then the CN_x film is destroyed even earlier.

A part of the spectrum where a feature denoted with E is situated stays almost the same at varying thicknesses of the CN_x film.

In Fig. 3 C K_α emission band of the CN_x film ($d = 2.5$ nm) obtained at 2 keV (curve 1) is compared with the spectrum of a hydrogenated carbon (a-C:H) film [19] (curve 2). The CN_x spectrum is similar to that of a-C:H with the exception of better separation of C, D and E features. These spectral features were observed in the C K_α emission band of a CN_x film studied in Ref. [13] at the same energies (Fig. 3, curve 3).