Effect of deposition temperature on chemical composition and electronic properties of amorphous carbon nitride (*a*-CNx) thin films grown by plasma assisted pulsed laser deposition

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ABSTRACT

The effect of deposition temperature and nitrogen inclusion in amorphous carbon (*a*-C) films, deposited by plasma enhanced pulsed laser deposition, on chemical composition and electronic transport has been studied. *a*-CNx films were deposited on Si (100) by pulsed ArF laser ablation of a graphite target, under N_2 atmosphere. A radiofrequency (13.56 MHz RF) apparatus was used to generate plasma of excited nitrogen species, and its effect on nitrogen uptake and CNx film formation has been studied. Chemical and micro-structural changes associated to increased deposition temperature and nitrogen incorporation were examined by x-ray photoelectron spectroscopy; electrical properties were analyzed by the four-point-probe methods. Temperature-dependent conductivity measurements are tentatively interpreted and discussed in reference to chemical composition.

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1. Introduction

Carbon nitride (CNx) is a very interesting material for many different applications, ranging from tribological type, like wear-resistant coating, to optical and electronic engineering. The synthesis of a crystalline material, however, has been proved to be most elusive, and most attempts resulted in an amorphous *a*-C:N alloy, with a variable range of nitrogen concentrations [1]. The amorphous structure (*a*-C:N) exhibits good and exploitable properties, like high hardness value, very low friction coefficient, chemical inertness, and variable controllable electrical conductivity and band-gap, as a function of relative N/C composition [2]. Many experiments have been made in the past to deposit carbon nitride thin films using physical vapour deposition techniques, direct current (DC) and radio frequency (RF) magnetron sputtering [3], electron cyclotron resonance [4], ion beam or ion beam assisted deposition [5,6] and reactive pulsed laser deposition (PLD) [7,8].

PLD is one of the most widely used methods of deposition for *a*-CN, because of its specific features. The carbon bond configuration in PLD films of *a*-C and *a*-CN type is highly dependent on the energy (wavelength) of the laser radiation, viz. ultraviolet, visible and infrared (UV, Vis, and IR), used for the ablation [9,10]. The average kinetic energy of the particles in the UV (~6.2 eV) radiation "plume", is very suitable to generate sp³-bonded carbon [9], even if the high energetic particles striking the growing film can produce high compressive stress and problems in film stability and adhesion [11], quite similar to problems observed for sputtered films [32].

Nitrogen incorporation in the films can be improved using a RF or DC nitrogen glow discharge with a proper bias voltage, since the negative voltage plays a dominant role in the tetrahedral C–N bond formation and suppression of graphite-like CN state [12–18].

In our work, we studied the effect of deposition temperature and N_2 plasma on physical–chemical and electronic properties of carbon nitride thin films. We used a specific DC biased plasma configuration, to improve adhesion and film quality. Selected samples were analyzed by x-ray photoelectron spectroscopy (XPS), and evaluated for electronic properties by the four-contact in-line probe measurements, as a function of deposition temperature.

2. Experimental details

2.1. Preparation of films

Carbon nitride thin films were prepared by PLD technique. We used an ArF excimer laser (Lambda Physik COMPex 102), 10 ns duration, pulse energy of ~57 mJ, with a corresponding fluence of ~2.7 J/cm² on the target. The laser beam was focused at an angle of 45° on a pyrolytic graphite target (99.999% purity). High-purity N_2 (99.999%) was used as reactance gas. During the deposition, the target was rotated to ensure a uniform erosion of the surface. The

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substrates were mounted on a heated holder, at a distance of ~5 cm. An RF source was used to generate plasma of nitrogen in the chamber. The scheme of the experimental set-up is shown in Fig. 1. In order to generate concentrated plasma localized near the substrate, a ring-shaped electrode, connected to a negative DC bias voltage, was placed between the target and the (grounded) substrate, close to the substrate, at a distance of ~1.5 cm. Before depositions the chamber was evacuated to ~5.0×10^{-7} mbar. The substrates were p-type Si <100> wafers, cleaned ultrasonically in cyclo-hexane. The N_2 flux was regulated by a flow-meter to a working pressure of ~2.0×10^{-2} mbar. The experimental parameters are synthesized in Table 1.

2.2. Spectroscopic characterization (XPS)

XPS experiments were carried out by an ESCALAB MkII (VG Scientific Ltd., U.K.) spectrometer, equipped with a standard Al K_α excitation source and a 5-channeltron detection system. Photoelectron spectra were collected at 20 eV constant pass energy of the analyser and a base pressure in the analysis chamber of 10^{-8} Pa. The binding energy (BE) scale was calibrated by measuring Au 4f spectrum from sputter-cleaned Au of 99.99% foil and setting Au $4f_{7/2}$ peak to BE = 84.0 eV. The samples were mounted on the holder by using an Au mask, which ensured the grounding of the samples. The accuracy of experimental BE scale was ± 0.1 eV. The curve fitting is carried out with a mixture of Gaussian and Lorentzian functions.

2.3. Electrical characterization (the method)

Electrical characterization is a useful method to investigate the influence, on physical properties, of structure and composition of deposited films. Temperature-assisted electrical measurements, indeed, allow determining the charge-carrier transport mechanisms. The temperature-dependent electrical characterization has been performed by the "four-contact in-line probe" in a vacuum chamber (~1×10^{-2} mbar). This method allowed us to measure the film sheet resistance under dark conditions. The set-up scheme is shown in Fig. 2. Injecting a bias current I_{Bias} by a current source (Keithley 224) into the outer probes, and measuring by a voltmeter (Keithley 182) the induced voltage drop V_M, between the inner probes, the sheet resistance R_S and the film resistivity ρ can be

obtained, under the thin-film approximation conditions ($t \ll s$), according to Eq. (1):

$$R_S = \frac{\pi}{\ln 2} \times \frac{V_M}{I_{Bias}}, \qquad \rho = R_S \cdot t, \qquad (1)$$

where, s is the distance between two contacts, and t the film thickness. Measurements have been performed varying the temperature T, from room temperature (RT) up to 350 °C (about 623 K), under vacuum conditions, to avoid film structural modifications and oxidation.

The silicon substrate used has a measured electrical resistivity of about 35 Ω cm, a value larger than the deposited layers, from 1 to 4 orders of magnitude. Therefore, we considered a weighed parallel conductance between film and silicon, for the higher resistivity film and, as a first approximation, assumed that the substrate gives no contribution to the measured dark electrical conduction, for the lower resistivity samples.

3. Results and discussion

3.1. Spectroscopic characterization (XPS)

A study of the C–N chemical binding states has been performed, in order to characterize the deposited C–Nx compounds, trying also to correlate the chemical properties to electrical behavior. The chemistry of carbon and nitrogen compounds is very complex and it is not an easy point to ascribe the chemical shifts measured to well-defined and unique compounds. In addition, the XPS technique allows determining the chemical states of the C and N atoms at the very surface of the films, that is, within the escape depth of the electrons (~10 nm), and the data should be considered as indicative of the whole film structure. Our results, however, can be considered quite accurate and extensible to real volume composition of the film, since they were confirmed by XPS depth profiling carried out for two samples. The profiling by 2.0 keV Argon ion (Ar$^+$) cyclic sputtering practically did not change the chemical composition: only the signal of superficial oxygen disappeared completely after the first cycle of sputtering, while the C1s and N1s peaks remained constant through the film thickness.

Both C1s and N1s spectra are broad, thus revealing the presence of several different types of bond, C1s is also asymmetric at the high-energy side. The N1s spectra are more symmetric and can be decomposed in two or three Gaussian peaks [Fig. 3]. Peak de-convolution has been proposed, since the first C–N film preparation experiments, by many authors [19–23]: the N1 peak component (~398.2 eV) has been assigned to a C–N sp^3 (tetrahedral type) bond; the N2 (~400.5 eV) assigned to a sp^2 graphite-type trigonal C–N bond, and N3 (~402.5 eV) assigned to oxidized compounds or N=N type bonds.

The C1s spectra, peaked at 285.3 eV, are generally broad and asymmetric at higher binding energy, revealing the presence of different types of binding states, and relative de-convolution and assignments are more cumbersome and debated. Our spectra have been de-convoluted into four or five components, using mainly Gaussian fit. The peaks correspond to binding energy values of about 284.4 and 285.2, 286.2 and 287.9 eV, and higher values ($\geq$289. 5 eV) for oxidized surfaces.

The C1 component (~284.4 and 285.2 V) has been assigned, respectively, to a sp^2 and sp^3 C–C type bond; C2 (~286.2 eV) assigned to a sp^2 graphite-like C=N bond; C3 (~287.8 eV) assigned to sp^3 bond of C N; and C4 (~289.5 eV) assigned to oxidized carbon and aliphatic C–N [22–26]. The fifth component (C=O bonds) was present only in some samples containing higher amount of superficial oxygen.

The relative concentrations of main chemical species were determined from the ratios of the area of each Gaussian peak component to the whole original curve. By using these concentrations,
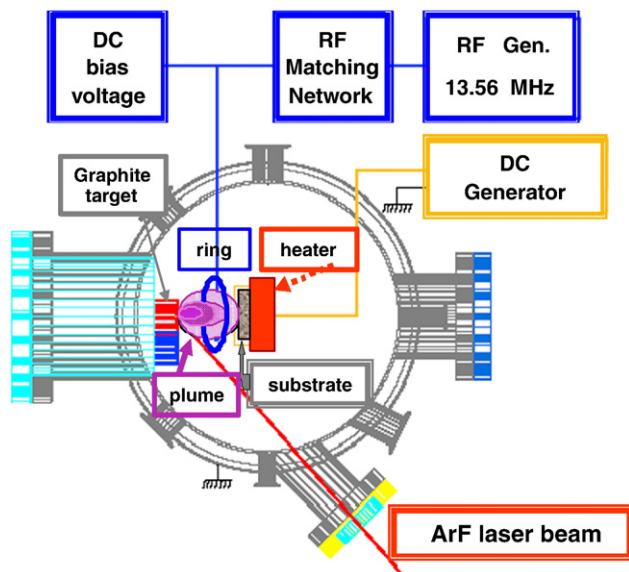

Fig. 1. The RF plasma assisted PLD apparatus, with the DC biased annular ring close to the substrate: the electrical scheme.