



Short communication

Spectroscopic investigation of the physicochemical origin of the spontaneous delamination of the sputtered amorphous carbon nitride films

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ABSTRACT

We present in this study a spectroscopic investigation of the delamination of the amorphous carbon nitride (a-CN_x) films deposited by RF magnetron sputtering of a graphite target in Ar/N₂ gas mixture. The microstructure of the studied films have been analysed prior and after their delamination. The origin of the observed spontaneous delamination have been elucidated in terms of chemical reactions between water and CN bonds at the a-CN_x/Si interface, which support delamination crack advance.

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The mechanical stability of coated materials has been a subject of considerable attention [1–7]. In the design of such devices, adhesion is a critical parameter governing the mechanical behavior and reliability of a thin film on a substrate. From the numerous studies, the delamination along the interface is found to be one of the major failure mechanisms occurred in various thin film/substrate systems [1,2,4]. However, significant fundamental as well as the microstructural properties of the deposited films still remain with most current approaches to predict this failure mode [6–10].

The aim of the present study is to investigate the microstructure origin of the observed spontaneous delamination of sputtered amorphous carbon nitrides (a-CN_x) films [8], which affect their interesting properties as promising protective coatings [11–14]. The microscopic origin of these mechanical properties seems to be attributed to their specific microstructure, which contains different configuration of the C–N bonds (sp¹, sp² and sp³) [15–18]. These structural parameters are also known to depend strongly on the deposition conditions [15,16,18]. Therefore, the structural integrity and reliability of these films appear to be a

great challenge. Fourier transform infra red (FTIR) absorption spectroscopy were used to characterize the microstructure of the a-CN_x films prior to and after their delamination, in order to study an insight of possible microstructural changes occurring during delamination.

In the present study, the a-CN_x, about 0.8 μm, were deposited on Si (1 0 0) substrates using an RF (13.56 MHz) magnetron sputtering technique of a graphite target. The films were grown by varying the nitrogen partial pressure (NPP) ratio in the Ar/N₂ sputtering gas 0–100% with a total discharge pressure of 1 Pa and at value of the RF power about 150 W. The distance between the two electrodes was kept constant at 7 cm. More details about the technique and the plasma parameters can be found elsewhere [18]. The thickness *h* of the deposited films was determined using a Dektak 3ST profilometer.

The different type of CN bonds were investigated using a Bruker Fourier transform infra red (FTIR) spectrometer at room temperature over a large wavenumber range (400–4000 cm⁻¹) with a resolution of 2 cm⁻¹ and averaging over 30 scans. The profiles of telephone cord buckles are characterized along deferent chords, by using the atomic force microscope (AFM) in tapping mode. The AFM images were taken in tapping mode (Digital Instruments) at 2 nm resolution. The refractive index (*n*) was determined by optical transmission measurements, in the

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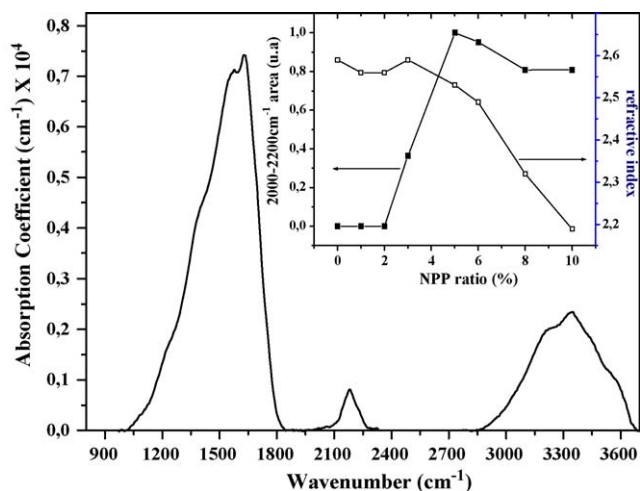


Fig. 1. FTIR spectra of amorphous carbon nitride films deposited under total nitrogen pressure 1.0 Pa and in the range 900–3600 cm^{-1} in their as-deposited state. The inset shows the variation of the refractive index n and the integrated intensity of the band lying between 2000 and 2200 cm^{-1} versus the NPP ratio. The line is only a guide for the eyes.

300–3000 nm range using a Varian Cary 5 spectrometer. The residual stresses in the films were determined by measuring the curvature of the Si substrate before and after deposition of films with the profilometer Dektak 3ST using the Stoney equation [19].

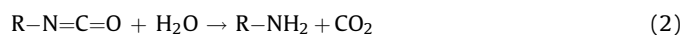
We present in Fig. 1 a typical infrared spectrum of a-CN_x film in the range 900–3600 cm^{-1} . The spectrum indicates three absorption bands at 900–1800 cm^{-1} , 2000–2500 cm^{-1} , and 2800–3700 cm^{-1} regions. The absorption lying between 900 and 1800 cm^{-1} can be resolved into sub-bands at 1220, 1400, 1570 and 1650 cm^{-1} . The peak around 1220 cm^{-1} can be attributed to sp^3 C–N bonds, while the peak around 1650 cm^{-1} can be assigned to C=N double bonds [15–18]. The m-odes at 1400 and 1570 cm^{-1} are a purely electronic effect [16,17]. The weak absorption bands around 2200 and 2235 cm^{-1} are attributed to isocyanate groups (N=C=O), and the stretching vibration of the C≡N triple bonds (the nitrile groups), respectively. The inset figure shows the variation of both the refractive index n (determined at 2 μm , wave length where there is no absorption), and the integrated intensity of the isonitrile vibration band (C≡N triple bonds) obtained from FTIR spectra, for $0 \leq \text{NPP ratio} \leq 10\%$.

The analysis of these spectra versus the NPP ratio suggests the presence of a large quantity of sp^2 bonds (the chain-like structures) and to the formation of N–H and C≡N terminating bonds along with voids. The variation of the refractive index can well be correlated to the IR measurements. A transition, from a dense material to a less dense, is that carbon nitride films can be explained by the lower covalence of N as compared to C atoms and to the release of the internal constraints by the carbon nitride films leading to a lower mean coordinance and atom density. Based on the impurity model [20,21], the intrinsic stress of sputtered a-CN_x has been analysed as a result of the competition between tensile stress, due to deposition technique (soft technique) and the nitrogen content which reduces the degree of over-constraining in the films, and compressive stress coming from pressure induced by the interaction between gaseous inclusions (O–H for example) [20–22]. Indeed, the low average energy of the incident particles obtained by SRIM (in the range of 10–20 eV) and the resulting low density of the deposited films, lead to low value of residual stress [21]. This tendency is accentuated by nitrogen incorporation, which reduces the degree of over-constraining in the films and leads to interlinking of Csp^2 sites by chains, with no significative clustering of the sp^2 phase in rings, according to IR data reported above.

It was reported that C₂N₂ is a precursor of the deposition of our RF magnetron a-CN_x films [21]. At given NPP ratio (i.e., h), the amount of the energy of the incident particles (i.e., bias voltage V_b) can affect both the nature and the sizes of the particles in the plasma and so the nature of CN hybridisation state within the deposited films. At low RF power (lower than 10 eV), the first process induces an aggregation of the incidental particles which form columns, which tend to coalesce as increasing RF power, leading to a slightly increase of the tensile stress. Thus, the resulting microstructure has a significant porosity, which favors the enhancement of the distortion of the graphitic plane (the gaseous inclusions effect) increasing the disorder and leading to intrinsic stress relaxation. At higher RF power, the energetic carbon sputtered particles (over 20 eV), can strike these radicals and brake the C₂N₂ molecules. The total stress increases due to a significant loss of the C≡N bonds modifying porosity geometry and leading to a loss of the amount of all the gaseous inclusion and inducing a decrease of the compressive stress [21,22].

At given RF power, the evolution of the intrinsic stress versus the NPP ratio (i.e., the film thickness h) can be explained according to the amount of the C≡N bonds within the films. We report in Fig. 2 the variation of the intrinsic stress versus the film thickness reported on Fig. 2. The inset shows the variation of h versus the NPP ratio. Indeed, the observed low values of the internal stresses can be connected to the nitrogen content and the resulting hybridisation states. As reported above, the increase of h (i.e., NPP ratio) induces the increase of the porous character of the a-CN_x films and their contamination by species as OH bonds, and so the compressive part of the intrinsic stress (the effect of interaction between gaseous inclusions), which can induce a spontaneous delamination and spalling of the a-CN_x films. For the studied a-CN_x films, we can legitimately attribute the evolution of the film delamination to the strong effect of water as it was reported for the BN films [9]. The porosities are preferred sites for the initiation of film delaminations. Obviously, at these defects, water molecules can rapidly migrate through the film to the film/substrate interface. The resulting high compressive stress can induce a spontaneous delamination the a-CN_x films deposited on silicon reported in Fig. 3. These images reveal that delamination appears sinusoidal (telephone cord) and proceeds by the propagation of the blister edge.

In order to examine the physicochemical mechanism governing the delamination crack advance, we compare in Fig. 4 typical IR absorption spectra for samples in their as-deposited state prior and after delamination [23]. The analysis of the bands reveals the decrease of the intensity of the isonitrile vibration band and the increase of sp^3 C–N and sp^2 C=N bonding. This mechanism of the dissociation/recombination of the CN bonds is accompanied by the increase of the CO (band around 1700 cm^{-1}), OH and NH bonds. A possible reaction of water and oxygen with CN or with nitrogen dangling bonds can explain the changes of the microstructure of the studied films. Normally, volume expansion accompanying the increase of amount of the O–H bonds and the resulting reactions along the a-CN_x/Si interface should drive the delamination crack [8,9]. In addition, where the a-CN_x films were delaminated, the liberation of N as NH₂ and the formation of both CO₂ and H₂O seem to be likely (Fig. 4). A possible hydrolysis of some groups as nitrile groups (R–C≡N) and isocyanate groups (R–N=C=O) can occur.



The dissociation/recombination mechanism of these different bonds reveals the endothermic character of the reaction (2). Using the Hess law, the resulting energy balance sheet of reaction gives $\Delta H \approx 1.82$ eV. Consequently the loss of nitrogen bonding as NH₂

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