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Structure and optical properties of boron nitride thin films deposited by radio-frequency sputtering on polycarbonate

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Abstract. Thin optical protective coatings of boron nitride, $\sim 1 \mu\text{m}$ thick, were deposited at low substrate temperature on polycarbonate (PC) and fused silica substrates by r.f. magnetron sputtering using a mixture of Ar + N₂ as the sputtering gas. The structure and composition of the deposited layers were studied by Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering spectroscopy (RBS). The optical characterization of the coated sample was carried out by measuring the ultraviolet–visible transmittance at different wavelengths and the strength of adhesion of the deposited layers to the plastic substrate was analysed by a scratch test. The deposited layers grow with hexagonal structure, the resulting layers being nearly stoichiometric, and are highly transparent in the visible range on both substrates examined; the measured optical band-gap of the coating was 4.6 ± 0.1 eV. The strength of adhesion to the polycarbonate was found to be dependent on the substrate pre-deposition treatment: ion etching of the PC surface before coating deposition gives rise to films with good adherence as a consequence of the formation of a mixed interface layer where C \equiv N chemical bonds were observed by FTIR.

Thin films of crystalline boron nitride (BN) can be prepared by using various deposition techniques and, depending on the deposition conditions, the resulting layers can have hexagonal (h-BN) or cubic (c-BN) structure. Although most of the scientific investigations deal with the synthesis of c-BN layers (this material is in fact nearly as hard as diamond), h-BN layers also present many interesting properties. Among them, the most important are their high chemical inertness and phase stability [1], the high mechanical hardness which is close to 4000 *H* [2] and the low friction coefficient [3]; moreover, h-BN is a good insulating material and, as a thin film, presents values of the electronic band-gap ranging from 3.8 eV for boron-rich films [4] to 4.9–5.6 eV for stoichiometric layers [5, 6]. Although this material is generally considered for application as protective coatings and gate insulators in metal–insulator–semiconductor field-effect transistors (MISFETs) [7], the above properties suggest that it can also be used as an optical protective coating for those polymeric materials which are of interest in the ophthalmic industry as substitutes for the traditional eyeglass lenses. Optical lenses made of polycarbonate (PC) are, in comparison to other plastic lenses, thinner and lighter in weight, more flexible and impact resistant; in addition they offer ultraviolet (UV) protection [8]. On the other hand the softness of this material requires the presence of a protective coating on both the surfaces of the lens.

In this paper we report on the low-temperature deposition of highly transparent h-BN thin films on polycarbonate substrate by using reactive r.f. magnetron sputtering of sintered h-BN

with nominal purity of 97 at.% as the target material and an Ar+N₂ mixture as the sputtering gas. The compositional and structural analysis of the deposited layers was carried out by Rutherford backscattering spectroscopy (RBS) and Fourier transform infrared spectroscopy (FTIR), the optical characterization was done by measuring the UV–visible transmittance spectrum, the strength of adhesion between the coating and the substrate was evaluated by a CSEM Scratch Tester and the film thickness was measured by a Dektat II profilometer.

Before the deposition process, polycarbonate substrates, 3 mm thick, were placed in an ethanol bath, ultrasonically cleaned for ten minutes and then dried in an oven at 40 °C for two hours. Substrate surface ion etching and BN coating deposition were sequentially carried out in a r.f. magnetron sputtering apparatus using a mixture of 97 at.% Ar and 3 at.% N₂ as the working gas. After plasma ignition at 150 W r.f. power and 1.5 Pa gas pressure, the substrate holder was r.f. biased at –150 V for five minutes to promote surface cleaning of the substrate by ion etching and coating adhesion by formation of an interface region between the polymer and coating [9, 10]. The shutter covering the target was kept closed during this stage. As measured by a thermocouple in contact with the back of the PC sample, the substrate temperature never exceeded 310 K, which is much lower than the deformation temperature of polycarbonate (~410 K). BN deposition was then carried out at 150 W target power and 0.5 Pa gas pressure without substrate bias to limit the onset of stresses during the growth: using these experimental parameters, we obtained a BN deposition rate of 4 nm min⁻¹ and the substrate temperature after two hours' processing was lower than 320 K.

The atomic composition of the deposited BN layers was studied by Rutherford backscattering spectroscopy using a 1.8 MeV ⁴He⁺ beam incident normally to the sample surface; a Si surface detector was positioned at an angle of 165° relative to the incident beam direction. In figure 1 we present a typical RBS spectrum of a thick BN film deposited on a PC surface; in the figure a numerical simulation of the spectrum calculated using a home-made simulation code based on the stopping power data reported in the literature is also shown. Assuming a BN density of 2.25 g cm⁻³, the spectrum is compatible with a stoichiometric BN film 1.1 μm

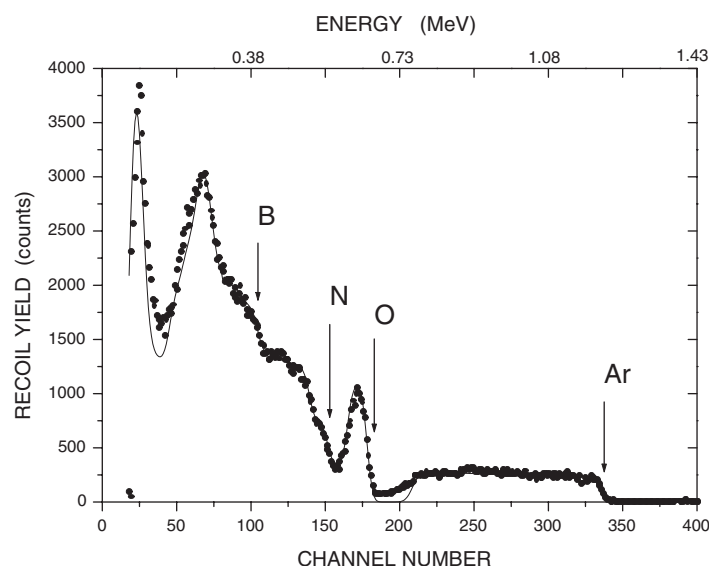


Figure 1. The RBS spectrum of h-BN-coated polycarbonate; the solid line represents the numerical simulation of the experimental data (see the text).

thick presenting a B-rich oxidized surface layer: these results are in agreement with Auger analysis carried out on BN samples deposited on (100)-oriented Si substrates using the same deposition parameters [12].

The crystalline phase of the deposited BN layers was examined by FTIR using (100)-oriented Si wafers as substrates covered by PC films: being PC infra-red active, this experimental set-up was chosen to increase the intensity of the signal obtained for the BN deposit with respect to the signal due to the substrate. For this analysis the PC films were deposited by spinning a liquid solution of polycarbonate granulate and CH_2Cl_2 on silicon: slow vaporization of the solvent at room temperature gives rise to PC films typically in the 1–2 μm thickness range. Figure 2 shows the FTIR spectrum of $\sim 1 \mu\text{m}$ BN on $\sim 1 \mu\text{m}$ PC and, in the inset, the FTIR spectrum of the PC film: the peaks at $\sim 1400 \text{ cm}^{-1}$ and $\sim 800 \text{ cm}^{-1}$ correspond to the B–N stretch vibration in h-BN(0001) and B–N–B bend vibrations out of the plane h-BN(0001) obtained for the sp^2 -bonded BN [11], thus indicating the growth of BN layers having a hexagonal structure. BN films deposited with similar deposition conditions on (100)-oriented Si substrate have revealed, by their glancing-angle x-ray diffraction (XRD), nanocrystalline structure with grain dimensions close to 3 nm [12]. As an interesting feature of the BN-coated PC spectrum, we observe the presence of absorption lines at $\sim 2300 \text{ cm}^{-1}$, possibly indicating the presence of $\text{C}\equiv\text{N}$ chemical bonds.

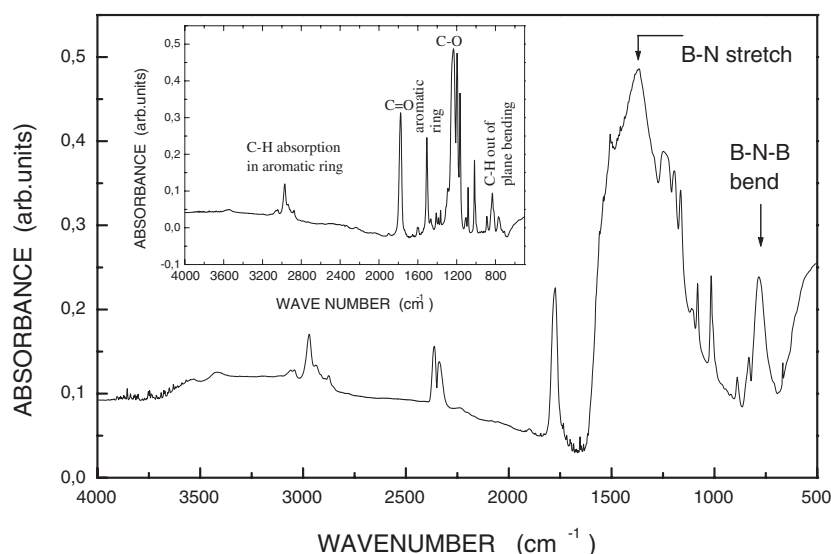


Figure 2. The FTIR spectrum of 1 μm thick h-BN coating deposited on PC films ($\sim 1 \mu\text{m}$ thick). In the inset we show the FTIR spectrum obtained for an uncoated PC film; we have labelled some of the most important absorption lines.

The optical transmittance of the h-BN-coated PC sample was measured in the 190–800 nm wavelength range using a UNICAM ultraviolet–visible double-beam spectrophotometer. In figure 3 we present the spectral characteristic of the $\sim 1 \mu\text{m}$ h-BN-coated PC sample and the corresponding spectrum obtained for the uncoated PC substrate. Comparing the spectra, we observe that the deposited BN coating is nearly as transparent as the substrate and that the h-BN coating does not alter the onset of the absorption of the PC substrate. In the inset of figure 3 we present the transmittance spectrum corresponding to a $\sim 1 \mu\text{m}$ thick h-BN film deposited on fused silica. From this spectrum we estimated [13] an absorption coefficient of the order of

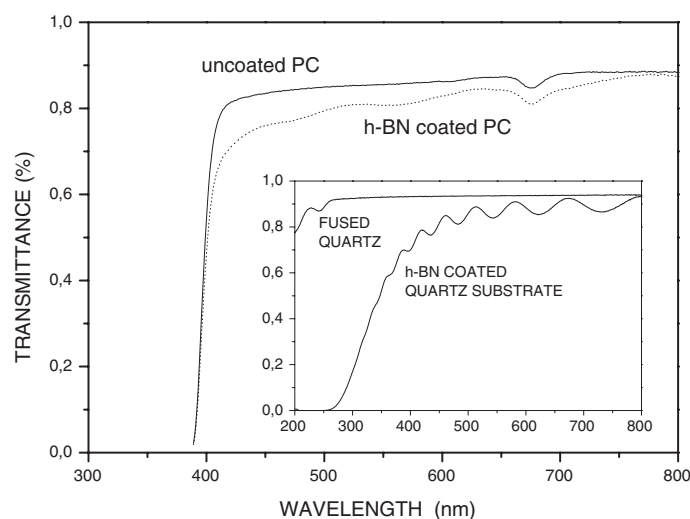


Figure 3. UV-visible transmittance spectra of uncoated and h-BN-coated bulk polycarbonate (3 mm thick); in the inset we also report the transmittance spectrum of h-BN-coated fused quartz (see the text).

10^4 cm^{-1} and, by extrapolation of the linear portion of the square of the absorption coefficient against photon energy, an optical band-gap energy value of $4.6 \pm 0.1 \text{ eV}$; both quantities are in good agreement with the value recently reported in the literature [14] for stoichiometric h-BN thin films.

A CSEM Scratch Tester equipped with a hemispherical Rockwell C diamond stylus of $200 \mu\text{m}$ radius was used for the evaluation of the strength of adhesion between the coating and the substrate. The critical load was determined from the applied normal force at which the first delamination occurred and the scratched area was observed with an optical microscope. In figures 4 and 5 we present micrographs (magnification $\times 200$) of two scratches on the h-BN sample deposited on bulk PC: figure 4 is pertinent to an h-BN coating deposited with plasma pre-treatment, figure 5 to a coating deposited without surface pre-treatment. In both figures scratch (a) corresponds to a load lower than 3 N while scratch (b) corresponds to a load of 4–5 N. While the h-BN sample that was not pre-treated undergoes a complete delamination during the test, we can observe that the treated one is delaminated only at the higher load; on closer inspection, we observe that the deposited layers present a paved-like effect, without debonding of material between the boundaries of these pavings.

The increased adhesion strength of a thin BN coating on a polymeric substrate after surface ion etching by low-pressure plasma is a well known effect [15] and is related to the formation of a thick interface region between the polymer substrate and the coating having specific chemical bondings. Bergeron *et al* [9], for example, observed by ellipsometry that the interfacial region is composed of cross-linked PC layers followed by a less atomically dense region between the polymer and the film in which the deposited layer is covalently bonded to the substrate. Although we plan to analyse this aspect in a more extended paper, it is worth remembering that the FTIR spectrum in figure 2 indicates the presence of $\text{C}\equiv\text{N}$ chemical bonds, as shown by the IR absorption band at $\sim 2300 \text{ cm}^{-1}$: RBS analysis revealed that C contaminants in the BN layers are below the detection limit (1–2 at.%) and thus the $\text{C}\equiv\text{N}$ bond, if actually present, probably results from the chemical bonding between C atoms of the PC substrate and N dangling bonds of the BN deposited layers. It is important to note that such IR adsorption

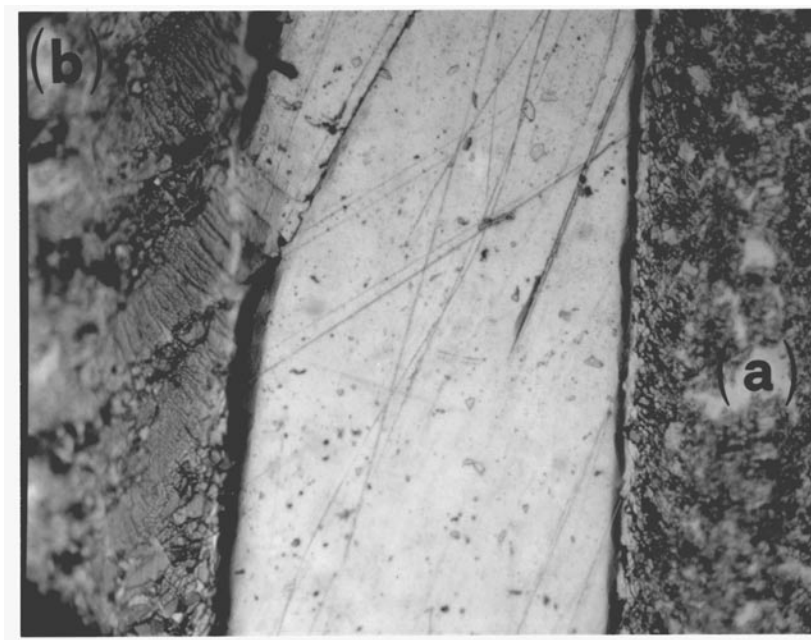


Figure 4. An optical micrograph of scratches on 1 μm thick h-BN film deposited on polycarbonate after substrate plasma etching; scratch (a) is related to the 3 N load, scratch (b) to a 4–5 N load.



Figure 5. An optical micrograph of scratches on 1 μm thick h-BN films deposited on polycarbonate without substrate plasma etching; scratch (a) is related to the 3 N load, scratch (b) to a 4–5 N load.

lines were not observed when the h-BN film was deposited on PC surfaces that were not pre-treated where, as reported above, the adhesion strength is quite low.

In conclusion, we succeeded in depositing BN thin films as optical protective coatings on polycarbonate substrates by r.f. magnetron sputtering. Using the appropriate deposition parameters it was possible to carry out the process keeping the substrate temperatures lower than the deformation temperature of the polymer. The deposited BN shows a hexagonal phase (h-BN) and has nanocrystalline structure. In the visible range the coatings are optically transparent and characterized by a good strength of adhesion to the substrate when the deposition process follows the ion etching of the substrate. Moreover, the good strength of adhesion between the h-BN and PC opens the way for the deposition of BN layers with cubic structure (c-BN) on polymer substrates. Indeed, it was proved that the c-BN phase is stabilized by the growth of an initial h-BN layer having appropriate hardness to sustain the intrinsic stress of the cubic material [12]. As a protective optical coating, c-BN presents properties which are competitive with those of other coating materials being the second hardest material, after diamond, and presenting high band-gap values, typically close to 6 eV [14].

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