

Preparation and Characterization of Nanocrystalline h-BN Films Prepared by PECVD Method

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This work describes a systematic study of the preparation of nano-crystalline thin h-BN films by Plasma-Enhanced Chemical Vapor Deposition (PECVD) technique. The samples were prepared at low temperatures using B_2H_6 and N_2 as gas precursors. It is shown that the flow ratio among these gases has an important influence on the size of the crystallites (deduced by Raman spectroscopy). The B_2H_6/N_2 flow ratio was varied from $1,6 \times 10^{-2}$ to $6,7 \times 10^{-4}$ leading to films presenting a crystallite size, which varied from 90 nm to amorphous, respectively. The XRD spectra show two peaks at 2 values around 42° and 44° , which are associated to $\langle 110 \rangle$ and $\langle 100 \rangle$ h-BN crystalline directions, indicating, a $\langle 002 \rangle$ preferential orientation for the h-BN crystallites. The thermo-mechanical properties, as stress, hardness, and Young modulus were also studied and correlated with the structural properties. The composition of the films was obtained by RBS and EDS indicating Boron to Nitrogen ratio, close to stoichiometry for all the studied deposition conditions.

I Introduction

In analogy to the carbon system, BN can exist in different crystallographic phases, among them the hexagonal and the cubic modifications; h-BN and c-BN have received great attention in view of coating applications. Like graphite h-BN consists of sp^2 -bonded hexagons. In h-BN, the boron and nitrogen atoms alternate in sequence of hexagonal layers. Sub modifications with higher disorder in the layer sequence are possible. Nevertheless, the h-BN has been considered as one of the most promising fine ceramics due to its high electrical resistivity, excellent thermal conductivity and extremely low dielectric constant [1-7]. It has also been developed as a potential alternative for fiber coatings in ceramic matrix composites on account of its lubrication and corrosion-resistant characteristics [7].

Different PVD (physical vapor deposition) and CVD (chemical vapor deposition) deposition methods to prepare BN have been reported, normally in temperatures above $600^\circ C$ [8-11]. To prepare BN at low temperature is advantageous, however depending on the final thickness the films present structural instability related to internal stress. In this way the knowledge of the mechanical properties of these materials, such as stress, hardness, elastic modulus, and thermal expansion coefficient is of great interest. It is well known that the thermo mechanical properties of thin films are

strongly correlated with the film structure such as defects, voids, network strain and the mean coordination number. In this paper, we present a systematic study of the influence of the substrate temperature and diborane to nitrogen flow rate on the structural and thermo-mechanical properties of the hexagonal boron nitride thin films prepared by PECVD method at low temperatures (below $400^\circ C$).

II Experimental

The Boron Nitride thin films were prepared using a standard 13.56 MHz radio frequency PECVD reactor, capacitively coupled, and utilizing different mixtures of (B_2H_6/N_2) as gas precursors. The set-up has been described in detail elsewhere [12, 13]. The rf power, substrate temperature, diborane to nitrogen flow rate, and the total pressure were systematically varied from one deposition to the other in order to analyze the effect of these parameters on the films properties.

Rutherford backscattering (RBS), X-ray photoelectron spectroscopes (XPS), and Energy Dispersive X-ray (EDS) spectroscopy and Elastic Recoil detect analyses (ERDA) were used to determine the chemical composition of the samples. In addition, XPS spectra were performed to analyze the short structural configuration of the h-BN films. The infrared absorption spectra were

obtained by FTIR (in a Bio-Rad spectrometer) in films deposited onto c-Si substrates, in the 200-4000 cm^{-1} wave-number range. The micro-Raman spectra were obtained with a Renishaw spectrometer in backscattering configuration, at room temperature using the 514.5-nm line of argon laser and X50 amplifier microscope. XRD measurements were performed in a Philips spectrometer using a Cu source in a low angle system to confirm the nano-crystalline phase.

Stress measurements were taken from films deposited onto $3 \times 25 \times 0.4 \text{ mm}^3$ (111)-Si bars using a Sloan profilometer to determine the radius of curvature of the film-substrate composite. The stress was then calculated by the Stoney equation [14]:

$$\sigma = [E / (1 - \nu)] (t^2 / 6dR) \quad (1)$$

where E , ν and t are the Young's modulus, Poisson's ratio, and thickness of the substrate, R and d are the radius of curvature and the thickness of the film, respectively. The hardness and Young Modulus were obtained in a Nanohardness system at different steps of measurements.

III Results

The compositional analyses indicate that the produced films are close to stoichiometry with the B/N ratio varying from 1 to 1.15 depending on sample preparation and experimental conditions. The concentration of carbon, oxygen and other elements found as contaminants was low but increase for samples prepared with low substrate temperature. Both molecular hydrogen and hydrogen bonded to boron and nitrogen increase when the substrate temperatures decrease as observed by ERDA and infrared spectra, respectively. The deposition rate varied from 2×10^{-2} to 3.3×10^{-1} A/s and the sample thickness from 0.35 to 0.8 μm .

The XPS spectra for h-BN thin films prepared keeping all the deposition parameters constant and varying the substrate temperature are presented in Fig. 1. The hexagonal phase of boron nitride compound presents the B 1s core level at 190.5 eV [15]. All our BN samples present a B 1s-core level at 190.3 eV very close to the hexagonal BN phase. However, the samples prepared at room temperature present a low shoulder band at 192 eV, which is associated to boron oxide [15], in accordance to composition analyses, which indicates a higher presence of oxygen, compared to samples prepared at 340 $^{\circ}\text{C}$. In Fig. 2, the infrared spectra for the same samples presented at figure 1 are shown. The absorption band observed around 780 cm^{-1} and 1380 cm^{-1} are related to the BN hexagonal phase [16] and the absorption bands centered at 2450 cm^{-1} and 3250 cm^{-1} are related to hydrogen bonded to boron and nitrogen, respectively. The FTIR analysis as a function of

the deposition temperature shows that for higher temperatures the hexagonal crystallite size, as indicated by the FWHM of the h-BN absorption band at 1380 cm^{-1} , increases. For lower temperatures the hydrogen content of the films increases as indicated by the N-H stretching band at 3250 cm^{-1} . The deposition rate also increased for decreasing temperatures, varying from 9×10^{-3} to 3.3×10^{-1} A/s. The maximum sample thickness attained for 6 hrs deposition was 0.8 μm .

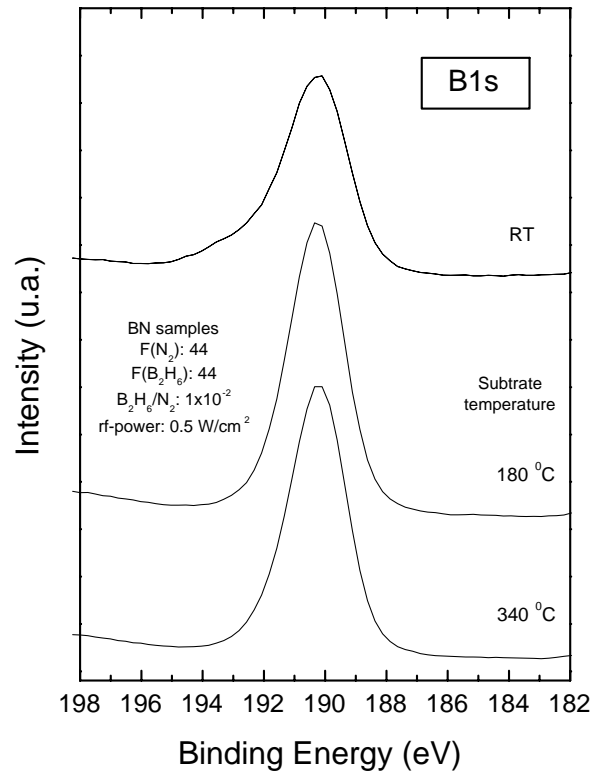


Figure 1. XPS spectra, showing the Boron 1s core level for samples grown at different substrate temperatures.

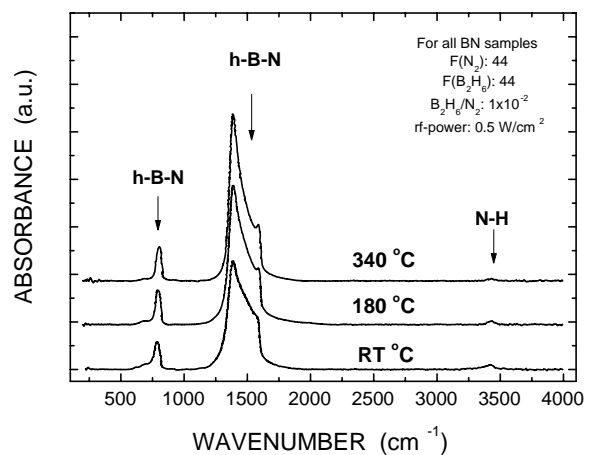


Figure 2. FTIR spectra for BN samples prepared at different substrate temperatures.

The average grain size of the hexagonal crystallites was also estimated through Raman Spectroscopy. The Raman spectra of hexagonal BN samples present an absorption band in 1380 cm^{-1} , according to the study by Nemanich *et. al.* [17] it is possible to estimate the average grain size of the nano-crystals present in the samples using the following relation:

$$\Gamma_{1/2} = \frac{1447}{L_a} + 8.70 \quad (2)$$

Where $\Gamma_{1/2}$ is a FWHM of the Lorentzian curve fitting the absorption band and L_a represents the equivalent grain size of the nano-crystals present in the sample. Fig. 3 presents the results obtained applying this equation to samples prepared at the same condition but changing the diborane flow. As it can be observed, the estimated average grain size of the h-BN thin film increases when the B_2H_6 flow increases. In the inset the XRD spectra for the sample with 50 \AA of crystalline size is shown and peaks for 42.3 and 44.3 degrees, associated to the $\langle 100 \rangle$ and $\langle 101 \rangle$ directions of BN hexagonal phase are evident.

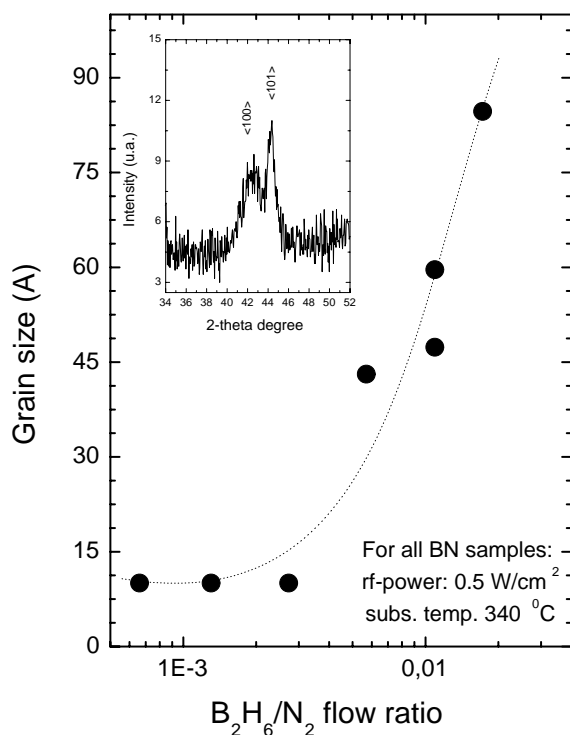


Figure 3. Grain size as a function of the substrate temperature of the BN samples obtained using the equation 2. In inset a XRD spectra of the equivalent 50 \AA of grain size.

The results for the intrinsic stress for the BN samples are shown in Fig. 4 (b), as it can be observed, the stress presents a minimum for substrate temperature around $180\text{ }^\circ\text{C}$. The hardness and Young Modulus for the same hexagonal BN samples are shown in Fig. 4(a). The hardness is below 4 GPa and presents an

opposite behavior compared to the stress as the substrate temperature increases. In contrast, the Young modulus does not present an evident correlation with the substrate temperature.

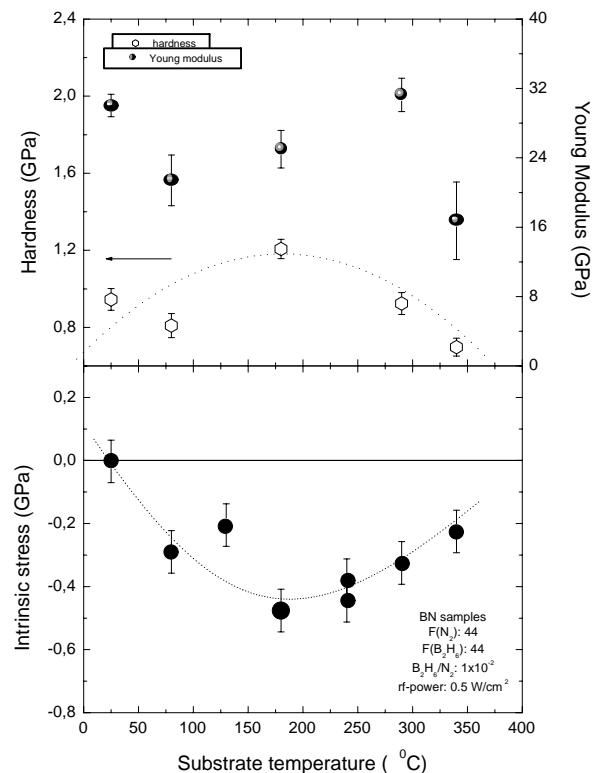


Figure 4. (a) Hardness and Young Modulus as function of substrate temperatures for the BN samples, and (b) BN samples intrinsic stress as function of the substrate temperature.

IV Discussion.

Infrared absorption spectroscopy is the most widely used method for BN films structural characterization since the hybridization states, sp^2 or sp^3 , of the B-N bond are easily distinguished through well-identified absorption's bands. The h-BN and turbostratic phases are characterized by two infrared active TO phonons, giving a strong and asymmetrical absorption band E_{1u} at about 1380 cm^{-1} attributed to in-plane stretching and a weaker band A_{2u} near 800 cm^{-1} resulting from an out-of plane B-N-B bending mode [16]. Thus the results shown in figure 2 combined with those in figures 1 and 3 indicate that it is also possible to grow Hexagonal BN samples with good structure and large grain size by the PECVD technique at low temperatures.

It was observed that the fundamental parameters to induce large grain size are the $\text{B}_2\text{N}_6/\text{N}_2$ flow ratio and low rf power [12, 13]. In the literature it is observed that the bulk values of the mechanical constants such as hardness, elastic modulus and thermal expansion coefficient, of the h-BN crystals oriented with the c-axis

perpendicular to the substrate surface [6] are very close to the exhibited by our hexagonal BN samples.

The values obtained for the hardness, the elastic modulus and the thermal expansion coefficient are comparable with those reported for h-BN. The hardness, and stress present opposite behavior with the substrate temperature, the hardness exhibits a maximum and the internal stress a minimum around 180 °C. At this point more study is necessary to understand this behavior, but it is possible to get a hardest h-BN thin film at low temperatures.

V Conclusions

Boron nitride thin films with different structure were obtained by the PECVD technique. The fraction of hexagonal and amorphous phases in the thin films is extremely dependent on the B₂H₆ flow and H₂ dilution. The crystallite size for the hexagonal grains increases for increasing temperatures and B₂H₆ flow as well as for low rf power density. The measured thermo mechanical properties of the BN samples did not show serious variations with the deposition conditions. In addition, the hexagonal BN nano-crystals present in the samples are well oriented and of good size.

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