

# Mechanical properties of boron nitride thin films obtained by rf-pecvd at low temperatures

J. Vilcarromero, M.N.P. Carreno and I. Pereyra,  
 Grupo de Novos Materiais, University of São Paulo,  
 CEP 0524-970, P.O Box 61548, SP, Brazil

This work describes the thermomechanical and structural modifications in RF-PECVD boron nitride thin films induced by the deposition conditions. The samples were prepared at low temperatures (below 400 °C) using B<sub>2</sub>H<sub>6</sub>, N<sub>2</sub> and H<sub>2</sub> gaseous mixtures. The B<sub>2</sub>H<sub>6</sub>/N<sub>2</sub> flow ratios, the B<sub>2</sub>H<sub>6</sub> flow, the N<sub>2</sub> flow, the substrate temperature the RF power and the H<sub>2</sub> dilution were varied. The thermomechanical properties, as stress and hardness, are also studied and correlated with the structural properties. It is found that the films present a mixture of hexagonal and amorphous phases and, under certain conditions, evidences of cubic phase. The fraction of these phases as well as the crystallite size, deduced by Raman spectroscopy, depend strongly on the B<sub>2</sub>H<sub>6</sub> flow, the B<sub>2</sub>H<sub>6</sub>/N<sub>2</sub> flow ratio and on the H<sub>2</sub> dilution. Boron to Nitrogen ratio, close to stoichiometry was obtained for all the studied samples.

## 1. Introduction

Boron nitride (BN) is a member of Group III-nitrides, which has deserved great attention due to its particular properties, among them the ability to form strong covalent bonds. This material has a wide range of applications in electronics, nuclear energy and metallurgy as wide gap semiconductor, super-hard and lubricant coatings, refractory material, etc [1-4]. Several PVD and CVD methods of deposition to prepare BN have been utilized [3, 5-8]. The deposition of uniform high-purity films onto irregularly shaped surfaces, exhibiting some fraction of cubic phase have been reported, utilizing CVD techniques, in opposition to PVD methods. The growth of BN samples by thermal CVD is usually performed at processing temperatures close to 1000 °C which is a limiting factor for many uses. On the other hand, plasma-enhanced CVD (PECVD) processes, typically below 400 °C, allow to overcome this temperature limitation expanding the variety of applications in the semiconductor and metallurgical industries. However, the PECVD BN thin films tend to have an important amorphous component mainly due to the low preparation temperatures. In addition, the deposition of BN samples exhibiting a mixture of cubic and hexagonal crystalline phases, using higher-density plasma sources such as inductively coupled RF discharges, has also been reported [9].

One of the main problems of low temperature BN is its structural instability that limits the final thickness of the films. In this way, the knowledge of the mechanical properties of these materials, such as the stress, the elastic modulus, and thermal expansion coefficient (TEC), is of great interest since it contributes to the stability and to the reliability of the manufactured devices and coatings. It is well known that the thermomechanical properties of thin films are strongly correlated with the film structure such as defects, voids, network strain and the mean coordination number. However a systematic study relating these properties, for Boron Nitride films, has not yet been reported. In this paper, we initiate a systematic study of the influence of the deposition parameters such as the substrate temperature and the diborane to nitrogen flow ratio on the

structural and thermomechanical properties of boron nitride thin films prepared by PECVD method.

## 2. Experimental

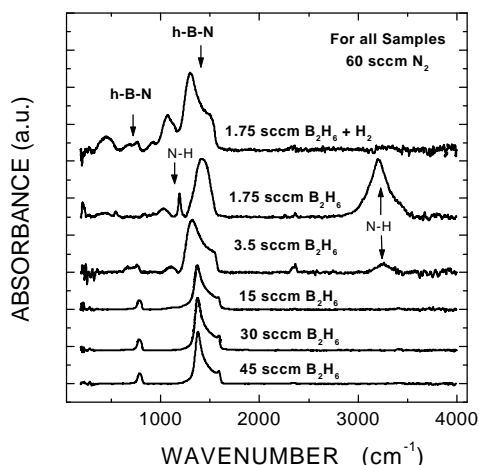
The BN samples were prepared using a standard 13.56 MHz radio frequency PECVD reactor, capacitively coupled, and utilizing different mixtures of (B<sub>2</sub>H<sub>6</sub> / N<sub>2</sub> / H<sub>2</sub>) as gas precursors. The set-up has been described in detail elsewhere [10]. The RF power, the substrate temperature, the diborane flow, the nitrogen flow, the total pressure, and the Hydrogen dilution were systematically varied from one deposition to the other in order to analyze the effect of these parameters on the films properties.

Rutherford Back Scattering (RBS), X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersive X-ray Spectroscopy (EDS) were used to determine the chemical composition of the samples. The infrared absorption spectra were obtained by FTIR (in a Bio-Rad spectrometer) on films deposited onto c-Si substrates, in the 200-4000 cm<sup>-1</sup> wave-number range. The micro-Raman spectra were obtained with a Renishaw spectrometer in back-scattering configuration, at room temperature using the 514.5 nm line of argon laser and X50 amplifier microscope.

Stress measurements were taken from films deposited onto 3x25x0.4 mm<sup>3</sup> (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 [11]:

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

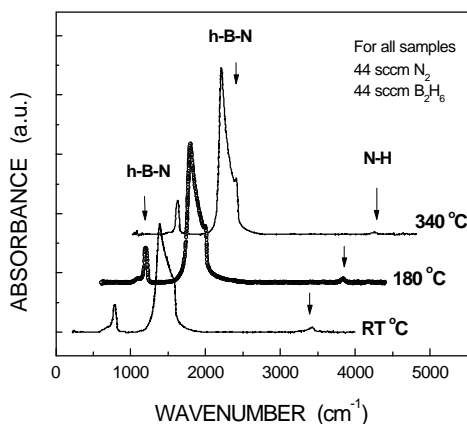
where E,  $\nu$  and t are the Young's modulus, Poisson's ratio, and thickness of the substrate, R and d are the radius of curvature and the thickness of the film, respectively.



**Figure 1.** FTIR absorption spectra for BN samples prepared with constant deposition parameters and variable B<sub>2</sub>H<sub>6</sub> flow. All the samples were grown with 60 sccm of N<sub>2</sub> and the upper curve is for a sample grown with 1,75 sccm of B<sub>2</sub>H<sub>6</sub> and 100 sccm of H<sub>2</sub>.

**3. Results**

The XPS, EDS and RBS experiments lead to a B/N ratio in the films varying from 0.9 to 1.15 depending on sample preparation and on the experimental conditions. Carbon, Oxygen and other elements were detected as contaminant, their concentration being higher for samples prepared with lower B<sub>2</sub>H<sub>6</sub> flow and additional hydrogen dilution, which promote an undesirable sputtering in the walls of the reactors and lead to lower deposition rates.

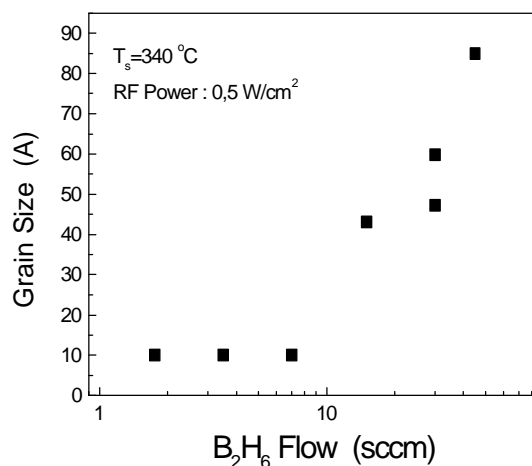


**Figure 2.** FTIR absorption spectra for BN samples prepared at different temperatures

In figure 1 the infrared spectra of the BN samples prepared keeping all the deposition parameters constant and varying the B<sub>2</sub>H<sub>6</sub> flow are depicted. The absorption band observed around 780 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> are related to hexagonal phase of the BN samples. The absorption bands centered at 2450 cm<sup>-1</sup> and 3250 cm<sup>-1</sup> are related to hydrogen bonded to boron and nitrogen, respectively. It is also appreciated that diminishing diborane flows decrease

the fraction of the hexagonal phase and for the lower flows increasing hydrogen incorporation is observed, also a small peak centered at 1100 cm<sup>-1</sup> appears. The figure 1 also show the FTIR spectra for a sample grown with the lowest B<sub>2</sub>H<sub>6</sub> flow (1,75 sccm) but adding 100 sccm of H<sub>2</sub> to the gaseous mixtures. It is found that H<sub>2</sub> dilution eliminates the N-H and B-H bonds. Increasing even more the hydrogen dilution and decreasing the B<sub>2</sub>H<sub>6</sub> flow decreases further the fraction of hexagonal phase and increases the band at 1100 cm<sup>-1</sup>, which might be due to the presence of BN cubic phase.

The FTIR analysis as a function of the deposition temperature shows that for higher temperatures the hexagonal crystallite size, as indicating by the FWHM of the h-BN absorption band at 1380 cm<sup>-1</sup>, increases. For lower temperatures the hydrogen content of the films increases as indicated by the N-H stretching band at 3250 cm<sup>-1</sup> in the FTIR spectra shown in figure 2. The deposition rate also increased for decreasing temperatures, varying from 9 x 10<sup>-3</sup> to 3.3 x 10<sup>-1</sup> A/s. The maximum sample thickness attained for 6 hrs. deposition was 0.8 μm.



**Figure 3.** Grain size (obtained using the equation 2) as a function of the B<sub>2</sub>H<sub>6</sub> flow for the samples of figure 1, grown with 60 sccm of N<sub>2</sub>, a substrate temperature of 340 °C and a rf power density 0,5 W/cm<sup>2</sup>.

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<sup>-1</sup>, according to the study by Nemanich et. al. [12] 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. Figure 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 sizes of the h-BN thin film increase when the  $B_2H_6$  flow increases.

The results for the intrinsic stress for the BN samples are shown in table 1. It is observed that the intrinsic stress decrease as the total pressure and the hydrogen dilution increase. Positive values of stress are indicating compressive stress. In figure 4 the behavior of the intrinsic stress of the films with the substrate temperature is depicted, it is observed that the stress presents a minimum for substrate temperature around 180 °C.

**Table 1.** Intrinsic stress of BN samples growth by PECVD method with a substrate temperature of 340 °C, rf-power of 1 W/cm<sup>2</sup>, and at different flow rates.

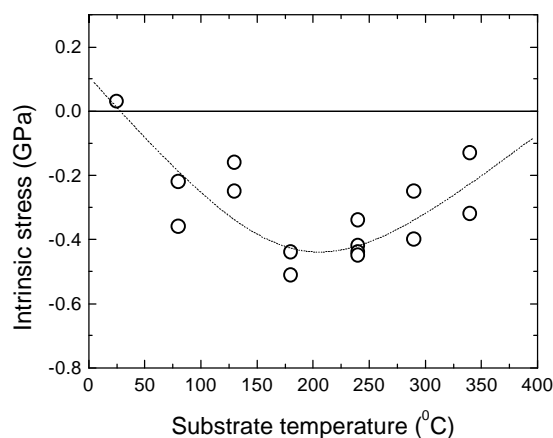
F (N <sub>2</sub> ) sccm	F (B <sub>2</sub> H <sub>6</sub> ) sccm	F(H <sub>2</sub> ) sccm	Stress (GPa)
120	3.5	100	-0.69
240	7	160	-1.14
360	10.5	300	-3.35
180	5.25	150	-1.26
150	4.3	125	-1.15
150	2.15	125	-0.22
150	1.08	125	-2.05
150	1.08	230	-3.41
150	1.08	350	-2.12
150	1.08	151	-0.99
150	1.08	185	-1.03

The hardness of the hexagonal BN samples presents values below 4 GPa. The hardness for samples with less hexagonal phase could not be determined due to the very small thickness of the films. The elastic modulus for the same samples was determined by nano-indentation and by an optical method, leading to values around 12 GPa, the thermal expansion coefficient for these samples was also determined by an optical method giving values in the order of  $-8.7 \times 10^6$  GPa. These constants did not show important changes when the deposition parameters were varied.

#### 4. Discussions

In a previous work, we observed that decreasing the  $B_2H_6$  flow induces the onset of the cubic phase on the BN samples. In this work, we decreased even further this flow as well as the  $B_2H_6/N_2$  flow ratio and observed the formation of hydrogen bonds (curve with 1.75 sccm of  $B_2H_6$  of the figure 1) and an increase in the band at 1100 cm<sup>-1</sup>. The addition of extra hydrogen in the gaseous mixture inhibits the hydrogen bonds and increases even more the band at 1100 cm<sup>-1</sup>. Even though Fourier Transform IR spectroscopy is one of most important tools to determine the BN structure, particularly the cubic phase, some precautions have to be taken interpreting the spectra

in order to avoid ambiguous or mistaken results. Normally, the absorption band around 1100 cm<sup>-1</sup> in the infrared spectra is associated to the cubic phase of the BN samples. But, it is possible also to associate it with the stretching vibration of Si-O and/or B-C bonds, which might be present in the samples as contaminant [13]. It is important to point out that contamination is more serious for deposition conditions that lead to lower deposition rates, which at the same time are the ones that favor the growth of the cubic phase. On the other hand, the results in figs. 1 and 2 show, unambiguously, that it is possible to get hexagonal BN samples with good structure by the PECVD technique, with average crystallite size above 90 nm.



**Figure 4.** Intrinsic stress as a function of the substrate temperature of the BN samples.

The values obtained for the hardness, the elastic modulus and for the thermal expansion coefficient are comparable with those reported for h-BN and did not show important variations with the deposition conditions.

The equivalent grain size deduced by the Raman spectra indicates that is possible to obtain large hexagonal nano-crystals in BN samples even at low temperatures. The hardness, the elastic modulus and the thermal expansion coefficient values of these hexagonal BN samples are similar to bulk values observed to h-BN crystals oriented to c-axis perpendicular to substrate surface [1]. In this sense, our samples present a very good performance of the growth nano-crystals.

#### 5. Conclusions

Boron nitride thin films with different structures were obtained by the PECVD technique. The fraction of hexagonal, amorphous and cubic phase of the thin films is extremely dependent on the  $B_2H_6$  flow and H<sub>2</sub> dilution. The crystallite size for the hexagonal grains increases for increasing temperatures and  $B_2H_6$  flow and at low rf power density. The measured thermomechanical properties of the BN samples did not show serious variations with the deposition conditions. In addition, the nano-crystals

presents in the hexagonal BN samples are well oriented and of good size.

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