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**Experimental evidence of the role of intericosahedral chains in the hardness of boron carbide films  
deposited by sputtering**

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## ABSTRACT

The relationship between structure and mechanical properties of sputter-deposited boron carbide films was investigated. Changes in the structure induced by annealing were characterized in terms of chemical composition, chemical bonding and concentrations of defects and of trapped impurities. The creation of new intericosahedral chains for higher annealing temperatures was revealed by infrared and Raman measurements, and the intensity of the infrared band at  $1500\text{ cm}^{-1}$  was found to be related with the hardness. The content of trapped Ar atoms and of open-volume defects are insensitive to relatively high annealing temperatures and do not influence the recovery of the hardness. Our results suggest annealing as a pathway to enhance the mechanical properties of boron carbide films.

Boron carbide can be as hard as 41 GPa [1] and is one of the hardest known materials, while at high temperatures it is the hardest one [2]. It combines low mass density, high wear resistance and high thermal stability, and the tribological properties can be improved by the formation of a superficial layer of boric acid [3-5]. It can be synthesized with several phases corresponding to different stoichiometries [6]. Within the range of 8-20 % of carbon, it is ideally described by a rhombohedral unit cell with icosahedral arrangement of 12 atoms at its vertices, in addition to a three-atom chain along the crystallographic *c*-axis that coincides with the unit cell main diagonal [6,7].

Despite the attractive characteristics of this material, the complexity of its structure, the existence of several stable and metastable phases, and the structural modifications that occur because of compositional changes, all impose difficulties in establishing a clear relationship between deposition conditions and film properties. A survey of the literature showed that in films deposited with nearly the same conditions, the mechanical properties can differ considerably [8]. In this work, we studied the relationship between the structure and hardness of sputter-deposited boron carbide films and established a direct correlation between the presence of intericosahedral chains and hardness.

Amorphous boron carbide films were deposited onto Si (100) by dc-magnetron sputtering from a B<sub>4</sub>C target at a working pressure of 5 mTorr of Ar. Prior to deposition, sputter-cleaning was performed to eliminate the natural oxidation of the target. The input power was fixed at 400 W, and the target bias, plasma current, substrate bias and temperature were -710 V, 0.55 A, -200 V and ~60 °C, respectively. The deposition rate was 0.9 Å/s and films with thickness 3600 Å were obtained. Thermal annealing was carried out in a vacuum furnace (base pressure of ~1x10<sup>-7</sup> Torr) for 30 minutes from 400 to 800 °C. The samples were allowed to cool in vacuum before removal to ambient environment.

The composition of the films was determined by nuclear reaction analysis (NRA) and x-ray photoelectron spectroscopy (XPS). NRA used ( $\alpha,\alpha$ ) reactions with B<sup>11</sup> and C<sup>12</sup> at an energy of 5.39 MeV [9], and the final amount of B was estimated by considering the relative abundance of B<sup>11</sup> as 80.1 %. XPS measurements used Mg  $\kappa_\alpha$  excitation and were done on *in-situ* sputter-eroded samples. The amount of trapped Ar in the films was determined by Rutherford backscattering spectrometry (RBS) using a 2 MeV He<sup>+</sup> beam.

Chemical bonding was investigated at room temperature by Fourier transform transmission infrared spectroscopy carried out in vacuum ( $\sim 2$  Torr) and by micro-Raman scattering spectroscopy with 100 x magnification using the 488 nm  $\text{Ar}^+$  laser line as the excitation source with 100 mW emission power.

Positron annihilation spectroscopy (PAS) was carried out using a monoenergetic ( $\pm 5$  eV) beam from 100 eV up to 20 keV. For each beam energy, the Doppler broadened spectra of the  $\gamma$  photons were analyzed to obtain the  $S$  parameter, i.e., the fractional area of the central region of the spectrum ( $511 \pm 0.7$  keV). The analysis was restricted to positron energies up to 4 keV that corresponds to a mean penetration depth of  $\sim 1500$  Å in  $\text{B}_4\text{C}$  in order to avoid any influence of the substrate.

Load and displacement indentation measurements were performed with a Nanoindenter II from NanoInstruments with a maximum load of 20 mN. Six independent indentations were carried out in each sample at different spots. Data analysis was carried out as described in [8].

Since changes in the composition are known to affect the structure and properties of boron carbide [7,10], eventual changes due to annealing were checked. The B:C ratio of the as-deposited and annealed films was determined by XPS and NRA to be 4:1. This is illustrated by the perfect overlap of the NRA spectra from the as-deposited and 800 °C annealed films, Fig. 1.

Figure 2a presents the infrared spectra of the as-deposited and annealed films. Two broad bands can be observed, one centered at  $\sim 1100$   $\text{cm}^{-1}$  and the other at  $\sim 1500$   $\text{cm}^{-1}$ . The band at 1100  $\text{cm}^{-1}$  is assigned to B-C bonds in the icosahedra [11], and the asymmetric lower frequency tail of this band contains the contributions of the vibrations of the amorphous boron network [12]. The band at 1500  $\text{cm}^{-1}$  is associated with the anti-symmetric stretching of B-C bonds in the linear chain that interconnects the icosahedra [7,13]. The infrared results show that while annealing at increasing temperatures does not induce major changes in the icosahedral arrangement, it leads to a higher intensity of the 1500  $\text{cm}^{-1}$  band. The observation of new B-C bonds originated in the intericosahedral chains suggests the creation of additional chains. A similar result was also observed by Raman spectroscopy where a peak at  $\sim 545$   $\text{cm}^{-1}$ , which is associated with intericosahedral chain vibrational modes [10], is observed in the annealed samples only (Fig. 2b). The broad bands between  $\sim 700$  and 1200  $\text{cm}^{-1}$  are related to icosahedral

modes which are not sensitive to annealing, in agreement with our infrared spectroscopy results. No sign of graphitic inclusions was observed.

We observed that higher annealing temperatures lead to an increase of the hardness from 20 to 26 GPa. The intrinsic conditions for high hardness are high bond (or electronic) density, short bond length and a high degree of covalent bonding [14], while the experimentally measured hardness of a material is strongly affected by the presence of defects. Because of this, we investigated the effect of annealing on the concentrations of open-volume defects and of trapped impurities. The as-deposited films contain  $\sim 7 \times 10^{21}$  at/cm<sup>3</sup> trapped Ar atoms which can block the formation of B-C bonds [8]. RBS results show that the Ar content remained the same up to annealing temperatures of 600 °C and decreased by 25 % after 800 °C annealing. The concentration of open-volume defects were obtained in terms of the *S* parameter which corresponds to the total number of positron annihilation events with low momentum electrons (valence electrons) [15,16]. Since annihilation of positrons localized in open-volume defects is enhanced relative to the defect-free material, an increase of the *S* value can be associated with an increase of the amount of defects [15,16]. The PAS results (not presented) show that the defect distribution is uniform along the thickness of the films and that it does not change due to annealing. In fact, the average *S* value of the as-deposited and 800 °C annealed samples are 0.462 and 0.464 ( $\pm 0.001$ ), respectively. Also, the absence of changes in the shape of the curve indicates that a new class of defects was not generated due to annealing. Clearly, neither changes in the composition nor the behavior of the concentration of open-volume defects or of the content of trapped Ar atoms can be directly correlated to the enhancement of the hardness. In fact, our data indicate a direct correlation between the hardness and the formation of B-C bonds in the intericosahedral chains. This trend is clearly demonstrated in Fig. 3 where the the formation of B-C bonds, as indicated by the intensity of the absorption band at 1500 cm<sup>-1</sup>, is plotted against hardness for boron carbide films annealed at increasing temperatures. Our results find additional support in theoretical calculations of the elastic properties and mechanical stability of boron-based materials that showed that the strength against compression comes from the chains that interconnect the icosahedra, explaining why  $\alpha$ -boron that does not have intericosahedral chains is soft, while boron carbide is hard [17].

In summary, we showed that the hardness of boron carbide is directly related to the presence of intericosahedral chains. Our results point to post-deposition annealing as a pathway to enhance the mechanical properties of these films. Moreover, it was found that the concentration of open-volume defects and of trapped Ar atoms which are insensitive to the effects of relatively high temperature annealings are not related to this process.

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## Figure captions

**Figure 1** – NRA spectra of the as-deposited and 800 °C annealed boron carbide films showing the intensity of the  $C^{12}$  and  $B^{11}$  peaks, as indicated. No variation in the composition of the films was found due to annealing.

**Figure 2** – a) Infrared spectra showing the anneal-induced evolution of the band at  $1500\text{ cm}^{-1}$  associated to B-C bonds in the intericosahedral chains. b) Raman spectra of the as-deposited and 800 °C annealed films. The arrow indicates the vibrational mode related to the intericosahedral chains that is observed in the annealed samples only.

**Figure 3** – Correlation between the hardness and the amount of B-C bonds in the intericosahedral chains as revealed by the area of the band at  $1500\text{ cm}^{-1}$ .

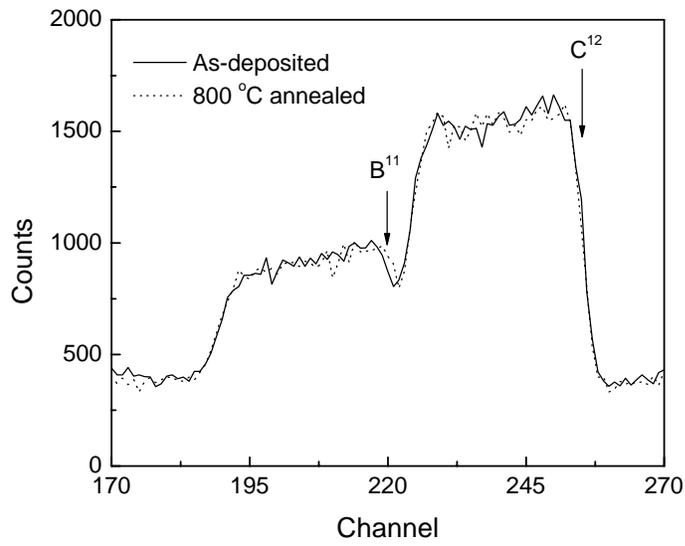


Figure 1 - L.G. Jacobsohn et al.

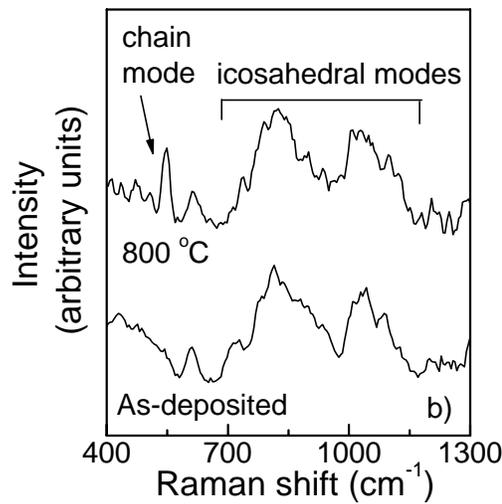
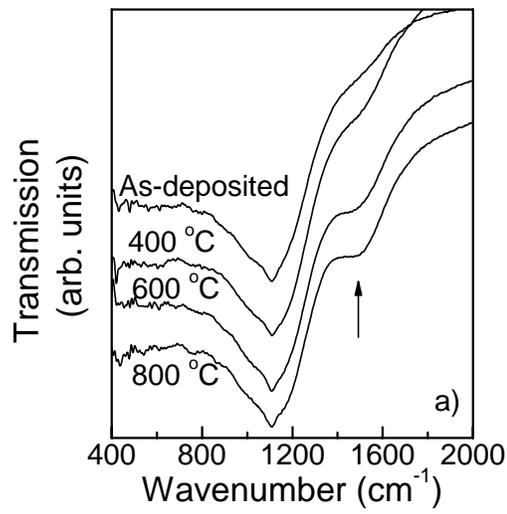


Figure 2 - L.G. Jacobsohn et al.

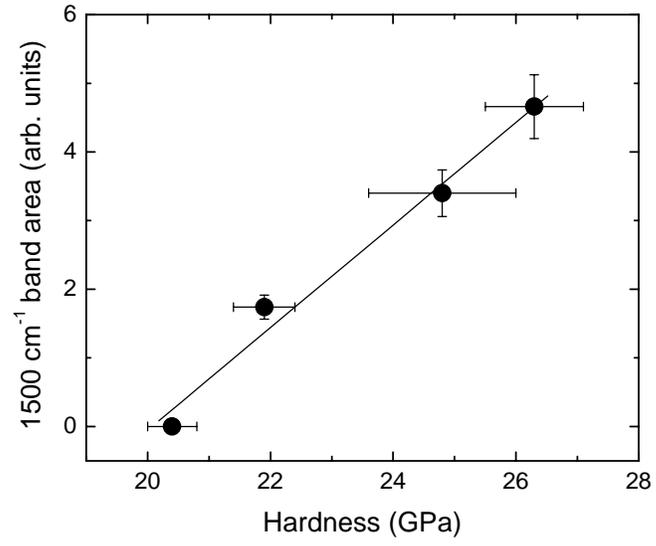


Figure 3 - L.G. Jacobsohn et al.