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Hard BC_xN_y thin films grown by dual ion beam sputtering

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Abstract

Boron carbonitride thin films were deposited by sputtering of a B_4C target with $Ar-N_2$ ion assistance. BC_xN_y films were grown onto Si (001) at room temperature. The chemical composition and the type of bonding were determined by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The hardness of the films was measured with a nanoindenter. The chemical analysis of the samples indicates the formation of two different compounds, a ternary BC_xN_y and a binary carbonitride CN_x. All the films showed high hardness, in the range 16–33 GPa, which clearly increases as the BC_xN_y content in the sample increases. In this study the highest hardness (i.e. 33 GPa) was obtained when the BC_xN_y content in the sample was 50%. The average composition of this BC_xN_y was estimated by XPS as 20 at.% carbon and 12 at.% nitrogen.

Keywords: BCN; CN; Hardness; XPS

1. Introduction

In the last few years, B–C–N systems have attracted much attention for hard coating applications as they are expected to combine the excellent properties of B_4C, CN_x and BN, e.g. high hardness, low friction coefficient, high wear resistance and high thermal stability. The deposition and characterization of ternary BC_xN_y thin films have been the subject of numerous experimental works [1–10]. Besides other deposition techniques (CVD, RF magnetron sputtering, laser), Ion Beam Assisted Deposition (IBAD) is one of the potential techniques for producing these coatings due to the possibility of adjusting the deposition parameter independently [11,12].

Regarding the chemical composition of the BC_xN_y system, in spite of several XPS analyses found in the literature [9,13] the formation of a stable ternary boron carbon nitride compound still remains unsolved. In fact, most of the analyses reported [2,14] indicate the formation of different mixtures of CN_x and BN_x phases. More recently, however, Linss et al. [9] have reported the formation of ternary compounds, BC_xN_y, in which all three elements are bonded to each other if at least one of them has a low concentration in the film.

In this study we have used a dual ion beam sputtering system to deposit BC_xN_y films on Si substrates. The chemical composition and the type of bonding were determined by X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy. The hardness of the films was measured with a Berkovich-tip nanoindenter.

2. Experimental

Boron carbonitride films were deposited on Si(100) substrates in a dual ion beam sputtering system at a base pressure of 10^{-7} Torr. The system has a 3 cm Kaufmann-type ion source to sputter a high purity B_4C target with inert Ar^+ ions at an angle of incidence of 45° from the target normal, while a low energy end-Hall ion source is used to bombard the film during its growth with a controlled mixture of Ar^+ and N_2^+ ions at an incidence of 30° from the sample normal. The sputter conditions were kept constant at a current density of 1 mA/cm^2 and energy of 500 eV. The energy of the assisting N_2^+ ions was kept constant at 60 eV while the current density was varied to obtain BC_xN_y films with different compositions. The films were grown at room temperature in a water-cooled copper sample holder. The sample holder was situated at ≈ 10 cm from the target and was rotated at 2 rpm during deposition to improve homogeneity.

In order to obtain information about the bonding, transmission FTIR spectra in the range of 550 to 7000 cm^{-1} were recorded in a Bruker IFS66V infrared spectrometer with a resolution of 4 cm^{-1}. Additionally, the samples were charac-

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terized by X-ray photoemission spectroscopy in a PHI 3027 spectrometer using MgK_α radiation ($h\nu = 1253.6$ eV) and a pass energy of 50 eV. Peak area ratios of the B1s, C1s, N1s and O1s core levels were used to determine the composition using the sensitivity factors given by the manufacturer [15].

The hardness was measured with a CSEM Nano-Hardness QC indenter with a Berkovich diamond tip. Load-unload curves were performed at a maximum load of 10 mN. This process was systematically repeated 10–20 times in well separated places. The curves were analyzed following the Oliver and Pharr method [16].

3. Results and discussion

Fig. 1 shows the hardness of each of the films as a function of the current density J of the N_2^+ ions. For comparison we have included the values corresponding to quartz and sapphire measured with the same system. In general we observe values of high hardness (i.e. above 16 GPa) for all the BC_xN_y films studied in this work, between those for quartz and sapphire. The hardness obtained for the film at $J = 0$ µA cm^{-2} is in agreement with reported values [17] for B_4C films. For the maximum current ion density, i.e. $J = 33$ µA cm^{-2}, the hardness decreases to 18 GPa, but this value is higher than the expected hardness for h-BN films (~12 GPa) as well as BCN films grown by CVD [18]. The hardness dependence in BCN films with the N content has already been studied by several groups [19–22]. All found that hardness decreases linearly with nitrogen content; however, in this work, a very interesting behavior was observed in the films when the incorporated nitrogen was in the low range ($J < 10$ µA cm^{-2}). Fig. 1 indicates that the hardness shows a maximum of 33 GPa for a current density of $J(N_2^+)$ ~6–8 µA cm^{-2}. The increase observed for the hardness at low nitrogen doses is not inconsistent with the reported works [19–22], since they did not perform a detailed study for low nitrogen content and probably could not have detected this behavior.

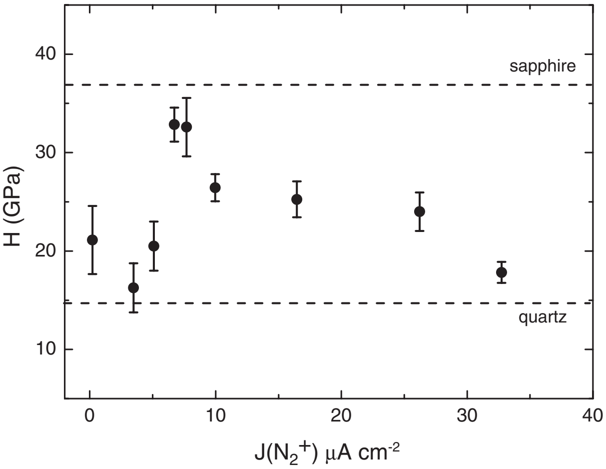

Fig. 1. Hardness of BCN films as a function of the nitrogen ion current density. Quartz and sapphire hardness values (dotted line, as labeled) are included for comparison.

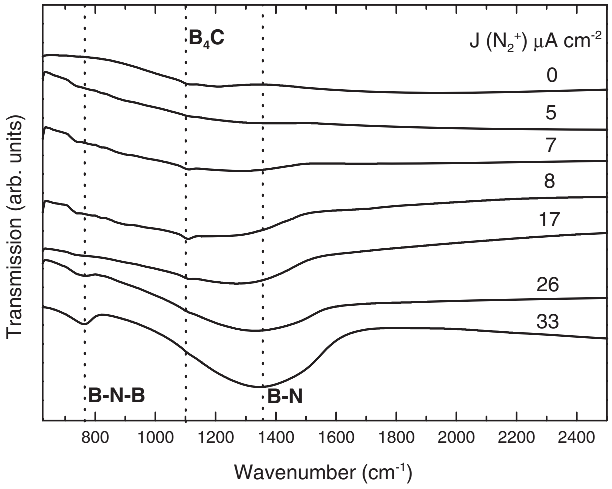

Fig. 2. FTIR spectra of different BCN films; the nitrogen ion current density is labeled for each spectrum.

The bonding characteristics of these films were investigated by infrared spectroscopy XPS. Fig. 2 shows the FTIR spectra (625–2500 cm^{-1}) of some samples, and the current density of the nitrogen ions is labeled for each spectrum. The figure shows continuous changes in the deposited films from B_4C target ($J = 0$) as the N_2^+ assistance is increased. For $J = 0$ µA cm^{-2} the FTIR spectrum shows only a characteristic absorption band around 1100 cm^{-1} due to B–C and/or polarized B–B bonds [21]. However, for the maximum current density, i.e. $J = 33$ µA cm^{-2}, the FTIR spectrum shows two vibrational bands, one weak at 765 cm^{-1} and the other intense at 1360 cm^{-1}, associated with B–N–B and B–N stretching bonds, respectively [9]. As J increases, we observe the appearance of a broad peak at 1200 cm^{-1}, which shifts towards 1400 cm^{-1}. Furthermore, the asymmetry of the band decreases especially at lower wavenumbers, suggesting that the number of B–B and/or B–C bonds is decreasing. Moreover, when nitrogen is incorporated into the films, appears the B–N–B bonding at 735 cm^{-1}, which becomes more intense and shifts to 765 cm^{-1} for $J > 17$ µA cm^{-2}. It is worth pointing out that several bonds should contribute to the broad absorption structure observed between 1100 and 1600 cm^{-1}. The B–C bond has been reported [17] to induce a band between 1100 and 1250 cm^{-1}, while by the B-rich films show the maximum absorption at 1100 cm^{-1} and the C-rich ones at 1250 cm^{-1}. Moreover, the formation of C–N and C═N bonds would give contributions around 1300 and 1600 cm^{-1}, respectively [23–25]. Therefore, it is difficult to determine unambiguously the origin of this peak. However, Fig. 2 allows three different set of spectra to be distinguished: those corresponding mainly to B_4C ($0 \leq J \leq 5$ µA cm^{-2}), those associated with a maximum content of nitrogen ($J > 25$ µA cm^{-2}) and those at intermediate ion current densities ($7 \leq J < 25$ µA cm^{-2}), where both the contributions, associated with B–C bonds and with B–N bonds, can be observed. This indicates that significant structural changes occur when the J current increases.

We performed X-ray photoelectron spectroscopy of the films. Fig. 3 shows the respective XPS spectra of the core