

Stress in boron nitride nanofilms prepared by rapid thermal annealing *

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Boron Nitride (BN) nanofilms (5-7 nm) were prepared by Rapid Thermal Annealing (RTA) of boron layers deposited on sapphire (Al_2O_3) substrates in NH_3 ambient in vacuum (5×10^{-2} Torr). The RTA process temperatures used were: 800, 1000, 1200 and 1400 °C, each applied for times of 15, 30, 60 and 180 s. The mechanical stress in the BN films, as a function of these processing parameters of the RTA process and its correlation to other film characteristics, were studied. Stress measurements showed that a transition from compressive to tensile stress occurs. The stress changed over a wide range of values, depending on the RTA process parameters. For example, the stress in the film before annealing is compressive, viz $-1.75 \times 10^{10} \text{ N.m}^{-2}$, and after RTA for 15 s, it is tensile with values of 0.75, 1.41, 2.65 and $2.28 \times 10^{10} \text{ N.m}^{-2}$ for annealing temperatures of 800, 1000, 1200 and 1400 °C respectively. The stress increase is due to increased nitrogen sorption on the substrate and the formation of BN films at higher (1200-1400 °C) temperatures. Boron nitride film morphology shows that films annealed at 800-1000 °C exhibit a homogeneous morphology, while for those annealed at 1200 °C, a needle-like morphology starts to be formed. Our results show that stress is in good correlation with XPS and the ohmic resistance measured for these films. Mechanical stress results are discussed on the basis of the N/B ratio and phase transformations in the boron nitride films.

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1. Introduction

Boron nitride (BN) thin films are useful as electric insulators because of their high electric resistivity, of the order of $10^{13} \Omega \cdot \text{cm}$. Until now, however, such a superior property is not yet fully applied in the industry. Studies on new methods for preparing good quality BN films would bring new opportunities to exploit its electronic and mechanical properties. A number of authors have reported data on such films prepared by different methods, and their characterization [1-7]. Depending on the film synthesis method, different structural aspects of the BN phases can develop, and hence the yield stress would be also of a different type [4]. To our knowledge, few authors have reported on the mechanical stress behaviour, especially in thin BN films [4, 5]. The purpose of this paper is to present the preparation technique, Rapid Thermal Annealing (RTA), as a way for producing BN nanofilms and to study the mechanical stress as a function of the processing parameters of the RTA process. The films were also characterized by XPS, IR spectra, SEM and resistance

measurements by a four-point method. The relationships between different properties will assist in the understanding of the film structure.

2. Experimental

Substrates of c-face sapphire (Al_2O_3) of 330 μm thickness were used. Boron of 99.999 % purity was first deposited by vacuum evaporation (5×10^{-5} Torr), in order to produce a nanofilm of about 5 nm thickness. The boron "precursor" was converted into BN during RTA in a reactor in an ammonia atmosphere, using 12 sccm NH_3 flow and a working pressure of 5×10^{-2} Torr. As a result, BN films of 7 nm thickness were obtained. The thicknesses were measured by ellipsometry. The temperature in this reactor could be raised to 2500 °C from room temperature in 2 s. In this study, temperatures of 800, 1000, 1200 and 1400 °C were applied to the B - Al_2O_3 structures for times of 15, 30, 60 and 180 s.

The Newton's rings method was used with an adapted microscope, to determine the mechanical stress in the film [8]. The stress was calculated by measuring the sample's radius of curvature before and after RTA. Once the

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curvature change was obtained, the yield stress, which is proportional to this change, was found. With this technique, it was possible to determine not only the magnitude but also the bending direction of the BN-Al₂O₃ system, and hence distinguish between compressive and tensile stress. The error in the curvature determination was different for each sample, and thus for simplicity the highest error of 10% was taken as representative in all cases.

3. Results

Fig. 1 shows the boron nitride stress behaviour as a function of the annealing time, at four temperatures. Fig. 2 presents the results of an XPS analysis of the film N/B ratio, also as a function of the annealing time for the same annealing temperatures. The morphology of films produced at 800 and 1400 °C, both annealed for 60 s, are presented in Fig. 3 and Fig. 4 respectively.

It is worth mentioning, first, that a general trend is evident for the influence of the RTA process on the mechanical stress. The stress is compressive for the original B-Al₂O₃ structure, while it becomes tensile after RTA at all process durations and temperatures studied. The stress value with only a boron film as deposited is as high as -1.75×10^{10} N.m⁻². The highest value of tensile stress at an annealing temperature of 1400 °C and an annealing time of 60 s is clearly seen in Fig. 1. It is interesting to note that for the same annealing time, but at 1200 °C, the lowest tensile stress is obtained. This means that the process temperature plays a dominant role in the stress changes. It is easily seen that at low temperatures (800 and 1000 °C) the stress changes between 60 and 180 s are very small – 1.94 to 1.99 and 1.77 to 1.86×10^{10} N.m⁻² respectively. This is in accord with the significance of the influence of temperature on the stress.

Fig. 2 shows that with increasing annealing temperature and time, a trend to an increased N/B ratio is observed. Looking at Fig. 1 and 2 together, the tendencies in the stress behaviour for 800 and 1000 °C are similar to those of the N/B ratio from the XPS analysis. A further increase in the ratio to 0.72 for 1400 °C, and 180 s annealing time is accompanied by a corresponding stress decrease.

SEM images of the film morphology are displayed in Figs. 3 and 4 – homogeneous to needle-like films.

4. Discussion

The bonding energy of Al-O in Al₂O₃ is 0.0053 keV [9]. The bonding energy of K-electrons in boron is two orders of magnitude higher, at 0.166 keV, than that in Al₂O₃. Thus, this appears consistent with the experimental findings of compressive stress for the B-Al₂O₃ structure, because the process of formation of the boron film

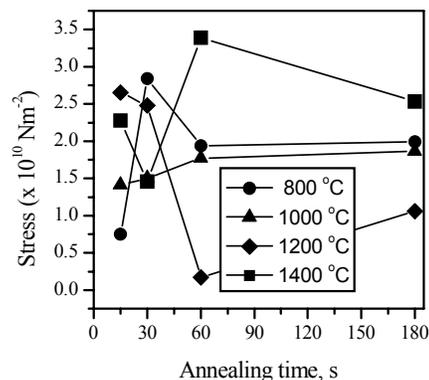


Fig. 1. Mechanical stress dependence of the BN-Al₂O₃ system on RTA time at constant temperatures.

would be accompanied by a ‘crumpling’ force effect. When the RTA process is applied to this structure, ammonia starts to decompose into atomic nitrogen, even at low temperatures. This highly reactive species reacts with boron to different extents, depending on the annealing temperature. The comparative atomic radii of B and N can explain in part the stress transition from compressive to tensile. Actually, the boron atomic radius is 0.04 nm, while that of nitrogen is 0.03 nm.

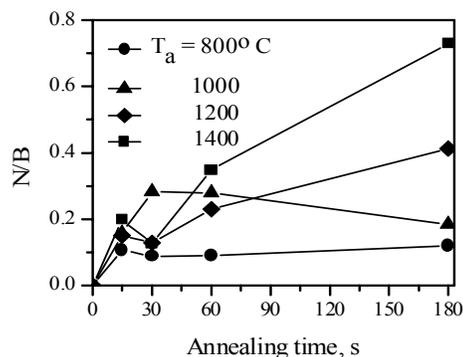


Fig. 2. N/B ratio taken from XPS analysis as a function of the annealing time at four constant temperatures.

In terms of stress this means that N, being three-fold coordinated, and being of higher atomic mass than B, in adapting to the boron during the thermal shock, stretches the system Al₂O₃-BN_x. Because of the complex bonding environment, this statement is additionally verified.

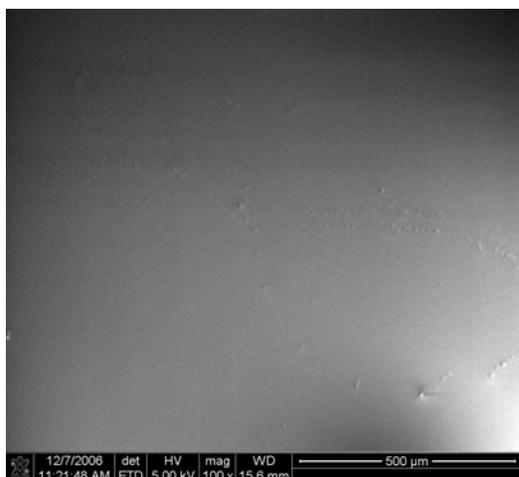


Fig. 3. Morphology of a BN_x film produced at 800 °C RTA for 60 s.

The term “bond strength” is used to mean the mechanical strength of the bond, i.e. the force constant resisting distortion, which can be taken from the IR absorption spectrum. Two IR active phonons have been identified at frequencies of 798.2 and 1370 cm^{-1} . The first is characteristic of all BN films studied. The second is characteristic of films prepared at only 1400 °C at 180 s. The 1370 cm^{-1} mode is a stretching of the B-N bond in the plane, and the 798.2 cm^{-1} mode is a bending of the B-N-B bond between the planes [4]. These modes are closely related to the IR-active modes, which are typical of hexagonal BN [10]. Moreover, other authors report [3] that nanofilms of hexagonal structure exhibit tensile stress, as in our case. As concerns the stress magnitude, it is in good agreement with the experimental observations published by other groups, though the methods of producing the BN films are different [11].

To gain some insight into the mechanical stress changes, and to correlate them to the structure of the films, they are discussed in parallel with the results on the N/B ratio and XPS analysis for the same annealing times and temperatures. The low values of the N/B ratio at 800 °C are signs of a prevailing physical adsorption without B-N bond formation. As can be seen in Fig.1, stress changes follow a behaviour similar to the N/B ratio. The observed maximum of $N/B = 0.28$ at 1000 °C and the subsequent decrease to 0.19 show that active adsorption centres of N atoms are initially saturated, and then the desorption from the substrate follows. In the first 60 s of the RTA process, at 800 and 1000 °C, B-N bonds are not yet formed, nor is a BN film formed. Since the B-N bond concentration is responsible for the stress changes, this is why the tensile stress varies over a wide range of values. For low temperatures, viz 800 and 1000 °C, only some intermediate B-N bonds are realized, and the stress increases. The strong stress increase, by a factor of roughly 3.5 at 800 °C, is due to the formation of an intermediate phase BN_x [12], which changes the ‘film’ density. For high temperatures, i.e. 1200 and 1400 °C, the processes of nitrogen adsorption

and desorption are very dynamic, and the basic phase transformations are in progress. Now the number of B-N bonds increases and this accounts for the highest stress value at 1400 °C. Further evidence of this stress behaviour is revealed by XPS analysis, with the help of the binding energy of N 1s and B 1s in the first 60 s [12]. The stable position of the N 1s peak at 402 eV, and of the B 1s peak at 188.3 eV are indications of there being no significant quantity of B-N bonds formed. All experimental data together show that the annealing times of up to 60 s are those when the beginning of B-N bond formation starts, in order to form a nanofilm of BN.

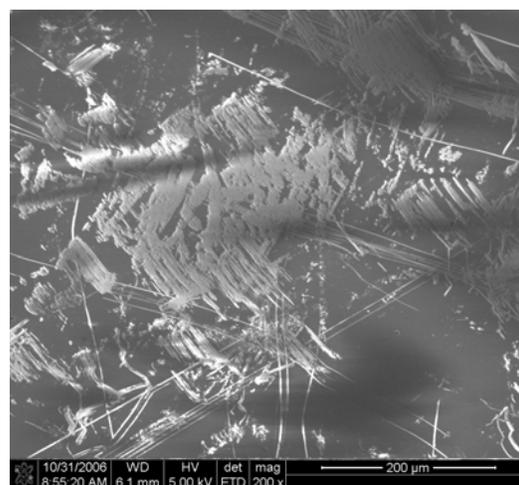


Fig. 4. Morphology of a BN_x film produced at 1400 °C RTA for 60 s.

Another macro-property of BN studied, the ohmic resistance, also assists in unravelling the complex stress changes, especially at 800 °C. The drastic increase in the stress (15 to 30 s) is well correlated with a resistance increase, taking into consideration the starting resistance of $6.7 \times 10^5 \Omega \cdot cm$ for a boron film to $9 \times 10^5 \Omega \cdot cm$ with 15 s RTA applied. At higher RTA durations, the stress magnitude decreases, or remains nearly constant, as does the resistance. A similar tendency is observed for 1000 °C, i.e. the slight increase of the stress is accompanied by a slight increase in the resistance. The resistance for the BN film produced at 1400 °C for 180 s is 3 orders of magnitude less ($2.7 \times 10^2 \Omega \cdot cm$) than for those annealed at 800 °C. This small value is in correspondence with the released stress, as commented upon below.

The gradual stress changes, from 60 to 180 s, compared to those that arise for times up to 60 s can be assigned to the chemisorption of nitrogen, which is the most clearly manifested at 1400 and 1200 °C. The closest value of the N/B ratio to 1 is 0.72 from the results presented in Fig.2, i.e. the film produced at 1400 °C is the closest to stoichiometric. For this reason, a 25% release of tensile stress is observed. Additionally, our earlier study [12] shows N 1s and B 1s peak shifts, respectively to 398.4 eV and 191.3 eV at 1400 °C. According to other authors [13], these values are the typical binding energies,

which guarantee the BN composition. Furthermore, SEM studies on the morphology of these films show that low temperature RTA for 60 s does not lead to morphological film changes (Fig.3), while at 1400 °C a needle-like morphology is observed (Fig.4). This is in good correlation with the highest value of stress obtained at 60 s RTA.

5. Conclusions

In this paper, we have studied the mechanical stress in BN nanofilms produced by RTA. The stress generated in the system Al_2O_3 -BN is tensile. The dependence of the stress on annealing time at different annealing temperatures exhibited a wide range of values for the first 60 s. This was associated with the dynamical balance between the processes of nitrogen adsorption and desorption. Stress data are an indication that complete BN films start to be formed at temperatures of about 1200 °C, when chemical adsorption is more significant than physical adsorption. The stress decrease at 1400 °C and annealing time of 180 s fully corresponds to the closest to the stoichiometric composition ratio of N/B, to the needle-like film morphology, to the characteristic of hexagonal BN peaks in the IR spectra, and to resistance measurements. Both tensile stress and substrate temperature play important roles in ordering the structure. The properties studied show that RTA could be used as a new useful option for producing BN nanofilms which could be in competition with the other methods of film production.

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