DEPOSITION OF BORON NITRIDE FILMS BY IBAD TECHNIQUE : EFFECT OF THE ION BOMBARDMENT.

M. A. DJOUADI.
Laboratoire Bourguignon des Matériaux et Procédés ENSAM Cluny 71250 Cluny

ABSTRACT

In an attempt to decrease the intrinsic stress of IBAD BN films and improve their adhesion, collisional effects on the intrinsic stress of the deposited layers were investigated by using on the one hand, a pur nitrogen ion beam, on the other hand, a mixed beam of argon and nitrogen. Bilayers were deposited under pur nitrogen assistance by varying the elaboration conditions (E, FN/FB) during growth. Surprisely the average stress remains constant whatever the experimental conditions. In fact the second deposition step always induces in the burried layer a peak of stress in the interfacial region. Boron nitride films were also deposited by using a mixture of nitrogen and argon ions for assistance during growth. On condition that nitrogen-to-boron flux ratio should be high enough to synthesize stoichiometric material, tetrahedral bonds in BN films are formed when argon-to-boron flux ratio and accelerating voltage exceed interdependent threshold values. The investigations of the structure of deposited films followed by stress measurements have shown that the high levels of obtained stress (up to -10 GPa) are due to a change of mechanical properties of the synthesized material when it goes from hexagonal structure to cubic one.

INTRODUCTION

Boron nitride (BN) is one of the most interesting materials of the III-V compounds, from both a practical and fundamental scientific viewpoint [1]. BN crystallizes in two forms : a cubic zinc blende and a hexagonal structure. Many potential applications of deposited BN, such as for wear-resistant coatings or optical layers, are limited by the intrinsic stress in thin films. In a previous paper [2], thermal effects were studied in BN and Si_3N_4 layers, the intrinsic stress can be always reduced below -1 GPa by a post-deposition annealing at a temperature less than 1000°C. On the contrary, when the deposition temperature is varied up to 600°C, the stress in IBSD Si_3N_4 layers is not significantly reduced and, for IBAD BN films, it is even greater than expected from the development of the thermal stress.

In the present work, we investigate collisional effects on the intrinsic stress of the deposited layers by using on the one hand, a pur nitrogen ion beam, on the other hand, a mixed beam of argon and nitrogen.

EXPERIMENTAL

The deposition conditions have been described elsewhere [3]. Ion-beam-assisted evaporation has been performed in a high-vacuum system (base pressure < 10^{-8} mbar) under a work pressure less than 3 10^{-5} mbar. A home-made electrostatic reflex ion source with a 3 grids extraction optics delivers a 100 mm diameter ion beam neutralized by a plasma-bridge. In this work, the ion energy has been varied from 0.25 to 2 keV and the ion-current from 0.20 to 0.50 mA/cm^2, with a boron deposition rate of 0.16 nm/s. Depositions at room temperature were done with a water-cooled substrate holder. A second substrate holder can be resistively heated up to 700°C. The thickness of BNx layers has been measured by using a Dektak profilometer. The internal stress of the films was estimated by measuring curvature radii of the Si substrate, by using the Newton's rings method.

RESULTS AND DISCUSSION

Effect of varying energy and fluxes

Deposition at nitrogen/boron flux ratio FN/FB=0.5 and energy E=1keV followed by a second deposition at FN/FB=1 and E=0.5keV have been performed with substrate temperature of 150°C. The total thickness of the samples was measured and found to be 0.8 µm. But the thicknesses of the superficial and burried layers are not accessible by measurement. However, by measuring the evaporation rate of boron by means of quartz oscillator and the arriving rate of nitrogen, on the growing film, using current density measurements we can estimate the thickness at 0.5 µm for the first layer and 0.3 µm for the second.
The resulting average stress does not differ significantly from that observed in a stochiometric film deposited at nearly room temperature i.e. -2.5 GPa. At the time we expected a decrease of the average stress which would be given by the average stress value of the first layer (-1.2 GPa) and the second (-2.6) weighted by their respective thicknesses : i.e. -1.7 GPa. In order to understand such a behavior stress profiles have been measured. The variation of substrate curvature is given in figure 1 as a function of film thickness. The stress in the upper layer is homogeneous and equal to -2.6 GPa as expected. In the burried layer, two different stress values can be observed, near the interface with the substrate, in a slab of a about 350 nm, the stress is equal to -1.2 GPa wich corresponds nearly to the value of a stochiometric film deposited at E=0.5 keV. But near the interface with the second deposit, the stress value is found to approach a surprising high value of -3.9 GPa. The second deposition step induced in the burried layer a peak of stress in the interfacial region. These results are similar to those obtained by performing a deposition/annealing/deposition sequence of hexagonal boron nitride films [2].

Further analysis of this phenomenon needs a detailed structural characterization of the films. However, it is demonstrated that the spatial extent of the ion-peening effect may exceed several tens of nanometers at 500 eV .

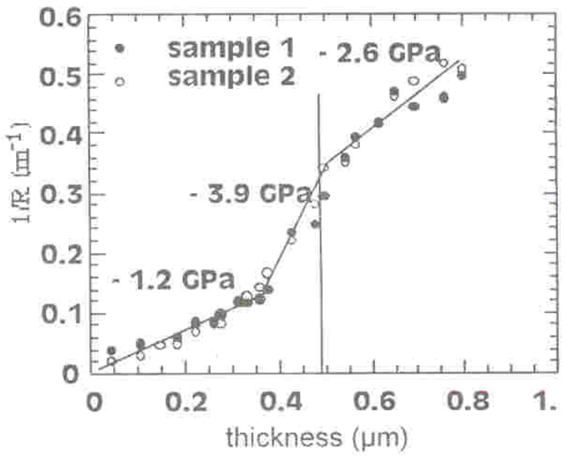


Figure 1 : $1/R$ vs d_f. Conditions : E=1keV FN/FB=1 and E = 0.5 keV, FN/FB = 0.5

__Effect of using argon and nitrogen ions__

BN films were deposited by using a mixture of nitrogen and argon ions for assistance during growth. On condition that nitrogen-to-boron flux ratio should be high enough to synthesize stoichiometric material, tetrahedral bonds in BN films are formed when argon-to-boron flux ratio and accelerating voltage exceed interdependent threshold values, which depend slightly on incident angle of the beam, but not on the substrate temperature above 200°C [4, 5]. The study of the stress in cBN films was done by fixing the substrate temperature to 400°C and $F_N/F_B>1$. The mesured stress is reported in Fig. 2 versus ion energy for two argon to boron flux rates 0.4 and 0.5. For energy below 550 eV a weak value of stress is obtained, above this energy the absolute value of the internal stress increases drastically and reaches a value of 9.5 GPa, after this maximum it decreases again with increasing energy until 3 GPa. These results are similar to those reported by several authors [6, 7, 8].

For explaining the transition from h-BN to cBN, MacKenzie and al [6] assumed that the incorporation of argon in the film, at a level of approximately 1%, may play an important role in creating stress and help to promote the growth of the c-BN phase. This interpretation is not in agreement with two of our results :

First, in Fig. 2 we have reported with the dotted line the variation of stress with ion energy for hBN films (curve b).The comparaison of curves (a) and (b) shows that below 550 eV the use of argon ions decreases the internal stress in the films as long as the structure of the layers is hexagonal. In order to explain such a behavior, it can be assumed that the bombardment of the film during growth, by argon ions, creates voids in the bulk of synthesized material. This hypothesis was verified by measuring the density of the obtained films wich lies in the range of 2 to 2.1 whereas the measured density of films deposited under assistance of pur nitrogen ion beam are greater then 2.28 [3]. In addition, other workers [9] have measured the argon concentration incorporated in their BN films. They have found that the content of argon is @ 0.2%-0.3% for both the h-BN/t-BN and c-BN films. We can assume therefore that the argon incorporation is not responsable for the films transition from h-BN to cBN.

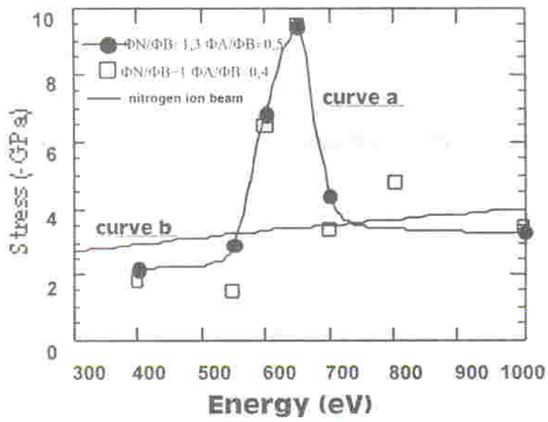
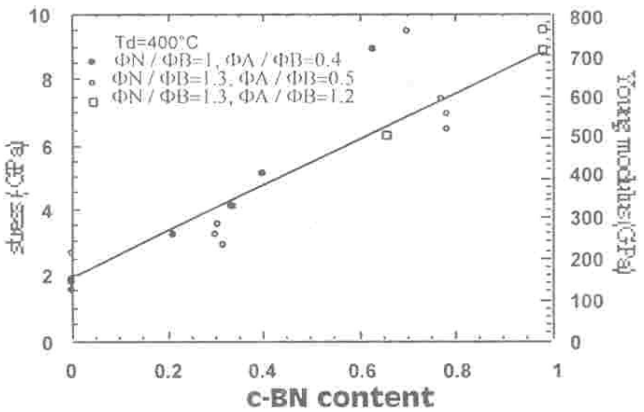


Figure 2 : Variation of the stress versus energy at a constant Ar^+ and N_2^+ ion flux.

Second, the behavior of the stress and cBN content vs energy is similar, so the variation of internal stress with cBN proportion is reported Fig. 3. It can be observed that the stress varies almost linearly with the content of cBN and this variation is similar to that of the Young modulus calculated for a mixture of cBN an hBN. For the hBN thin films and bulk cBN, the $(Y_f)/(1-n_f)$ ratios are respectively equal to 1.8 and $7x10^{11}$ N/m^2 [5].

Regarding of these results it can be assumed that the high levels of obtained stress are not due to argon incorporation but may be due to a change of mechanical properties of the synthesized material when it goes from hexagonal structure to cubic one.



Fiure 3 : Variation of the stress and calculated Young modulus (straight line) versus c-BN content.

REFERENCES

1) C. Weissmantel in *Thin films from free atoms and particles*, Ed. K.J. Klabunde, Academic Press,Orlando, 1985, p.153

2) M.A. Djouadi, D. Bouchier Materiel Modification by Energtic Atoms and Ions. Ed.K.S. Grabowski, S.A. Barnett, S.M. Rossnagel, K. Wasa, MRS Proceedings, **263**, 185 (1992).

3) O. Burat, D. Bouchier, V. Stambouli and G. Gautherin, Jpn, J.Appl. Phys , **30**, 1469-1474 (1991).

4) M.A. Djouadi, University Thesis, Université Paris XI, Orsay, October 1993.

5) D. Bouchier, G. Séné, M.A. Djouadi and P. Möller Nuc. Instr. & Meth. in Physics Research B 89 (1994) 369-372

6) D. R. Mackenzie, W. D. Macfall, W. G. Sainty, C. A. Davis and R. E. Collins, Diamond and Related Material, 2 (1993) 970-976.

7) K. Bewilogua, J. Buth, H. Hübsch and M. Grischke, Diamond and Related Material, 2 (1993) 1206-1210

8) D. J. Kester, K. S. Ailey and R. F. Davis, J. Mater. Res. Vol. **8**. No. 6. Jun 1993

9) T. A. Friedmann, P. B. Mirkarimi, D. L. Medlin, K. F. Mccarty, E. J. Klaus, H. A. Johnsen, M. J. Mills and D. K. Ottesen, J. Appl. Phys. **76** (5) 1 september 94 3088-3101.