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Properties of BN_x nanolayers prepared by rapid thermal annealing♣

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The possibility for preparation of boron nitride nanolayers with thickness of 3-7 nm, using Rapid Thermal Annealing (RTA), as well as the properties of the obtained films in dependence of the technological conditions are investigated. Boron nitride layers were prepared as follows: thin boron films were deposited on sapphire (Al_2O_3) substrates by vacuum evaporation. The resulting B/Al_2O_3 structures were submitted to RTA in ammonia (NH_3) ambient at annealing temperatures of 800, 1000, 1200 and 1400 ^oC, for annealing times of 15, 30, 60 and 180 s. The resulting films were studied using X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy, Fourier Transform InfraRed Spectroscopy and Raman Spectroscopy. The resistance of the films was measured by a four-probe method. It was established that RTA increases the resistivity of the films. The XPS data undoubtedly show the formation of B-N bonds. The obtained BN films have a hexagonal structure, with a needle-like surface morphology.

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1. Introduction

Because of the superior mechanical and optical properties of hexagonal and cubic boron nitride, thin film deposition of BN has recently gained wide interest. Various chemical vapour deposition (CVD) [1,2] and physical vapour deposition (PVD) [3,4] techniques have been successfully used for the deposition of BN thin films. Extensive work was reported on modifications of the deposition methods and selection of growth conditions for preparation of high-quality BN thin films. Most of the CVD or PVD deposition methods, however, yield polycrystalline BN material with a porous structure. The volume fraction of the micropores depends on the deposition parameters. Cubic BN (cBN) in particular has significant potential in the field of thin film applications. Having a Vickers hardness of about 5000 kg mm^{-2}, cBN is the second hardest material, after diamond [5]. It has a high resistance to oxidation at temperatures up to 1300 ºC [6], and unlike diamond films, cBN can be doped producing "p" and "n" type semiconductors. In fact, an UV emitting p-n junction photodiode has already been made in bulk cBN. Infrared (IR) [7-12] and Raman [13-14] spectroscopy were used to investigate BN thin film optical and structural properties. The aim of this work is to investigate the possibility for preparing BN nanofilms by Rapid Thermal Annealing (RTA) of boron films in ammonia ambient, in the temperature range 800-1400 ^oC, for different annealing times.

2. Experimental details

Boron films with thickness d = 3-7 nm were deposited on sapphire substrates (c-face) by vacuum evaporation. The purity of the boron precursor was 99.999 %. After the deposition, the B/Al_2O_3 structures were submitted to Rapid Thermal Annealing in an ammonia atmosphere at various temperatures (T_a) and annealing times (t_a), as given in Table 1. The RTP system (schematically shown in Fig. 1) uses a resistively heated tungsten plate on which the samples are placed.

Table 1 Technological conditions of the process.

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Parameters	Range
Temperature, T_a (°C)	800, 1000, 1200, 1400
Duration, t_a (s)	15, 30, 60, 180
NH_3 pressure (Torr)	5×10^{-2}
NH_3 flow (sccm)	12

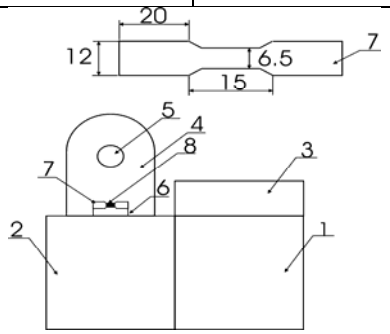


Fig. 1. Schematics of the RTP system: 1- system electronics, 2-vacuum system, 3-operation block, 4- vacuum camera, 5 - windows, 6- electrodes, 7-heater(dimensions in mm), 8- substrate.

The assigned temperature in the range 800-1400 ºC was reached after 2 s. Prior to the treatment, the system was evacuated to 5×10^{-5} Torr. The films were characterized by means of X-ray Photoelectron Spectroscopy (XPS), Secondary ElectronMicroscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy. The resistivity of the layers was measured by the four-probe method.

3. Results and discussion

The results from FTIR investigations show that starting at the annealing temperature of 1200 ºC the hexagonal phase of BN is formed predominantly. The obtained spectra contain features in the range 794-798 cm^{-1} and 884 cm^{-1}, characteristic of hexagonal BN [15,16]. As an illustration, Fig. 2 depicts FTIR spectra of B layers treated at 1400 ºC. The formation of hexagonal BN is also confirmed by Raman spectroscopy [17,18]. Peaks in the range 750 and 1370-1400 cm^{-1} have been found (Fig. 2b). The presence of the peak at ~ 418 cm^{-1} in the Raman spectra is attributed to the signal from the Al_2O_3 substrate, visible due to the small film thickness. (The peak corresponding to Al in the Raman spectra of Al_2O_3 is at ~ 400 cm^{-1}). The resistance of the as-deposited boron films was $6.7x10^{11}$μΩcm. RTA increases the resistance of the films, which is interpreted by the incorporation of nitrogen and the formation of B-N bonds. The influence of the annealing time on the resistivity, however, depends on the T_a. For the lowest T_a (800º C), the film's resistance increases for t_a = 15 s and then decreases for the longer annealing times (it is 9, 8.2, 8 and $7.7x10^{11}$ μΩcm for t_a = 15, 30, 60 and 180 s, respectively). The observed decrease is most probably due to the desorbtion of the nitrogen, taking place at the longer t_a. For the rest of the processing temperatures (1000-1400 °C) the resistivity increases with increased duration of the annealing. We attribute this behaviour to the increased amount of nitrogen bonded to B, i.e. the formation of B-N bonds in the layers. After treatment at 1000 °C, the resistance is 7.8, 8.2, 8.7 and $9.4x10^{11}$ μΩcm for 15, 30, 60 and 180 s, respectively. For annealing temperatures above 1000º C, the resistance strongly depends on the quantity of the forming B-N bonds; for 1400°C and t_a = 180 s the resistance is about $8.2x10^{11}$ μΩcm.

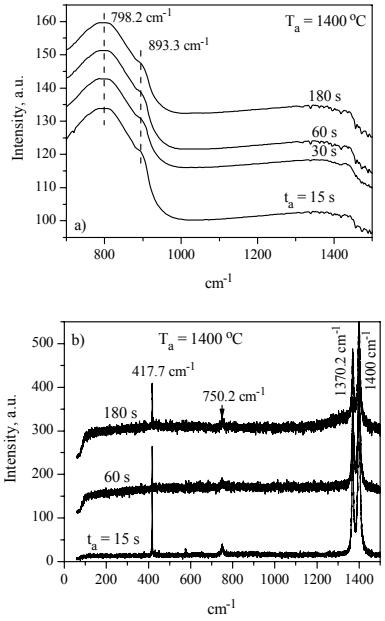
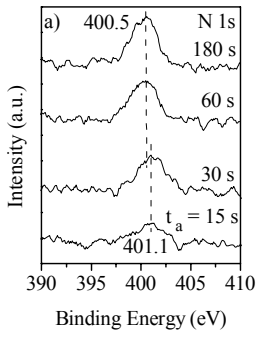


Fig. 2. FTIR (a) and Raman (b) spectra of BN_x films obtained at T_a = 1400 ºC, for different annealing times.

Fig. 3 illustrates the N 1s and B 1s XPS spectra of films treated at the lowest annealing temperature used (800º C). A slight shift of the N 1s peak is observed after treatment at t_a > 30 s. The N 1s line is placed at a lower binding energy, about 0.6 eV smaller than that of the 15 and 30 s annealed samples. The B 1s peaks do not change their position upon variation of the treatment time.



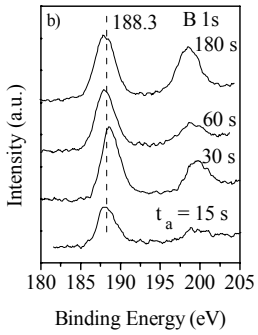
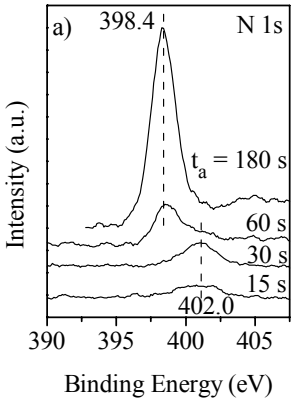


Fig. 3. N 1s (a) and B 1s (b) XPS spectra of films formed at 800 ºC for different t_a.

These results suggest that T_a = 800 °C does not lead to the formation of B-N bonds. The analysis of the spectra of samples treated at T_a = 1200 and 1400 ºC clearly indicates the formation of B-N bonds. The N 1s and B 1s spectra of films obtained at 1400 ºC are presented in Fig. 4 (the data for T_a = 1200º C demonstrate the same tendencies). As seen, the longer t_a result in a higher intensity of the N 1s peak. Annealing at $t_a \geq 60$ s leads to a well-pronounced shift of the N1 s peak to lower binding energies. For t_a = 60 and 180 s, the N 1s line appears at 398.4 eV (for the shorter t_a the peak is placed at 402.0 eV). The position of the B 1s peak is constant (189.0 eV) for t_a up to 60 s, and shifts to 191.3 eV for t_a = 180 s. The observed shift of the binding energy of the N 1s and B 1 s XPS lines after 180 s is a clear indication of the formation of B-N bonds. Furthermore, the binding energy for N1s and B1s corresponding to 180 s treatment at 1400 ºC are in good agreement with the BN data in [19]. The SEM investigations show the creation of a needle-like morphology upon processing of the B



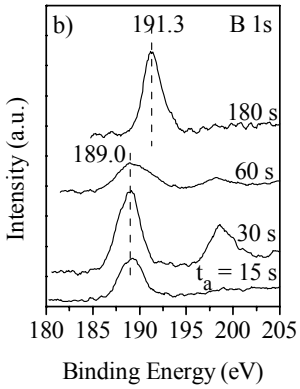


Fig. 4. Evolution of N 1s (a) and B 1s (b) XPS spectra with the annealing time of films obtained at 1400º C.

films at T_a > 1000 ºC. Fig. 5 shows the surface morphology of an as-deposited boron film and a sample treated at 1200 ºC for 180 s. The formation of agglomerates and needle-like morphology is

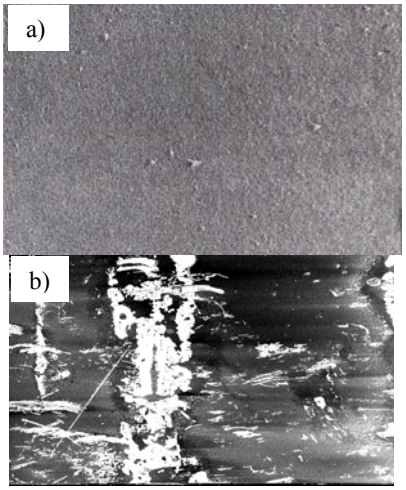


Fig. 5 Surface morphology of an as-deposited boron film (a) and a layer treated at 1200 ºC for 180 s.

clearly seen. The needle-like morphology is thought to be due to the interface stress between boron layers and the substrate treated at this high temperature.

4. Conclusion

It was established that ultrathin BN_x layers could be prepared by a RTA process in ammonia ambient. The formation of B-N bonds was confirmed through XPS analysis, and the optimal technological conditions are annealing temperatures above 1200 ºC, and annealing times longer than 60 s. The structure of the obtained films corresponds to the hexagonal phase (as indicated by FTIR), with a needle–like surface morphology.

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