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BN coatings deposition by magnetron sputtering of B and BN targets in electron beam generated plasma

A S Kamenetskikh[1,2], N V Gavrilov[1], O V Koryakova[3] and S O Cholakh[2]

[1] Institute of Electrophysics, 620016, 106 Amundsen str., Yekaterinburg,Russia
[2] Ural Federal University, 620002, 19 Mira str., 620002 Yekaterinburg, Russia
[3] Institute of Organic Synthesis, 620137, 22 Sofia Kovalevskayastr., Yekaterinburg, Russia

E-mail: alx@iep.uran.ru

Abstract. Boron nitride coatings were deposited by reactive pulsed magnetron sputtering of B and BN targets (50 kHz, 10 μs for B; 13.56 MHz for BN) at 2–20 mA/cm^2 ion current density on the substrate. The effect of electron beam generated plasma on characteristics of magnetron discharge and phase composition of coatings was studied.

1. Introduction

Boron nitride (BN) coatings have been used in various fields of science and technique due to their unique features. It is known there are several polymorphic modifications of BN, including superhard (up to 72 GPa) cubic c-BN phase [1]. RF magnetron sputtering of dielectric targets made of hexagonal h-BN is mostly used for deposition of BN coatings by PVD methods. Coatings with high c-BN content are formed when conducting targets of B_4C are used in DC or DC pulsed mode, however this coatings contains more than 5 % of C contamination [2]. The specific resistance of boron drops lower than 1 Ω·cm when target are heated till ~600 °C that allows using B-target in DC sputtering systems [3].

Intensive ion assistance is a necessary condition for deposition of coating with high c-BN content by vacuum-plasma methods. Coatings containing ~80–90 % of c-BN are formed in narrow range of ion current density and energy [4]. To increase the ion current density during BN coating deposition by magnetron sputtering, unbalanced magnetic field [5] or ion-beam assistance are often used [6]. In the present work ion current density on the samples was regulated in the range 2–20 mA/cm^2 by adjustment of the current of low-energy (~10^2 eV) electron beam injected into the working chamber. In previous work the authors showed high efficiency of such method of plasma parameters control [7]. The aim of the work is the study of the effect of ion component of electron beam plasma on the characteristics of magnetron discharge with B and h-BN targets and on the phase composition of coatings.

2. Experimental technique

The sketch of experimental system is shown in figure 1. Plasma generation system included a plane balanced magnetron *1* and a source of broad (50 cm^2) electron beam *2*, placed on the vacuum chamber *3* 330 mm in diameter. Discs 80 mm in diameter and 4 mm thick made of B and h-BN (99.9 % purity) were used as sputtering targets. B target was sputtered in DC pulsed mode (50 kHz, 10 μs) with amplitude of discharge current up to 1 A; h-BN target was sputtered in RF mode (13.56 MHz) with discharge power 200 W. Discharge with self-heated hollow cathode made of titanium nitride [7] was used in the electron

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source. Discharge current was regulated in the range of 2–30 A and discharge voltage changed from 300 V to 25 V. Energy of electron beam during the coating deposition was 100 eV.

Coatings were deposed on polished surfaces of samples 15×15 mm made of silicon and steel AISI430. Samples were ultrasonically cleaned in acetone solution before placing into the chamber. The working chamber was pumped off till 10^{-2} Pa by turbomolecular pump. Samples were cleaned by ion etching in Ar plasma generated by electron beam. Pulse bias of samples during ion etching was 500 V (50 kHz, 10 μs), ion current density – 2 mA/cm^2. The bias voltage during coatings deposition was 200 V.

Gas mixture Ar/N_2 was feed through electron source. Coatings were deposited under constant gas flow rates Q_{Ar}/Q_{N_2} – 30/7 (sccm) in the mode of B target sputtering and 3/1 in the mode of h-BN target sputtering; total gas pressure was 0.12 and 0.04 Pa, correspondingly.

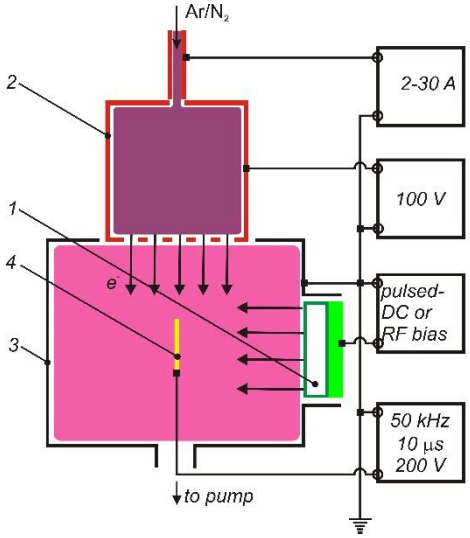

Figure 1. The diagram of experiment: *1* – magnetron, 2 – electron source, *3* – working chamber, *4* – samples.

The coatings was analyzed by IR-Fourier spectroscopy. The spectra of frustrated total internal reflection of the coatings were registered on IR-Fourier spectrometer ”Nicolet 6700” (Thermo Electron Corporation) using “Smart orbit” add-in device with diamond crystal. Intensity of peaks and squares under optic density curve was calculated using ”Omnic” program.

3. The effect of electron beam generated plasma on characteristics of magnetron discharge with B cathode

Characteristics of magnetron discharge with B target are determined significantly by temperature dependence of boron electric resistance. Heating of B target in discharge plasma at constant current amplitude is accompanied by discharge voltage decrease by several hundred V during ~10^2 s. Current voltage characteristic for steady state discharge (figure 2) has non-monotonic character. Increase of discharge current from 0.1 to 0.5 A leads to rise of target temperature by 450 °C and to corresponding decrease of specific resistance by ~10^5 Ω·cm^2; the voltage across the discharge gap is reduced by 110 V. Specific resistance of B target does not significantly affect the magnitude of discharge voltage at further growth of discharge current. The right branch of dependence curve corresponds to typical current voltage characteristic of magnetron discharge [8].

The increase of electron beam current till 25 A leads to decrease of magnetron discharge voltage from 580 to 60 V (figure 3). The drop of discharge voltage is determined by ions, which arrived from beam plasma. Ion current density (j_i) grows monotonically along with beam current increase and reaches ~23 mA/cm^2 at 25 A. Figure 4 shows the dependencies of magnetron discharge voltage (obtained at beam current 5 A) and frequency of ionizing collisions of electrons with gas atoms, calculated from the ratio $\nu_i \sim \sigma_i(\upsilon)\cdot\upsilon$ (where σ_i is the cross section of electron impact ionization; υ – electron velocity), on accelerating voltage of electron source. It is seen that frequency of ionizing

collisions reaches maximum value at electron energy ~250 eV; magnetron discharge voltage is minimum (~440 V) in this case.

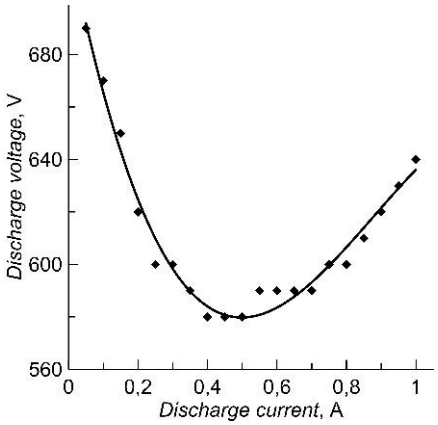

Figure 2. The voltage current characteristic of magnetron discharge with B target.

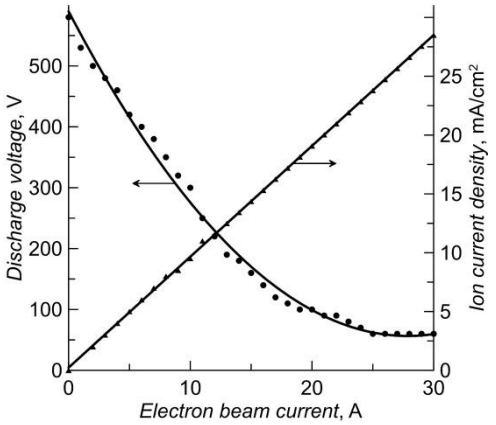

Figure 3. The dependencies of magnetron discharge voltage and density of ion current from the beam plasma on the beam current.

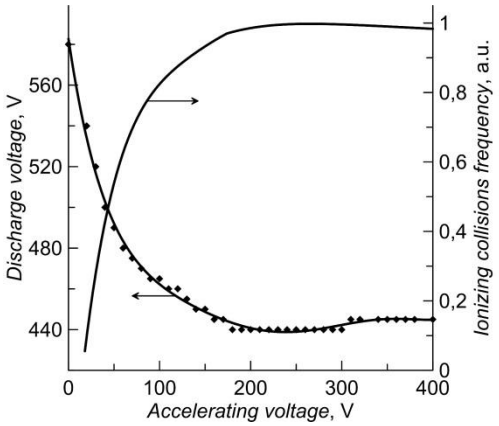

Figure 4. The dependencies of magnetron discharge voltage and frequency of ionizing impact of electrons with gas atoms on accelerating voltage of the electron source.

4. The effect of beam plasma on the phase composition of BN coating

The IR spectra of BN coatings deposed on Si substrate in B target sputtering mode are shown at figure 5. At all IR spectra a line with wavenumber ~1080 cm^{-1} corresponding to c-BN phase can be seen. It is known that wavenumber 1004 cm^{-1} corresponds to c-BN peak in the stress-free samples [9]. Observed shift of the peak towards large values of wavenumber indicates the presence of intrinsic stresses in the coating. Their value estimated from the ratio obtained in [10] is 13 GPa. Such a high level of intrinsic stresses impairs the coatings adhesion, so the maximum thickness of adhesive BN coatings obtained in B target sputtering mode did not exceed ~1 μm.

According to [4], relative content of c-BN in coatings (n_c) can be estimated from the ratio of intensities of peak at 1080 cm^{-1} and peak at 1366 cm^{-1}, corresponding to h-BN phase. The increase of electron beam current from 5 to 20 A, providing the change of ion fluence ratio to the number of atoms per square unit of the coating Φ/N from 3 to 24, is accompanied by n_c growth from 0.67 to 0.83.

Besides c-BN and h-BN phases, a phase having wurtzite structure (w-BN), corresponding to the line with wave number 1171 cm^{-1} [11] (figure 5) as well as fullerene-like (e-BN) phase with lines 907, 1260, 1409 and 1580 cm^{-1} [12] presents in the coating. The e-BN phase was first revealed after exposing of high dynamic loads achieved by explosive method on h-BN powder [13]. In work [11] e-BN phase was observed in coatings deposited by RF sputtering of h-BN target.

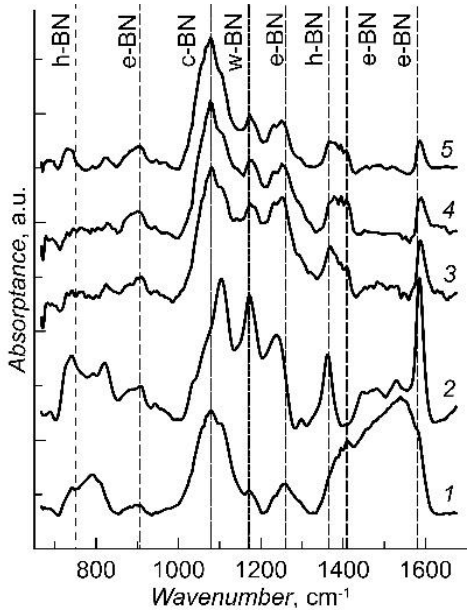

Figure 5. IR spectra of BN coatings deposited in B target sputtering mode. Electron beam current: *1* – 2; *2* – 5; *3* – 10; *4* – 15; *5* – 20 A.

The authors of the work [11] describe the appearance of e-BN phase in the coating as follows. The h-BN clusters (which are in state of sp^2-hybridization) are sputtered from target surface, acquired enough energy to form sp^3 bonds during interaction with plasma particles and form structure with ratio of sp^2 and sp^3 bonds 1:1 on coating surface. In coatings deposited by reactive magnetron sputtering of one-component target in DC pulsed mode, e-BN phase was first revealed. The intensity of e-BN phase peaks decreases under the increase of electron beam current. According to [11], the growth of energy transmitted by plasma particles to atoms of the coating facilitates formation of a large number of sp^3 bonds, hence the concentration of phases h-, e-, w- and c-BN in the coatings is increases along with the growth of beam current. In our experiment conditions for e-BN formation are created already at electron beam current 2 A providing Φ/N ratio ~2.4. Further j_i increase promotes preferential c-BN formation.

IR the spectra of coatings obtained by RF sputtering of h-BN target are shown at figure 6. The coatings with main phase h-BN are formed when the ratio Φ/N changes from ~3 to 14 in the range of beam current 2–8 A. In the spectra the peaks corresponding to e-BN (1580, 1409 cm^{-1}) are also observed, however their intensity at beam currents below 14 A is significantly lower than intensity of h-BN peak (~1340–1360 cm^{-1}). Phase c-BN appears in coatings at electron beam currents more than 8 A. Relative content of c-BN reaches maximum 0.58 at beam current 12 A and decrease sharply to 0.05 at further current increase.

The peak of c-BN phase lays in the range of wavenumbers 1022–1038 cm^{-1}. The intrinsic stress of coatings estimated from the peak shift value is ~5 GPa, that is significantly lower than in coatings deposited in the mode of B target sputtering. According to the model of static stresses [14], the minimum level of intrinsic stresses necessary for c-BN formation makes ~4 GPa, and the content of c-BN at stress value ~5 GPa reaches 55–60 % that correlates with obtained results.

Thus, at comparable values of Φ/N the level of intrinsic stress in the coatings deposited by RF sputtering of h-BN target is ~2.5 times lower than in coatings obtained by DC pulsed sputtering of B target. This improves adhesion of coatings and allows to make them thicker. The main advantage of B target sputtering mode (under conditions of Ar-N_2 plasma generation by broad electron beam) consists in higher content of c-BN (~0.6–0.8) in coatings that is achieved in wide range of Φ/N ratio (from 3 to 24).

5. Conclusions

Two variants of BN coating deposition – by RF magnetron sputtering of h-BN target and DC pulsed sputtering of B target – were compared under conditions of the coating exposure in the plasma of low-energy (100 eV) electron beam. Ions from electron beam plasma facilitate initial heating of B target

and reduce magnetron discharge voltage. Changing of electron beam current allows controll the ratio of ion fluence to the number of atoms in the coating in the range of 2–24 and optimization of the conditions of c-BN phase formation. Maximum content of c-BN phase in coatings obtained by B and h-BN targets sputtering, made 83 and 58 %, and the levels of intrinsic stresses are 13 and 5 GPa, correspondingly.

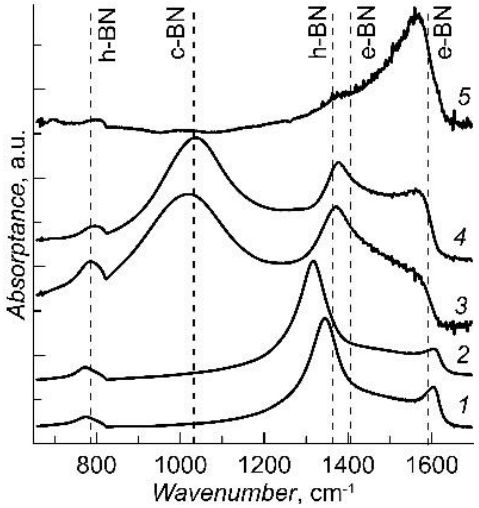

Figure 6. IR spectra of BN coatings deposited in h-BN target sputtering mode. Electron beam current: *1* – 0; *2* – 6; *3* – 10; *4* – 12; *5* – 14 A.

Acknowledgment
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