Reactive Magnetron Sputtering Deposition of Nanocomposite Al-Si-B-N Coatings[1]

K.V. Oskomov, A.D. Korotaev*, N.S. Sochugov, A.A. Soloviev

High current Electronics Institute SB RAS, 2/3 Akademichesky Ave., Tomsk, 634055, Russia
Phone: +7-3822-49-16-51, Fax: +7-3822-49-24-10, E-mail: oskomov@lae.hcei.tsc.ru
**Siberian Physical-Technical Institute, 1 Novosobornaya Sq., Tomsk, 634050, Russia*

Abstract – A composite ∅ 12 cm magnetron target (Al 80 at. %, Si 15 at. %, B 5 at. %) has been sputtered by DC power in an Ar/N_2 ambient. Nitrogen partial pressure, substrate temperature and bias have been varied during deposition experiments.

The optimum nitrogen partial pressure for deposition of stochiometric nitride film was found to be 0.04–0.08 Pa at partial argon pressure of 0.24 Pa. Magnetron discharge voltage and current were equal to 470 V and 1 A correspondingly, and film growth rate was as high as 0.4–0.6 nm/s under these conditions. In the case of lower nitrogen flow rate deposited coatings contained soft metal phase, while at higher nitrogen flow rate the target poisoning occurred. The coatings deposited at substrate temperature of 400 °C were amorphous for XRD and their hardness was close to that of bulk AlN (20–21 GPa).

It is shown that ion bombardment of the films growing on conductive substrates is an effective way to increase their hardness. During the bombardment it was necessary to prevent charging of the film surface since the coating was insulating. So, only use of bipolar pulsed substrate bias voltage resulted in sufficient increase of the coating hardness (up to 25 GPa), while DC and unipolar pulsed bias voltage did not lead to the film hardening. XRD study of the film revealed predominantly AlN hexagonal structure with (0002) texture and grain size of about 20 nm.

1. Introduction

Study of superhard nanocomposite nitride-based n-Me(1)N/a-phase [1] and n-Me(1)N/Me(2) [2] coatings have been attracting much attention in the last decades (here n-Me(1)N denotes hard nanocrystalline metal nitride, Me(1)=Ti, Zr, W, V, Al; a-phase means hard amorphous phase of SiN_x, BN_x, TiB_2, $Si_xB_{1-x}N$; Me(2) is a soft metal that is immiscible with the hard nitride Me(1)N) (Fig.1). It is connected both with fundamental interest in superhardness (>40 GPa) phenomenon and prospective applications of these coatings as oxidative corrosion and wear resistant ones [1]. The fundamental interest is stimulated by an absence of consistent explanation of the superhardness origin. Except strong covalent bond Me(1)-N, the nanocomposite structure and phase composition are also strongly affects hardness of the coatings. Among the well-known factors increasing the coatings hardness one can mention: 1) decrease of Me(1)N grain size up to 10 nm and less with segregation of a-phase or Me(2) phase at the Me(1)N grain boundaries, 2) generation of defects and intrinsic compressive stress in the coatings. Up to present time several deposition methods and many elemental compositions for production of nanocomposite coatings have been studied. There are CVD (n-TiN/a-Si_3N_4, n-$Ti_xAl_{1-x}N$/a-Si_3N_4, n-TiN/a-BN) [1], vacuum cathode arc PVD (Ti-Al-Si-N, Ti-B-N) [3], and magnetron sputtering PVD (n-TiN/Cu, n-AlN/Cu, n-ZrN/Y, Al-Si-Cu-N, Ti-B-Cu-N etc.) [2]. In the case of CVD, the deposited films consist of equiaxial very fine (about 3 nm) grains of Me(1)N separated by very thin (about 0.1 nm) layer of a-phase. These films are ultrahard (up to 100 GPa), very stable and corrosion resistant up to 800–1000 °C. However, usually CVD technologies are not highly productive and environmentally friendly.

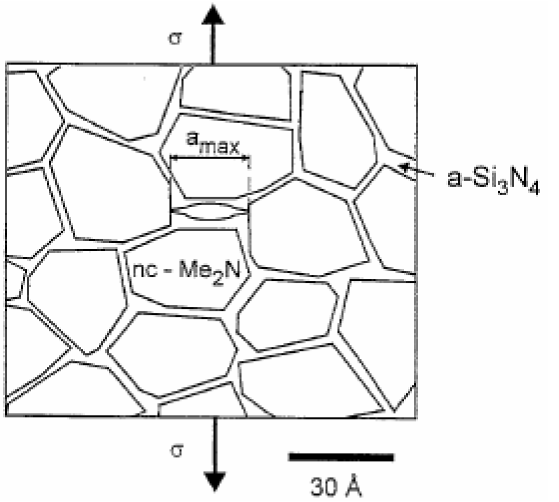

Fig. 1. Schematic representation of a nanocomposite coating structure

The PVD methods, especially, the magnetron sputtering, are easily scalable for mass production and safe for ecology. But coatings deposited by mag-

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[1] This work was supported by RFBR grant No. 05-08-01277 and CRDF BHRE grant No. Y2-EP-16-07

netron sputtering PVD demonstrate a variety of possible structures, phase and chemical compositions and, thus, more complex and ambiguous relations between them and the films properties. For example, Musil reports that both amorphous and nanocrystalline textured (002) cubic Al-Cu-N [4] and Al-Si-Cu-N [5] coatings are harder than 50 GPa have similar hardness value. Moreover, in some cases superhard films deposited by magnetron sputtering PVD show much lower thermal stability compared to films with the same chemical and phase composition deposited by CVD [6]. The reason is high density of defects produced under intensive ion bombardment during the film growth. Thus, the versatility of structures and properties of superhard nanocomposite nitride films produced by magnetron sputtering PVD, make them interesting for investigation both from fundamental and technological point of view.

Thus, the goal of the work was to investigate the main factors of Al-Si-B-N films magnetron sputtering PVD process that affect the coatings properties.

2. Experimental

For the experiments we chose Al-Si-B-N system that is close to already investigated Al-Cu-N [4] and Al-Si-Cu-N [5], which were shown to form superhard (up to 60 GPa) nanocomposite nitride coatings of n-AlN/Cu and n-$Al_xSi_{1-x}N$/Cu. The lack of the above films is the soft metal phase (Cu), which prevents growth of fine nanograins and moving of dislocations there, but can not prevent the grains sliding because of weak interface between the soft metal and nitride phase. Adding boron instead of copper we hoped to attain segregation of hard nitrides (such as a-BN) at grain boundaries and to create strong interfaces between n-$Al_xSi_{1-x}N$ and a-BN.

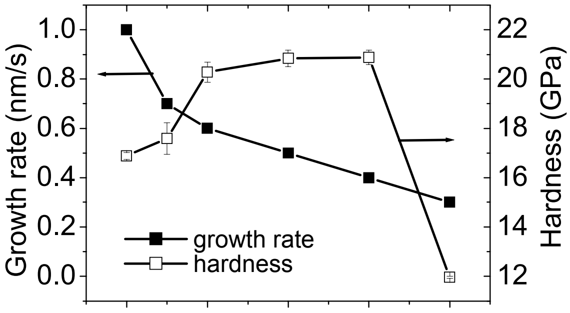

Fig. 2. Al-Si-B-N film growth rate and hardness vs. nitrogen partial pressure at p(Ar)=0.24 Pa and T(substrate)=400 °C (lines are given as eye-guides)

All the experiments have been performed at laboratory-made deposition equipment. A composite 12 cm magnetron target (cathode) (Al 80 at. %, Si 15 at. %, B 5 at. %) has been used for the experiments. At the first stage of the investigation DC reactive magnetron sputtering of single target in an Ar/N_2 ambient has been chosen because of its more simple realization compared to the case of multiple targets. The magnetron discharge current was stabilized at 1 A, argon flow rate (125 sccm) and pumping speed have been kept constant, while nitrogen flow rate (and thus, partial pressure) was varied and the discharge voltage has been set up in a self-consistent manner depending on the latter parameter. Two more parameters being varied are temperature at the substrate (by a resistive heater) and a substrate bias voltage.

The nanocomposite nitride Al-Si-B-N films have been deposited on glass, silicon, stainless steel and WC-Co substrates. Thickness of the deposited coatings was measured by an *MII-4* interferometer (*LOMO*, Russia). X-ray difractometer *Shimadzu* was used for determination of the coatings phase composition and the grain size. For investigation of the surface morphology, *Solver P47* atomic-force microscope (*NT-MDT*, Russia) was used and contact mode of surface imaging was applied. To investigate the hardness and elastic modulus of the coating surface layer, a *NanoTest 600* nanoindenter (*MicroMaterials*, Great Britain) was used. The maximum indenter penetration depth did not exceed 5—10 % of the film thickness. Dependences of the penetration depth of the diamond Berkovich indenter into the coating on the applied force in the loading and unloading stages were analyzed by the Oliver and Pharr method [7]. The final values of the hardness and elastic modulus were obtained by averaging the results of five measurements.

3. Results and discussion

As the first step, an optimum nitrogen flow rate and partial pressure were found. The dependence of the film growth rate on nitrogen partial pressure (Fig. 2) is a typical for the reactive magnetron sputtering process. At low nitrogen partial pressure, the sputtering occurs mainly in metal mode, while with increase of nitrogen flow rate, the sputtering shifts to the reactive mode. The optimum nitrogen partial pressure was found to be 0.04—0.08 Pa at argon partial pressure of 0.24 Pa, when transparent and hard Al-Si-B-N films were deposited. The hardness is about 20—21 GPa, which is close to the hardness of stochiometric aluminum nitride. At lower nitrogen partial pressure the coatings contain high percent of metal (Al) and become softer (Fig. 2). At higher N_2 pressure the film growth rate becomes sufficiently lower because of the target poisoning. This also leads to arcing at the cathode and inclusion of microdroplets into the growing films that makes it opaque and less hard (Fig. 2).

It was also found that higher temperature at the substrate was necessary for deposition of hard films with good adhesion. So, rather thick (>1 micron) coatings of Al-Si-B-N deposited at 200 °C at the substrate were completely delaminated after, while the coatings deposited under the same conditions, but at 400 °C at the substrate, were tightly adhered. In both cases the films were amorphous for XRD, but their morphology was different. In Fig. 3 one can see AFM images of Al-Si-B-N films deposited at 200 °C and 400 °C at the substrate. The film deposited at 400 °C consist of bigger grains (about 100 nm) compared to 200 °C (about 30–50 nm) due to higher temperature and surface mobility of adatoms. Taking into account the results of XRD examination, these grains seem to be agglomerates of very small subgrains (about 1 nm), which are unresolved by XRD. Such two-level structure is in good agreement with previous research in the field of nanocomposite materials [8] and with facts of easy amorphization of AlN [4, 5].

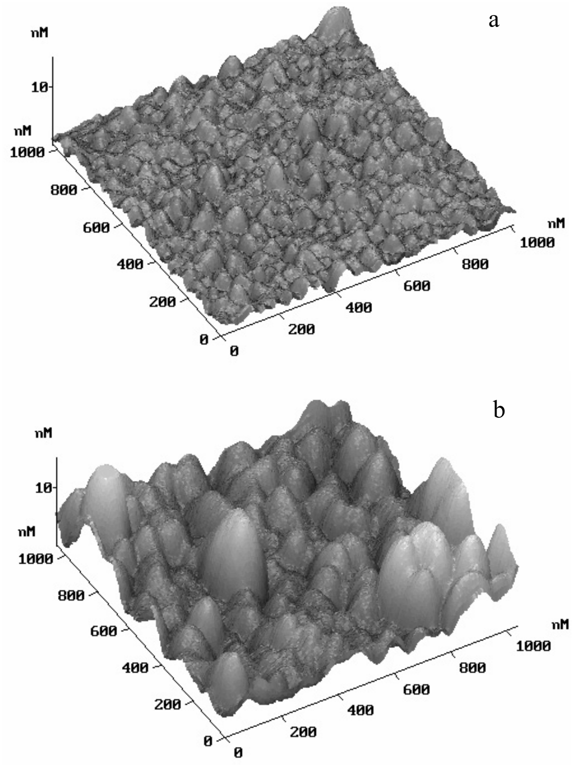

Fig. 3. AFM images (1000×1000×15 nm^3) of Al-Si-B-N films deposited at 200 °C (a) and 400 °C (b) at the substrate at p(N_2)=0.04 Pa and P(Ar)=0.24 Pa

Substrate bias voltage was shown to be crucial factor affecting the Al-Si-B-N structure and hardness since ion bombardment of the films is known as an effective way to increase their hardness. During the bombardment it was necessary to prevent charging of the film surface since the coating was insulating. So, only use of bipolar pulsed substrate bias voltage resulted in sufficient increase of the coating hardness, while DC and unipolar pulsed bias voltage did not lead to the film hardening. Typical waveform of the bipolar voltage is presented in Fig. 4. The frequency was equal to 25 kHz, the width of negative and positive pulses was equal to 30 мs and 10 мs, correspondingly. The amplitude of positive pulse was as high as 20% of the negative one. In Fig.5 it is clearly seen that bipolar substrate bias voltage of –500 V (+100 V) was optimum for deposition of the most hard (25 GPa) Al-Si-B-N films. XRD study of such film revealed predominantly AlN hexagonal structure with (0002) texture and grain size of about 20 nm, which is typical for magnetron sputtering deposited superhard nanocomposite films [4, 5]. Probably, in the case of lower bias voltage, the energy of ion bombardment is not sufficient for transformation of the film structure from amorphous to nanocrystalline state, while the case of higher bias voltage requires further investigations.

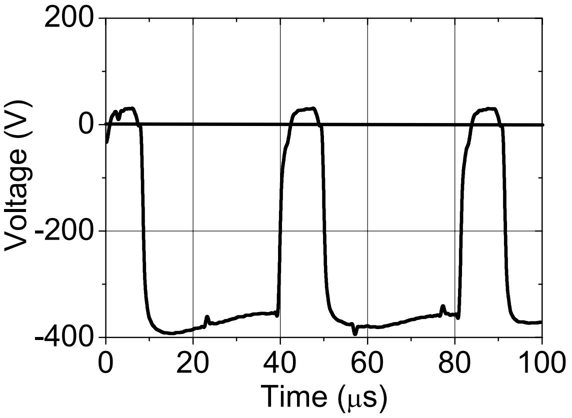

Fig. 4. A typical waveform of bipolar substrate bias voltage

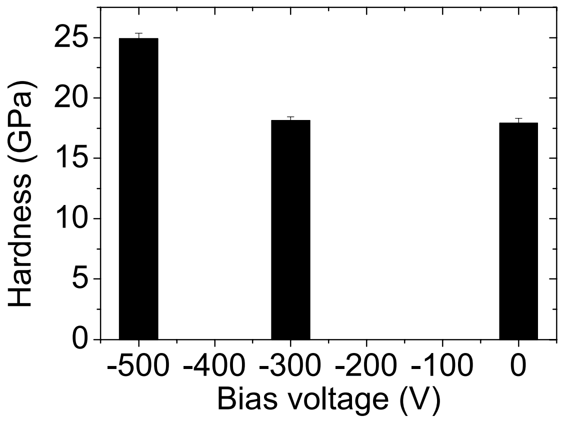

Fig. 5. Hardness of Al-Si-B-N films vs. amplitude of negative pulse of bipolar bias voltage

Conclusion

Al-Si-B-N films produced by DC reactive magnetron sputtering PVD of the composite 12 cm magnetron target (Al 80 at. %, Si 15 at. %, B 5 at. %) have been studied.

The optimum nitrogen partial pressure for deposition of stochiometric nitride film was found to be

0.06–0.08 Pa at total gas pressure of 0.35 Pa. Magnetron discharge voltage and current were equal to 470 V and 1 A correspondingly, and film growth rate was as high as 0.7 nm/s under these conditions. In the case of lower nitrogen flow rate deposited coatings contained soft metal phase, while at higher nitrogen flow rate the target poisoning occurred. The coatings deposited at substrate temperature of 400 °C were amorphous for XRD and their hardness was close to that of bulk AlN (16–17 GPa).

Ion bombardment of the films growing on conductive substrates is an effective way to increase their hardness. Use of bipolar pulsed substrate bias voltage of –500 V (+100 V) resulted in sufficient increase of the coating hardness (up to 26 GPa) due to deposition of nanocrystalline hexagonal structure with (0002) texture and grain size of about 20 nm.

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