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GROWTH AND PHYSICAL STRUCTURE OF AMORPHOUS BORON CARBIDE DEPOSITED BY MAGNETRON SPUTTERING ON A SILICON SUBSTRATE WITH A TITANIUM INTERLAYER

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Abstract. Multilayer amorphous boron carbide coatings were produced by radiofrequency magnetron sputtering on silicon substrates. To improve the adhesion, titanium interlayers with different thickness were interposed between the substrate and the coating. Above three hundreds nanometer, the enhanced roughness of the titanium led to the growth of an amorphous boron carbide with a dense and continuing columnar structure, and no delamination effect was observed. Correspondingly, the adhesion of the coating became three time stronger than in the case of a bare silicon substrate. Physical structure and microstructural proprieties of the coatings were investigated by means of a scan electron microscopy, atomic force microscopy and X-ray diffraction. The adhesion of the films was measured by a scratch tester.

Keywords: boron carbide, magnetron sputtering, titanium, interlayer, scratch test.

1. Introduction

Boron B_4C carbide is one of the most relevant material because of its very interesting characteristics such as high hardness, good electronic and tribological properties, chemical and thermal stability [24, 18, 9]. At room temperature, boron carbide is the third hardest known material and above 1100 °C is the hardest one [22]. The films of few microns show good performance on cutting tools [9] and can be used as mirrors with high reflectivity in the ultraviolet range [4]. Boron-based coatings can also be very useful in neutrons detection application [17] due to their high neutron absorption cross section. Several techniques such as chemical vapor deposition, plasma enhanced chemical vapor deposition [1], hot filament chemical vapor deposition [6], ion beam assisted evaporation [7], and vacuum arc deposition technology [11] were utilized to synthetize boron carbide films. Magnetron sputtering [5] is one of the most used technique in thin film deposition on industrial scale due to its application at low temperature and without dangerous gases. Coatings produced by this technique often show internal stress induced from the deposition conditions. In order to reduce the stress of the deposited coatings, many suitable deposition recipes have been studied and optimized in terms of deposition parameters [9, 26, 8], and several methods such as post-process annealing have been explored [13]. In several cases, examples are reported in literature on the possibility to control thin films stress by using a multilayer structure [14, 25, 23] or to increase the adhesion by interposing a metallic inter-layers between the substrate and the coating [20, 12, 10, 19]. Mechanical proprieties, time stability and adhesion to the substrate are fundamental requirements to achieve useful coatings in many applicative fields.

In this study we report on the structure of an amorphous boron carbide (a-B_4C) coating prepared by radio frequency (RF) magnetron sputtering as function of the titanium interlayer (Ti-i) thickness deposited on (100) silicon substrate at room temperature. We found that a-B_4C films are time instable if deposited on bare silicon or in presence of Ti-i with thickness lower than $100 \div 150$ nm. In some cases the coatings start to delaminate and peel off in a few hours after being taken out of the deposition chamber. As Ti-i thickness further increases up to 400 nm thickness, the films show a very good stability and adhesion. Emphasis is given to the relationship between substrate roughness and physical structure of the sputter-deposited a-B_4Cs. Physical structure and microstructural proprieties of the a-B_4C coating and Ti interlayers are determined by scan electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). A comparison between the adhesion of a-B_4C coating to the bare silicon and to a 400 nm Ti coated silicon is reported as measured by a CETR UMT-2 scratch tester.

2. Material and Methods

Amorphous boron carbide films and Ti interlayers were prepared by RF (13.56 MHz) magnetron sputtering of a B_4C and Ti targets, respectively. Silicon substrates were ultrasonically cleaned with acetone and ethanol, and carefully placed on the grounded substrate holder kept at 7 cm distance from the RF powered electrode. The vacuum before deposition was less than 1×10^{-4} Pa and the substrate temperature was monitored by using a K thermocouple placed in contact with the sample. High purity Ar (99.9 %) gas was introduced into the chamber through a mass flow controller and a gate valve was used to adjust the pressure during the process. Three samples of Ti interlayer with thicknesses of 25 nm, 200 nm, and 400 nm were sputter-deposited on Si substrates in the same experimental conditions for 4, 30 and 60 minutes, respectively, implying a 6.6 nm/min constant deposition rate. The RF power was fixed at 150 W and the plasma pressure at 1 Pa. Amorphous boron carbide was deposited on bare and Ti-coated silicon substrates with a multilayer structure which consists in the growth of four layers at two different pressure. For the first and third layer, the working pressure was fixed at 2 Pa, while, for the second and fourth layer a pressure of 0.8 Pa was used. The morphological properties and physical structure of the films were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM measurements were made in air by a Nano-RTM AFM System (Pacific Nanotechnology, Santa Clara, CA, USA) operating in close contact mode. Silicon conical tips of 10 nm radius mounted on silicon cantilevers of 1250 nm length, 42 N/m force constant and 320 kHz resonance frequency were used. Images were processed and analyzed by means of the NanoRule+TM software provided by Pacific Nanotechnology. SEM measurements were performed using a ZEISS Supra System with an accelerating voltage of 15 kV. The structural properties studied by X-ray diffraction measurements were performed with a wide angle Siemens D-500 diffractometer (WAXD) equipped with a Siemens FK 60-10 2000 W tube. The radiation was a monochromatized Cu $K\alpha$ beam with wavelength $\lambda = 0.15418$ nm. The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from 10 to 80 2θ at 0.02 2θ intervals by means of a silicon multi-cathode detector Vortex-EX (SII). Scratch test measurements were made in compliance with the European standard UNI EN 1071-3-2005 by using a CETR UMT-2 tester equipped with a Rockwell C standard spherical diamond indenter of 50 µm radius and a 400× optical microscope.

3. Results and Discussion

Figure 1 shows SEM cross-section micrographs of the boron carbide coatings grown on bare Si substrate and on different Ti-i thicknesses. The cross sectional view allows to determine the B−C deposited coating thickness, which is about 0.5 micron (obtained by a sequential deposition of four layers), implying a deposition rate of about 0.9 nm/min.

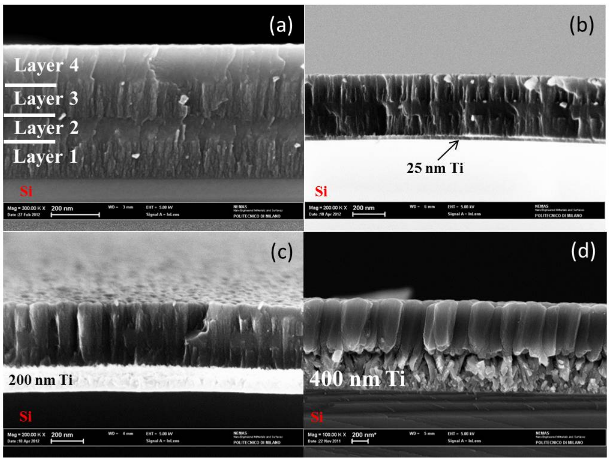

Figure 1. SEM cross-section images of the boron carbide coatings deposited on (a) bare Si, and on (b) 25 nm, (c) 200 nm, (d) 400 nm of Ti interlayer thickness.

As expected, amorphous boron carbide starts to growth with columns (Fig. 1a) much thinner than the ones deposited on Si substrate with a 25 nm Ti interlayer. This can be clearly related with the high flatness of Si substrate (R_{rms} less than 0.1 nm) and with the poor surface diffusion due to the high working pressure. At 25 nm Ti-i thickness (Fig. 1b), the coating exhibits both fine columnar structure (layer 1 and 3) and compact structure (layer 2 and 4). The interface separation of the four layers is quite clear. The four layer structure becomes less pronounced as the Ti interlayer thickness increases further up to 200 nm (Fig. 1c). The columnar structure becomes more continuous and the interface separation less visible. As the Ti-i thickness further increases (Fig. 1d), the layered structure completely disappeared and the coating assumes a continuous columnar structure. The coating structure remained columnar as the Ti-i thickness increased above 400 nm. We have observed that the coatings without Ti-i gradually start to delaminate after being taken out of the coating chamber and brought in atmospheric pressure at room temperature. These stresses can be caused by the large discrepancy between the lattice parameters of the (100) silicon plane and the structure of the growing coating. The delamination effect has also been found with Ti-i thickness less than 100 ÷ 150 nm. The introduction of a Ti interlayer with thickness above 200 nm produced a B−C stable coatings. The effect of the Ti interlayer is likely to decrease the internal stress at the substrate-film interface, thus smoothing the difference in lattice parameters between the thin film and the substrate.

X-ray diffraction has been used to characterize the structure. The diffraction (Fig. 2) spectrum of the boron carbide deposited on 400 nm Ti interlayer reveals the amorphous character of the coating.

This result also applies to the other coatings with different Ti-i thicknesses.

The analysis shows, besides the reflection at an angle of 69.3 degree corresponding to the (100) Si substrate, some crystallographic orientations of

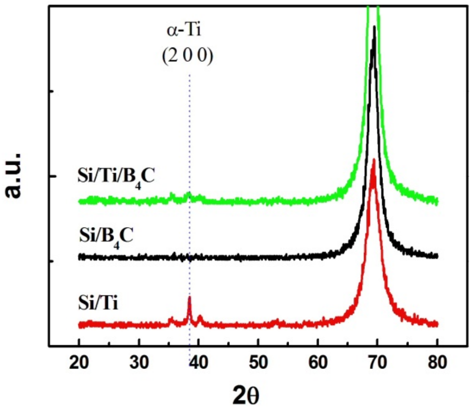

Figure 2. XRD spectra of amorphous boron carbide deposited on 400 nm of Ti-interlayer (green line) and bare Si (black line); for comparison, the spectrum of Ti interlayer (red line) is also reported.

the hexagonal α-titanium phase [2, 21]. The main orientation is (002) at a 2θ angle of 38.5 degree; other three less intense peaks are visible.

The columnar geometry depends on the substrate topology, because it results from the competition between the growth of the irregularities and the surface atoms diffusion [16, 15]. The substrate roughness influences strongly the initial stage of the coating growth [3] and it also plays an important role in the evolution of the physical structure. Surface roughness usually increases during the deposition, and in some cases [27], columnar structures gradually appear in sputtered thick films in correspondence of a certain roughness value.

As shown in Fig. 3, the roughness of the Ti interlayer increases as a function of the thickness. Correspondingly, an increase of the lateral dimension of the a-B_4C columns is observed (Fig. 1). Furthermore, the interface of each layers becomes less clear until it disappears at a value of about 300 nm of Ti-i thickness. Another interesting feature to note is that above this thickness the samples (Fig. 1d) show dense and continue columns independent of which working pressure has been used.

As previously reported in literature [3], if the surface adatoms diffusion length is longer than the irregularities characteristic length, the roughness of the deposited coating is smoothed out and the coating becomes denser. So we explain the growth features of our coatings by this notion. Decreasing the working pressure, when the deposition is switched from layer 1 to layer 2 (Fig. 1a), the energy released from the particles at the surface will be higher, consequently, the increased surface adatoms diffusion length will give rise to an a-B_4C denser layer. With regard to the sample d (Fig. 1), the a-B_4C coating has started to grow with a large basal lateral dimension of the columns and, when the pressure was decreased, the growth

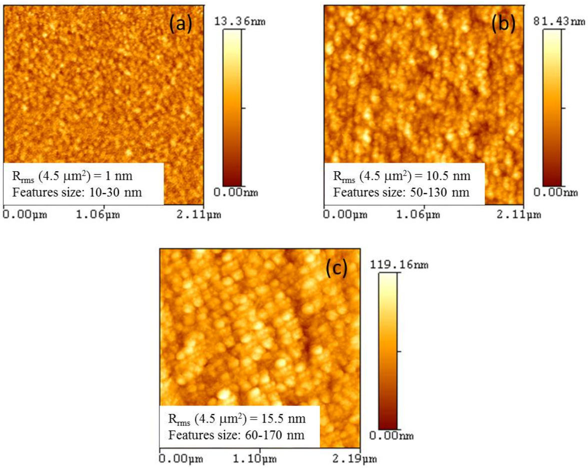

Figure 3. AFM images of Ti-i interlayers of thickness a) 25 nm, b) 200 nm and c) 400 nm; the root mean square roughness is indicated with R_{rms}.

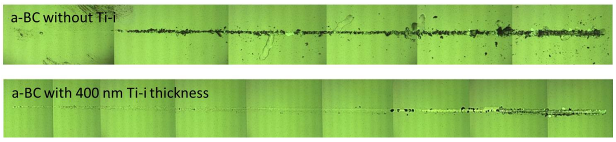

Figure 4. Optical micrographs of the scratch track generated from the indenter on a-B_4C deposited on bare and 400 nm Ti coated silicon substrate.

was proceeded with the same texture of the previous layer. We estimate that at this value of Ti-i roughness, an equilibrium between surface adatoms diffusion length and roughness length scale of the substrate was achieved. We emphasize that, during the deposition process, the temperature of the substrate was very low (about 320 K), indicating that thermal induced surface diffusivity can be neglected.

In order to investigate the mechanical properties of the coatings, scratch test measurements have been performed on a-B_4C films grown on bare silicon and on 400 nm of Ti-i thickness. The scratches were performed by progressive load scratch test (PLST) mode in which the applied normal load increases linearly with time. The slide velocity of the indenter and the applied load were fixed to 9.0 mm/min and 9.0 N/min, respectively. A comparison between the two scratch test clearly shows an increase of the adhesion, that becomes three times stronger in the presence of Ti-i, thus changing from 1.4 N (without Ti-i) to 5.1 N (with Ti-i). The destructive effect generated by the indenter while scratching along the two samples is shown in Fig. 4.

4. Conclusions

Boron carbide has been deposited by magnetron sputtering on silicon substrate with different titanium interlayer thickness. Ti thickness above 300 nm leads to the growth of a-B_4C with a dense and continue columnar structure. In this case, no delamination effects were found. Correspondingly, scratch test measurements show that the adhesion of the a-B_4C coating becomes three times stronger. We attribute this result to the Ti-i which decreases the internal stress at the substrate-film interface. This result is connected to the enhanced roughness of Ti-i which induces the growth of a dense and continue columnar structure.

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