Experimentální Analýza Napětí 2011
Experimental Stress Analysis

Effect of temperature treatment on mechanical properties of amorphous boron carbide thin films

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Abstract: Nanoindentation tests have been performed to investigate the effect of temperature treatment on mechanical properties (hardness and elastic modulus) of magnetron sputtered amorphous boron carbide thin films. Variations in a film thickness and internal stress were studied as well. Films were investigated in two ways (i) after annealing in air for one hour at temperatures of 300, 400, 500 and 600 °C (ii) in-situ high temperature measurements at 100, 200, 300 and 400 °C. Increasing the annealing temperature up to 500 °C leads to the stress reduction, slight decrease of the thickness and increase in the film hardness. However already at 600 °C the dramatic film thickness reduction takes place. Hot stage nanoindentation tests show that surface hardness and elastic modulus are almost constant with temperature up to 400 °C.

Keywords: Boron carbide, Nanoindentation, Mechanical properties, Hardness

1. Introduction

Boron carbide (B_4C), which has a high melting point (2450 °C), is the third hardest material after diamond and cubic boron nitride. In addition it exhibits many other attractive properties, such as high elastic modulus and wear resistance combined with low mass density and high chemical stability [1]. Boron carbide coatings are considered to be a promising candidate for a wide range of applications as a protector or cutting tool.

Because of its high application potential it is of particular interest to investigate its mechanical properties at conditions which are close to those experienced in service, especially at elevated temperatures. The structural and compositional changes can take place on the film surface and as a result the mechanical properties can change.

Oxidation of bulk B_4C starts at temperatures above 550 °C [2, 3] with formation of B_2O_3 and CO_2 [4]. Although the oxidation can be insignificant for bulk material, in the case of thin film with thickness of several microns it can be vital.

In this paper, the influence of air annealing at temperatures up to 600 °C on thickness, mechanical properties and structure was investigated. The depth sensing indentation experiments were performed at room temperature as well as at elevated temperatures up to 400 °C.

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2. Experimental details

Amorphous boron carbide films with composition close to stoichiometric B_4C were deposited on the unheated substrate Si(111) by DC-magnetron sputtering of hot-pressed B_4C target using the Leybold-Heraeus Z 550 M sputtering plants. Additional bias voltage was not applied during the deposition process.

The structure of the film was studied by micro-Raman spectroscopy (λ=514.5 nm, Renishaw Ramascope, Model 1000). The polarization of the scattered light was not analyzed; the frequencies of the Raman features observed were taken directly from the spectra without any deconvolution. The film composition was determined by electron probe X-ray microanalysis (EPMA).

Amorphous boron carbide thin films were additionally annealed in air at 300, 400, 500 and 600 °C for one hour. The film thickness, compressive stress and hardness were measured after each annealing.

The nanoindentation experiments were performed using NanoTest NT600 instrument equipped with Berkovich indenter at load of 10 mN [5]. The hardness and reduced elastic modulus were determined from load-displacement curves according to the analysis developed by Oliver and Pharr [6]. The reduced elastic modulus that takes into account the effect of diamond indenter is defined as

$$E_r = E/(1-\nu^2), \qquad (1)$$

where E and ν are the Young's modulus and the Poisson's ratio.

The maximal penetration depth of indenter did not exceed ~15 %, therefore we do not take into account any influence of Si(111) substrate on the measured values of mechanical properties. On the other hand the indenter penetration is large enough to reduce possible errors associated with surface roughness, size effects or indenter calibration. The average values of hardness and reduced elastic modulus were calculated from 5 independent measurements.

Furthermore, high temperature nanoindentation tests were performed on one as-deposited film. Hardness and reduced elastic modulus were determined at room temperature and elevated temperatures of 100, 200, 300 and 400 °C. The film was continuously annealed during the test. The NanoTest system was equipped with a computer-control heating stage for measurement at elevated temperatures. Heating was applied to both indenter and the sample utilizing separate temperature control. This isothermal contact ensures that there is not heat flow during the indentation process.

The intrinsic stresses of the films were calculated using Stoney's classical equation [7]. The radii of curvature of the substrate before and after coating deposition as well as film thickness were measured by Tencor Alfa-Step profilometer.

3. Results and discussion

3.1. Annealing in the air

Amorphous character of investigated films was established using Raman spectroscopy. Fig.1 illustrates the Raman spectra of studied films and sputtered polycrystalline B_4C target for comparison.

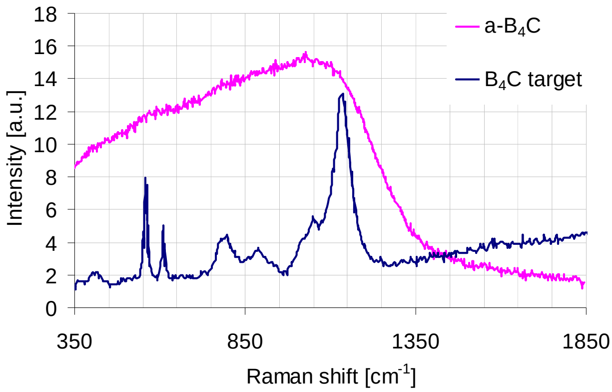

Fig. 1. Raman spectra of studied amorphous boron carbide thin film and polycrystalline B_4C target

Film thickness as a function of the annealing temperature (1 hour in the air) is illustrated in Fig. 2. The thickness of as-deposited film is 1.16 µm and remains stable up to 400 °C. Small thickness reduction with the value of 40 nm starts at 500 °C. Although such decrease is insignificant for bulk material, in the case of thin films it plays a vital role. Further increase of annealing temperature up to 600 °C leads to a dramatic reduction of film thickness. The oxidation proceeds very intensively and the film becomes very inhomogeneous at the same time. It should be noted that the film totally disappear during annealing at 600 °C for several hours.

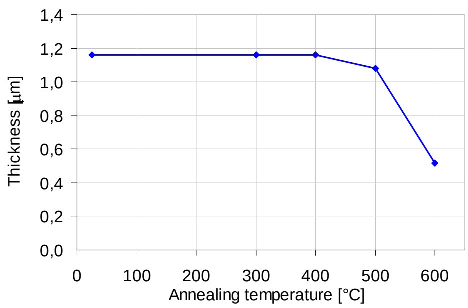

Fig. 2. Thickness of a-B_4C films as a function of annealing temperature in air

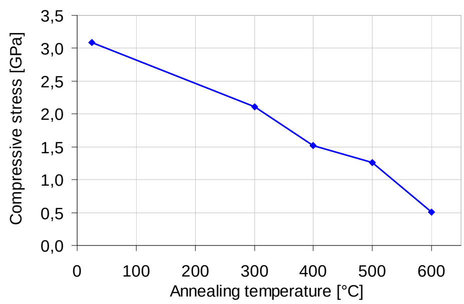

Fig. 3. Compressive stress of a-B4C films as a function of annealing temperature in air

Internal compressive stress gradually decreases with the annealing for all temperatures up to 600 °C, as is shown in Fig. 3. Indentation hardness slightly increases up to 500 °C. Both of these facts can be attributed to some ordering of the film structure that takes place during annealing. However, already at 600 °C a significant drop in hardness is observed. This can be a result of increasing effect of softer Si substrate due to a rapid decrease of film thickness and/or of changes in chemical composition of the film surface. However, practically no changes in chemical composition were observed after annealing at 300, 400, 500 and even 550 °C in comparison to as-deposited films: ~78% at. of boron and ~22% of carbon [8]. Fig.5 illustrates that reduced elastic modulus remains almost steady up to 500 °C and than decreases slightly. It is apparent that the data for 600 °C scatters widely, which could be attributed to the changes of the film surface due to intensive oxidation.

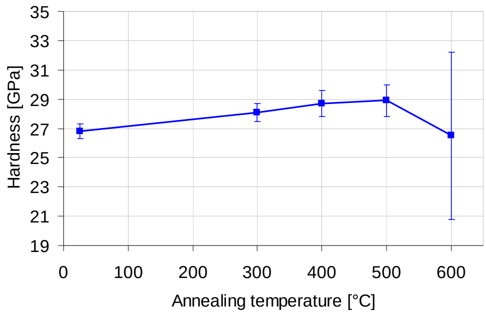

Fig. 4. Hardness of a-B_4C films as a function of annealing temperature in air.

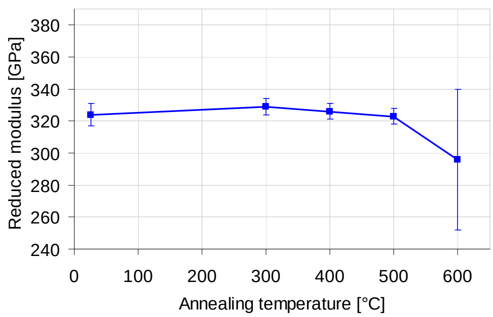

Fig. 5. Reduced elastic modulus of a-B_4C films as a function of annealing temperature in air.

3.2. High temperature nanoindentation

In addition to annealing experiments the *in situ* high temperature nanoindentation measurements were performed. The goal of this type of test was to investigate the thermal stability and high temperature performance of the a-B_4C films.

Fig.6. shows the variation of hardness with temperature on the sample surface in the range of 26-400 °C. It has been proved that hardness of silicon remains stable up to 400-500 °C [9]. Hence, the changes in mechanical properties of films with temperature should not be attributed to the effect of Si(111) substrate.

First, the increase of temperature results in slight reduction in hardness with the minimum at 200 °C. The hardness gradually rises with further increasing the temperature. Reduced modulus increases slowly with temperature up to 200 °C and then levels out. It is worth noting that hardness and modulus shows similar trends like in the case of annealing experiments at temperatures up to 400 °C.

At 300 and 400 °C, hardness and modulus scatter strongly. Visual examination showed that the first changes in surface morphology were observed after experiments at 300 °C. It should be emphasized that sample is exposed to the final temperature for thermal stabilization before measurement for approximately three hours. The whole period of high temperature exposure at a specific temperature was about 24 hours.

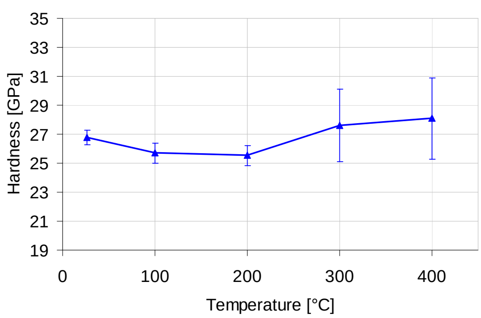

Fig. 6. Hardness of a-B_4C films measured at different temperatures in air.

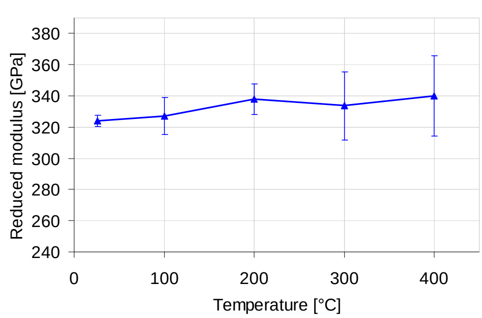

Fig. 7. Reduced elastic modulus of a-B_4C films measured at different temperatures in air.

4. Conclusion

An examination of the mechanical characteristics of temperature-treated amorphous boron carbide thin films with composition close to B_4C was presented.

Air annealing for one hour does not have any effect on thickness and composition up to 400 °C. Increase of annealing temperature up to 500 °C leads to the stress reduction, slight decrease of the thickness and increase in the film hardness. However, already at 600 °C the dramatic film thickness reduction takes place. Simultaneously the oxidation proceeds very intensively and the film becomes inhomogeneous.

Hot stage nanoindentation tests show that surface hardness and elastic modulus are almost constant with temperature up to 400 °C. This agrees with annealing experiment, though the changes in surface morphology are shifted down to 300 °C as a result of longer exposure to specific temperature, specifically about 24 hours. Thus the upper operational temperature of the a-B_4C films in the air is limited also by the expected operational time.

Acknowledgement

This work has been supported by the Operational Program Research and Development for Innovations - European Regional Development Fund (CZ.1.05/2.1.00/03.0058) and co-financed from European Social Fund and State financial resources (CZ.1.07/2.3.00/20.0017) and by the Academy of Sciences of the Czech Republic, research projects No. AVOZ10100520 and KAN301370701.

References

[1] Kulikovsky V., Vorlicek V., Bohac P., Ctvrtlik R., Stranyanek M., Dejneka A. and Jastrabik L., “Mechanical properties and structure of amorphous and crystalline B_4C films,” *Diamond & Related Materials*, **18**, pp. 27-33 (2009). ISSN 0925-9635Surname

[2] Lavrenko V.A., Pomytkin A.P., Kislyj P.S. and Grabchuk B.L., “Kinetics of high-temperature oxidation of boron carbide in oxygen,” *Oxidation of Metals*, **10**(2), pp. 85-95 (1976). ISSN 0030-770X.

[3] Gogotsi G.A., Gogotsi Y.G. and Ostovoj D.Y., “Mechanical behaviour of hot-pressed boron carbide in various atmospheres,” J*ournal of Materials Science Letters*, **7**(8), pp. 814-816 (1988). ISSN 0261-8028.

[4] Li Y.Q. and Qiu T., “Oxidation behaviour of boron carbide powder,” *Materials Science and Engineering: A*, **444**(1-2), pp. 184-191 (2007). ISSN 0921-5093.

[5] Ctvrtlik R., Stranyanek M., Bohac P.and Jastrabik L., “NanoTest NT600 – A device for analyse of mechanical properties of materials,” *Materials Structure*, **13**(2), pp. 90-93 (2006). ISSN 1211 – 5894.

[6] Oliver W.C. and Pharr G.M., “An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments,” *Journal of Materials Research*, **7**(6), pp.1564-1583 (1992). ISSN 0884-2914.

[7] Stoney G.G., “The tension of metallic films deposited by electrolysis” *Proceedings of the Royal Society A*, **9**, pp. 172-175 (1909). ISSN 0950–1207.

[8] Kulikovsky V., Vorlicek V., Ctvrtlik R., Bohac P., Jastrabik L. and H. Lapsanska, “Effect of air annealing on mechanical properties and structure of amorphous B_4C films,” *Surface and Coatings Technology*, **205**(16), pp. 4052-4057 (2011). ISSN 0257-8972.

[9] Vandeperre L.J., Giuliani F., Lloyd S.J. and Clegg W.J., “The hardness of silicon and germanium,” Acta Materialia, **55**(18), pp. 6307-6315 (2007). ISSN 1359-6454.