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Mechanical properties of pulsed laser deposited nanocrystalline SiC films

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ABSTRACT

The mechanical properties of nanocrystalline SiC thin films grown on (100) Si at a substrate temperature of 1000 °C under a CH_4 atmosphere using the pulsed laser deposition (PLD) technique were investigated. Nanoindentation results showed that films exhibited hardness values around 36 GPa and Young modulus values around 250 GPa. Scratch tests found that films were adherent to the substrate, with critical load values similar to those recorded for other hard coatings deposited on significantly softer Si substrates. Wear tests performed at a temperature of 900 °C showed that films exhibited friction coefficients and wear rates very similar to those measured at room temperature, due to the presence of C–C bonds as evidenced by X-ray photoelectron spectroscopy investigations. These results recommend such coatings for demanding high temperature applications such as nuclear fuel encapsulation.

1. Introduction

Due to its excellent mechanical, optical, thermochemical, electronic and electrical properties SiC has been extensively investigated for potential uses in microelectronics [1,2], hard and protective coatings for tools [3,4], water splitting [5] and bio-applications [6]. More recently, it has been suggested that due to its very low neutron absorption cross section, SiC could be used in the nuclear industry as encapsulating coatings for nuclear fuel in next generation reactors [7,8]. For such applications the deposited SiC films are expected to maintain their properties at temperatures between 500 and 800 °C and even higher, up to 1000 °C, in the case of an emergency if an accident occurs.

The deposition of high quality SiC films to study their properties is a challenging process due to their low sputtering yield, high melting temperature and reactivity with oxygen [1–4]. Progress has been recently made using CVD, ion beam or sputtering techniques [1–8]. By using the Pulsed Laser Deposition (PLD) technique, good quality SiC films that are very useful for properties investigations were also synthesized [9–14]. The use of a high laser fluence, a very low residual vacuum, high purity CH_4 and high repetition rates were necessary to grow the films [15]. Results obtained from simulations of the X-ray reflectivity curves acquired from the PLD grown films showed that they possess a low surface roughness (rms values < 1 nm) and a density around 3.20 g/cm^3, almost identical to the tabulated value for bulk SiC. Grazing incidence X-ray diffraction studies showed the films were nanocrystalline while X-ray photoelectron spectroscopy investigations found that films contained in bulk a rather low oxygen concentration, below 2–3 at.%. The results of systematic nanoindentation investigations and wear tests performed at room temperature and 900 °C on PLD grown SiC films are presented below.

2. Experimental details

The PLD experimental set up used to deposit films has been described previously [15]. It uses a KrF excimer laser (λ = 248 nm, pulse duration τ = 25 ns, 8 J/cm^2 fluence, 40 Hz repetition rate) to ablate SiC polycrystalline targets (Angstrom Sciences) in a stainless steel chamber. The ultimate pressure in the deposition chamber was in the low 10^{-6} Pa. Since the properties of the deposited films improved with the increase of the substrate temperature, we restricted our investigations to films deposited using the maximum temperature of 1000 °C achievable in our

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deposition system. Moreover, because the wear testing of such films involved experiments at 900 °C, it was not very useful to deposit them at lower temperatures. Series of films were deposited at 1000 °C on Si substrates (MEMC Electronic Materials, Inc.) for 27,000 and 14,000 pulses (generic names SiC_17 and SiC_18, respectively) under a high purity of 2×10^{-5} mbar of CH_4. After deposition, films underwent a 1 h anneal at the deposition temperature and then were slowly cooled at room temperature at a rate of 5 °C/min. As mentioned in the Introduction part, the crystalline structure, surface roughness, mass density, elemental composition, and optical properties of these films were previously reported [15]. According to ellipsometry measurements, the thickness of the deposited films were around 1 μm and 0.5 μm, ±5% on an area of 2 cm^2 for the SiC_17 and SiC_18 series of samples, respectively.

The mechanical properties of the thin films were investigated using a nanoindentation device produced by CSM Instruments (NHT-2) equipped with a Berkovich diamond tip. To minimize substrate contributions, the indentation experiments were performed controlling the depth penetration of the indenter, between 80 and 120 nm and 40 and 150 nm at maximum loads ranging from ~4 to ~7 mN and ~1 to ~11 mN for samples SiC_17 and samples SiC_18, respectively. The hardness and reduced modulus were determined following the model of Oliver and Pharr [16]. On each series of samples, a matrix of measurements, with X and Y displacements of 0.05 mm, have been made, with the following protocol: linear loading, loading rate = 100 nm/min, pause during full load 2 s (in order to minimize the creep effect), and unloading rate = 100 nm/min. Considering the thickness variation of PLD grown films only the indentations that were located on the central area of the films were taken into consideration. The load resolution of the apparatus is 40 nN, with a usable indentation load range between 0.1 and 500 mN. The thermal drift, which can influence the measurements with indentation depths lower than 100 nm, is countered with the use of a zirconium reference ring, which is in contact with the sample surface. The reference ring also acts as a local environmental enclosure to passively protect the measurement location from air currents, sound waves and changes in humidity and temperature. Furthermore the environmental temperature and humidity are kept constant during measurement sessions. For comparison purposes, nanoindentation measurements were performed on the silicon substrate, with the following protocol: Berkovich diamond indenter, linear loading, 300 nm penetration depth, loading and unloading rates of 1000 nm/min.

The scratch tests were performed on a Micro Scratch Tester (CSM Instruments) using a 100Cr6 steel tipped indenter with a Rockwell geometry (tip radius = 100 μm). The load was applied progressively, from 0.03 N to 9 N for samples SiC_17, and from 0.03 to 8 N for samples SiC_18, with a speed of 1 N/min. The length of the tests was set at 3 mm, being confined to the samples' area of relatively uniform thickness. Three tracks were made on each measured sample, with a displacement on the *Y* axis of 0.2 mm between each track. The critical load values were obtained after optical analysis of the wear tracks, and these are defined as follows: Lc_1 – the load necessary for the emergence of the first cracks in the film; Lc_2 – the load corresponding to the first delamination of the film; Lc_3 – the load responsible for the delamination of more than 50% of the film from the wear track. Mechanical wear tests were carried out at 25 °C and 900 °C in air atmosphere using a dry ball-on-disk tribometer from CSM Instruments. The bearing balls were made out of Si_3N_4 having a diameter of 5 mm. The normal load was set at 1.00 N, the maximum linear speed at 0.05 m/s and the stop condition at 2400 cycles.

The chemical composition of the films was investigated by X-ray photoelectron spectroscopy (XPS) on a Physical Electronics PHI 5000 VersaProbe II using monochromatic Al K_α radiation (1486.6 eV). Sputtering of the surface was done with 2 kV Ar ions while the sample was rotated to ensure a uniform removal rate.

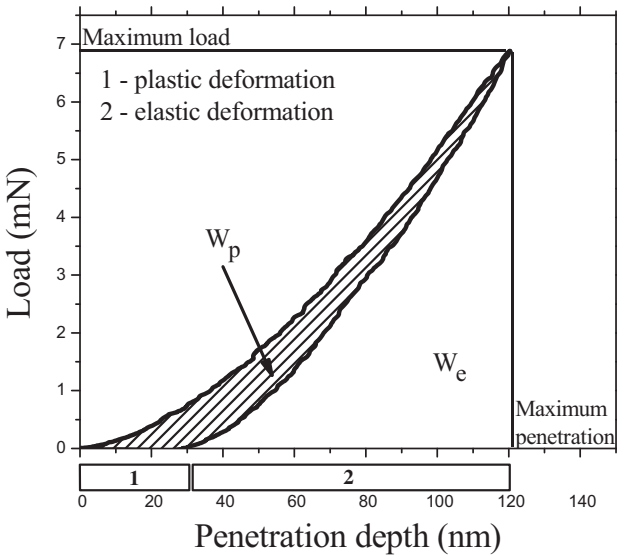

Fig. 1. Loading–unloading curves for a penetration depth of 120 nm recorded for a sample SiC_17.

3. Results and discussion

Nanoindentation measurements were performed in multiple locations on several samples, with different penetration depths. The representative results are presented in Table 1. Overall, the results showed that the films were very hard, exhibiting values from ~32 to ~41 GPa for both samples, while the elastic modulus values were around 250–260 GPa, typical values for good quality SiC films [17,18]. However, upon further investigation of the data, several observations can be extracted. Fig. 1 represents a typical loading–unloading curve for a penetration depth of 120 nm recorded for sample SiC_17. From the evolution of the loading–unloading curves, it can be observed that the film exhibited a very small degree of plastic deformation. A similar evolution was noticed for the remaining measurements, regardless of the penetration depth, which leads to the conclusion that the mechanical characteristics are relatively homogeneous throughout the measured thickness of the films. This observation can be supported by a more in-depth analysis of the loading–unloading curves. By analyzing the load–displacement response, one can extract other mechanical metrics apart from the hardness (H_{it}), such as the plastic work ratio (u_p), defined as:

$$u_p = \frac{W_p}{W_t} \quad (1)$$

where W_t is the total work of indentation which is separated into an elastic (W_e) and a plastic (W_p) component (as seen in Fig. 1). These parameters are extracted from the experimentally measured loading–unloading curve. Higher u_p values denote a material with a higher ability to dissipate energy in plastic deformations.

Fig. 2 presents the variation of the plastic work ratio as a function of the penetration depth. One can observe that, for both samples, the plastic work ratio is stabilized in the penetration depth interval 80–120 nm. Following this interval, the plastic work ratio rises abruptly for the thinner sample up to a value of ~0.31. This phenomenon should be expected, considering that the penetration depth for this particular measurement reaches 30% of the total film thickness (500 nm). The physics and technique of nanoindentation measurements in films thinner than 0.5 μm is still a matter of