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Mechanical properties of ZrC thin films grown by pulsed laser deposition

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ZrC thin films were grown by the pulsed laser deposition technique on (001) Si, (111) Si and (001) sapphire substrates. The structure and composition of the films were investigated by x-ray diffraction, x-ray reflectivity, and Auger electron spectroscopy investigations. Films grown at temperatures higher than 700 °C under very low water vapor pressures exhibited a high degree of crystallinity. According to x-ray diffraction and pole figure investigations, ZrC films deposited on (001) Si are very well aligned with the substrate, both in-plane and out of plane, in a cube on cube manner. ZrC films deposited on (111) Si and sapphire grew with the (111) axis perpendicular to the substrate, while in-plane orientation depended on the particular orientation of the substrate. Nanoindentation measurements showed higher values of the hardness for higher crystallinity. For the highest crystalline quality, (111) ZrC films deposited on sapphire, values over 450 GPa for the elastic modulus and 30.4 GPa for the hardness were measured.

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1. Introduction

ZrC is a refractory compound, characterized by a high melting temperature of 3530 °C [1], excellent thermal stability, high hardness, and a low work function for electron emission of 3.3 ~ 3.5 eV [2]. Thin films of ZrC have important applications in vacuum electronics or micromechanics [3-5]. ZrC also exhibits lower lattice mismatch and thermal expansion coefficient difference with Si than ZrN, making it a potential good candidate for metallization or diffusion barriers structures for Si-based electronic devices, especially if it could be grown epitaxially. Many techniques such as e-beam bombardment [4,5], chemical vapor deposition [6], magnetron sputtering [7], or laser cladding [8] have been used to grow thin ZrC films. However, it appears that it is quite difficult to obtain high crystalline quality films because of its high melting temperature, low vapor pressure and Zr atoms affinity for oxygen. Pulsed laser deposition (PLD) is one of the best techniques that can overcome these difficulties and be successfully employed to grow crystalline ZrC films [9,10]. By optimizing the deposition conditions we were able to obtain epitaxial ZrC films on single crystal substrates. The structure, composition and mechanical properties of these films are described below.

2. Experiment

The film depositions were conducted in an all-metal vacuum chamber using a KrF excimer laser (λ = 248 nm). The laser parameters used were 10 J/cm^2 fluence and 10 Hz repetition rate. The films were deposited for different times in order to obtain thicknesses from around 20 to about 100 nm, on (001) and (111) Si or (001) sapphire substrates at temperatures up to 850 °C. Just prior to deposition the Si substrates were heated up to 900 °C for 20 min under vacuum to remove the native oxide. Depositions were performed under residual vacuum or a low C_2H_2 or CH_4 atmosphere. Special care was taken to maintain low vapor pressures during depositions, below 1.33 × 10^{-6} Pa, as measured with a residual gas analyzer attached to the deposition chamber.

The films surface and interfacial roughness, mass density and thickness were obtained by simulating the measured x-ray reflectivity (XRR) spectra acquired with a Panalytical X'Pert MRD system. The same instrument was used for structural characterization in symmetric and grazing incidence x-ray diffraction (XRD and GIXD). Pole figure measurements were acquired both from the films and substrates for texture characterization. The chemical composition of the films was investigated by Auger electron spectroscopy (AES, Perkin Elmer 510 system).

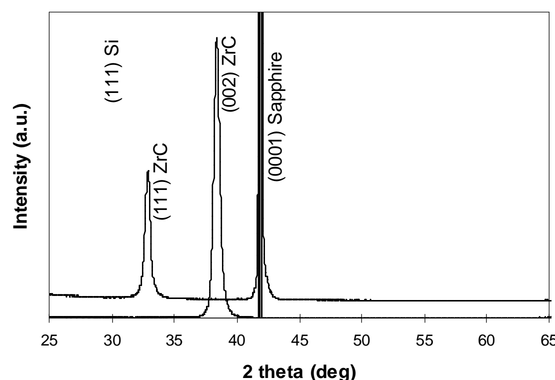

Fig. 1. XRD spectra of ZrC films deposited at 750 °C on various substrates.

Automated indention pattern grids with indention spacing of 5 μm were programmed to run on original

substrates and coated substrates with a Hisitron TriboIndenter. Tests were run in displacement control with a total displacement range of 15 to 70 nm. The samples thicknesses used for nano-indentation test were around 70~100 nm. The sample surfaces were carefully cleaned before the measurements. A Berkovich diamond indenter with a total included angle of 142.3º, a half angle of 65.3º, and a tip radius of 100~200 nm was used for indentation. A tip area function was generated by curve fitting a plot of area versus contact depth from indentations on a fused quartz standard with a modulus of 72 GPa and a Poisson's ration of 0.168. Unloading force displacement curves were analyzed to determine reduced modulus and hardness using a method first described by Doemer and Nix [11] and later refined by Oliver and Pharr [12].

3. Results and discussion

The acquired theta-2theta XRD diffraction spectra showed that the ZrC films deposited above 500 °C were crystalline, while those deposited above 700 °C were highly textured, especially for sapphire and (001) Si substrates as one can see in Fig. 1. ZrC deposited on sapphire or (111) Si exhibited a (111) texture, while those deposited on (001) Si exhibited a (001) texture. To check the presence of other crystalline orientations, grazing incidence XRD investigations, which are more sensitive to the surface region, were performed for the highly textured films at incidence angles of 1° and 2°. Typical spectra acquired at omega=2° and presented in Fig. 2, showed that films deposited on sapphire substrates exhibited barely visible humps in the spectra, indicating a very small amount of grains possessing other crystalline orientations than that with the (111) axis perpendicular to the substrate. Films deposited on (001) Si and (111) Si substrates exhibited some small diffraction peaks, more so for the (111) Si substrates, corresponding to cubic ZrC orientations (a=0.469 nm, JCPDS 35-0784), similar to those observed in the spectrum acquired from the pure ZrC target.

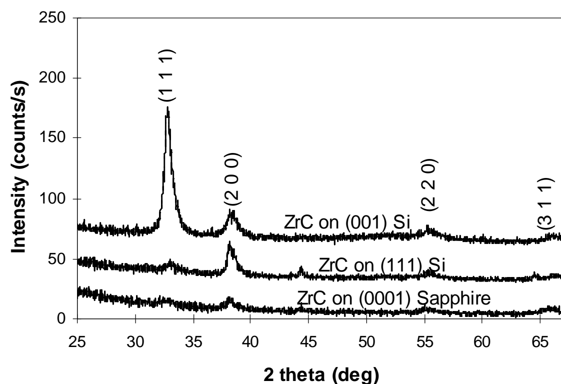

Fig. 2. GIXD spectra (Ω=2°) of ZrC films deposited at 750 ^{o}C on various substrates.

The density of these high crystalline quality films and their surface roughness, estimated by modeling the acquired XRR spectra using the Wingixa™ software from Panalytical and a three-layer model (interfacial layer, ZrC film, and contamination layer), was around 6.7 g/cm^3 and 0.6-0.7 nm, respectively, regardless of the substrate type. The density values are a good indication that films are compact stoichiometric ZrC [13]. The surface contamination layer density was around 4~5 g/cm^3 indicating the presence of an oxide or hydroxide compound. AES investigations confirmed that the first 2.0~3.0 nm of the ZrC films were heavily contaminated with oxygen. However, once the topmost layer was removed by Ar ion sputtering, the oxygen content dramatically decreased to values below 5%. Under our best vacuum conditions during depositions, ZrC films exhibiting oxygen atomic concentrations as low as 2.1 % have been obtained.

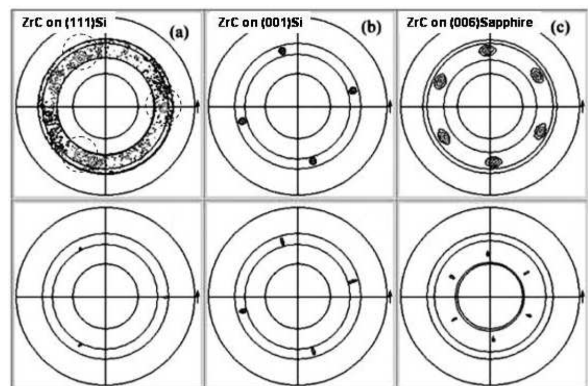

Fig. 3. Pole figures of the ZrC films (top row) and their substrates (lower row): a) (001)ZrC and (004)Si for a film deposited on (111)Si, respectively; b) (111)ZrC and (111) Si for a (001)ZrC film deposited on (001)Si; (c) (111) ZrC and (116) sapphire for a (111)ZrC deposited on sapphire.

The in-plane crystalline orientation of the deposited films was investigated by pole figure measurements of several diffraction peaks for both the films and the substrates. Typical pole figure results for ZrC films deposited on (001) Si and sapphire together with those of their substrates are displayed in Fig. 3. One can clearly see that the films were exhibiting a rather good in-plane texture as well, therefore being epitaxial. ZrC films deposited on (001) Si exhibited an in-plane orientation such as [100] Si // [100] ZrC and out of plane orientation [001] Si // [001] ZrC, which corresponds to cube on cube growth. The misfit, estimated from the lattice parameters was of the order of 13.6%, a large value that can explain the rather large areas of the peaks seen in the pole figures. The films deposited on sapphire or (111) Si grew with their [111] axis perpendicular to the substrate and an in-plane orientation where [110] ZrC // [210] sapphire or [110] ZrC // [110] Si. Instead of the usual three-fold symmetry as seen for the substrate, a six-fold symmetry caused by twinning was observed for these ZrC films.

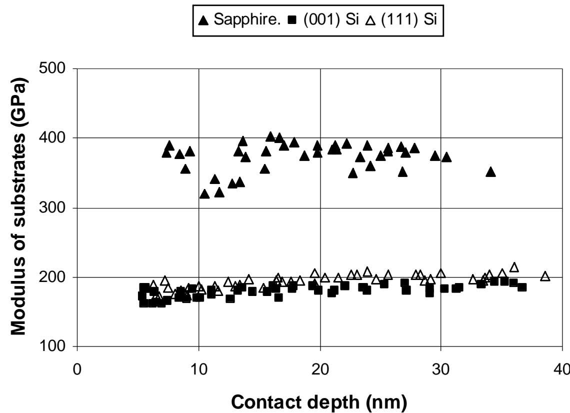

Fig. 4. Elastic moduli values versus indentation depth of the as - received sapphire, (001) Si, and (111) Si substrates used for film growth.

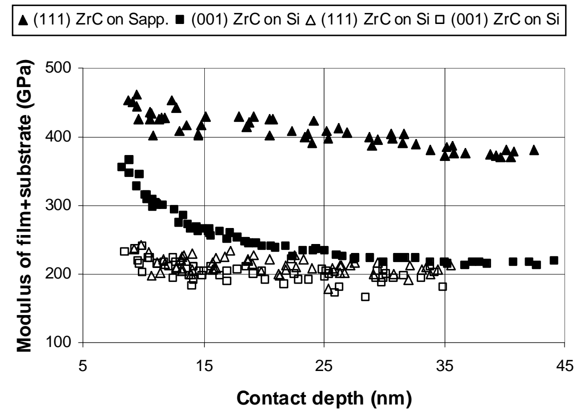

Fig. 5. Combined elastic modulus values versus indentation depth of the ZrC films and substrates.

The elastic modulus of film and substrate as a function of contact depth was simply calculated from the measured reduced modulus, assuming that the compliance of sample and indenter is combined as springs in series [14]. The modulus values measured from the as-received substrates are displayed in Fig. 4, while the values measured from ZrC films is displayed in Fig. 5. As one can see in Fig. 5, as the contact depth is increased (hence applied force), the values of the moduli are approaching the values measured for the substrates only. Since the combined film and substrate modulus is strongly decreasing with the depth of penetration from the value of the modulus of the hard film towards that of the softer substrate system [15], a value of over 450 GPa of elastic modulus can be estimated for the highest crystalline quality (111) ZrC (t ~ 100 nm) on sapphire. For relatively thinner and lower crystalline quality (open triangles and squares, t ~ 70 nm) samples, the substrate effect was very dominant and the films modulus barely influenced the measurements. Figs. 6 and 7 show the variations of hardness as a function of contact depth for Si substrates and ZrC films, respectively. Since hardness is affected by the plastic deformation of the soft substrate beyond 20 nm contact depth, the hardness data obtained only below 20 nm contact depth was used for calculations. The results show that the higher crystal quality films (solid squares: 27.5 GPa, solid triangles: 30.4 GPa) have higher hardness than that of lower crystalline quality films (open squares: 19.6 GPa, open triangles: 17.6 GPa). This maximum hardness is comparable the maximum hardness (30.2 GPa) reported recently [7] for ZrC.

5. Conclusions

In summary, by using the pulsed laser deposition technique under very low water vapor pressures and high substrate temperatures, epitaxial ZrC films were deposited on single crystalline substrates. On (001) Si the ZrC films grew along the [001] axis while on (111) Si and (001) sapphire they grew along the [111] axis. Pole figure measurements showed that ZrC films exhibited in-plane orientation too, depending on the type of substrate. Grazing incidence x-ray diffraction investigations evidenced the presence in these films of a rather small fraction of randomly oriented crystallites. The films mass density was around the tabulated value of 6.7 g/cm^3 while the surface morphology was very smooth, with a roughness value (rms) of 0.6 ~ 0.7 nm. High value of hardness (30.4 GPa) and elastic modulus (over 450 GPa) were obtained for high crystalline quality (111) ZrC deposited on sapphire substrate.

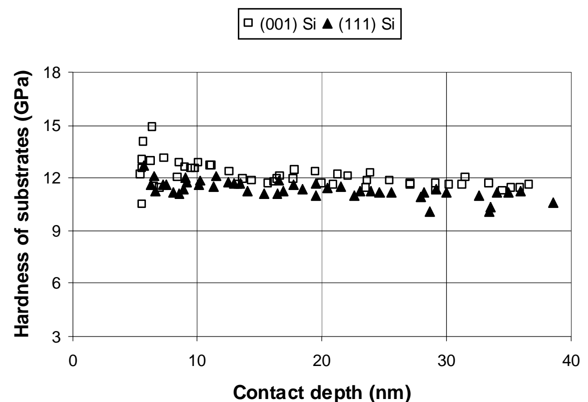

Fig. 6. Hardness values versus indentation depth of as-received substrates used for the growth of films.

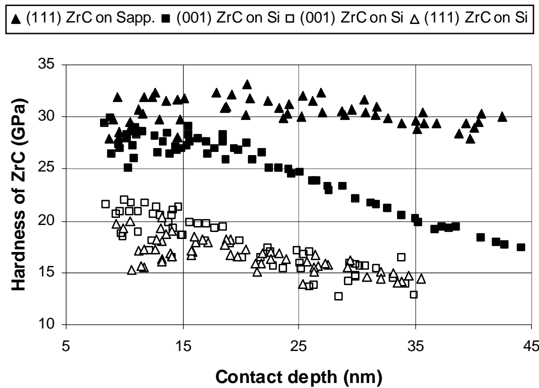

Fig. 7. Hardness values versus indentation depth of ZrC films grown on different substrates.Solid triangles and squares correspond to samples that exhibited a higher degree of in-plane texture.

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Invited Lecture

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