

Pulsed laser deposition of crystalline ZrC thin films

V. Craciun^{a,*}, D. Craciun^b, J.M. Howard^a, J. Woo^a

^a Major Analytical Instrumentation Center, Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA

^b Laser Department, National Institute for Laser, Plasma, and Radiation Physics, Bucharest, Romania

Received 31 July 2006; received in revised form 6 November 2006; accepted 28 November 2006

Available online 9 January 2007

Abstract

ZrC thin films were grown on Si substrates by the pulsed laser deposition (PLD) technique under various conditions. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), X-ray diffraction and reflectivity, spectroscopic ellipsometry, and four point probe measurements were used to characterize the properties of the deposited films. It has been found that crystalline films could be grown only by using laser fluences higher than 5 J/cm² and substrate temperatures in excess of 500 °C. For a fluence of 10 J/cm² and a substrate temperature of 700 °C, cubic ZrC films ($a=0.469$ nm) exhibiting a (200)-texture were deposited under vacuum or low pressure C₂H₂ atmosphere. These films were smooth, with surface roughness values below 1.0 nm and mass densities around the tabulated value of 6.7 g/cm³. AES depth profiling investigations showed oxygen contamination around 7% in the bulk region. Despite the relatively high levels of oxygen contamination, the deposited ZrC films were very conductive. The use of a low C₂H₂ pressure atmosphere during deposition had a small beneficial effect on crystallinity and stoichiometry of the films.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Thin films; ZrC; Laser ablation; Refractive coatings

1. Introduction

ZrC is a refractory compound characterized by a high melting temperature, excellent thermal stability, high hardness and a low work function for electron emission [1]. It crystallizes in the B1 type lattice (NaCl) and can exhibit a wide range of ZrC ratios and oxygen contaminants [2]. Its applications range from tribological and protective coatings for tools to high brightness electron emission coatings [3,4]. Because of its refractory nature, chemical inertness, and high hardness it has been difficult to synthesize sharp tips for field emitter arrays from bulk ZrC. An alternative approach is to coat Si or Mo tips, which are easier to fabricate, with a thin ZrC film to improve their electron emission properties [5]. Nonetheless, it is still a challenge to deposit high quality ZrC films at processing temperatures that are low enough to be compatible with Si technology [6–8].

Pulsed laser deposition (PLD) is recognized as a technique that can allow a decrease of the substrate temperature with respect to other deposition techniques while preserving the high quality of

the deposited films. There have been several reports describing the growth of ZrC films by the PLD technique [8–10]. We extended these studies to a wider range of deposition conditions to further improve the properties of the deposited ZrC films and report the results here.

2. Experiment

The depositions were conducted in a typical PLD system using a KrF excimer laser ($\lambda=248$ nm). The laser parameters used were 2–10 J/cm² fluence and a 5 Hz repetition rate. The films were deposited for different times from a polycrystalline ZrC target (Plasmaterials, Inc.) on p⁺⁺ Si (100) substrates supplied by MEMC Electronic Materials, Inc that were cleaned in acetone, ethanol, then dipped for 5 min. in 1% HF solution, rinsed in deionized water and finally blown dry with high purity nitrogen. The substrate temperature during deposition was from 300 up to 800 °C. Depositions were performed under residual vacuum (low 10^{−4} Pa) or under a C₂H₂ atmosphere.

The films surface and interfacial roughness, mass density and thickness were investigated by X-ray reflectometry (XRR, Panalytical X'Pert MRD system, using Cu K_α radiation). The

* Corresponding author.

E-mail address: vcrac@mse.ufl.edu (V. Craciun).

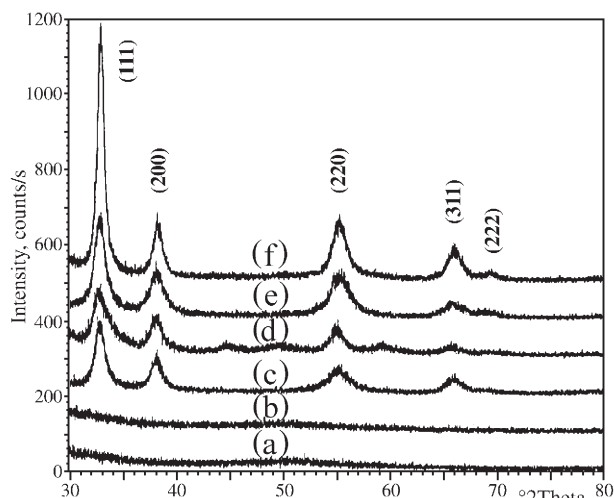


Fig. 1. GIXD spectra ($\omega=1^\circ$) of ZrC films deposited under various conditions; C_2H_2 pressure, laser fluence, and substrate temperature were: (a) 1.3×10^{-1} Pa, 6 J/cm², 500 °C; (b) 1.3×10^{-3} Pa, 3 J/cm², 600 °C; (c) 1.3×10^{-3} Pa, 8 J/cm², 600 °C; (d) 1.3×10^{-2} Pa, 10 J/cm², 600 °C; (e) 1.3×10^{-2} Pa, 10 J/cm², 700 °C; (f) 1.6×10^{-1} Pa, 10 J/cm², 600 °C.

same instrument was used for structural characterization in symmetric and grazing incidence X-ray diffraction (XRD and GIXD). The chemical composition and bonding of the films were investigated by X-ray photoelectron spectroscopy (XPS) in a PHI model 5100 ESCA system using Mg K α radiation (1253.6 eV). A Perkin-Elmer PHI 660 system was used for Auger electron spectroscopy (AES) investigations. The obtain an elemental depth profiling of the deposited films, AES measurements were collected after cycles of 15 s Ar ion sputtering (4 kV, 1 μ A/cm²) of the films until the Si substrate was reached. The thickness and optical properties of the films were also measured by spectroscopic ellipsometry (Woollam M-88 system) using a Lorentz model for the optical constants of the films and compared with results obtained from the

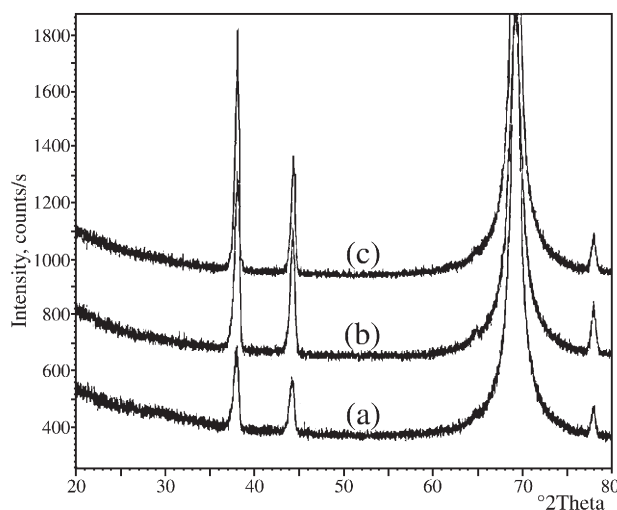


Fig. 2. XRD spectra of thin films deposited from a Co-doped ZrC target under various conditions; C_2H_2 pressure, laser fluence, and substrate temperature were: (a) 2.7×10^{-1} Pa, 2 J/cm², 300 °C; (b) 1.3×10^{-1} Pa, 3 J/cm², 500 °C; (c) 1.3×10^{-1} Pa, 6 J/cm², 500 °C.

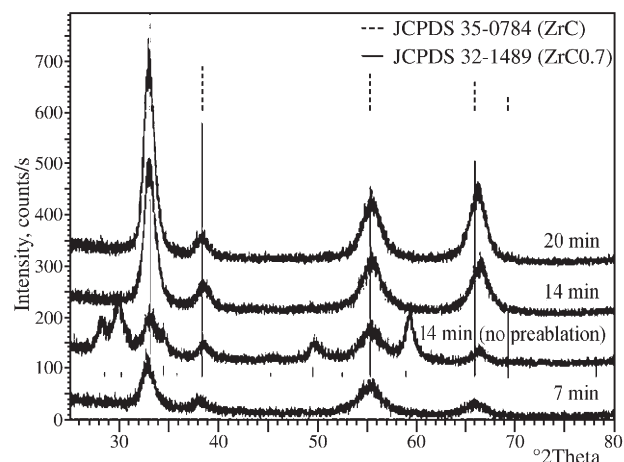


Fig. 3. GIXD spectra ($\omega=1^\circ$) of ZrC films deposited for various times at 700 °C under vacuum. The standard position of diffraction lines from ZrC and ZrC_{0.7} are also shown.

simulations of the XRR spectra. Preliminary four point probe measurements were conducted to assess the electrical conductivity of the deposited films.

3. Results and discussion

XRD investigations of the targets showed that they were crystalline, with diffraction lines corresponding to cubic and stoichiometric ZrC ($a=0.469$ nm) [11]. No other phases were identified in the diffraction patterns. Fig. 1 displays GIXD spectra acquired at an incidence angle of 1° from films deposited under various conditions. It is apparent that the deposition of crystalline films requires the simultaneous use of high substrate temperatures and laser fluences. All the diffraction lines observed in the spectra correspond to the cubic ZrC, being identical to those observed from the pure ZrC target.

One of the targets used was Co-doped ZrC. It is worth mentioning that films grown from the Co-doped ZrC target surprisingly exhibited sharp diffraction lines even for a substrate

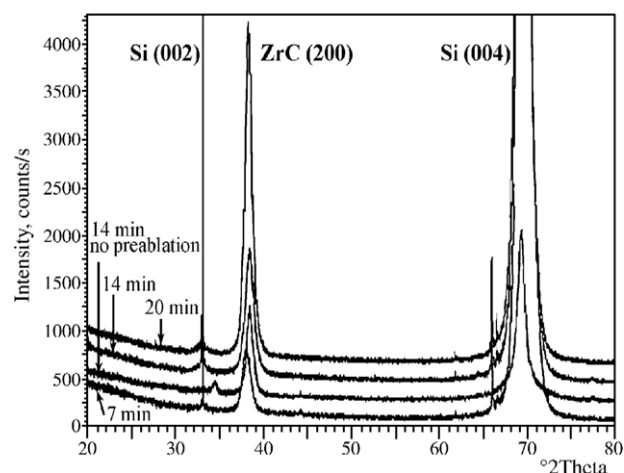


Fig. 4. XRD spectra of ZrC films deposited for various times at 700 °C under vacuum.

Download English Version:

<https://daneshyari.com/en/article/1676445>

Download Persian Version:

<https://daneshyari.com/article/1676445>

[Daneshyari.com](https://daneshyari.com)