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Structural, mechanical, electrical and wetting properties of ZrN_x films deposited by Ar/N_2 vacuum arc discharge: Effect of nitrogen partial pressure

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ABSTRACT

Non-stiochiometric zirconium nitride (ZrN_x) thin films have been deposited on silicon substrates by vacuum arc discharge of (N_2 + Ar) gas mixtures at different N_2 partial pressure ratio. The microstructure, mechanical, electrical and wetting properties of these films are studied by means of X-ray diffraction (XRD), micro-Raman spectroscopy, Rutherford back scattering (RBS) technique, conventional micro-hardness testing, electrical resistivity, atomic force microscopy (AFM) and contact angle (CA) measurements. RBS results and analysis show that the (N/Zr) ratio in the film increases with increasing the N_2 partial pressure. A ZrN_x film with (Zr/N) ratio in the vicinity of stoichiometric ZrN is obtained at N_2 partial pressure of 10%. XRD and Raman results indicate that all deposited films have strained cubic crystal phase of ZrN, regardless of the N_2 partial pressure. On increasing the N_2 partial pressure, the relative intensity of (1 1 1) orientation with respect to (2 0 0) orientation is seen to decrease. The effect of N_2 partial pressure on micro-hardness and the resistivity of the deposited film is revealed and correlated to the alteration of grain size, crystallographic texture, stoichiometry and residual stress developed in the film. In particular, it is found that residual stress and nitrogen incorporation in the film play crucial role in the alteration of micro-hardness and resistivity respectively. In addition, CA and AFM results demonstrate that as N_2 partial pressure increases, both the surface hydrophobicity and roughness of the deposited film increase, leading to a significant decrease in the film surface free energy (SFE).

1. Introduction

Transition metal nitride coatings, mainly based on titanium, chromium and zirconium, are used as protective coatings against wear and corrosion [1]. Furthermore, they are widely used as optical and decorative coatings [2]. Zirconium nitrides exhibit very interesting properties such as high hardness, high melting point, high corrosion resistance [3]. Their optical, mechanical and electrical properties intensively depend on the nitrogen composition [4,5]. The stoichiometric zirconium nitride (ZrN) is metallic-like and thermodynamically stable phase with a golden yellow color. However, like TiN, the ZrN compound has a considerable range of nonstoichiometry and it is usually designated as ZrN_x. The resistivity of ZrN_x films is influenced by the nitrogen quantity embedded into the film. The resistivity of ZrN_x films varies from 15 to 200 $\mu\Omega$ cm [6], depending on the N_2 content in the film. Therefore, the connection among the resistivity, density, stoichiometry, preferred orientation, and grain size and wetting properties of ZrN_x films, as well as how these material characteristics are influenced by the nitrogen content during deposition, is remains an important issue. In particular, the effect of deposition parameters on wetting and SFE of ZrN is scarcely studied in the literature [7].

Various techniques has been utilized to synthesize ZrN_x thin films, including reactive magnetron sputtering [8–11], chemical vapor deposition (CVD) [12], pulsed laser deposition (PLD) [13], ion-beam assisted deposition (IBAD) [14], plasma nitridation [4] and vacuum arc discharge deposition [15]. Among them, reactive magnetron sputtering is the most used technique for this purpose. However, Vacuum arc discharge begins to attract more and more attention as an effective technology for the deposition of high-quality films of metals, alloys, carbon (amorphous diamond) and compounds [16,17]. This is due to its several advantages such as low voltage discharge (12–40 V), the generation of charged particles have high energy (some tens eV in the order of magnitude) [15–18], and the low effect of the reactive gas composition on the characteristics of the vacuum arc discharge during the reactive deposition [18]. It results in the formation of a denser film and it strongly reduces surface defects, such as voids and columnar growth. It provides to be an attractive method owing to its high efficiency, control of composition and structure of the films and high adhesion force between film and its substrate.

The present research work is devoted to investigate the influence of N_2 partial pressure ratio on microstructure, mechanical,

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electrical and wetting properties of ZrN_x films deposited on Si substrates by vacuum arc discharge technique.

2. Experimental details

ZrN films were prepared by vacuum arc deposition using a V-1000 "U" system from a pure zirconium metallic target. The residual pressure was lower than 3×10^{-6} Torr. Films were deposited on a Si(1 0 0) substrate in argon/nitrogen mixtures discharge with a total pressure 3 mTorr at different nitrogen partial pressure ranged from 0% to 100%. During deposition, the arc current was maintained at 150 A, and the substrate rotated continuously around the vertical central axis at chamber temperature. The crystallographic properties of the prepared films were studied by X-ray diffraction (Stoe StadiP Transmission X-ray diffractometer). The RBS analysis were performed at the 3 MV HVEE™ tandem accelerator [19] using a $^4He^+$ beam of 2.0 MeV. The Raman spectra excited by a He–Ne 20 mW laser with wavelength 632.817 nm were measured in 180° back scattering configuration at room temperature using a micro-Raman system HR 800, Jobin Yvon-Horiba. The RBS spectra were treated using the computer code SIMNRA [20]. Backscattered particles were detected at 170° using passivated ion-implanted detector with resolution of 12 keV. Micro-hardness measurements were performed using a HX-1000 micro-hardness tester with Vickers indenter at loading force varying from 15 to 75 gram force (gF) with the time of indentation kept constant at 15 s. Tescan Vega II XMU scanning electron microscope (SEM) was used for determining the thickness of the prepared samples and indentation dimensions in micro-hardness. The electrical resistivity measurements were carried out using an automated measurement set up of Keithley – 237 Source-Measure Unit (SMU).

The contact angles were obtained using the sessile drop method with OCA 15 plus, SCA 20, Data Physics Instrument GmbH. The digital drop image was processed using an image analysis system that calculated both the left and right contact angles from the shape of the drop with an accuracy of ±0.1°. Contact angles were measured for each ZrN_x film using 3 µl drops of either, double distilled water, ethylene glycol or Diiodomethane. The effect of the N_2 partial pressure ratio on the surface topography and roughness of the deposited film investigated by AFM measurements using AFM (easyScan II, Nanosurf AG, Switzerland) with 5 µm scanner in tapping mode.

3. Results and discussion

3.1. Deposition rate and RBS analysis

The thickness of deposited ZrN_x films is evaluated from SEM cross sectional observations and the variation of the deposition rate with the N_2 partial pressure is plotted in Fig. 1. A systematic decrease in the deposition rate with the increase of the N_2 partial pressure is revealed. In similarity to the general mechanism of reactive sputtering, the observed variation in the deposition rate can be explained by target poisoning by reactive gas (0%, 10–100% N_2) [21,22].

The composition and density of ZrN_x films were examined by using RBS and the result is depicted in the Fig. 2. It can be observed that the atomic concentration of nitrogen to zirconium (N/Zr) in ZrN_x films increases with increasing N_2 partial pressure during deposition. All films deposited at N_2 partial pressure above 10% contain over-stoichiometry nitrogen (N/Zr > 1), whereas the film deposited at 10% N_2 is close to stoichiometric ZrN structure with Zr/N ratio of 0.91.

3.2. Structural analysis

Fig. 3 shows XRD patterns of ZrN_x films deposited at the different N_2 partial pressure. The spectra of the film deposited in pure Ar

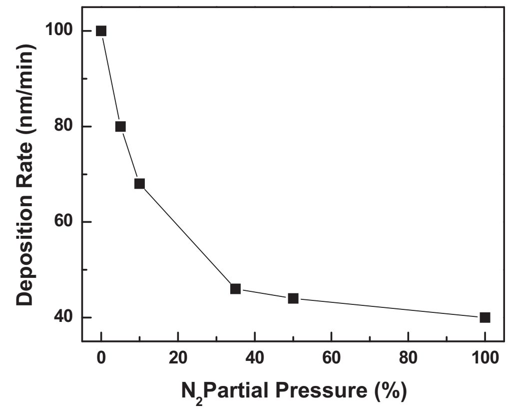

Fig. 1. Deposition rate as a function of nitrogen partial pressure (0–100%).

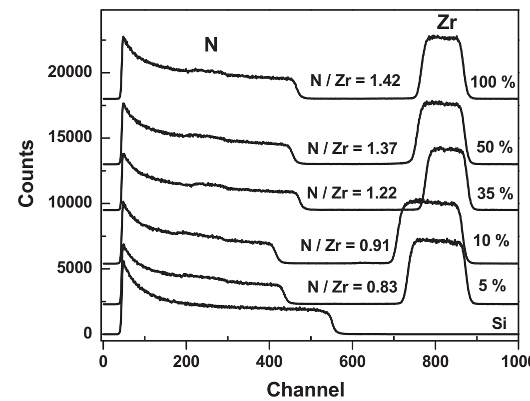

Fig. 2. RBS spectra obtained with 2 MeV $4He^+$ beam for Si substrate and ZrN_x films deposited at different N_2 partial pressure.

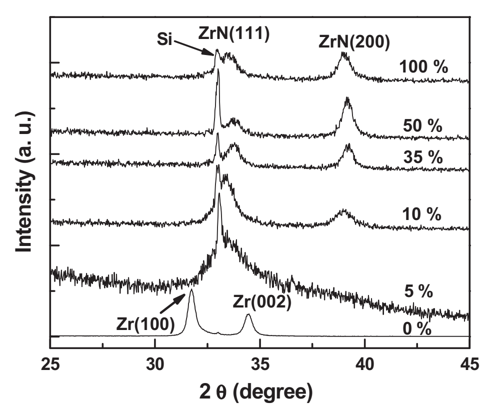

Fig. 3. XRD pattern of the ZrN_x films deposited at different N_2 partial pressure.

discharge shows two diffraction peaks at 2θ = 31.7° and 34.43° that are assigned to (1 1 1) and (2 0 0) crystallographic planes in Zr film, respectively. On introducing the nitrogen, two peaks corresponding to (1 1 1) and (2 0 0) planes of cubic ZrN crystal phase, are observed in spectra of the deposited films. The impact of N_2 partial pressure ratio on the position, broadening and relative intensity of these two peaks can be clearly observed. The relative intensity of (2 0 0) peak with respect to that of (1 1 1) peak increases with increasing N_2 partial pressure ratio in the discharge. The relative intensity $[I_r(1 1 1) = I(1 1 1)/I(1 1 1) + I_r(2 0 0)]$ and the relative area