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Structural and electrical resistivity characteristics of vacuum arc ion deposited zirconium nitride thin films

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ABSTRACT

Zirconium nitride (ZrN) thin films were grown on glass and aluminum substrates using a dual cathodic arc ion deposition technique. The effects of various negative bias voltages and flow ratios of N_2/Ar on the stoichiometric ratio of nitrogen to zirconium (N/Zr), deposition rate, structure, surface morphology and electrical resistivity of the ZrN layer were investigated. Rutherford backscattering spectroscopy measurements indicated a drop in the deposition rate and a slight increase in stoichiometric ratio (N/Zr) with the increase of bias voltage up to −400 V, although the latter still remained slightly less than unity (~0.92). Deposition rate of the film showed an increase with the argon addition. X-ray diffraction patterns depicted mostly polycrystalline nature of the films, with preferential orientation of (2 0 0) planes in the −100 V to −300 V bias voltage range. For 70–50% nitrogen and at a bias voltage of −400 V, the (1 1 1) orientation of ZrN film predominated. The films were smoother at a lower bias of −100 V, while the roughness increased slightly at a higher bias voltage possibly due to (increased) preferential re-sputtering of zirconium-rich clusters/islands. Changes in the resistivity of the films were correlated with stoichiometry, crystallographic orientation and crystalline quality.

1. Introduction

Transition metal nitrides are popular as wear and corrosion-resistant coatings. Among these, zirconium nitride (ZrN) offers relatively higher thermal stability, higher hardness, better tribological properties, lower electrical resistivity and higher corrosion resistance [1–4]. In general, an interlayer of metallic zirconium and preferential orientation of (1 1 1) are considered desirable for corrosion protection [5,6] and reduced diffusivity [7], respectively.

The energy of the incident particles/species on the growing film surface plays an important role in physical vapor deposition (PVD) processes. ZrN coatings are mostly prepared by thermal evaporation or DC magnetron sputtering. The latter is preferred for relatively higher energy of the adatoms reaching the substrate. There are numerous reports on ZrN films, prepared by DC magnetron sputtering deposition at various nitrogen conditions and bias voltages. Cathodic arc ion deposition is in many ways similar to DC magnetron sputtering, but it offers comparatively higher throughput and larger fraction of ions (in addition to the neutral species) of the target material. Particularly due to bias applied on the substrate, ions of argon and nitrogen extracted from plasma with an optimal kinetic energy, impart their energy to the surface atoms and thus enhance

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their mobility which facilitates the formation of dense and adherent coatings [8–10]. Nitrogen content in the plasma also affects the quality of ZrN film [11,12].

In the present study, thin films of ZrN have been deposited on glass/aluminum substrate with a pre-deposited Zr layer using a dual cathodic arc ion technique. The inter-metallic layer was grown for the improvement of ZrN film adhesion. The purpose of this work was to establish an empirical correlation between deposition parameters (substrate bias voltage and flow ratio of N_2/Ar) and the stoichiometric ratio, film texture (crystallographic orientation), surface morphology and electrical resistivity of ZrN film. Aluminum and glass substrates were selected to study the dependence of the films orientation on the choice of substrates.

2. Experimental

A commercial dual cathodic arc ion deposition system was employed for Zr/ZrN thin films growth. The system was equipped with two cathodes and two Kaufman ion sources as shown in a schematic diagram of Fig. 1. To get higher throughput of the depositing species/particles, both targets were utilized. The base vacuum obtained in the growth chamber was $\sim 10^{-4}$ Pa. The targets were two zirconium discs (Purity: 99.99%).

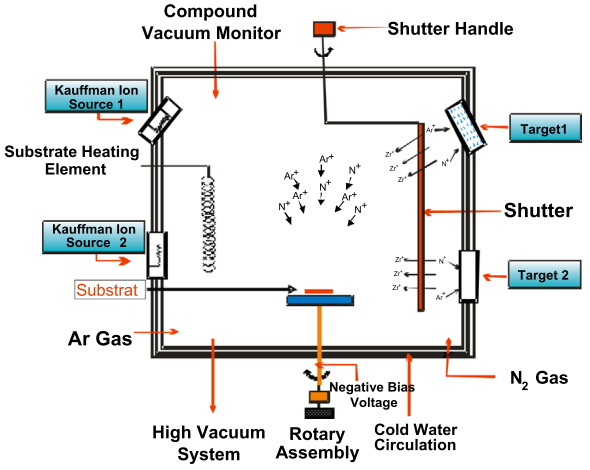

Fig. 1. Schematic diagram of the deposition chamber.

Electropolished aluminum strips and glass discs were employed as substrate. These were rinsed in de-mineralized water and acetone, followed by ultrasonic cleaning in trichloroethylene for about 15 min. Deposition temperature was measured with the help of a thermocouple attached to the base of substrate holder. To avoid/minimize contamination of growing films by oxygen and other impurities, a three-stage procedure was adopted. In first step, the chamber was evacuated and substrates were degassed at 150 °C temperature to remove adsorbed species on the substrates. Secondly, the substrates were sputter-etched for 15 min using two Kauffman argon ion sources (1 keV each). Lastly, to clean the targets surfaces, pre-sputtering of the targets in pure argon atmosphere was performed for 10 min. During pre-sputtering, the substrates were shadowed by shutter. Two series of experiments were conducted coded as series A and B as described in Table 1. In series A, pure Ar gas was injected in the synthesis chamber and its flow was adjusted at 28 sccm. The arcs were created to settle the target current and bias voltage at 80 A and −100 V, respectively. Once the parameters established and targets were cleaned, shutter from targets front was removed and metallic species were allowed to deposit on the substrate surface. Metallic thin film was grown for a period of 5 min. Temperature during film growth was maintained in a range of 80–100 °C, as it rapidly rises during film growth owing to the high throughput of a cathodic arc ion process. After the completion of metallic coating, only nitrogen (N_2) gas (flow ~90 sccm) was injected and nitride layer was prepared for a period of 15 min keeping the current, bias voltage and temperature at 80 A, −100 V and 80–100 °C, respectively. Next samples of series-A (S_2 and S_3) were grown at −300 V and −400 V substrate bias, respectively while keeping the other parameters constant. In series-B samples, nitride film was deposited under different nitrogen conditions, ranging from 100% to 15% in the deposition chamber. The bias voltage was kept at −400 V for this series.

The atomic percent compositions and thicknesses of the films were measured by means of Rutherford backscattering (RBS) spectroscopy. A collimated 2.0 MeV $4He^{+2}$ beam produced by 5UDH-2 Pelletron was used having charge of 15 μC and current 35 nA. To control the orientation of samples relative to the $4He^{+2}$ beam, these were mounted on a high precision (0.01°) five-axis goniometer in a vacuum chamber. Au–Si barrier detector collected the backscattered particles. The detection angle

Table 1
Deposition parameters constant parameter (time of deposition for ZrN layer: 15 min).

Sample #	Flow ratio $N_2/(Ar+N_2)$%	Biasing (V)	Deposition pressure (Pa)
Series A			
S_1	100	−100	2×10^{-1}
S_2	100	−300	2×10^{-1}
S_3	100	−400	2×10^{-1}
Series B			
S_3	100	−400	2×10^{-1}
S_4	70	−400	2×10^{-1}
S_5	50	−400	2×10^{-1}
S_6	22	−400	2×10^{-1}
S_7	19	−400	2×10^{-1}
S_8	15	−400	2×10^{-1}