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Studies on zirconium nitride films deposited by reactive magnetron sputtering

H. B. Bhuvaneswari[2], I. Nithiya Priya[1], R. Chandramani[3], V. Rajagopal Reddy[2], and G. Mohan Rao*[1]

[1] Department of Instrumentation, Indian Institute of Science, Bangalore 560012 India
[2] Mysore university PG centre, Hassan
[3] Bangalore University, Bangalore

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This paper deals with the preparation of Zirconium Nitride films by DC reactive magnetron sputtering. Films were deposited on silicon substrates at room temperature. Nitrogen partial pressure was varied from $4x10^{-5}$ to $10x10^{-5}$ m bar and the effect on the structural, electrical, optical properties of the films was systematically studied. The films formed at a nitrogen pressure of $6x10^{-5}$ mbar showed low electrical resistivity of $1.726x10^{-3}$ Ω.cm. The deposited films were found to be crystalline with refractive index and extinction co-efficient 1.95 and 0.4352 respectively.

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Introduction

Transition metal nitride coatings such as ZrN/TiN have been extensively studied for industrial applications, such as hard coating [1,2], diffusion barrier in semiconductor technology [3-5], optical applications for heat mirrors [6-10] and decorative coatings [11-14] because of their outstanding properties.

Many researchers have studied transition nitride coatings deposited by reactive sputtering, ion plating, arc sputtering, and electron–beam evaporation. Among these methods, dc reactive magnetron sputtering is the most commercially practiced method because of its various advantages like high deposition rates on larger area substrates, control of the film composition, small substrate temp rise during film deposition, films with better adhesion and thickness uniformity. It also minimizes target poisoning.

The physical properties of ZrN films prepared by DC magnetron sputtering mainly depend on sputtering parameters such as nitrogen partial pressure, sputtering pressure, substrate temperature, apart from target – substrate distance, sputtering power and deposition rate.

In the present study, an attempt was made to deposit ZrN films by DC reactive magnetron sputtering at various sputtering pressures and study the effect on the physical properties of the films. We have tried to optimize the process parameters to prepare ZrN films with low electrical resistivity and good optical reflectivity.

Experimental

Zirconium Nitride films were deposited by dc reactive magnetron sputtering from a pure Zirconium (99.9%) disk of 100 mm diameter, mechanically clamped to a water-cooled magnetron cathode assembly. A variable

* Corresponding author: e-mail: gmrao@isu.iisc.ernet.in

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power supply was used for controlling the glow discharge. The pumping system was a diffusion pump-rotary pump combination, capable of giving an ultimate vacuum of $2x10^{-5}$ m bar. Nitrogen (99.99%) and Argon (99.99%) have been used as reactive and sputtering gases, respectively. The pressure was monitored with a pirani – penning gauge combination calibrated against argon gas using a McLeod gauge. Thin films of Zirconium nitride were deposited on glass and p type silicon (100 orientation and resistivity- 10 ohm.cm) substrates cleaned using standard techniques prior to deposition.

The deposition parameters maintained during the preparation of ZrN films are given in the table 1. Pre-Sputtering was done for 15-30 min in pure argon to remove oxide layer that had formed on the target surface during exposure to air. After pre-sputtering, the reactive gas was introduced through a needle value and was stabilized at the desired partial pressure. The crystallographic structure of the films was analyzed with X-ray diffractometer (Siefert x-ray diffractometer) using cu-kα radiation. (λ= 1.54 A^0). Electrical resistivity of the films was measured using 4-point probe technique. Optical reflectance of the films was measured with Hitachi (330A) double beam spectrophotometer. The thickness of all the films was found out using stylus method. The refractive index (n) extinction coefficient (k) were calculated from the optical reflectance data [15]. The surface topography was studied using scanning electron microscopy.

Table 1 Sputtering parameters maintained during the deposition of ZrN films.

Deposition method	DC reactive magnetron sputtering
Sputtering target	Zirconium (99.9 percent, 100 mm dia)
Substrate to target distance	90 mm
Total gas pressure (N_2+Ar)	$5x10^{-4}$ m bar
Nitrogen partial pressure.	(4-10) x 10^{-5} m bar
Substrate temp	ambient temperature (no deliberate heating)
Cathode potential (V)	257 – 345 V
Cathode current (I)	200 m A

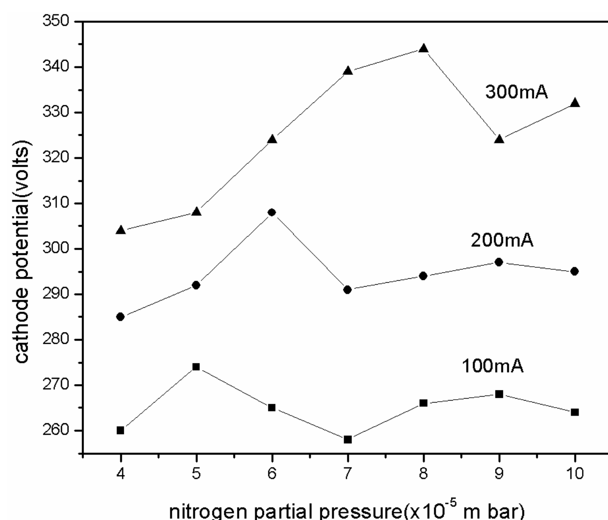

Fig. 1 Current – Voltage characteristics during reactive sputtering of Zirconium at different nitrogen partial pressures.

Results and discussion

The ZrN films prepared by DC reactive magnetron sputtering were uniform and highly adherent to the substrate. The thickness of the films investigated was in the range of 650 – 1200 Å. In a reactive sputtering process, the reactive gas pressure plays an important role on the glow discharge characteristics and on the deposition rate.

Figure 1 shows glow discharge characteristics in reactive sputtering at different partial pressures of nitrogen. It shows that the cathode potential required to achieve a particular current is a strong function of N_2

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partial pressure. The dependency shows 3 distinct regions similar to the model explained by Mohan Rao and Mohan [16]. Initially the cathode potential shows an increase up to 274 volts as the nitrogen partial pressure is increased to 5 x10^{-5}mbar. Later it is seen that cathode potential gradually decreased from 274 volts to 258 volts with increase in nitrogen partial pressure from 5x10^{-5} mbar to 7 x10^{-5} mbar. Beyond this pressure, the cathode potential increases with further increase in nitrogen partial pressure. The initial increase may be due to depletion of electrons in the glow discharge due to negative ion formation, which necessitates higher cathode potential to maintain a constant current. At higher nitrogen pressures, due to the target poisoning effects the secondary electron emission from the partially nitrided target is high and this is evident in the reduction in the cathode potential. At still higher nitrogen pressures, the conductivity of zirconium nitride, which is less than that of pure zirconium, comes into picture and thus an increase in the cathode potential is seen. The explanation is plausible when one observes that the critical nitrogen pressure at which target poisoning starts is higher at larger discharge currents. The sputtering yield of zirconium nitride is less than that of pure zirconium and this is reflected on the deposition rates as seen from the figure 2. Incidentally the above explanation on the cathode potential assumes importance when one sees that the pressure at which the deposition rate reduces is similar to the one at which cathode potential reduces, indicating the target poisoning effects.

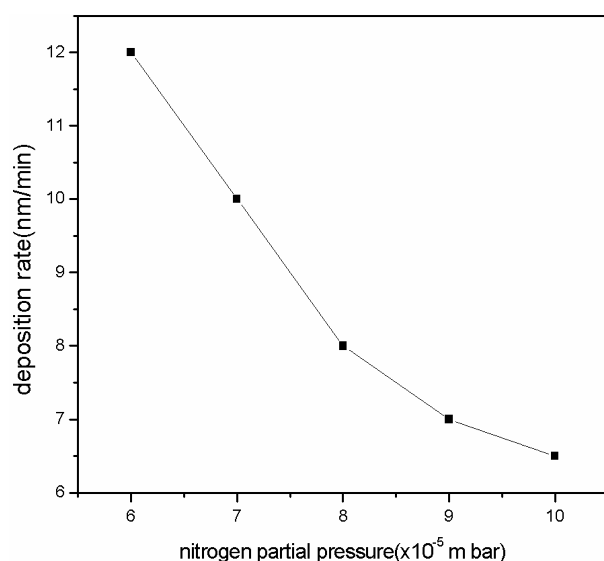

Fig. 2 Deposition rate as a function of nitrogen partial pressure.

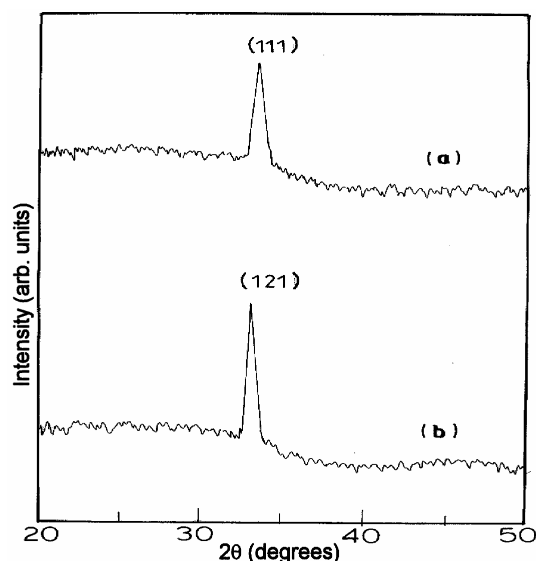

Fig. 3 X-ray diffraction pattern for ZrN films deposited at different nitrogen pressures a. 6x10^{-5} mbar and b. 7x10^{-5} mbar.

Zirconium nitride is known to exit in two different forms. One is metallic form corresponding to the composition of ZrN and Zr_2N, where as, Zr_3N_4 is an insulating form. Fig 3 shows the X-ray diffraction data for the films prepared at partial pressure of 6 - 7 x10^{-5} m bar. Films formed at lower partial pressure (less than 5x10^{-5} mbar did not show the formation of ZrN but indicated only Zirconium phase. Films formed beyond 6 x10^{-5} m bar showed ZrN peaks corresponding to 121 and 111 phases.

Variation of electrical resistivity (ρ) of film is as shown in figure 4. The electrical resistivity of the films formed at a pressure of 6x10^{-5} m bar was found to be 1.726x10^{-3} Ω cm. As N_2 partial pressure was increased to 8x10^{-5} m bar, 'ρ' increased to a value of 48.28x10^{-3}Ω cm. At low N_2 partial pressures, the sputtered Zirconium atoms can reach the substrate with less collision, resulting to a slightly high Zirconium content in films, which leads to low electrical resistivity. As the nitrogen partial pressure is increased, the reactivity between Zr and N_2 increases, resulting in compound formation on the substrate.

The good electrical resistivity of the films can be due to free electrons, which are characteristics of a good conducting sample. The resistivity values are quite similar to those reported in literature [17,18].

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The optical constants for ZrN films have been calculated using the optical reflectance data using the relation [15];

$$\lambda_{max} = 2n_1 t/m \quad \text{for conditions, } n_0 < n_1 < n_2$$

Where n_0 , $n_1 n_2$ are refractive index of air, film and substrate and m is the order of reflectance maxima.

The extinction coefficient 'k' of the film was calculated using the relation

$$k = \lambda\alpha/4\Pi$$

Where

$$\alpha = 2.303/t \log(1/R)$$

α is the absorption coefficient, R is the percentage of reflectance and t is the thickness of the film.

The refractive index and extinction coefficient were found to be 1.95 and 0.4352 respectively for the films deposited at a nitrogen partial pressure of 6×10^{-5} mbar. These values agree well with those reported by Straboni etal [17,18] for zirconium nitride films prepared by dual ion beam sputtering technique.

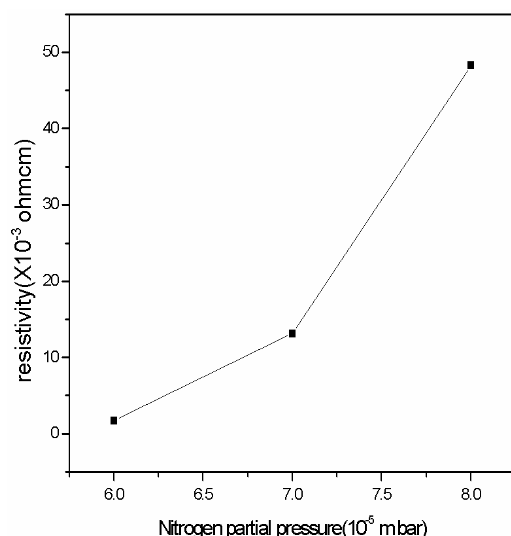

Fig. 4 Electrical resistivity of ZrN films as a function of nitrogen pressure.

Conclusions

ZrN films were prepared onto glass and silicon substrates by dc reactive magnetron sputtering technique using metallic Zirconium target in an argon and Nitrogen atmosphere. A systematic study was made on the influence of partial pressure of N_2 partial pressure. Structural studies revealed that the films were crystalline in nature with 111 and 121 orientation. Electrical resistivity increased from 1.726×10^{-3} to 48.28×10^{-3} ohm.cm with increase in nitrogen pressure from 6 to 8×10^{-5} mbar. The refractive index and the extinction coefficient are 1.95and 0.43 respectively. Further studies are in progress to study the zirconium nitride coating as a conducting layer in schottky devices and MOS structures.

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