

Effect of nitrogen flow ratio on structure and properties of zirconium nitride films on Si(100) prepared by ion beam sputtering

SHAHAB NOROUZIAN^{1,2,*}, MAJID MOJTAHEDZADEH LARIJANI³ and REZA AFZALZADEH²

¹Physics Department, Iran University of Science and Technology, P.O. Box 16765-163, Tehran, Iran

²Physics Department, K. N. Toosi University of Technology, P.O. Box 16315-1618, Tehran, Iran

³Agricultural, Medical and Industrial Research School, P.O. Box 31485-498, Karaj, Iran

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Abstract. In this study, zirconium nitride thin films were deposited on Si substrates by ion beam sputtering (IBS). Influence of $N_2/(N_2+Ar)$ on the structural and physical properties of the films has been investigated with respect to the atomic ratio between nitrogen and zirconium. It was found that the thickness of layers decreased by increasing the $F(N_2)$. Moreover, crystalline plane peaks such as (111), (200) and (220) with (111) preferred orientation were observed due to strain energy which associate with (111) orientation in ZrN. Also, the fluctuation in nitrogen flow ratio results in colour and electrical resistivity of films.

Keywords. Zirconium nitride; ion beam sputtering; reactive; flow ratio.

1. Introduction

The fourth-column transition metal mono-nitrides have interesting properties resulting from their exhibition of both covalent and metallic bonding characteristics. Covalent crystalline properties are high melting points, extreme hardness and brittleness and excellent thermal and chemical inertness (Hubler *et al* 2001; Rodriguez *et al* 2002). The metallic characteristics are electrical conductivity and metallic reflectance. A gold-like appearance results from high reflectance of the materials at the red-end of the visible spectrum with low reflectance near the ultraviolet region (Schlegel *et al* 1977). The reflectance spectrum is a specific property of these materials. Zirconium nitride is a memorable ceramic with cubic (rock-salt) structure that its good mechanical, electrical and optical properties have attracted many researchers in the last few decades. This is because of various applications such as hard and refractory coatings with resistance against wear, fatigue and corrosion in industry and medicine, and also, it can be employed as an alternative to gold in decorative coatings due to its golden colour (Constantin and Miremad 1999; Streit *et al* 2003; Westlinder *et al* 2005). In this work, ion beam sputtering method used for deposition of Zirconium nitride on Si substrate with various $N_2/(N_2+Ar)$ flow ratios and physical and structural properties of films have been investigated.

2. Experimental

2.1 Sample preparation

Silicon wafers, Si(100), polished on one side, with 5 Ω cm electrical resistant were ultrasonically cleaned in ethanol at RT for 5 min and then immediately washed in acetone (C_3H_6O) and dried with clean hot air prior to loading into the deposition chamber. The target was zirconium plate with 99.999% purity which was deposited under conditions reported in our previous study (Larijani *et al* 2009). The coating chamber was evacuated to a base pressure of 1.2×10^{-3} Pa. Sputtering was commenced by introducing pure Ar (% 99.999) and N_2 (% 99.999) gas into the chamber. The working pressure was kept constant at 2.3×10^{-3} Pa and the total flow rate of (Ar + N_2) mixed gas was maintained at 60 sccm. The ions of Ar and N_2 were accelerated toward the target with a fixed energy of 2.2 keV and current density of 1.5 mA/cm² throughout the experiments. The substrate temperature during deposition was 400 °C. All experimental conditions were repeated for six times by the corresponding variation of $N_2/(N_2+Ar)$ flow ratio ($F(N_2)$).

2.2 Characteristic measurement

The thicknesses and composition of the films were determined using Rutherford backscattering (RBS) analysis with energy spectra of 1.5 MeV He^+ . The ion beam impinges on the sample surface at normal incidence and backscattered at a detection angle of 165° from ZrN films. RBS data obtained by studding films were analysed using SIMNRA software. The structural characteristics of the obtained samples were revealed by X-ray diffraction (XRD), Philips PW1800 at

*Author for correspondence (sh.norouzian@yahoo.com)

40 kV voltage and 30 mA current in the 2θ range from 30–65°. The morphology of films has been observed by scanning electronic microscopy (SEM) measurement. The reflected light was measured and characterized by Carry-5000 spectrophotometer and electrical resistance of films evaluated by four-point-probe technique.

3. Results and discussion

3.1 Structure

The thickness of films obtained from the Rutherford backscattering spectroscopy (RBS) measurements has been illustrated in table 1.

As shown in table 1, thickness of layers was decreased by increasing the $F(N_2)$. The ratio of sputtered atoms is related to the number of incident atoms and their mass (Wasa *et al* 2004). Increasing in flow ratio ($F(N_2)$) leads to Ar atoms decreasing and as a result, the deposition rate is decreased. Also, this effect may be due to the interaction of target by nitrogen ions and, consequently, the formation of zirconium nitride at the target surface which has less sputtering yield than pure Zr (Huang *et al* 2002). This behaviour had been observed in our previous work over SS304 substrates (Larijani *et al* 2009).

At high flow ratio, sample S_6 , the film will be amorphous. This can be explained by the absence of stable phases in the nitrogen-rich zone of ZrN system or by the influence of deposition parameters and substrate nature on film structure (Benia *et al* 2002).

The peaks of Ar in RBS spectra were detected and shown in figure 1. It may be due to implantation of the Ar ions into the surface during film deposition.

X-ray diffraction (XRD) results are presented in a graph in figure 2. In this figure, different crystalline plane peaks can be observed such as (111), (200) and (220). The preferred orientation is (111) for all samples, except sample S_1 . This fact can be explained by the model suggested by Pelleg and coworkers (1991), confirmed later by Greene *et al* (1995). The preferential orientation is determined by competition between two thermodynamic parameters: the surface free energy and strain energy.

According to Williamson and Hall analysis, microstrain (η) in film is dependant on the magnitude of peak broadening (Birkholz 2006):

$$FWHM = \frac{0.9\lambda}{D \cos \theta} + \eta \tan \theta, \quad (1)$$

Table 1. Thickness and packing factor of films for different $F(N_2)$.

Sample	S_1	S_2	S_3	S_4	S_5	S_6
$(N_2/(N_2+Ar)\%)$	10	15	25	50	65	80
Thickness (μm)	3.84	3.63	3.50	3.25	3.15	1.45

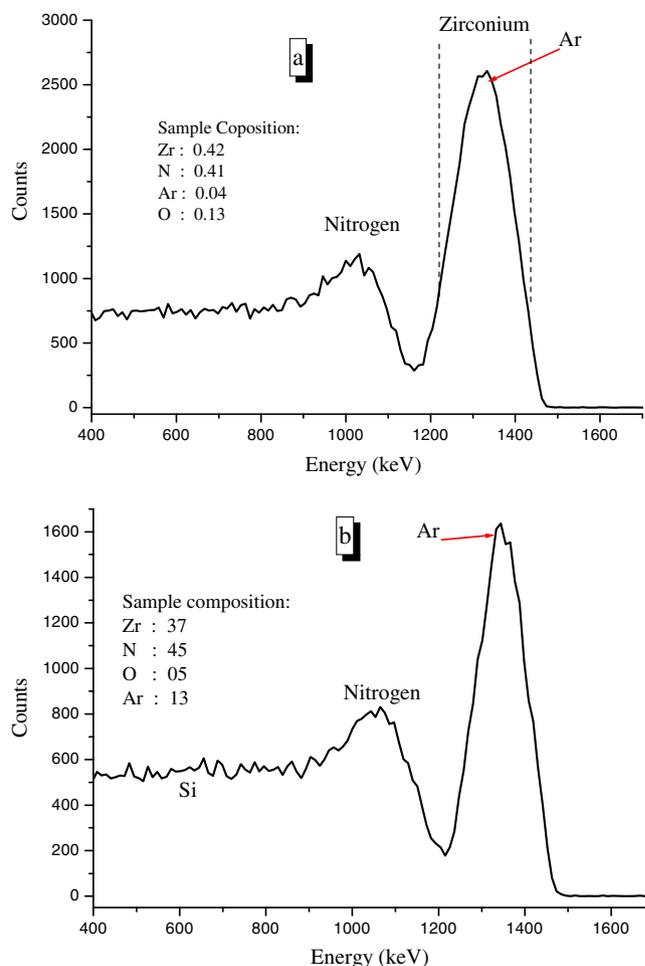


Figure 1. Typical Rutherford backscattering spectrum of ZrN films: a. $F(N_2)=15$ and b. $F(N_2)=65$.

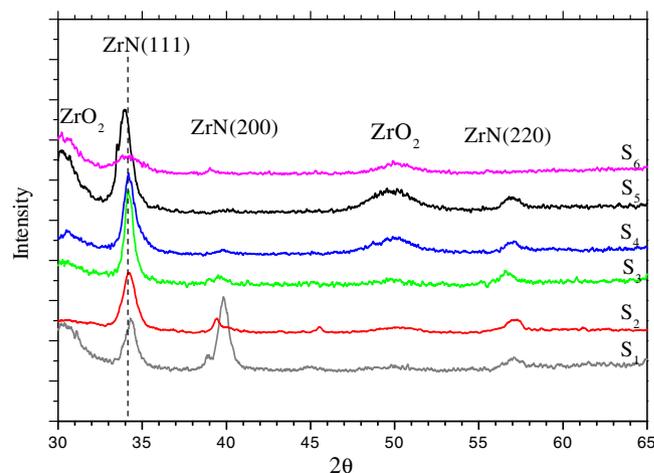


Figure 2. X-ray diffraction patterns of ZrN films.

where λ is X-ray wavelength (1.54 Å) and D the average grain size in sample. For ZrN, the strain energy associated with (111) plane similar to S_4 sample is about 2-4, which is greater than surface energy associated with (200) plane. The

shift in Zr (111) in sample S5 and widening of the corresponding diffraction line, an expansion of the reticular constant due to implantation of Ar atoms in the layer and also an interstitial atom of nitrogen dissolved in a lattice are seen.

Meanwhile, crystalline peak of ZrO₂ appearing in the structure may be attributed to oxygen impurity in the Ar or N₂ gas sources or residual gas in the chamber.

3.2 Electrical properties

Electrical characteristics of films were investigated by measuring electrical resistivity of all samples and using the four-point-probe method. Figure 3 shows electrical resistivity as a function of nitrogen flow ratio, F(N₂). The sample's resistivity increases by intensifying the F(N₂), especially when the flow ratio is greater than 50% (figure 3).

Since F(N₂) varies from 10 to 65%, the resistivity increases from $21 \times 10^{-4} \Omega\text{cm}$ to $115 \times 10^{-4} \Omega\text{cm}$. As a result, for stoichiometric ZrN, all the 2*p* states of the nitrogen atoms (N:1*s*²2*s*²2*p*³) which are entirely situated below the Fermi level filled with three of four electrons in the 4*d* and 5*s* states of zirconium atoms (Zr:[Kr]4*d*²5*s*²). If more nitrogen atoms are introduced in the ZrN_{*x*} structure, more 2*p* states will be filled. Therefore, film resistivity will be enhanced. Furthermore, putting more nitrogen atoms in the ZrN_{*x*} structure (at the flow ratio above 65%) changes the stoichiometry of films and causes further scattering by introducing more disorder (structural defects, dislocations, etc) (Larijani *et al* 2006). This change also causes the resistivity to increase. Moreover, with increasing nitrogen flow, the stoi-

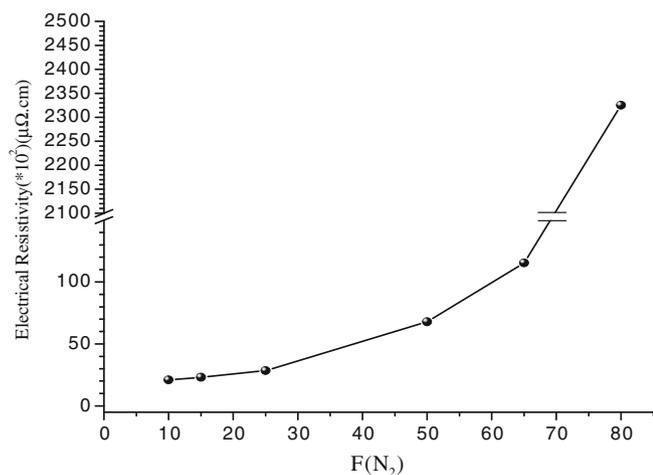


Figure 3. Electrical resistivity of ZrN films as a function of nitrogen flow.

chiometric ZrN would be changed by incorporation of nitrogen atoms in interstitial sites and formation of other phases like Zr₃N₄, when the nitrogen atoms relax in response to the Zr vacancy, nature of the inter-atomic interactions is significantly changed and the lattice constant slightly expanded resulting in insulating behaviour (Ching *et al* 2002).

4. Conclusions

The variation of nitrogen flow ratio changes the thickness, colour, electrical resistivity and reflectance of ZrN films. In this study, thickness of layers was decreased by increasing the F(N₂), it can be due to reducing Ar atoms as sputtering atoms and composition of nitrogen and Zr ions at the target surface. The preferred orientation of films from X-ray diffraction analysis was (111), the strain energy causes growth in (111) plane direction. The number of free electrons in the layers could be decreased by increment in nitrogen flow ratio, so electrical conductance of the film have been reduced which also caused colour change in the film.

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