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Effect of Nitrogen Flow Rates on Phase Transformation Structures of ZrN Thin Film Deposited by Reactive Magnetron Sputtering

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ABSTRACT

Zirconium nitride has outstanding properties as high hardness, high refractive index, high thermal and chemical stability and low electrical resistivity. It has been widely applied as hard and protective coating on mechanical tools, decorative coating and diffusion barrier in the microelectronic industry. In this research, the phase transformation structures of zirconium nitride thin films were prepared by a reactive DC magnetron sputtering system. In the procedure, the nitrogen gas (N_2) was applied onto zirconium (Zr) deposited on unheated silicon wafer (100). Thus zirconium nitride thin film was deposited at N_2 flow rates in the range of 1.0 to 4.0 sccm, with argon flow rate of 6 sccm. The sputtering current and deposition time were set at 0.6 A for 15 minutes. The structures, microstructures and thickness of the deposited film were characterized by X-ray diffraction (XRD), Raman spectroscopy, and Atomic Force Microscopy (AFM). The XRD results revealed that the structures of zirconium nitride films deposited at N_2 flow rates of 1.0, 2.0, 3.0-4.0 sccm were ZrN, Zr_3N_4 and its amorphous, respectively. The AFM results showed the average film thickness was acceptable in that it was varied from 94.0 to 228.1 nm when N_2 flow rates were oppositely varied from 1.0 to 4.0 sccm. From overall, this study will further help to predict and control the reliable phase transformation structures of zirconium nitride.

Key words: Zirconium nitride; Phase transformation; DC magnetron sputtering; X-ray diffraction pattern.

INTRODUCTION

Zirconium nitride has been recognized as prominent material of high hardness, exceptional thermal and chemical stability with a low electrical resistivity. Thus, it has been widely employed as protective and decorative coating and a diffusion barrier in microelectronics industry. In general, there are many methods to fabricate Zirconium nitride film such as ion beam-assisted method [2], cathodic arc evaporation method [5], sputtering method [6], etc. Among these methods, reactive magnetron sputtering has a very important method because the stoichiometry of the deposited film can be controlled and a metal target can be used. In addition, it is one of the simplest methods and is widely used in industry. The previous literature, effect of the sputtering reactive gas mixture between sputtering and reactive gas reactive magnetron sputtering on several structures of Zirconium nitride film was investigated [1,3,4]. However, there is no investigation and understand about the effect of sputtering parameters on the film structure and morphology. Thus in this work, the effects of nitrogen flow rate on the structure and morphology of thin film deposited at a fixed high argon flow rate were studied.

Materials and Methods

Zirconium nitride thin films were deposited on Si wafer (100) using home-built DC unbalanced magnetron sputtering system. The vacuum chamber has diameter of 310 mm and height of 370 mm. Metallic zirconium with purity of 99.99% and a diameter of 3 inch was used as a sputtering target. The base pressure of deposition chamber was about 5 x 10^{-5} mbar. Ar (99.99% purity) and N_2 (99.99% purity) were used as sputtering and reactive gases, respectively. The zirconium target was initially sputtered for 6 min to remove the surface oxide after reaching the base pressure. The Ar gas flow rate is 6

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sccm, monitored with pressure gauge. The flow rate of N_2 was varied in the range of 0.0 sccm to 6.0 sccm, as the parameter for observing structure and morphology of the film. The deposition current and deposition time were kept constant at 0.6 A and 15 minute, respectively. Crystal structure of films was characterized by X-ray diffraction technique with Cu-K_α radiation (λ=1.54056Å) and XRD patterns were recorded at grazing incidence angle (3°) in the 2θ range of the 20º- 60º with a scan rate of 0.02º. The thickness and morphology of films were analyzed using atomic force microscopy (NanoScope III) in a tapping mode.

Results and Discussions

The crystallinity and structure of zirconium nitride film system were investigated by X-ray diffraction measurements. Fig. 1 shows X-ray diffraction pattern of the zirconium nitride film system grown on Si(100) substrates. The XRD results indicate differences of structural formations of the film from α-Zr, α-$ZrN_{0.28}$, ZrN, Zr_3N_4 and to amorphous with increasing of N_2 flow rate. At 0.0 sccm, the film is in α- Zr phase of hexagonal structure. The formation of $ZrN_{0.28}$ was detected at 0.6 sccm. The intensity peak of α-$ZrN_{0.28}$ phase disappeared for the N_2 flow rate 0.9 sccm, and the structure is the ZrN in (111) plane. As the flow rate was increased to 1.2 sccm, the two orientations in (111) and (200) planes of ZrN phase were formed. These planes remain as the structures of the films with decreasing in intensity until the N_2 flow rate was up to 1.5 sccm. At 2.0 sccm, ZrN phase completely disappeared and the formation of Zr_3N_4 phase was detected instead. Finally, the occurrences of amorphous structure were detected for the N_2 flow rate above to 3.0 sccm.

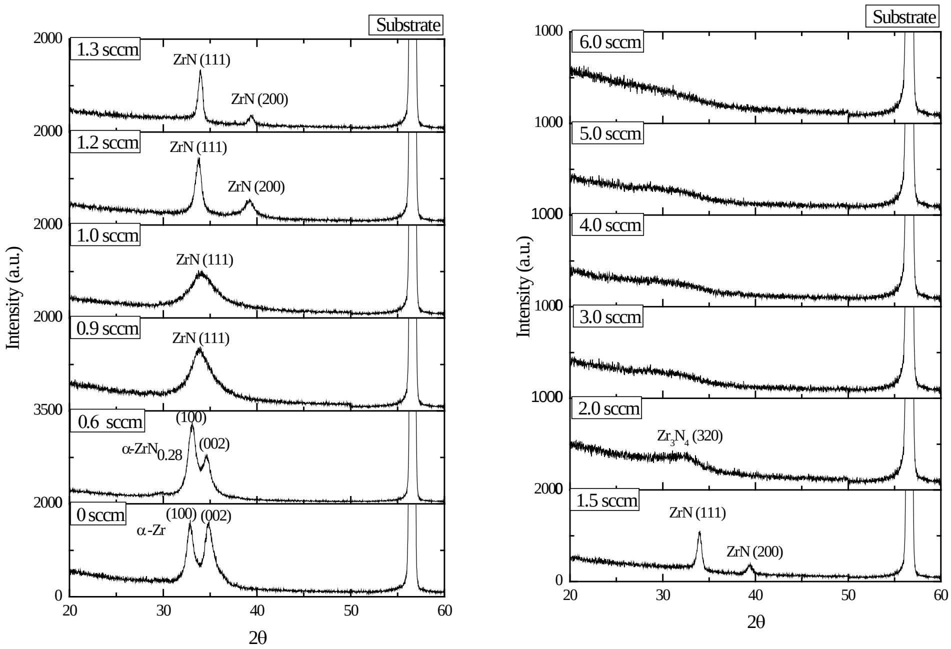

Fig. 1: X-ray diffraction patterns for Zr-N films deposited with various N2 flow rates at Zr current of 0.6 A and deposition time of 15 minutes.

The AFM technique was used to study the surface morphology such as roughness, grain size and measure the thickness of the films. Figure 2 show the three – dimensional images of zirconium nitride thin films as a function of N_2 flow rate. The results show that the variation of root-mean-square roughness (r.m.s.) and grain size relate with variation of structure as presented in Table 1.

The thickness of zirconium nitride films was measured from the section analysis of 2D-AFM images. Figure 3 shows a typical film thickness analysis of zirconium nitride films deposited at a sputtering current of 0.6 A and a deposition time of 15 min. Three values of the film thickness were measured by scanning the tip of AFM at three different areas, shown in Figure.3, and the results are shown in Table 1. It was found that the average film thickness increased with increasing N_2 flow rates and varied from a minimum value of 85.6 nm to a maximum value of 276.0 nm.

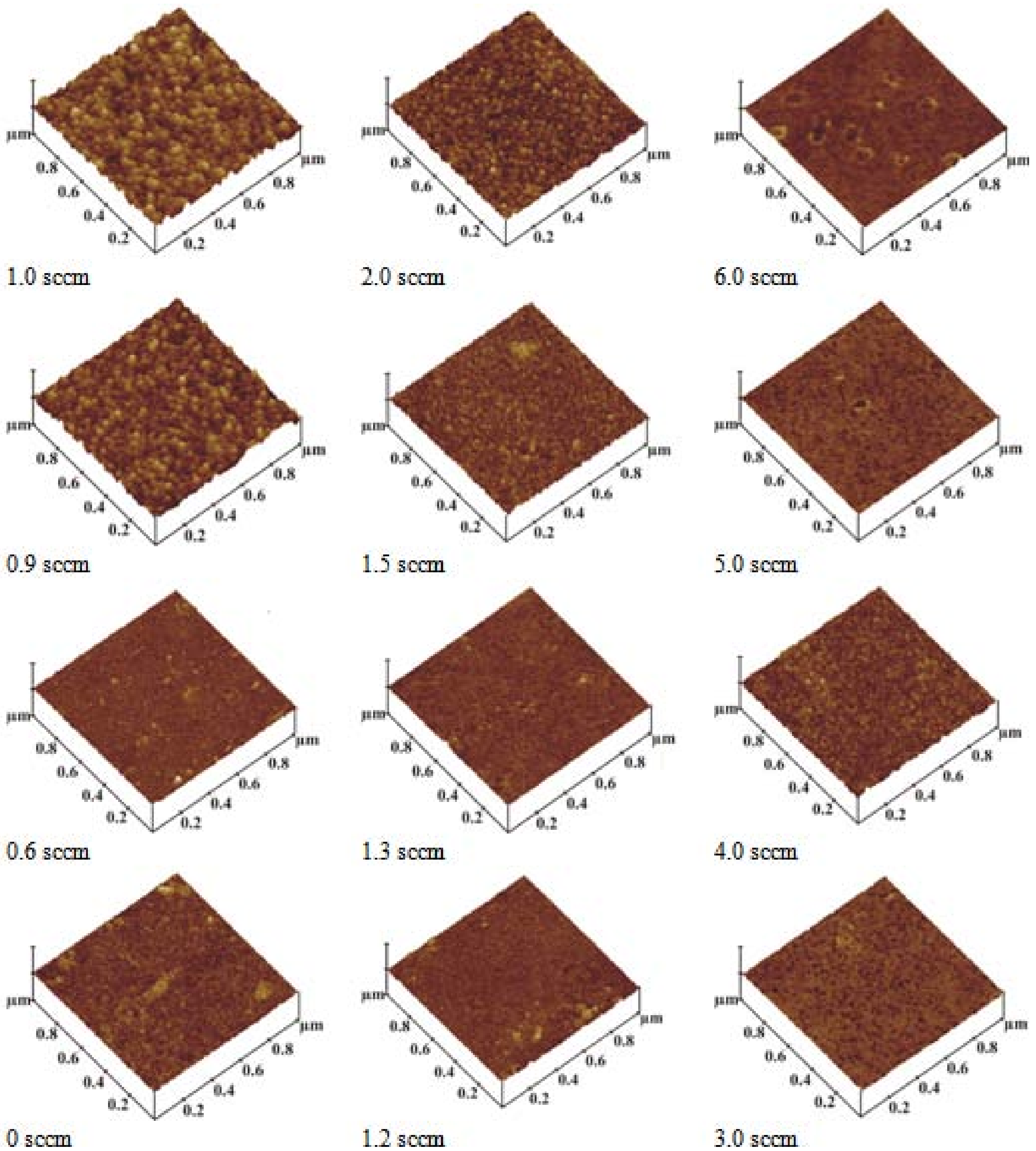

Fig. 2: Surface morphologies of zirconium nitride films (3D images) deposited with various N_2 flow rates at Zr current of 0.6 A and deposition time of 15 minutes.

Table 1: Variation of structure, thickness, roughness and grain size of zirconium nitride film system deposited with different N_2 flow rates.

No.	N_2 Flow Rate (sccm)	structure	thickness (nm)	roughness r.m.s. (nm)	grain size (nm)
1	0	α-Zr	276.0	2.45	33.99
2	0.6	α-$ZrN_{0.28}$	264.7	1.92	25.49
3	0.9	ZrN	246.8	0.74	16.01
4	1.0	ZrN	228.1	0.77	16.01
5	1.2	ZrN	179.5	1.50	17.97
6	1.3	ZrN	148.2	1.27	12.42
7	1.5	ZrN	135.8	1.30	10.78
8	2.0	Zr_3N_4	106.5	0.76	13.48
9	3.0	amorphous	99.5	0.52	11.44
10	4.0	amorphous	94.0	0.66	11.07
11	5.0	amorphous	88.3	0.51	9.48
12	6.0	amorphous	85.6	0.42	10.78

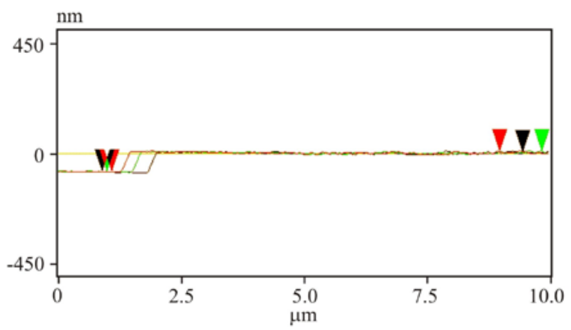

Fig. 3: Section analysis of zirconium nitride films at a constant sputtering current of 0.6 A and a deposition time of 15 min.

Variation of structure, thickness, roughness and grain size of zirconium nitride film system deposited with different N_2 flow rates are shown in the Table 1. When the N_2 flow rate fed into the chamber is 0.0 sccm, the roughness and grain size of film are 2.45 nm and 33.09 nm, respectively. The staring structure shows α-Zr of the Zirconium target. The structure change of α-Zr into α-$ZrN_{0.28}$ is found at the N_2 flow rate of 0.6 sccm with roughness and grain size of 1.92 nm and 25.49 nm. At the N_2 flow rate of 0.9-1.0 sccm, the occurrence of ZrN phase in (111) plane was detected with the little roughness and grain size in the interval of 0.7 and 1.6 nm, respectively. The ZrN phase with the (111) and (200) planes are revealed at the N_2 flow rate of 1.2-1.5 sccm. The values of roughness and grain size are found to be higher with increased the N_2 flow rate at this rate. Occurrence of Zr_3N_4 phase at N_2 flow rate of 2.0 sccm was presented with the smooth of the film with the roughness and grain size as 0.76 nm and 13.48 nm, respectively.

Finally, at the N_2 flow rate of 3.0 sccm and above the amorphous structure is revealed with the roughness and grain size in the range of 0.51-0.66 nm and 9.48-11.44 nm, respectively.

Conclusion:

In the present investigation, Zirconium nitride thin films were deposited on Si wafer (100) using home-built DC unbalanced magnetron sputtering system. The effects of nitrogen flow rate on the structure and morphology of thin film deposited at a fixed high argon flow rate were investigated. The structural formations of the film from α-Zr to α-$ZrN_{0.28}$, ZrN, Zr_3N_4 and amorphous confirmed by XRD are found with increased N_2 flow rate from 0.0 to 6.0 sccm. The surface morphology such as roughness, grain size and the thickness of the films are evaluated by AFM technique. Thickness of the films, determined by line scan at three different areas, is increased with increased N_2 flow rates. Variations of roughness and grain size correspond to the structural change of zirconium nitride thin film from α-Zr to α-$ZrN_{0.28}$, ZrN, Zr_3N_4 and amorphous, respectively.

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