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Variation of color in Zirconium nitride thin films prepared at high Ar flow rates with reactive dc magnetron sputtering

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Abstract

This study is to evaluate a color variation of the zirconium nitride thin film deposited at N_2 flow rates in the range of 0.0 to 6.0 sccm, whereas the high Ar flow rate is fixed at 6 sccm. The thin films were deposited on unheated silicon wafer (100) with a reactive DC magnetron sputtering. The deposition current and deposition time were 0.6 A and 15 minutes, respectively. The color of films was measured using a spectrophotometer on CIE L*a*b* color index. The surface morphology and thickness of the films were investigated by atomic force microscopy (AFM). The structure was characterized by X-ray diffraction (XRD). The XRD results reveal the structures changes of film system from α-Zr, α-$ZrN_{0.28}$, ZrN, Zr_3N_4 and finally amorphous with the increasing of N_2 flow rate. The average film thickness was varied from a minimum value of 85.8 nm to a maximum value of 276.0 nm. In the study, colors of the deposited film were changed from silver, dark brown, brown and to blue. Interestingly, it was found that no golden color zirconium nitride film were obtained under the interested conditions.

Keyword: Zirconium nitride; Reactive sputtering; Thin film

1. 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

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methods to fabricate Zirconium nitride film such as ion beam-assisted method [2], cathodic arc evaporation method [3], sputtering method [4], etc. However, among of these methods, reactive magnetron sputtering can change chemical compositions to obtain several structures of the deposited film such as ZrN, Zr_2N, Zr_3N_4 and ZrN_2 [5] via the control the sputtering reactive gas mixture between sputtering and reactive gas, which several beginners may face with the problem on controlling such conditions, i.e. how to choose gas mixture ratio for the perspective condition, e.g. Zr_3N_4.

In addition, many researchers reported the effect of the reactive gas flow rate, such as nitrogen, on chemical compositions and color of the film [3-6]. However, no one has a clear point on the relationship between color and such chemical compositions. In part, instead of determining the chemical composition of the film using X-ray diffraction technique, we believe that color of the films may be another way capable of indicating the film structure such as a gold film refers to ZrN [3-4, 6].

Thus in this work, the effects of nitrogen flow rate on the color of thin film deposited at a fixed high argon flow rate were studied. The colors of the films in relation to the structure were reported as a novel technique for identifying the film structure. This parameter obtained also could be very useful in decorative coating applications which may require specific.

2. Experimental procedures

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 5×10^{-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 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 color variation 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=1.54056 Å) 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 of films was analyzed using atomic force microscopy (NanoScope III) in a tapping mode. A spectrophotometer (UV-VIS-NIR 3100 Shimadzu) was employed for the color measurement at room temperature in the wavelength range of 380-780 nm. The films deposited on Si wafer were measured in the CIE L*a*b* color system (see Fig. 2), whose coordinates are L*, a* and b*, respectively. The L* axis, indicating lightness, runs from top to bottom. The maximum value of L* is 100, representing a perfect reflecting diffuser. Its minimum value is zero, which represents black. The a* and b* axes have no specific numerical limits. However, the positive value of a* refers to red, whereas its negative value refers to green. Also, the positive value of b* indicates yellow, but its negative value indicates blue.

3. Results and discussions

The colors of zirconium nitride film deposited on Si (100) substrates at different N_2 flow rates, while kept the Ar flow rate at a fixing value of 6 sccm. Fig. 1 shows examples of the films having different colors. The colors are silver, dark brown, yellow and dark blue for the N_2 flow rates of 0, 1.5, 2.0 and 6.0 sccm, respectively.

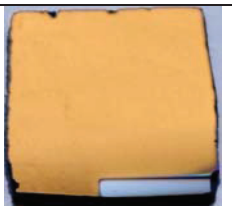
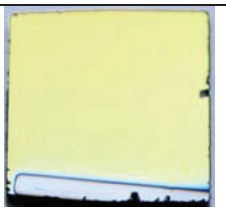
silver	brown	green- yellow	dark blue
			
N_2 = 0.0 sccm	N_2 = 1.5 sccm	N_2 = 2.0 sccm	N_2 = 6.0 sccm

Fig. 1. Color variation of zirconium nitride films. At N_2 flow rates of 0.0, 1.5, 2.0 and 6.0 sccm, the film colors are silver, dark brown, yellow and dark blue, respectively

Fig.2 shows the relations between lightness and color of the film (in the CIE L*a*b* color system) and the N_2 flow rates. When the N_2 flow rate is at 0 and 0.6 sccm, the film exhibited a silver color, corresponding to table 1 with the lightness (L*) of 82 and 85. At the flow rate of 0.9, 1.0 and 1.2 sccm, the lightness of the film was increased to 93, 91 and 87 relating with more intense of pale yellow, respectively. The films exhibited dark brown color with the N_2 flow rate of 1.3-1.5 sccm. As the flow rate is up to 2.0 sccm, the film shows yellow with the lightness of 90. At flow rate above 2.0 sccm, a decreasing trend of lightness occurs and its color turns to more dark blue and with decreasing lightness. Interestingly, the results found that the golden color is not evident in the N_2 flow rate of 0 - 6.0 sccm while the Ar flow rate was fixed at 6.0 sccm.

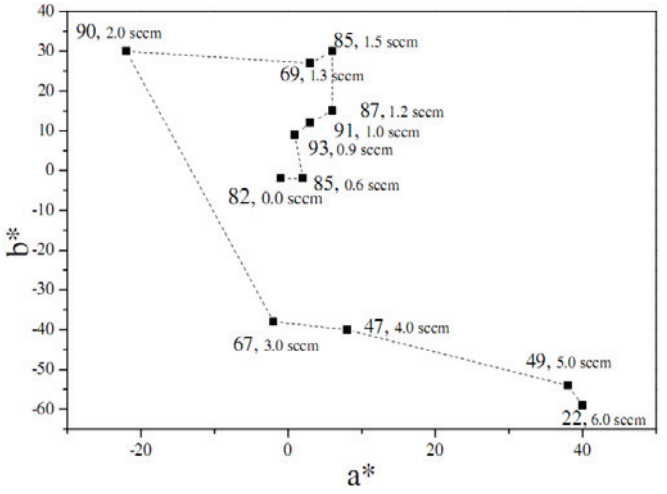


Fig. 2. Color of the zirconium nitride films in CIE L*a*b* color index in two dimensions of zirconium nitride film system. The given numbers of each point represent the value of lightness (L*) and N_2 gas flow rate

The crystallinity and structure of zirconium nitride film system were investigated by X-ray diffraction measurements. Figure 3 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 was 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.

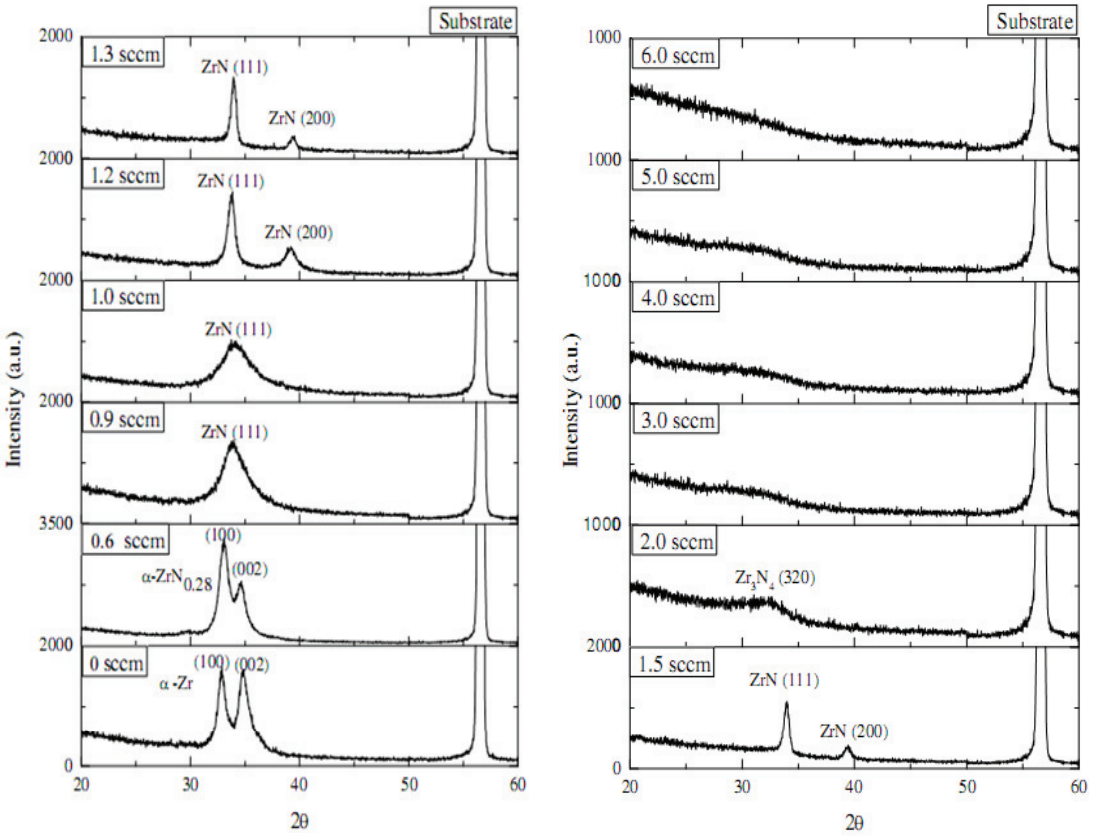


Fig. 3. X-ray diffraction patterns for Zr-N films deposited with various N_2 flow rates at Zr current of 0.6 A and deposition time of 15 minutes

From the summarized results in the table 1, when the N_2 flow rate is 0.0 sccm, or no nitrogen is fed into the chamber, color of film is silver and exhibited the structure as α –Zr which is the color of Zirconium target. Color of α-$ZrN_{0.28}$ formed at the N_2 flow rate of 0.6 sccm is similar to that of Zirconium target. At the N_2 flow rate of 0.9-1.2 sccm, the occurrence of ZrN phase in (111) plane was detected with the color of the film show in pale yellow. With the N_2 flow rate of 1.3-1.5 sccm, the (111) and (200) planes of ZrN phase revealed with dark brown color. Occurrence of Zr_3N_4 phase at N_2 flow rate of 2.0 sccm was presented with the yellow color of the film. Finally, the amorphous structure was shown at the N_2 flow rate of 3.0 sccm with films in blue color and it's color become darker blue for N_2 flow rate beyond 3 sccm.

It should be noted that, above 2.0 sccm, the color of films are not easily identified with the film structure because many factors can affecting the film color such as thickness, contamination of oxygen, etc. In addition, the average film thickness was varied from 276.0 to 85.6 nm decreasing with higher N_2 gas flow rate. The average thickness of each film was calculated from three different areas of AFM

scanning. The decreasing of deposition rate with increasing of N2 gas flow rate corresponds with previous studies [7].

Table 1. Variation of thickness, observed color, and structure of zirconium nitride film system deposited with different N_2 flow rates

No.	N_2 flow rate (sccm)	average thickness (nm)	observed color	structure
1	0.0	276.0	silver	α –Zr
2	0.6	264.7	silver	α – $ZrN_{0.28}$
3	0.9	246.8	pale yellow	ZrN
4	1.0	228.1	pale yellow	ZrN
5	1.2	179.5	pale yellow	ZrN
6	1.3	148.2	dark brown	ZrN
7	1.5	135.8	dark brown	ZrN
8	2.0	106.5	yellow	Zr_3N_4
9	3.0	99.5	blue	amorphous
10	4.0	94.0	blue	amorphous
11	5.0	88.3	dark blue	amorphous
12	6.0	85.6	dark blue	amorphous

4. Conclusion

Colors of the zirconium nitride film, prepared on Si (100) substrates, were changed from silver, pale yellow, dark brown, blue to dark blue, when N_2 flow rate further increases. Each color of the film may be potential for indicating the film structure in zirconium nitride film system. For example, silver refers to α-Zr or α-$ZrN_{0.28}$. Pale yellow and brown refer to ZrN. Although the relationship between color and structure of the film of the N_2 flow rate above 2.0 sccm is limited due to many parameters affecting, we can roughly say that yellow and blue refer to Zr_3N_4 and amorphous, respectively. To have further understanding on the relationships between color and structure of the film, it would be worth to study with different types of substrate, e.g. glass, stainless steel, etc. In our work, at fixed Ar flow rate of 6 sccm, the results interestingly indicate that the range of golden color with varying N_2 flow rate of 0.0 to 6.0 sccm can not occurred.

Acknowledgements

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References

[1] M. Östling, S. Nygren, C.S. Petersson, H. Norström , R. Buchta , H. – O. Blom and S. Berg. Comparative study of the diffusion barier properties of TiN and ZrN. *Thin Solid Films* 1986;**145**:81-88.

[2] W. Ensinger, K. Volz and M. Kiuchi. Ion beam – assisted deposition of nitrides of the 4th group of transition metals. *Surf. Coat. Technol.* 2000;**128-129**:81-84.

[3] S. Niyomsoan, W. Grant, D.L. Olson and B. Mishra. Variation of color in titanium and zirconium nitride decorative thin films. *Thin Solid Films* 2002;**415**:187-194.

[4] M. Nose, M. Zhou, E. Honbo , M. Yokota and S. Saji. Colorimetric properties of ZrN and TiN coatings prepared by DC reactive sputtering. *Surf. Coat. Technol.* 2001;**142-144**:211-217.

[5] I.A. Khan, M. Hassan, R. Ahmad , A. Qayyum , G. Murtaza , M. Zakaullah and R.S. Rawat. Nitridation of zirconium using energetic ions from plasma focus device. *Thin Solid Films* 2008;**516**:8255-8263.
[6] E. Budke, J. Krempel-Hesse, H. Maidhof and H. Schüssler. Decorative hard coatings with improved corrosion resistance. *Surf. Coat. Technol*. 1999;**112**:108-111.
[7] P. Klumdoung, P. Asanithi, S. Chaiyakun and P. Limsuwan. Variation of color in Zirconium nitride thin films prepared by reactive dc magnetron sputtering. *Adv. Mater. Res.* 2011;**214**:320-324.