Characterization of sputtered zirconium nitride films deposited at various argon:nitrogen ratio

Nicky P. Patel¹, Kamlesh V. Chauhan¹, Jaydeep M. Kapopara¹, Nayan N. Jariwala¹, Sushant K. Rawal²

¹CHAMOS Matrusantha Department of Mechanical Engineering, Chandubhai S. Patel Institute of Technology (CSPIT), Charotar University of Science and Technology (CHARUSAT), Changa-388421, Gujarat, India.
²Department of Mechanical Engineering, McMaster University, 1280 Main St., W. Hamilton, ON, L8S 4L7, Canada

Corresponding author: sushantrawal@outlook.com

Abstract. Zirconium nitride films were deposited by reactive magnetron sputtering using argon as inert gas and nitrogen as reactive gas. The nitrogen flow rate in argon:nitrogen ratio was increased from 4sccm to 20sccm by an increment of 4sccm. The effect of increment in nitrogen flow rate on various properties of deposited zirconium nitride films are reported in this paper. The structural characterization was done by X-Ray diffraction which confirms (011) peak of Zr3N4 and a very low intensity (111) peak of Zr3N4. Optical properties was investigated by Uv-Vis-NIR spectrophotometer which showed that the films were transparent and maximum transmittance observed was around 82%. The wettability properties was investigated by contact angle goniometer which showed the films were hydrophobic and maximum contact angle achieved was 99.5°.

KEY WORDS: Zirconium nitride; Sputtering; Contact angle; Wettability.

1. Introduction

Transition metal nitrides have stimulated many scientific interest because of their properties such as high hardness, good wear and oxidation resistance that permit to use them as hard coating [1]. Zirconium nitride (ZrN) have been extensively studied for industrial applications as hard coatings,
optical applications for heat mirrors and decorative coatings and many more outstanding properties. The optical and mechanical properties of ZrN depends on nitrogen composition [2].

The physical properties of these compounds are influenced by parameters such as nitrogen to zirconium atomic ratio [3], bias effect [4, 5, 6], deposition time [7], gas flow rate [8, 9] and deposition temperature [10, 11].

It was observed from the literature review that wettability properties of zirconium nitride thin films are not much explored. The objective of the present work is to deposit thin films by using zirconium as target material and nitrogen gas as reactive gas. The effects of varying nitrogen flow rate on structural, optical and wettability properties of reactive sputtered zirconium nitride films are inspected.

2. Experimental details

Zirconium nitride coatings were deposited on corning glass substrates in a specially crafted chamber (Excel Instruments, India) by reactive magnetron sputtering. The target material of 50.8mm diameter zirconium with purity of 99.999% was used. The chamber was initially evacuated to about base pressure of $6 \times 10^{-4}$ Pa, by a turbo molecular pump backed up with a rotary pump. The argon and nitrogen gas flow of high purity was injected into the chamber and the flow of gas rate was controlled by Mass Flow Controller procured from ALICAT instruments, USA. The details of experiment is given in table 1 below:

| Table 1. Experimental parameters for depositing zirconium nitride thin films |
|---------------------------------|------------------|
| Target                          | Zr (99.999%)     |
| Substrate                       | Corning glass    |
| Target-substrate distance       | 50 mm            |
| Base pressure                   | $6 \times 10^{-4}$ Pa |
| Sputtering Pressure             | 1.5 Pa           |
| Gas Ratio (Ar:N$_2$ in sccm)    | 20:20, 20:16, 20:12, 20:08, 20:04 |
| Respective sample names         | R20, R16, R12, R08, R04 |
| Rf Power                        | 180W             |
| Substrate temperature           | 510°C            |

The structural properties of zirconium nitride thin films was characterized by X-Ray Diffractometer (XRD) using Bruker D2 phaser, advance diffractometer with Cu-K$_\alpha$ radiation having wavelength 1.54Å. The surface morphology of zirconium nitride thin films was done by scanning electron microscope (EVO-18, Emitech, model no. SC7620) and atomic force microscope (Nano surf easy scan 2). Optical properties of zirconium nitride thin films was done by UV-Vis-NIR spectrophotometer (Shimadzu 3600). Contact angle measurement using water as a liquid was done on contact angle goniometer (Rame Hart 290).
3. Results and discussion

The XRD patterns for zirconium nitride thin films deposited at Ar:N2 gas ratio of 20:20, 20:16, 20:12, 20:08, 20:04 with sample names R20, R16, R12, R08 and R04 are shown in figure 1. When Ar:N2 ratio was 20:20, (011) peak of Zr3N4 having very low intensity was observed. A very low intensity peak (111) of Zr3N4 was also observed when nitrogen gas flow was 20 sccm. As the flow rate of nitrogen decreases to 16, 12 and 8sccm the intensity of the peak (011) increases subsequently. The (011) peak with maximum intensity was observed at the least flow rate of nitrogen at 4sccm for sample R04.

Klumdoung et al. (2010) observed patterns of XRD for zirconium nitride coatings prepared at different deposition time of 15, 30 and 60 minutes [7]. XRD pattern showed that ZrN thin films have orthorhombic Zr3N4 phase with only (011) peak.

Zhiguo et al. (2005) noticed that on rising the flow rate of nitrogen, XRD peaks of zirconium nitride get to be weaker and widened, which can be associated with smaller grain sizes. They demonstrated that zirconium nitride was synthesized and lattice parameters of orthorhombic phase were a = 0.97, b = 1.08, c = 0.33 nm. The decrease in grain size and increment in the N2+ ion density was observed as the proportion of nitrogen in the film increases [9]. Singh et al. (2013) observed that there was a slight increment in lattice parameter which relied upon nitrogen flow rate as abundance nitrogen can occupy interstitial positions that leads to subsequent increase of lattice parameter. Other than formation of ZrN
phase, major reflections representing $\alpha$-Zr$_3$N$_4$ phase was also observed. Poorly crystallized films were observed with the increment of nitrogen flow rate up to 10sccm [8].

So the presence of well intense (011) peak of zirconium nitride thin films at Ar:N$_2$ gas ratio of 20:04sccm and decline in intensity with increase in the gas ratio is consistent with literatures. We were able to observe (011) peak of zirconium nitride thin films at Ar:N$_2$ gas ratio of 20:20sccm corresponding to high nitrogen flow rate of 20sccm. The average crystallite size of the samples in this work was calculated by Scherrer formula [4]. The average crystallite size of zirconium nitride thin films decreases from ~9 to ~7nm with increase in Ar:N$_2$ gas ratio from 20:4 to 20:20. The (011) peak for Zr$_3$N$_4$ becomes broad and short with increase in gas ratio, that results in smaller grain size with increase in gas ratio.

The surface morphology of zirconium nitride thin films was investigated by SEM. The images of zirconium nitride thin films for samples R04 and R20 are shown in figure 2. It was observed that zirconium nitride thin films had a columnar structure and grain size of coating decreases with increase in gas flow rate. Larijani et al. (2009) synthesized zirconium nitride thin films and studied the impact of nitrogen flow proportion and noticed a thick columnar structure of ZrN film built up. They attributed the reason of having such structure at low temperature may be because of adatom surface mobilities quickened in the experiment by energetic ions bombardment on developing film that might have affected the surface. This perception was relevant to that of reported work by different authors somewhere else [12].

![Figure 2. SEM images of zirconium nitride films for samples R04 and R20](image_url)

Lopez et al. (2005) investigated SEM images by performing EDX investigation on the surface. The coating displayed a fibrous polycrystalline structure that consisted of numerous columnar crystalline grains packed organized with each other, which is characteristic for low-temperature deposition magnetron sputtering deposition process, as many authors have beforehand reported [13]. So the results are in a good agreement with most studies dealing with the growth of zirconium nitride thin films.
The surface topography of zirconium nitride thin films was also characterized by an AFM system. The AFM images of zirconium nitride films of samples R04 and R20 are shown in figure 3. The roughness values was in the range of 0.6649nm and 0.8719nm for Ar:N₂ ratio of 20:04 and 20:20 sccm for samples R04 and R20 respectively which clearly shows that the surface smoothness reduces with increase in Ar:N₂ ratio.

Figure 3. AFM images of zirconium nitride films for samples R04 and R20

Khan et al. (2015) studied the results of AFM images for zirconium nitride coatings developed at various nitrogen condition and bias voltages. They observed that coatings were genuinely smooth, as the variation stays just a couple of nanometers in Z-height. The decline in roughness may possibly be because of the film quality and better density as consequence of granting higher energy to surface atoms amid film development [11]. In our case, it was observed that decrease in Ar:N₂ gas ratio leads to highly intense (011) peak of zirconium nitride thin films. The smoothness of film increases and decline in surface roughness values was observed that are in agreement with literatures.

The transmittance spectra of zirconium nitride films deposited at various Ar:N₂ gas ratio is shown in figure 4. It can be noticed clearly that as nitrogen flow rate increase transmittance of film fairly increases. The average maximum range of transmittance is around 82% for Ar:N₂ gas ratio of 20:20 sccm which decreases to about 65% for Ar:N₂ gas flow rate of 20:04 sccm. Klumdoung et al. (2010) studied transmittance spectra in the wavelength range of 190-2100nm for Zr₃N₄ film deposited at different deposition times. Films that are coated for a longer time had lower transmittance. The average optical transmittance of films was found to be 69.3% [7]. The transmittance graphs of zirconium nitride shows clearly that deposited zirconium nitride films are transparent and are in good agreement with literature.
Figure 4. Transmittance spectra of zirconium nitride films prepared at various Ar:N₂ gas ratio

The contact angle and surface energy of zirconium nitride films deposited at various Ar:N₂ gas ratio is shown in figure 5. It is clearly observed that a steady increase in contact angle was found with increase in Ar:N₂ gas ratio.

Figure 5. Surface energy and contact angle of zirconium nitride films prepared at various Ar:N₂ gas ratio
The films deposited at Ar:N₂ gas ratio of 20:20 sccm had a contact angle of 99.5° which proves that the film deposited has a hydrophobic property. The lowest contact angle 95.0° was found at Ar:N₂ gas flow rate of 20:04 sccm. The surface energy is inversely related with the contact angle as the contact angle increases the surface energy decreases as evident from figure 5. At low nitrogen flow rate of 4sccm the surface energy tends to be 26.15mJ/m² and at maximum flow rate of 20sccm the surface energy was 23.31mJ/m². Rawal et al. (2011) reported that surface structure/roughness height is very important in achieving a hydrophobic state. In addition to contact areas on a rough surface, the size scale of surface structures determines the contact angle of a drop of a water on the surface [14]. When the films are hydrophobic, the surface energies are lower as compared to the films that are hydrophilic. Hence the results are in agreement with the literatures.

Surface roughness and contact angle of zirconium nitride films prepared at various Ar:N₂ gas ratio is shown in figure 6. A gradual decline in values for both parameters is observed for zirconium nitride films with decrease in nitrogen flow rate. The figure shows how the increase in flow rate affects surface roughness along with contact angle. The films deposited shows hydrophobic property (contact angle greater than 90°) and the average contact angle was around 97.52°. It was observed that there is a gradual rise in contact angle with corresponding rise in roughness and greater contact angle values indicates that there is decline in wettability [15]. The result shows good agreement with the literature.
4. Conclusion

It was observed that decrease in Ar:N₂ gas ratio leads to highly intense (011) peak for zirconium nitride films. Average crystallite size of zirconium nitride films decreases from ~9 to ~7nm with increase in Ar:N₂ gas ratio from 20:04 to 20:20. The average maximum range of transmittance was ~82% for Ar:N₂ gas ratio at 20:20 sccm which decreases to about ~65% for Ar:N₂ gas flow rate of 20:04 sccm. When tested with contact angle goniometer using water, the films deposited at Ar:N₂ gas ratio of 20:20 sccm had a contact angle of 99.5° which proves that the film deposited was a hydrophobic film. At low Ar:N₂ gas ratio of 20:04 the surface energy tends to be 26.15 mJ/m² and at maximum Ar:N₂ gas ratio from 20:20 sccm the surface energy was 23.31mJ/m².

5. Acknowledgement

This work has been supported by AICTE grant number 20/AICTE/RIFD/RPS (POLICY-III) 24/2012-13 authorized under Research Promotion Scheme (RPS). We are grateful to President and Provost of CHARUSAT for supporting this experimental work. We are appreciative to Head, Dr. K. C. Patel Research and Development Centre (KRADLE) subsidiary to Charotar University of Science and Technology (CHARUSAT), India for conceeding authorization to utilize different equipment’s available in their characterization laboratory.

6. References

[1] Vetter J., Rochotzki R., Thin Solid Films 192 (1990) 253.
[2] Pichon L., Girardeau T., Straboni A., Lignou F., Perriere J., Frigerio J.M., Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 147 (1999) 378.
[3] Gruss K. A., Zheleva T., Davis R. F., and Watkins T. R., “Characterization of zirconium nitride coatings deposited by cathodic arc sputtering,” vol. 107, pp. 115–124, 1998.
[4] Rizzo A., Signore M. A., Mirenghi L., Tapfer L., Piscopiello E., Salernitano E., and Giorgi R., “Sputtering deposition and characterization of zirconium nitride and oxynitride films,” Thin Solid Films, vol. 520, no. 9, pp. 3532–3538, 2012.
[5] Chou W., Yu G., and Huang J., “Bias effect of ion-plated zirconium nitride film on Si (100),” vol. 405, no. March 2001, pp. 162–169, 2002.
[6] Pilloud D., Dehlinger A. S., Pierson J. F., Roman A., and Pichon L., “Reactively sputtered zirconium nitride coatings : structural , mechanical , optical and electrical characteristics,” vol. 175, pp. 338–344, 2003.
[7] Klumdoung P., Chaiyakun S., Limsuwan P. “Asian Journal on Energy and Environment,” vol. 11, no. 01, pp. 60–68, 2010.
[8] Singh A., Kuppusami P., Khan S., Sudha C., Thirumurugesan R., Ramaseshan R., Divakar R., Mohandas E., and Dash S., “Applied Surface Science Influence of nitrogen flow rate on microstructural and nanomechanical properties of Zr – N thin films prepared by pulsed DC magnetron sputtering,” Appl. Surf. Sci., vol. 280, pp. 117–123, 2013.
[9] Zhiguo Z., Tianwei L., Jun X., Xinlu D., and Chuang D., “N-rich Zr – N films deposited by unbalanced magnetron sputtering enhanced with a highly reactive MW-ECR plasma B,” vol. 200, pp. 4918–4922, 2006.
[10] Fragiel A., Staia M. H., Muñoz-saldaña J., Puchi-cabrera E. S., Cortes-escobedo, C. and Cota L.,
“Influence of the N₂ partial pressure on the mechanical properties and tribological behavior of zirconium nitride deposited by reactive magnetron sputtering,” vol. 202, pp. 3653–3660, 2008.

[11] Khan S., Mehmood M., Ahmad I., Ali F., and Shah A., “Materials Science in Semiconductor Processing Structural and electrical resistivity characteristics of vacuum arc ion deposited zirconium nitride thin films,” *Mater. Sci. Semicond. Process.*, vol. 30, pp. 486–493, 2015.

[12] Larijani M. M., Elmi M., Yari M., Ghoranneviss M., Balashabadi P., and Shokouhy A., “Surface & Coatings Technology Nitrogen effect on corrosion resistance of ion beam sputtered nanocrystalline zirconium nitride films,” *Surf. Coat. Technol.*, vol. 203, no. 17–18, pp. 2591–2594, 2009.

[13] Lopez G. and Staia M. H., “High-temperature tribological characterization of zirconium nitride coatings,” vol. 200, pp. 2092–2099, 2005.

[14] Rawal S. K., Kumar A., Chawla V., Jayaganthan R., and Chandra R., “Structural, optical and hydrophobic properties of sputter deposited zirconium oxynitride films,” *Mater. Sci. Eng. B*, vol. 172, no. 3, pp. 259–266, 2010.

[15] Rawal S. K., Chawla A. K., Jayaganthan R., and Chandra R., “The influence of various sputtering parameters on structural, wettability and optical properties of Zr2ON2 thin films,” *Mater. Sci. Eng. B*, pp. 1–8, 2013.