Deposition of zirconium nitride thin films produced by reactive DC magnetron sputtering

Pattarinee Klumdoung¹,²,³*, Surasing Chaiyakun ², Pichet Limsuwan¹,³

¹Thin Film Technology Research Laboratory, Department of Physics, Faculty of Science, King Mongkut’s University of Technology Thonburi, Bangkok 10140 Thailand.

²Vacuum Technology and Thin Films Research Laboratory, Department of Physics, Faculty of Science, Burapha University, Chonburi, Thailand.

³Research Centre in Thin Film Physics, Thailand Centre of Excellence in Physics.

*Author to whom correspondence should be addressed, email: posterland@hotmail.com

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Abstract

Zirconium nitride thin films were deposited on unheated silicon wafer (100) and glass slide by reactive dc magnetron sputtering. The flow rate of Ar and N₂ during sputtering was maintained at 6 and 3 sccm, respectively. The sputtering current (I) was kept constant at 600 mA. The zirconium nitride films were deposited at different times of 15, 30 and 60 min, respectively. The surface morphology and thickness of the films was investigated by atomic force microscopy (AFM). The structure was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The colour of films deposited on glass slide was measured using a spectrophotometer with a reference to CIE L*a*b* colour index. The optical transmission was determined by a UV-VIS-NIR spectrophotometer. The XRD and TEM results show that the structure of film is an orthorhombic phase of Zr₃N₄. The optical transmittance and energy band gap of Zr₃N₄ film in the wavelength range of 300-2100 nm was found to be 69.3% and 2.1- 2.3 eV, respectively.

Keywords: dc magnetron sputtering, zirconium nitride, Thailand

Introduction

Since zirconium nitride has outstanding properties as high hardness, 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 [1]. The only stable compound in the Zr-N binary system is ZrN of
NaCl-type crystal structure [2], but it is possible to obtain the zirconium nitride, ZrNₓ, with a considerable range of non-stoichiometry (x<2) varying the deposition conditions. The nitrogen-rich films are semi-transparent and much less conducting than zirconium mononitride [3]. In particular, the Zr₃N₄ phase shows extraordinary mechanical and electrical properties in many applications [4]. Although it is generally difficult to vary and to control the nitrogen concentration in nitride thin films in order to obtain higher nitrides, there is a strong scientific interest toward these materials [5]. The Zr₃N₄ thin films have been synthesized by high-pressure laser-heated diamond anvil cell1, novel modified filtered cathodic arc, reactive dual ion beam sputtering and direct current (DC) reactive magnetron sputtering [6-8]. Many studies have been performed in order to understand the relationships between the processing parameters, the film structure and properties. 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.

In this research the effect of varying deposition time on structural and optical properties of zirconium nitride film is studied.

**Experimental Procedures**

Zirconium nitride thin films were deposited on glass slide and Si wafer (100) using a home-built DC unbalanced magnetron sputtering system. The vacuum chamber has a 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 5x10⁻⁵ mbar. Pure Ar (99.99%) and N₂ (99.99%) were used as sputtering and reactive gases, respectively. Zirconium target was sputtered for 6 min to remove the surface oxide after reaching the base pressure. The flow rates of Ar and N₂ were kept at constant values of 6 and 3 sccm, respectively, regardless of total pressure. The discharges were generated by a DC power supply at a constant current of 0.6 A. The deposition was carried out at different times of 15, 30 and 60 min.

The substrates used were glass slides for surface roughness analysis and optical transmittance, carbon coated copper transmission electron microscopy (TEM) grids for microstructure analysis and silicon wafers (100) for crystal structure analysis.

The crystal structure of films was characterized by X-ray diffraction technique with Cu-Kα radiation (λ=1.54056 Å) and XRD patterns were recorded at grazing incidence angle (3°) in the 20 range of 20°-80° with a scan rate of 0.02°. The crystalline structure and orientation of the films deposited on the TEM grids were investigated by transmission electron microscopy (Jeol, JEM-2100) working at 160 kV. The surface morphology and its root-mean-square (r.m.s.) roughness and film thickness of the films deposited on glass substrates were analyzed using atomic force microscopy (NanoScope III) in a tapping mode.

A spectrophotometer (UV-VIS-NIR 3100 Shimadzu) was employed for the optical characterization. Optical transmittance of films was performed in a wavelength range from 190 nm to 2100 nm. The colour of films deposited on glass slide sample was measured using a spectrophotometer with a reference to CIE L*a*b* colour index.
Results and Discussion

Structural results

Figures 1(a)-(c) show the two- and three- dimensional images by atomic force microscopy (AFM) obtained from three sample surfaces deposited at a sputtering current of 0.6 A and different deposition times of 15, 30 and 60 min, respectively. The surface roughness of the three sample surfaces shown in Figs.1 (a)-(c) was found to be 0.307, 0.635 and 0.756 nm, respectively. It is seen that the surface roughness increases with increasing deposition time.

Figure 1. Surface morphologies of zirconium nitride films (2D images, left and 3D images, right) deposited at a constant sputtering current of 0.6 A and different deposition times of: (a) 15 min, (b) 30 min and (c) 60 min.
The grain size of zirconium nitride films was estimated from the 2-D AFM images in Figs. 1(a)-(c) and the grain sizes are given in Table 1. It is seen that the average grain size increases with increasing deposition time.

Table 1. Variations of thickness, surfaces roughness and the grain size of zirconium nitride films deposited with three different deposition times.

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Thickness (nm)</th>
<th>R.M.S. roughness (nm)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>79.6</td>
<td>0.307</td>
<td>8.823</td>
</tr>
<tr>
<td>30</td>
<td>206.9</td>
<td>0.635</td>
<td>9.804</td>
</tr>
<tr>
<td>60</td>
<td>265.6</td>
<td>0.756</td>
<td>10.784</td>
</tr>
</tbody>
</table>

The thickness of zirconium nitride films was measured from the section analysis of 2D-AFM images. Figure 2 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 Fig.2, and the results are shown in Table 1. It was found that the average film thickness varied from a minimum value of 79.6 nm to a maximum value of 265.6 nm.

Figure 2. Section analysis of zirconium nitride films at a constant sputtering current of 0.6 A and a deposition time of 15 min.

The crystallinity and structure of zirconium nitride films were investigated by XRD measurements. Figures 3 shows XRD patterns of zirconium nitride film grown on Si wafers (100) substrates at three different deposition time of 15, 30 and 60 min. From XRD pattern, all deposited Zr-N thin films exhibited the orthorhombic Zr$_3$N$_4$ phase and only (011) plane was observed. Furthermore, the film crystallinity increases with the increase of deposition time.
Figure 3. XRD pattern of Zr$_3$N$_4$ films deposited at 15, 30 and 60 min on Si(100), respectively.

Figure 4. (a) HRTEM images and (b) SAED images of Zr$_3$N$_4$ thin films deposited at a constant sputtering current of 0.6 A and different deposition times of 15 min.

Figure 4 shows a typical high-resolution transmission electron microscopy (HRTEM) image and the corresponding selected-area electron diffraction (SAED) patterns of Zr$_3$N$_4$ thin films deposited at a sputtering current of 0.6 A and deposition time of 15 min. However, the HRTEM images and SAED patterns obtained at deposition times of 30 and 60 min are very similar, and hence only the results on Zr$_3$N$_4$ thin films deposited at 15 min are presented.

As observed in Fig. 4(a), showing the HRTEM images of Zr$_3$N$_4$ thin films deposited at a sputtering current of 0.6 A, polycrystalline growth can be identified from the random orientation of several lattice planes. One measured d-spacings were indexed in the figure. The corresponding SEAD patterns, Fig.4 (b), were used for phase determination. The electron diffraction patterns display rings, indicating polycrystalline structure. In the diffraction rings
the d-values correspond to the (011), (421) and (450) planes of the crystalline Zr₃N₄ phase in the Joint Committee on Powder Diffraction Standard-International Center for Diffraction Data (JCPDS-ICDD) card no. 87-0843.

**Optical properties**

Table 2 shows the coordinates of CIE colour index of Zr₃N₄ deposited at different times. The plot of colour coordinates in Table 2 is shown in Fig. 5. It is seen from Fig. 5 that the colour of Zr₃N₄ film is yellow for deposited film of 15 min and become red-brown for longer deposition time.

**Table 2. CIE L*a*b* colour index of three Zr₃N₄ films deposited at different times.**

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Thickness (nm)</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>79.6</td>
<td>56.00</td>
<td>-20.44</td>
<td>2.25</td>
</tr>
<tr>
<td>30</td>
<td>206.9</td>
<td>59.95</td>
<td>1.76</td>
<td>2.01</td>
</tr>
<tr>
<td>60</td>
<td>265.6</td>
<td>60.99</td>
<td>9.23</td>
<td>0.42</td>
</tr>
</tbody>
</table>

![Colour Space Diagram](image)

**Figure 5.** Lab colour space in two dimensions of Zr₃N₄ films were deposited at 15, 30 and 60 min, respectively.

As can be seen from Table 2, the lightness of film increases and the colour becomes darker as the film thickness increases.
Figure 6. Transmission spectra of Zr$_3$N$_4$ films were deposited at 15, 30 and 60 min, respectively.

Fig. 6 shows transmittance spectra in the wavelength range of 190 – 2100 nm of Zr$_3$N$_4$ film deposited at different times. When films were coated for a longer time, transmittance was lower. It shows that films are darker because of the increase in thickness. The optical transmittance of films found as 69.3%.

It can be seen from Fig. 6 that the transmission shifts to the longer wavelength with the increase of deposition time. The calculated transmittance values in the range of UV, VIS and NIR are given in Table 3.

Table 3. Transmittance values of films deposited at different times.

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Thickness (nm)</th>
<th>%T$_{UV}$</th>
<th>%T$_{VIS}$</th>
<th>%T$_{NIR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>79.6</td>
<td>70.69</td>
<td>75.54</td>
<td>3.91</td>
</tr>
<tr>
<td>30</td>
<td>206.9</td>
<td>81.35</td>
<td>48.85</td>
<td>-0.84</td>
</tr>
<tr>
<td>60</td>
<td>265.6</td>
<td>78.72</td>
<td>52.34</td>
<td>-1.30</td>
</tr>
</tbody>
</table>

Table 3 shows the maximum percentage transmittance in visible range of film deposits is 15 min. When the film thickness increases, transmittance spectra shift in the right hand direction. Increasing film thickness can be explained by determinative path difference of refraction and transmission rays. Effects on each percentage transmittance of film thickness are different.

The energy band gap can be calculated from Eq.(1) [9]

$$\alpha h\nu = A(h\nu - E_g)^2 \quad \text{(1)}$$

where $\alpha$ is absorption coefficient and $h\nu$ is photon energy.

The absorption coefficient was calculated from optical transmittance spectra in Fig. 6. Then the photon energy ($h\nu$) and the value of $(\alpha h\nu)^{1/2}$ were obtained. The relation between $(\alpha h\nu)^{1/2}$
and photon energy (hv) is shown in Fig. 7 and the energy band gap was determined. The energy band gap (Eg) for all Zr3N4 films was found to be in the range of 2.1 to 2.3 eV.

![Graph](image)

**Figure 7.** Dependence of \((a\nu)^{1/2}\) on photon energy of Zr3N4 films deposited at 15, 30 and 60 min, respectively.

**Conclusions**

Zirconium nitride thin films deposited on unheated silicon wafer (100) and glass slide by reactive dc magnetron sputtering were studied. The sputtering current (I) was kept constant at 600 mA. The zirconium nitride films were deposited at different times of 15, 30 and 60 min, respectively. The surface morphology and thickness of the films was investigated by atomic force microscopy (AFM). The structure was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The colour of films deposited on glass slide was measured using a spectrophotometer with a reference to CIE L*a*b* colour index. The optical transmission was determined by a UV-VIS-NIR spectrophotometer. The XRD and TEM results show that the structure of films is an orthorhombic phase of Zr3N4. The optical transmittance and energy band gap of Zr3N4 film in the wavelength range of 300-2100 nm was found to be 69.3% and 2.1-2.3 eV, respectively.
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