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Wettability And Optical Studies Of Films prepared from Power Variation Of Co-Sputtered Cr And Zr Targets By Sputtering

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Abstract

The aim of this paper is to investigate the effect of power variation on thin films deposited by co-sputtering metal targets of chromium and zirconium by reactive magnetron sputtering. The well crystalline chromium oxide and zirconium oxynitride films with different orientations are observed only when the power for one of the target is equal to or more than 90W. The contact angle and surface energy of the deposited films were measured by contact angle measuring system. The deposited films exhibit hydrophobic behavior with the increase of target powers and the contact angle of 90° or more is observed when the power for one of the target is 90W or more. The refractive index and packing density of the deposited films increases gradually with the increase of target powers. The band gap of chromium oxide and zirconium oxynitride films increases with the increase of their respective target powers.

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Keywords: Wettability; Contact Angle; Optical Properties; Sputtering; Oxynitride;

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1. Introduction

Physical vapour deposition techniques are widely used for the deposition of transition metal oxide thin films. Binary, ternary or multinary compounds are currently prepared from alloyed, segmented or composite targets [1-5]. Reactive magnetron sputtering is one such well-known process to synthesize various metallic oxides, nitride or carbide films using a metallic target and a reactive gas mixture (i.e., Ar-O$_2$, Ar-N$_2$ or Ar-CH$_4$) [6-8]. Recently metal oxynitride films are also being prepared by this process using various reactive gas mixtures (Ar-O$_2$-N$_2$, O$_2$-N$_2$ or He-O$_2$-N$_2$). The major advantage of using reactive magnetron sputtering is that the flow of reactive gases can be controlled precisely, which determines the O and N content in oxynitride films [9]. If a sputtering system is configured in such a way that two different target materials can be sputtered, with the power to each of the targets controlled independently than such an arrangement is called reactive co-sputtering. The motivation is creation of controlled mixtures of materials in the film deposited by this process. Reactive co-sputtering is appealing because it can deposit films otherwise unrealizable. Co-sputtering of two different materials has typically been accomplished with ion beam sputtering or the use of RF or DC supplies to deliver power to sputtering targets in diode or magnetron configurations. [10-11]. In the last few decades, recent developments tend towards such multi-target sputtering, since such systems allow the synthesis of new types of coatings (multi-layers, alloys, graded compositions, etc.) and so this is a useful way to achieve attractive properties [5,12-15]. Thus, this method has been widely used for mechanical, optical, electronic or magnetic applications [8].

The objective of this work is to deposit films by reactive co-sputtering of two different metal targets of Cr and Zr respectively. Oxygen and nitrogen were used as reactive gases that may lead to formation of respective metal oxide, nitride or oxynitride films. The effect of power variation on the structural, wettability and optical properties of the deposited films is investigated in the present work.

2. Experimental Details

Chromium (Cr) and zirconium (Zr) metallic targets (99.99% pure, 2 in. diameter and 5-mm thick) were used to deposit co-sputtered transition metal based films on corning glass substrates by reactive magnetron sputtering. The targets were arranged confocally for co-sputtering and the substrate to target distance was kept constant at 50 mm during deposition. The substrates were cleaned by rinsing in ultrasonic baths of acetone and methanol. The base pressure was better than 5x10$^{-4}$ Pa and the sputtering was carried out in a helium atmosphere along with oxygen and nitrogen as reactive gases. The flow rates of helium, oxygen and nitrogen were 10sccm, 1.3sccm and 40sccm respectively. The deposition time, temperature and gas pressure were kept constant at 60 minutes, 500°C and 2.0 Pa respectively for all depositions. Before starting the actual experiment, targets were presputtered for 15 min with a shutter located in between the target and the substrate. This shutter is also used to control the deposition time. First the power of zirconium target was kept constant at 30W and the power of chromium target was varied as 60W, 90W and 120W respectively represented by samples CZ-1, CZ-2 and CZ-3. Sample CZ was deposited by keeping the power of both targets at 75W. Finally the power of chromium target was kept fixed at 30W and power of zirconium target was varied as 60W, 90W and 120W which are represented by samples ZC-1, ZC-2 and ZC-3.

Structural characterization of the deposited samples was done by X-ray diffractometer (XRD) using Bruker D8 Advance diffractometer with Cu Kα radiation of wavelength 1.54 Å. The surface morphology of films was characterized using atomic force microscope (NT-MDT Ntegra). The elemental analysis of these films was carried out using an energy dispersive X-ray analysis (FEI, Quanta 200F). The wettability studies of films were done by contact angle measurement system (Kruss DSA 100 Easy Drop) to find the contact angle of water with films. The thickness of samples was determined by Surface Profilometer (Ambios Technology XP-200). Optical transmission and absorption of the films were measured by UV–Vis–NIR spectrophotometer (Varian Cary 5000).
3. Results and Discussions

The XRD graphs of co-sputtered chromium oxide and zirconium oxynitride films are shown in figure 1. The chromium oxide films when the power of Cr target is 60W for sample CZ-1 is amorphous. When the power of Cr target is increased to 90W represented by sample CZ-2, the deposited films shows (1 0 4) and (1 1 6) oriented Cr$_2$O$_3$ phase. The further increase of Cr target power to 120W shows the evolution of (0 1 2) oriented peak of Cr$_2$O$_3$ phase along with its (1 0 4) and (1 1 6) oriented peaks and is represented by sample CZ-3. For all these three cases the power of Zr target was fixed at 30W. When the power of both the Cr and Zr targets were kept at 75W for sample CZ the deposited films are amorphous.

For sample ZC-1 when the power of Zr target is kept 60W, the deposited zirconium oxynitride films shows evolution of (2 2 2) peak of γ-Zr$_2$ON$_2$ phase. When the power of Zr target is increased to 90W for sample ZC-2, well oriented (2 2 2) peak of γ-Zr$_2$ON$_2$ phase with its weakly crystalline (4 4 0) peak is observed. The intensity of (2 2 2) & (4 4 0) peaks increases and traces of (3 1 1) oriented peak of γ-Zr$_2$ON$_2$ is observed when the power of Zr target is 120W for sample ZC-3. The power of Cr target for all three samples was fixed at 30W.

When the powers of targets are increased, the atoms can be ejected from the target easily due to high energy imparted to the targets. So the electron and ions that hit the targets can easily sputter the atoms from the targets thereby increasing the proportion of sputtered atoms, ions and molecules in the plasma. The increase of the power thus increases the amount of atoms impinging on the substrate for a set period of time, favouring the formation of respective phases as per deposition conditions. So this may be the reason for the evolution of various phases of chromium oxide and zirconium oxynitride films with different textures upon increasing the power of Cr and Zr targets respectively. The increase in power of both targets thus increases the deposition rate and hence an increase in thickness of the deposited chromium oxide and zirconium oxynitride films is observed which is summarized in table 1. The average crystallite size calculated by Scherrer formula [16,17] of the deposited chromium oxide and
zirconium oxynitride films is also given in table 1.

Table 1: Calculated parameters of co-sputtered chromium oxide and zirconium oxynitride films.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sputtering power of targets</th>
<th>Cr (at.%)</th>
<th>Zr (at.%)</th>
<th>O (at.%)</th>
<th>N (at.%)</th>
<th>Avg. d(XRD) (nm)</th>
<th>Band Gap (eV)</th>
<th>Thickness (nm) by Profilometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZ-1</td>
<td>Cr (60W) – Zr (30W)</td>
<td>23</td>
<td>11</td>
<td>65</td>
<td>01</td>
<td>-</td>
<td>2.11</td>
<td>157 ± 10</td>
</tr>
<tr>
<td>CZ-2</td>
<td>Cr (90W) – Zr (30W)</td>
<td>33</td>
<td>06</td>
<td>58</td>
<td>03</td>
<td>46±3</td>
<td>2.28</td>
<td>280 ± 10</td>
</tr>
<tr>
<td>CZ-3</td>
<td>Cr (120W) – Zr (30W)</td>
<td>39</td>
<td>03</td>
<td>54</td>
<td>04</td>
<td>40±3</td>
<td>2.42</td>
<td>359 ± 10</td>
</tr>
<tr>
<td>CZ</td>
<td>Cr (75W) – Zr (75W)</td>
<td>29</td>
<td>26</td>
<td>43</td>
<td>02</td>
<td>-</td>
<td>2.88</td>
<td>146 ± 10</td>
</tr>
<tr>
<td>ZC-1</td>
<td>Cr (30W) – Zr (60W)</td>
<td>10</td>
<td>21</td>
<td>67</td>
<td>02</td>
<td>-</td>
<td>3.21</td>
<td>124 ± 10</td>
</tr>
<tr>
<td>ZC-2</td>
<td>Cr (30W) – Zr (90W)</td>
<td>04</td>
<td>35</td>
<td>55</td>
<td>06</td>
<td>7±1</td>
<td>3.30</td>
<td>236 ± 10</td>
</tr>
<tr>
<td>ZC-3</td>
<td>Cr (30W) – Zr (120W)</td>
<td>02</td>
<td>52</td>
<td>40</td>
<td>06</td>
<td>8±1</td>
<td>3.37</td>
<td>285 ± 10</td>
</tr>
</tbody>
</table>

The 3D AFM images of chromium oxide and zirconium oxynitride films are shown in figure 2. The increase in power of both targets leads to increase in thickness and surface roughness of the deposited films. The surface roughness of 1.9, 3.0 and 3.8 nm for chromium oxide films is observed for samples CZ-1, CZ-2 and CZ-3 respectively. The surface roughness for sample CZ is 2.4nm when the power of both targets is kept 75W. The surface roughness of samples ZC-1, ZC-2 and ZC-3 are 0.7, 2.1 and 2.3nm respectively.

The contact angle and surface roughness of the deposited chromium oxide and zirconium oxynitride films are shown in figure 3. The contact angle increases from 76.2° to 93.2° for the chromium oxide films with the increase in power.
of Cr target and fixed power of Zr target.

Similarly the contact angle increases from 75.1° to 93.3° for zirconium oxynitride films with the increase in power of Zr target at fix power of Cr target. When the power of both targets is fixed at 75W, the observed contact angle is 82.1° for sample CZ. So a transformation from hydrophilic to hydrophobic behaviour is observed for chromium oxide and zirconium oxynitride films with the gradual increase of respective target powers. The hydrophilic behaviour at low target powers can be attributed to the amorphous films that give lower surface roughness and thickness values. With the increase of target powers the film structure changes from amorphous to crystalline leading to evolution of various phases. The increase in thickness and surface roughness of the films are also observed. So greater contact angle are observed for films deposited at target power ≥90W. The surface energies are calculated by two methods namely Owen-Wendl and Wu methods the details are discussed elsewhere [18,19]. The surface energies of the chromium oxide and zirconium oxynitride films are summarized in table 2.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>( \gamma_{S} ) (mN/m)</th>
<th>( \gamma_{d} ) (mN/m)</th>
<th>( \gamma_{S}^{P} ) (mN/m)</th>
<th>( \gamma_{d}^{P} ) (mN/m)</th>
<th>( \gamma_{S}^{P} ) (mN/m)</th>
<th>( \gamma_{d}^{P} ) (mN/m)</th>
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</thead>
<tbody>
<tr>
<td>CZ-1</td>
<td>31.02</td>
<td>19.35</td>
<td>11.67</td>
<td>37.28</td>
<td>22.67</td>
<td>14.6</td>
</tr>
<tr>
<td>CZ-2</td>
<td>20.35</td>
<td>12.7</td>
<td>7.65</td>
<td>27.37</td>
<td>16.93</td>
<td>10.44</td>
</tr>
<tr>
<td>CZ-3</td>
<td>18.06</td>
<td>11.27</td>
<td>6.79</td>
<td>25.18</td>
<td>15.65</td>
<td>9.54</td>
</tr>
<tr>
<td>CZ</td>
<td>26.36</td>
<td>16.44</td>
<td>9.91</td>
<td>32.99</td>
<td>20.20</td>
<td>12.79</td>
</tr>
<tr>
<td>ZC-1</td>
<td>32.07</td>
<td>20.00</td>
<td>12.06</td>
<td>38.24</td>
<td>23.23</td>
<td>15.01</td>
</tr>
<tr>
<td>ZC-2</td>
<td>19.54</td>
<td>12.19</td>
<td>7.35</td>
<td>26.6</td>
<td>16.48</td>
<td>10.12</td>
</tr>
<tr>
<td>ZC-3</td>
<td>18.15</td>
<td>11.33</td>
<td>6.83</td>
<td>25.27</td>
<td>15.7</td>
<td>9.57</td>
</tr>
</tbody>
</table>

The surface energies calculated by both methods are in good agreement with each other. The surface energies are higher initially for both chromium oxide and zirconium oxynitride films when the powers of both targets are lower. The films are hydrophilic at lower powers of targets which results in higher surface energies of the films. When the films are hydrophobic, the surface energies are lower as compared to the films that are hydrophilic. A gradual decline in their values is observed as the contact angle and surface roughness of the films increases with increase in
power of both targets. Similar trend is observed for films prepared by reactive magnetron co-sputtering titanium and zirconium targets [20] and chromium and titanium targets [21].

Figure 4: Transmission spectra of co-sputtered chromium oxide and zirconium oxynitride films at different variation of Cr and Zr target powers.

The transmission spectra of chromium oxide and zirconium oxynitride films are shown in figure 4. The transmission of chromium oxide films is lower as compared to zirconium oxynitride films. The transmission of chromium oxide films decreases with the increase in power of Cr target. Initially the films are amorphous, thinner and have lower surface roughness values at low power of Cr target. When the power is increased, films are crystalline, thicker and surface roughness also increases for the deposited films. These may have led to decline in the transmission of the deposited films with increase in power of the targets.

Figure 5: Variation of refractive index and packing density for co-sputtered chromium oxynitride and zirconium oxynitride films at different variation of Cr and Zr target powers.
The refractive index of the film was calculated from the transmission data from the model proposed by Manifacier et al. [22] the details are given in detail elsewhere [19]. The film packing density is calculated using the expression Bragg and Pippard model explain in detail elsewhere [23,24]. The variation of refractive index with the film packing density of chromium oxide and zirconium oxynitride films is shown in figure 5. The refractive index and the film packing density increases with increase in the power of respective targets. The increase in target powers leads to more availability of the metal atoms that result in formation of crystalline films and increase in the deposition rate of the deposited films. So this might have led to increase in film packing density due to increase in thickness of the deposited films with increase in respective target powers.

The optical band gap of the films was determined by the absorption coefficient ($\alpha$) from the absorption spectra of the films using the Tauc relation [25], which is described in detail elsewhere [17]. The band gap of the deposited chromium oxide and zirconium oxynitride films are shown in figure 6. The band gap of chromium oxide films are 2.11, 2.28 & 2.42eV for samples CZ-1, CZ-2 and CZ-3 respectively. The band gap of 2.88eV is observed for sample CZ when the power of both targets is kept at 75W.

The band gap values of 3.21, 3.30 & 3.37eV of zirconium oxynitride films are observed for samples ZC-1, ZC-2 & ZC-3 respectively. With increase in the power of respective targets, the Cr and Zr atoms content as given in table 1 for chromium oxide and zirconium oxynitride films increases. This also favours the formation of the respective phases as evident from the XRD graph in figure 1. So with the increase in the power of metal targets, a change in atomic concentration and structure of the deposited films are observed. Moreover, the thickness of the deposited films also increases with increase in power of the targets. So the absorption coefficient of the films also increases giving higher band gap values for the films with the increase in the power of the respective targets.

4. Conclusions

When the powers of Cr and Zr targets are low (60W), the deposited chromium oxide and zirconium oxynitride films are amorphous. The thickness and surface roughness increases for chromium oxide and zirconium oxynitride films
with the increase of their respective target powers. This also leads to change in the contact angle and the deposited chromium oxide and zirconium oxynitride film gets transformed from hydrophilic to hydrophobic. The transmission of the chromium oxide and zirconium oxynitride films decreases with increase in the power of their respective targets. The band gap values of the deposited chromium oxide increases from 2.11 to 2.42eV and from 3.21 to 3.37eV for zirconium oxynitride films with their respective target powers.

5. References