Pulsed Bias Effect on Crystallinity and Nano-Roughness of Ti6Al4V-N Films Deposited by Grid Assisted Magnetron Sputtering System

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This paper reports the effect of pulsed bias in comparison with DC bias on reactive deposition of Ti6Al4V-N films, obtained by Grid Assisted Magnetron Sputtering. The results obtained by X-Ray diffraction (XRD), Energy Dispersive X-ray Fluorescence Spectrometer (EDX) and Atomic Force Microscopy (AFM) show that bias condition affects the crystalline texture and change the roughness and morphology of the films. The DC bias favors the film crystallinity, however the pulsed bias produces smoother films.

Keywords: sputtering, pulsed voltage bias, Ti6Al4V-N film

1. Introduction

Nanostructured surfaces have found growing applications in different areas like optoelectronics, physical chemistry, optics and photonics, photovoltaic cells, photocatalysis, cellular biology, microbiology, biochemistry, electrical and electronic engineering, mechanical and aerospace engineering, among other fields. Based-plasma processes are correlated with the nanotechnology development. Among these processes we can highlight the magnetron sputtering, for deposition of nanostructured films1. In magnetron sputtering systems, the energy delivered to the film comes from external heating, chemical reactions on the surface and collisions with electrons, ions, radicals and neutral atoms2,3. The total amount of energy transferred to the film is the difference between the total inlet energy and the dissipated energy. It promotes the nucleation and growth of the film and affects their stoichiometry and adhesion to substrate.

For magnetron sputtering systems, the energy delivered to the substrate during the film deposition depends of several process variables, such as: power source (e.g. DC, pulsed magnetron sputtering (PMS), high power pulsed magnetron sputtering (HIPIMS) and modulated pulsed power magnetron sputtering (MPP))2-5; the anode-cathode geometry6,7; the magnetic field configuration8-10, and the substrate bias11,12. These variables are not independent and it is difficult to do a correlation between them13. The ion bombardment control has received great attention due to the possibility of change the film structure in micro and nanometer scales. Moreover it can improve the adherence of the films to the substrate and change the crystallographic texture and roughness of the films14. Nevertheless, few studies have been done in relation to the control of the pulsed substrate bias15-17. Due the interest in Ti alloys films, this paper investigates the effect of pulsed bias voltage ($V_{bias}$) in comparison with DC bias on crystallinity and roughness of Ti6Al4V-N films obtained by reactive deposition, using a grid assisted magnetron sputtering system. Ti6Al4V alloy was chosen due to your resistance to wear and fatigue, weathering and corrosion. It has been applied in aerospace and medicine with a good combination of mechanical, chemical, physical and biocompatibility18,19. The morphological properties of these films were analyzed by X-Ray diffraction (XRD), Energy Dispersive X-ray Fluorescence Spectrometer, (EDX) and Atomic Force Microscopy (AFM).

2. Experimental Details

The depositions were carried out in a stainless steel chamber with 28.0 cm in diameter and a height of 24.0 cm. The chamber walls are grounded. The target-substrate distance was fixed in 7.0 cm, being the target a planar disk Ti6Al4V (99.6% purity, 100mm diameter). Between the target and the substrate there is a grounded AISI 304 stainless steel grid that acts as the discharge anode, making plasma maintenance easier6. The cathode (12.4 cm in diameter) is mounted on an unbalanced magnetron. A mask shield system allowed the introduction of six samples for each deposition cycle. While a deposition was performed over one sample, another five samples were kept protected by a mask and so on. All films were deposited on substrates of AISI 304 stainless steel during 30 minutes. The magnetron discharge voltage was set at 440 V resulting in a current around 1.0 A. The substrate temperature was set in 300°C and it was controlled by a heating system consisting of four 250 W halogen lamps and a temperature control system. The pressure in the chamber was measured by two Pirani gauges.
The gases mass flow rate (Ar 99.99% and N₂ 99.99%) were measured by mass flow controllers. The voltage source used to generate the plasma was a switching power supply, with current control from 0.0A to 2.0A and voltage up to –1000V related to the ground. The samples were electrically isolated from the chamber walls (grounded), enabling the negative bias of the substrate with respect to the ground, as shown in Figure 1. The bias power supply used in this work allowed us change the pulsed bias between 0 and –300V (peak to peak at 1.0 kHz) and the adjustment of duty cycle or “time on”/“time off” periods.

During the “time off” the substrate was under floating potential. The ratio “time on”/“period” is called “duty cycle”. The depositions were carried out using 20% duty cycle as well DC bias. It was used a low “duty cycle” value (20%) just to compare with DC mode, where the ions bombardment is continuum.

The samples were characterized by AFM Nanosurf Nanite B S200 model at contact mode for surface morphology and roughness characterization in nanometer scale. The formation of crystalline phases was examined by XRD. The thickness was measured by an indirect method using Energy Dispersive x-ray spectrometer (EDX) Shimadzu EDX-720.

### 3. Results and Discussion

Three values of bias voltage were studied: –100V, –200V and –300V at 1.0kHz frequency and 20% duty cycle. For comparison it was used DC bias. The Figure 2 shows the voltage and current waveforms for duty cycle of 20%. At bottom of this figure it is shown the voltage (in V) and on top the current (in mA). It is possible to see that the bias current drops toward zero when the voltage is switched off. When the current reaches zero, the sample is in floating potential. It was used the traditional method of the hysteresis curve to determine the proportion of N₂/Ar flow (reactive and inert gas flow to the chamber) for stoichiometric film deposition with high deposition rate. The optimal point for stoichiometric Ti6Al4V-N film deposition, corresponding to 2.2 sccm and 2.6 sccm for N₂ and Ar flow respectively (N₂/Ar = 0.85).

The average current in pulsed mode is lower than in DC mode, as can be seen in Table 2. However the peak current density (at peak pulse voltage) is significantly higher than DC bias current. This means that peak power delivered to substrate is higher in pulsed mode, although the average power is higher in DC mode.

Average film thickness of the samples was 0.4±0.2μm for all samples. The exception was the film deposited at \( V_{bias} = –300V \) in DC mode, in which we observed a thinner film with thickness approximately 0.05mm. At this voltage the ions acquire sufficient energy to produce considerable re-sputtering of ad-atoms during the deposition, resulting in a thinner film.

X-ray diffraction spectra (Figure 3) show three peaks of high intensity at 2θ angles of 37.2°, 42.8°, 74.6°, relative to the AISI 304 stainless steel substrate. The peaks relative to Ti6Al4V-N films appears at 20 angles of 37.2°, 42.8°, 62.1° indicating the formation of crystal planes (111), (200) and (220) of TiN respectively. At bias voltage of –100V and –200V, it is possible to see more intense (111) and (200) peaks for DC bias mode than for pulsed mode. However at –300V bias it is possible to observe more intense peaks (111), (200) and (220) for pulsed mode (20% duty cycle, 1kHz). The high power delivered to the substrate due to pulsed mode results in a higher deposition rate.
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Bombardment at –300 V DC promotes resputtering and probable amorphization of the film. On the other hand, for –300 V bias in pulsed mode also occurs bombardment by energetic ions, but the intermittent ion bombardment (20% on) is sufficient to allow the adatoms diffusion and time (80% off) for nucleation and growing of the grains on substrate surface.

The topographies of film surfaces are shown in Figure 4 and were obtained with atomic force microscopy – AFM. Pictures have dimensions of 5mm × 5mm. The roughness values are shown in Table 3. The roughness is higher for films deposited under DC bias for –100 V and –200 V and for –300 V pulsed bias. Films with higher roughness have more intense peaks (111), (200) and (220) of TiN in XRD pattern, that are the samples corresponding to DC bias –100 V and –200 V and pulsed bias –300 V at 1kHz and 20% duty cycle. The smoother films are corresponding to pulsed bias –100 V and –200 V and less intense peaks in XRD spectra. It indicates that the growing of crystalline films results in rougher surfaces. This can be attributed to formation of crystalline texture on the surface due a preferential growing direction of the grains.

Table 2. Substrate current bias obtained for different voltages and bias modes.

<table>
<thead>
<tr>
<th>Bias mode</th>
<th>–100 V DC</th>
<th>–100 V, 20%, 1kHz</th>
<th>–200 V DC</th>
<th>–200 V, 20%, 1kHz</th>
<th>–300 V DC</th>
<th>–300 V, 20%, 1kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density (µA/cm²) Peak</td>
<td>30</td>
<td>85</td>
<td>70</td>
<td>120</td>
<td>140</td>
<td>170</td>
</tr>
<tr>
<td>Power density (mWatt/cm²) Peak</td>
<td>3.0</td>
<td>8.5</td>
<td>14.0</td>
<td>8.0</td>
<td>42.0</td>
<td>51.0</td>
</tr>
</tbody>
</table>

Table 3. Roughness Ra of films.

<table>
<thead>
<tr>
<th>Bias mode</th>
<th>DC</th>
<th>–100 20%, 1kHz</th>
<th>–200 20%, 1kHz</th>
<th>–300 20%, 1kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughness (Ra)</td>
<td>5.3nm</td>
<td>1.9nm</td>
<td>5.0nm</td>
<td>2.3nm</td>
</tr>
</tbody>
</table>

Figure 3. XRD spectra (a) –100VDC × –100V, 20%, 1kHz, (b) –200VDC × –200V, 20% 1kHz, (c) –300VDC × –300V, 20% 1kHz.
4. Conclusion

The effects of pulsed and DC substrate bias on the surface morphology and crystallinity of Ti6Al4V-N films deposited by Grid Assisted Magnetron Sputtering were investigated. Pulsed bias causes changes in crystallinity and nano-roughness. Different combinations of bias values (voltage, frequency and duty cycle) can provide appropriate energy delivery and time for adatoms diffusion in the growing film.

Surface morphology and nano-roughness of the films are changed by the bias mode. In pulsed bias, the bombardment lasted less time, so, it was possible to observe that smoother films were yielded in pulsed bias. The growth of crystalline...
films induces rougher surfaces due to preferential directions of nano-crystal growth.

The choice of frequency, duty cycle and voltage can be used to grow films with the same crystal planes observed with DC bias, but with smoother surfaces. For DC mode bias, significant changes were not observed in film roughness; however, amorphous films can be produced as well as there-sputtering of adatoms from the substrate, when it is biased with high voltage (for example $V_{\text{bias}} = -300\text{V}$).

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**References**


