CHAPTER 6

Role of the substrate on the growth of titanium nitride thin film

In Chapter 5, the effect of working pressure on the preferred orientation of titanium nitride thin film was studied. In this chapter the substrate induced preferred orientation of the titanium nitride thin film deposited onto plasma nitried substrate is presented.

6.1 Introduction

Titanium nitride (TiN) films have been investigated widely for their very interesting properties such as high hardness, wear and corrosion resistance, low resistivity, etc. The high hardness value makes it applicable to coat cutting tools, thereby increasing the life of the tool [1]. As a decorative coating, the luxurious golden yellow color of TiN finds its application in many industries [2]. In microelectronic, application of the low resistivity and diffusion barrier property of TiN is of great demand [3-4]. TiN coating by magnetron sputtering has developed rapidly over the last decade in such a way that it has become an established process of choice for the deposition of a wide range of industrially important coatings. But due to their unsuitability for the use with many substrate materials such as low alloy steel and titanium alloys and the lack of load-bearing support provided by the substrate, these coatings have certain limitations. To address these problems and to extend the commercial viability of advanced PVD processes, duplex processes have been developed [5]. Physical vapor deposition of TiN on pre-nitried steel is a good example of a duplex process. Components treated in this way exhibit low wear characteristics of the ceramic coating, combined with the high load-bearing capacity and high fatigue strength characteristics of the nitried layer. Also, it has been reported by Gredic et al. [6] that the
plasma nitriding prior to coating deposition strongly improves the adhesion properties of the hard coating.

It is important to note that most of the TiN coatings are reported to exhibit a preferential crystallographic orientation [7-9] which affects the mechanical behavior of the coatings. The preferential orientation depends on the various process parameters and on the nature of the substrate surface [10]. Dependence of the preferred orientation of TiN on the process parameters like working pressure is discussed in the Chapter 5. This chapter reports thoroughly on the difference in the preferred orientation observed in the DC-sputtered TiN coatings deposited under various conditions onto the bare AISI M2 and plasma-nitried AISI M2 substrate. The AISI M2 high-speed steel (HSS) (0.86% C, 6.0% W, 5.0% Mo, 4.1% Cr, 1.9% V, and 0.5% Co, in wt.%) is selected as the substrate material because it is mostly used as a cutting tool material.

6.2 Experimental set up and diagnostic procedure

Disc-shaped samples of 20 mm in diameter and 4 mm in thickness, made from the AISI M2 high speed steel are prepared to mirror polish finish by standard metallographic method and cleaned with acetone before processing. Plasma nitriding is done in a different arrangement. The schematic diagram of the planar magnetron sputtering system as well as plasma nitriding system used in this study is described respectively, in the section 2.2 and the section 2.5 of the Chapter 2. Initially, the samples of AISI M2 high speed steel are placed on the sample holder which is negatively biased. The vacuum chamber is evacuated to 1 Pa. The glow discharge is generated using a DC pulsed power supply (1000V, 3A, 0-100KHz) with a gas mixture composition of 80% N₂ -20% H₂. The working pressure of 5 mbar and a voltage of 550 V are maintained during the process. The samples are kept at a temperature
of 500°C with an accuracy of ±10°C, which is read on a temperature indicator using a J-type thermocouple. An external heater is used to heat the negative biased sample holder. After 24 h, AISI M2 samples are cooled with nitrogen gas and latter taken out from the chamber when the samples attained room temperature. It was obtained from the XRD studies of the deposited thin films in the Chapter 5 that lower working pressure (less than 0.5 Pa) favors the preferential growth of TiN (111) on bare AISI M2 high speed steel. Keeping this fact into account, the TiN thin film is deposited onto bare as well as the plasma nitrided high speed steel below 0.5 Pa. The working pressures at $3 \times 10^{-1}$ Pa and input power of 300 W are fixed during the deposition of the samples. During the deposition the values of nitrogen partial pressure ($P_{N_2}$) are varied from $1 \times 10^{-2}$ to $8 \times 10^{-2}$ Pa. Equal duration of TiN deposition at the above mentioned values of nitrogen partial pressures results thin film of thickness 2.90µm to 1.97µm. To clean the substrate surfaces prior to the deposition and improve film’s adhesion, the bare and plasma-nitrided substrates are pre-treated by Ar plasma in a sputtering chamber for 10 min with a bipolar power supply bias of -300 V. Phase composition of all the untreated and treated samples are studied by X-ray diffraction (XRD) using a XRD3000PTS diffractometer (GE Inspection Technologies, Ahrensburg, Germany) with the CuKα radiation ($\lambda = 1.5406$ Å) in the Bragg-Brentano configuration operated at 40 keV and 50 mA. XRD patterns are recorded with step durations of 4 s at each step in the angular range of 30° to 90°. In order to find out the substrate induced TiN growth, we need to compare the texture coefficients of the various TiN diffraction peaks deposited on the bare and pre-plasma nitrided substrate. Information regarding the preferred orientation of the different planes is obtained by measuring the
intensities of the diffraction peaks and as such, the texture coefficients corresponding to the various planes. The thickness of the deposited films is determined by properly calibrated quartz crystal thickness monitor model no. DTM-101 provided by Hind HiVac, Bangalore, India.

6.3 Results and discussions

6.3.1 Langmuir probe study of the magnetron plasma

The magnetron discharge plasma at the above mentioned values of working pressure is scanned by the cylindrical Langmuir probe to obtain the value of ion and the electron density. The important production and loss mechanism in the nitrogen added argon plasma is already described in the section 5.3 of the Chapter 5. When nitrogen is added at a fixed working pressure, the densities of the nitrogen related ions such as N$_2^+$, N$_3^+$, and N$_4^+$ should increase and Ar$^+$ ions should decrease for obvious reasons. However, due to the higher rate coefficients of the recombination reactions of the nitrogen related ions (Reactions 3, 4 and 9 of Table 5.1, section 5.3 of Chapter 5) the loss mechanisms of electrons become dominant over its production mechanisms. As a result a gradual decrease of density of electron with increasing nitrogen partial pressure is also observed. Following the procedure of the mean ion mass as explained in the Chapter 2, the density of Ar$^+$ ions in the discharge is calculated and as mentioned already, it is found to decrease with addition of nitrogen in the argon discharge. As the sputtering yield of titanium target to Ar$^+$ ions is greater than the other positive ions present in such discharge, therefore higher value of deposition rate is achieved at lower nitrogen partial pressure. Accordingly, the TiN films deposited with nitrogen partial at 1 x 10^{-2} Pa have the maximum thickness. The modulation of electron and
Ar⁺ ion density and TiN deposition rates as a function of nitrogen partial pressure are given in Fig. 6.1.

![Graph showing the variation of electron and Ar⁺ ion density with nitrogen partial pressure.](image)

**Figure 6.1** Effect of nitrogen partial pressure on (a) the variation of electron and Ar⁺ ion density in nitrogen added argon plasma (b) the film deposition rate.

**6.3.2 XRD studies of the plasma nitrided AISI M2 high speed steel**

The X-ray diffraction patterns with CuKα radiation is used to identify the formed phases in the plasma nitrided samples.

![XRD pattern of bare and plasma nitrided AISI M2 high speed steel.](image)

**Figure 6.2** X. R. D pattern of bare and plasma nitrided AISI M2 high speed steel
The formation of the nitrided layer of different structures can be controlled by N\textsubscript{2}/H\textsubscript{2} gas composition [12]. Fig. 6.2 shows the diffraction patterns of the bare and plasma-nitrided sample, respectively. These figures reveal that all intense peaks on the bare substrate are assigned to α-Fe-phase. On the plasma nitrided substrate the most intense peaks are assigned to \(\varepsilon\)-Fe\textsubscript{2.3}N and \(\gamma'\)-Fe\textsubscript{4}N phases while the peaks of α-phase are disappeared. It is worth mentioning that the hexagonal closed packed (hcp) \(\varepsilon\)-nitride exhibits a higher hardness than the face centered cubic (fcc) - \(\gamma'\)-nitride [13].

### 6.3.3 XRD studies of the deposited titanium nitride thin films

The phase composition and texture in polycrystalline TiN thin film deposited onto the bare and plasma-nitrided AISI M2 high-speed steel are analyzed by X-ray diffractometer. Fig. 6.3 shows X-ray spectra for TiN coating on (a) bare AISI M2 sample and (b) plasma-nitrided AISI M2 substrate at different values of nitrogen partial pressures. The coatings deposited onto the above mentioned substrates show the presence of (111), (200), and (220) TiN diffraction peaks and α Fe(110) peak on the bare sample. All iron nitride phases like \(\varepsilon\) Fe\textsubscript{2.3}N and \(\gamma'\) Fe\textsubscript{4}N are observed even after deposition of the TiN coating onto the plasma-nitrided substrate. It is clear from the Fig. 6.3(a)-(b) that the orientation of TiN is clearly influenced by deposition and substrate conditions. On the bare samples, higher intensity of the TiN (111) peak is observed compared to the TiN (200) and TiN (220) peaks. However at higher nitrogen partial pressure an increased intensity of TiN (220) peak is noticed. On the plasma-nitrided samples, the relative intensity of diffraction peak is different than the bare samples. Here, the intensity of the TiN (200) peak is dominant over the other TiN diffraction peaks. From the observed intensity of the diffraction planes, it is possible to calculate the texture coefficients \(T_c\) of a particular diffraction plane that represents the
Figure 6.3(a) X.R.D patterns of TiN deposited on the bare AISI M2 substrate.

Figure 6.3(b) X.R.D patterns of TiN deposited on the plasma nitrided AISI M2 substrate.

degree of preferred orientation. On bare substrate a TiN(111) preferred orientation is observed. The minimization of the strain energy [14, 15] as a responsible factor for such preferred orientation of the TiN films on the bare AISI M2 substrate was explained in
details in the Chapter 5. It is worthwhile to mention again that for the deposited TiN thin films with such high value of thickness (greater than 1.90 μm), (111) preferred orientation is the result of relieving strain energy [16]. It is also interesting to mention that decrease of the thin film thickness at the higher value of nitrogen partial pressure promotes more open diffraction planes like the TiN(220) on the bare substrate. However, the texture growth of TiN films deposited onto the plasma-nitrided high-speed steel is different. In this case the (200) preferred orientation is observed at the various deposition conditions. The value of the texture coefficient of the different TiN peaks deposited onto the bare and plasma nitrided AISI M2 high speed steel is given in the Table 6.1.

Table 6.1: Value of texture coefficient (Tc) of TiN peaks deposited on bare and plasma nitrided high speed steel

<table>
<thead>
<tr>
<th>Nature of the substrate</th>
<th>Tc on bare AISI M2 steel</th>
<th>Tc on pre-plasma nitrided AISI M2 steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiN(111)</td>
<td>TiN(200)</td>
</tr>
<tr>
<td>Wp (Pa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1x10^-2</td>
<td>1.79</td>
<td>0.20</td>
</tr>
<tr>
<td>3x10^-2</td>
<td>1.44</td>
<td>0.72</td>
</tr>
<tr>
<td>5x10^-2</td>
<td>1.31</td>
<td>0.57</td>
</tr>
<tr>
<td>8x10^-2</td>
<td>1.18</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Note that the bold indicates the preferred TiN peaks deposited onto bare and pre-plasma nitrided substrate.
It is clear from the table that minimization of strain energy cannot explain the texture of TiN films on the plasma-nitrided substrate and as such, we have to look for the substrate-induced texture growth in this case.

6.3.4 Effect of substrate on the texture growth of the TiN films

Very few investigation reports the contribution of substrate surface structure [17-18] on the preferential growth of TiN thin film. It can be seen from the XRD analysis that near-surface crystallography affects the orientation of TiN film subsequently grown on them. The XRD analysis of the plasma-nitrided samples shows the presence of $\gamma'$Fe₄N and $\varepsilon$Fe₂₃N diffraction peak leading to the formation of compound layer on the surface of the substrate. The inter-atomic spacing of $\gamma'$Fe₄N planes of the plasma-nitrided substrate is found to be very similar to the TiN diffraction planes. Earlier studies [3, 18-21] of the TiN growth on the plasma-nitrided substrate have reported the preferred orientation of TiN (220) plane but the compositions of the hydrogen-nitrogen gases for plasma nitriding in those studies are different from the one used in this investigation. Finally in order to explain the preferential growth of the TiN (200) peak on the plasma-nitrided substrate in our study, we have compared the inter-planar distances (d) of $\gamma'$Fe₄N planes of the plasma-nitrided surface with the TiN diffraction planes on bare substrate and are listed in the Table 6.2. Both TiN (200) and $\gamma'$Fe₄N (111) planes are closed pack. Also, from Table 6.2, it is clear that the inter-atomic spacing between TiN (200) planes and $\gamma'$Fe₄N (111) planes are very similar, i.e., an atomic mismatch of only 0.23%. Thus, interfacial strain at the substrate (111)/coating (200) interface would be very low [22]. This factor may be responsible for higher degree of preferred orientation of TiN (200) plane on plasma-nitrided substrate.
Table 6.2 Inter-atomic spacing between TiN planes and $\gamma'$Fe$_4$N planes

<table>
<thead>
<tr>
<th>Phases</th>
<th>$\gamma'$Fe$_4$N</th>
<th>TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d(nm)</td>
<td>d(nm)</td>
</tr>
<tr>
<td>(111)</td>
<td>0.2191</td>
<td>0.2440</td>
</tr>
<tr>
<td>(200)</td>
<td>0.1901</td>
<td>0.2141</td>
</tr>
<tr>
<td>(220)</td>
<td>0.1351</td>
<td>0.1487</td>
</tr>
</tbody>
</table>

Note the similarity of calculated values (italics) for inter-planar distances of $\gamma'$Fe$_4$N (111) plane and TiN (200) plane.

Since different iron nitride phases are present on plasma-nitried surface, additional investigations of the coating/substrate interface using HR SEM and TEM are necessary.

6.4 Conclusion

The chapter reports the growth of TiN texture on the bare and plasma-nitried AISI M2 high-speed steel. While there are many reports available in the literature regarding the growth of TiN as a function of the deposition parameters on Si and bare substrate, very few investigations is available regarding the effect of substrate such as the plasma nitried surface on the growth of TiN texture. In this study, the substrate-induced texture growth of TiN is clearly visible on the plasma-nitried high-speed steel substrate. While the TiN (111) plane preferentially grows on the bare AISI M2 substrate, the TiN (200) orientation is preferred on the plasma-nitried substrate. The matching of the inter-planar distances of the TiN (200) plane with $\gamma'$Fe$_4$N plane of the plasma-nitried substrate is believed to be a factor responsible for this preferred orientation.
References


