Investigation of Influence of Gas Ratio on the Electron Temperature in TiN Magnetron Sputtering Deposition System

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In this work, a nanolayer of titanium nitride which produced by the magnetron sputtering system is synthesized. Moreover the effect of plasma parameters on the electron temperature is studied. Electron temperature has a significant effect on the plasma coating system properties. The results show that, increasing the working pressure and nitrogen ratio in the system causes decreasing electron temperature.

1- Introduction
Owing to high hardness, wear resistance, and thermal stability, TiN thin film is commercially used in the tool industry as a protective film to prolong the service life of substrate materials and improving the tribological performance of tools and machine parts in industrial applications. The progress of micro-electromechanical systems (MEMS) is driving the demand for ultra-thin (less than 0.5 Am) protective and functional nitride coatings [1, 2].

Direct current (DC) sputtering has become a very popular technique to develop a wide variety of thin films including nitrides. Using this method it is possible to deposit compound films with controlled microstructure and composition.

In the past few decades, progress in understanding physics and chemistry of ionized gases has led to the widespread acceptance of plasma technology for surface modification in different types of industrial applications [3]. During ionization process for titanium nitride deposition, the electrical discharge enhances the surface interactions. Plasma produces active nitrogen and titanium species and results to the momentum and energy transportation to the surface. Hence optimizing the production of these active species in electrical discharge plasma is essential because it leads to better control of surface interactions during the film growing process and producing a layer with better quality [4]. It requires fundamental understanding of the plasma characteristics in the experimental conditions.

The electron temperature is one of the most important parameters of the plasma which influences on the production of active species by inelastic collisions. Measuring electron temperature in different experimental conditions of electrical discharge helps to better understanding of the particle collision process, plasma reactions and active species concentration in the plasma [5]. Most of the plasma diagnostic techniques are either electrical or optical in nature. The electrical technique which is used for electron temperature and density measurement is Langmuir probe. But it has some remarkable problems [6]. Therefore, optical diagnostic methods have been developed.

Optical emission spectroscopy (OES) has been extensively used to identify and characterize the excited and ionized species in glow discharge plasma. In glow discharge plasma, electron collisions excite some of the active species to the higher electronic states. These species decay and emit photon with characteristics wavelength [7]. The basic assumption in this technique is that, the intensity of specific emission wavelengths of excited state depends on the species concentration in excited state.

This work provides an appropriate insight about the species that influence on the reactivity of magnetron sputtering plasma in order to improve the coated films and nanolayers. The different experimental conditions can affect on the electron temperature in the magnetron sputtering plasma. In this investigation, we study the effect of working pressure and nitrogen ratio on the electron temperature.

2- Experimental Setup
In this experiment, argon-nitrogen gas mixture is used as the working gas. The sputtering chamber is a glass chamber which will be accompanied by titanium cathodic target (purity 0.99999). The plasma is generated in the glow discharge regime, for titanium nitride deposition. Experiments are arranged in different applied electrical powers: 90, 110, 130 and 150 W. Working gas pressure is from about 0.05 mbar to 0.09 mbar and the ratios of nitrogen gas to the total gas are adjusted on 10%, 20% and 30%. Each experiment continues for 40 min. During the experiments, OCEAN OPTICS spectrometer (HR2000) is used to detect the plasma spectra.
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3- Results and Discussion

The electron temperature, which affects the plasma reactivity can be evaluated from the Ar-I spectral lines intensity, using Boltzmann’s plot method. If the LTE approximation is valid in the plasma, a linear dependence of the logarithm of the normalized population density on the excitation energy can be found (which called as the Boltzmann plot (equation 1)) [9]:

$$\ln \left( \frac{I_{\lambda, k_i}}{g_{k_i} A_{k_i}} \right) = - \frac{E_k}{k_B T} + C$$

(1)

where $\lambda_{k_i}$ is the wavelength, $I_{\lambda_i}$ is the measured intensity, $A_{k_i}$ is the transition probability, $g_{k_i}$ is the statistical weight of upper levels, $C$ is a constant for a certain atomic species, and $T$ is the equilibrium temperature. Furthermore, if the respective upper levels are populated only by inelastic collisions of the electrons the measured temperature can be considered as the electron temperature.

Figure 1 shows an optical emission spectrum of the titanium nitride plasma at 150W input power. In this experiment the working gas pressure is set at 0.05 mbar. The ratio of nitrogen gas is 20%.

![Figure 1: Emitted spectrum of Titanium nitride plasma deposition for apply power 150W, working pressure 0.05 mbar, and nitrogen gas ratio 20%.](image)

Using a number of Ar-I spectral lines that have a common lower energy level, the electron temperature is calculated from the slope of the Boltzmann plot.

The data for the recorded Ar-I spectral lines are given in Table 1. Figure 2 represents the value of $\ln (I/\lambda A)$ versus the energy of the upper level for each considered transition, and the electron temperature is obtained from the slope according to the equation 1.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$g_{k_i} A_{k_i} (10^6 S^{-1})$</th>
<th>$E_k$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>696.5431</td>
<td>19.2</td>
<td>107496.4166</td>
</tr>
<tr>
<td>706.7218</td>
<td>19.0</td>
<td>107289.7001</td>
</tr>
<tr>
<td>738.3980</td>
<td>42.4</td>
<td>107289.7001</td>
</tr>
<tr>
<td>811.5311</td>
<td>232.0</td>
<td>105462.7596</td>
</tr>
<tr>
<td>912.2967</td>
<td>56.7</td>
<td>104102.0990</td>
</tr>
</tbody>
</table>

One of the factors which influences on the electron temperature is the nitrogen gas ratio. Figure 3 shows that the electron temperature in plasma increases with decrease of nitrogen ratio. This fact may be explained as follows: The ionization cross sections and ionization potentials are nearly the same for Ar and N2 [~2.5×10$^{-20}$ m$^{-2}$ and ~ 15.7 eV, respectively], so these parameters are not likely to explain the increase in electron temperature with decrease of nitrogen ratio.

A possible explanation for the variation of the electron temperature is the difference in the electron energy distribution function (EEDF) especially in the high energy tail. This is probably due to a higher secondary electron yield at the target in the presence of argon in the discharge [10]. The other possible reason may be the Penning ionization of Ti atoms because in penning ionization which results in the argon neutral ground state atom, a titanium ion and an energetic electron can be produced.

![Figure 2: Boltzmann’s plot used to estimate the electron temperature.](image)

This mechanism and possibly other charge-exchange reactions can provide high-energy electrons, which may account for the increase in average electron temperature upon the addition of titanium atoms by
sputtering. Figure 3 also describes the effect of filling gas pressure on the electron temperature. The decrease in electron temperature with increase in filling pressure may be explained by the collisional loss of the electron energy. When pressure in the chamber increases, it causes an increase in the number of collisions between the electrons and the other plasma species. Therefore increasing the transferred energy from the electrons to the plasma species causes the plasma temperature to increase and the electron temperature to decrease [11].

![Figure 3: Electron temperature changes in addition argon gas for a constant input power 150 W.](image)

4- Conclusion

In this work, a TiN nanolayer was deposited on the stainless steel substrate. The effect of the different experimental conditions on the electron temperature was investigated. As it explained before, the electron temperature was an important factor in the magnetron sputtering plasma. It has been seen that a decrease of nitrogen ratio in the plasma has been caused an increase in the electron temperature while an increase in working pressure reduces the electron temperature.

5- Reference

[1] H. Kupfer, F. Elstner, G. Hecht, F. Richter, TiN formation by reactive magnetron sputtering, Department of Physics, Technical University of Chemnitz, Germany.


