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Preparation and Optimization of High Quality TiN Films

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Abstract

TiN thin films have been deposited by DC reactive magnetron sputtering method on glass substrates. The effects of the substrate temperature and the substrate bias voltage on the structural, optical and electrical properties of the films were studied by using XRD, STM, optical transmission and resistivity measurements. The bias voltage was varied in the 0 to 200 V range for two substrate temperatures, 100 °C and 300 °C.

The results showed that the substrate bias voltage influenced the stoichiometry and structure of the films. The smoothest and least porous TiN films were prepared at about 160 V substrate bias voltage and 300 °C substrate temperature. The electrical resistivity of the TiN films decreased with increasing substrate temperature and increasing thickness. It is found that the optical transmission of the films in the visible region were enhanced by increasing the substrate bias voltage for the same substrate temperature. In addition, optical transmission was improved by the TiN/MgF_2 two layer AR coating.

Key Words: TiN, Magnetron Sputtering, Ion Bombardment, Optical transmission, Antireflection coating.

1. Introduction

TiN films have interesting properties such as exceptional hardness, high wear resistance, high melting point, good chemical inertness, thermodynamic stability and golden-yellow colour [1-10]. Hence, they are widely used as wear and corrosion resistant coatings and for surface decoration. In addition, due to their high electrical conductivity, TiN films are used in several areas of microelectronics such as diffusion barriers, Schottky contacts and contact layers in solar cells [3-11]. Recently, TiN films have become very important for anti-reflection (AR) and anti-static (AS) coatings in optical applications [8,11-14]. TiN coatings are also used for orthopaedic prostheses, cardiac valves and dental prostheses [20]. This study reports the effect of substrate temperature and substrate bias voltage on the properties of the TiN films.

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2. Experimental

2.1. Preparation of films

TiN thin films have been deposited on silicon and quartz substrates by DC reactive magnetron sputtering. High purity (99.999%) Ar and N_2 were used as the sputtering and reactive gases, respectively. The system had a water cooled planar magnetron sputter source (1" US' GUN II). The target used was a Ti (99.9% purity) disk with a 2.54 cm diameter and 3.2 mm thickness. The Ti target was sputter-cleaned prior to each deposition for 15-20 minutes. The discharge power on the Ti target was 50 W and the substrate to target distance was about 5 cm. The base pressure of the vacuum system was 5×10^{-7} Torr. During experiments, the total gas pressure was kept at 4×10^{-3} Torr. The films were deposited with a 15% nitrogen gas partial pressure in a nitrogen-argon gas mixture. Films were deposited at the substrate temperatures of 100 and 300 °C. The substrate bias voltage was varied from 0 to 200 V.

2.2. Film characterization

The electrical resistivity of the TiN films was measured by the four-point probe method. The crystallographic orientation of the TiN films was examined by means of a Philips PW1140/00 diffractometer using CuK_α radiation ($\lambda = 1.542$ Å) with a Ni filter. A stylus profilometer was employed for determining the film thickness. The surface topography of the prepared films was analyzed by using scanning tunnelling microscopy (STM). Optical transmittance spectra were measured using a Varian Carry 5E spectrophotometer from 200 nm to 2000 nm and showed that the grown films were highly transparent in the visible region.

3. Results and Discussion

3.1. Electrical properties

Stoichiometric TiN films were determined to have a low and stable electrical resistivity. In stoichiometric TiN, the first interband transition particularly occurs at the same energy as in gold colour wavelength and this compound therefore exhibits a gold-like colour [18]. The electrical properties of the TiN films depend on the stoichiometry and the structure. The final structures and the electrical properties of the TiN films also have a close relationship with the nitrogen partial pressure, the substrate temperature and the negative bias voltage V_s applied on the substrate. A negative bias voltage applied to the substrate during the film deposition improves the quality of the films and to obtain an electrical resistivity comparable to that of the TiN single crystals, 30 $\mu\Omega$cm [2,5,6].

In this study, the bias voltage was varied between 0 and 200 V at two different substrate temperatures, 100 and 300 °C. In Figure 1 and Figure 2, a linear decrease can be seen in electrical resistivity with increasing substrate bias voltage for the same substrate temperature. There is a clear correlation between growth temperature and resistivity of the films, such that with a lower substrate temperature the films have a higher resistivity.

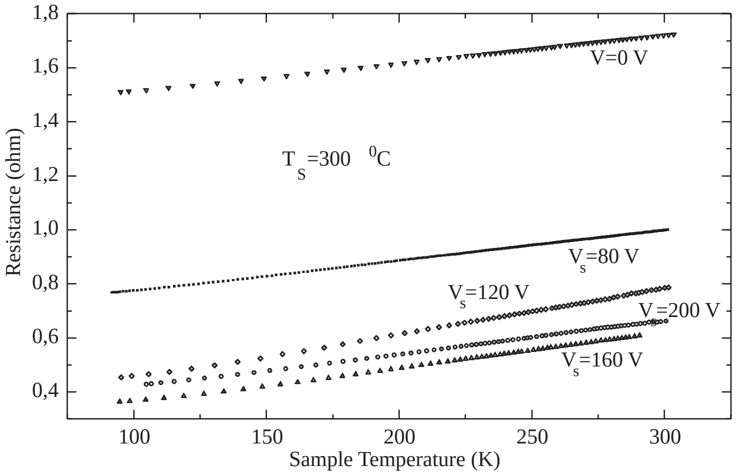

Figure 1. The variation of electrical resistivity with the substrate bias voltage for TiN films that were prepared at 300 °C substrate temperature.

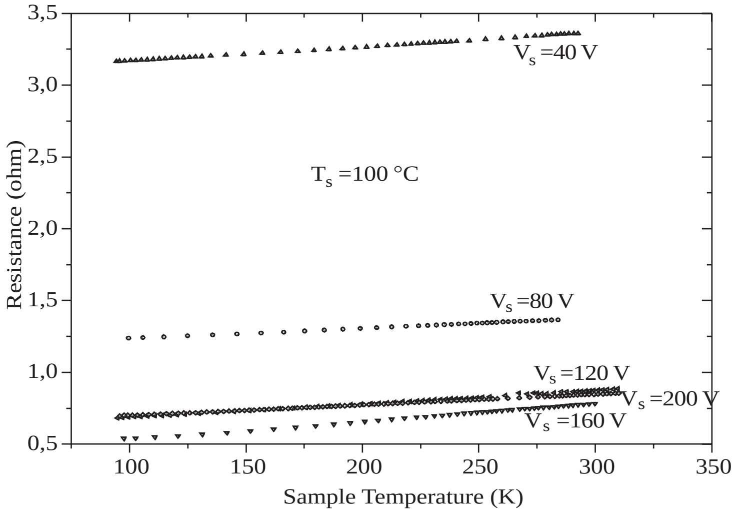

Figure 2. The variation of electrical resistivity with the substrate bias voltage for TiN films that were prepared at 100 °C substrate temperature.

The optimal value of the bias voltage was determined to be 160 V for both substrate temperatures. The electrical resistivity of the films began to increase beyond the optimal bias voltage value. The resistivity of the 1500 Å TiN film was about 40 $\mu\Omega$cm at room temperature (Figure 3, inset). The temperature coefficient of resistivity $\left[TCR = \frac{1}{R}\frac{dR}{dT}\right]$ was calculated from the resistivity measurements. It was found that a clear increase is observed in the TCR with varying substrate bias voltage from 0 to 160 V for two substrate temperatures (Figure 3). A density increase is expected due to the elimination of voids with increasing substrate bias voltage and temperature. The increase of substrate bias voltage and/or temperature increases the mobility of adatoms promoting more closely packed structures.

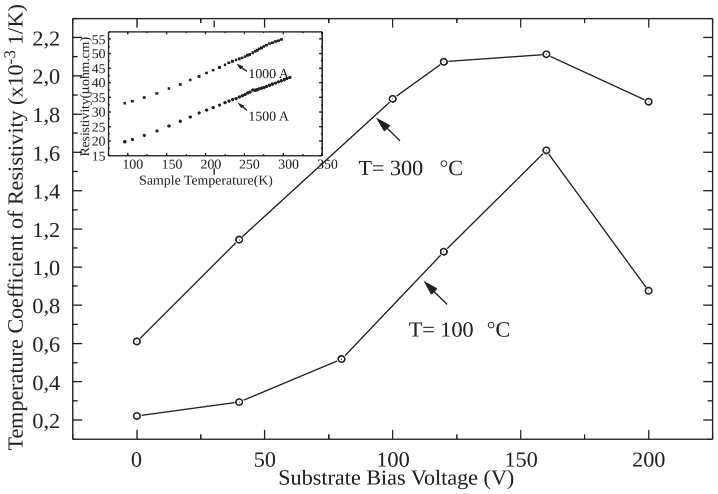

Figure 3. Substrate bias voltage dependence of TCR for two substrate temperatures.

3.2. XRD and STM

The variation of the electrical resistivity also has a close relation with the variation in preferred orientation [8]. The (111) orientation is the most commonly observed one, although the (200) and (220) orientations were also reported. TiN films that have high (111) peak intensity also have high resistivity [8]. However, the (111) peak was usually observed for TiN coatings of approximately 2 μm thickness [16]. In this study, the orientations were (200) and (220) for unbiased condition at 300 °C substrate temperature. (220) and (200) planes contain both nitrogen and titanium atoms [17]. However, at 120 V bias voltage the texture became (220)-dominated for the same substrate temperature (Figure 4). There was a window for the growth of the preferred orientation at approximately 100-200 eV/atom [16]. It is clear that the preferred growth of a plane depends greatly on the substrate bias voltage.

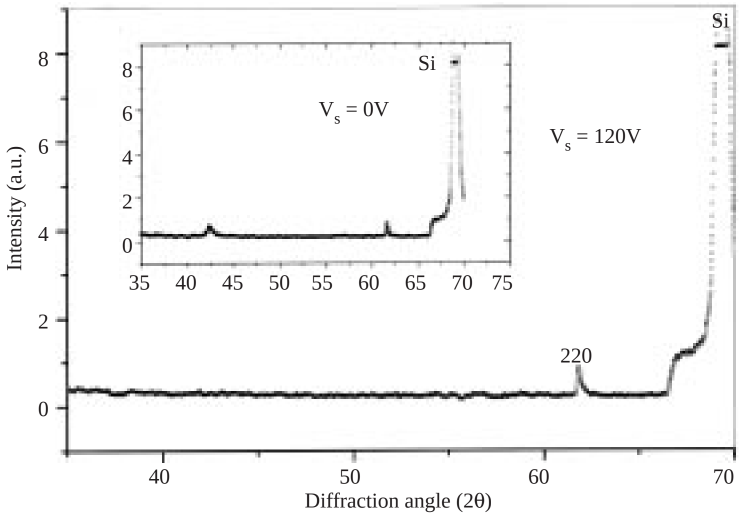

Figure 4. The X-ray diffraction of TiN films that were prepared at different bias voltages for 300 °C substrate temperature.

The voids of the structure decreased with increasing substrate bias voltage from 0 to 160 V at 300 °C substrate temperature, as the sequence of the STM micrographs reveal in Figure 5. Thus, uniformity of the films was improved with substrate biasing up to an optimal value and the renucleation was observed to start above a critical bias value. In addition, substrate temperature was believed to control the diffusion of atoms during the film growth [17]. Figure 6 shows the variation of the surface topography of TiN films with temperature. Results indicate that the high density, closely-packed film growth was promoted with increasing substrate temperature.

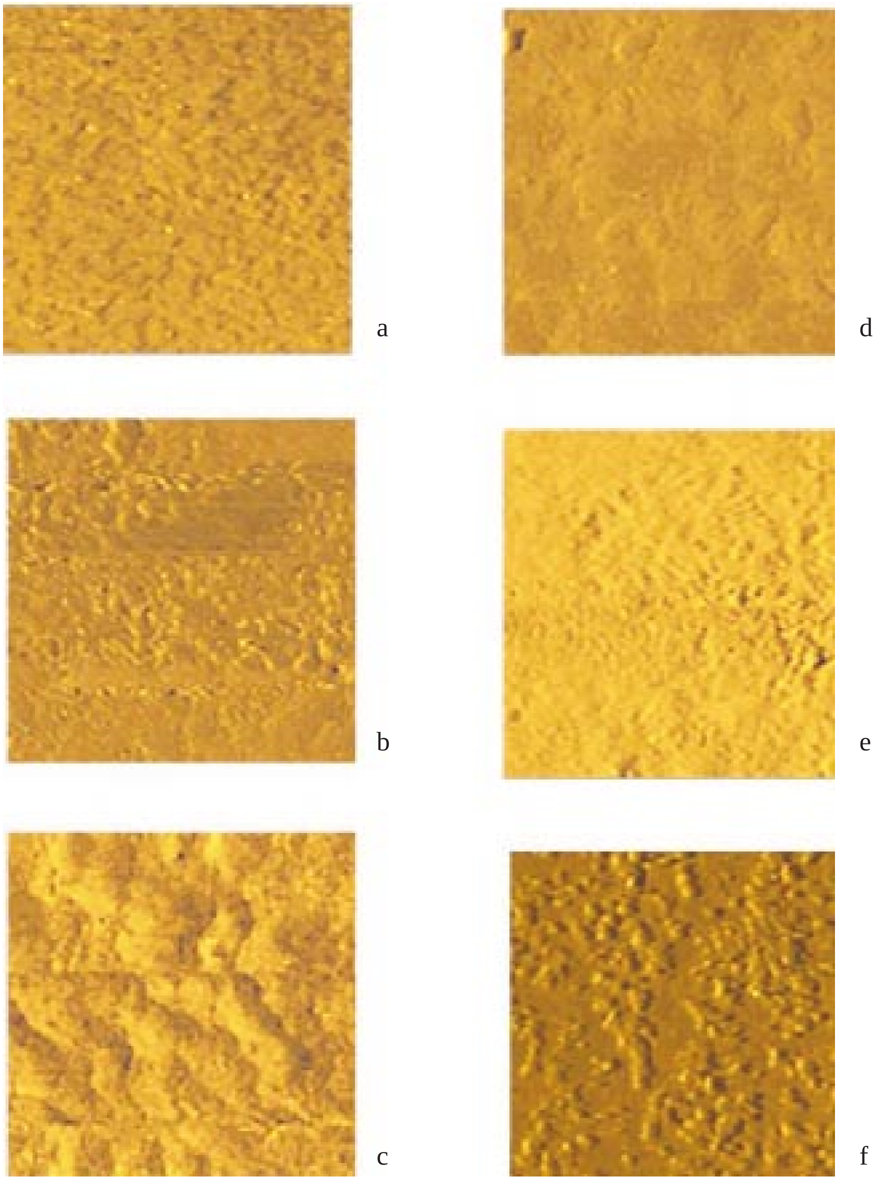

Figure 5. STM micrographs show the variation of surface morphology with increasing substrate bias voltage at 300 °C substrate temperature (a. V_s = 0V, b. V_s = 40V, c. V_s = 80V, d. V_s = 120V, e. V_s = 160V, f. V_s = 200V).

3.3. Optical properties

One of the main applications of TiN is solar control window coating. Very thin TiN films have been suggested as antireflection (AR) and antistatic (AS) layers for display in optical coatings [11,12]. Spectral transmittance in UV, visible, and near IR wavelengths depend on the N/Ti ratios [12]. TiN can be used as a heat mirror because of its stability at high temperatures and because of its high reflectivity in the infrared region.

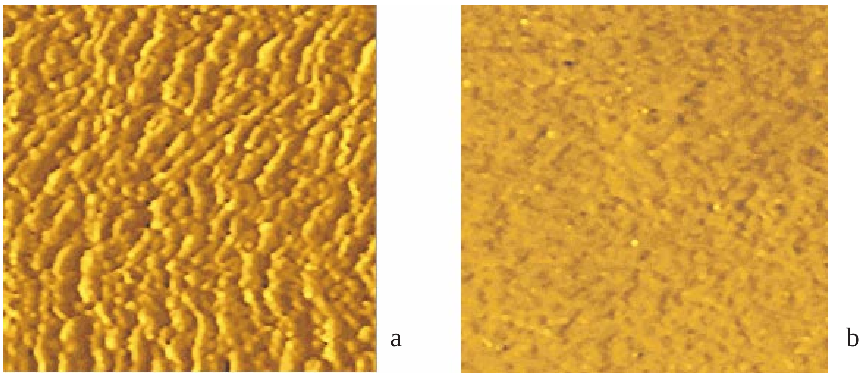

Figure 6. The difference between the surface topography of unbiased TiN films with varying substrate temperature (a. $T_s = 100$ °C, b. $T_s = 300$ °C).

Film thickness has to be optimised for the desired region of visible transmission. The optical transmissions of various TiN films as a function of the wavelength are measured. Figure 7 and Figure 8 show that the optical transmission of the TiN films increases with increasing substrate bias voltage for both substrate temperatures in the visible region. However, the transmission of the films that are prepared at $T = 100$ °C substrate temperature is higher than that prepared at $T = 300$ °C. As can be observed in these figures, transmission curves have a high symmetry with respect to $\lambda_0 = 450$ nm in the visible region. The thickness of TiN films is very important to get wide band AR coatings, as shown in Figure 9. While transmission is increasing, the width of the AR band is broadened with decreasing thickness of the films. A good agreement is seen in Figure 9 between the experimental $T(\lambda)$ curves and the calculated $T(\lambda)$ curves in the visible spectrum; the latter were obtained via the "Essential Macleod" software package.

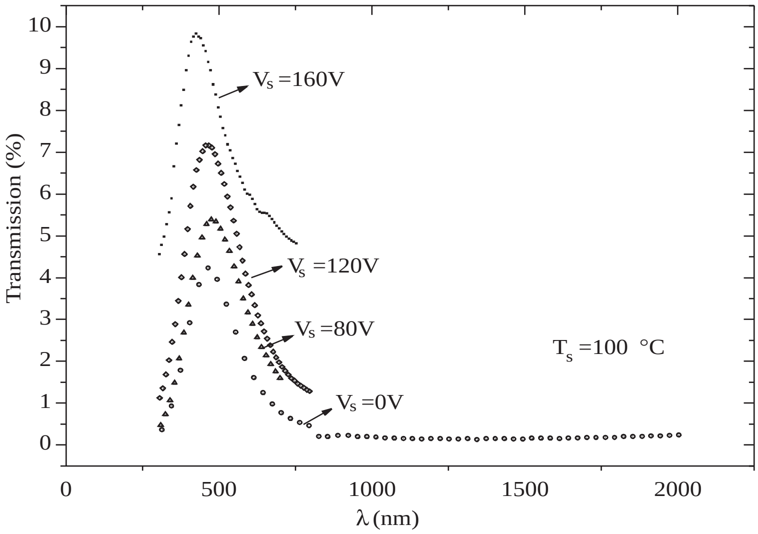

Figure 7. Transmission spectra vs. wavelength for TiN films that were prepared at constant substrate temperature (100 °C) with increasing substrate bias voltage.

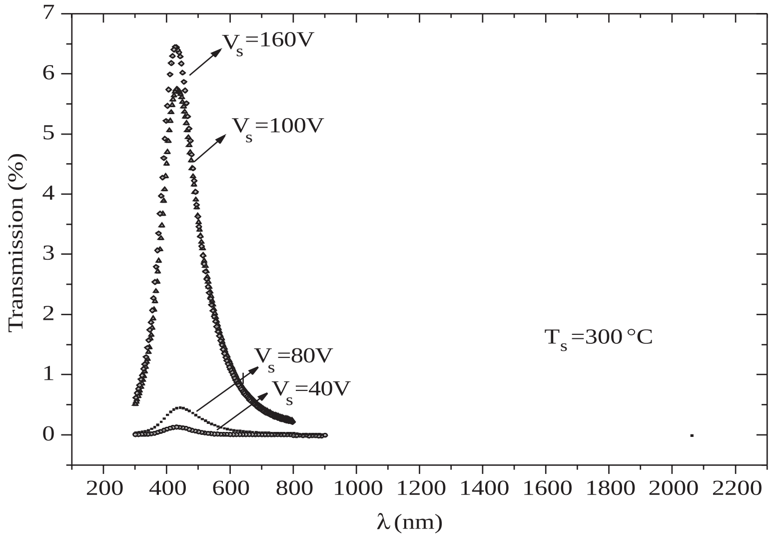

Figure 8. Transmission spectra vs. wavelength for TiN films that were prepared at constant substrate temperature (300 °C) with increasing substrate bias voltage.

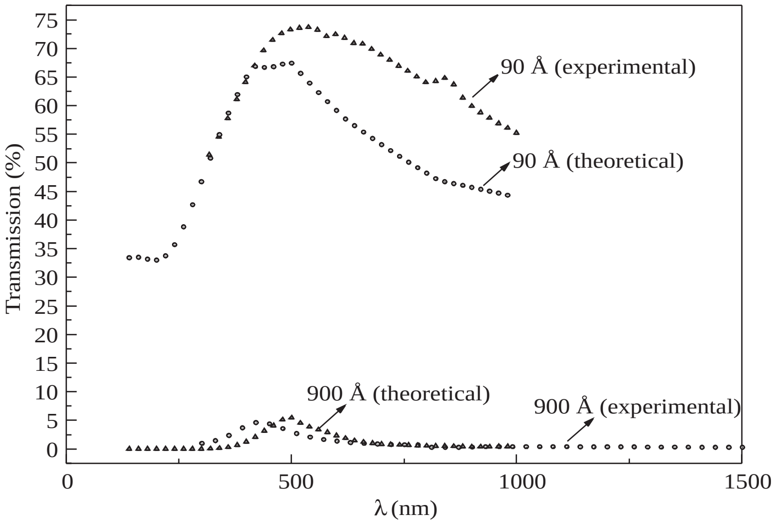

Figure 9. Experimental and theoretical optical transmittance vs. wavelength for TiN films of different thicknesses.

AR coatings reduce the intensity of the reflection in a desired wavelength region with appropriate design of the right materials. The purpose of all thin film design techniques is to obtain an optimal solution. In this study, two layer AR coatings were prepared in order to increase the optical transmittance of the prepared TiN films in the visible region. According to the two layer AR coating theory for nonabsorbing films and for normal incidence radiation, reflection is reduced to zero when $\sqrt{n_s} = n_2/n_1$, where n_s, n_1 and n_2 are the refractive indices of substrate, bottom coating, and top coating, respectively. The optical thickness of the layers were taken as a quarter wavelength $d = \lambda_0/4n$ for the reflected waves to interfere destructively, where λ_0 is the reference wavelength [21]. Thus, we decided that MgF_2 is a convenient material to deposite on TiN for broadband AR coating in the visible region according to the two layer antireflection coating theory where $n_s = 1.52$, $n_{2(MgF2)} = 1.38$, $n_{1(TiN)} = 1.70$ [8]. The required MgF_2 thickness was calculated from the well-known quarter-wave layer thickness relationship [21]. MgF_2 is deposited on TiN films by using the thermal evaporation method. The peak transmittance of a two-layer coating, TiN/MgF_2, was improved to 42% from 26% after AR coating at $\lambda_0 = 450$ nm, as shown in Figure 10.

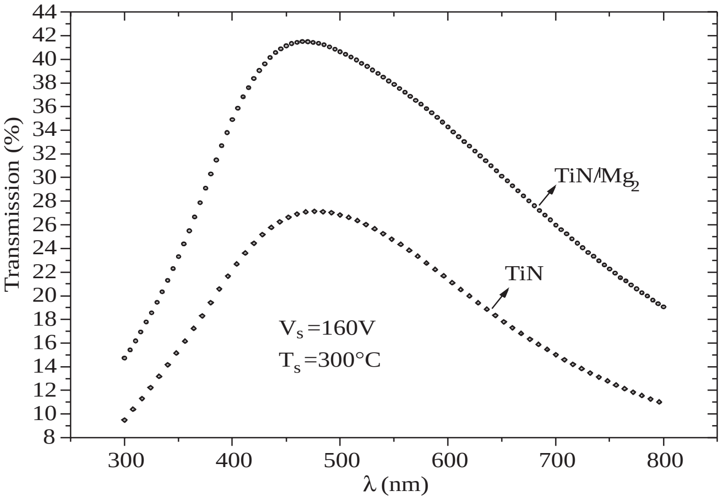

Figure 10. Transmission spectra vs. wavelength for two layer TiN/ MgF_2 AR coatings on quartz substrates. $T_{max}(\lambda) = 42\%$ at $\lambda = 450$ nm for TiN/MgF_2(TiN;$T_s = 300$ °C, $V_s = 160$V).

4. Conclusion

It is determined that the substrate bias voltage, the substrate temperature, the discharge power and the nitrogen partial pressure are fundamental parameters for growing high quality of the TiN films. In this study, the electrical resistivity and the surface topography of the prepared films were improved by adjusting the substrate temperature and bias voltage to the optimal values. According to the electrical resistivity measurement and STM results, the optimal value of the substrate bias voltage was found to be $V_s = 160$ V for the substrate temperature of 300 °C.

In addition, optical transmission of TiN was determined to be affected by the bias voltage and the substrate temperature as well. Maximum optical transmission values were obtained for 160 VDC at $T_s = 100$ °C. Higher substrate temperatures are believed to anneal out Ti vacancies that are needed for higher transmission. It has been determined that the two layer TiN/MgF_2 coatings resulted in higher visible transmission values than the single layer TiN coatings.

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