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Effect of nitrogen concentration on titanium nitride thin film formation

Abstract. This paper presents the study of the influence of argon/nitrogen gas concentration ratio in the of reactive magnetron sputtering process on the formation of titanium nitride (TiN) thin films. The addition of 5% nitrogen to the gas mixture is sufficient for the formation of titanium nitride films. It was found that changing the concentration of nitrogen in the reactive gas mixture affects the morphology of the surface, in particular, increasing the concentration of nitrogen leads to an increase in surface roughness of the resulting TiN films. According to the results of Raman spectroscopy, there is a dependence of the ratio of peak areas (TO + LO)/(TA + LA) observed in the regions of 603, 175 and 315 cm^{-1}, respectively, on the N_2 concentration. The X-ray Photoelectron Spectroscopy (XPS) analysis results show that increasing the nitrogen content in the reactive gas leads to a decrease in the oxygen concentration in the thin films. The results deepen the understanding of the synthesis of TiN thin films and their potential for the development and improvement of materials for various applications including microelectronics, optics, and coatings.
Key words: titanium nitride, gas concentration, reactive magnetron sputtering, Raman spectroscopy, XPS analysis

Introduction

Titanium nitride (TiN) is one of the most important materials in the field of materials science due to its largely unique properties and is used in a wide range of practical applications, from optoelectronics to the development of radiation resistant devices [1-3]. For instance, recently, Solovan M.M. et al. have developed a new type of photodiode made of a combination of titanium nitride and cadmium zinc telluride, which is characterized by high detectivity, fast response and radiation resistance, making it ideal for use in space or in radioactively contaminated environments [3]. TiN also has high mechanical hardness, chemical stability and biocompatibility, which greatly expands its range of applications as a coating for implants, in fuel cells, photocatalysis and as an abrasion-resistant coatings for highly loaded parts [4-7]. The appeal of TiN lies in its ability to provide high adhesion and abrasion resistance, structural integrity and durability, which is the reason for its use in various industries [8].

There are several methods for the fabrication of titanium nitride coatings, including chemical vapor deposition [9-11], plasma-enhanced chemical vapor deposition [12-14], e-beam evaporation [15-17], direct nitriding of metallic titanium [18], magnetron sputtering [19-23], cathodic cage plasma deposition [24,25], and various other approaches. However, the production of high-quality TiN thin films remains a major challenge [12]. One of the methods for controlled growth of thin films is magnetron sputtering, which is a physical vapor deposition process where the target material is bombarded with high-energy ions to release particles that subsequently deposit onto a substrate, forming a thin film. The advantage of this technique lies in its ability to provide uniform and dense coverage, precise control of film thickness, and the capability to deposit films onto various substrates [26]. However, controlled growth of TiN films with specified structural and chemical characteristics is still a difficult task. One of the methods of controlling the resulting films is to change the ratio of argon and nitrogen (Ar/N_2) concentrations [27-28].

This study investigates the effect of gas concentration on the properties of TiN thin films. This study contributes to a better understanding of the formation of TiN thin films. Through a comprehensive approach and by using modern methods for characterization of physical, optical and structural properties, the influence of the Ar/N_2 reactive gas ratio in the reactive magnetron sputtering process on the formation of TiN films was revealed.

Materials and Methods

2.1. Materials

TiN thin film was deposited on a p-type silicon (100), aluminum foil (99.9%) and quartz glass substrates by reactive DC magnetron sputtering in Ar + N_2 atmosphere. The reactive sputtering gas was a mixture of argon (99.999 %) and nitrogen (99.9 %) supplied by Ihsan Technogas LLP, with the different Ar/N_2 volume ratio. The 2-inch diameter sputtering target was cut from a flat 5 mm thick VT1-00 grade titanium wafer (99.9%).

2.2 TiN thin film deposition

The experimental setup was a HEX modular thin film deposition system from Korvus Technology Ltd. Using a turbomolecular pump, the pressure in the chamber was reduced to 4×10^{-4} Pa. The chamber was then vented with a mixture of Ar/N_2 gases, each at a flow rate of 100 sccm, for 2 minutes to remove possible contaminants in the gas delivery system, and then evacuated to a vacuum. Before sputtering onto the substrate, the target was pre-sputtered at 3.5 Pa and 300 W to remove the oxide layer by Ar, until the plasma color became the dark blue color characteristic of titanium [29]. Simultaneous use of three types of substrates in the sputtering process is necessary to study the films by different techniques. Thin film sputtering was carried out at a pressure of 3.9 Pa and a power of 100 W. The volume concentration of nitrogen was varied from 5 to 25% in steps of 5%. During the sputtering process, the substrates were maintained at room temperature, specifically 25°C. Room temperature deposition is crucial for compatibility with various substrates, particularly those that are sensitive to heat. This expands the applicability of TiN thin films to a broader range of substrates. The film thickness for each sample was 10 nm. This uniform thickness was achieved and verified using a quartz crystal microbalance (QCM), ensuring high precision and reproducibility across all experiments.

2.3 Characterization of TiN

The chemical composition of the TiN films was analyzed using an X-ray photoelectron spectrometer (XPS) with a monochromatic X-ray source Al-Kα radiation at 1486.6 eV (NEXSA, Thermo Scientific). Raman spectra and AFM images were acquired using a Solver Spectrum instrument from NT-MDT, using red He-Ne laser with a wavelength of 633 nm and a diffraction grating with spectral resolution of 4 cm^{-1} for Raman measurements.

Results and Discussion

3.1. Surface morphology analysis

The change in the microstructure of TiN_x thin films mainly depends on the Ar/N_2 ratio in the sputtering gas [27]. Figure 1 shows AFM images of TiN_x thin films synthesized at different sputtering gas concentrations.

Figure 1 shows that the surface of the films is rather rough with a number of globular structures of 10-15 nm in diameter. Statistical analysis of the AFM data revealed that the root mean square roughness, which is one of the dispersion parameters characterizing roughness, changes from 0.960 nm to 0.796 nm for 10 and 25 % of N_2, respectively. Thus, higher Ar concentration leads to a decrease in surface roughness, which may be due to an increase in the intensity of ion bombardment of the target, resulting in more uniform film growth. The main reason is the aggregation of small particles and reduction of grain boundaries during deposition, which leads to surface roughness [27]. Another roughness parameter is kurtosis which is a measure of the sharpness of the peaks on the sample surface. Thus, the comparison of these values – 21.46 and 9.48 for 10 and 25% N_2 samples – additionally indicates that the Ar/N_2 ratio affects the roughness of the resulting TiN_x films.

3.2. The structural characteristics of thin films

Figure 2 shows the Raman spectroscopy results for TiN_x thin films deposited at different N_2 gas concentrations. All samples studied demonstrate similar Raman spectra where the Raman bands at 175, 315, and 603 cm^{-1} are related to the transverse acoustic (TA), longitudinal acoustic (LA), and transverse optical (TO) and longitudinal optical (LO) TiN modes, respectively[30-33]. These characteristic Raman bands serve as critical indicators of the structural integrity and composition of the TiN films, confirming the successful synthesis of TiN thin films under various N_2 gas concentrations.

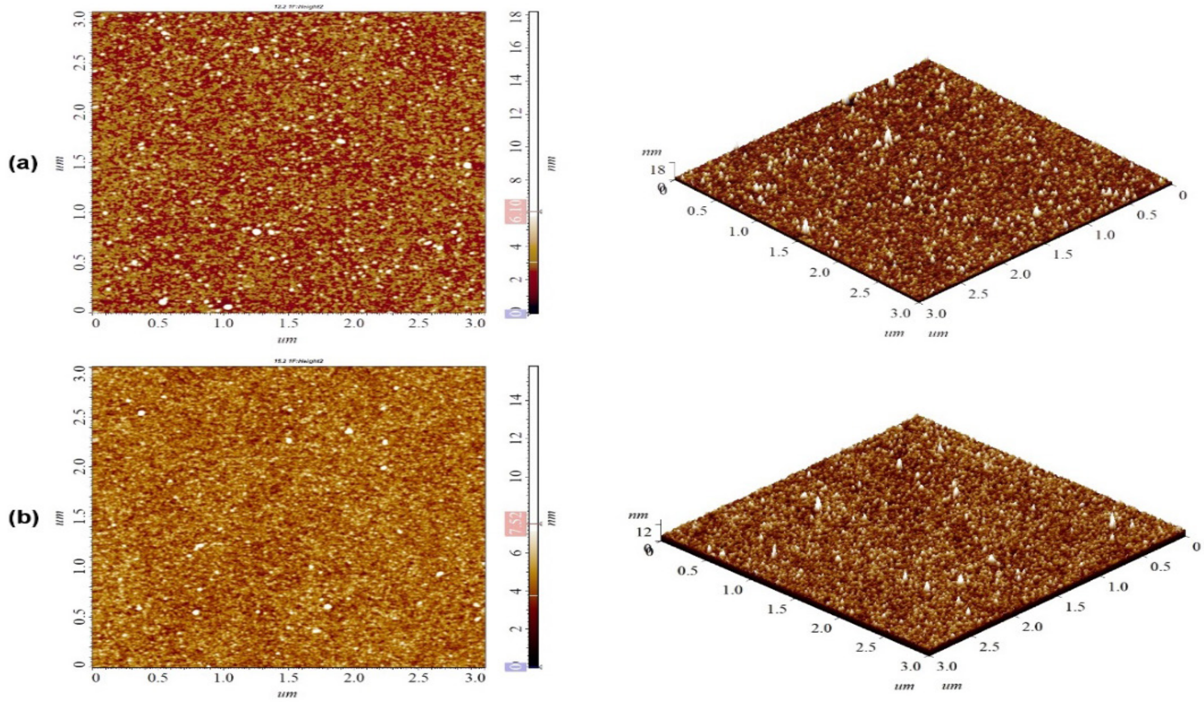

Figure 1 – AFM analysis of surface morphology of TiN_x thin films deposited on silicon substrate with (a) 10% and (b) 25% N_2 concentration

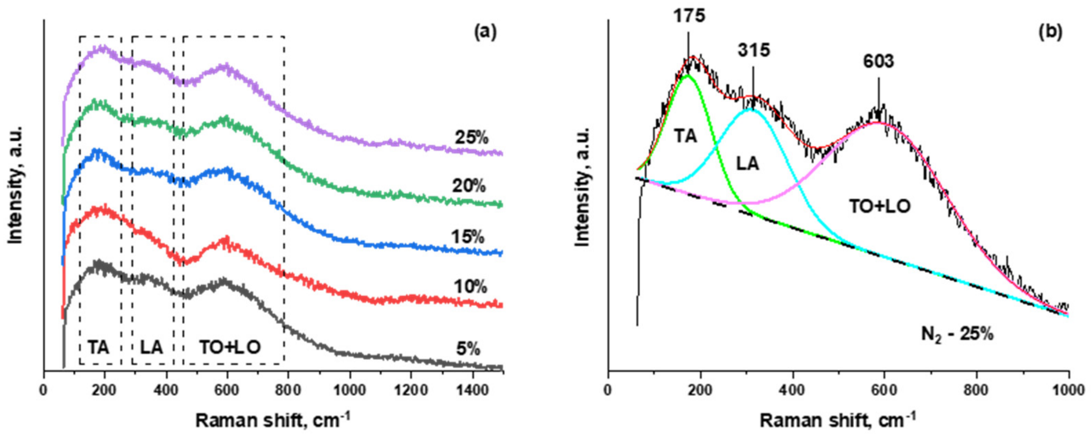

Figure 2 – Raman spectra of TiN_x thin films on Al substrate deposited at (a) different N_2 gas concentration and (b) deconvolution of Raman spectra for 25% N_2 gas concentration

It is also noteworthy that there is a change in the peak intensity of these Raman bands when the amount of nitrogen is changed during the sputtering process. The change in peak intensity as a function of the amount of nitrogen during sputtering indicates non-stoichiometric characteristics of the thin films. The ratio of Raman peak areas (TO + LO)/(TA + LA) can provide information about the nitrogen concentration in nonstoichiometric TiN_x [24,31]. The highest nitrogen concentration is observed at N_2=15% ((TO + LO)/(TA + LA)=1.5). When even 5% N_2 is introduced, the nitrogen concentration remains at a relatively high level (((TO + LO)/(TA + LA)=1.4). Increasing the nitrogen concentration above 15% does not lead to an increase in its concentration in the composition of TiN films.

Figure 3 shows the X-ray Photoelectron Spectroscopy (XPS) analysis of TiN deposited on a silicon substrate. This analysis offers valuable insights into the chemical composition and bonding states of the TiN thin film. In the XPS spectrum shown in Figure 4, characteristic peaks corresponding to the core levels of titanium and nitrogen can be seen. In addition, it can be seen that the obtained films contain oxygen.

For a more detailed view of the chemical composition, peak-fitted XPS core level spectra analysis was performed in both the Ti 2p and N 1s regions for TiN films deposited under two different conditions: at 5% and 25% N_2 concentration, as displayed in Figure 4.

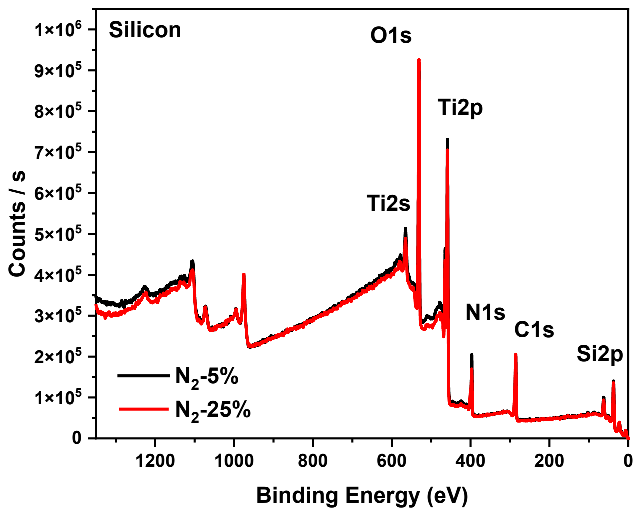

Figure 3 – XPS analysis of TiN film on silicon substrate

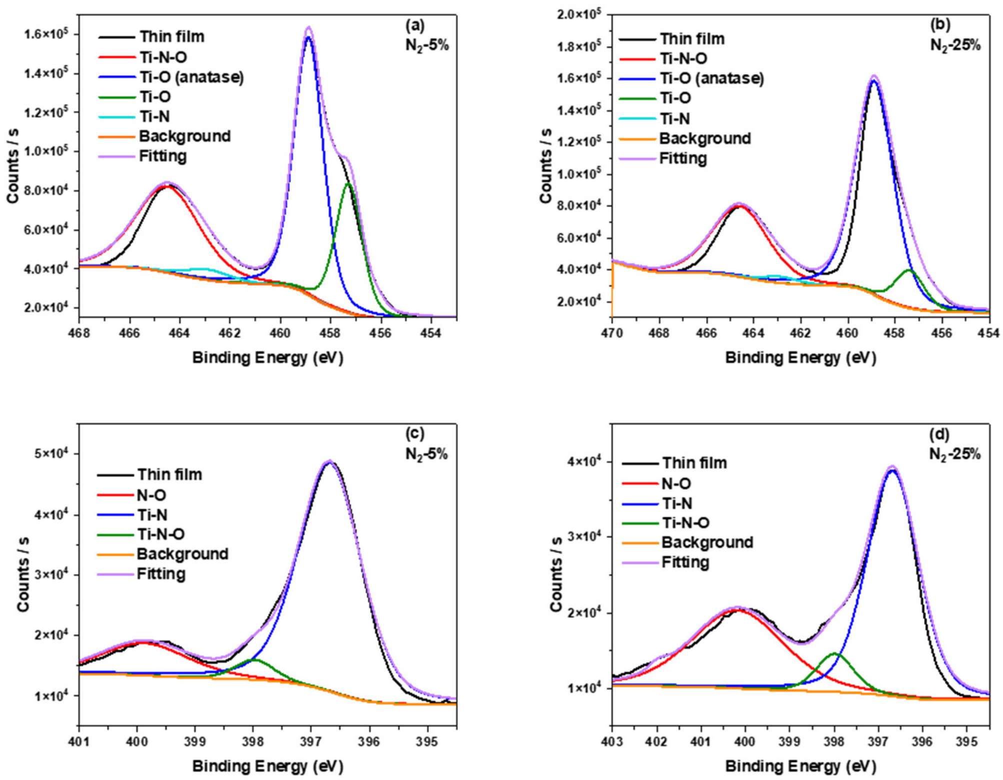

Figure 4 – Deconvoluted Ti 2p XPS peak of TiN on a silicon substrate at (a) 5% and (b) 25% N_2 gas concentrations, and deconvoluted N 1s XPS peak at (c) 5% and (d) 25% N_2 gas concentrations

As shown in Figure 4, increasing the nitrogen concentration in the reactive gas mixture affects the structural properties of the film. There is a significant reduction in the area of the Ti-O peak at binding energies around 457 eV when the nitrogen content is increased to N_2=25%, as compared to N_2=5%. This reduction suggests a decrease in the amount of oxygen in the film. Additionally, the intensity of the Ti-N peak also decreases, which is consistent with the results obtained from Raman spectroscopy analysis. In summary, it can be assumed that increasing the nitrogen concentration in the reactive gas mixture leads to a more active interaction of oxygen with nitrogen (NO_x), which reduces the amount of oxygen ions during the sputtering of the target material, and leads to a decrease in the oxygen content within the thin films [34-36]. However, the oxygen content in the films remains high for all samples, which can be explained by the surface oxidation of TiN thin films during vacuum breakage. As reported by Piallata et al., low-temperature vacuum break leads to bulk oxidation of the substrates [37]. Additionally, Jaeger et al. have reported that oxygen can react with TiN to form titanium oxides or oxynitrides, which possess a different electronic structure compared to pure TiN. Oxygen contamination complicates the quantitative analysis of TiN XPS spectra. The formation of titanium oxides or oxynitrides results in the overlapping of spectral characteristics, making it difficult to accurately determine the composition and electronic structure of the TiN sample [38]. These findings provide valuable insights into the chemical composition and potential oxygen-related defects in TiN thin films, contributing to a deeper understanding of their formation, properties and behavior [39].

Conclusion

In this work, the complex processes of the formation of titanium nitride (TiN) thin films using reactive magnetron sputtering and the effect of argon and nitrogen concentration in the gas mixture were investigated. The results indicate that changing the Ar/N_2 ratio in the gas mixture for sputtering has a significant effect on the surface morphology of TiN thin films. In particular, with increasing argon concentration, a smoother surface of the films is observed, which is explained by the enhanced ion bombardment of the target material and, thus promoting a more uniform growth of the films. Structural analysis conducted using Raman spectroscopy has demonstrated that the nitrogen content in TiN films varies depending on the concentration of N_2. Specifically, an increase in the N_2 concentration in the reactive gas up to 15% leads to an enhancement of nitrogen concentration in the TiN_x films. However, further increases in the nitrogen concentration result in a reduction of nitrogen content in the thin films. Concurrently, this increase in nitrogen concentration contributes to a decrease in oxygen content, which is confimed by XPS data. Thus, this study significantly extends the understanding of the synthesis of TiN thin films and has practical implications for the development and improvement of materials for various applications, including microelectronics, optics, and surface coatings, among others.

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