Absorption Characteristics of Ag-doped Titanium Nitride Nanostructures Prepared by Reactive Co-sputtering

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Abstract
In this work, nanostructured silver-doped titanium nitride (Ag-doped TiN) thin films were deposited on glass substrates by dc reactive co-sputtering technique. Results showed that the low nitrogen content in the gas mixture leads to enhance the absorbance of the prepared films due to the contribution of local surface plasmon resonance (LSPR) of silver nanoparticles in the titanium nitride matrix. On the other hand, the high content of nitrogen in the gas mixture leads to lower absorbance due to the degradation of structural and optical properties of the prepared nanostructures as a result of increasing defects and surface oxidation.

Keywords: Titanium nitride; Silver dopant; Absorption characteristics; Reactive sputtering
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1. Introduction

Titanium nitride (TiN) is a promising transition compound exhibiting both metallic properties (high conductivity) and excellent optical properties (high refractive index and absorption in UV and visible regions). These properties make TiN a possible alternative of noble metals in the applications of plasmonics and photonic thin films [1-3]. However, the main challenge against using TiN in practical applications is the control of charge carriers and frequency of LSPR to be compatible with the targeted application, especially biomedical, energy and sensing [4-6]. Therefore, TiN structures are doped with silver (Ag) as an active strategy to enhance their optical and electrical properties as the high electronic mobility and relatively low plasmonic energy of silver allow modifying the free electron density as well as adjusting the effective refractive index of the TiN nanostructures [7-9]. Moreover, incorporation of Ag nanoparticles into the TiN matrix leads to induce synergetic effects, such as enhancement of local electromagnetic field and absorption efficiency in the visible and near-infrared (NIR) regions [10]. This explores many applications such as high-sensitive LSPR devices, thin-film solar cells for enhanced light harvesting, photothermal coatings for medical and environmental applications, and nanophotonic devices [11-14].

The final properties of the Ag-doped TiN nanostructures crucially depend on the preparation method. Reactive sputtering is one of the most reliable method to prepare Ag-doped TiN nanostructures. In this method, Ag concentration and gas mixing ratio are the most important parameters to be optimized in order to control the size distribution and density of Ag nanoparticles within the TiN matrix in addition to the TiN crystallinity and phase formation [15-18]. Accordingly, the understanding of relationship between Ag-doped TiN preparation parameters and properties, in addition to the UV-visible absorption and Fourier-transform infrared (FTIR) spectroscopy are reasonably necessary to design nanostructures with enhanced and controlled performance to satisfy the requirements of the next generation of plasmonics, photonics and their applications. This represents the aim of this work.

2. Experimental Part

Titanium Nitride (TiN) nanostructures were prepared and doped with silver (Ag) using a DC reactive closed-field unbalanced magnetron sputtering technique. A DC power supply was used to apply maximum discharge voltage of 2.5 kV and discharge current of 19 mA between the discharge electrodes inside stainless steel deposition chamber. This chamber was initially evacuated down to 10^{-3} mbar using an Edwards double-stage rotary pump with 8 m^3/h suction capacity. A co-sputtering configuration of the highly-pure (99.99%) Ti and Ag targets was employed as shown in Fig. (1). The area of stainless steel not covered with Ti target was covered with Teflon host in order to keep only Ti and Ag targets bare to glow discharge plasma column.

3. Results and Discussion

Figure (2) shows the absorption spectra of the Ag-doped TiN nanostructures prepared in this work using different Ar:N_2 gas mixtures in the spectral range of 300-800 nm. In general the absorbance reasonably decreases with wavelength for all samples. It is a

typical behavior for semi-metallic or transition metal compounds as the free electrons contribute to the absorption at longer wavelengths (>550nm) while the absorption is higher at shorter wavelengths due to the transitions from occupied to unoccupied bands. At 300 nm, the sample S4 shows the highest absorbance (~0.75) while the sample S1 shows the lowest absorbance (~0.3). This is attributed to the formation of much more stoichiometric TiN at higher content of nitrogen in the gas mixture. This increases the electronic state density near Fermi level and hence increases the absorption coefficient. On the contrast, the samples prepared at lower nitrogen content shows lower absorbance due to the formation of nitrogen-poor TiN phase or to the formation of excess metallic titanium that causes weaker interaction with the light in the visible region. It is observed that the effect of nitrogen content is much clearer at high photon energy (shorter wavelengths) while the absorption is supported by the local surface plasmon resonance (LSPR) absorption due to doping silver particles. This contribution is not reasonably affected by changing nitrogen content in the gas mixture. Furthermore, the decrease in absorbance beyond 375 nm may be an indication for enhancing crystallinity and reducing defects, which make these nanostructures appropriate for transparent conducting oxide (TCO) or heat reflective films.

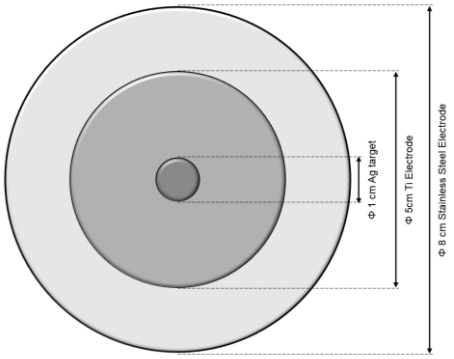

Fig. (1) The configuration of co-sputtering employed in this work using Ti and Ag targets

The inset figure shows the absorption spectra in the 350-510 nm region where the LSPR peaks can be distinctly observed with apparent dependency on the content of nitrogen in the gas mixture. The sample S4 shows the highest absorbance (~0.067) at 350 nm with a decreasing tail at longer wavelengths. This refers to a high concentration of silver nanoparticles with narrow distribution as well as reduced nitrogen-rich TiN matrix that limits the particles accumulation. A small red shift can be observed from 400 (S1) to 410 nm (S4) due to the increase in silver nanoparticle size or the variation of dielectric constant of the matrix due to the reduction of nitrogen, which weakens the plasmonic light trapping.

A contradicting behavior of absorption may be expected when the nitrogen content in the gas mixture is decreased since the sputtered titanium atoms not bonding to nitrogen atoms are also deposited on the substrate. These metallic Ti atoms support the deposited Ag atoms and hence increase the reflectance of the prepared film, which necessitate a corresponding decrease in absorbance. However, this effect might be neglected due to the stronger effect of LSPR contribution to the absorbance.

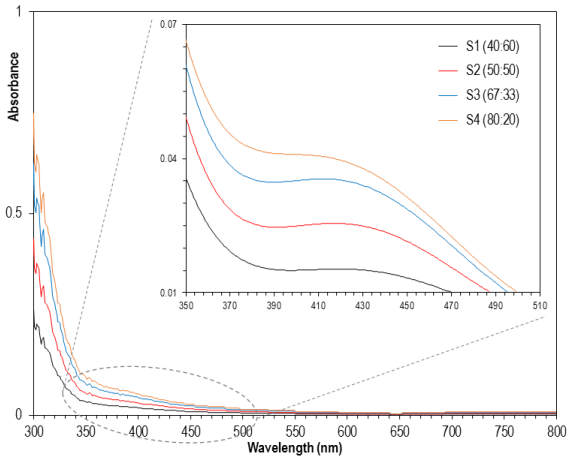

Fig. (2) Absorption spectra of the Ag-doped TiN nanostructure samples prepared in this work at different nitrogen contents in the Ar:N_2 gas mixture (S1 for 40:60, S2 for 50:50, S3 for 67:33, S4 for 80:20)

Figure (3) shows the Fourier-transform infrared (FTIR) spectra of the prepared samples in the wavenumber range of 4000-400 cm^{-1}. The effect of nitrogen content in the gas mixture on the electronic and vibrational configuration of the prepared materials can be observed. The peaks within 400-600 cm^{-1} are ascribed to the Ti-N stretching and N-Ti-N bending modes while the Ti-O stretching mode can be expected due to slight surface oxidation since the vacuum pressure of 10^{-3} mbar does not ensure complete removal of oxygen from the deposition chamber. The peaks belonging to the Ag-Ag metal lattice vibration can be assigned at 402 and 557 cm^{-1}. In the range of 600-700 cm^{-1}, the Ag-O metal oxide bending mode can be seen too. The distinct peak seen at 877 cm^{-1} is attributed to the Ti=N stretching mode. No distinct peaks ascribed to the formation of Ag-N or Ti≡N were observed, which means that the nitridation of sputtered titanium atoms was the major event over than the nitridation of Ag atoms or metallic bonding of Ag-Ti system.

All peaks and bands seen in the region 1000-4000 cm^{-1} are resulted from the inevitable impurities and contaminants adsorbed from the atmosphere while the samples were transferred from the chamber to the FTIR lab. The FTIR results confirm that the lower nitrogen content in the gas mixture supports the electronic and vibrational configurations of the Ag-doped TiN structures to be suitable for the applications of plasmonics and optical coatings, whereas the high nitrogen content leads to a

degradation in the structural characteristics due to increasing defects and surface oxidation.

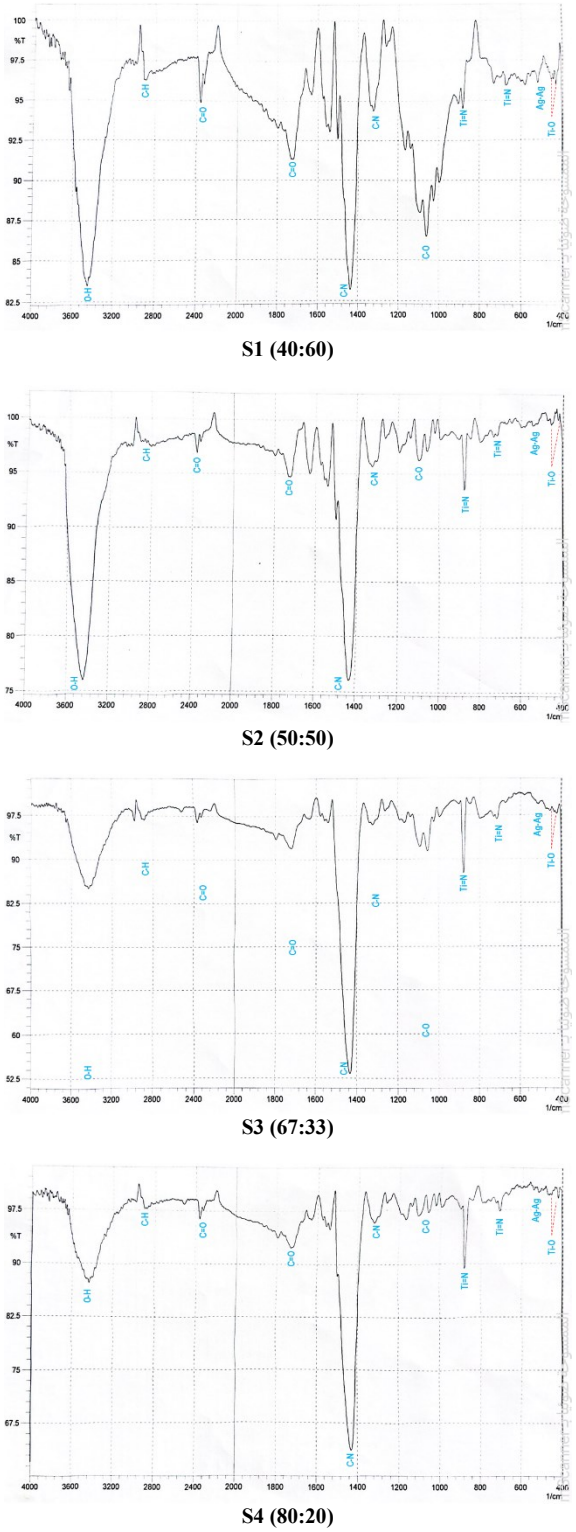

Fig. (3) FTIR spectra of the Ag-doped TiN nanostructure samples prepared in this work at different nitrogen contents in the Ar:N_2 gas mixture

4. Conclusion

In concluding remarks, nanostructured Ag-doped TiN thin films were successfully prepared by DC reactive co-sputtering technique as a simple and efficient configuration of co-sputtering of Ti and Ag targets was employed. The prepared nanostructures revealed the role of nitrogen content in the gas mixture in supporting their absorption by the LSPR of Ag dopants at low nitrogen content while the high content caused a degradation in the properties of these nanostructures due to the increase in defects and surface oxidation.

References

[1] E. Mohammadpour et al., "Enhancement of thermal and mechanical stabilities of silicon doped titanium nitride coating by manipulation of sputtering conditions", *J. Mater. Res. Technol.*, 17 (2022) 1122-1131.

[2] E. Abualgassem et al., "Optical and magnetic properties of cobalt doped TiN thin films grown by RF/DC magnetron sputtering", *J. Magnet. Magnet. Mater.*, 550 (2022) 169023.

[3] S.I. Goreninskii et al., "Long-term biocompatibility of fluoropolymer vascular grafts enhanced via magnetron-sputtered silicon-doped titanium nitride coatings", *Colloids Surf. A: Physicochem. Eng. Aspects*, 735 (2026) 139480.

[4] V. Jokanović et al., "Detailed phisyco-chemical characterization of the multilayered thin films based on titanium oxynitride and copper doped titanium nitride obtained by different PVD techniques", *Vacuum*, 195 (2022) 110708.

[5] G. Zhao et al., "Study on the electrical and optical properties of vanadium doped TiN thin films prepared by atmospheric pressure chemical vapor", *J. Alloys Compd.*, 569 (2013) 1-5.

[6] Q. Wang et al., "Formation and high-temperature stability of Mg-doped titanium nitrides in MgTi treated steel: Experiment and first-principles calculation", *Mater. Characteriz.*, 232 (2026) 115954.

[7] P. Zheng et al., "Modulating the structure of iron-doped titanium nitride deposited on a nitrogen-doped carbon catalyst for the oxygen reduction reaction in Zn–air batteries", *Catal. Sci. Technol.*, 12(24) (2022) 7408-7416.

[8] J. Shi et al., "Study on capacitance properties of the sputtered carbon doped titanium nitride electrode material for supercapacitor", *Vacuum*, 198 (2022) 110893.

[9] M. Maarouf et al., "Negative magnetoresistance in iron doped TiN thin films prepared by reactive magnetron sputtering", *J. Magnet. Magnet. Mater.*, 514 (2020) 167235.

[10] H. Liu et al., "Effect of copper-doped titanium nitride coating on angiogenesis", *Mater. Lett.*, 269 (2020) 127634.

[11] S. Sedira et al., "Physical deposition of carbon doped titanium nitride film by DC magnetron sputtering for metallic implant coating use", *Appl. Surf. Sci.*, 295 (2014) 81-85.

[12] C. He et al., "Magnetic field-regulated glow discharge sputtering for enhanced depth-profiling and antibacterial analysis of Ag-doped TiN coating", *Mater. Today Bio*, 33 (2025) 102034.
[13] W. Shao et al., "Effect of cluster interface structure on the spontaneous escape behavior of silver in ion plating coatings and its inhibition mechanism", *Thin Solid Films*, 664 (2018) 6-11.
[14] J. Cheng et al., "Research on magnetron sputtering thin films as electrode materials for supercapacitors", *Chem. Eng. J.*, 509 (2025) 161242.
[15] F.J. Al-Maliki et al., "Enhanced photocatalytic activity of Ag-doped TiO_2 nanoparticles synthesized by DC Reactive Magnetron Co-Sputtering Technique", *Opt. Quantum Electron.*, 52 (2020) 188.
[16] O.A. Hammadi, F.J. Kadhim and E.A. Al-Oubidy, "Photocatalytic Activity of Nitrogen-Doped Titanium Dioxide Nanostructures Synthesized by DC Reactive Magnetron Sputtering Technique", *Nonl. Opt. Quantum Opt.*, 51(1-2) (2019) 67-78.
[17] R.A.H. Hassan and F.T. Ibrahim, "Preparation and Characterization of Ni-doped TiO_2 Nanostructures for Surface Cleaning Applications", *Iraqi J. Appl. Phys.*, 17(1) (2021) 3-8.
[18] N.A.H. Hashim, F.J. Kadhim and Z.S. Abdulsattar, "Characterization of Electrochromism and Photoelectrochromism of N-Doped TiO_2 and Co_3O_4 Thin Films Prepared by DC Reactive Magnetron Sputtering: Comparative Study", *Iraqi J. Appl. Phys.*, 19(1) (2023) 5-12.

