Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 15(2), 470-478, 2025
Journal of the Institute of Science and Technology, 15(2), 470-478, 2025

ISSN: 2146-0574, eISSN: 2536-4618

Fizik / *Physics* **DOI: 10.21597/jist.1537596**

Araştırma Makalesi / *Research Article*

Geliş tarihi / *Received*: 04.09.2024 **Kabul tarihi / *Accepted*: 02.01.2025**

Atıf İçin: Mak, A., K., Öztürk, O. ve Karabulut, M. (2025). Akıllı Cam Uygulamaları için Nano Ölçekli Ta:TiO_2 Şeffaf İletken Katmanların İncelenmesi. *Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, 15(2), 470-478.

To Cite: Mak, A., K., Öztürk, O. & Karabulut, M. (2025). Investigation of Nanoscale Ta:TiO_2 Transparent Conductive Layers for Smart Glass Applications. *Journal of the Institute of Science and Technology*, 15(2), 470-478.

Akıllı Cam Uygulamaları için Nano Ölçekli Ta:TiO_2 Şeffaf İletken Katmanların İncelenmesi

Ali Kemal MAK[1*], Osman Öztürk[1] Mevlüt KARABULUT[1]

Öne Çıkanlar:

- Bu makale, EC uygulamaları için şeffaf iletken oksit ince filmlere odaklanmaktadır
- Böyle bir kalınlık ölçeğinde ilk çalışma
- Literatüre katkı sağlayan bir çalışma

Anahtar Kelimeler:

- Elektrokromik
- Ta:TiO_2
- Magnetron Sıçratma
- TCO
- Akıllı Camlar

ÖZET:

Artan enerji ihtiyacını karşılamaya dönük yeni ve alternatif enerji kaynaklarının araştırılması için dünya genelinde yoğun bir çaba harcanırken mevcut enerji kaynaklarının verimli kullanılması da son derece önemli hale gelmiştir. Akıllı cam uygulamalarına yönelik çalışmalarda iletken oksit tabaka olarak TCO kullanımı gerekmektedir. Özellikle elektrokromik malzemelerde iletken oksit tabaka ile uygulanan küçük bir voltaj ile şeffaf/renkli hale dönüştürülebilen elektrokromik camlar enerji tasarruflu binaların önemli bileşenlerinden biridir. Toplamda 5 tabakadan oluşan tam bir EC cihazın iki tabakası şeffaf iletken tabaka olup uygulamada genellikle ITO kullanılmaktadır. Bu projede WO_3 temelli EC cihazlarında ITO ya alternatif olarak tantal katkılı TiO_2 filmleri araştırıldı. Farklı kalınlıklardaki Ta:TiO_2 filmleri radyo frekansı magnetron saçtırma yöntemi ile alttaş sıcaklığı 500 ºC tutularak büyütüldü. Elde edilen filmlerin yapısal, morfolojik, optik ve elektrik özellikleri XRD, SEM, AFM, UV-vis-NIR, XPS ve Hall etkisi ölçümleri ile gerçekleştirildi. Ta katkılı filmler için TiOx filminin kalınlığı 90 Å olarak sabit tutulurken Ta tabakalarının kalınlıkları ise 6 Å, 12 Å ve 18 Å olacak şekilde değiştirildi. XRD ölçümlerinden bütün filmlerin amorf yapıda büyüdükleri gözlenirken XRR ölçümlerinden ise filmlerin tabaka yoğunluklarının Ta miktarı arttıkça arttığı görüldü. Katkısız TiO_2 filminin geçirgenliği % 90 civarında iken Ta katkısı ile filmlerin geçirgenliklerinde azalma gerçekleşmiştir. Ta katkısıyla yüzey kabalığı başlangıçta azalırken miktar arttıkça artmıştır. XPS spektrumlarının analizinden Ta 4f bandının 26-27 eV aralığında olduğu ve bu değerin Ta_2O_5 fazına karşılık geldiği bulunmuştur. Ti 2p bandları 457-459 eV aralığında olup bu değerler TiO_2 fazını işaret etmektedir. Ta miktarlarıyla bu piklerin bağlanma enerjilerinde kaymalar gözlenmiştir..

Investigation of Nanoscale Ta:TiO_2 Transparent Conductive Layers for Smart Glass Applications

Highlights:

- This paper focuses on transparent conductive oxide thin films for EC applications
- The first study on such a thickness scale
- A study that contributes to the literature
-

Keywords:

- Electrochromism
- Ta:TiO_2
- Magnetron Sputtering
- TCO
- Smart Glasses

ABSTRACT:

An intense effort has been given globally to the investigation of new and alternative renewable energy sources in order to meet the increasing energy needs of societies. On the other hand, effective usage of energy sources is also an important issue. TCO should be used as a conductive oxide layer in smart glass applications. Especially in electrochromic (EC) materials, electrochromic glasses, which can be converted into transparent / colored with a small voltage applied with a conductive oxide layer, are one of the important components of energy-saving buildings. A complete EC device has a total of 5 layers including two transparent conducting layers, usually ITO in application. In this paper, tantalum doped TiO_2 films have been investigated as an alternative to ITO for WO_3 based EC devices. Ta:TiO_2 films of different thicknesses were grown on glass substrates that were heated to 500 ºC by radiofrequency magnetron sputtering. The structural, optic and morphological properties of the films were investigated by means of XRD, XRR, SEM, AFM, UV-vis-NIR, XPS and Hall effect measurements. The thickness of TiO_2 films was kept constant at 90 Å while the thickness of Ta films were varied as 6 Å, 12 Å and 18 Å. XRD analysis showed that all of the films were amorphous. The XRR measurements indicated that the layer density increased with increasing Ta content. The transparency of undoped TiO_2 film had a transparency of 90 % and decreased with Ta doping. Addition of Ta initially caused a decrease in the surface roughness after which it increased. The binding energy of Ta 4f band was in the 26-27 eV range indicating the Ta_2O_5 phase while the binding energy of Ti 2p bands were found to be in 457-459 eV interval, indicating the TiO_2 phase. A shift was observed in the positions of these bands with the Ta content..

[1]Ali Kemal MAK (**Orcid ID:** 0000-0002-5380-0314), Osman ÖZTÜRK (**Orcid ID:** 0000-0002-9729-8792), Mevlüt KARABULUT (**Orcid ID:** 0000-0002-0227-318X) Gebze Technical University, Department of Physics, Kocaeli, Türkiye

***Sorumlu Yazar/*Corresponding Author**: Ali Kemal MAK, e-mail: alikemalmak@gtu.edu.tr

INTRODUCTION

Transparent conductive oxide (TCO) films are materials used in several areas including optoelectronic devices such as solar cells, infrared anti-reflective and smart displays with their high transmittance and low resistance (Yang, 2018). Indium tin oxide (ITO) is the most widely used among TCOs and it has characteristic properties such as high transmittance and low resistance. It has a resistance as low as $1x10^{-4}$ Ω.cm, a wide band gap of 3.2 eV and a transmittance of over 80 %. In addition to these properties. Optical and electrical properties were tried to be increased by doping with different materials (Tsutsumi et al., 2024). It also has disadvantages such as poor chemical resistance, limited resources and high cost (Yang, 2018), (Bhosle, 2006), (Yan, 2017). (Alizadeh et al., 2022; Tsutsumi et al., 2024). Due to these disadvantages, research is being carried out for the development of different TCO materials. Aluminium and gallium-doped zinc oxide (Bhosle, 2006), which has similar properties to TCO, shows properties at a level that may be attractive. Another interesting candidate is tantalum-doped titanium oxide (TaTO) with an optical transmittance of over 90 % and it has resistance of $2\text{-}3x10^{-4}$ Ω.cm (Yang, 2018). Among many semiconductor materials, TiO_2 is an interesting material due to its photo-electrochemical properties and chemical stability (Hitosugi, 2005). TiO_2 is an interesting semiconductor material due to its transmittance in the visible region, convenient band structure and chemical resistance at low atmospheric pressure (Mazzolini, 2015). Doping of TiO_2 with group V elements (such as Ta, Nb) resulted in a resistivity value of is $2x10^{-4}$ Ω.cm which is reported to be due to the replacement of Ti atoms in the lattice by dopant atoms (Mazzolini, 2015; Furubayashi, 2005).

The aim of this study is to study alternative materials to the materials used as conductive oxide layers in smart glass applications. As known, conductive oxide materials such as ITO (Terzini et al., 2000), AZO (Agura et al., 2003) and GaZO (Wong et al., 2011) are widely used in smart glass applications such as electrochromic. The search for alternative materials continues today as it has in the past and different material studies will continue to be studied in the future.

MATERIALS AND METHODS

Tantalum-doped titanium oxide thin films were obtained by magnetron sputtering (MS) (Chandra Sekhar et al., 2016; Tajima et al., 2008) technique using the ultra-high vacuum chamber (Fig.1) in the surface physics laboratory of the Physics department of Gebze Technical University. Table 1 shows the coating parameters of $Ta:TiO_2$ thin films.

Figure 1. Ultr-High vacuum chamber photo

Table 1. Coating Parameters of Ta:TiO_2 Films

TiOx Power (W)	Ta Power (W)	Working Pressure (mb)	TiOx-Ar/O_2 (sccm)	Ta-Ar/O_2 (sccm)	TiOx-Coating Time (sec)	Ta-Coating Time (sec)	TiOx-QCM-Thickness (Å)	Ta-QCM-Thickness (Å)	Substrate Temp. (℃)
45	0	5.23E-3	4/1	0	2416	0	100	0	500
45	5	4.84E-3	4/1	2/0	2480	9	90	6	500
45	5	5.3E-3	4/1	2/0	2397	18	90	12	500
45	5	5.4E-3	4/1	2/0	2365	29	90	18	500

Schematic illustration of film structures is given in Fig. 2. The films were obtained by layer-by-layer co-sputtering method. Before the TiO_x and Ta films were grown, the growth rates were optimized for each material. A 3-inch Ti metal target material was used to grow the TiO_2 films. Similarly, a tantalum layer was obtained using a 3-inch Ta target material. While coating the TiO_2 layer, Ar/O_2 gases were introduced to the chamber in a ratio of 4/1 sccm during the TiO_2 coating while the Ta layer was grown in a full argon environment. The substrates were heated to 500 ℃ during the coatings to help better adhesion of Ta layer with the TiO_x layer. In order to increase the amount of Ta in the structure and control the conductivity of Ta:TiO_x thin films investigated as a TCO material. The characterization of Ta:TiO_x films were done by in-situ XPS measurements and ex-situ XRD, XRR, UV-VIS-NIR, SEM, AFM and Hall Effect measurements.

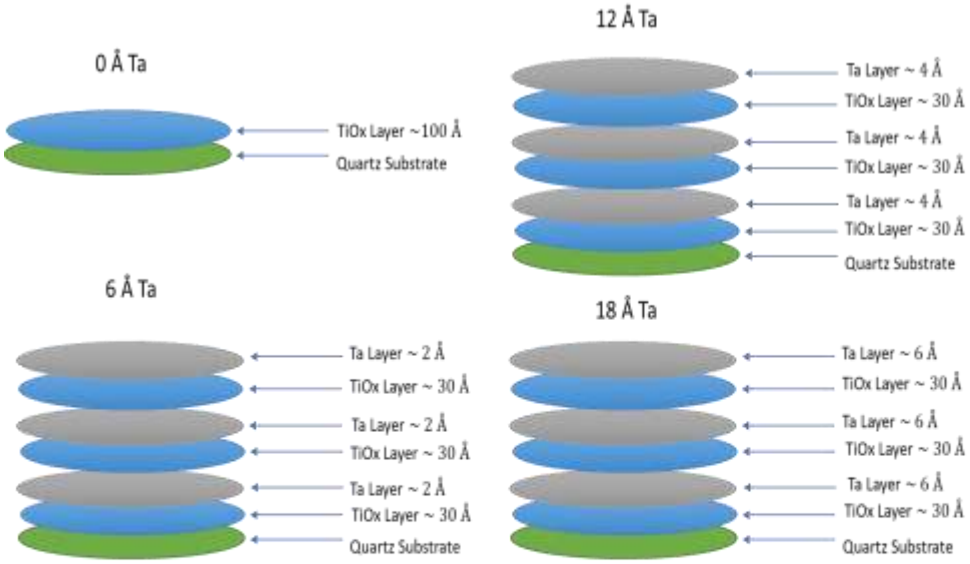

Figure 2. Schematic illustration of Ta:TiO_2 films

RESULTS AND DISCUSSION

A total of four undoped and Ta doped TiO_x thin film samples were obtain in this study. The thicknesses of the samples were determined by quartz crystal microbalance (QCM). The thickness of the undoped TiO_2 film was 90 Å and kept constant while Ta was added with a total thickness of 6, 12 and 18 Å. The structures of the obtained films were studied by X-ray diffraction (XRD) method. The XRD patterns given in Fig. 3 show that the Ta:TiO_2 films grew in amorphous structure.

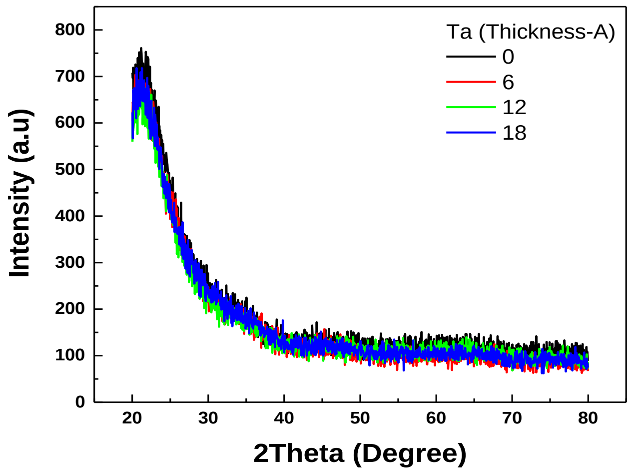

Figure 3. XRD pattern of Ta:TiO_2 films

The results obtained from the X-ray reflection (XRR) measurements performed on Ta:TiO_2 films are given Table 2. There is a difference of about ±2 nm between the film thicknesses obtained from XRR measurements compared to the QCM results. In the QCM technique, the oscillation frequency of the quartz crystal is proportional to the change in the mass of the film on the crystal per unit area. In addition, it is observed that the layer densities of films increase as the amount of Ta increases.

Table 2. XRR Result of Ta:TiO_2 films

Ta Power (W)	Ta QCM (Å)	TiOx QCM (Å)	Thickness XRR (Å)	Layer Density (gr/cm^{3})
5	0	100	73	3.77
5	9	90	75	3.84
5	12	90	75	3.86
5	18	90	104	3.90

The optical properties of Ta:TiO_2 films were examined with UV-vis-NIR spectrometry. The transmittances of Ta:TiO_2 thin films are given in Fig.4. While the transmittance of the undoped TiO_2 film is about 90 %, a decrease in the transmittance value has been observed with the addition of Ta. The transmittance decreased from 85 % to 80 % and 63 % when the thickness of the Ta layers were increased from 6 Å to 12 Å and 18 Å, respectively.

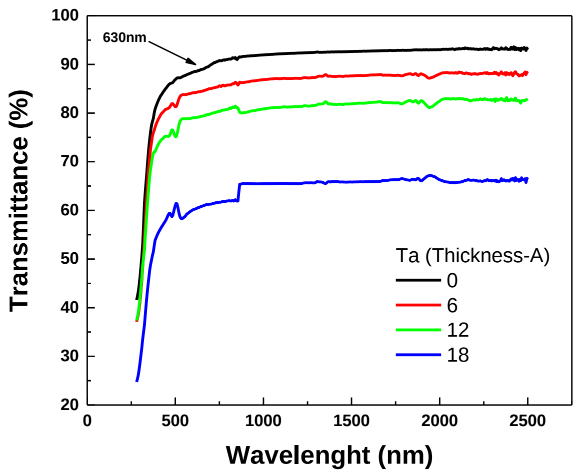

Figure 4. UV-VIS result of Ta:TiO_2 films

SEM cross sectional images of the films are given in Fig. 5. From these images, it can be seen that TiO_2 and Ta-doped TiO_2 films have been grown on the quartz substrates and thoroughly bonded to the substrate. Although the TiO_x and Ta were grown on the substrates layer by layer as shown schematically in Fig. 2, it is observed that the TiO_x and Ta layers come together as a single layer as intended which is as a result of holding the substrate at 500 °C during coating. The thicknesses of the films were also measured from the cross-section images at three different points. The thicknesses of Ta-doped TiO_2 films determined from SEM cross-sectional images and QCM measurements provided seen at Table 3. There is a big difference between the thickness obtained from QCM and the thickness results obtained from SEM cross-section measurements. Similar differences have been observed in the literature between the film thicknesses determined by QCM and SEM techniques (Deki, 1997), (Kao, 2022). In addition, the density of the film layer is used when determining the thickness in QCM, and there may be a difference between the actual value and the value used in calculations.

Figure 6 shows the AFM images of TiO_2 thin films. It is observed that with an increase in the amount of Ta, the clusters decrease on the surface. The surface roughness results obtained from AFM are given in Table 3. The surface roughness of the undoped TiO_2 sample was observed to be high compared to all other Ta-doped samples. In Ta-doped TiO_2 films, on the other hand, the surface roughness increases slightly with increasing Ta content.

Table 3. Thicknesses and AFM surface roughness of Ta: TiO_2 thin films

Ta QCM Thickness (Å)	TiO_x QCM Thickness (Å)	All Film SEM Thickness (Å)	Surface Roughness (Å)
0	100	248	16
6	90	149	4.5
12	90	136	5.6
18	90	149	6

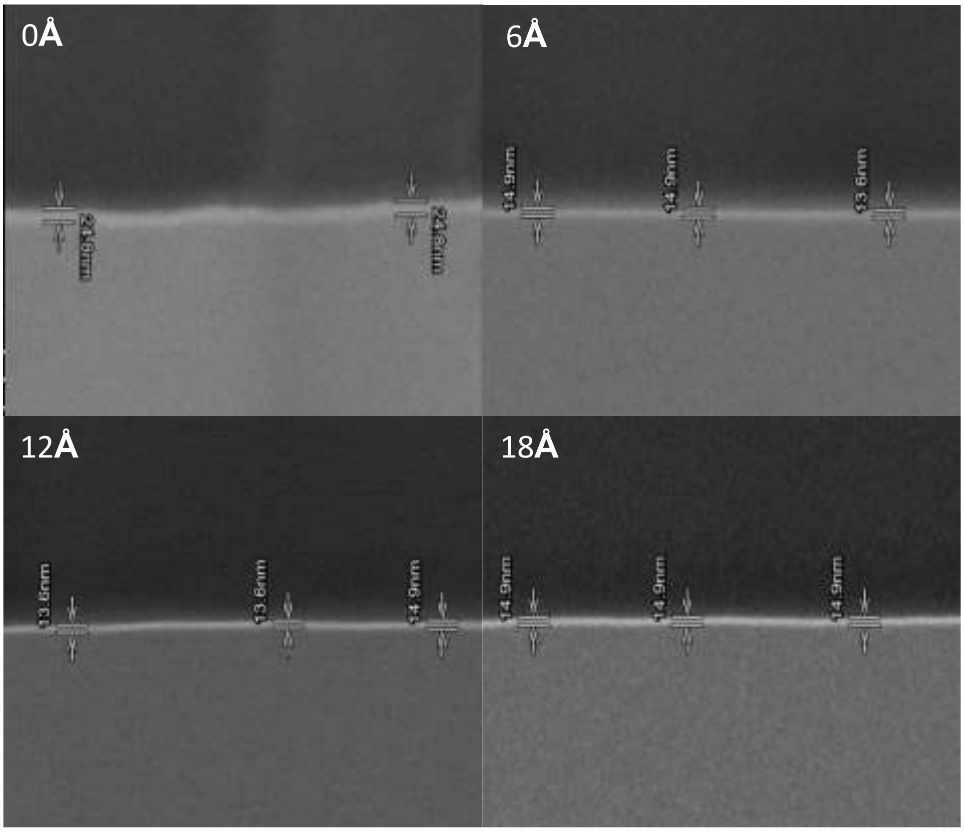

Figure 5. SEM Cross-Sectional images of Ta:TiO_2 thin films

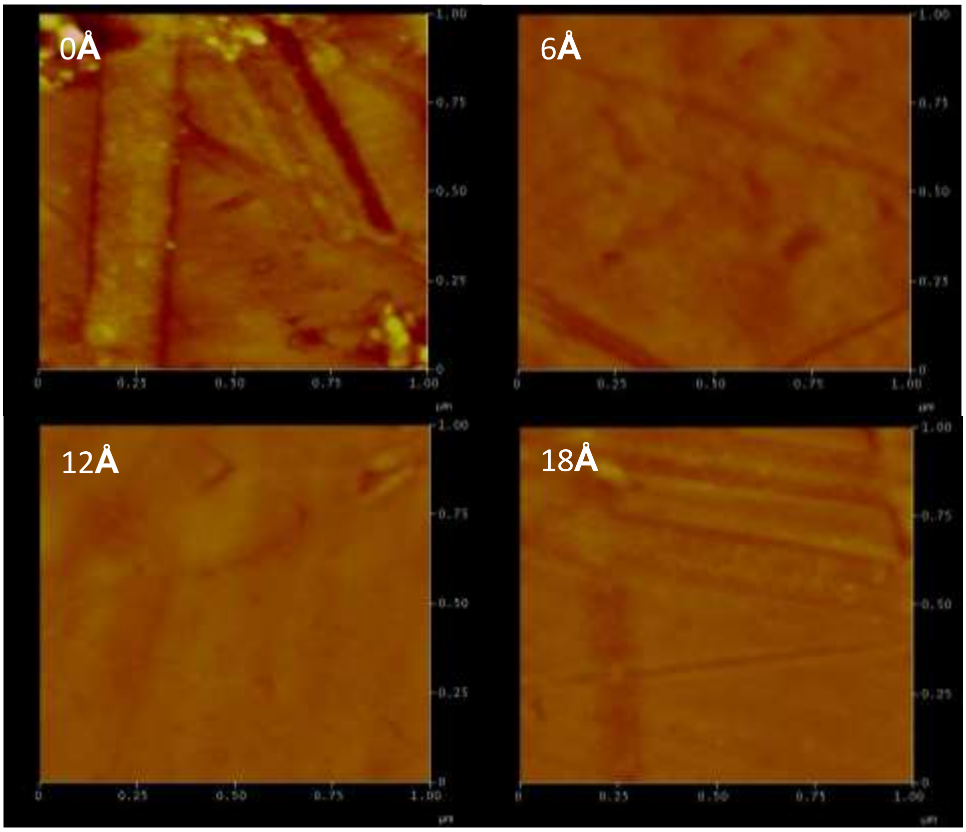

Figure 6. AFM images of Ta:TiO_2 thin films

The chemical composition of the undoped and Ta-doped TiO_2 films as investigated by XPS method. XPS results of Ta:TiO_2 thin films are given Table 5 and in Fig.7-9. The high resolution XPS spectra in Figs. 7-9 are given according to the thickness of the total Ta layer in the films. With the calculations made, the amounts of tantalum in the Ta:TiO_x structure were determined (Liu et al., 2018). The binding energies (BE) of Ta 4f band (Fig. 7) were observed in the 26-27 eV interval and this corresponds to the Ta_2O_5 phase. Similarly, the BEs of O 1s bands (Fig. 8) were observed in the 528-531 eV interval. These values are in the metal oxide range (Moulder, 1992). The BEs of Ti 2p bands (Fig. 9) have been observed in the 457-459 eV interval which indicates the TiO_2 phase (Yan et al., 2017). In Fig. 8, the O 1s peak was observed at a BE of 528.1 eV in the undoped TiO_2 film, and shifted to higher BEs with initial Ta doping and was observed at 529.9 eV when the Ta thickness reached 12 Å. However, when the thickness of the Ta layer was further increased to 18 Å, the O 1s peak again showed a shift towards low energy. Similar shifts were observed in the Ta 4f and Ti 2p bands (Yan et al., 2017)**.**

Table 4. XPS result of Ta:TiO_2 thin films

Ta Thickness (Å)	Ta (%)
0	0
6	2.4
12	4.8
18	5.7

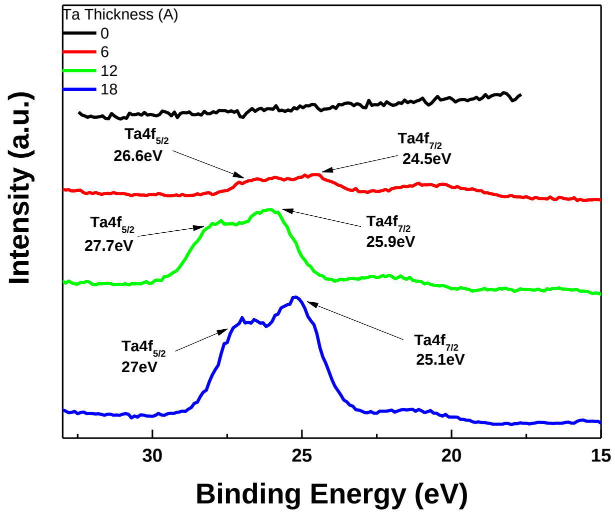

Figure 7. XPS spectra of Ta 4f band

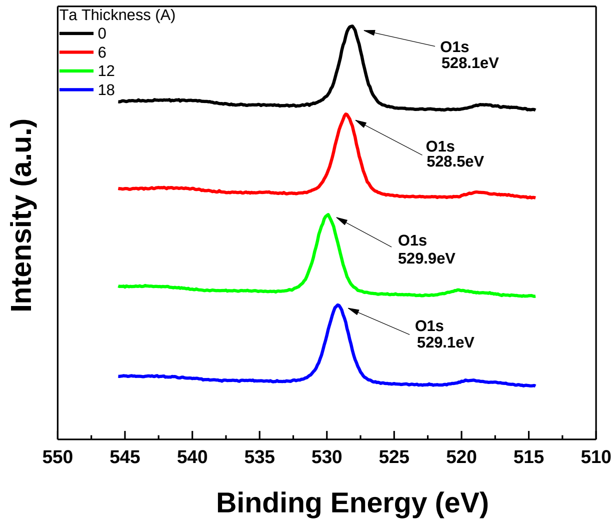

Figure 8. XPS spectra of O 1s band

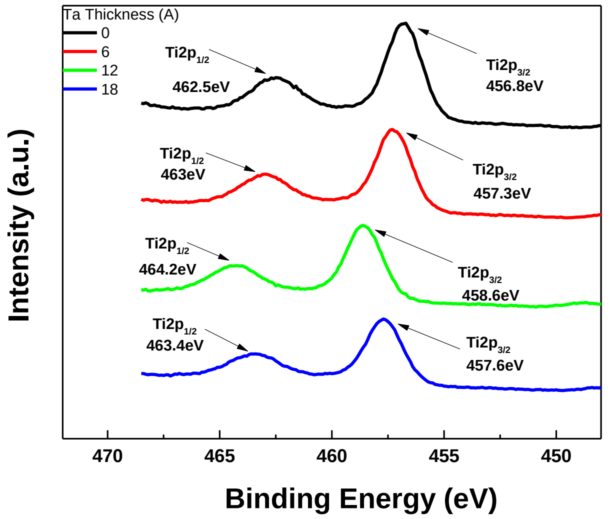

Figure 9. XPS spectra of Ti 2p band

CONCLUSION

The aim of this study is both to develop a material that can be an alternative to the widely used TCOs and to obtain thinner films. In addition, in smart glass applications, it is important to study thinner films and eliminate additional processes such as heat treatment, given the toxicity of commonly used materials, their high thickness and difficulty in achieving low resistance levels. The surface resistances of ITO transparent conductive layers used in smart glasses and especially in electrochromic applications are in the range of 8-20 Ω. The electrical resistances of the Ta:TiO_2 films that we have studied was measured by Hall effect and 4-point methods. Despite all the attempts, the resistance values have been outside the measurement scales of the devices used. There may be several reasons for this. The first thing that comes to mind is that the substrate may have been contacted when taking the contacts for measurements because of the small thickness. While the probes are being pressed in the 4-point method. The film may be damaged while the solders are being taken in Hall effect measurements. Another reason for this may be that the films are in an amorphous structure. Because the films obtained in the literature are generally in a crystalline structure (Hitosugi et al., 2005; Nurfani et al., 2016; Yan et al., 2017). In addition, since the films are reactive coated with co-sputtering, oxidation may have occurred during Ta coating. These effects may have caused the high resistance of the films. Resistance values in the literature are in the $1x10^{-2}$ to $1x10^{-4}$ Ω.cm interval (Chen, 2011) Crystalline TiO_2 films are reported at 400 °C in the literature, but all the films we obtained are amorphous. This may vary depending on the coating system used, coating parameters and the target material used (metallic or ceramic). By increasing the film thicknesses and temperature, crystal films and low surface resistance can be obtained. The amount of tantalum can be reduced and a higher transmittance value can be obtained. There are no TCO in such low thicknesses in the literature. In the literature, it is usually around 1000-10000 Å (Kafizas, 2013). In addition, the target materials used are mostly ceramic target materials which makes it possible to make coating only in argon medium. The absence of oxygen during coating will ensure that tantalum is not oxidized or oxidized much less.

ACKNOWLEDGEMENTS

This study was supported by Gebze Technical University Scientific Research Department within the scope of GTU BAP 2021-A-102-06 "Investigation of Nanoscale Ta:TiO_2 Transparent Conductive Layer for Smart Glass Applications".

Conflict of Interest

No conflict of interest was declared by the authors.

Author's Contributions

Ali Kemal Mak: Conceptualization, methodology, investigation, formal analysis, writing the original draft, writing-review&editing, Osman Öztürk: writing-review&editing, formal analysis, Mevlüt Karabulut: writing-review&editing, supervision.

REFERENCES

Agura, H., Suzuki, A., Matsushita, T., Aoki, T., & Okuda, M. (2003). Low resistivity transparent conducting Al-doped ZnO films prepared by pulsed laser deposition. Thin Solid Films, 445(2), 263–267. https://doi.org/10.1016/S0040-6090(03)01158-1.

Alizadeh, A., Rajabi, Y., & Bagheri–Mohagheghi, M. M. (2022). Effect of crystallinity on the nonlinear optical properties of indium–tin oxide thin films. Optical Materials, 131(May), 1–11. https://doi.org/10.1016/j.optmat.2022.112589.

Bhosle, V., & Narayan, J. (2006). Microstructure and electrical property correlations in Ga: ZnO transparent conducting thin films. Journal of applied physics, 100(9).

Chandra Sekhar, M., Nanda Kumar Reddy, N., Verma, V. K., & Uthanna, S. (2016). Structural, optical and electrical properties of DC reactive magnetron sputtered (Ta2O5)1−x(TiO2)x thin films. Ceramics International, 42(16), 18870–18878. https://doi.org/10.1016/j.ceramint.2016.09.034.

Chen, D. M., Xu, G., Miao, L., Nakao, S., & Jin, P. (2011). Sputter deposition and computational study of M-TiO2 (M= Nb, Ta) transparent conducting oxide films. Surface and Coatings Technology, 206(5), 1020-1023.

Deki, S., Aoi, Y., Asaoka, Y., Kajinami, A., & Mizuhata, M. (1997). Monitoring the growth of titanium oxide thin films by theliquid-phase deposition method with a quartz crystal microbalance. Journal of Materials Chemistry, 7(5), 733-736.

Furubayashi, Y., Hitosugi, T., Yamamoto, Y., Inaba, K., Kinoda, G., Hirose, Y., ... & Hasegawa, T. (2005). A transparent metal: Nb-doped anatase TiO2. Applied Physics Letters, 86(25).

Hitosugi, T., Furubayashi, Y., Ueda, A., Itabashi, K., Inaba, K., Hirose, Y., Kinoda, G., Yamamoto, Y., Shimada, T., & Hasegawa, T. (2005). Ta-doped anatase TiO2epitaxial film as transparent conducting oxide. Japanese Journal of Applied Physics, Part 2: Letters, 44(33–36), 2–5. https://doi.org/10.1143/JJAP.44.L1063.

Kafizas, A., Noor, N., Carmalt, C. J., & Parkin, I. P. (2013). TiO 2-based transparent conducting oxides; the search for optimum electrical conductivity using a combinatorial approach. Journal of Materials Chemistry C, 1(39), 6335-6346.

Kao, P. C., Hsu, C. J., Chen, Z. H., & Chen, S. H. (2022). Highly transparent and conductive MoO3/Ag/MoO3 multilayer films via air annealing of the MoO3 layer for ITO-free organic solar cells. Journal of Alloys and Compounds, 906, 164387.

Liu, Y., Peng, Q., Zhou, Z. P., & Yang, G. (2018). Effects of Substrate Temperature on Properties of Transparent Conductive Ta-Doped TiO2 Films Deposited by Radio-Frequency Magnetron Sputtering. Chinese Physics Letters, 35(4), 2–7. https://doi.org/10.1088/0256-307X/35/4/048101.

Mazzolini, P., Gondoni, P., Russo, V., Chrastina, D., Casari, C. S., & Li Bassi, A. (2015). Tuning of electrical and optical properties of highly conducting and transparent Ta-doped TiO2 polycrystalline films. The Journal of Physical Chemistry C, 119(13), 6988-6997.

Moulder, J. F., Stickle, W. F., Sobol, P. E., & Domben, K. D., 1992. X-ray photoelectron spectroscopy (XPS), Handbook of Adhesion, 2nd ed., Perkin-Elmer Corp., 621–622.

Nurfani, E., Kurniawan, R., Muhammady, S., Marlina, R., Sutjahja, I. M., Winata, T., Rusydi, A., & Darma, Y. (2016). Effect of Ta concentration on the refractive index of TiO2:Ta studied by spectroscopic ellipsometry. AIP Conference Proceedings, 1725(May), 2–6. https://doi.org/10.1063/1.4945511.

Tajima, K., Yamada, Y., Bao, S., Okada, M., & Yoshimura, K. (2008). Proton conductive tantalum oxide thin film deposited by reactive DC magnetron sputtering for all-solid-state switchable mirror. Journal of Physics: Conference Series, 100(8), 082017. https://doi.org/10.1088/1742-6596/100/8/082017.

Terzini, E., Thilakan, P., & Minarini, C. (2000). Properties of ITO thin films deposited by RF magnetron sputtering at elevated substrate temperature. Materials Science and Engineering B: Solid-State Materials for Advanced Technology, 77(1), 110–114. https://doi.org/10.1016/S0921-5107(00)00477-3.

Tsutsumi, N., Ootsuki, D., Ishida, T., & Yoshida, T. (2024). Anomalous Carrier Enhancement with Lightly Mn Doping in Indium – Tin Oxide Thin Films Studied by Hard X-ray Photoemission Spectroscopy. 104801, 2–7. https://doi.org/10.7566/JPSJ.93.104801

Wong, L. M., Chiam, S. Y., Huang, J. Q., Wang, S. J., Chim, W. K., & Pan, J. S. (2011). Examining the transparency of gallium-doped zinc oxide for photovoltaic applications. Solar Energy Materials and Solar Cells, 95(8), 2400–2406. https://doi.org/10.1016/j.solmat.2011.04.013.

Yan, Y., Lee, J., & Cui, X. (2017). Enhanced photoelectrochemical properties of Ta-TiO2 nanotube arrays prepared by magnetron sputtering. Vacuum, 138, 30–38. https://doi.org/10.1016/j.vacuum.2016.12.049.