

Transparent Ta doped SnO₂ films deposited by RF co-sputtering

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Abstract – Tantalum doped tin oxide (TaTO) has the potential to surpass the more commonly used transparent electrode, fluorine doped tin oxide (FTO), in terms of electrical conductivity as it avoids the self-compensating F interstitial defects that limit FTO. However, high mobility TaTO has only been deposited by pulsed laser deposition (PLD), a slow, expensive and non-scalable technique. In this work, TaTO was deposited by RF co-sputtering of SnO₂ and Ta₂O₅. A range of sputtering parameters were investigated varying the tantalum content and substrate temperature. Resistivities of $8.5 \times 10^{-3} \Omega\text{cm}$ were achieved under the best conditions, corresponding to a carrier concentration of $4.4 \times 10^{19} \text{ cm}^{-3}$ and Hall mobility of $16.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ along with transmission of $>75\%$ across the visible and near infrared was achieved. X-ray diffraction patterns informed that the limitation of the co-sputtering deposition method arose from uneven distribution of dopant throughout the films.

Index Terms – Conductive films, Doping, Sputtering, Tin Compounds.

I. INTRODUCTION

Photovoltaic (PV) devices require a transparent electrode to extract carriers while still allowing photons to enter the absorber. This requires a material with usually mutually exclusive properties of transparency and conductivity; such materials are called transparent conductors (TCs). The most commonly used TCs are transparent conductive oxides (TCOs) which are degenerately doped wide band gap metal oxide semiconductors [1].

While a wide range of TCOs are used for PV devices, fluorine doped tin oxide (FTO) is the most widely used. FTO has respectable electrical and optical properties with resistivities as low as $4 \times 10^{-4} \Omega\text{cm}$ and $>85\%$ transparency in the visible [2].

However, these fall short of the values for tin doped indium oxide (ITO) which is the TCO which currently presents the best properties. ITO is not used for commercial photovoltaics as the high cost of indium makes it unsuitable for such large-scale applications [3]. Also, issues can arise when using an ITO transparent electrode in CdTe devices as the indium may diffuse into the *p*-type CdTe absorber layer and dope it *n*-type [4].

FTO, while affordable and suitable, is unable to match the electrical properties of ITO. This is due to the presence of self compensating interstitial fluorine defects which act as acceptors. This self-compensation limits the carrier mobility to about $35 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and prevents it from reaching the values predicted for SnO₂ using scattering models [5].

Due to these factors it is highly desirable to find a new dopant for tin dioxide which would allow it to match the electrical properties of ITO for a fraction of the cost and is free of the self-compensation mechanisms identified in FTO.

Experimental evidence suggests that we can expect TaTO to be free of the self-compensation observed in FTO. Tantalum is of interest in this regard as the tantalum doped tin oxide (TaTO) deposited by pulsed laser deposition (PLD) has demonstrated carrier mobilities in excess of $80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and resistivities as low as $1.8 \times 10^{-4} \Omega\text{cm}$ [6]. However, PLD is not an industrially scalable technique, so this work aims to investigate the use of the more scalable deposition technique of RF sputtering. TaTO deposited by this method has so far reached mobilities of $25.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with films of sheet resistance of $5.4 \times 10^{-4} \Omega\text{cm}$ and carrier concentrations of $4.5 \times 10^{20} \text{ cm}^{-3}$ [7].

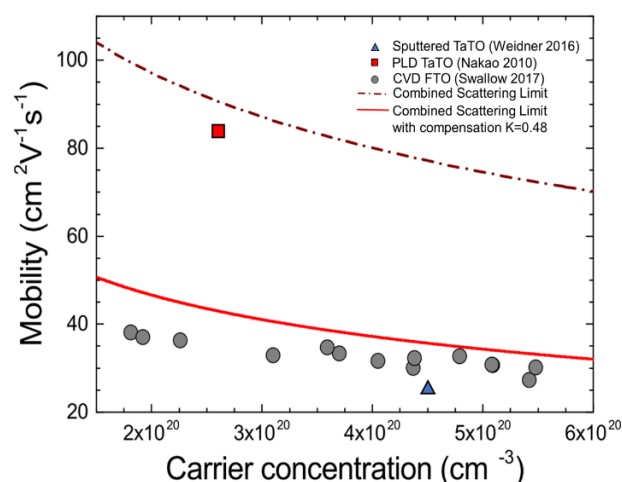


Fig. 1. Record mobilities for TaTO deposited by PLD and RF-sputtering and for CVD deposited FTO compared to modelled combined scattering limits with and without self compensation [5]-[7].

Swallow *et al.* reported Hybrid density functional theory calculations of the formation energy of several likely defects as a function of Fermi level in FTO [5]. For FTO, interstitial fluorine (*F_i*) acceptors become the most energetically favourable defect when the Fermi level is raised to 4.15 eV above the valence band maximum or higher. For Fermi levels below this value, substitutional fluorine donors on the oxygen site (*F_o*), the desirable position for the fluorine atoms, is favourable. *F_i* defects acting as acceptors reduce the carrier density in *n*-type materials while still acting as scattering centres and therefore reduce the conductivity by reducing both carrier

concentration and mobility. This means that at doping densities that raise the Fermi level to 4.15 eV or higher the limiting self-compensation will be present. Alternative dopants could surpass FTO by being free of this self-compensation mechanism.

Evidence that TaTO is free of this limitation comes from comparing literature values to calculated limits on mobility. Figure 1 shows the highest mobilities of TaTO found in the literature for both PLD and sputtered compared to those measured for commercially available FTO deposited by chemical vapour deposition (CVD).

The figure also shows an upper limit for mobility due to scattering based on the Brooks-Herring model [8] for a range of carrier concentrations and the upper limit adjusted for self-compensation due to interstitial defects with a self-compensation factor, K , of 0.48 where K is the ratio of acceptors to donors, N_{D^+}/N_{A^+} .

All data points for the CVD deposited FTO fall below the self-compensation limit as expected. However, the previous record for sputtered TaTO also falls below it with only the PLD deposited TaTO surpassing it. Moreover, the PLD deposited TaTO almost reaches the upper limit of mobilities for the measured carrier concentration. This is compelling evidence that TaTO has the potential to surpass FTO in terms of electrical properties.

Here we present the results of co-sputtering SnO_2 and Ta_2O_5 to grow uniform and graded TaTO films. Co-sputtering has the advantage over single target sputtering that a wide range of doping densities can be investigated without having to create a new target each time. Here we present the obtained resistivities for samples having a range of doping densities and deposited at a range of substrate temperatures. The results of Hall measurements on the best samples are also presented.

II. EXPERIMENTAL RESULTS

Tantalum doped tin oxide thin films were deposited by RF sputtering using an ATC Orion Series Sputtering System (AJA International). Deposition was by co-sputtering from separate targets for the host material and dopant. In this case the host target was SnO_2 and the dopant was introduced using Ta_2O_5 . Films were deposited onto $5 \times 5 \text{ cm}^2$ soda-lime glass substrates under an argon pressure of 5 mTorr. Depositions lasted one hour. Here, two investigations have been performed. In the first the Ta_2O_5 target power was varied with fixed substrate temperature and in the second, having optimised the sputtering power ratio, the substrate temperature was varied. The tantalum content of the films was controlled using the ratio of power supplied to the two targets. For this investigation the power applied to the SnO_2 target was kept at 200 W while the power applied to the Ta_2O_5 target was varied between 36 and 75 W. The initial power of 36 W was chosen to correspond to 2.5 % atomic tantalum since this was the doping concentration of the high mobility TaTO previously reported. This power was based on target calibrations and assumed that all Ta would be incorporated. Films were deposited with the Ta_2O_5 target at 36, 40, 45, 50 and 75 W

and a substrate temperature of 300°C . Sheet resistance was measured using a four-point probe and thickness was measured using a surface profilometer trace over a masked step on the film. The values obtained from these were used to calculate the resistivity of the films. Film thicknesses for all films were between 475 and 525 nm. The lowest resistivity was achieved at 45 W with $\rho = 2.3 \times 10^{-2} \Omega\text{cm}$. Figure 2 shows the full set of results for resistivity with varying power applied to the Ta_2O_5 target and substrate temperature.

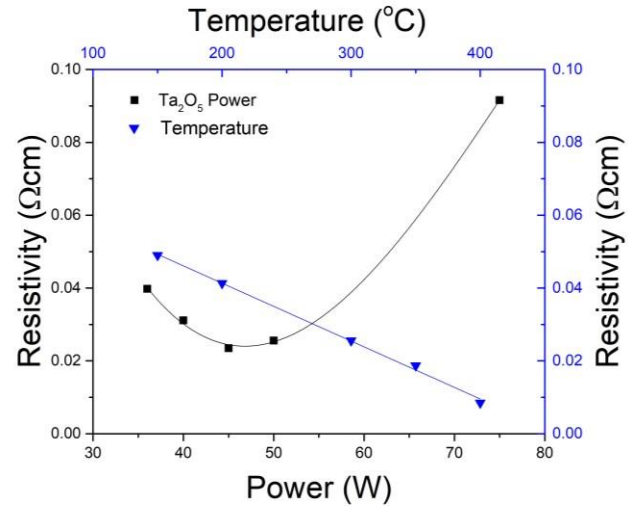


Fig. 2. Resistivity and of TaTO thin films deposited by RF co-sputtering of and SnO_2 over a range of Ta_2O_5 sputtering powers and substrate temperatures for a deposition length of one hour. Lines presented are to show the general trend in each data set.

With the power ratio optimised, the substrate temperature was varied between 150 and 400°C to further optimise the deposition. This investigation was performed at the identified optimum power ratio of 45:200 W. Other deposition parameters were kept the same as in the previous investigation. The resistivity of the films was determined. Figure 2 shows the variation in resistivity with temperature.

Figure 3 shows the transmission spectrum measured over the range of $\lambda = 250\text{-}1500 \text{ nm}$. The average transmission across the visible and near infra-red range ($\lambda = 390\text{-}1500\text{nm}$) as the more commonly used method of using just the visible range ignores a significant portion of the spectrum which solar cells with narrower band gaps absorb.

It was found that neither the substrate temperature nor the target power ratio had any significant effect on the transmission of the film with the value varying only by less than $\pm 1.5\%$ across the entire range and an average of around 76%. The transmission spectrum for the film with best electrical properties had an average transmission of 75.6% in the visible and near infrared range, making it optically suitable for photovoltaic applications.

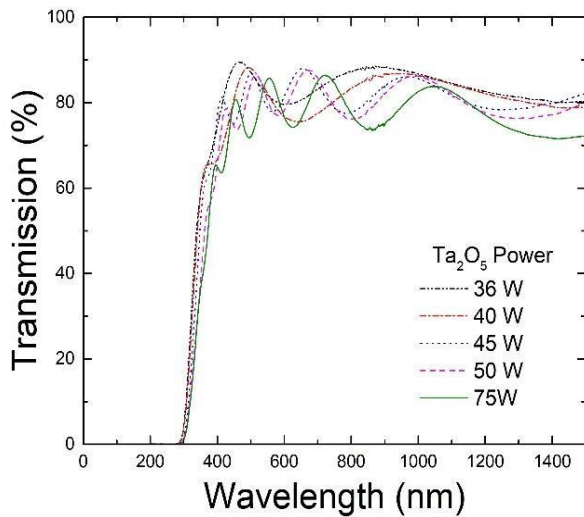


Fig.3. The transmission spectrum for TaTO sample sputtered at a power ratio of 45:200W and substrate temperature of 300

The figure shows shifts in the interference fringes in the spectrum with varying sputtering power on the Ta₂O₅ target. The frequency of these fringes is dependent on the thickness and the refractive index of the film. As the thickness of the films were relatively consistent this can be attributed to a change in refractive index with increased power on the Ta₂O₅ target. An increased frequency in the fringes corresponds to a decrease in refractive index. This is consistent with increased power on the dopant target resulting in a higher doping density as increasing free electron concentration decreases the refractive index.

A linear decrease in resistivity with increasing substrate temperature can be observed with the films with the best electrical properties deposited with a substrate temperature of 400 °C. Hall measurements were made on the best sample which had a resistivity of $8.5 \times 10^{-3} \Omega\text{cm}$. The Hall mobility was $\mu = 16.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the carrier concentration was $n = 4.4 \times 10^{19} \text{ cm}^{-3}$.

These properties are inferior to all those presented in figure 1. This may be a result of poor tantalum incorporation or introduction of some crystalline defects due to the co-sputtering method.

X-ray diffraction patterns were obtained for each film using a Rigaku smart lab in parallel beam geometry using a copper x-ray source.

There is evidence in the literature that this is generally the case for co-sputtered TCOs as the lowest resistivity examples of each TCO deposited by co-sputtering are always significantly more resistive than the best sample deposited from a single doped target [9]-[11].

X-ray diffraction patterns of each of the films are presented alongside the theoretical diffraction patterns for SnO₂ and Ta₂O₅ in figure 4. In all measured diffraction patterns, the largest peak is the SnO₂ (101) peak at 33.9° . However, in the theoretical diffraction pattern for SnO₂ the (110) peak at 26.6° is the largest peak. This means that all films deposited share the same preferred orientation

towards the (101) plane. As previous investigations into the diffraction pattern of TaTO deposited by other methods do not demonstrate this preferred orientation [12, 13], this is most likely a characteristic of the co-sputtering deposition method. crystallinity with increasing substrate temperature.

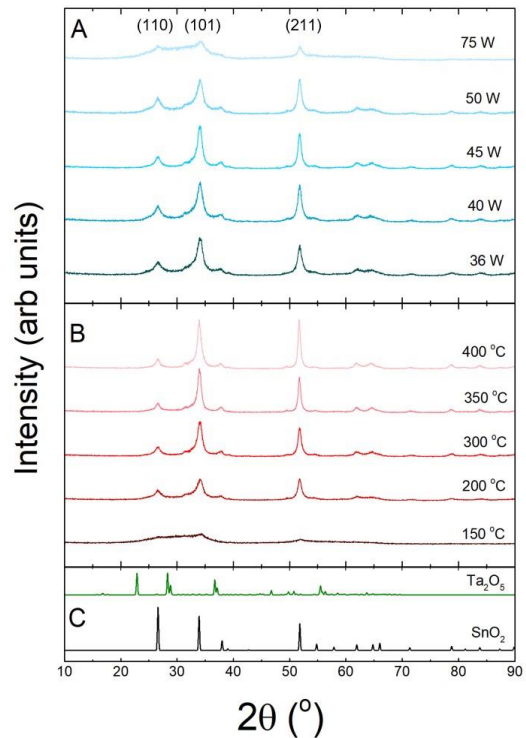


Fig. 4. Background X-Ray diffraction patterns for A films with varied Ta₂O₅ sputtering power; B films with varied substrate temperature; and C The calculated theoretical diffraction patterns for SnO₂ and Ta₂O₅.

A clear trend can be seen in Figure 4B that increased substrate temperature corresponds to increased film crystallinity. This is further demonstrated in Figure 5 shows a linear relationship between the relative intensity of the (101) peak and the substrate temperature. This trend also means that the resistivity of the films decreases with increased crystallinity. Changes in crystallinity can also be observed with changing Ta₂O₅ power in Figure 4A. The most crystalline film in this set is the one deposited with 45 W supplied to the Ta₂O₅ target which is also the least resistive of the films. Figure 6A shows the SnO₂ (101) peaks for the different samples plotted on the same axis to demonstrate this trend more clearly while figure 6B shows both the relative intensity of the (101) peak and the resistivity of the films as a function of Ta₂O₅ power.

From the figure a trend relating resistivity to crystallinity becomes clear. With lower or higher than optimal Ta₂O₅ sputtering rate crystallinity deteriorates to the point where at the highest sputtering power, 75 W, the resulting film appears to be predominantly amorphous. This supports the idea that that the changes in the electrical properties observed with changing Ta₂O₅ power is predominantly

caused by changes in crystallinity rather than the Ta content of the films.

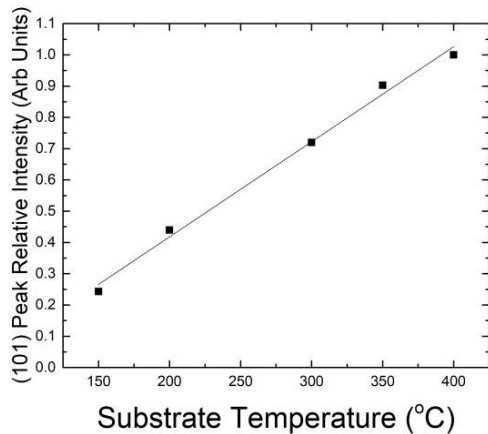


Fig. 5. The relative intensity of the SnO₂ (101) peak in the TaTO background subtracted x-ray diffraction with changing substrate temperature showing increased crystallinity with increasing substrate temperature.

This phenomenon has been previously observed in co-sputtered aluminium doped zinc oxide, AZO, but has not widely been reported or discussed [14]. However, it is widely accepted that increased crystallinity corresponds to higher conductivity in TCOs.

Another feature of the diffraction spectra is the presence a shoulder on the left-hand side of the (101) at approximately 31.5° and an extra small peak at approximately 49.4°, neither of which correspond to peaks present in the theoretical patterns for SnO₂[15] or Ta₂O₅[16]. These extra features are clearly present in all the spectra excluding the primarily amorphous samples deposited at 150 °C and with a Ta₂O₅ power of 75 W.

These two features are just to the left of the (101) and the (220) peaks which are the two largest peaks in each spectrum. This indicates that these features may be related to these two reflections. Introduction of substitutional Ta atoms onto Sn sites can be expected to increase the lattice parameters of the SnO₂ unit cell due to the relative sizes of Ta and Sn atoms.

Based on Bragg's law, an increase in the SnO₂ lattice parameters of around 10% would place the (101) and (211) at the positions of the two extra features.

This implies that the films contain two distinct alloy compositions. The first corresponds to SnO₂ with little to no Ta content so that the lattice parameter remains unchanged. The second, SnO₂ with high Ta content substituting on the Sn site so that the interatomic spacing and therefore the lattice parameters increase. The majority of each film consists of the low Ta content material as the peaks corresponding to SnO₂ are significantly more intense than the shifted peaks. The peaks from reflections other than the (101) and (211) planes are not visible for the high Ta component of the films, as they are expected to be of a magnitude comparable to the noise in the data.

This means that there is an uneven distribution of the dopant throughout the films with the tantalum content clustering together to form a secondary alloy composition large enough to create discrete x-ray reflections.

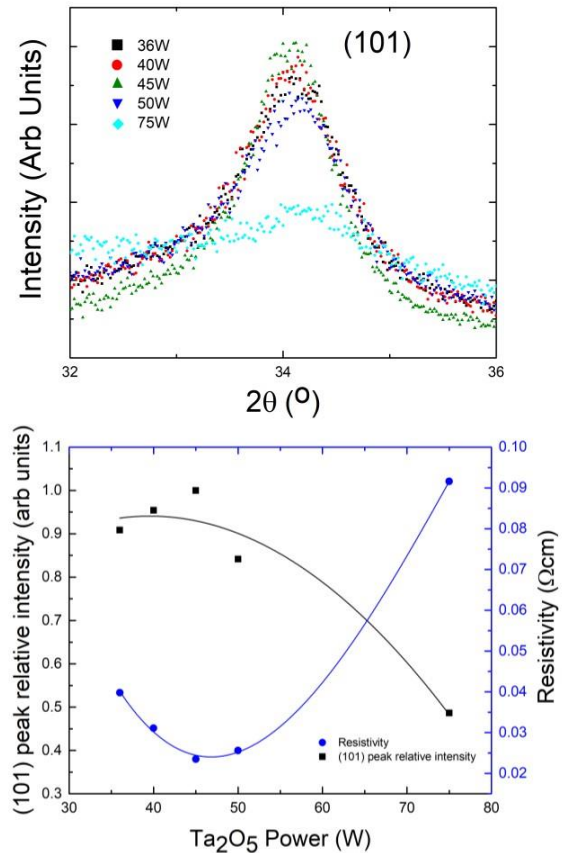


Fig. 6. A The SnO₂ (101) peak from the diffraction patterns for the TaTO films deposited with different Ta₂O₅ powers and B the relative intensity of the SnO₂ (101) peak in the TaTO background subtracted x-ray diffraction patterns and the resistivity of the thin films with Ta₂O₅ sputtering power. Lines are to show the general trends.

The tantalum not being evenly distributed throughout the films as a donor could therefore be the limiting factor on the conductivity of films deposited by the co-sputtering deposition method. This combined with the trend between improved crystallinity of the films and reduced resistivity means that the greatest impact of changing the Ta₂O₅ power is not on the doping density and in fact the film crystallinity due to the formation of multiple phases and the crystallinity is therefore the limiting factor on the films conductivity.

III. CONCLUSION

Previous reports of PLD-grown TaTO provides evidence that its performance should be able to surpass the widely used FTO. In this initial work on co-sputtering of TaTO, the best electrical properties achieved are a resistivity of $8.5 \times 10^{-3} \Omega\text{cm}$, carrier density of $4.4 \times 10^{19} \text{ cm}^{-3}$ and a Hall mobility of $16.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. These properties do not surpass those of FTO or the record for single-target-sputtered

TaTO. This is tentatively attributed to a limiting issue with the co-sputtering deposition method as close-to-record electrical properties have never been achieved for any TCO using this deposition method.

A trend between the crystallinity and the power applied to the Ta₂O₅ target was observed in the XRD patterns along with evidence of a second Sn_{1-x}Ta_xO₂ component of the films with high Ta content. This indicated that improved electrical properties of certain films arose from improved doping uniformity and crystallinity rather than increased incorporation of tantalum as a donor impurity.

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