

Characterization of Ti/SnO₂ Interface by X-ray Photoelectron Spectroscopy

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The Ti/SnO₂ interface has been investigated in situ via the technique of x-ray photoelectron spectroscopy. Thin films (in the range from 0.3 to 1.1 nm) of titanium were deposited on SnO₂ substrates via the e-beam technique. The deposition was carried out at two different substrate temperatures, namely room temperature and 200 °C. The photoelectron spectra of tin and titanium in the samples were found to exhibit significant differences upon comparison with the corresponding elemental and the oxide spectra. These changes result from chemical interaction between SnO₂ and the titanium overlayer at the interface. The SnO₂ was observed to be reduced to elemental tin while the titanium overlayer was observed to become oxidized. Complete reduction of SnO₂ to elemental tin did not occur even for the lowest thickness of the titanium overlayer. The interfaces in both the types of the samples were observed to consist of elemental Sn, SnO₂, elemental titanium, TiO₂, and Ti-suboxide.

tin

titanium

tin oxide

X-ray photoelectron spectroscopy

1. Introduction

Tin oxide (SnO₂) has attracted significant attention due to its interesting properties. It is proving to be a possible alternative to TiO₂ as an electron transporting layer in perovskite solar cells. The oxide has a lower crystallization temperature than that of TiO₂. The TiO₂ film requires a high annealing temperature (>450 °C) to obtain high quality films. This increases both the possibility of chemical interaction with the underlying substrates and interdiffusion [1][2]. The lower formation temperature makes it easier to crystallize and dope the tin oxide. Many materials as dopants (such as Mg, Li, Al, and Sb) to SnO₂ have been investigated [3][4][5][6]. Tin oxide therefore becomes suitable for use in flexible solar cells, tandem solar cells, and large-scale commercialization at a lower cost [7][8][9]. It has been found to have excellent chemical stability, UV-resistance, and good antireflection as compared to TiO₂. For example, Yahi et al. [10] have reported the average transmittance of SnO₂ films to be around 80%. These properties increase the stability and lifespan of the devices [11].

The tin oxide and titanium oxide (TiO₂) have found applications as gas sensors [12][13][14][15][16], photocatalysts [17][18][19][20][21], photovoltaic [22][23][24], optoelectronics [25][26][27][28], etc. Nanocomposites of these two oxides have found use in technological applications in various fields [29][30][31][32][33][34][35][36]. To increase the photocatalytic activity of photocatalysts, creation of nanocomposite of these two oxides (SnO₂ and TiO₂) represents a promising method. These two oxides bear some resemblance in terms of their material properties such as their structure, wide band gap, high transmittance, multi-valency state, and high melting point. SnO₂ plays an essential role in nanocomposite structures with TiO₂ due to the production of more hydroxyl radicals in such a composite compared

to other oxides such as ZnO, WO₃, and Fe₂O₃ [37]. A wide range of properties that could be obtained in the TiO₂-SnO₂ nanocomposites depend upon their synthesis method and precursor type. Several studies have been focused on the creation of TiO₂-SnO₂ nanocomposites in order to increase their photoactivity. Various methods used for the creation of the nanocomposites include sol-gel [38][39][40][41], hydrothermal synthesis [42][43], chemical vapor deposition [44], spray and laser pyrolysis [45][46][47], coprecipitation [48][49], and green [50]. The significant differences that exist between the present investigation and those employed by other researchers lie primarily in the method of preparing the Ti/SnO₂ interface. In the present investigation, thin films of tin and titanium were deposited by the technique of electron-beam evaporation. Since the depositions have been carried out under high vacuum, such a method of preparation provides a contaminant free specimen.

In the present investigation, the chemical reactivity at the titanium-stannic oxide (Ti/SnO₂) interface has been investigated as a function of the thickness of the titanium overlayer and the substrate temperature. Thin films of titanium were deposited onto the stannic oxide substrate. The deposition of the titanium overlayer was performed under two different processing conditions: the substrate kept at ambient temperature and at 200 °C during the deposition. The 200 °C temperature was chosen in order to view significant changes at the interface. The interfaces have been characterized in situ by the technique of XPS. This technique is sensitive to the changes in the chemical states and thus becomes suitable for this investigation [51].

2. Room Temperature Deposition

2.1. Sn 3d Region

In order to analyze the experimental data from the Ti/SnO₂ interface, spectral data from elemental tin and tin oxide were recorded. For this purpose, a 20 nm thick film of tin was deposited on a silicon substrate at room temperature. The spectrum from this sample is shown as curve (a) in **Figure 1**. In this spectrum the 3d_{5/2} and 3d_{3/2} core level peaks are observed to be at BE values of 484.95 and 493.18 eV, respectively. These values are in agreement with those reported for elemental tin by other researchers [52][53]. The spectrum indicates that under the deposition conditions used in this investigation, tin gets deposited as elemental tin on silicon. The tin oxide (SnO₂) was formed by oxidizing a similar sample of tin in a quartz tube furnace. The spectrum obtained from this sample is included as curve (b) in **Figure 1**. The core level peaks obtained from the SnO₂ sample are seen to be shifted to the high BE side as compared to those for elemental tin. The BEs of the 3d_{5/2} and 3d_{3/2} core level peaks in this curve are measured to be 486.93 eV and 495.56 eV, respectively, and are in agreement with those reported by other researchers [52][53].

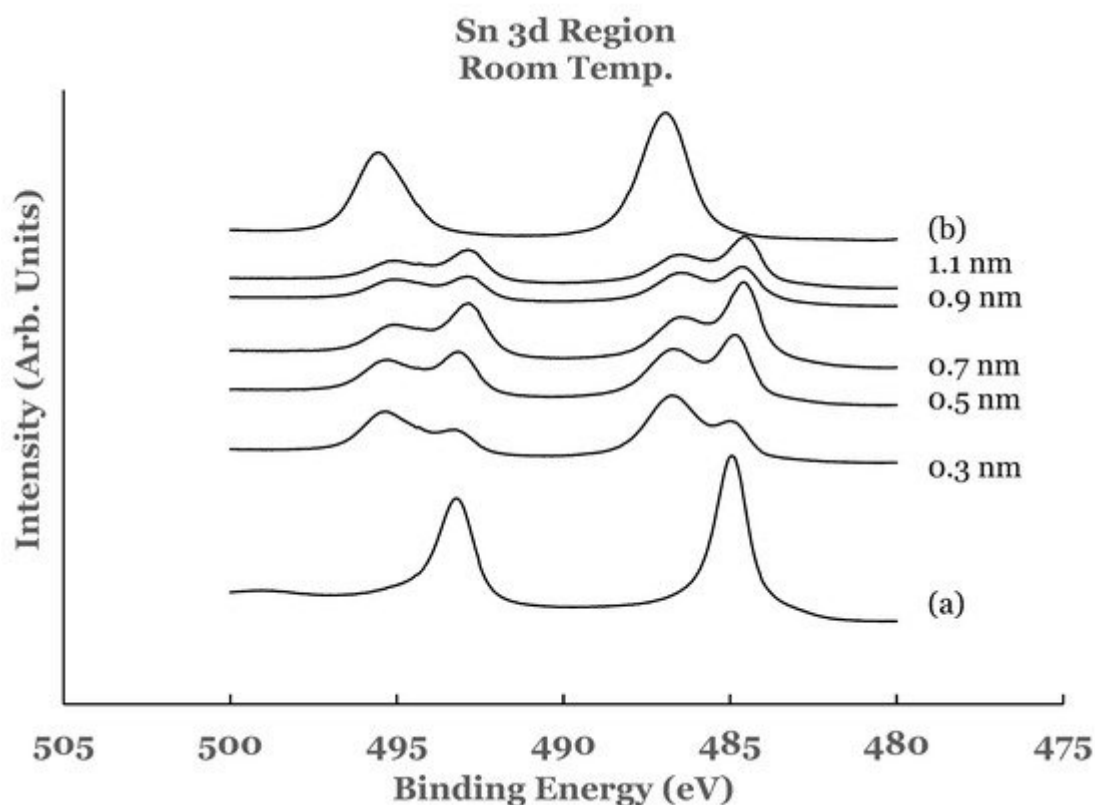


Figure 1. Spectral data in the Sn 3d region as a function of the thickness of the titanium overlayer. The overlayer was deposited at room temperature. Curve (a) corresponds to elemental Sn while curve (b) corresponds to SnO₂.

Figure 1 also includes the high resolution spectra in the 3D region of tin obtained from the Ti/SnO₂ interfaces for the different thicknesses of the titanium overlayer. These spectra are normalized to have equal intensity at 482 eV. The normalization of the spectra facilitates comparison for increase or decrease in the intensity in the core level region. The spectrum from the 0.3 nm sample shows the presence of a shoulder on the low BE side of each of the tin oxide core level peaks. Upon comparison with the elemental spectrum, the presence of this shoulder is attributed to the presence of elemental tin at the Ti/SnO₂ interface. The spectral features therefore indicate that the room temperature deposition of the 0.3 nm overlayer of titanium on SnO₂ results in the partial reduction of the oxide into elemental tin. This is corroborated by the investigation of the 2p region of titanium in these samples, as explained later in this paper.

The spectral data from the 0.5, 0.7, 0.9, and 1.1 nm thick titanium overlayers are similar to those observed for the 0.3 nm sample. In all of these samples, there is no change in the shape of the spectral features. The intensity of the core level peaks corresponding to SnO₂ is observed to decrease while that due to elemental Sn to increase as a function of the thickness of the titanium overlayer. Only a partial reduction of SnO₂ is observed even with the lowest thickness of the titanium overlayer.

To estimate the amounts of the SnO₂ and elemental Sn present at the interface, a curve fit was carried out to the spectral data. An example of curve fit is given in **Figure 2** for the 1.1 nm sample. A Shirley background was subtracted from the spectrum before the curve fit. The elemental and the oxide spectra were scaled to match the

spectral data from the sample. The relative percentages of SnO₂ and elemental Sn were determined from the areas under the corresponding fitting curves, normalized to the total area of the 3D peak. Plots of the percentage composition of SnO₂ and elemental Sn thus determined as a function of the thickness of the titanium overlayer are shown in **Figure 3a,b**. The dashed lines serve as a guide to represent the trend in the data. From these figures it is observed that SnO₂ shows a decreasing trend while elemental Sn shows an increasing trend with the increase in the titanium overlayer. The decrease in SnO₂ is significant until 0.5 nm Ti overlayer and then it becomes gradual for thicknesses greater than this. This can be understood from the amount of titanium available to interact with SnO₂ at the interface. Till 0.5 nm thickness, significant amount of titanium interacts with SnO₂. As the thickness increases, the underlying layers prevent further interaction with the SnO₂ substrate. The study therefore indicates the presence of SnO₂ and reduced elemental tin at the Ti/SnO₂ interface.

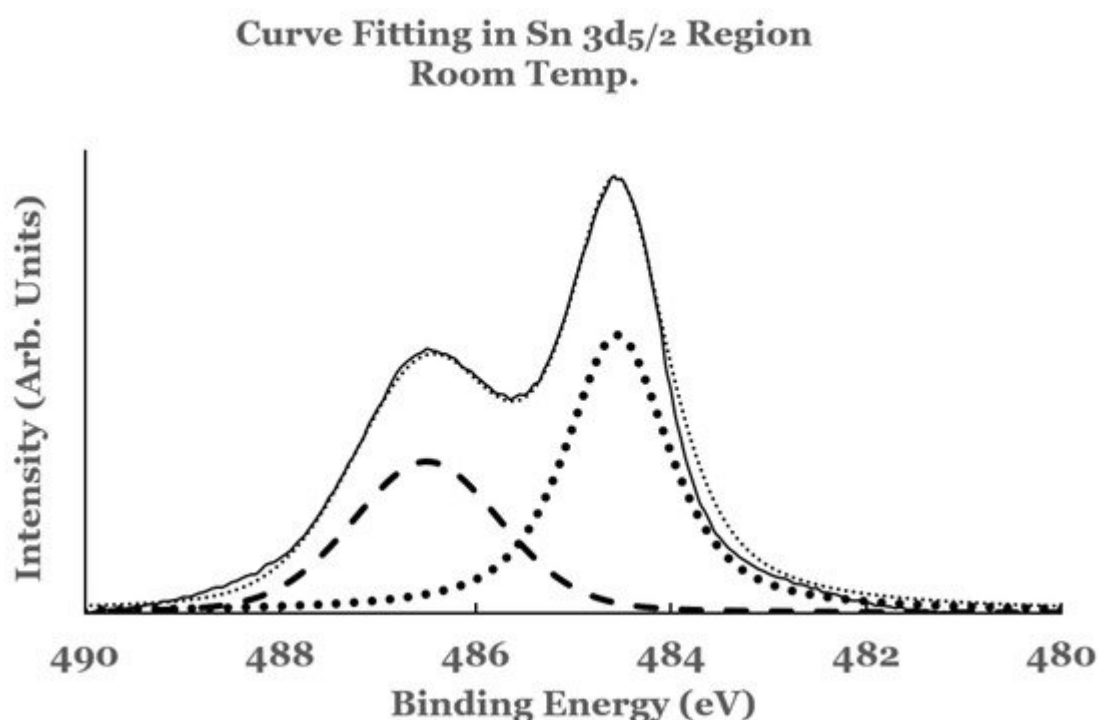


Figure 2. Curve fit for the 3d_{5/2} region of tin for the 1.1 nm titanium overlayer deposited at room temperature. The thin solid line represents the experimental data. The thick dotted line represents the spectrum from elemental Sn while the thick dashed line that from SnO₂. The thin dotted line represents the superposition from elemental Sn and SnO₂.

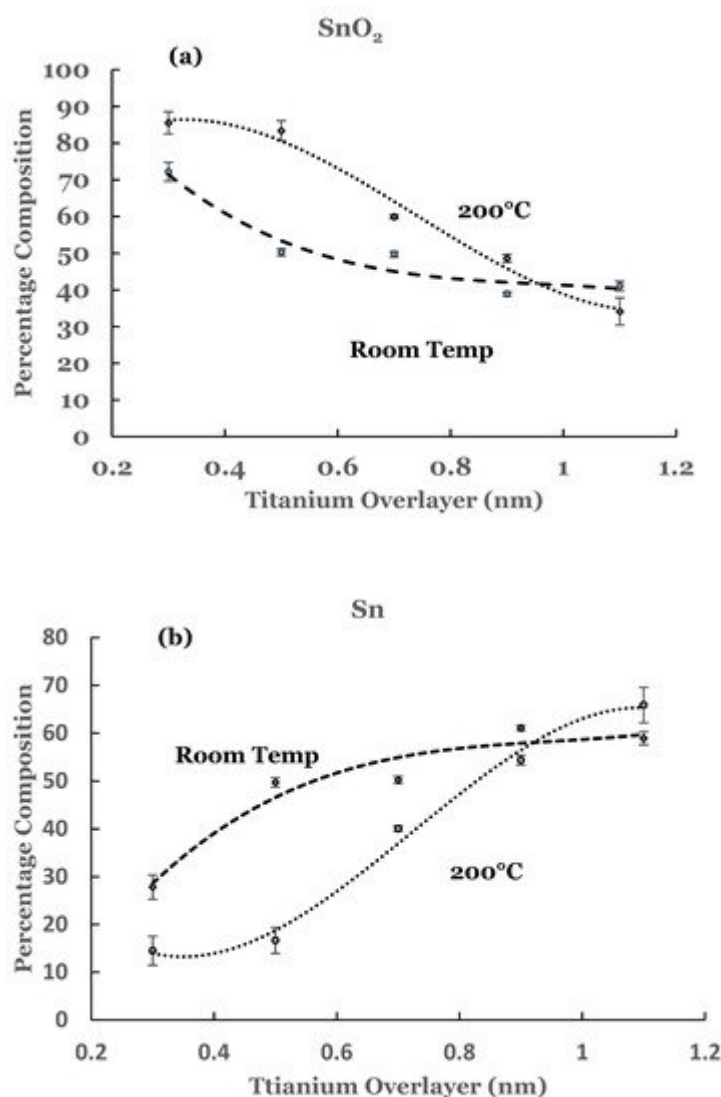


Figure 3. (a) Percentage composition of SnO₂ as a function of the thickness of the titanium overlayer in the two sets of samples, and (b) percentage composition of elemental Sn as a function of the thickness of the titanium overlayer in the two sets of samples. The lines serve as a guide for the trend in the data. The error bars are also included.

2.2. Ti 2p Region

The titanium 2p region in the samples investigated are shown in **Figure 4**. The spectra are normalized to have equal intensity at 450 eV. The data from elemental titanium and TiO₂ are also included in this figure. The spectrum of elemental titanium was obtained by depositing about 20 nm of elemental titanium on a silicon substrate (Ti/Si). The spectrum from this sample is shown as curve (a) in **Figure 4**. The spectral features show BE values of 454.1 and 460.2 eV, respectively, for the 2p_{3/2} and 2p_{1/2} core level peaks. These values are in agreement with those reported in literature for elemental titanium [54][55]. The titanium oxide (TiO₂) was formed by oxidizing the Ti/Si sample in an oxygen environment using a quartz tube furnace. The spectrum obtained from the oxide is included as curve (b) in **Figure 4**. The core level peaks in this spectrum are observed to be broader and shifted to the high BE side as compared to those for elemental titanium. The BEs of the 2p_{3/2} and 2p_{1/2} core level peaks are

measured to be 458.9 and 464.7 eV, respectively. These values are in good agreement with those reported by other researchers for TiO₂ [56][57].

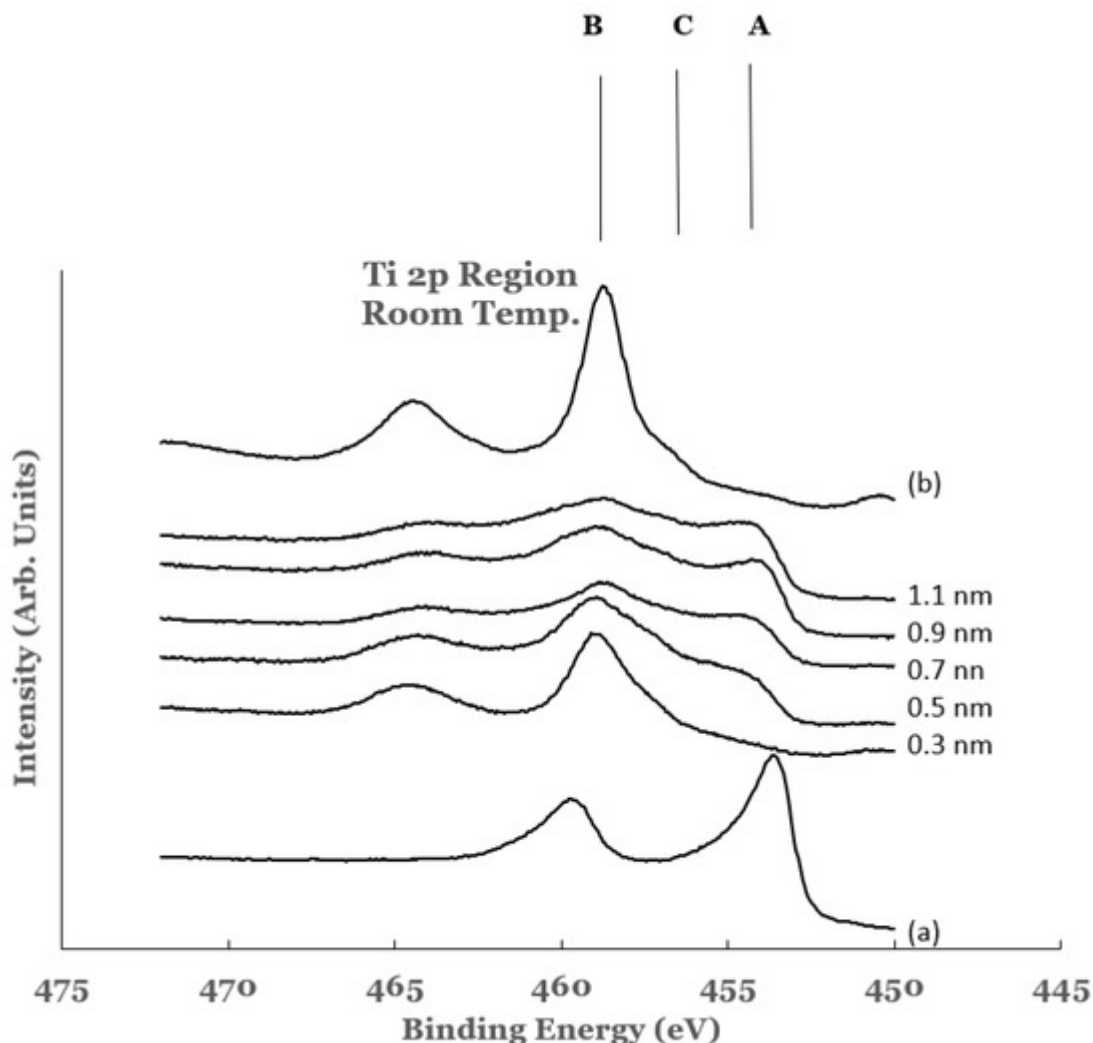


Figure 4. Spectral data in the Ti 2p region as a function of the titanium overlayer. The overlayer was deposited at room temperature. Vertical lines represent the positions of the 2p_{3/2} core level of titanium in the different chemical states of titanium. Line A represents the position of the 2p_{3/2} core level for elemental Ti, line B that for TiO₂, and line C that for Ti-suboxide. Spectrum (a) corresponds to that for elemental Ti while spectrum (b) to that for TiO₂.

The 2p region of titanium in all of the spectra from the Ti/SnO₂ samples is observed to contain broad spectral features. The presence of these features indicates chemical reactivity at the Ti/SnO₂ interface. The features can be divided into three regions: region A (centered around 453 eV), region B (centered around 458 eV), and region C (centered around 456 eV). The intensities in these regions are compared with those from elemental Ti and TiO₂ to estimate the extent of the chemical reactivity. Region A corresponds to that from the 2p_{3/2} core level peak of elemental titanium. It represents the amount of elemental titanium left unreacted from the overlayer. It is observed to increase as a function of the thickness of the overlayer. Region B corresponds to that from the 2p_{3/2} core level peak of titanium in TiO₂. It represents the amount of TiO₂ formed at the interface as a result of chemical interaction between Ti and SnO₂. In the 0.3 nm sample, larger intensity in region B and a very small intensity in region A are

observed. The increase in the intensity in region A and the decrease in the region B for other samples are attributed to the increase and decrease of elemental Ti and TiO₂, respectively, at the interface. The spectral data therefore indicate intense chemical reaction at the Ti/SnO₂ interface. The amount of unreacted titanium is observed to increase with the increase in the thickness of the Ti-overlayer. The extent of the chemical reactivity at the interface is observed to decrease with this increase.

A curve fitting was also performed in the 2p region to estimate the amounts of the constituents present at the interface. A Shirley background was subtracted from the experimental curve before the curve fit. The spectra from elemental Ti and TiO₂ were superimposed on the experimental curve. For this, their intensities were scaled to match one end of the spectrum. An example of such a curve fitting is shown in **Figure 5** for the 1.1 nm sample. Due to the asymmetric shape of the core level peaks of titanium, a complete match of the fitted curve with the experimental one was not possible. Any excess intensity of the fitted curve was subtracted from the total area before estimating the percentage concentration. It is evident from this figure that the region C consists of additional intensity. This intensity is due to the suboxide of titanium resulting from incomplete chemical interaction between titanium and SnO₂ at the interface. The results therefore show that the interface consists of TiO₂, elemental Ti, and Ti-suboxide. The amounts of TiO₂, unreacted Ti, and suboxide of Ti have been estimated from the spectral data. The areas under the curves were determined using the trapezoidal method. The relative percentage of each of the constituents was determined from these areas, normalized to the total area of the spectrum. The variations in the percentage of TiO₂, elemental Ti, and Ti-suboxide in these samples as a function of the thickness of the titanium overlayer are shown in **Figure 6a–c**. The lines in these figures represent the guides for the variations. The TiO₂ shows an initial decrease followed by saturation beyond the 0.5 nm of the titanium overlayer. The Ti-suboxide and unreacted titanium are observed to increase initially followed by flattening off for the same thickness of the titanium overlayer. These trends are in accord with those observed for elemental Sn and SnO₂.

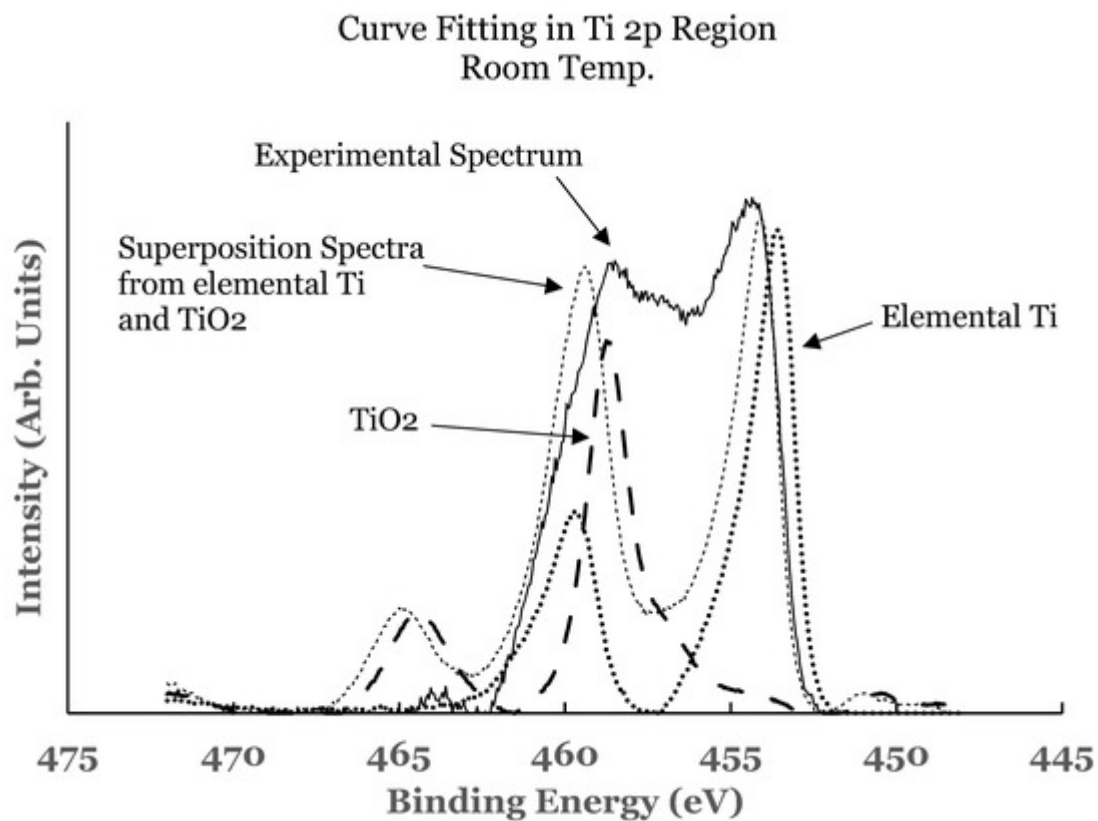


Figure 5. Curve fit for the 2p region of titanium for the 1.1 nm overlayer deposited at room temperature. The thin solid line represents the experimental data. The thick dotted line represents the spectrum from elemental Ti while the thick dashed line that from TiO₂. The thin dotted line represents the superposition from elemental Ti and TiO₂.

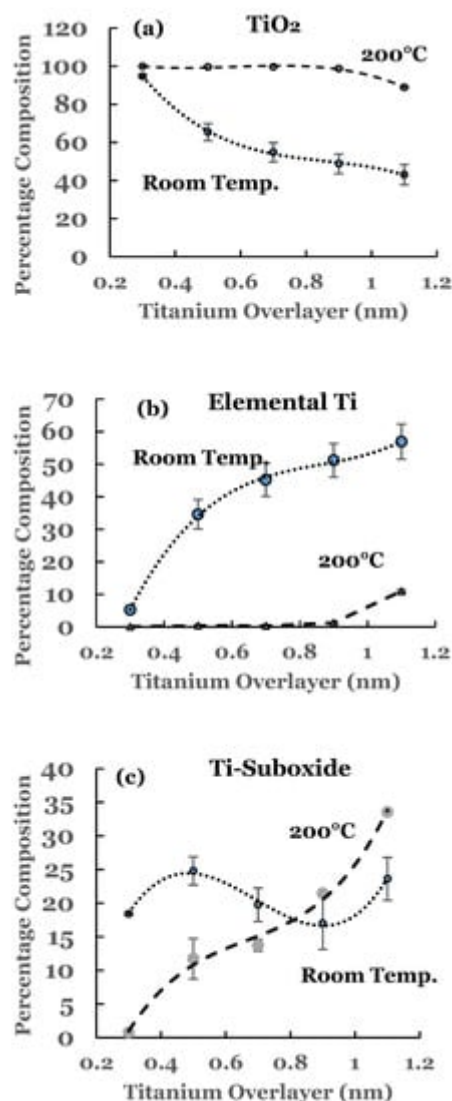


Figure 6. (a) Percentage composition of TiO₂ as a function of the thickness of the titanium overlayer in the two sets of samples; (b) percentage composition of elemental Ti as a function of the thickness of the titanium overlayer in the two sets of samples; (c) percentage composition of Ti-suboxide as a function of the thickness of the titanium overlayer in the two sets of samples. The lines serve as a guide for the trend in the data. The error bars are also included.

Different researchers have employed different techniques of curve fitting to quantify the presence of the constituents in a specimen. Saric et al. [58] have investigated the oxidation of cobalt metal by low-energy oxygen bombardment at room temperature. They have estimated the concentration fraction of CoO and Co₃O₄ in the samples through curve fitting. The 2p_{3/2} core level of elemental cobalt was fitted with an intense asymmetric peak with two small additional peaks. In the oxidized samples, they observed that at least eight fitting components were required to obtain a good fit. Due to the possibility of the presence of other sub-oxides of cobalt and the overlap of the fitted peaks, their method may not fully account for the fraction concentration of the constituents. Hong et al. [59] have investigated the Fe/CuO interface. They have estimated the amount of unreacted iron and Fe₂O₃ at the interface by modeling the spectra from the elemental iron and pure Fe₂O₃. The fitted spectra were calculated with the constraint: $x + y = \text{thickness of the deposited overlayer}$ with x being the thickness of the elemental iron and y

that for Fe₂O₃. The values of x and y were varied to get a good fit with the experimental curve. These methods may work if there were no sub-oxides present. In the present investigation, scaling the intensities of the peaks is expected to account for the various components to scale accordingly. Hence, the method of curve fitting employed in the present investigation is suitable for the estimation of the suboxide at the interface.

3. Substrate Temperature (200 °C) Deposition

3.1. Sn 3d Region

The high resolution spectra in the 3d region of tin obtained from the Ti/SnO₂ interfaces for the titanium overlayer deposited at a substrate temperature of 200 °C are shown in **Figure 7**. These spectra are normalized to have equal intensity at 482 eV. The spectrum from the 0.3 nm sample shows the presence of shoulder on the low BE side of each of the tin oxide core level peaks. The presence of this shoulder is attributed to the reduction of SnO₂ to elemental tin by the titanium overlayer. The intense peaks in this spectrum are due to the SnO₂. The spectral features therefore indicate that the deposition of titanium at this substrate temperature results in the partial reduction of the oxide into elemental tin. The spectral data from the 0.5, 0.7, 0.9, and 1.1 nm thick titanium overlayers are similar to those observed for the 0.3 nm sample. In all of these samples there is no change in the shape of the spectral features. The intensity of the core level peaks corresponding to SnO₂ is observed to decrease while that due to elemental Sn to increase as a function of the thickness of the titanium overlayer. As in the previous case, only a partial reduction of SnO₂ is observed even with the lowest thickness of the titanium overlayer.

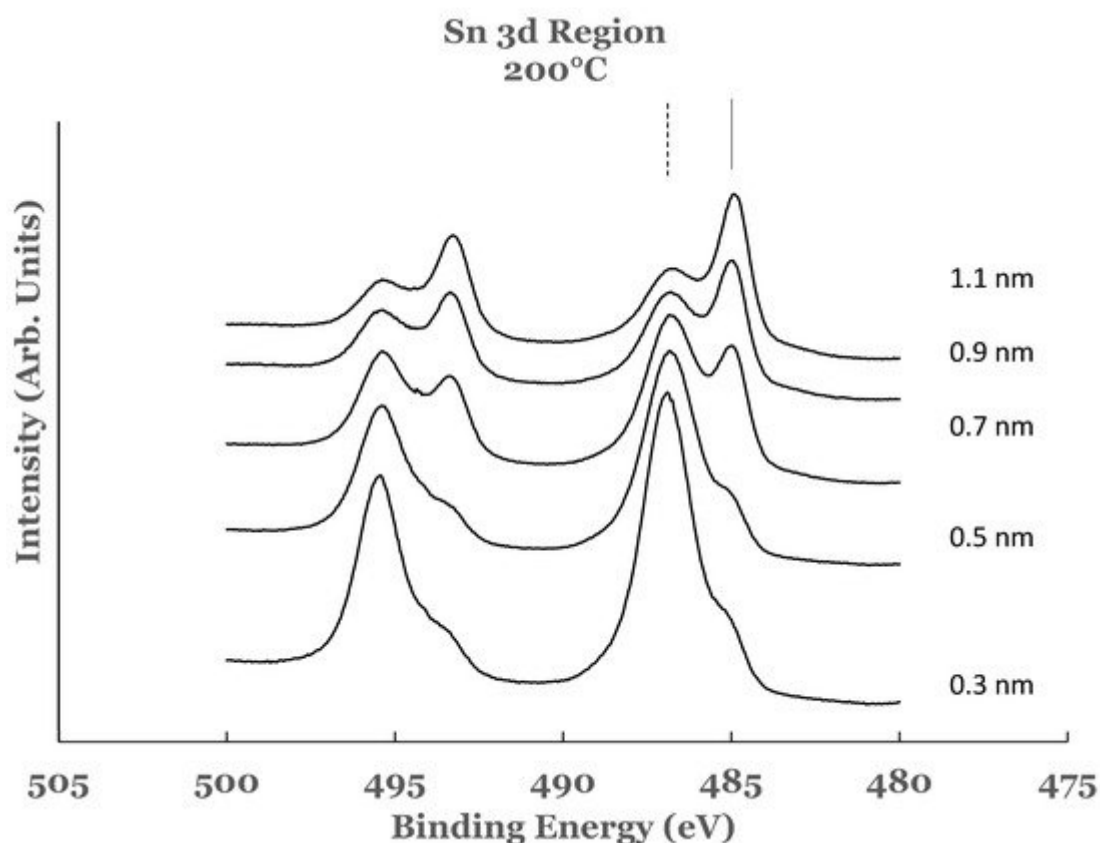


Figure 7. Spectral data in the Sn 3d region as a function of the titanium overlayer. The overlayer was deposited at the substrate temperature of 200 °C. The vertical lines represent the positions of the 3d_{5/2} core level. The solid line corresponds to elemental Sn while the dashed line to SnO₂.

The amounts of SnO₂ and elemental Sn at the interface were estimated for these samples also. For this purpose a curve fit to the spectral data was performed as explained earlier. An example of curve fit is given in **Figure 8** for the 1.1 nm of titanium on SnO₂. The relative percentages of SnO₂ and elemental Sn were determined from the areas of the corresponding fitting curves, normalized to the total area of the 3d peak. Plots of the percentage compositions of SnO₂ and elemental Sn, thus determined as a function of the thickness of the titanium overlayer, are also included in **Figure 3a,b**. The dashed lines serve as a guide to represent the trend in the data. For these samples, a decreasing trend in SnO₂ while an increasing trend in elemental Sn are observed with the increase in the titanium overlayer. Some differences exist when comparing these data with the room temperature data. The SnO₂ concentration starts from a higher value in such samples and continues to show a decreasing trend for thicknesses greater than 0.9 nm. Similarly, the elemental Sn starts from a lower value and continues to show an increasing trend. The data from these samples therefore suggest that the titanium overlayer continues to interact with the underlying SnO₂ layer for thicknesses greater than 0.9 nm. The increased interaction at the interface can be attributed to the thermal diffusion of the titanium overlayer into the underlying SnO₂ in such samples. The study therefore indicates the presence of SnO₂ and elemental Sn in greater amounts in such samples.

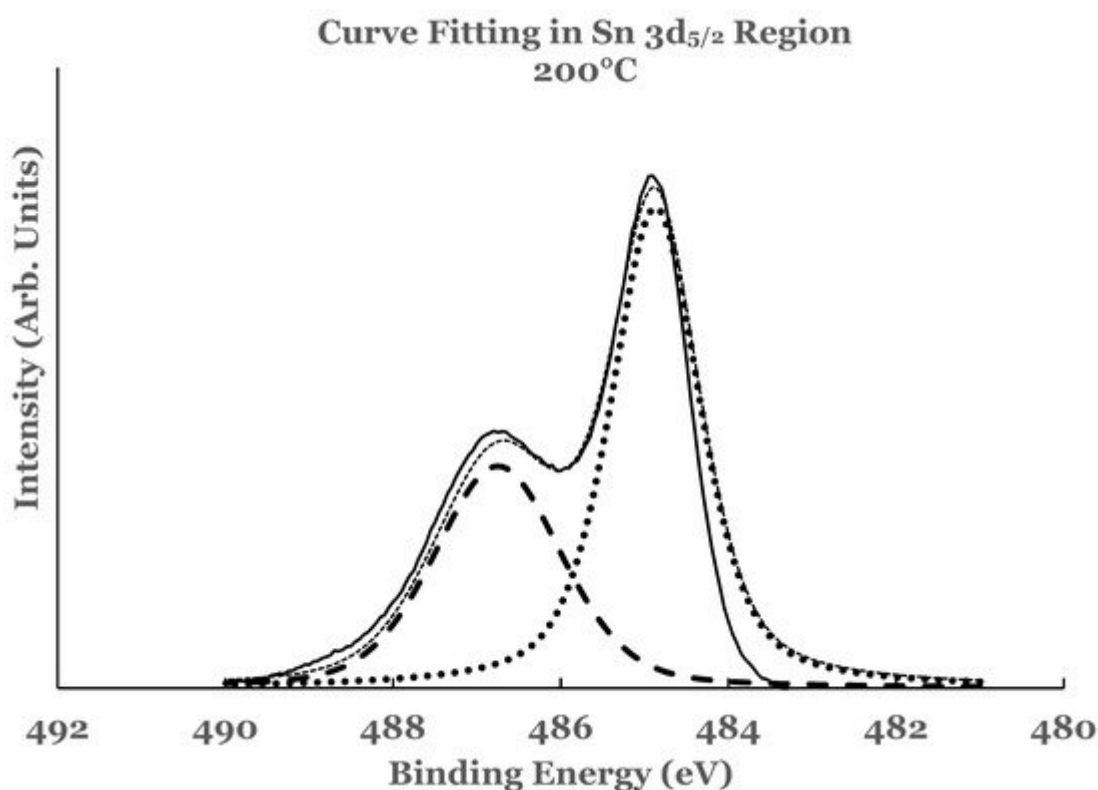


Figure 8. Curve fit for the 3d_{5/2} region of tin for the 1.1 nm titanium overlayer deposited at substrate temperature of 200 °C. The thin solid line represents the experimental data. The thick dotted line represents the spectrum from

elemental Sn while the thick dashed line that from SnO₂. The thin dotted line represents the superposition from elemental Sn and SnO₂.

3.2. Ti 2p Region

The high resolution spectra in the 2p region of titanium obtained from the Ti/SnO₂ interfaces for the titanium overlayer deposited at a substrate temperature of 200 °C are shown in **Figure 9**. The spectra are normalized to have equal intensity at 450 eV. The spectral features in these samples exhibit considerable chemical reactivity at the Ti/SnO₂ interface. The intensity in the region A (centered around 453 eV and corresponds to the 2p_{3/2} core level of titanium in elemental titanium) is observed to increase for thicknesses greater than 0.5 nm. A large intensity in the region B (centered around 458 eV and corresponds to that from the 2p_{3/2} core level peak of titanium in TiO₂) is observed in all of the samples. The intensity of this spectral feature is observed to decrease with increase in the overlayer thickness. The intensity in region C (centered around 456 eV and corresponds to that from the Ti-suboxide) is observed to increase for thicknesses greater than 0.5 nm. The spectral data therefore indicate intense chemical reaction at the Ti/SnO₂ interface. The increase in the amount of unreacted titanium with the increase in the thickness of the Ti-overlayer represents a decrease in the extent of the chemical reactivity at the interface. A decrease in the intensity in region C is observed in these samples when compared with the room temperature data. This is interpreted as an increase in the TiO₂ content in such samples resulting from the diffusion of the titanium overlayer into the underlying SnO₂ layer.

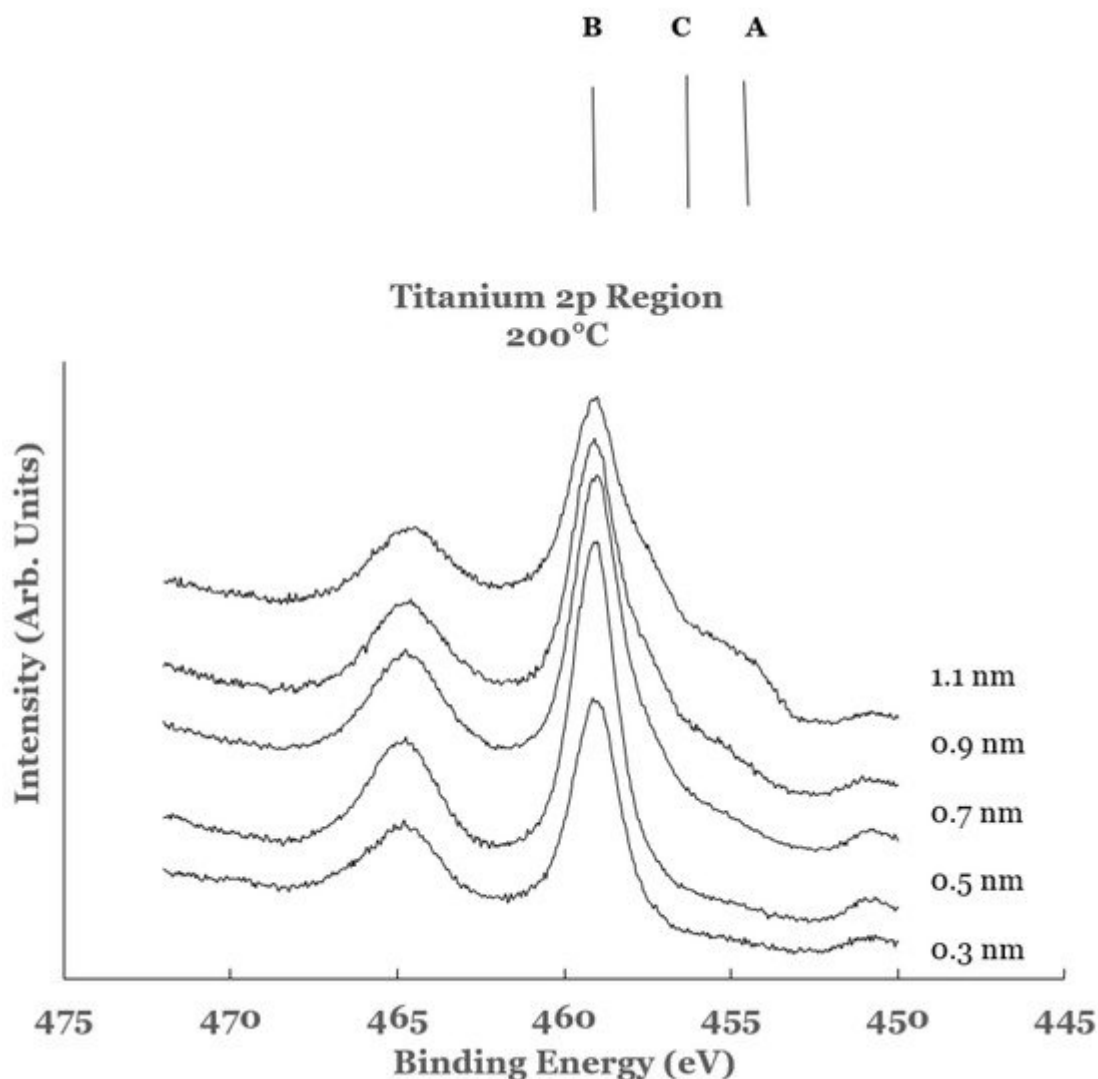


Figure 9. Spectral data in the Ti 2p region as a function of the titanium overlayer. The overlayer was deposited at the substrate temperature of 200 °C. Vertical lines represent the positions of the 2p_{3/2} core level of titanium in the different chemical states of titanium. Line A represents the position of the 2p_{3/2} core level for elemental Ti, line B that for TiO₂, and line C that for Ti-suboxide.

A curve fitting was also performed in the 2p region in these samples to estimate the amount of the constituents present at the interface. The details of curve fitting have been outlined earlier. An example of such a curve fitting is shown in **Figure 10** for the 1.1 nm sample. It is evident from this figure that the region C consists of additional intensity. This intensity is due to the suboxide of titanium resulting from incomplete chemical interaction between titanium and SnO₂ at the interface. The results therefore show that the interface consists of TiO₂, elemental Ti, and Ti-suboxide. The amounts of TiO₂, unreacted Ti, and suboxide of Ti have also been estimated from the spectral data of such samples.

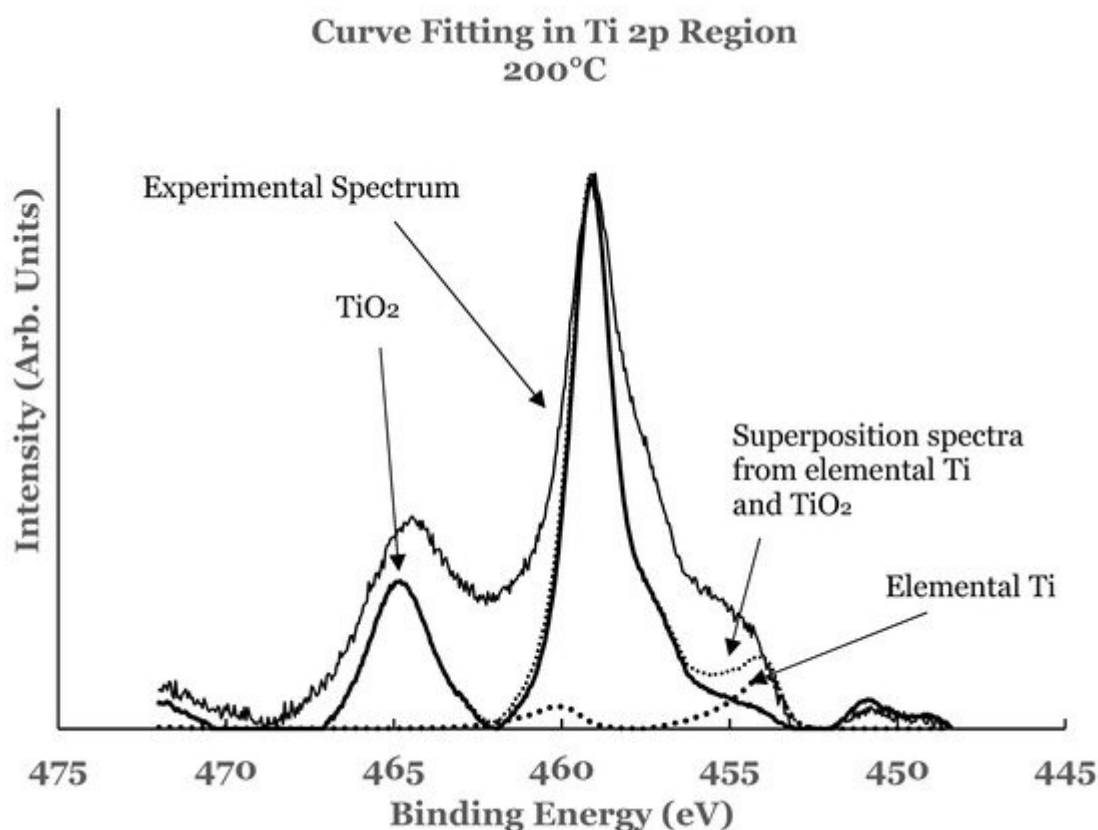


Figure 10. Curve fit for titanium for the 1.1 nm overlayer deposited at 200 °C substrate temperature. The thin solid line represents the experimental data. The thick dotted line represents the spectrum from elemental Ti while the thick solid line that from TiO₂. The thin dotted line represents the superposition from elemental Ti and TiO₂.

The variations in the percentage of TiO₂, elemental Ti, and Ti-suboxide in these samples as a function of the thickness of the titanium overlayer are also included in **Figure 6a–c**, respectively. The lines in these figures represent the guides for the variations. The percentage of TiO₂ is observed to be around 100% till 0.9 nm thickness of the overlayer. This is followed by a decrease in its concentration beyond this thickness. The thermal diffusion of the Ti overlayer makes more titanium to be available for chemical interaction with SnO₂. When compared with the room temperature data, the spectral data for these samples indicate complete oxidation of the titanium overlayer till 0.9 nm thickness. This variation is corroborated by the variation in the percentage for elemental Ti (**Figure 6b**). The elemental titanium is near zero and shows an increasing trend beyond the 0.9 nm thickness. The trend is markedly different from that of the room temperature data. The unreacted titanium shows a rather sharp increase in the percentage for the first two samples in the case of the room temperature deposition. This increase then becomes gradual for thicknesses beyond 0.5 nm. The variation in the Ti-suboxide is also included **Figure 6c** for these samples. Significant variation in the percentage is observed for thicknesses beyond 0.5 nm. The room temperature data, on the other hand, shows variation around 20% for all of the samples. The trends are in accord with those observed for elemental Sn and SnO₂.

The interfacial reaction between Ti and SnO₂ can be understood by considering the Gibbs free energy of the involved products. Gamsjager et al. ^[60] have compiled the Gibbs free energy data for SnO₂ from various sources.

The table A-58 in that reference lists a range of values between –367 and –372 kJ/mol. These values have been measured over a temperature range 673–1380 K. Schaefer has also compiled various values (Table 8 in Ref. [61]) from different researchers. For the present investigation, a value of –407 kJ/mol has been used for SnO₂. Kim and Kang [62] have listed experimental values of the Gibbs free energy for various titanium oxides. The value of –659 kJ/mol has been used for TiO₂ in the present calculation.

The spectral data for the room temperature Ti/SnO₂ interface show the interfacial reaction to occur as:



Titanium exhibits oxidation states of +2, +3, and +4. The Ti-suboxide can therefore be attributed to the presence of Ti₂O₃ near the interface. The above reaction can then be written as:



Considering the above mentioned Gibbs free energy for the involved constituents (the value for Ti₂O₃ is –1430 kJ/mol, [63]), the Reaction (2) results in an approximate value for the change in Gibbs free energy as –1891 kJ/mol. This indicates that such an interfacial reaction can proceed thermodynamically.

For the deposition at the substrate temperature of 200 °C, the reaction occurs according to the following equation:



which is also favored thermodynamically (change in Gibbs free energy is approximately –742 kJ/mol). The data also suggest that TiO₂ is more readily formed at the interface when the substrate temperature is increased.

The partial reduction of SnO₂ to SnO can also occur according to:



The value of the Gibbs free energy for the formation of SnO is –253 kJ/mol [64]. This yields a value of –1893 kJ/mol for the above reaction. However, the spectral data indicate that such a reaction is not favorable under the experimental conditions.

The analysis of the data thus provides a picture of the contents at the interface. The oxidized titanium and the reduced tin are present at the interface. As the titanium overlayer increases, the interfacial TiO₂ layer serves as a barrier for further oxidation of titanium. Due to less availability of oxygen away from the interface, the subsequent titanium overlayer gets partially oxidized. This occurs until after a certain thickness the titanium overlayer results in the unreacted titanium. The present investigation points to the need for more experiments to establish a correlation between the amount of constituents and the substrate temperatures. The electrical properties of these interfaces can then be explored against particular device applications.

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