Using I–V characteristics to investigate selected contacts for SnO_2:F thin films

Shadia. J. Ikhmayies[1,†] and Riyad N Ahmad-Bitar[2]

[1] Al Isra University, Faculty of Information Technology, Department of Basic Sciences-Physics, Amman 16197, Jordan
[2] University of Jordan, Faculty of Science, Physics Department, Amman 11942, Jordan

Abstract: Fluorine doped tin oxide (SnO_2:F) thin films were prepared on glass substrates by the spray pyrolysis (SP) technique at different substrate temperatures between 380–480 ℃. The microstructure of the films was explored using scanning electron microscope observations. An investigation of selected contacts for the films was performed through the analysis of the I–V measurements which were taken in the dark at room temperature. Indium, aluminum and silver were selected as contacts where two strips of each metal were vacuum-evaporated on the surface of the film. The resistivity of the films was estimated from the linear I–V plots. It was found that the smallest resistivity was obtained using silver contacts, while the largest resistivity was obtained by using indium contacts. This is because silver diffuses in the film and participates in doping, while aluminum and indium cause compensation effects when they diffuse in the film. The best linear fit parameters are those of films with aluminum contacts, and the worst ones are those of films with indium contacts. Annealing was found to improve the electrical properties of the films, especially those deposited at a low substrate temperature. This is because it is expected to encourage crystal growth and to reduce the contact potential which leads to the formation of an alloy. Annealed films are more stable than un-annealed ones.

Key words: ohmic contacts; I–V characteristics; annealing; tin oxide
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1. Introduction

An ohmic contact is defined as one in which there is an unimpeded transfer of majority carriers from one material to another, i.e., the contacts do not limit the current. With ohmic contacts the disturbing effect of the barriers is removed and measurements of the electrical characteristics can be made with confidence. The way to achieve such a contact is by doping the semiconductor heavily enough so that tunneling is possible. Lee *et al*.[1] say that ohmic contact resistance is strongly dependent on doping concentration because the tunnelling process is more dominant at high doping levels.

Linear current–voltage characteristics, particularly at low voltages, is a criterion for the perfection of the contacts[2]. Obviously, the value of the electrical resistivity will depend on the characteristics of the contact. The obtained resistivity depends on the way by which it is measured. If for example, the measurement was made between two electrodes on the same side, an apparent (surface) resistivity would be obtained. If however, the measurement was made with electrodes on opposite faces, a (volume) resistivity would be obtained which may be different from the former one[3]. The fabrication of ohmic contacts frequently includes a high temperature step, so that the deposited metals can either alloy with the semiconductor, or the high-temperature anneals reduce the unintentional barrier at the interface[4]. Metals commonly used as contacts of SnO_2 are Ag[5], Au[6] and In[5, 7, 8].

A lot of studies have been performed to research ohmic contacts; for example, Smith[2] studied the properties of ohmic contacts of CdS single crystals, in a former study we [3] made a comparison between selected contacts of CdS:In thin films, Lee *et al.*[1] investigated the low ohmic contact resistance of GaN by employing a XeCl excimer laser. But to the best of our knowledge no such studies were found about the ohmic contacts of SnO_2 single crystals or thin films. All that we found in the literature are works discussing the electrical properties of SnO_2 thin films using ohmic contacts such as Shanthi *et al.*[9], Fantini and Torriani[10], and Zaouk *et al.*[11] who did not mention the type of contacts, Banerjee *et al.*[5] and Geraldoa *et al.*[8] who used In contacts, and Banerjee *et al.*[5] who used Ag contacts. So, there is a lack of experimental and theoretical work regarding the ohmic contacts of SnO_2.

The objective of this work is to make a comparison between a set of ohmic contacts for SnO_2 thin films; indium, aluminum and silver by using current–voltage characterization. These metals were chosen for this study because of the suitability of their work functions; the work function of In is about: 4.09 eV[12], and the work functions of Ag and Al are 4.31 and 4.20 eV[13] respectively. These values are close to the electron affinity of SnO_2 (4.8 eV)[14], so all of these metals can make ohmic contacts with SnO_2:F thin films. To the best of our knowledge, we are the first study to use aluminum as a contact for SnO_2:F, and we are the first study to compare a set of ohmic contacts for SnO_2:F thin films.

2. Experimental part

The spray pyrolysis technique (SP) was used to produce the SnO_2:F thin films. The precursor solution was made by dissolving 5.0×10^{-2} moles of stannous chloride ($SnCl_2{\cdot}2H_2O$) with 5.71×10^{-2} moles of hydrofluoric acid (HF) in 45 mL of methanol, 40 mL of distilled water and 10 mL of HCl (about

† Corresponding author. Email: shadia_ikhmayies@yahoo.com
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36% HCl). The ratio of fluorine ions to tin ions in the solution was 1.14 which is approximately the same as Gordillo *et al.*[15], in which they got the best quality SnO_2:F thin films. This ratio is not necessarily the same as that in the films due to the dynamic nature of the spray pyrolysis.

The substrates are ordinary glass microslides with dimensions of $2.5 \times 6 \times 0.1$ cm^3. The substrate temperatures were in the range 360–480 ℃. Prior to the deposition of the films, the substrates were ultrasonically cleaned in methanol for at least 15 min. The spray rate was usually in the range 15–18 mL/min. The optimum carrier gas pressure for this solution flow rate was around 5 kg/cm^2.

Aluminum, indium and silver were used to make the contacts for the SnO_2:F thin films. Two strips of the contact material were deposited on the surface of the film by vacuum evaporation, where the separation distance is 2–3 mm. The thickness of each strip was more than 0.4 μm, its length was 1 cm and its width was 1 mm. The I–V measurements were taken at room temperature by a system that consists of a Keithley 2400 source meter capable of measuring 10^{-11} A, which was interfaced by an IBM computer. The sample in question was placed in a brass cell which is shielded by an aluminum box. Some films were annealed in a nitrogen atmosphere at 400 ℃ by using the annealing system described in Ref. [16].

The transmittance of the films was measured in the wavelength range λ = 290–1100 nm by using a double beam Shimadzu UV 1601 (PC) spectrophotometer in respect to a piece of glass of the same kind as the substrates. The minima and maxima in the transmittance curves were used to estimate the film thickness as follows[17]:

The transmittance at a certain maximum was considered as T_{max}, the transmittance at the next minimum as T_{min} and dispersion is negligible, then a parameter ρ_{T} was defined by the approximate form,

$$\rho_{\text{T}} = \frac{T_{\text{max}}}{T_{\text{min}}} \cong \frac{\left(n_1^2 + n_0^2\right)\left(n_1^2 + n_2^2\right)}{2n_1^2\left(n_0^2 + n_2^2\right)}, \quad (1)$$

where n_0, n_1, and n_2 are the refractive indices of air, film, and glass respectively, and the condition $n_0 < n_1$ and $n_2 < n_1$ was satisfied. Solving Eq. (1) for n_1 to have

$$n_1 = \left\{ -\left(n_0^2 + n_2^2\right)(1 - 2\rho_{\text{T}}) + \left[\left(n_0^2 + n_2^2\right)(1 - 2\rho_{\text{T}})^2 - 4n_0^2 n_2^2\right]^{1/2} \Big/ 2 \right\}^{1/2}, \quad (2)$$

and the film thickness is given by

$$t = \frac{\lambda_{\text{max}}\lambda_{\text{min}}}{4n_1\left(\lambda_{\text{min}} - \lambda_{\text{max}}\right)}, \quad (3)$$

where λ_{min} and λ_{max} are the values of the wavelength at a certain maximum and the next minimum respectively. The estimated values of film thickness are in the range 100–350 nm.

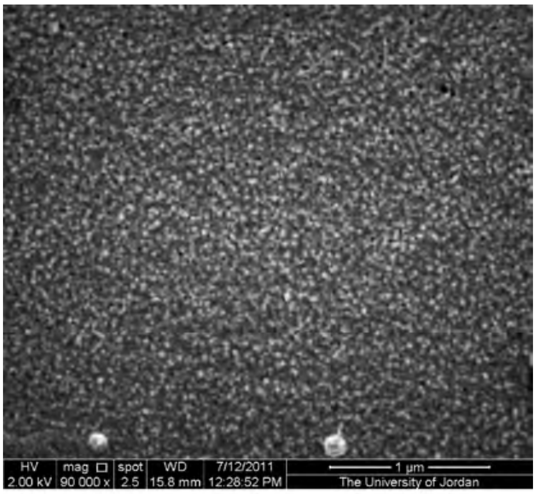
The surface morphology of the films was analyzed before depositing the contacts by a FEI scanning electron microscope (Inspect F 50) for some films (the films deposited at different substrate temperatures), and by a LEITZ-AMR 1000A scanning electron microscope for other films (the as-deposited and annealed films).

3. Results and discussion

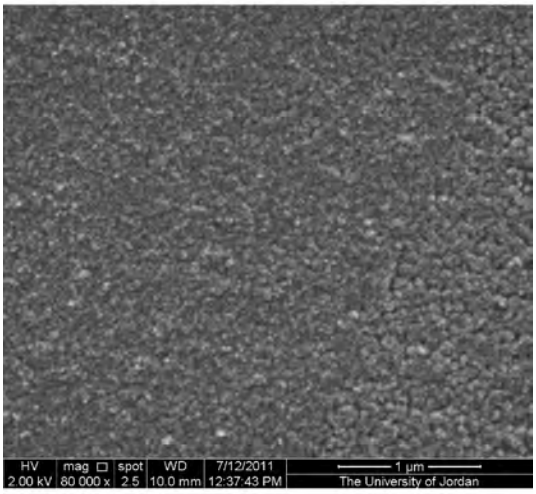
Polycrystalline, fluorine doped tin oxide (SnO_2:F) thin films were produced by the spray pyrolysis technique on glass substrates at different substrate temperatures. Figure 1 depicts the scanning electron micrographs for a set of films prepared at three different substrate temperatures; 400, 450 and 450 ℃, taken by a FEI scanning electron microscope (Inspect F 50). The films appear to be uniform, in tact and fully covered with material. The effect of the substrate temperature is apparent where the size of the crystallites appears to increase with the increase in the substrate temperature. Annealing is known to encourage crystal growth and increase the grain size, but when the films are prepared at high substrate temperatures its effect diminishes and becomes unapparent. Figure 2 displays the SEM micrographs for a film deposited at T_{s} = 480 ℃ before and after annealing taken by a LEITZ-AMR 1000A scanning electron microscope. The comparison between the two micrographs did not show a considerable difference, but the uniformity of the film improved a little after annealing.

Some of the criteria of the perfection of the contacts are linear current–voltage characteristics, particularly at low voltages, and the absence of photovoltaic effects[2]. At lower voltages, the contact resistance dominates. Most of the voltage will appear across the contact resistance and very little across the bulk of the film. Indium, aluminum and silver were used as contacts for SnO_2 : F thin films, all of them could make ohmic contacts. The I–V measurements were recorded at room temperature in the voltage range 0–1 V. Figure 3 displays these plots for two SnO_2 : F thin films deposited at T_{s} = 380 ℃ (Fig. 3(a)) and 460 ℃ (Fig. 3(b)) with the three aforementioned contacts having similar geometries deposited on the surface of each film. As the figure shows, all of the curves are linear, so linear fits were performed and the resistivity was calculated using the slope of the straight lines and the relation $R = \frac{\rho L}{A}$, where R is the resistance taken from the slope of the straight lines, L is the length in the direction of the current which equals the distance between the contacts, and A is the area perpendicular to the current which is equal to the length of the contact multiplied by the film thickness. The values of the resistivity and the parameters of the linear fits R^2, F, and the standard deviation SD are inserted in Table 1.

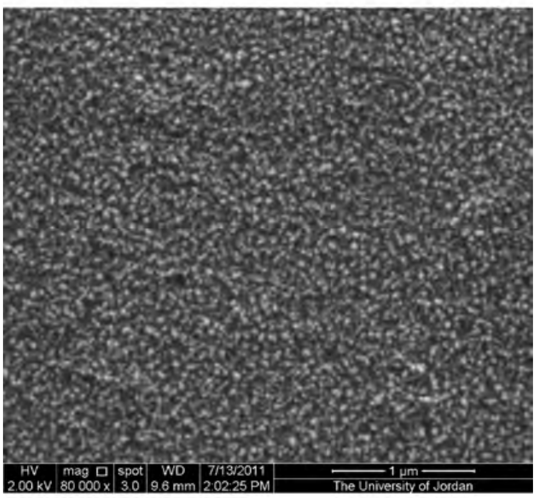
From Fig. 3 and Table 1 it is first noticed that the smallest resistivity was obtained from the data taken using the silver contacts, while the largest resistivity was for the data taken using indium contacts. Second, it is also noticed that the resistivity was smaller in the case of the higher substrate temperature for the three contacts. This is not the subject of this paper, but the relation between resistivity and substrate temperature was discussed elsewhere[18]. Remembering that the results were also affected by the difference in film thickness in the two cases, where the films deposited at 380 ℃ have a thickness of about 350 nm, while those deposited at 460 ℃ have a thickness of about 100 nm. This can be understood by knowing that the resistivity decreases with film thickness as discussed in Ref. [19]. A comparison of the linear fit parameters for the three contacts shows that Al has the best R^2 values and SD values at the two substrate temperatures, and it has the best F value at the higher substrate temperature. On the other hand, In has the worst fitting parameters of the set, where it has the



(a)



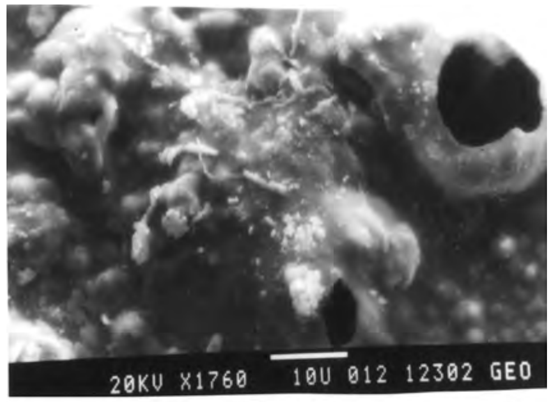
(b)



(c)

Fig. 1. SEM micrographs of SnO_2:F thin films prepared at different substrate temperatures. (a) 400 ℃. (b) 450 ℃. (c) 480 ℃. Note: the magnification in (a) is 90000 × while in (b) and (c) it is 80000.

largest SD, the smallest F value and the smallest R^2 values in both cases. This means that the best linearity or ohmicity is obtained by using the Al contacts.



(a)

(b)

Fig. 2. SEM micrographs for a film (a) before annealing and (b) after annealing.

To explain these results, first we refer to the fact mentioned in Section 1; that is the work function of silver is the closest to the electron affinity of SnO_2, while that of indium is the farthermost. Second, in the case of Al and In contacts, we expect that some compensation mechanisms will play a role in the film, which reduces the amount of free charge carriers. This is supported by Pan *et al.*[20] who mentioned that p-type SnO_2 films have been prepared by Al or In doping. So when these two metals are used to form contacts they penetrate the films and cause compensation effects. The ionic radius of Al is smaller than that of Sn, so it can substitute it in the crystal lattice and cause a shrink in the SnO_2 lattice, and then a decrease in the lattice parameters. The ionic radius of In is larger than that of tin, so when it substitutes it in the crystal lattice it can enlarge the lattice of SnO_2 and then causes an increase in the lattice parameters. The increase in lattice parameters in the case of In contacts and the decrease in them in the case of Al contacts is thought to be the reason of the larger resistivity of films with indium contacts and the smaller resistivity of films with Al contacts. Silver is expected to take an interstitial position in the crystal lattice, so it makes the film n-type and then increases the number of free charge carriers.

To improve the contacts and then improve the electrical properties, a heat-treatment is recommended, so a film of thickness 100 nm with silver contacts, which was deposited at 380 ℃, was heat-treated in nitrogen at 400 ℃ for several times and hence has different annealing periods. The I–V plots for this film are shown in Fig. 4. Since the relations are linear, a

Table 1. Values of the resistivity deduced from Figs. 1(a) and 1(b) beside the linear fit parameters for each case.

T (℃)	380	380	380	460	460	460
Contact	Ag	Al	In	Ag	Al	In
ρ (Ω·cm)	22.7	141.8	1089.5	0.4	1.1	1.4
R^2	1	1	0.99735	0.99997	1	0.99985
SD	8.62×10^{-3}	3.36×10^{-3}	3.25×10^{-2}	0.26	1.55×10^{-2}	0.18
F	4.52×10^{8}	7.62×10^{7}	1.39×10^{4}	8.87×10^{5}	3.41×10^{7}	1.48×10^{5}

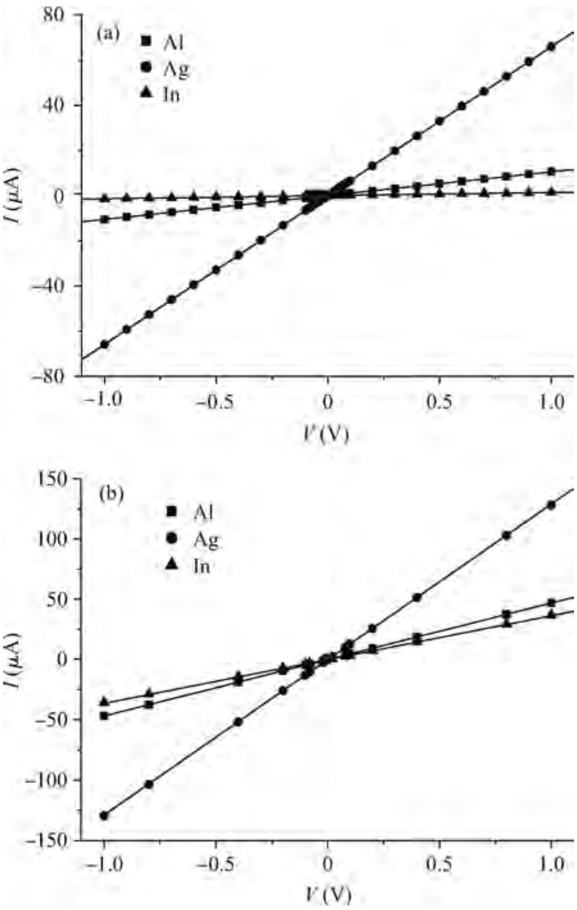


Fig. 3. The I–V characteristics and the linear fits for two SnO_2:F thin films with three different contacts, but deposited at different substrate temperatures. (a) $T_s = 380$ ℃. (b) $T_s = 460$ ℃.

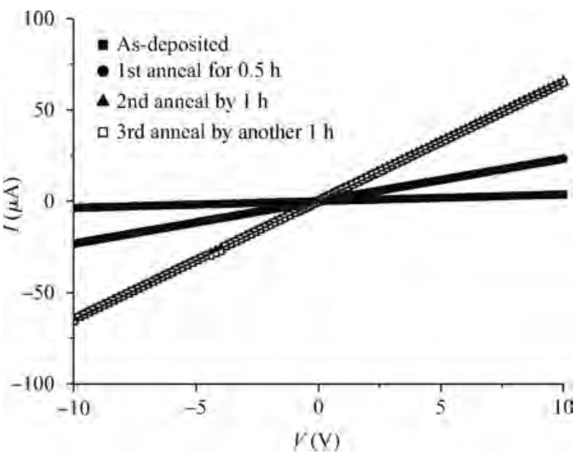


Fig. 4. The I–V plots and linear fits for a film with Ag-contacts annealed in a nitrogen atmosphere at $T = 400$ ℃.

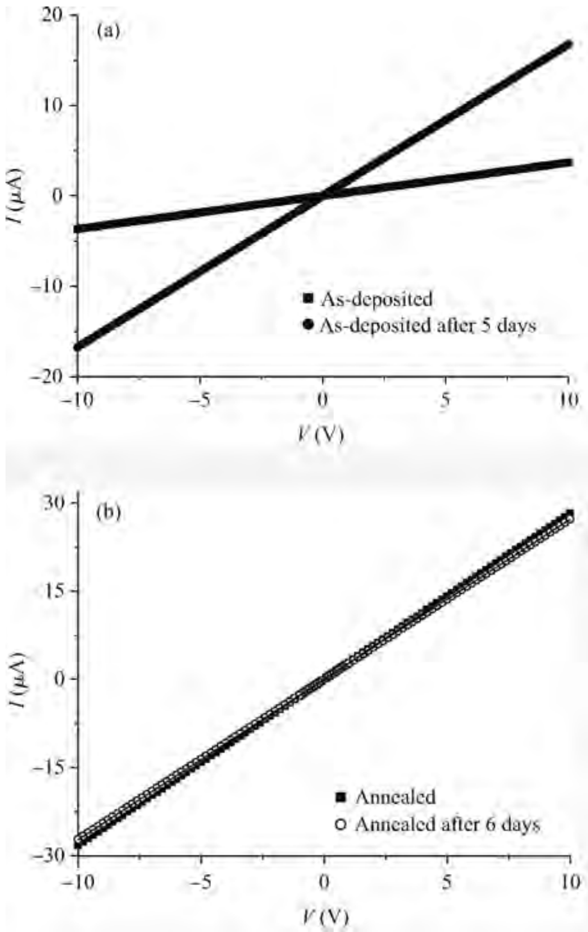


Fig. 5. The stability of the I–V characteristics with time for SnO_2:F thin films with silver contacts for (a) as deposited film and (b) annealed film. The linear fits are also shown.

linear fit was performed for each case and the deduced values of the resistivity and the parameters of the linear fit are inserted in Table 2. As the table shows, the first annealing for half an hour had decreased the resistivity by a factor of more than 6, while the second annealing for an hour (i.e. the total annealing period was 1.5 h) had decreased the resistivity from its value without annealing by a factor of more than 17. At this stage the color of the silver contacts had completely changed which is evidence of the formation of a silver-tin alloy after annealing. This alloy forms an ohmic contact as found by Mohammad and Abdul-Ghafor[21]. The third annealing for another hour (i.e. a total annealing period of 2.5 h) did not decrease the resistivity, but slightly increased it. The improvement in the conductivity is not totally due to the formation of the silver–tin alloy but it is also related to the completeness of crystal growth and the enlargement of grain size after annealing[22, 23]. An inspection of

Table 2. Resistivity and parameters of the linear fits for the curves in Fig. 4.

Treatment	As-deposited	0.5 h 1st anneal	1 h 2nd anneal	Another 1 h 3rd anneal
ρ (Ω·cm)	90.57	14.32	5.11	5.14
R^2	0.99999	1	0.99999	0.99996
SD	6.85×10^{-3}	1.66×10^{-2}	0.13	0.25
F	9.9×10^6	6.8×10^7	8.6×10^6	2.4×10^6

Table 3. The values of the resistivity and linear fit parameters obtained from the curves in Fig. 5.

Treatment	As-deposited	As-deposited after 5 days	Annealed	Annealed after 6 days
ρ (Ω·cm)	90.57	19.91	11.85	12.24
R^2	0.99999	1	1	1
SD	6.85×10^{-3}	1.20×10^{-2}	1.26×10^{-2}	1.02×10^{-2}
F	9.9×10^6	6.7×10^7	1.7×10^8	2.5×10^8

the linear fit parameters shows that the standard deviation SD increases with annealing and the worst values of R^2, SD and F are those of the data obtained after the third annealing.

To check the stability of the contacts, the I–V plots for as-deposited and annealed films with silver contacts were measured twice separated by a period of 5 or 6 days. The results are displayed in Fig. 5, where Figure 5(a) shows the plots regarding the as-deposited film for two sets of data separated by a period of 5 days, and Figure 5(b) shows the plots regarding the annealed film for two sets of data separated by a period of 6 days. Linear fits were performed for each set of data and the resistivities were deduced and inserted in Table 3 beside the fit parameters. As Table 3 shows, the resistivity of the as-deposited film had decreased by a factor of more than 4.5 after 5 days. This result proves that silver diffuses in the film and causes the increase in the number of free charge carriers. But for the annealed film (as seen in Table.3) a negligible increase in the resistivity had occurred after 6 days, which means that there is no diffusion of silver and no change in the state of the electrodes. The inspection of the linear fit parameters shows that better R^2 and F values are obtained for the as-deposited film after 5 days, and better R^2, SD and F values are obtained for the annealed film after 6 days. So, not only does the annealed film have stable contacts, but it also has better linearity in the I–V plots, or in other words better ohmicity. We conclude that annealing is a necessary step in order to have ohmic and stable contacts.

4. Conclusions

Polycrystalline SnO_2:F thin films were prepared by the SP technique on glass substrates. SEM micrographs showed that the grain size and surface morphology is dependent on the substrate temperature. Three different metallic contacts (Ag, Al, and In) were used and the I–V plots were recorded and analyzed. The I–V characteristics were used to compare the suitability of these contacts for SnO_2:F thin films. It was found that all of them could form ohmic contacts, but silver was the best because it results in the smallest resistivity due to its diffusion in the film and then increasing the number of free charge carriers. aluminum gives the best linear fit but it diffuses in the film and causes compensation effects, which results in the reduction of the number of free charge carriers and then an increase of the resistivity. Indium was the worst in the set because it results in the highest resistivity due to compensation effects and the worst fit parameters. Annealing is a necessary step to improve the contacts because it reduces the barrier height at the metal–semiconductor interface and results in the formation of an alloy. The effect of the annealing period was investigated and it was found that 2.5 h is enough to get the optimum results at which a silver–tin alloy was formed. The annealed contacts are stable with time, while un-annealed contacts are unstable.

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