Effect of platinum doping on the structural and electrical properties of SnO₂ thin films

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ABSTRACT
The investigation of Pt doping effect on the structural and electrical properties of SnO₂ thin films was aimed in this study. For this purpose, the polycrystalline pure and Pt-doped SnO₂ thin films were deposited onto n-type silicon substrate and the Pt sputter power was varied as 0 (un-doped), 2, 5 and 7 W by using radio frequency confocal sputtering system. The structural properties of the samples were analysed by X-ray diffraction measurements. The structural results show that the 5 W Pt-doped SnO₂ sample has better crystallinity than the other samples. The results of the electrical measurements as current–voltage, capacitance–voltage and conductance–voltage were also obtained and discussed in detail for fabricated diodes. The analysis of electrical characteristics shows that the use of different Pt doping has significant effect on electrical properties of such devices. The study also provides an improved supplemental understanding to the related technologies which use Pt-doped SnO₂ materials.

1. Introduction
Transparent conductive oxide materials have attracted significant interest due to their prospective applications in electro-optic and electrochemical devices.[1] Among them, SnO₂ has been extensively used as a n-type semiconductor material which exhibits a fairly high electrical conductivity (10³ S/cm), along with a direct wide bandgap (3.6 eV).[2,3] It has also unrivalled characteristics such as high transmittance in the ultraviolet-visible region and high reflectance in infrared region, high electrical conductivity, high melting point, metal-like conductivity, absence of toxicity, easy doping, easy tailoring and abundance in nature.[4,5] Thus, SnO₂ has been used in a number of applications such as electrode materials in solar cells,[6] transistors,[7] light emitting diodes,[8] flat panel displays,[9] gas sensors,[10] special catalysts,[11] high density energy storage material,[12] conductive film,[13] high performance capacitor,[14] dynamic random-access memory (RAM),[15] rechargeable lithium batteries,[16] resistors,[17] transparent heaters,[18] electrode ceramics[19] and antistatic coatings.[20]
It is clearly seen from the reported results that the properties of the films and devices are strongly influenced by the method and the conditions of the deposition.[21] Thus, the deposition method choosing is quite important. In the literature, the pure and doped SnO₂ thin films have been obtained by using a variety of techniques such as chemical vapour deposition,[22] physical vapour deposition,[23] pulsed laser deposition,[24] spray pyrolysis,[25] hydrothermal method,[26] sol-gel method,[27] evaporation,[28] co-precipitation[29] and sputtering.[30] In this study, a sputtering method was chosen due to the fewer pinholes, higher purity, better adhesive quality, simpler preparation and lower cost than others.[2]

The electrical properties of the SnO₂ based devices such as the selectivity, stability, sensitivity and detecting efficiency can be improved with the adjusting of nanostructured coatings.[21] These properties can also be enhanced by doping pure SnO₂ with small amounts of noble metals such as Pt, Pd and Bi dispersed on the surface of a semiconductor.[31–33] The results of doping many d-block transition metals and rare earth elements in SnO₂ have been reported in literature.[34–36] The results of tailoring electrical properties of this non-stoichiometric 4d metal oxide depend on the doping, grain size, pore and surface defects. Additionally, the detecting efficiency of SnO₂ is based on its electrical property changes that are mainly depended on the homogeneity, elemental composition, point and oxygen defects distribution, chemisorbed oxygen species and oxygen vacancies of the film.[37–41] Moreover, many researchers have studied the dielectric behaviour of SnO₂ nanostructures which is concerned with the storage and dispensation of electric and magnetic energy.[42] SnO₂ nanostructures possess ultrahigh dielectric constant in the low frequency region.[43] On this basis, a detailed study on the structural and electrical properties of the SnO₂ thin films is of great importance to develop SnO₂ devices.[44]

In this paper, the Pt doping effect was investigated on the structural and electrical properties of SnO₂ thin films. For this purpose, the Pt sputter power was varied as 0 (undoped), 2, 5 and 7 W. The SnO₂ thin films were deposited onto n-type silicon substrate by using radio frequency confocal sputtering (co-sputtering) system at room temperature. The structural parameters as the crystal quality, grain size, dislocation density and strain were determined by X-ray diffraction (XRD) measurements. After that, the samples were fabricated as the Au/Pt:SnO₂/n-Si/Au Schottky barrier diodes (SBDs). The electrical properties of the Au/Pt:SnO₂/n-Si/Au SBDs were obtained by using current–voltage (I–V), capacitance–voltage (C–V) and conductance–voltage (G/ɷ–V) data. After detailed investigation on the properties of SnO₂ thin films, it can be said that the present study effectuates an important contribution to the literature about the Pt-doped SnO₂ thin films and its related device applications.

2. Experimental details

Au/Pt:SnO₂/n-Si/Au SBDs were fabricated on the phosphorus doped (n-type) Si substrates with 380 ± 25 μm thickness, (100) orientation and 1–10 Ωcm resistivity. Prior to the fabrication, 2” n-type Si substrate was decreased in organic solvent of CHClCClL₂, CH₃COOH and CH₃OH, etched in a sequence of H₂SO₄ and H₂O₂, 25% HF, a solution of 7 HNO₃:1 HF:40 H₂O, 25% HF and finally quenched in deionised water with resistivity of 18 MΩcm for a prolonged time.[45] The fabrication process can be successively separated into three parts as ohmic contact formation, SnO₂ deposition and Schottky contact
formation. The back side of substrate was mounted onto the stainless steel holders and loaded into the magnetron co-sputtering system (Nanovak NVTS-500). The Au ohmic contact with 200 ± 1 nm thickness was then formed by deposition of high purity gold (Au) (99.999%) at 400 °C under 4.8 × 10⁻³ mbar vacuum and the substrate was annealed at 360 °C to achieve good ohmic contact behaviour. After that, the substrate was cut into the 1 cm² pieces and all pieces were cleaned with acetone and ethanol. The substrates were separately replaced to upper surface right after the cutting and cleaning step. After all, as seen from Table 1, un-doped and Pt-doped SnO₂ thin films with 100 ± 1 nm thickness were deposited onto the upper surface of the substrates by using high purity (99.995%) SnO₂ target at room temperature. The film thickness was also confirmed by stylus type profilometer. In order to investigate the Pt doping effect on the properties of the SnO₂ thin films, the Pt sputter power was varied as 0 (un-doped), 2, 5 and 7 W. The other deposition parameters such as SnO₂ sputter power, temperature, pressure, argon flow and target distance were kept constant at whole depositions. Thus, they were called as S001, S002, S003 and S004 and given in Table 1. In this way, the Pt:SnO₂/n-Si structures were ready for their characterisations and fabrications.

After the deposition processes, the structural properties of the samples were analysed by a high resolution X-ray diffractometer (D-8 Bruker). After that, the samples were fabricated for the electrical characterisations of the Au/Pt:SnO₂/n-Si/Au SBDs. The 1 mm dot-shaped Au rectifier contacts with 150 ± 1 nm thickness were formed onto SnO₂ thin films by the deposition of high purity (99.999%) Au at room temperature. In this way, the Au/Pt:SnO₂/n-Si/Au SBDs were ready for determining their electrical characterisations. Schematic representation of fabricated SBD was given in Figure 1.

The electrical properties of the Au/Pt:SnO₂/n-Si/Au SBDs were investigated using I/V, C/V and G/ω—V data. These data were obtained by using a semiconductor parameter analyser (Keithley 4200) and an impedance analyser (HP 4192 A LF) system. The C/V and G/ω—V measurements were achieved in the frequency range of 100 Hz—1 MHz at room temperature.

3. Results and discussion

3.1. Structural properties

The ω-2θ XRD patterns of the samples were shown in Figure 2. All the observed diffraction peaks agree well with the tetragonal structure of SnO₂ from Joint Committee of Powder Diffraction Standards (JCPDS) Card No. 41-1445. As seen from Figure 2, the high intense peak comes from n-Si substrate while the other peaks that belong to the SnO₂, SnO, SiO₂ and Pt.
It can be seen from Figure 2 that there are Si (400), Si (200), SnO\textsubscript{2} (101), SnO\textsubscript{2} (310), SnO\textsubscript{2} (311), SnO\textsubscript{2} (202), SnO\textsubscript{2} (320), SnO (100) and Pt (220) peaks. That means the deposited SnO\textsubscript{2} thin films have polycrystalline structure.

As seen in Table 2, the structural parameters of the three samples such as the grain size ($D$), dislocation density ($\delta$) and strain ($\varepsilon$) values were calculated. They were obtained from the equations given by

\begin{align*}
D &= \frac{0.9\lambda}{\beta \cos \theta} \quad (1) \\
\delta &= \frac{1}{D^2} \quad (2) \\
\varepsilon &= \frac{1}{\tan \theta} \left( \frac{\lambda}{D \cos \theta} - \beta \right) \quad (3)
\end{align*}

where $\lambda$ is the X-ray wavelength (1.540 Å), $\theta$ is the peak angle value in the $\omega$-2$\theta$ scans, $hkl$ are the Miller indices and $\beta$ is the full width at half maximum (FWHM) value of the SnO\textsubscript{2} peaks.[46]

It is seen from Table 2 that the grain size of the S001, which is the un-doped one, is lower than the others. On the contrary, S003 has the highest grain size and lowest dislocation density. It means that it has better crystallinity than the others. On the other hand, the FWHM of reflection peaks which is related with the grain size can be relevant to the crystal quality of the polycrystalline thin films.[47]

It can be seen from Figure 3 that, when the SnO\textsubscript{2} thin films were doped with Pt, the FWHM which is encoded in triangle decreased (except S002). It is expected from S003 that when the FWHM decreased, the grain size increased and dislocation density decreased and, thus, the crystallinity of the film increased. However, for the other samples, the crystallinity of the films was not increasing with the decreasing FWHM. The scientists observed similar phenomenon in ‘Al doped Zinc Oxide’ and ‘Zn doped SnO\textsubscript{2}’ in the literature.[48,49]

Furthermore, the lattice spacing ($d$) which is between two different crystallographic planes and lattice parameters ($a$ and $c$) of the tetragonal structure of SnO\textsubscript{2} can be
Figure 2. The $\omega$-2$\theta$ XRD spectra of the samples.
determined by using Equations (4) and (5):

\[ d = \frac{\lambda}{2\sin \theta} \]  \hspace{1cm} (4)

\[ \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \]  \hspace{1cm} (5)

where \( h, k \) and \( l \) are the Miller indices of the reflection plane. Thus, the lattice parameters of S003 were found as \( a = b = 4.739 \text{ Å} \) and \( c = 3.279 \text{ Å} \) by using Equation (5) and related parameters. However, the well-known pure tetragonal SnO\(_2\) has the lattice parameters as \( a = b = 4.738 \text{ Å} \) and \( c = 3.187 \text{ Å} \).\(^{[49]}\) Accordingly, there was a slight increase in the lattice constant of S003 compared to pure SnO\(_2\), which indicates that some of the Pt\(^{4+}\) ions (with ionic radius 7.7 nm) incorporate into the Sn\(^{4+}\) sites of the SnO\(_2\) (7.2 nm) lattice.\(^{[50]}\)

### 3.2. Forward and reverse bias I–V characteristics

The experimental \( I–V \) characteristics of Au/Pt:SnO\(_2\)/n-Si/Au SBDs were investigated at room temperature. The \( \ln I–V \) graph was drawn with obtained data and given in Figure 4.

![Graph showing FWHM, Grain Size, and Dislocation Density](image)

**Figure 3.** The calculated FWHM and grain sizes for the SnO\(_2\) thin films.
In order to quantitatively analyse the SBDs, the standard thermionic emission theory was used as follows [51]:

\[
I = I_0 \exp \left( \frac{q(V - IR_s)}{nkT} \right)
\]  

(6)

where \( q \) is the electronic charge, \( n \) is the ideality factor, \( k \) is the Boltzmann’s constant and \( T \) is the absolute temperature in Kelvin. The term \( IR_s \) is the voltage drop across the series resistance of the diode. \( I_0 \) is the saturation current which is derived from the straight line intercept of \( \ln I - V \) plot at zero bias voltage.[52] Thus, it is expected as

\[
I_0 = AA^* T^2 \exp \left( - \frac{q\Phi_B}{kT} \right)
\]

(7)

where \( \Phi_B \) is the effective barrier height at zero bias, \( A \) is the rectifier contact area, \( A^* \) is the effective Richardson constant (112 A cm\(^{-2}\) K\(^{-2}\) for n-type Si).

The \( \Phi_B \) was determined from the extrapolated \( I_0 \) and given by the relation:

\[
\Phi_B = \frac{kT}{q} \ln \left( \frac{AA^* T^2}{I_0} \right)
\]

(8)
Additionally, $n$ can be derived from the slope of linear region of the forward-bias $\ln I - V$ plot.\cite{53,54} It is given by

$$n = \frac{q}{kT} \left( \frac{dV}{d(\ln I)} \right)$$  \hspace{1cm} (9)$$

As can be seen from Figure 4, the similar behaviour was observed due to the effects of some factors such as series resistance, interface states and interfacial layers. The linear region narrows and deviates from linearity.\cite{55} The higher values of ideality factor can also indicate that an interfacial layer arises between metal and semiconductor. This layer can be formed either during surface preparation or fabrication processes.\cite{56}

The experimental values of $n$ and $\Phi_B$ were calculated as 2.30, 2.21, 2.70 and 1.44; 0.66, 0.73, 0.68 and 0.71 eV for S001, S002, S003 and S004 SBDs, respectively. These values were given in Table 3.

The $n$, $\Phi_B$ and $R_s$ were also determined by using Cheung and Cheung functions.\cite{57} These functions were given as

$$\frac{dV}{d(\ln I)} = n \left( \frac{kT}{q} \right) + IR_s$$  \hspace{1cm} (10)$$

$$H(I) = V - n \left( \frac{kT}{q} \right) \ln \left( \frac{I}{AA * T^2} \right) = IR_s + n\Phi_B$$  \hspace{1cm} (11)$$

Figures 5 and 6 show the experimental $dV/d(\ln I)$ vs. $I$ and $H(I)$ vs. $I$ plots for all the samples at room temperature. The plots give a straight line for the data of the downward curvature region in the forward-bias $I - V$. Therefore, the $dV/d(\ln I)$ vs. $I$ plot's slope gives the $R_s$ value, while the $y$-axis intercept gives the $n$ value. The $R_s$ and $\Phi_B$ values can be also obtained from $H(I) - I$ plot with the same method.

Thus, the $R_s$ and $n$ values from $dV/d(\ln I)$ vs. $I$ plot were found as 977.63, 891.63, 225.48 and 1366.90 $\Omega$; 2.08, 2.74, 4.73 and 1.45 for S001, S002, S003 and S004 SBDs respectively. The $R_s$ and $\Phi_B$ values from $H(I) - I$ plot were found as 770.66, 805.34, 161.37 and 987.68 $\Omega$; 0.72, 0.81, 0.87 and 0.77 eV for S001, S002, S003 and S004 SBDs, respectively. These values were given in Table 3. The $R_s$ values obtained from $dV/d(\ln I) - I$ and $H(I) - I$ plots were in agreement with each other.

### Table 3. The experimental $I - V$ results.

| Parameters | Method       | S001   | S002   | S003   | S004   |
|------------|--------------|--------|--------|--------|--------|
| $I_0 (\mu A)$ | $\ln I - V$  | 76.80  | 4.81   | 44.00  | 11.60  |
| $N$        | $\ln I - V$  | 2.30   | 2.21   | 2.70   | 1.44   |
| $\Phi_B$ (eV) | $\ln I - V$  | 0.66   | 0.73   | 0.68   | 0.71   |
| $H(I)$     | $\ln I - V$  | 0.72   | 0.81   | 0.87   | 0.77   |
| $Rs$ ($\Omega$) | $dV/d(\ln I)$ | 2.08   | 2.74   | 4.73   | 1.45   |
| $F_B$      | $\ln I - V$  | 0.62   | 0.81   | 0.80   | 0.71   |
| $H(I)$     | $\ln I - V$  | 977.63 | 891.63 | 225.48 | 1366.90|
| $Rs$ ($V$) | 770.66       | 805.34 | 161.37 | 987.68 |
| $F_B$      | 524.71       | 641.24 | 426.78 | 838.38 |
| $R_i$      | 242.36       | 749.78 | 127.36 | 280.94 |
| $R_{sh}$ ($M\Omega$) | 11.90 | 20.56  | 5.73   | 7.49   |
Additionally, the series resistance ($R_s$) and shunt resistance ($R_{sh}$) were obtained by using Ohm’s law ($R_i = \frac{dV_i}{di}$). The structure resistance ($R_s$)–applied bias voltage ($V_i$) graph was drawn with the experimental $I$–$V$ data and given in Figure 7.

It can be seen from Figure 7 that the structure resistance comes near to the maximum values in the reverse bias region, while it goes to the minimum at sufficiently
high forward-bias voltage. The minimum and maximum regions correspond to the series and shunt resistances, respectively.[56] Thus, the values of $R_s$ were found as 242.66, 749.78, 127.36 and 280.94 $\Omega$ for S001, S002, S003 and S004 SBDs, respectively. The values of $R_{sh}$ were found as 11.90, 20.56, 5.73 and 7.49 M$\Omega$ for S001, S002, S003 and S004 SBDs, respectively. Therefore, it can be said that the $R_{sh}$ values as high as possible and the $R_s$ values as low as possible as expected. The obtained values were also given in Table 3.

For the comparison of results, Norde method which was modified by Lien was also used to determine $R_s$ and $\Phi_B$.[58,59] The $F(V)$ function was defined in this method as

$$F(V, \gamma) = \frac{V}{\gamma} - \frac{q}{kT} \ln \left( \frac{I(V)}{AA \cdot T^2} \right)$$  \hspace{1cm} (12)

where $I(V)$ is current value derived from $I-V$ curve and $\gamma$ is a dimensionless integer greater than the ideality factor of diode.

When the minimum point of the $F(V)-V$ plot was determined, the value of $\Phi_B$ and $R_s$ can be derived as following, where $F(V_{\text{min}})$ and $V_{\text{min}}$ are coordinates of minimum point.
in the $F(V)$ vs. $V$ plot shown in Figure 8.[59]

$$\Phi_B = F(V_{\text{min}}) + \frac{V_{\text{min}}}{\gamma} - \frac{kT}{q}$$  \hspace{1cm} (13)

$$R_s = \frac{kT}{qI_{\text{min}}} (\gamma - n)$$  \hspace{1cm} (14)

where $I_{\text{min}}$ is the value of the forward-bias current corresponding to $V_{\text{min}}$.

The values of $\Phi_B$ obtained from Equation (13) were found as 0.62, 0.81, 0.80 and 0.71 eV for S001, S002, S003 and S004 SBDs, respectively. The values of $R_s$ obtained from Equation (14) were found as 524.71, 641.24, 426.78 and 838.38 $\Omega$ for S001, S002, S003 and S004 SBDs, respectively. The obtained values were also given in Table 3.

3.3. Forward and reverse bias C–V and $G/\omega$–V characteristics

The useful details about the structural changes and transport mechanism of the device can be generated by using the impedance spectroscopy. It is the most usable and preferable
technique to determine the dielectric properties of the nanomaterials.\textsuperscript{[60]} The dielectric properties of nanomaterials are also very sensitive to the local electric field distribution in the sample. Therefore, the dielectric properties such as the dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and ac electrical conductivity ($\sigma_{ac}$) are very important for the selection of materials for device applications.

Figure 9 shows the experimental $C-V$ curves of the Au/Pt:SnO$_2$/n-Si/Au SBDs at 1 MHz frequency at room temperature. As shown in Figure 9, each $C-V$ curve has three regimes as an accumulation, depletion and inversion region. The voltage axis shifts due to the presence of interface states, at Si/SnO$_2$ interface, barrier inhomogeneous and oxide layer at the metal–semiconductor interface.\textsuperscript{[61]} It can be said that the maximum capacitance was obtained with the S003 SBD.

Figure 10 shows the measured $G/\omega-V$ characteristics of SBDs at 1 MHz. It can be seen from Figure 10 that the values of conductance increased in the S003 SBD.

Additionally, the frequency dependence of dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and ac electrical conductivity ($\sigma_{ac}$) were evaluated from the measured $C-V$ and $G/\omega-V$ data in the frequency range of 100 Hz–1 MHz at room temperature.

The complex permittivity ($\varepsilon^*$) was determined using Equation (15) after measuring the capacitance and conductance of the samples.\textsuperscript{[51,52,62]}

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

where $\varepsilon'$ is the real part of complex permittivity which describes the stored energy and $\varepsilon''$ is the imaginary part of complex permittivity which describes the dissipation energy and $i$ is root square of $-1$. The complex permittivity formula can be rewritten as a function of capacitance and conductance. Thus, the frequency dependence of $\varepsilon'$ and $\varepsilon''$ were
determined by using Equations (16) and (17). \[51,62\]

\[
\epsilon' \epsilon_0 = \frac{C}{C_i} = \frac{C d_i}{\epsilon_0 A} \quad (16)
\]

\[
\epsilon'' = \frac{G}{\omega C_i} = \frac{G d_i}{\epsilon_0 \omega A} \quad (17)
\]

where \( C \) is the measured value of the capacitance of the device, \( d_i \) is the interfacial insulator layer thickness, \( \epsilon_0 \) is the electric permittivity of free space (\( \epsilon_0 = 8.85 \times 10^{-14} \text{ F/cm} \)) and \( A \) is the rectifier contact area of the diode in cm\(^2\). The maximal capacitance of the sample corresponds to the interfacial insulator layer capacitance (\( C_i = \epsilon' \epsilon_0 A / d_i \)) in the strong accumulation region. Thus, from Equations (16) and (17), the quantity of \( \tan \delta \) can be expressed as follows \[51,62\]:

\[
\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (18)
\]

Normally, the dielectric constant cannot be changed with the voltage frequency and temperature. However, it can be affected from polarisation mechanism which has a distinctive relaxation frequency. In addition, the dielectric properties of materials also depend on the structural properties and fabrication procedures of the sample.\[63,64\]

The room temperature frequency dependent dielectric constant graph was shown in Figure 11. It can be seen from Figure 11 that the dielectric constant of all devices decreases with increase in frequency. The observed features can be explained with Maxwell–Wagner type interfacial polarisation and Koops phenomenological theory.\[65,66\] It was also found that the dielectric constant of the Pt-doped SnO\(_2\) devices exhibited lower

**Figure 10.** The forward and reverse bias \( G/\omega - V \) characteristics of SBDs at 1 MHz.
value than the pure SnO$_2$ diode. This decreasing may be due to the smaller dielectric polarisability and bigger ionic radius of dopant ions than the parent ions. This is also consistent with the wide bandgap band semiconductors have a lower dielectric constant.\[67\]

This behaviour of dielectric constant can also be clarified with the hopping model. The carrier exchange mechanism between different metal ions can impress upon the dielectric constant and ac conductivity. The hopping of electrons within the grain and grain boundaries can adapt to the applied ac field at lower frequencies. However, the electrons cannot follow the applied ac field at the higher frequencies. Thus, the electrons that are reaching the grain boundaries reduce; thus, the polarisation decreases which decreases the dielectric constant.\[68\]

In nanomaterials, inhomogeneity such as defects and space charge formation in the interphase layers can trap the current. Therefore, it can result in a dielectric loss. Figure 12 shows the room temperature frequency dependent dielectric loss graph. The dielectric loss also exhibits a similar behaviour with the dielectric constant. It was seen that the dielectric loss decreases with the increase in frequency and immediately after it remains constant for all Pt-doped SnO$_2$ samples.

It can be attributed to the Debye-like relaxation mechanism and the interfacial/space charge polarisation effect.\[67,69\] Thus, these types of materials can be used in high frequency device applications due to exhibition of a stable dielectric constant and dielectric loss behaviour at higher frequencies.

Figure 13 shows the variation of ac conductivity ($\sigma_{ac}$) values as a function of frequency for SBDs. It was observed that the ac conductivity was nearly constant up to 500 kHz and, thereafter, increases slightly in all samples. Additionally, the conductivity decreases with Pt-doping. This type of behaviour was also observed in ’Ni doped TiO$_2$ nanoparticles’.\[70\]
It is also important to know whether the SBDs are n-type or p-type. This information can be obtained by calculating the capacitance between grains boundary, then by applying the following Mott–Schottky expression [71–73]:

\[
\left( \frac{1}{C} - \frac{1}{2C_0} \right)^2 = \frac{2}{q\varepsilon_\varepsilon_0 N_d} (\Phi_B + V)
\] (19)
where

\[ \frac{1}{C_0} = 2 \left( \frac{2\Phi_B}{qe_0N_D} \right)^{1/2} \]  

(20)

and \( q \) is the electronic charge, \( \varepsilon_s \) is the dielectric constant of n-type Si (11.8 \( \varepsilon_0 \)), \( \varepsilon_0 \) is the dielectric constant of vacuum (8.85 \( \times 10^{-14} \) F/cm), \( N_D \) is the doping concentration and \( V \) is the applied voltage.

Thus, the plotting \( (1/C-1/(2C_0))^2 \) versus applied voltage according to Equation (19) should yield a straight line. Figure 14 shows the relation between \( (1/C-1/(2C_0))^2 = f(V) \) as function of applied voltage. When the slope of \( (1/C-1/(2C_0))^2 - V \) graph is positive, hence, the semiconductor device is n-type. Similarly, when the slope of \( (1/C-1/(2C_0))^2 - V \) graph is negative, the semiconductor device is p-type.[71]

It can be seen from Figure 14 that the slope of \( (1/C-1/(2C_0))^2 - V \) graph is linear and positive, hence, the SBDs are also n-type. The results are also given in Table 4.

Figure 15 shows the reciprocal of the squared capacitance per unit area as a function of the bias at constant frequency (1 MHz). It can be seen from Figure 15 that the \( C^{-2} - V \) plots were linear. This linearity of the curves can be indicated with the uniformity of the donor concentration in the depletion region. It can be also said that the interface states cannot follow ac signal at high frequency regions.[52]

Table 4. The electrical parameters of SBDs obtained from \( C^{-2} - V \) data at 1 MHz.

| Sample | Type | \( V_0 \) (V) | \( V_d \) (V) | \( N_D \) (cm\(^{-3}\)) | \( \varepsilon_F \) (eV) | \( W_0 \) (cm) | \( \Delta\Phi_B \) (meV) | \( \Phi_B \) (eV) |
|--------|------|---------------|---------------|-----------------|-----------------|----------------|-----------------|----------------|
| S001   | n    | 0.705         | 0.731         | 1.041 \( \times 10^{15} \) | 0.197           | 9.572 \( \times 10^{-5} \) | 13.648          | 0.914           |
| S002   | n    | 0.516         | 0.542         | 6.070 \( \times 10^{14} \) | 0.211           | 1.079 \( \times 10^{-4} \) | 11.066          | 0.741           |
| S003   | n    | 0.345         | 0.370         | 1.483 \( \times 10^{15} \) | 0.187           | 5.712 \( \times 10^{-5} \) | 13.949          | 0.544           |
| S004   | n    | 0.534         | 0.542         | 8.525 \( \times 10^{14} \) | 0.202           | 9.260 \( \times 10^{-5} \) | 10.956          | 0.751           |
It can be possible that the doping concentration ($N_D$), Fermi energy level ($E_F$), depletion layer width ($W_D$), built-in voltage at zero bias ($V_0$), diffusion potential at zero bias ($V_d$), image force barrier lowering ($\Delta \Phi_B$) and barrier height ($\Phi_B (C-V)$) can be obtained from the $C^{-2}-V$ characteristics of SBDs at 1 MHz by using the following equations.

If the $C/V$ measurements at 1 MHz are considered, the depletion layer capacitance in SBD can be expressed as \[C^{-2} = \frac{2(V_0 + V_R)}{q\varepsilon_s\varepsilon_0 A^2 N_D} \text{ (21)}\]

\[N_D = \frac{2}{q\varepsilon_s\varepsilon_0 A^2 \left( \frac{d(C^{-2})}{dV} \right)} \text{ (22)}\]

where $q$ is the electronic charge, $\varepsilon_s$ is the dielectric constant of n-type Si (11.8 \(\varepsilon_0\)), $\varepsilon_0$ is the dielectric constant of vacuum ($8.85 \times 10^{-14}$ F/cm), $A$ is the diode area, $N_D$ is the doping concentration, $V_R$ is the reverse bias voltage and $V_0$ is the built-in voltage at zero bias. It can be determined from the extrapolation of $C^{-2}-V$ plot and given as

\[V_0 = V_d - \frac{kT}{q} \text{ (23)}\]

The $\Phi_B (C-V)$ values were also calculated by using the following relation:

\[\Phi_B(C - V) = V_0 + \frac{kT}{q} + E_F - \Delta \Phi_B \text{ (24)}\]
where $\Delta \Phi_B$ is the image force barrier lowering and given by [74]

$$\Delta \Phi_B = \left( \frac{qE_m}{4\pi\varepsilon_0\varepsilon_0} \right)^{1/2} \tag{25}$$

where $E_m$ is the maximum electric field. $E_m$ was obtained from the following relation:

$$E_m = \left( \frac{2qN_DV_d}{\varepsilon_0\varepsilon_0} \right)^{1/2} \tag{26}$$

$E_F$ is obtained from

$$E_F = \frac{kT}{q} \ln \left( \frac{N_C}{N_D} \right) \tag{27}$$

$N_C$ is the effective density of states in the semiconductor conductance band which is obtained from

$$N_C = 4.82 \times 10^{15} \frac{T^{3/2}}{m_e^*} \left( \frac{m_e^*}{m_0} \right)^{3/2} \tag{28}$$

where $m_e^*$ is the effective mass of the electron, $m_0$ is the rest mass of the electron.

Additionally, the $W_D$ was also derived by using Equation (29) [75]:

$$W_D = \left( \frac{2\varepsilon_0\varepsilon_0V_d}{qN_D} \right)^{1/2} \tag{29}$$

The obtained values of $V_0$, $V_d$, $N_D$, $E_F$, $W_D$, $\Delta \Phi_B$ and $\Phi_B$ (C–V) were presented in Table 4. The similar results have been reported in the literature.[61]

In general, n-type metal oxide nanomaterials are also shaped due to oxygen vacancies, which change the crystallographic structure and lead to a donor level below but close to the conduction band.[76] It means that the Fermi energy level ($E_F$) is also low when it is doped. It can be seen from Table 4 that the Fermi energy level ($E_F$), built-in voltage at zero bias ($V_0$), diffusion potential at zero bias ($V_d$) and barrier height ($\Phi_B$ (C–V)) of S003 are lower than the other SBDs.

4. Conclusion

This study investigated the properties of the SnO$_2$ thin films depended on Pt doping concentrations. In order to investigate the Pt doping effect, the Pt sputter power was varied as 0 (un-doped), 2, 5 and 7 W. Thus, the samples were called as S001 (un-doped), S002 (2 W Pt-doped), S003 (5 W Pt-doped) and S004 (7 W Pt-doped). The structural and electrical characteristics of the samples were obtained by XRD, $I–V$, $C–V$ and $G/\omega–V$ measurements. XRD results show that S003 has better crystallinity, which is depended on the FWHM, grain size and dislocation density, than the others. It can be seen from the
electrical results that the Pt-doped samples have lower $\Phi_B$ and higher $R_{sh}$ values. It was also observed that the $\varepsilon'$ and $\varepsilon''$ show a similar behaviour, they decrease and, thereafter, remain constant for all the samples. Additionally, $\varepsilon'$ and $\varepsilon''$ decrease with Pt-doping. The $\sigma_{ac}$ was nearly constant up to 500 kHz and, thereafter, increases slightly in all samples. $\sigma_{ac}$ decreases with Pt-doping.

In summary, the structural and electrical characteristics of the SnO$_2$ samples were significantly affected by the Pt-doping. Although the preferable features of all doped samples, S003 has come into prominence due to its better properties. As a result, it can be said that S003 type SnO$_2$ thin films can be more convenient for SnO$_2$ based electro-optic and electrochemical device applications.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**References**

[1] Bargougui R, Oueslati A, Schmerber G, et al. Structural, optical and electrical properties of Zn-doped SnO$_2$ nanoparticles synthesized by the co-precipitation technique. J Mater Sci Mater Electron. 2014;25:2066–2071. doi: 10.1007/s10854-014-1841-2.

[2] Gui T, Hao L, Wang J, et al. Structure and features of SnO$_2$ thin films prepared by RF reactive sputtering. Chin Opt Lett. 2010;8:134–136. doi: 10.3788/COL2010081.0134.SnO.

[3] Kamble VB, Bhat SV, Umarji AM. Investigating thermal stability of structural defects and its effect on d0 ferromagnetism in undoped SnO$_2$. J Appl Phys. 2013;113:244307. doi: 10.1063/1.4812382.

[4] Ginley DS, Bright C. Transparent conducting oxides. MRS Bull. 2000;25:15–18. doi: 10.1557/mrs2000.256.

[5] Chopra KL, Major S, Pandya DK. Transparent conductors — a status review. Thin Solid Films. 1983;102:1–46. doi: 10.1016/0040-6090(83)90256-0.

[6] Snaith HJ, Ducati C. SnO$_2$-based dye-sensitized hybrid solar cells exhibiting near unity absorbed photon-to-electron conversion efficiency. Nano Lett. 2010;10:1259–1265. doi: 10.1021/nl903809r.

[7] McDowell MG, Sanderson RJ, Hill IG. Combinatorial study of zinc tin oxide thin-film transistors. Appl Phys Lett. 2008;92:2007–2009. doi: 013502\r10.1063/1.2828862.

[8] Li Y, Yin W, Deng R, et al. Realizing a SnO$_2$-based ultraviolet light-emitting diode via breaking the dipole-forbidden rule. NPG Asia Mater. 2012;4:e30. doi: 10.1038/am.2012.56.

[9] Isono T, Fukuda T, Nakagawa K, et al. Highly conductive SnO$_2$ thin films for flat-panel displays. J Soc Inf Disp. 2007;15:161–166. doi: 10.1889/1.2709738.

[10] Nelli P, Faglia G, Sberveglieri G, et al. The aging effect on SnO$_2$ Au thin film sensors: electrical and structural characterization. Thin Solid Films. 2000;371:249–253.
[11] Hagemeyer A, Hogan Z, Schlichter M, et al. High surface area tin oxide. Appl Catal A Gen. 2007;317:139–148. doi: 10.1016/j.apcata.2006.09.040.

[12] Paek SM, Yoo E, Honma I. Enhanced cyclic performance and lithium storage capacity of SnO2/graphene nanoporous electrodes with three-dimensionally delaminated flexible structure. Nano Lett. 2009;9:72–75. doi: 10.1021/nl802484w.

[13] Bernardi MIB, Soledade LE, Santos IA, et al. Influence of the concentration of Sb2O3 and the viscosity of the precursor solution on the electrical and optical properties of SnO2 thin films produced by the Pechini method. Thin Solid Films. 2002;405:228–233. doi: 10.1016/S0040-6090(01)01770-9.

[14] Yan J, Khoo E, Sumboja A, et al. Facile coating of manganese oxide on tin oxide nanowires with high-performance capacitive behavior. ACS Nano. 2010;4:4247–4255. doi: 10.1021/nn100592d.

[15] Scott JF. High-dielectric constant thin films for dynamic random access memories (Dram). Annu Rev Mater Sci. 1998;28:79–100. doi: 10.1146/annurev.matsci.28.1.79.

[16] Budaya C, Jeon BJ, Lee JK. High thermal performance of SnO2:F thin transparent heaters with scattered metal nanodots. ACS Appl Mater Interfaces. 2015;7:57–61. doi: 10.1021/acsami.4b14071.

[17] Borse RY, Garde AS. Electrical and gas sensing properties of SnO2 thick film resistors prepared by screen-printing method. Sensors Transducers. 2008;97:64–73.

[18] Pena J, Perez-Pariente J, Vallet-Regi M. Textural properties of nanocrystalline tin oxide obtained by spray pyrolysis. J Mater Chem. 2003;13:2290–2296. doi: 10.1039/b304830f.

[19] Gaggiotti G, Galdikas A, Kaciulis S, et al. Temperature dependencies of sensitivity and surface chemical composition of SnO2 gas sensors. Sensors Actuators B Chem. 1995;25:516–519. doi: 10.1016/0925-4005(95)00352-9.

[20] Li Y, Peng R, Xiu X, et al. Growth of SnO2 nanoparticles via thermal evaporation method. Superlattices Microstruct. 2008;50:511–516. doi: 10.1016/j.spmi.2011.08.013.

[21] Tian ZM, Yuan SL, He JH, et al. Structure and magnetic properties in Mn doped SnO2 nanoparticles synthesized by chemical co-precipitation method. J Alloys Compd. 2008;466:26–30. doi: 10.1016/j.jallcom.2007.11.054.
Tadeev AV, Delabouglise G, Labeau M. Influence of Pd and Pt additives on the microstructural and electrical properties of SnO$_2$-based sensors. Mater Sci Eng B. 1998;57:76—83. doi: 10.1016/S0921-5107(98)00251-7.

Azam A, Ahmed AS, Chaman M, et al. Investigation of electrical properties of Mn doped tin oxide nanoparticles using impedance spectroscopy. J Appl Phys. 2010;108:094329. doi: 10.1063/1.3506691.

Azam A, Ahmed AS, Ansari MS, et al. Study of electrical properties of nickel doped SnO$_2$ ceramic nanoparticles. J Alloys Compd. 2010;506:237—242. doi: 10.1016/j.jallcom.2010.06.184.

Chang S-S, Jo MS. Luminescence properties of Eu-doped SnO$_2$. Ceram Int. 2007;33:511—514. doi: 10.1016/j.ceramint.2005.10.021.

Shimizu Y, Egashira M. Basic aspects and challenges of semiconductor gas sensors. MRS Bull. 1999;24:18—24. doi: 10.1557/S0883769400052465.

Schierbaum KD, Weimar U, Göpel W, et al. Conductance, work function and catalytic activity of SnO$_2$-based gas sensors. Sensors Actuators B Chem. 1991;3:205—214. doi: 10.1016/0925-4005(91)80007-7.

Sangaletti L, Depero LE, Allieri B, et al. Oxidation of Sn thin films to SnO$_2$ micro-Raman mapping and X-ray diffraction studies. J Mater Res. 1998;13:2457—2460.

Kılıç Ç, Zunger A. Origins of coexistence of conductivity and transparency in SnO$_2$. Phys Rev Lett. 2002;88:095501. doi: 10.1103/PhysRevLett.88.095501.

Zhang Y, Yu K, Li G, et al. Synthesis and field emission of patterned SnO$_2$ nanoflowers. Mater Lett. 2006;60:3109—3112. doi: 10.1016/j.matlet.2006.02.055.

Mehraj S, Ansari MS. Structural, dielectric and complex impedance properties of Cd doped SnO$_2$ nanoparticles. J Nanoeng Nanomanuf. 2013;3:229—236. doi: 10.1166/jnan.2013.1137.

Chenari HM, Hassanzadeh A, Golzan MM, et al. Frequency dependence of ultrahigh dielectric constant of novel synthesized SnO$_2$ nanoparticles thick films. Curr Appl Phys. 2011;11:409—413. doi: 10.1016/j.cap.2010.08.011.

Acciarri M, Canevali C, Mari CM, et al. Nanocrystalline SnO$_2$-based thin films obtained by sol-gel route: a morphological and structural investigation. Chem Mater. 2003;15:2646—2650. doi: 10.1021/cm031002w.

Şafak-Asar Y, Asar T, Altundal Ş, et al. Investigation of dielectric relaxation and ac electrical conductivity using impedance spectroscopy method in (Au/Zn)/TiO$_2$/p-GaAs(110) Schottky barrier diodes. J Alloys Compd. 2015;628:442—449. doi: 10.1016/j.jallcom.2014.12.170.

Cevatışlı C, Özçelik S. Barrier enhancement of Ge MSM IR photodetector with Ge layer optimization. Superlattices Microstruct. 2015;88:685—694. doi: 10.1016/j.spmi.2015.10.034.

Maniv S, Zangvil A. Controlled texture of reactively rf-sputtered ZnO thin films. J Appl Phys. 1978;49:2787.

Fu E-G, Zhuang D-M, Zhang G, et al. Properties of transparent conductive ZnO:Al thin films prepared by magnetron sputtering. Microelectron J. 2004;35:383—387. doi: 10.1016/S0026-2692(03)00251-9.

Ni J, Zhao X, Zhao J. P-type transparent conducting SnO$_2$:Zn film derived from thermal diffusion of Zn/SnO$_2$/Zn multilayer thin films. Surf Coat Technol. 2012;206:4356—4361. doi: 10.1016/j.surfcoat.2012.04.031.

Khairy M, Mohamed MM. SnO$(\beta$-Bi$_2$O$_3$)/Bi$_2$Sn$_2$O$_7$ nanohybrids doped with Pt and Pd nanoparticles: applications in visible light photocatalysis, electrical conductivity and dye-sensitized solar cells. Phys Chem Chem Phys. 2015;17:21716—21728. doi: 10.1039/C5CP02066B.

Rhoderick EH, Williams RH. Metal-semiconductor contacts. 2nd ed. Oxford: Clarendon Press; 1988.

Sze SM. Physics of semiconductor devices. 3rd ed. Hoboken (NJ): John Wiley & Sons. Inc.; 2007.

Card HC, Rhoderick EH. Studies of tunnel MOS diodes I. Interface effects in silicon Schottky diodes. J Phys D Appl Phys. 1971;4:1589—1601. doi: 10.1088/0022-3727/4/10/319.

Knaci B, Özen Y, Kızılkaya K, et al. Effect of alloy composition on structural, optical and morphological properties and electrical characteristics of Ga$_x$In$_{1-x}$P/GaAs structure. J Mater Sci Mater Electron. 2013;24:1375—1381. doi: 10.1007/s10854-012-0937-9.
Kinaci B, Asar T, Çetin SS, et al. Electrical characterization of Au/ZnO/TiO2/n-Si and (Ni/Au)/ZnO/TiO2/n-Si Schottky diodes by using current-voltage measurements. J Optoelectron Adv Mater. 2012;14:959–963.

Taşçıoğlu İ, Altundal Ş, Polat İ, et al. The effect of metal work function on the barrier height of metal/CdS/SnO2/In–Ga structures. Curr Appl Phys. 2013;13:1306–1310. doi: 10.1016/j.cap.2013.04.010.

Cheung SK, Cheung NW. Extraction of Schottky diode parameters from forward current-voltage characteristics. Appl Phys Lett. 1986;49:85–87. doi: 10.1063/1.97359.

Norde H. A modified forward I-V plot for Schottky diodes with high series resistance. J Appl Phys. 1979;50:5052–5053. doi: 10.1063/1.325607.

Lien CD, So FCT, Nicolet MA. An improved forward I-V method for nonideal Schottky diodes with high series resistance. IEEE Trans Electron Devices. 1984;ED-31:1502–1503. doi: 10.1109/T-ED.1984.21739.

Şafak Asar Y, Asar T, Altundal Ş, et al. Dielectric spectroscopy studies and ac electrical conductivity on (AuZn)/TiO2/p-GaAs(110) MIS structures. Philos Mag. 2015;95:2885–2898. doi: 10.1080/14786435.2015.1081301.

Tataroğlu A, Altundal Ş. Characterization of interface states at Au/SnO2/n-Si (MOS) structures. Vacuum. 2008;82:1203–1207. doi: 10.1016/j.vacuum.2007.12.014.

Nicollian EH, Brews JR. MOS (metal oxide semiconductor) physics and technology. Hoboken (NJ): Wiley Interscience Publication; 1982.

Ulrich RK, Schaper I.W. Integrated passive component technology. Hoboken (NJ): Wiley - IEEE; 2003.

Blythe AR, Bloor D. Electrical properties of polymers. Cambridge: Cambridge University Press; 1979.

Maxwell JC. Electricity and magnetism. Oxford: Clarendon Press; 1892.

Koops CG. On the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies. Phys Rev. 1951;83:121–124. doi: 10.1103/PhysRev.83.121.

Pandian SK, Karthik K, Sureshkumar K, et al. Effect of Mn-doping on structural, optical, and dielectric properties of SnO2 nanoparticles by coprecipitation method. Mater Manuf Process. 2012;27:130–134. doi: 10.1080/10426914.2011.557130.

Mehraj S, Ansari MS, Alimuddin. Structural, electrical and magnetic properties of (Fe, Co) co-doped SnO2 diluted magnetic semiconductor nanostructures. Phys E Low-Dimens Syst. Nanostruct. 2015;65:84–92. doi: 10.1016/j.physe.2014.08.016.

Yang H, Lin Y, Wang F, et al. Chemical synthesis of K0.5Na0.5NbO3 ceramics and their electrical properties. Mater Manuf Process. 2008;23:489–493. doi: 10.1080/10426910802104070.

Karthik K, Pandian SK, Jaya NV. Effect of nickel doping on structural, optical and electrical properties of TiO2 nanoparticles by sol–gel method. Appl Surf Sci. 2010;256:6829–6833. doi: 10.1016/j.apsusc.2010.04.096.

Batal MA, Jneed FH. Tin oxide n-type semiconductor inverted to p-type semiconductor prepared by sol-gel method. Energy Procedia. 2011;6:1–10. doi: 10.1016/j.egypro.2011.05.001.

Mukae K, Tsuda K, Nagasawa I. Capacitance-vs-voltage characteristics of ZnO varistors. J Appl Phys. 1979;50:4475–4476. doi: 10.1063/1.326411.

Fernández-Hevia D, de Frutos J, Caballero AC, et al. Mott–Schottky behavior of strongly pinned double Schottky barriers and characterization of ceramic varistors. J Appl Phys. 2002;92:2890–2898. doi: 10.1063/1.1498968.

De Visschere P. Image forces and MIS Schottky barriers. Solid State Electron. 1986;29:873–875. doi: 10.1016/0038-1101(86)90006-7.

Tataroğlu A. Comparative study of the electrical properties of Au/n-Si (MS) and Au/Si3N4/n-Si (MIS) Schottky diodes. Chin Phys B. 2013;22:068402. doi: 10.1088/1674-1056/22/6/068402.

Shao S, Wu H, Jiang F, et al. Regulable switching from p- to n-type behavior of ordered nanoporous Pt-SnO2 thin films with enhanced room temperature toluene sensing performance. RSC Adv. 2016;6:22878–22888. doi: 10.1039/C5RA24736E.