

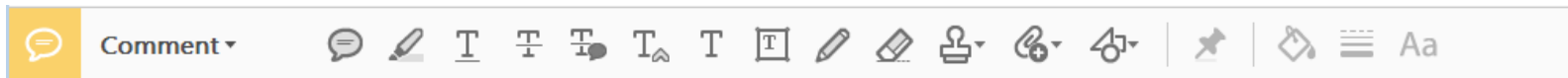
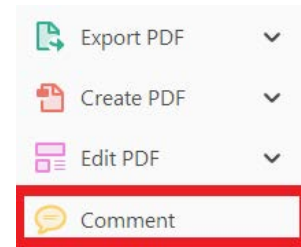
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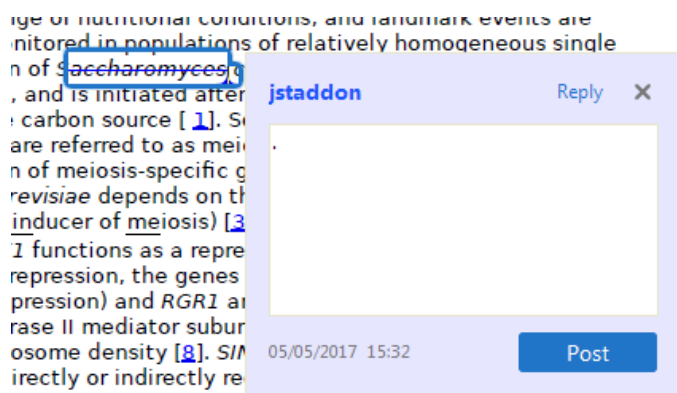


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
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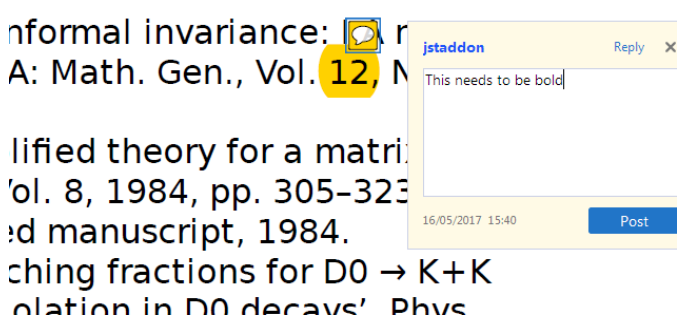
1. Small size (35-250 amino acids).
2. Absence of similarity to known proteins.
3. Absence of functional data which could not be the real overlapping gene.
4. Greater than 25% overlap at the N-terminus terminus with another coding feature; over both ends; or ORF containing a tRNA.

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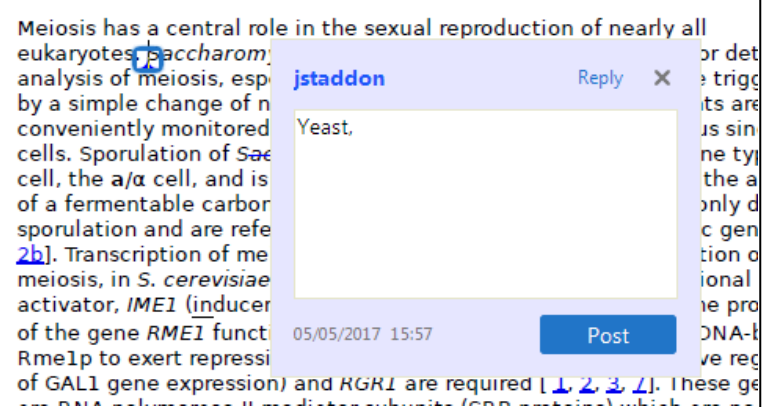


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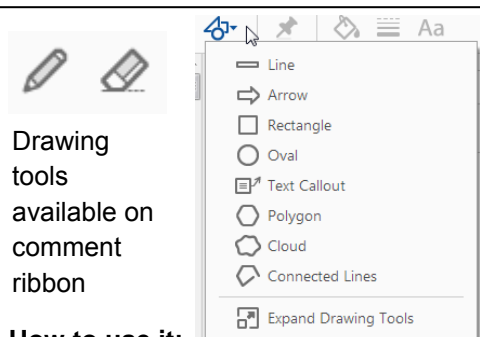
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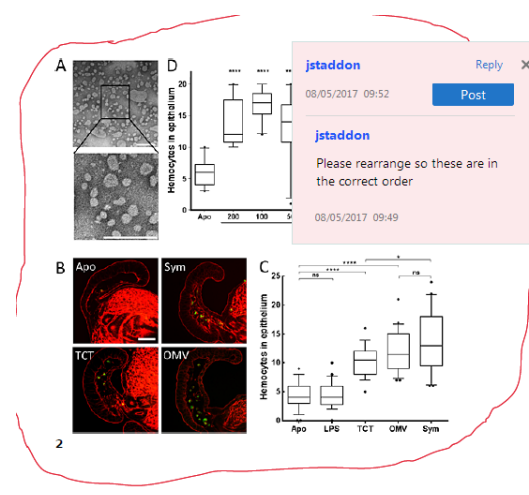


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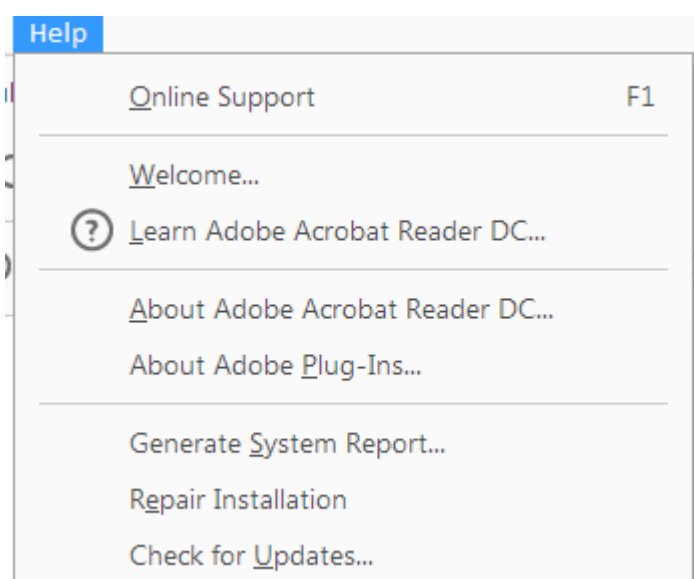
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Surface Dielectric Tunnel Barrier Induced by Mn Doping in SnO₂ Micro- and Nanostructures

Manuel¹ Herrera, David Maestre,* and Ana Cremades

Electrical properties of undoped and Mn doped SnO₂ microplates and rods have been studied by electron beam induced current (EBIC) in a scanning electron microscope (SEM), and I–V curves acquired at room temperature. AFM measurements reveal the formation of numerous terraces at the (–101) surface of the analyzed Mn-doped SnO₂ microplates, which also exhibit high carrier recombination processes at their central region, as confirmed by combined EBIC and cathodoluminescence (CL) measurements. A diffusion length for minority carriers about 205 nm is obtained by EBIC measurements. Different electrical conduction mechanisms, such as Fowler-Nordheim, Direct Tunneling and Poole-Frenkel, have been evaluated in the electrical analysis of the samples. Mn doped microplates show lower conductivity than the undoped microrods. Moreover the height of the surface tunnel barrier is increased by Mn doping, as confirmed by the analysis of the I–V curves acquired under transversal configuration. A value of the relative dielectric constant ϵ_r about 7.3 has been estimated for the probed SnO₂ microstructures.

1. Introduction

SnO₂ is a semiconductor with a direct wide bandgap of about 3.6 eV (at 300 K) that receives significant attention due to their applications as gas sensors, solar cells, or catalyst.^[1–4] Moreover, SnO₂-based elongated micro- and nanostructures can be also used as building blocks in optoelectronic devices. The combination of good electrical conductivity, due to the intrinsic oxygen deficiency, together with high transparency in the visible range makes this material one of the most exploited transparent conductive oxides (TCO). Moreover, Mn doping can induce variations in the SnO₂ electrical and optical properties, together with magnetic functionality, what motivates its study. This

semiconductor has also been proposed for spintronic applications due to the ferromagnetic properties observed at room temperature, particularly in Mn-doped SnO₂ thin films and nanostructures.^[5–8] The use of spin-MOSFET's with gate electrodes composed by a ferromagnetic material with the insertion of a dielectric barrier at the gate, enhances the spin accumulation at the semiconductor at room temperature due to the increase of interface resistance by the formation of a tunnel barrier.^[9,10] On the other hand, tunnel barriers produced as dielectric layers in semiconductors, or dielectric tunnel barriers, demonstrate direct applications in the fabrication of information storage devices,^[11] such as floating gate field-effect transistors used in cellular phones, and digital cameras. These barriers are fabricated and investigated mainly from materials with high dielectric constant, such as Al₂O₃, SiO₂, Ta₂O₅, HfO₂ and ZrSi_xO_y,^[12] and less have been done on the potential candidate SnO₂ so far. In some of these applications, the mechanisms involved in the electronic conduction strongly influence the final device performance, hence a deep study of these processes is required.

Previously, we reported that the presence of Mn induced changes in the growth conditions and the morphology of Mn-doped SnO₂ micro- and nanostructures grown by a vapor–solid method, as well as in their luminescence.^[13] Temperatures, around 1090 °C, are required to synthesize Mn doped SnO₂ microplates, with lengths of tens of microns, thickness below 1 μm and widths between 2 and 4 μm. Following this synthesis method, wires and belts could be fabricated as well. Electron backscattered diffraction measurements indicate that the microplates grow along the [101] direction. We also reported that the average of Mn content incorporated in the SnO₂ is around 1.6 at %, as measured by EDS, although the incorporation of Mn varies as a function of the probed surface of the microplate, as confirmed by XPS measurements.^[13] Facets with a higher amount of Mn are associated with increased luminescence due to a higher concentration of oxygen vacancies related defects, as the presence of Mn³⁺ substituting Sn⁴⁺ involves formation of oxygen vacancies to maintain charge neutrality. In this case, as a further investigation, we study the effects caused by Mn doping on the electrical properties of these SnO₂ micro- and nanostructures grown by a vapor–solid process. We report that the electrical conduction mechanism, at room temperature, in Mn

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Dedicated to Prof. Javier Piqueras

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1 doped SnO₂ elongated structures reveals the formation of a
2 dielectric tunnel barrier at their surface. The influence of Mn
3 doping in the formation of this tunnel barrier is discussed in this
4 work.

5 2. Experimental Section

6 The undoped and Mn doped SnO₂ microstructures analyzed in
7 this work were grown by a catalyst-free evaporation-deposition
8 method, following a procedure that we previously reported in
9 Ref. [13]. In order to synthesize Mn doped SnO₂ samples,
10 commercial powders of SnO₂ (Alfa Aesar 99.99%) and MnCO₃
11 (Alfa Aesar 99.9%) at 5 wt% were mechanically mixed in a
12 centrifugal ball mill and thermally treated under a controlled Ar
13 flow in a horizontal furnace operated at 1400 °C for 10 h under
14 low vacuum conditions (up to 1×10^{-2} mbar). A SnO₂ ceramic
15 substrate, previously sintered at 700 °C, was placed at the
16 downstream side of the furnace, where different elongated nano-
17 and microstructures grow by a vapor–solid process as a function
18 of the temperature.^[13] In particular, Mn doped SnO₂ microplates
19 are grown at 1090 °C. A reference sample of undoped SnO₂
20 microrods and wires, grown at 1040 °C, was also prepared by the
21 same method using pure SnO₂ as precursor.

22 The morphology of these micro- and nanostructures was
23 studied with a Leica 440 Stereoscan SEM operated at 10 kV and
24 500 pA. Atomic Force Microscopy (AFM) measurements were
25 performed at atmospheric pressure, using a Nanotech AFM
26 controlled by a Dulcinea software operated in contact mode with
27 commercial Si tips. For AFM observations, some of the
28 structures under study were placed onto a Si (100) substrate
29 and fixed with silver paint. The electrical properties of the as-
30 grown structures were studied by Electron Beam Induced
31 Current (EBIC) in a scanning electron microscope (SEM) at
32 room temperature and low vacuum conditions ($\approx 10^{-6}$ Torr).
33 Considering tin oxide as a n-type semiconductor, as commonly
34 reported, and work function values of about 4.5, 4.1, and 4.8 eV
35 for SnO₂, In and Au, respectively, either Schottky or ohmic
36 contacts will be obtained by Au/SnO₂ or In/SnO₂. For EBIC
37 measurements the Mn doped SnO₂ microplates were deposited
38 onto a Au/Si(100) substrate generating a SnO₂/Au Schottky
39 contact in planar configuration. The second electrode consists of
40 an electrochemically etched W tip coated with In attached to a
41 micromanipulator in a Leica 440 SEM, used to contact the
42 surface of the SnO₂ microplates as an ohmic contact (In/SnO₂)
43 in order to perform EBIC measurements. Local I–V measure-
44 ments have been also acquired under transversal configurations
45 in an SEM at room temperature and low vacuum conditions
46 ($\approx 10^{-6}$ Torr), using a Keithley 2400 as power supply and
47 amperemeter. The structures were placed onto a In/Si(100)
48 substrate, in order to obtain a SnO₂/In ohmic contact, while the
49 micro-manipulated In/W tip was used as the second electrode,
50 therefore the current flows through the structure.

51 3. Results and Discussion

52 SEM image in **Figure 1a** shows a Mn-doped SnO₂ microplate
53 with a length and width of about 30 and 5 μm , respectively, which
54 was placed onto a Si(100) substrate and fixed with silver paint to

be studied by AFM. **Figure 1b** shows an AFM image of the region
1 marked with a square in **Figure 1a**. The AFM study reveals a
2 surface formed by parallel terraces aligned along the growth
3 direction of the microplate, marked with an arrow in **Figure 1b**,
4 which has been previously identified as the [10-1].^[13] These
5 terraces, the concentration of which is higher in the central
6 region of the microplates, show the same triangular-ending
7 appearance observed in the microplates. The topographic profile
8 shown in **Figure 1c** corresponds to the line marked in the terrace
9 in **Figure 1b**, which indicates that terraces at the surface of the
10 microplate present a step-height of about 15 Å. EBSD study of
11 the Mn doped SnO₂ microplates revealed that their main surface
12 corresponds to the rutile (–101) plane.^[13] Considering that the
13 thickness of an atomic monolayer of the (–101) surface in SnO₂
14 is 5.2 Å, the terrace profiled in **Figure 1c** could roughly
15 correspond to three atomic monolayers. The correlative
16 EBSD-CL-XPS study referred in Ref. [13] enabled us to associate
17 the (–101) surface with a region of hindered Mn incorporation,
18 low presence of oxygen vacancies, and high concentration of
19 surface defects.

20 In this work, EBIC measurements in a SEM have been carried
21 out on the Mn doped SnO₂ microplates in order to analyze their
22 electrical behavior. **Figure 2a,b** show SEM and EBIC images,
23 respectively, of a Mn doped SnO₂ microplate placed onto a Au-
24 coated Si substrate and electrically connected with an indium-
25 coated W tip. A significant dark contrast along the central region
26 of the microplate is clearly observed in the EBIC image
27 (**Figure 2b**). Dark contrast in EBIC images corresponds to low
28 electric currents collected by the In/W tip electrode, which can
29 be attributed to a decrease of the charge carrier density due to
30 recombination of electron-hole pairs.^[14] Extended defects, such
31 as dislocations and grain boundaries, typically result in dark
32 EBIC contrasts, as they usually act as radiative recombination
33 centers.^[15–17] In this case, the presence of radiative recombina-
34 tion centers at the central region of the Mn doped SnO₂
35 microplates has been confirmed by CL measurements, as shown
36 in **Figure 2c** where the central region of the microplates appear
37 brighter. In particular the CL signal associated with the
38 microplates is dominated by a blue emission of 2.58 eV,^[13]
39 usually attributed to shallow levels in the SnO₂ electronic
40 structure involving surface defects, removal of oxygen vacancies,
41 and/or creation of oxygen interstitials.^[18] Therefore a higher
42 concentration of these defects should be present in the central
43 region of the microplates, showing a brighter CL signal, where
44 AFM measurements also indicate a higher presence of terraces.
45 **Figure 2d** shows an EBIC profile corresponding to the line
46 marked in the EBIC image (inset), which corresponds to the
47 central region of the microplate in **Figure 2b**. By neglecting
48 surface recombination, EBIC signal decays exponentially
49 following the expression $I \propto \exp(-x/L)$, where I is the EBIC
50 signal, x is the length from the bright region with high e-h
51 recombination, and L corresponds to the diffusion length of the
52 minority carriers. In this case, L was estimated using the fit of
53 **Figure 2d**, obtaining a value of (205 ± 18) nm, in agreement with
54 values reported for SnO₂ ceramic material between 0.2 and
55 $2 \mu\text{m}$.^[19]

56 I–V measurements have been performed on the Mn doped
57 SnO₂ micro and nanostructures, as well as on undoped SnO₂ low
58 dimensional structures, as a reference, by using ohmic contacts
59

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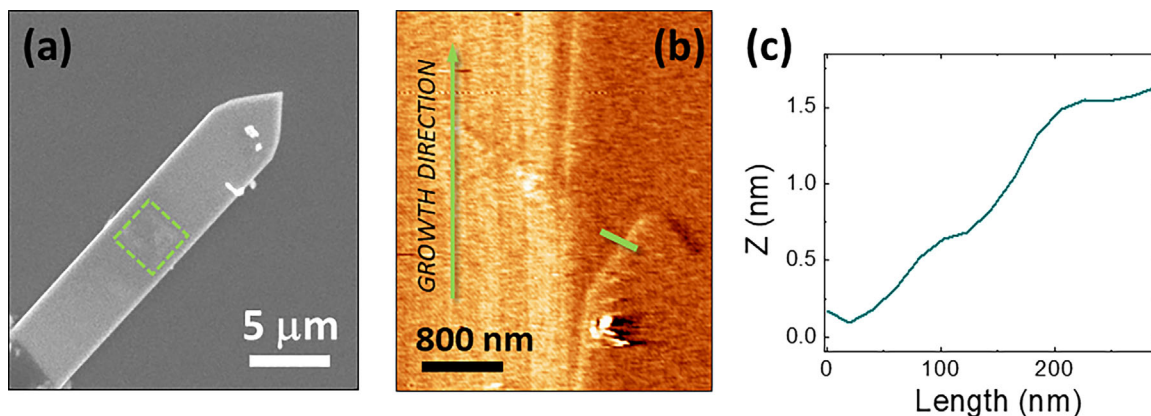


Figure 1. a) SEM image of a Mn doped SnO₂ microplate. b) AFM image obtained from the square marked in (a). c) AFM profile measured along the line marked in the terrace in (b).

1 under transversal configuration at low vacuum conditions in a
2 SEM. Different structures have been analyzed in this work, so
3 that the results here shown can be considered as representative
4 for the samples under study. In addition, different conduction
5 mechanisms have been considered in the analysis of the I–V
6 curves, such as ohmic conduction, Fowler-Nordheim tunneling
7 (FN), Direct Tunneling (DT), Poole-Frenkel (PF), Schottky
8 emission, or Space-Charge-Limited conduction (SCL). As the
9 I–V curves have been acquired in a SEM at room temperature,
10 temperature-related effects have not been considered in the
11 electrical analysis. Moreover, additional I–V curves have been
12 acquired as a reference contacting directly the In/W tip and the
13 In/Si substrate, without any SnO₂ structure in between. As the
14 corresponding I–V curves exhibit an ohmic behavior, we

disregard the presence of a possible dielectric layer at the In/W 1
tips or the In/Si substrate that could act as a potential barrier, 2
which will be further taken into account in the analysis of the I–V 3
curves. 4

Firstly, Mn doped SnO₂ microplates with an amount of Mn 5
about 1.6 at%, as those shown in Figure 1a, have been electrically 6
characterized. **Figure 3a** shows the I–V curve corresponding to a 7
microplate, with a thickness about 500 nm, electrically con- 8
nected between the In/Si substrate and the In/W tip, as observed 9
in the SEM image shown in the inset. Two bias regimes, below 10
and over 20 V, can be clearly appreciated in the corresponding 11
non-linear I–V curve shown in Figure 3a, which suggests 12
different conduction mechanisms involved for low or high bias 13
voltage. A continuous increase of the current intensity up to 14

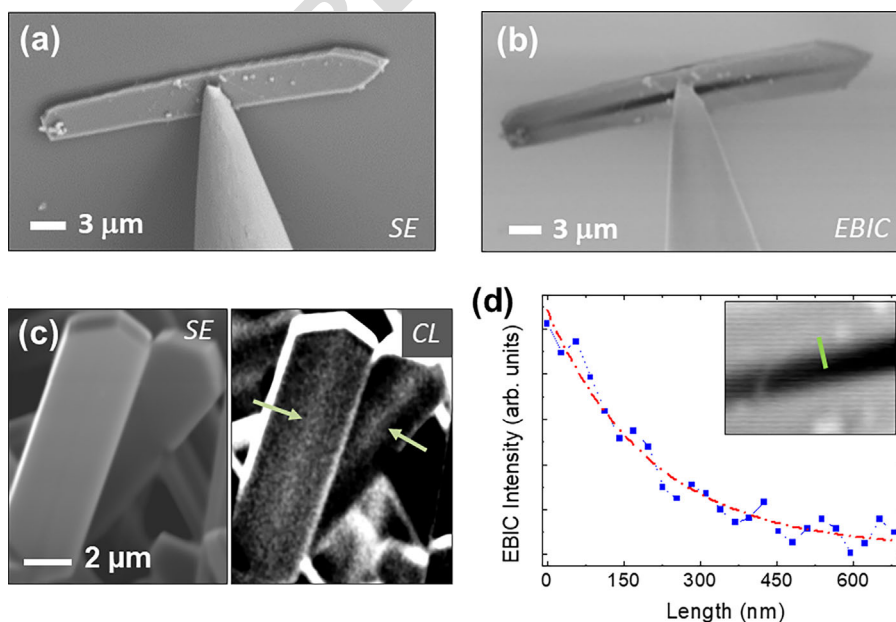


Figure 2. a) SEM and (b) EBIC images of a Mn doped SnO₂ microplate. c) SEM and CL images acquired from Mn doped SnO₂ microplates. d) EBIC profile measured at the contrasted EBIC region shown in the inset.

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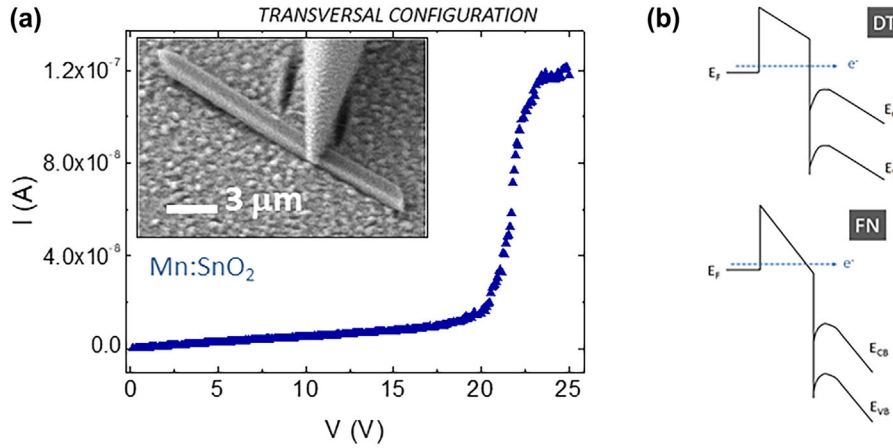


Figure 3. a) I–V curve acquired from a Mn doped SnO₂ microplate in transversal configuration. The inset shows the SEM image acquired before the measurement. b) Schematic descriptions of the direct-tunneling (DT) and Fowler-Nordheim (FN) conduction mechanisms.

1 several nA is observed when the applied voltage ranges between
2 0 and 20 V, while a strong increase of the current intensity up to
3 10⁻⁷ A is observed when the bias voltage is higher than 20 V, in
4 accordance to the variation in the specific barrier profile.

5 Among the conduction mechanisms considered in this study,
6 FN and DT can be fitted to the experimental I–V data in
7 Figure 3a. FN involves electrons tunneling through a triangular
8 potential barrier in the presence of a high electric field, while DT
9 occurs when electrons are able to tunnel through a trapezoidal
10 barrier not severely deformed at low electric fields (as shown in
11 the schemes in Figure 3b). The high voltage regime (higher than
12 20 V) in Figure 3a, can be interpreted on the basis of the Fowler-
13 Nordheim (FN) tunneling mechanism described by the
14 $I \propto V^2$ relation^[20]:

$$I(V) = \frac{A_{\text{eff}} \cdot q^3 m V^2}{8\pi h \phi_B d^2 m^*} \exp\left(\frac{-8\pi\sqrt{2m^*}\phi_B^{3/2}d}{3hqV}\right) \quad (1)$$

15 where A_{eff} is the effective contact area, ϕ_B is the barrier height,
16 and q , m^* , d , and h correspond to the electron charge, effective
17 electron mass for SnO₂, the separation between electrodes
18 (microplate thickness), and the Planck's constant, respectively.

19 This equation can be rewritten as:

$$\ln\left(\frac{I}{V^2}\right) = \ln\left(\frac{A_{\text{eff}} \cdot q^3 m}{8\pi h \phi_B d^2 m^*}\right) - \frac{8\pi\sqrt{2m^*}}{3hqV} \phi_B^{3/2} d \quad (2)$$

20 Therefore, the FN mechanism in the high bias regime can be
21 determined by a negative slope when plotting $\ln(I/V^2)$ versus $(1/V)$,
22 as shown in **Figure 4a**. Considering an effective mass for
23 electrons in SnO₂ of $m^* = 0.27m_0$ ^[21] a value of barrier height
24 about $\phi_B = (0.42 \pm 0.08)$ eV can be obtained from the linear fit
25 (Eq. 2) shown in Figure 4a. This result demonstrates that the FN
26 tunneling originates the increase of the current intensity at high
27 bias regime.

28 For the electrical conduction at low bias voltages between 0
29 and 20 V, a Direct-Tunneling (DT) mechanism has been
30 considered. This mechanism, for which tunneling of electric

charge occurs through a potential barrier, can be described by the
following equation^[22]:

$$I(V) = \frac{A_{\text{eff}} \cdot \sqrt{m\phi_B} q^2 V}{h^2 d} \cdot \exp\left(\frac{-4\pi\sqrt{m\phi_B} d}{h}\right) \quad (3)$$

where m is the free electron mass, ϕ_B corresponds to the height
of the potential barrier, and d is the width of the tunnel barrier.
Usually this equation is rewritten as:

$$\ln\left(\frac{I}{V^2}\right) = \ln\left(\frac{A_{\text{eff}} \cdot \sqrt{m\phi_B} q^2}{h^2 d}\right) - \frac{4\pi\sqrt{m\phi_B} d}{h} + \ln\left(\frac{1}{V}\right) \quad (4)$$

In this case, a DT mechanism can be identified as a linear fit
in a plot of $\ln(I/V^2)$ versus $\ln(1/V)$, as shown in Figure 4b, where
the slope should be ideally 1. The accurate linear fit, indicated
in Figure 4b, leads to a slope of (1.02 ± 0.01) with an R^2
coefficient of 0.998, thus confirming the linear dependence
expressed in Equation (4). However, despite the fact that the
experimental data can be linearly fitted yielding a remarkably
low value for the barrier height of $\phi_B = (0.7 \pm 0.2) \cdot 10^{-3}$ eV,
electron tunneling through a potential barrier with a width of
500 nm, the thickness of the microplate, results physically
improbable. Therefore, as some other conduction mechanisms
have been considered and discarded in the analysis of the low
bias regime, a modified direct tunneling mechanism is
proposed in this work. In this case, the transversal configura-
tion on which the I–V curves have been acquired, can be
modeled as two tunnel barriers (In/SnO₂ and SnO₂/In),
together with a current flow through the SnO₂ microplate.
Following this idea, the total bias voltage can be interpreted as
 $V_{\text{DT1}} + V_{\text{SnO}_2} + V_{\text{DT2}}$. The origin of the both tunnel barriers
could be related to the presence of surface states which can
promote formation of depletion layers at the SnO₂ surface. If
we assume that both In/SnO₂ and SnO₂/In barriers exhibit a
similar behavior, as both corresponds to the (-101) planes, the
total voltage, V , can be interpreted as $2V_{\text{DT}} + V_{\text{SnO}_2}$. Therefore,
Equation (3) can be rewritten as:

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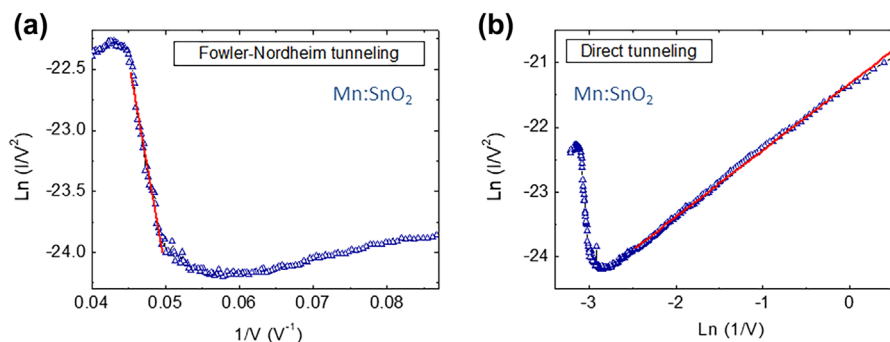


Figure 4. Fitting of the I–V curve in **Figure 3a** by using the models for (a) Fowler-Nordheim and (b) direct tunneling conduction mechanisms.

$$I(V) = \frac{A}{2e^{-B} + AR_{\text{SnO}_2}} V \quad (5)$$

1 with $A = \frac{A_{\text{eff}} \cdot \sqrt{m\phi_B q^2}}{h^2 d}$, $B = \frac{-4\pi \sqrt{m\phi_B d}}{h}$, and R_{SnO_2} is the electric resistance
2 of the SnO_2 .

3 In this case, d corresponds to the thickness of each tunnel
4 barrier formed at the surface of the Mn doped SnO_2 microplate,
5 in both contact regions, which in this work has been considered
6 as around 5 nm, by following the values reported in some other
7 works.^[23,24] For R_{SnO_2} a value of $200 \text{ M } \Omega^{-1}$ has been considered,
8 as estimated from the I to V curves shown in this work.

9 Therefore, Equation (5) can be expressed as:

$$\ln\left(\frac{I}{V^2}\right) = \ln\left(\frac{A}{2e^{-B} + AR_{\text{SnO}_2}}\right) + \ln\left(\frac{1}{V}\right) \quad (6)$$

10 We found that the plot $\ln(I/V^2)$ versus $\ln(1/V)$ should also
11 reveal a slope near to the unity. In this case, a value of
12 (1.02 ± 0.01) was estimated for the slope in **Figure 4b**, enabling
13 us to determinate the value for the barrier height of $\phi_B = (1.34$
14 $\pm 0.24) \text{ eV}$, which is more physically probable than the value of
15 ϕ_B obtained before, even when this model can be further
16 optimized.

17 Undoped SnO_2 rods have also been electrically analyzed in a
18 SEM under transversal configuration for comparison. A micro-
19 rod (250 nm thick) has been placed onto a In/Si substrate and
20 pinned with an In/W electrode to assure a good electrical contact,
21 as shown in the inset of **Figure 5a**. As a first difference with

respect to the Mn doped SnO_2 structures (**Figure 3a**), the I–V 1
curves from undoped SnO_2 do not show two clear bias regimes. 2
Moreover, current values obtained for undoped SnO_2 are some 3
orders of magnitude higher than those corresponding to Mn 4
doped SnO_2 acquired using a similar transversal configuration. 5
Actually, current values about 500 nA were achieved for undoped 6
 SnO_2 microrods with a bias voltage of 1 V, as shown **Figure 5a**, 7
while for Mn-doped SnO_2 microplates similar values of current 8
were not reached even with applied bias voltages of 25 V 9
(**Figure 3a**). Even when differences in the thickness of the probed 10
structures are considered in the electrical analysis, these results 11
indicate that undoped SnO_2 microrods show higher conductivity 12
than the Mn-doped SnO_2 microplates. FN and DT mechanisms 13
have been also evaluated in comparison with the analysis of the 14
I–V curves from Mn-doped SnO_2 . In this case FN tunneling is 15
not the dominant conduction mechanism, as data corresponding 16
to the higher bias values cannot be linearly fitted when plotting \ln 17
 (I/V^2) versus $1/V$. On the other hand, **Figure 5b** shows the linear 18
dependence when plotting $\ln(I/V^2)$ versus $\ln(1/V)$ for low 19
voltages, with a slope of (0.97 ± 0.01) , near to the theoretical 20
value of 1 corresponding to DT. As conventional direct tunneling 21
through a barrier of 250 nm, the thickness of the rod, is 22
physically improbable, again a modified direct tunneling (Eq. 5) 23
has been used to analyze the I–V curves, and a potential barrier of 24
 $\phi_B = (0.96 \pm 0.18) \text{ eV}$ has been estimated in this case. This value 25
is about 30% lower than the corresponding for Mn-doped SnO_2 , 26
obtained with a similar electrical analysis, which indicates that 27
Mn doping induces an increase in the barrier height. This higher 28
barrier height formed at the surface of the Mn-doped SnO_2 29

COLOR

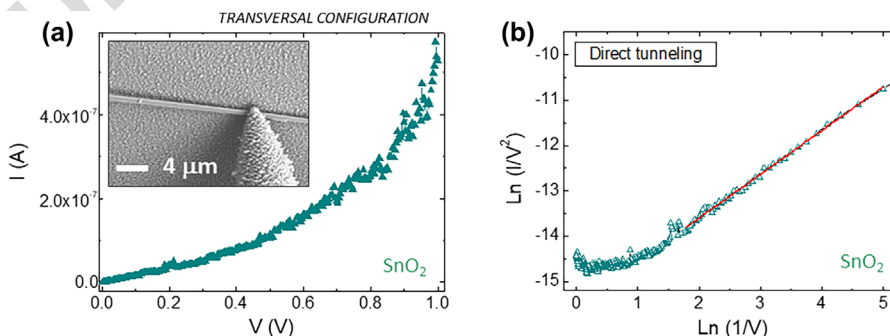


Figure 5. a) I–V curve acquired from an undoped SnO_2 microrod in transversal configuration. The inset in (a) shows the SEM image acquired before the measurement. b) Fitting of the I–V curve in (a) with the direct tunneling model.

1 microplates can be also associated with the increase in the
2 resistivity of the Mn doped samples, as compared with undoped
3 SnO₂.

4 As the presence of a dielectric layer acting as a potential
5 barrier at the In/W tip or the In/Sn substrate was previously
6 discarded, the electrical behavior deduced from the analysis of
7 the I-V curves, could indicate that a dielectric tunnel barrier is
8 formed at the probed (-101) surface of the Mn doped SnO₂
9 microplates. This barrier could be associated with a depletion
10 layer formed due to surface states on SnO₂ (-101), which
11 concentration would be increased for the Mn doped SnO₂
12 samples. Actually, previous cathodoluminescence measure-
13 ments revealed a lower concentration of oxygen vacancies
14 (V_O) in the Mn doped SnO₂ microplates,^[13] mainly at the (-101)
15 surface. This could explain the associated decrease in the
16 conductivity induced by Mn doping, as these V_O defects govern
17 the conductivity in SnO₂.^[25,26]

18 In this work, a Poole-Frenkel (PF) mechanism, generated by a
19 field-enhancement thermal excitation of trapped electrons into
20 the conduction band, has been also considered in the analysis of
21 the I-V curves. A scheme describing this trap-assisted
22 conduction mechanism is depicted as an inset in **Figure 6a**.
23 This mechanism follows the relation^[27]:

$$I = \frac{qN_c\mu V}{d} \exp\left(\frac{\beta_{PF} V^{1/2} - q\phi_{PF}}{k_B T}\right) \quad (7)$$

24 where ϕ_{PF} is the Poole-Frenkel barrier height, k_B the Boltzmann
25 constant, and β_{PF} is a coefficient related to the relative static
26 permittivity, or dielectric constant ϵ_r , of the material by:

$$\beta_{PF} = \sqrt{\frac{e^3}{d\pi\epsilon_0\epsilon_r}} \quad (8)$$

27 where ϵ_0 is the vacuum permittivity, ϵ_r is the dielectric constant of
28 SnO₂, e the electron charge and d corresponds to the

nanostructure length between contacts. Equation (7) can be
expressed as:

$$\ln\left(\frac{I}{V}\right) = \frac{\beta_{PF} V^{1/2}}{k_B T} - \frac{q\phi_{PF}}{k_B T} + \ln\frac{qN_c\mu}{d} \quad (9)$$

A value of $T = 300$ K has been considered in this analysis,
although higher values could be locally achieved, as high bias
voltages were used. According to Equation (9), PF mechanism
implies a linear dependence of $\ln(I/V)$ versus $V^{1/2}$, with slope
values usually ranging from 1 to 2. In the case of Mn-doped SnO₂
microplates, I-V data cannot be fitted to Equation (9), indicating
that PF is not the dominant conduction mechanism in this case.
On the other hand, a good correlation has been found for
undoped SnO₂ microrods (Figure 6a) in the region with voltages
higher than 0.5 V in Figure 5a, which suggests that the PF
mechanism is involved for high voltage values, complementary
to the direct tunneling observed for low bias. Figure 6a shows the
corresponding $\ln(I/V)$ versus $V^{1/2}$ curve, from which analysis a
value of 7.3 has been estimated for the dielectric constant ϵ_r .
Reports on the permittivity values of SnO₂ nanostructures are
scarce, and usually depend on the presence of dopants and
concentration of oxygen vacancies.^[28] Nevertheless, values for ϵ_r
between 2.5 and 9.5 have been reported for SnO₂,^[3,29] which
agrees with the value obtained in this work.

4. Conclusion

To summarize, in this work the electrical properties of undoped
and Mn doped SnO₂ microplates and rods have been analyzed by
EBIC technique and I-V curves acquired in transversal
configuration. Topographic characterization by AFM shows
formation of terraces at the (-101) surface of the Mn doped
SnO₂ microplates. Combined EBIC and CL imaging techniques,
reveal enhancement of carrier recombination along the central
region of the Mn-doped SnO₂ microplates. Based on the analysis
of the EBIC measurements, a value about 205 nm has been
estimated for the diffusion length of the minority carriers.
Electrical measurements confirmed that the presence of Mn
induces a decrease in the electrical conductivity of the probed
microstructures. Moreover, transition from direct tunneling to
Fowler-Nordheim tunneling conduction mechanisms was found
through the Mn-doped SnO₂ microplates. The analysis of the
electrical measurements considering direct tunneling points out
to an increase of the tunnel barrier through Mn doping. This
tunnel barrier could be associated with the presence of surface
states, the concentration of which is apparently enhanced by Mn
doping. A modified direct tunneling mechanism involving two
tunnel barriers at the front and rear surfaces of the probed
structures has been also proposed. Based on the Poole-Frenkel
mechanism, a value for the dielectric constant ϵ_r about 7.3 has
been estimated for the SnO₂ microrods.

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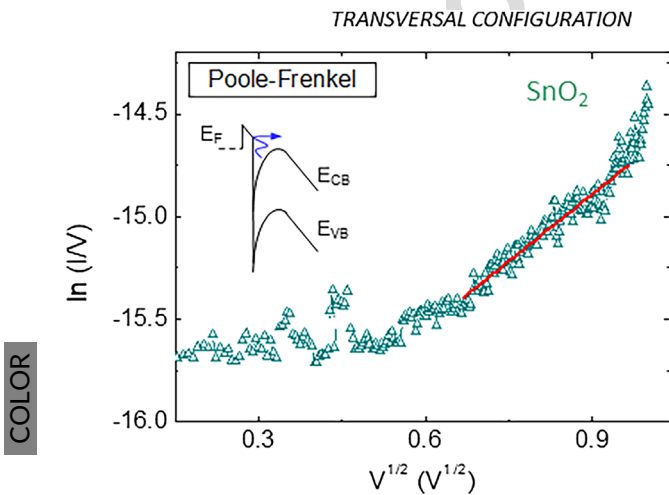


Figure 6. Fitting of the I-V curve shown in **Figure 5a** to the Poole-Frenkel
conduction mechanism. A scheme of the PF model is included as an inset.

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3 Conflict of Interest

4 The^{Q4} authors declare no conflict of interest.

Keywords

doping, EBIC, microplate, SnO₂

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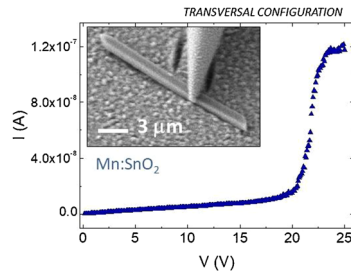
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ORIGINAL PAPER

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Surface Dielectric Tunnel Barrier Induced by Mn Doping in SnO₂ Micro- and Nanostructures



An electrical characterization of undoped and Mn doped SnO₂ microplates and rods, grown by a vapor–solid process, is performed. Mn doping induces a decrease in the electrical conductivity, as well as an increase of the surface dielectric tunnel barrier estimated from the analysis of the direct tunneling mechanism observed in the I–V curves.

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