



Electrical properties of TiO₂ thin films

A. Yildiz^{a,*}, S.B. Lisesivdin^b, M. Kasap^b, D. Mardare^c

^a Department of Physics, Faculty of Science and Arts, Ahi Evran University, Aşıkpaşa Kampüsü, 40040 Kırşehir, Turkey

^b Department of Physics, Faculty of Science and Arts, Gazi University, Teknikokullar, 06500 Ankara, Turkey

^c Faculty of Physics, Alexandru Ioan Cuza University, 11 Carol I Boulevard, 700506-Iasi, Romania

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ABSTRACT

The electrical properties of n-type titanium dioxide thin films deposited by magnetron-sputtering method have been investigated by temperature-dependent conductivity. We observed that the temperature dependence of the electrical conductivity of titanium dioxide films exhibits a crossover from $T^{-1/4}$ to $T^{-1/2}$ dependence in the temperature range between 80 and 110 K. Characteristic parameters describing conductivity, such as the characteristic temperature (T_0), hopping distance (R_{hop}), average hopping energy (Δ_{hop}), Coulomb gap (Δ_C), localization length (ξ) and density of states ($N(E_F)$), were determined, and their values were discussed within the models describing conductivity in TiO₂ thin films.

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1. Introduction

Titanium dioxide thin films have received a great deal of interest due to an important number of applications such as electrochromic, photovoltaic and microelectronic devices [1–3]. Although many structural and optical studies [4–8] were carried out for TiO₂, its electron transport properties remain back due to its high resistivity. In fact, in TiO₂ semiconductor thin films having a high energy gap in which compensation is nearly full, impurity band conduction may become significant even above room temperature [9]. Electrical conductivity processes are mainly due to hopping via impurity centers, while the contribution of intrinsic free carriers is negligible even at high temperatures. At high temperatures ($T > 300$ K), the measured conductivity of TiO₂ thin films is, generally, explained in terms of the simple thermally activated conduction ($\sigma = \sigma_0 \exp(-E_a/k_B T)$) mechanism [10]. At low temperatures ($T < 300$ K), the conductivity takes place through variable range of hopping (VRH) between the localized states, with thermal activation energy being smaller than E_a , instead of simple activated hopping [11,12].

In the theoretical description of VRH conduction process, it is assumed that when the density of electronic states is finite and the states are localized near the Fermi energy E_F , variable hopping will occur and $\ln(\sigma)$ is proportional to $T^{-1/4}$ (Mott law) [13]. If Coulomb repulsion between carriers is taken into account, $\ln(\sigma)$ is proportional to $T^{-1/2}$ (Efros–Shklovskii law) [14]. In the derivation of the latter dependence, it is assumed that one-electron density of states vanishes at the Fermi energy E_F , resulting in a soft Coulomb gap. The electron transport in this case is possible due to different hopping process, which activated in different temperature regions.

* Corresponding author. Tel.: +90 0386 252 80 50; fax: +90 0386 252 80 54.
E-mail address: yildizab@gmail.com (A. Yildiz).

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In this study, electrical conductivity measurements of titanium dioxide thin films were carried out in a temperature range of 13–320 K. The temperature-dependent conductivity of these films was explained in terms of VRH conductivity at both Mott and Efros–Shklovskii (ES) regime.

2. Experimental

Titanium dioxide films were deposited onto glass substrates by dc magnetron-sputtering method, using water vapors as reactive gas. By using water as reactive gas, we intended to lower the high resistivity that characterizes the stoichiometric titanium dioxide films. As experimentally observed, titanium dioxide films deposited with water vapor as reactive gas in certain conditions [15,16] have room-temperature electrical conductivity values of $0.1\text{--}1.0 (\Omega \text{ cm})^{-1}$, i.e. $10^8\text{--}10^9$ times higher than those corresponding to the stoichiometric films prepared using oxygen. This is a general observation, which indicates the possibility of increasing the carrier density in TiO₂ films with increasing the oxygen vacancy [15–17]. The target to substrate distance was 150 mm, the total pressure being set at 2×10^{-3} mbar. Argon was used as

Table 1
Values of film thickness (*d*), room-temperature conductivity (σ_{RT}) and values of the Mott VRH conduction parameters

Sample	<i>d</i> (nm)	σ_{RT} (Ω cm) ⁻¹	$\sigma_{0,Mott}$ (Ω cm) ⁻¹	$T_{0,Mott}$ (K)	<i>s</i>	$R_{hop,Mott}$ (nm)	$\Delta_{hop,Mott}$ (meV)	$N(E_F)$ (m ⁻³ eV ⁻¹)	$R_{hop,Mott}/\xi$
L31	450	2.390	1.53×10^6	2.41×10^6	0.26	9.39	45	6.34×10^{24}	3.92
L48	260	0.443	1.01×10^9	1.55×10^7	0.27	19.6	72	4.32×10^{23}	6.26
L27	230	0.125	4.79×10^9	6.54×10^7	0.25	39.9	103	3.61×10^{22}	8.97

sputtering gas. The reactive gas partial pressure was kept constant at 6×10^{-4} mbar during the deposition [15,16]. For low temperature measurements, the samples were cooled in a continuous He flow cryostat (Cti-Cryogenics-Helix Technology Corporation). An Alpha-Step profilometer was used for measuring the film thickness. Temperature-dependent electrical conductivity was measured using planar-type samples. Measurements were performed with a Keithley 196 electrometer in a temperature of 13–320 K. Thin gold films, separated by a gap of 0.5 mm, were used as electrodes.

The samples were deposited with the same deposition rate, 0.02 nm/s, but different deposition times, resulting in different thicknesses (Table 1). The substrate temperature was not the same during the deposition of the studied samples. The samples significantly denoted by L27, L31 and L48 were deposited at 270, 310 and 480 °C, respectively [10].

3. Results

In a previous work [10], it has been shown that the present TiO₂ thin films exhibited a simple thermally activated conduction in a temperature range of 310–468 K. However, in lower temperatures (13–305 K), temperature dependence of the electrical conductivity of these TiO₂ thin films (not shown here) indicates that the conductivity over this range of temperature is not characterized by constant activation energy. As it can be seen from Ref. [10], no single law can fit the entire curve. This suggests that there are two types of conduction mechanisms contributing to the conductivity in different temperature ranges. These two mechanisms may be distinguished experimentally by operating in appropriate two temperature ranges.

In TiO₂ thin films, the charge carriers are localized within grains and, therefore, transport of charge carriers is likely to be dominated by the variable-range hopping (VRH) mechanism. In this case, the conductivity is generally in the form

$$\sigma = \sigma_0 \exp \left[-\left(\frac{T_0}{T}\right)^s \right], \tag{1}$$

where T_0 is a characteristic temperature coefficient and σ_0 is a pre-exponential factor. The value of the exponent *s* depends critically on the nature of hopping process. In practice, on hopping conduction it is assumed that σ_0 in Eq. (1) is independent of the temperature. However, hopping theory predicts that $\sigma_0(T) = \sigma_0 T^{-2s}$ [18].

In the case of VRH, if the density of states at the Fermi level is constant, $s = 1/4$ for a three-dimensional (3D) system and $s = 1/3$ for a 2D system (Mott VRH). In this case, for a 3D system conductivity model is expressed as [13]

$$\sigma = \sigma_0 T^{-1/2} \exp \left[-\left(\frac{T_0}{T}\right)^{1/4} \right], \tag{2}$$

T_0 is a characteristic temperature coefficient which depends on the density of states $N(E_F)$ at the Fermi level in the form [19]

$$T_{0,Mott} = \frac{18}{k_B \xi^3 N(E_F)}, \tag{3}$$

where ξ is the localization length and k_B is Boltzmann's constant. On the other hand, if there is a gap, the so-called ‘‘Coulomb gap’’ at the

Fermi Level, $s = 1/2$ for both 3D and 2D systems (ES VRH). Then, for a 3D systems ES VRH conductivity model is expressed as [20]

$$\sigma = \sigma_0 T^{-1} \exp \left[-\left(\frac{T_0}{T}\right)^{1/2} \right], \tag{4}$$

T_0 is a characteristic temperature coefficient which is given by

$$T_{0,ES} = \frac{2.8e^2}{k_B \xi \varepsilon}, \tag{5}$$

where ε is the dielectric constant.

Fig. 1 shows the plot of $\ln(\sigma T^{1/2})$ against $T^{-1/4}$. The plot of $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ was found to have been linear at high temperatures (100–305 K). This indicates that the conduction in TiO₂ thin

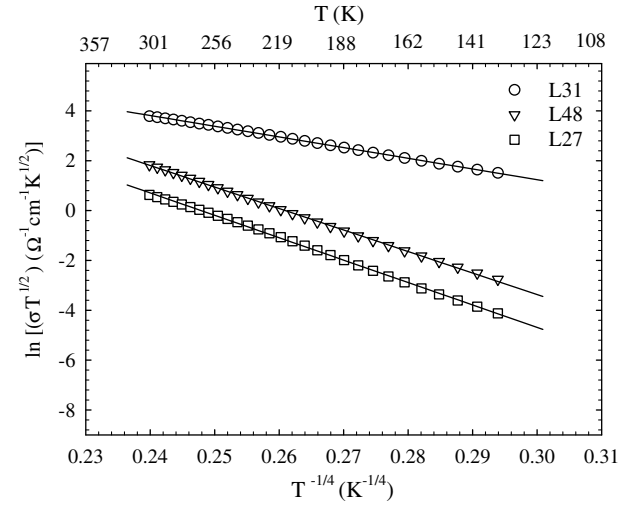


Fig. 1. Temperature dependence of the conductivity plotted as $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$. Solid lines are the best-fit lines with Eq. (2).

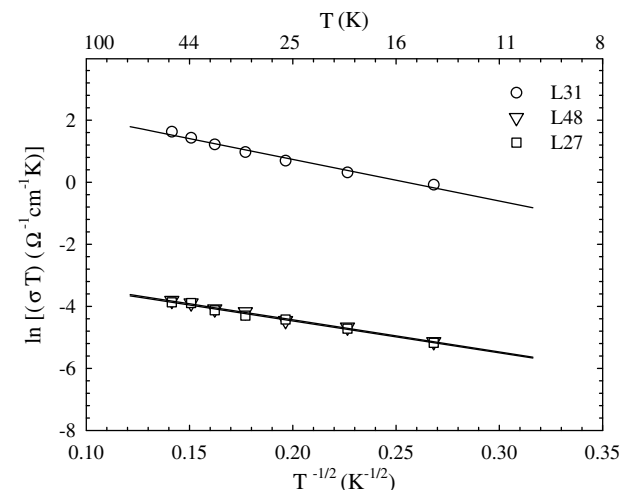


Fig. 2. Temperature dependence of the conductivity plotted as $\ln(\sigma T)$ vs. $T^{-1/2}$. Solid lines are the best-fit lines with Eq. (4).

Table 2
Values of the ES VRH conduction parameters

Sample	$\sigma_{0,ES} (\Omega \text{ cm})^{-1}$	$T_{0,ES} (\text{K})$	s	$R_{\text{hop},ES} (\text{nm})$	$\Delta_{\text{hop},ES} (\text{meV})$	$\Delta_C (\text{meV})$	$\xi (\text{nm})$	$R_{\text{hop},ES}/\xi$
L31	30.32	2.17×10^2	0.48	1.61	3.48	0.161	2.39	0.672
L48	0.115	1.16×10^2	0.51	1.55	2.54	0.025	3.15	0.494
L27	0.111	1.17×10^2	0.51	2.19	2.55	0.012	4.46	0.493

films is governed by Mott's VRH ($T^{-1/4}$ law) conductivity instead of a simple thermally activated hopping at high temperatures. As the temperature decreases below nearly between 80 and 110 K, there is a deviation from a conduction mechanism to another one. At low temperatures, when the measured data were plotted as $\ln(\sigma T)$ vs. $T^{-1/2}$ (Fig. 2) as indicated by the ES VRH $T^{-1/2}$ law, well-defined lines were obtained. Although the temperature dependence of the electrical conductivity of titanium dioxide films indicates that VRH occurs in a temperature range of 13–305 K, very nearly linear behavior on these plots is observed in a temperature range 125–305 K and 13–60 K, respectively.

In Figs. 1 and 2, a linear behavior is observed. However, it is difficult, to distinguish between the two regimes from this simple graphical analysis. In order to determine the value of the exponent s , σ_0 and T_0 in Eq. (1) more accurately, the conductivity data were analyzed in a similar way as described in Ref. [21]. By this way, the characteristic hopping parameters s , σ_0 , T_{Mott} and T_{ES} have been obtained. The results of fitting are given in Tables 1 and 2. The best fits were obtained for values of s in the vicinity of 1/4 and 1/2, in the high temperature regime and low temperature regime, respectively. This confirms that there can be Mott type of VRH at high temperatures and the ES type of VRH conduction at low temperatures in the studied samples.

4. Discussion

It can be seen from Table 1 that there is an increase of room-temperature conductivities (σ_{RT}) from 0.125 to 2.390 ($\Omega \text{ cm})^{-1}$, with the increase in the thickness of the films from 230 to 450 nm. To explain the differences observed in the electrical conductivities, it must be remembered that in polycrystalline thin films, transport mechanism of charge carriers is strongly influenced by grain size and the characteristics of grain boundaries [22]. The grain sizes depend on the deposition parameters. As the substrate temperature or the deposition time increases [10], we expect to obtain larger grains, with a smaller number of grain boundaries. The effect will be the decrease of the carriers scattering, and finally an increase of the electrical conductivity, as observed.

The total conductivity of the titanium dioxide films can be determined as the sum of the contributions from the Mott regime and ES regime. The conductivity is then expressed as

$$\sigma = \sigma_{0,\text{Mott}} T^{-2s} \exp \left[- \left(\frac{T_{0,\text{Mott}}}{T} \right)^s \right] + \sigma_{0,\text{ES}} T^{-2s} \exp \left[- \left(\frac{T_{0,\text{ES}}}{T} \right)^s \right]. \quad (6)$$

Using the values of characteristic hopping parameters s , σ_0 , T_{Mott} and T_{ES} given in Tables 1 and 2, the total conductivity of titanium dioxide films is given in Fig. 3. It can be seen from Fig. 3 that a good agreement is observed between the measured conductivity and the total conductivity predicted by Eq. (6). For all the samples $r^2 = 0.99$ ($r =$ correlation coefficient) were obtained, which indicate a satisfactory fit. Therefore, it is clear that the conductivity of titanium oxide films is governed by Mott's VRH mechanism at high temperatures, while the conduction mechanism changes from the Mott type to the ES type of VRH at low temperatures. This clearly suggests that titanium oxide thin films exhibit crossover from $T^{-1/4}$ to $T^{-1/2}$ dependence in the temperature range between 80 and 110 K.

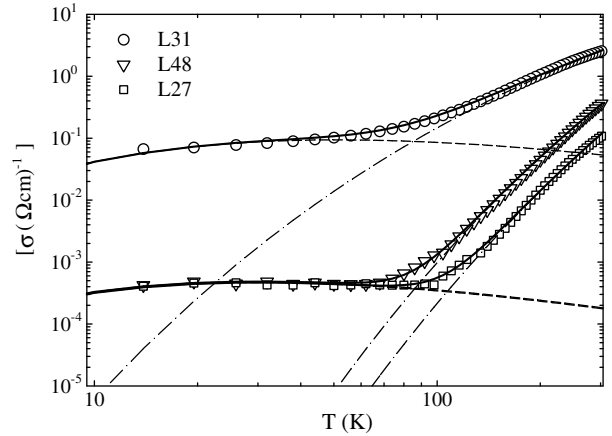


Fig. 3. Temperature dependence of the conductivity. Dash-dotted and dashed lines correspond to the fits to the experimental data by using the parameters given in Tables 1 and 2. Solid lines represent the total conductivity predicted by Eq. (6).

The hopping conduction is considered to be valid, if the hopping parameters satisfy the hopping conditions. For the ES type of VRH conduction, the temperature-dependent hopping distance (R_{hop}) and average hopping energy (Δ_{hop}) are calculated from Eqs. (7) and (8), respectively [14]

$$R_{\text{hop},ES}/\xi = \frac{1}{4} (T_{0,ES}/T)^{1/2}, \quad (7)$$

$$\Delta_{\text{hop},ES} = \frac{1}{2} k_B T (T_{0,ES}/T)^{1/2}. \quad (8)$$

The Coulomb gap energy (Δ_C) according to ES VRH theory [14] has been calculated from the following relation:

$$\Delta_C = e^3 N(E_F)^{1/2} / \epsilon^{3/2}. \quad (9)$$

Similarly, the temperature-dependent hopping distance (R_{hop}) and average hopping energy (Δ_{hop}) of the Mott type of VRH conduction are given as follows [19]:

$$R_{\text{hop},\text{Mott}}/\xi = \frac{3}{8} (T_{0,\text{Mott}}/T)^{1/4}, \quad (10)$$

$$\Delta_{\text{hop},\text{Mott}} = \frac{1}{4} k_B T (T_{0,\text{Mott}}/T)^{1/4}. \quad (11)$$

Kim et al. [23] measured dielectric constants (ϵ) of TiO_2 thin films with various ratios of the rutile phase. Our L27 and L31 samples are with 50%-rutile [10], and therefore the calculated dielectric constant (ϵ) is about 90 [23]. For L48, pure rutile structure [10], ϵ is about 127 [23]. Using these values of ϵ and $T_{0,ES}$ given in Table 2, localization length (ξ) can be obtained from Eq. (5). Then, other hopping parameters can be determined in both Mott VRH and ES VRH regime. These values are given in Table 1 and 2, respectively.

It can be seen from Table 1 that in the Mott regime, the Mott characteristic temperature $T_{0,\text{Mott}}$ increases with the decreasing conductivity. The increase in the characteristic temperature $T_{0,\text{Mott}}$ is reflected in the other hopping parameters as an increase in both hopping distance and average hopping energy, and as a decrease in the density of states. Also the obtained $T_{0,\text{Mott}}$ values are of the same order of magnitude as that found in a variety of titanium

oxide systems [24,25]. It is worth mentioning that the relation $R_{\text{hop,Mott}}/\xi \geq 1$, expected for VRH conduction, is satisfied with high $T_{0,\text{Mott}}$ values. $\sigma_{0,\text{Mott}}$ values, given in Table 1, are much larger; they vary from 1.53×10^6 to $4.79 \times 10^9 (\Omega \text{ cm})^{-1}$. Similar values of $\sigma_{0,\text{Mott}}$ were reported for various materials exhibiting high temperature VRH conduction. Zang and Tang [25] found that conductivity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ indicates a Mott VRH mechanism for $T > 90$ K. The fitting parameters $\sigma_{0,\text{Mott}}$ and $T_{0,\text{Mott}}$ were obtained as $2.48 \times 10^7 (\Omega \text{ cm})^{-1}$ and 5.38×10^7 K, respectively. Ziese and Srititiwarawong [26] found that $\sigma_{0,\text{Mott}}$ reaches $10^9 (\Omega \text{ cm})^{-1}$ for $T > 215$ K in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Hauser [27] suggested that $\sigma_{0,\text{Mott}}$ may reflect to a much greater extent than T_0 , the defect structure of the Sb films deposited by sputtering method.

In the ES VRH regime, the hopping parameters ($T_{0,\text{ES}}$, $R_{\text{hop,ES}}$, $\Delta_{\text{hop,ES}}$, ξ and Δ_C) are not significantly affected with the decreasing conductivity as seen in Table 2. It should be noted that the obtained parameters for both the Mott and the ES types of VRH are of the same order of magnitude as those found in a variety of systems [11,24–32]. Localization length (ξ) given in Table 2 is of the order 10^{-9} m, which is consistent with the expected magnitude in VRH regime [28]. However, the low values of $T_{0,\text{ES}}$ imply that localization length (ξ) is greater than $R_{\text{hop,ES}}$ in the examined temperature range of all the samples. The criterion $R_{\text{hop,ES}}/\xi \geq 1$ is not satisfied. This situation was also observed in three-dimensional (3D) films; In_xO_y [33], Ge [34] and CdSe [35] in either Mott VRH or ES VRH regime.

In addition to this, the obtained hopping parameters should satisfy the 3D VRH criterions

$$\Delta_{\text{hop}} > k_B T \text{ or } T_0 > T \quad (12)$$

and

$$d > R_{\text{hop}}. \quad (13)$$

In Eq. (13), film thickness (d) is a significant parameter to decide whether dimensionality of VRH is 3D. If $d \ll R_{\text{hop}}$ in a system, VRH tunneling can occur [36]. Note that our samples are of 3D, since the two conditions are well fulfilled at both Mott and ES regime for TiO_2 thin films. The average hopping energy (Δ_{hop}) and film thickness (d) are considerably greater than $k_B T$ and hopping distance (R_{hop}), respectively. Also, the obtained values of the exponent s given in Tables 1 and 2 are very close to 1/4 and 1/2, which confirm the availability of 3D VRH in the studied samples.

However, in the ES regime, the criterion $\Delta_C > \Delta_{\text{hop}}$ is not satisfied. The Coulomb gap is not greater than the average hopping energy. A small value of the Coulomb gap is due to the large value of the dielectric constant of TiO_2 . The crossover from Mott to ES VRH conduction with a small Coulomb gap has also been reported for TiO_2 and other systems [29,37]. Since the Coulomb gap is reduced at the metal–insulator (M–I) transition [31], our titanium oxide thin films are therefore close to the M–I transition.

5. Conclusion

In this study, the electrical properties of titanium dioxide thin films have been investigated by temperature-dependent conductivity. It has been observed that the temperature dependences of electrical conductivity of the investigated films exhibit a crossover

from $T^{-1/4}$ to $T^{-1/2}$ dependence in the temperature range between 80 and 110 K. Characteristic parameters describing conductivity, such as the characteristic temperature (T_0), hopping distance (R_{hop}), average hopping energy (Δ_{hop}), Coulomb gap (Δ_C), localization length (ξ) and density of states ($N(E_F)$), were determined, and their values were discussed within the Mott and ES VRH regimes.

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