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High temperature variable-range hopping conductivity in undoped TiO_2 thin film

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Electrical conductivity measurements in an undoped titanium dioxide thin film have been carried out as a function of temperature (180- 320 K). The film has been deposited onto glass substrates by a d.c. magnetron-sputtering method, using water vapors as reactive gas. Analysis of the data showed that temperature dependence on the electrical conductivity was well described by the Mott type variable range hopping (VRH) law, suggesting that the density of states at the Fermi level is constant in this temperature range.

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1. Introduction

Titanium dioxide (TiO_2) is attracting much attention because of its importance in both scientific and technological aspects. This material is used in a variety of applications such as optical filters [1], solar cells [2] and optical coatings [3]. In spite of tremendous success in device development, there is still its use in limited electrical applications in the TiO_2, due to its low conductivity. The wide forbidden band gap of TiO_2 results in excellent transparency to visible light, but its electrical conductivity at room temperature is less than 1 $(\Omega\ \text{cm})^{-1}$ [4]. The development of methods for modification of electrical properties of thin films of oxides is of great interest. [5]. For TiO_2, electrical conductivity process is mainly explained in the terms of the simple thermally activated conduction mechanism at high temperatures, while it is due to hopping via impurity centres at low temperatures. In the other hand, later is possible for TiO_2 situation even above room temperature, due to its high energy gap in which compensation is nearly full.

In this work, we carried out electrical conductivity measurements in an undoped titanium dioxide thin film, and we show that indeed in the impurity band regime the conductivity is governed by Mott type VRH at studied temperature range.

2. Experimental

Undoped titanium dioxide film was deposited onto glass substrates by d.c. magnetron-sputtering method, using water vapors as reactive gas [6, 7]. For low temperature measurements the sample was cooled in a continuous He flow cryostat (Cti-Cryogenics-Helix Technology Corporation). The phase and crystal structure of film were identified by X-ray diffraction (XRD) with a Rigaku Geigerflex (CuK_{α}) computer-controlled diffractometer. 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 180-320 K. Thin gold films, separated by a gap of 0.5 mm, were used as electrodes.

3. Results and discussion

In order to determine conduction mechanisms in undoped TiO_2 thin film, the temperature dependent conductivity was measured in a temperature range of 180-320 K. Arrhenius plot of the measured conductivity (σ vs $10^3/T$) was given in Fig. 1. The film thickness (d) and the measured room temperature conductivity (σ_{RT}) were also quoted in Table 1. The dependencies of the electrical conductivity versus inverse temperature, $\sigma = f(10^3/T)$ were investigated in a wide range of temperature (from 180 to 320 K), using the relation:

$$\sigma = \sigma_a \exp\left(-\frac{E_a}{kT}\right) \qquad (1)$$

where E_a is the thermal activation energy of the electrical conduction and σ_a is a parameter depending on the semiconductor nature. We found that the Arrhenius plot was not able to describe the data temperature range between 180 and 320 K in the studied sample. Instead of this, VRH conduction mechanism dominates in studied sample.

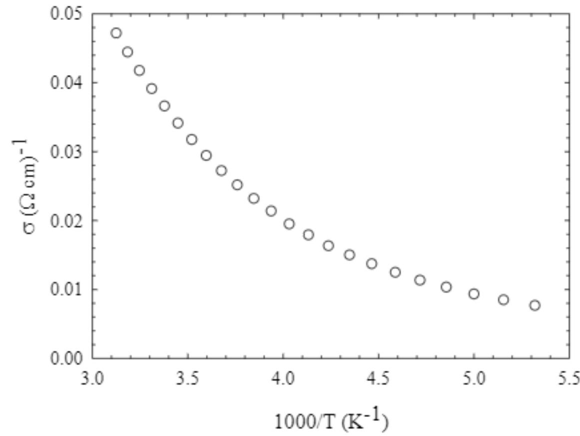

Fig. 1. Temperature dependence of the conductivity plotted as σ vs. $10^3/T$.

Table 1. Values of film thickness (d), room temperature conductivity (σ_{RT}) and values of the VRH conduction parameters obtained by analyzing the electrical conductivity data using the percentage deviation method.

d (nm)	σ_{RT} $(\Omega cm)^{-1}$	$N(E_F)$ $m^{-3}eV^{-1}$	$T_{0,Mott}$ (K)	$R_{hop, Mott}$ (nm)	$\Delta_{hop,Mott}$(meV)	s
295	0.003	8.81×10^{24}	2.37×10^{7}	6.96	80	0.236

As is well known, the general form of the VRH conductivity is given by

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^s\right], \qquad (2)$$

where σ_0 is a pre-exponential factor and T_0 is a characteristic temperature coefficient. The value of the exponent s depends critically on the nature of hopping process.

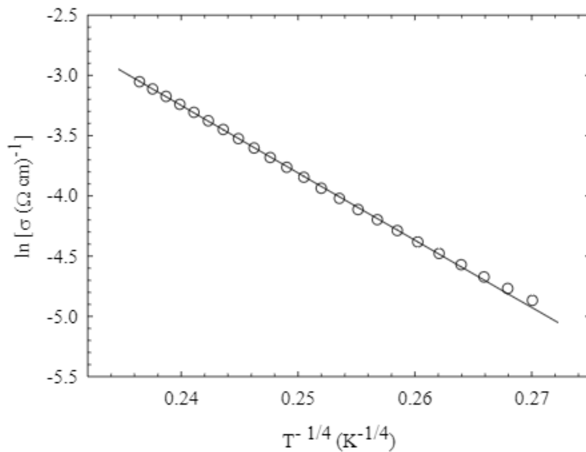

Fig. 2. Temperature dependence of the conductivity plotted as ln σ vs. $T^{-1/4}$. Solid lines correspond to the fit of Mott's law to the experimental data by using the parameters written in Table 1.

In the case of VRH, if the density of states at the Fermi level is constant, the VRH conductivity model is expressed with s = 1/4 in Eq. (2) (Mott law) [8]. T_0 is a characteristic temperature coefficient which depends on the density of states $N(E_F)$ at the Fermi level in the form [9]:

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

where ξ is the localization length and k_B is Boltzmann's constant.

On the other hand, if there is a gap at the Fermi Level, the VRH conductivity model is expressed with s =1/2 in Eq (2) (Efros-Shklovskii (ES) law). Similarly, T_0 is a characteristic temperature coefficient of the ES type of VRH conduction is given as follows [10]:

$$T_{0,ES} = \frac{2.8e^2}{k_B \xi \varepsilon}, \qquad (4)$$

where ε is the dielectric constant and e is value of the elementary charge of electron.

It was difficult to infer whether the Mott law or the Efros-Shklovski law was applicable to crystalline semiconductors. For a proper analysis one should use either Mott law or the Efros-Shklovski law explicitly, it must be determined exponent s with more precision. In order to obtain the exponent s with more accuracy, the experimental values of conductivity σ_i, and temperature T_i

were fitted to a curve of the form of Eq. (2) using σ_0, T_0 and s as adjustable parameters. The fitting procedure was as follows. Taking an arbitrary value of the parameter s, the relation was transformed variables using standard least-squares procedures. The validity of the fit was tested by a procedure proposed by Finlayson and Mason [11].The percentage deviation of the fitted curve from experimental points was calculated using the expression

$$\% dev = \left[\frac{1}{n} \sum_{i=1}^{n} \frac{100}{\sigma_i} \left\{ \sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T} \right)^s \right] - \sigma_i \right\}^{1/2} \right]$$

By this way the characteristic hopping parameters s, σ_0 and $T_{0,Mott}$ have been calculated. These were shown in Table 1. The best fits were obtained for values of s in the vicinity of 0.25. It clearly confirmed that there is Mott VRH conductivity in the sample in the temperature range between 180 and 320 K. The obtained $T_{0,Mott}$ value is of the same order of magnitude as found in variety of titanium oxide systems [12-14].

A good fit of the measured data is essential but not sufficient criterion for applicability of the VRH theory. The hopping parameters should satisfy the Mott requirements. Knowing $T_{0,Mott}$ and taking a reasonable value for ξ such as 10^{-9}m [15], $N(E_F)$ can be obtained from Eq. (3). Then, it is now possible to estimate other hopping parameters such as hopping distance $(R_{hop,Mott})$ and the average hopping energy $(\Delta_{hop,Mott})$[9]:

$$R_{hop,Mott} / \xi = \frac{3}{8} (T_{0,Mott} / T)^{1/4}, \qquad (5)$$

$$\Delta_{hop,Mott} = \frac{1}{4} k_B T (T_{0,Mott} / T)^{1/4}, \qquad (6)$$

Density of states $(N(E_F))$, the calculated value of hopping distance $(R_{hop,Mott})$ at 200 K and the corresponding value of average hopping energy $(\Delta_{hop,Mott})$ were shown in Table 1. In addition to this the obtained hopping parameters should satisfy the three dimension VRH criterions;

$$\Delta_{hop,Mott} > kT \text{ or } T_0 > T, \qquad (7)$$

and

$$d > R_{hop,Mott}. \qquad (8)$$

It can be seen from Table 1 that both two conditions are well fulfilled at studied sample. The average hopping energy $(\Delta_{hop,Mott})$ and film thickness (d) are considerably greater than k_BT and hopping distance $(R_{hop,Mott})$, respectively.

4. Conclusion

In this study, temperature dependences of electrical conductivity of undoped titanium dioxide have been investigated. The conductivity of the sample follows Mott's VRH conduction low in a temperature range between 180 and 320 K. This is confirmed by the value of VRH exponent, s, around 0.25.

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