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Non-adiabatic small polaron hopping conduction in Nb-doped TiO_2 thin film

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ABSTRACT

Transport properties of Nb-doped titanium oxide (TiO_2) thin film, obtained by a RF sputtering technique, have been investigated by means of the electrical conductivity and the Seebeck coefficient as a function of temperature (13–425 K). At high temperatures ($T>325$ K), temperature dependent behaviors of the electrical conductivity and the Seebeck coefficient confirm that the transport mechanism is the non-adiabatic small polaron hopping type. An excellent agreement between the theoretical and the experimental values of non-adiabatic polaron hopping energy ($W_H \approx 0.3$ eV) is obtained. The conductivity follows the Mott's variable range hopping conduction (VRH) at the temperature range of 200–325 K, while it exhibits a temperature-independent behavior at low temperatures ($T<200$ K). Various physical parameters of the present sample such as polaron radius, effective dielectric constant, polaron hopping energy, density of states at the Fermi level, polaron band width and polaron coupling constant are determined using small polaron hopping model.

1. Introduction

In the last decade, the transition metal oxides have received a great deal of attention due to their many technological applications [1–3]. TiO_2, an ionic transition metal oxide, is used in a variety of electronic applications such as solar cells [4] and photocatalysis [5]. The electrical conduction in the transition metal oxide materials is controlled by strong electron–phonon coupling which results in the formation of small polarons. The electrical conduction occurs by the hopping movement of small polarons between two different states of the transition metal ions in the temperatures higher than half of the Debye temperature [6]. In case of TiO_2, electrical conduction occurs by thermally activated small polaron hopping between Ti^{4+} and Ti^{3+} metal ions [7].

The electrical conductivity phenomenon has been studied in various Nb-doped materials by several groups [8,9], and it has been shown that the temperature dependence of the electrical conductivity can be explained well using the small polaron hopping model at high temperatures. It has been also reported that Nb doping induces a rise in the electrical conductivity due to electrons added from donor impurities in TiO_2 [10]. However, conductivity of TiO_2 is less than 10^{-7} $(\Omega\,\mathrm{cm})^{-1}$ at room temperature [10]. TiO_2 exhibits strong electron–phonon coupling that results low electron mobilities at room temperature. Since the mobility of TiO_2 is too small because of small polaron conduction in the material, electrical transport data are limited by the conductivity measurements [11]. Explaining the electrical properties of the transition metal oxides in a certain case requires the measurements of thermopower (Seebeck coefficient) and conductivity as a function of temperature. Then, a detailed investigation about the nature of charge carriers in transition metal oxides materials can be carried out. In order to get more information about the conduction mechanisms at high temperatures, the conductivity data of Nb-doped TiO_2 can be interpreted in terms of a phonon-assisted small polaron hopping model proposed by Mott [6]. On the other hand, it is possible to observe a change in conduction mechanism from small polaron hopping conduction to variable range hopping conduction (VRH) in transition metal oxides materials, as the temperature decreases.

The aim of the present work is to study the electrical conduction mechanism of Nb-doped TiO_2 thin film at the temperature range of 13–425 K. The temperature dependence of the Seebeck coefficient, which confirms the polaronic conduction, is investigated for the studied sample. The measured conductivity data are also analyzed in terms of the small polaron hopping conduction model at high temperatures ($325\,\mathrm{K}<T<425\,\mathrm{K}$), while Mott's VRH conduction model is used at the intermediate temperatures ($200\,\mathrm{K}<T<325\,\mathrm{K}$).

2. Experimental

The RF (13.56 MHz) sputtering technique has been used for depositing TiO_2 thin film. The target was a metallic titanium disk

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of 99.5% purity and 60 mm in diameter. Nb_2O_5 powder (99.9997%) was used, in order to obtain Nb-doped TiO_2 thin films [12]. The reactive gas (oxygen—99.998% purity) was maintained at a constant partial pressure of 0.03 Pa, the total pressure being set at 0.1 Pa. Argon (99.9997%) was the sputtering gas. The film has been deposited onto glass covered by 100 nm transparent indium tin oxide (ITO) (from Merck Balzers), at a temperature of 250 °C, with a deposition rate of 0.03 nm s^{-1}. The target to substrate distance was 250 mm. The RF power was 800 W.

X-ray diffraction (XRD) measurements have been carried out with a Rigaku Geigerflex computer-controlled diffractometer, with Cu K_α radiation. XRD patterns revealed a polycrystalline structure, with mixed anatase/rutile phases, which is consistent with its being deposited onto heated substrates. The weight percentage of the anatase phase is about 83% in the Nb-doped TiO_2 film [13].

The composition of the film has been investigated by electron probe micro-analysis. The calibration was made using the following standard materials: TiO_2, Nb_2O_3. The concentration value of impurity atoms represents a mean value obtained making measurements on several points for the sample. The studied sample is doped with 0.35 at% Nb [10].

In our experiments, the apparatus allows for determining the Seebeck voltage, ΔU, between two points of the film, having the temperature difference $\Delta T = T_2 - T_1$ [13]. The temperatures T_1 and T_2 were measured at the surface of the thin film, with the help of two thermocouples. In order to obtain the Seebeck voltage, a Keithley 6517A electrometer was used because of the high resistance of TiO_2 film [13]. Using the temperature independent relationship between the experimentally measured Seebeck coefficient and the fraction of reduced transition metal ions (C), C is calculated as 0.49 for the Nb-doped TiO_2 at the temperature range of 325–425 K.

Electrical resistance measurements were performed with a Keithley 617 electrometer at high temperatures (325–425 K) and with a Keithley 196 at low temperatures (13–325 K). Gold electrodes were used. As TiO_2 samples have big resistances, we used transverse geometry Au/TiO_2/ITO [10].

3. Results and discussion

Fig. 1 shows the temperature dependence of the conductivity for the Nb-doped TiO_2 thin film at the temperature range of 325–425 K. As shown in Fig. 1, the relationship ln (σT) against 1000/T is almost linear in the chosen temperature range, which indicates that the conduction mechanism of Nb-doped TiO_2 thin film is dominated by the thermally activated hopping small polarons. In this case, the conductivity data can be explained by Mott's small-polaron hopping model given for transition metal oxides [6]. According to this model, conductivity in the non-adiabatic regime is expressed as

$$\sigma = (\sigma_0/T)\exp(-W/kT), \tag{1}$$

where W is the activation energy and σ_0 is the pre-exponential factor given as

$$\sigma_0 = \nu_0 N e^2 R^2 C(1-C)\exp(-2\alpha R)/k, \tag{2}$$

where ν_0 is the optical phonon frequency ($\sim 10^{13}$ Hz), N is the concentration of the transition metal ions, C is the fraction of reduced transition metal ions, R is the average spacing between the transition metal ions given as $R = N^{-1/3}$ and α^{-1} is the localization length. In the adiabatic case, $\exp(-2\alpha R)$ reduces to 1 in Eq. (2). In order to explain the polaronic conduction mechanism in the studied Nb-doped TiO_2 thin film, Eq. (1) is fitted to measured conductivity data. The values of W and σ_0 are deduced from the fit at Fig. 1 as 0.54 eV and 1.8×10^3 $(\Omega\,\mathrm{cm})^{-1}$, respectively.

In a previous work [13], temperature dependent Seebeck coefficient was investigated for the Nb-doped TiO_2. In that study, a negative Seebeck coefficient was observed and it was nearly independent of temperature at the temperature range of 325–425 K, while it was decreased with the decreasing temperature below 325 K [13]. A negative Seebeck coefficient indicates n-type semiconductor i.e. the majority of charge carriers are electrons. In addition, temperature independence of Seebeck coefficient results very small activation energy, which can be neglected when compared with the activation energy (W) obtained from conductivity data. This suggests that the carriers in Nb-doped TiO_2 move by hopping in the localized states, and the electrical conduction can be interpreted in the frame of strong electron–phonon coupling that forms small polarons [14]. The relationship between the temperature independent Seebeck coefficient (S) and the fraction of reduced transition metal ions (C) was suggested by Heikes et al. [15] as

$$C = \left[1 + \exp\left[\frac{e(S - S_0)}{k}\right]\right]^{-1}, \tag{3}$$

where e is the electron charge, k is Boltzmann's constant and S_0 is a constant of proportionality between the heat transfer and the kinetic energy of an electron. $S_0 \geqslant 2$ suggests hopping due to large polaron and $S_0 < 1$ suggests the existence of small polaron. However, S_0 is generally predicted to be smaller than the S. From the experimental studies, there is considerable evidence that S_0 is negligible in the Eq. (3) [16,17]. Hence, we have simply approximated it as zero. Using the temperature independent Seebeck coefficient data [13], from Eq. (3) we can estimate a value of C as 0.49 for the Nb-doped TiO_2. By using Eq. (2), and taking the values of $\nu_0 = 10^{13}$ Hz, $C = 0.49$ and a reasonable value for α (such as 20 nm^{-1}) [18–20] for transition metal oxide doped materials, the average spacing between the transition metal ions, R, is determined to be 0.3 nm. The obtained value of R is of the same order of magnitude as found in variety of transition metal oxide systems [1,20,21]. However, if α would be assumed to be zero, the value of R would be unphysical. So, it can be expected that the non-adiabatic hopping conduction mechanism is presented in the studied sample. Now, polaron radius (r_p) can be calculated as 0.12 nm for the Nb-doped TiO_2 thin film using by relation [22]

$$r_p = \left(\frac{\pi}{6}\right)^{1/3}\frac{R}{2}. \tag{4}$$

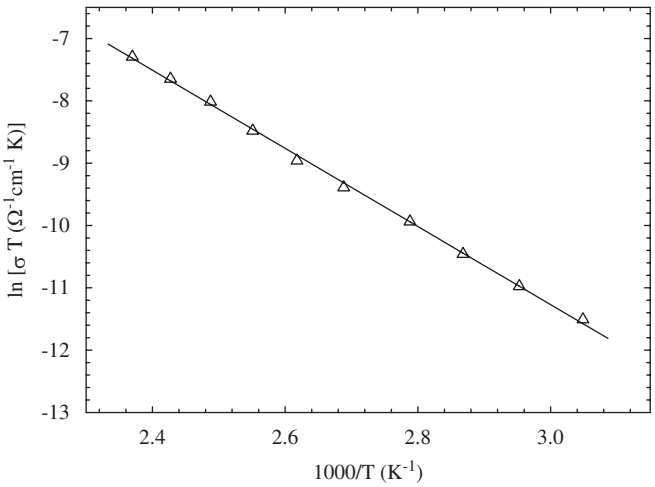

Fig. 1. Dependence of ln(σT) on reciprocal temperature for Nb-doped TiO_2. The line is least square fit to the data.

The value of effective dielectric constant ε_p is given by

$$\frac{1}{\varepsilon_p}=\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_s}, \tag{5}$$

where ε_∞ and ε_s high and static dielectric constant of the sample, respectively. In previous studies [23,24], values of ε_s and ε_∞ were reported as 371 and 5.93, respectively, for Nb-doped TiO_2. Using these values, ε_p can be calculated easily as 6. On the other hand, we can estimate value of ε_p as 5.54, considering Mott's small polaron hopping model with the relation by [6]

$$\varepsilon_p=\frac{e^2}{4Wr_p}. \tag{6}$$

Actually, the difference between the two values of ε_p is not large, which may confirm that the conduction mechanism of the studied sample can be explained by small polaron hopping model. Assuming a strong electron–phonon interaction, Austin and Mott [25] proposed that

$$W=W_H+W_D/2 \quad (\text{for } T>\theta_D/2),$$

and

$$W=W_D \quad (\text{for } T<\theta_D/4), \tag{7}$$

where W_H is the polaron hopping energy, W_D is the disorder energy arising from the energy difference of neighbors between two hopping sites and θ_D is the Debye temperature (530 K for TiO_2 [26]). The polaron hopping energy, W_H, is given as [27]

$$W_H=(e^2/4\varepsilon_p)(r_p^{-1}-R^{-1}). \tag{8}$$

From Eq. (8), the value of W_H is obtained as 0.32 eV for Nb-doped TiO_2. Recently, Deskins et al. [7] have applied a computational methodology that was proven to be successful for oxide materials. They have theoretically calculated the value of non-adiabatic activation energy nearly as 0.3 eV for both rutile and anatase form of TiO_2. Actually, the estimated our experimental finding (0.32 eV) is well consistent with the theoretical finding (0.3 eV) for Nb-doped TiO_2.

With the values of W and R, the density of states, $N(E_F)$ at the Fermi level is calculated using the relation [28]

$$N(E_F)=\frac{3}{4\pi R^3 W}. \tag{9}$$

The estimated value of $N(E_F)$ is $6.98\times10^{21}\,\text{eV}^{-1}\,\text{m}^{-3}$ for Nb-doped TiO_2. This value is of the same order of magnitude as found in variety of transition metal oxide doped materials [1,19]. It is difficult to decide whether the small hopping conduction is in the adiabatic or non-adiabatic region, merely using the temperature dependence of conductivity data. To better understand the nature of hopping conduction for the studied sample, it is necessary to perform a detailed analysis with using the following relations [29]:

$$J>\left(\frac{2kTW_H}{\pi}\right)^{1/4}\left(\frac{h\nu_0}{\pi}\right)^{1/2} \quad \text{(adiabatic)},$$

$$J<\left(\frac{2kTW_H}{\pi}\right)^{1/4}\left(\frac{h\nu_0}{\pi}\right)^{1/2} \quad \text{(non-adiabatic)}, \tag{10}$$

where J is the polaron band width. In the evaluation of the term on the right-hand side of Eq. (10) at 330 K, a value of 0.034 eV is obtained. On the other hand, J can be estimated independently using Dhawan's formula [27]

$$J\approx e^3(N(E_F)/(\varepsilon_p)^3)^{1/2}. \tag{11}$$

By using the previously obtained $N(E_F)$ and ε_p values in Eq. (11), J is calculated as 0.0033 eV. Since $J<0.034$ eV, we conclude that the conduction in Nb-doped TiO_2 is due to small polaron in the non-adiabatic regime.

The small polaron coupling constant γ_p, which is a measure of the electron–phonon interaction, can be estimated from the relation $\gamma_p=2W_H/h\nu_0$ [6]. The estimated value of γ_p is 16.1. Since γ_p is higher than 4 [28], there is a strong electron–phonon interaction in the present system. With the value of γ_p, the ratio of the polaron mass (m_p) to the rigid-lattice effective mass (m^*) can be obtained using the relation [28]

$$m_p=\frac{h^2}{8\pi JR^2}\exp(\gamma_p)=m^*\exp(\gamma_p). \tag{12}$$

The value of m_p/m^* is found as 9.82×10^6 which confirms that electron–phonon interaction is strong in the Nb-doped TiO_2 thin film. When non-adiabatic small polaron mechanism is operative, the carrier mobility is given by [30]

$$\mu=\left(\frac{eR^2}{kT}\right)\left(\frac{1}{\hbar}\right)\left(\frac{\pi}{4W_HkT}\right)^{1/2}J^2\exp(-W/kT). \tag{13}$$

The carrier density is also calculated, using the relationship $N_c=\sigma/e\mu$. The values of μ and N_c are estimated as $1.2\times10^{-9}\,\text{cm}^2/\text{V s}$ and $8.45\times10^{21}\,\text{cm}^{-3}$ at 420 K, respectively. The mobility is much smaller than $1\,\text{cm}^2/\text{V s}$ as predicted by small polaron model [6].

In the small polaron system, the conduction changes from the thermally activated small polaron hopping to the VRH conduction, with decreasing temperature [31]. According to the hopping theory, the VRH is generally to be valid at low temperatures [28]. However, it is possible for TiO_2 situation even above room temperature; due to its high-energy gap in which compensation is nearly full [11,32]. We, therefore, attempt to fit the Mott's VRH model to the experimental data of the Nb-doped TiO_2 thin film at the temperature range of 200–325 K. In the Mott's VRH model, the density of states at the Fermi level is assumed to be a constant. According to the Mott's VRH model, the conductivity is given as [28]

$$\sigma=\sigma_0\exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right], \tag{14}$$

where T_0 is a characteristic temperature coefficient which depends on the density of states $N(E_F)$ at the Fermi level. It is given as [28]

$$T_0=\frac{18\alpha^3}{kN(E_F)}. \tag{15}$$

Fig. 2 shows $\ln(\sigma)$ against $T^{-1/4}$ for the Nb-doped TiO_2. At high temperatures, Mott's VRH model fits to the conductivity very well as shown solid line in Fig. 2. At lower temperatures ($T<200$ K) the activation energy for the conductivity tends to zero and the VRH is not able to fit conductivity data of Nb-doped TiO_2. This temperature independent conductivity behavior is consistent with a behavior expected for small polaron conduction [31]. A similar temperature dependent conductivity behavior was also reported for $TiO_{2-\delta}$ [33].

A good fit of the measured data is essential but not sufficient criterion for applicability of the Mott's VRH model. The hopping parameters should satisfy the Mott's requirements ($R_{hop}\alpha\geqslant1$ and $W_{hop}>kT$). Here, R_{hop} is the temperature-dependent hopping distance and W_{hop} is the average hopping energy. These hopping parameters are given as [28]

$$R_{hop}=\left[\frac{9}{8\pi N(E_F)\alpha kT}\right]^{1/4}, \tag{16}$$

$$W_{hop}=\frac{3}{4\pi R_{hop}^3 N(E_F)}. \tag{17}$$

The characteristic temperature, T_0, is determined as 4.32×10^8 K from the slope of plot in Fig. 2. Using $\alpha=20\,\text{nm}^{-1}$ [18–20], we can

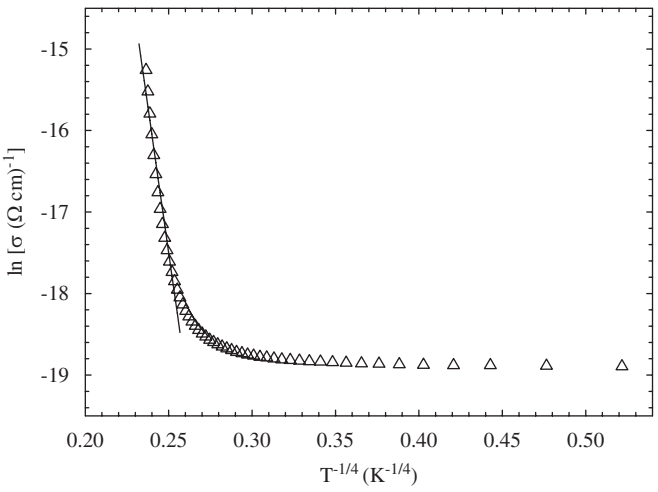

Fig. 2. Temperature dependence of the conductivity plotted as $\ln\sigma$ vs. $T^{-1/4}$. Solid line is the best-fit line with Eq. (14) at the temperature range between 200 and 325 K.

easily estimate the quantity of $N(E_F)$ as $6.04\times10^{19}\,\mathrm{eV}^{-1}\,\mathrm{m}^{-3}$ in the VRH regime. With $N(E_F)$, the values of $R_{hop}\alpha = 13$ and $W_{hop} = 224$ meV are obtained at 300 K. The requirements $R_{hop}\alpha \gg 1$ and $W_{hop} > kT$, which are essential for the validity of Mott's VRH model, is clearly satisfied.

4. Conclusion

The temperature dependence of the Seebeck coefficient and the conductivity are investigated in the Nb-doped TiO_2 thin film. The temperature dependence of the Seebeck coefficient and the conductivity data indicate that small polaron hopping conduction takes place at high temperatures ($T > 325$ K). The conductivity data of Nb-doped TiO_2 is successfully analyzed by the non-adiabatic small polaron hopping conduction theory in the examined temperature range. An excellent agreement between the theoretical and the experimental values of non-adiabatic polaron hopping energy ($W_H \approx 0.3$ eV) is obtained. Various physical parameters of the present sample are found to be appropriate for small polaron hopping regime. It has been found that the conduction mechanism at the temperature range of $200\,\mathrm{K} < T < 325\,\mathrm{K}$ in Nb-doped TiO_2 is due to variable range hopping mechanism. For temperatures below 200 K, the conductivity of Nb-doped TiO_2 exhibits a temperature independent behavior.

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