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Modeling the electrical transport in epitaxial undoped and Ni-, Cr-, and W-doped TiO₂ anatase thin films

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Electrical transport in undoped and Ni-, Cr-, and W-doped TiO₂ thin films on SrTiO₃(001) is modelled either with the sum of two thermally activated processes with exponential temperature dependence of conductivity, or with the sum of three-dimensional Mott variable-range hopping (VRH) and an activated process with low activation energy. The latter is interpreted for both models as small polaron hopping ($< \theta_D/4$). According to reduced chi-square values, the double activated model is superior for data of higher ordered films grown at 540 and 460 °C. For lower growth temperature, VRH plus activated conductivity fits partly better. For all dopants, n-type conductivity is observed. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4892811>]

TiO₂ is an interesting material for future electronic applications, such as memristor devices.¹ Doped TiO₂:Nb is a promising transparent conducting oxide with performance similar to In_{2-x}Sn_xO₃ and ZnO.² Furthermore, TiO₂:Nb is commonly used as n-type metal oxide semiconductor in new generation solar cells.³ The electrical transport of TiO₂ in its different polymorphs (anatase, rutile and brookite) was found to vary from metallic to insulating in dependence on the crystalline structure, growth conditions and type of dopant. Different models have been used to explain the experimental conductivity behaviour.²⁻¹⁰ A resistivity minimum in undoped epitaxial TiO₂ films grown under low oxygen pressure by pulsed laser deposition (PLD) could be reasonably explained by Mott variable-range hopping (VRH).⁴ Polycrystalline film samples with varying anatase to rutile ratios showed VRH in combination with small polaron hopping.^{5,6} The conductivity mechanisms of anatase single crystals and epitaxial thin films were explained by either large polaronic transport,^{7,8} metallic behaviour,² or metal-insulator transitions.^{9,10} In the search for p-type conducting TiO₂ doping with Al, Cr, and Ni was investigated in Refs. 11 and 12, where p-type conductivity was concluded only indirectly from field-effect transistor measurements. There are few other reports on electrical properties of doped TiO₂, such as epitaxial Fe- and Ni-doped films,¹³ Ni-doped ceramic,¹⁴ Cr-N codoped,¹⁵ and W-doped films.^{16,17}

In this Letter, we provide a comprehensive modeling of the conductivity mechanisms of undoped, and Ni-, Cr-, and W-doped TiO₂ thin films grown epitaxially on 5 × 5 mm² SrTiO₃(001) (STO) substrates. We use two fit models, i.e., first the sum of two thermally activated processes, and second VRH plus polaron hopping. The goodness of fits is discussed by means of reduced chi-square values in dependence on crystalline order of films.

The films were grown by PLD with varying growth temperatures from room temperature (RT) to 640 °C. The target was prepared by solid-state synthesis of TiO₂ powder (99.995% purity) together with pure NiO, Cr₂O₃ (99.97%),

or WO₃ powder (99.998%), to realize 5 at. % concentration of the dopants. Energy dispersive x-ray spectroscopy (EDX), measurements were done on Ni- and Cr-doped films grown at $T_S = 540$ °C, which revealed a 50% reduction of the dopant element concentrations during transfer from the PLD target into the film. The lateral homogeneity of chemical dopant distribution for Ni and Cr was examined by EDX mapping over 1 μm² film areas using a field emission electron microscope. See supplementary material for typical EDX maps.³⁸ No indication for dopant enrichment at grain boundaries can be deduced. The STO single crystals were HF-etched and annealed prior to PLD to ensure a TiO₂-terminated monolayer terrace structure at the surface. 30 000 laser pulses were applied during PLD which yield films thicknesses in the range of 450 to 650 nm as estimated with a surface profiler DEKTAK 3030. For more details about used PLD methods see Refs. 18 and 19. For the electrical measurements, 80 nm thin gold contacts were DC-sputtered at the corners of the films.

For X-ray diffraction (XRD) measurements, a Philips X'Pert diffractometer with focussing Bragg-Brentano optics with secondary graphite monochromator was employed. RT and temperature-dependent (30 to 300 K) electrical conductivity and Hall effect was measured in van der Pauw geometry.

The surface morphology and crystalline structure were studied for films grown at different substrate temperatures (T_S) using AFM images and XRD 2θ - ω -scans, see Fig. 1. The films grown above room temperature are granular, with increasing grain size by increasing growth temperature, as Fig. 1(a) shows. The film grown at room temperature shows a smooth line structure with monolayer terraces of a few Å step height. The Ni-, Cr- and W-doped films exhibit almost similar XRD patterns to Fig. 1(b) and are not shown here. The films grow preferentially in the anatase phase of TiO₂ with the following out-of-plane orientational relationship: TiO₂[001]_{anatase} || STO[001]. Only (004)_{anatase} and (008)_{anatase} peaks could be indexed in the XRD 2θ - ω -scans. The in-plane epitaxial relationship was determined to be TiO₂[100]_{anatase} || STO[100] by φ -scans of the asymmetric STO (110) and the (101)_{anatase}

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FIG. 1. (a) AFM images $10 \times 5 \mu\text{m}^2$ of Ni-doped TiO₂ films grown at the indicated temperatures at 6×10^{-5} millibar. The z-height full scales are 2.0; 2.9; and 180 nm for $T_s = 23$; 340; and 640°C , respectively. See supplementary material³⁸ for AFM images for other dopants. (b) XRD 2θ -scans (Cu K α) of undoped TiO₂ films grown at an oxygen partial pressure of 6×10^{-5} millibar and growth temperatures T_s as indicated. Peaks labelled A and R correspond to the anatase and rutile phase of TiO₂, respectively. The inset is a zoom-in on the anatase (004)-peak. The samples with rutile peaks grown at 640°C were not included in the conductivity investigations, see Fig. 3.

peaks (not shown). In addition, minor peaks of the rutile phase of TiO₂ were detected for the highest T_s . However, their intensity is several orders of magnitude lower as compared to the anatase peaks (Fig. 1), compare.^{13,20} This is due to the lower in-plane lattice mismatch of anatase and STO (+3.4%), as compared to rutile and STO (−14.6%, see JCPDS 2.00 card No. 84-1286, 84-1284, and 84-0444). With decreasing T_s , the intensity of the anatase-peaks decreases while the full width at half maximum (FWHM) increases (see Fig. 1). For growth below 300°C , the films are x-ray amorphous.

Films grown at oxygen partial pressures above 6×10^{-5} millibar up to 0.02 millibar were electrically highly insulating ($R > 10^{10} \Omega$) and any conductivity measurement failed (cf. Refs. 4 and 21). Hence, we only consider films grown at the lowest oxygen partial pressure of 6×10^{-5} millibar. Undoped TiO₂ (anatase) has a wide bandgap of 3.2 eV.⁹ It was shown that under Ti-rich, i.e., oxygen deficient growth conditions the number of oxygen vacancies and Ti interstitials increases (Refs. 4 and 22, see also Ref. 23), which act as donors in TiO₂.^{9,10,22,24} These defects introduce electrons which move via band conduction or hopping processes. With the used setup for DC Hall effect, the dominating charge carrier type in our samples could not be clearly determined, due to low Hall-mobilities below $1 \text{ cm}^2/\text{Vs}$ typical for hopping or small polaron conduction processes.^{25,26} In agreement with Refs. 9 and 10, we can confirm only n-type conductivity for all our films.

Fig. 2 shows RT conductivities of films grown at T_s from RT to 530°C . The measured conductivities vary by almost five orders of magnitude from 10^0 to 10^4 Sm^{-1} with T_s . For films grown above 500°C , i.e., with highest crystalline quality, the variation of conductivity with doping is surprisingly small, i.e., close to the performance deviations of different films grown with nominally identical PLD parameters such as substrate temperature and oxygen partial pressure. In contrast, films grown at RT show a significant decrease in conductivity by about one order of magnitude, due to the loss of crystalline ordering, as shown in Fig. 1. The Cr-doped films show the lowest conductivities in comparison to the undoped and Ni- and W-doped films grown at

the same conditions. Since Ti is in the Ti^{4+} state in the TiO₂-lattice,²⁷ Ni and Cr could act as acceptors²⁸ when built in at the Ti site, i.e., Ni in the Ni^{2+} state, and Cr in the Cr^{3+} or Cr^{2+} state. This could explain the decrease in conductivity for the Cr-doped films by compensation of donors. However, the assignment of dopant type of Ni and Cr defects in TiO₂ is controversially discussed in density functional theory calculations.^{28–30} W should behave as a donor as W^{5+} or W^{6+} when built in at a Ti site.

To obtain further insight into the transport properties, the temperature-dependent conductivity was measured from 300 K down to about 30 K (Figs. 3(a)–3(c)). Films grown at T_s of 530, 460, and 340°C were selected to cover the effect of crystalline order of the samples (cf. Fig. 1). Again, the general behaviour does not depend much on the dopant except Cr, as discussed already above with Fig. 2. Within the given temperature range, conductivity increases with decreasing T_s . It is apparent that the conductivity cannot be modelled with a single activation energy over the entire temperature range, i.e., $\sigma(T) \sim \exp(-E/k_B T)$. Instead, we have to consider a low temperature regime with low activation energy, and a high temperature mechanism ($T > T_X$) with

FIG. 2. Electrical conductivity at RT of undoped and doped TiO₂ films as indicated vs. substrate temperature T_s during PLD growth. All films were grown at an oxygen partial pressure of 6×10^{-5} millibar.

FIG. 3. (a)–(c) Arrhenius-plots of the electrical conductivity of TiO₂ films, doping, and substrate temperature T_s as indicated. Dashed lines are fits according to Eq. (1). (d) Arrhenius plots of the electrical conductivity for Ni-doped TiO₂ films grown at various substrate temperatures T_s as indicated. Fits according to Eqs. (1) and (4) are included for comparison of the models as indicated. The color code of graphs in (a) is valid for (a) to (c).

another activation energy. Therefore, the experimental conductivity was fitted first with a model of two thermally activated functions, see Ref. 21

$$\sigma(T) = \sigma_1 + \sigma_2 = \sigma_{01} \exp(-E_{A1}/k_B T) + \sigma_{02} \exp(-E_{A2}/k_B T). \quad (1)$$

σ_{0i} are temperature independent prefactors, E_{Ai} are activation energies ($i = 1, 2$), and k_B is Boltzmann's constant. The graphs according to Eq. (1) are included in Figs. 3(a)–3(c), and the parameters are collected in Table I. The transition temperature T_X is that temperature where both terms of (1) are equal, i.e., $\sigma_1 = \sigma_2$. The values of E_{A2} are very low compared to E_{A1} , expressing a weaker temperature dependence at lower temperatures, and thus, conduction different from simple thermal activation, see below.

The low temperature regime can be explained by the theory of small polarons^{26,31} with identical temperature dependence as in Eq. (1). Since in TiO₂ electrons and phonons are strongly interacting, the formation of polarons is possible and has been predicted theoretically^{22,32} and shown experimentally.^{5–8} Polarons are quasiparticles of electrons coupled to their own local polarization of the surrounding crystal. Interestingly, in ferroelectric hysteresis measurements of electrically insulating Ni- (and Cr-) doped TiO₂ films, we found hysteresis-like polarization-field dependencies which point to real field-dependent atomic displacements. Austin and Mott have proposed for small polaron conduction an activated behaviour with conductivity proportional to $\exp(-W/k_B T)$ with different regimes²⁶

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

$$W = W_D/2 \quad \text{for } T < \theta_D/4, \quad (3)$$

with W_H being the polaron hopping energy and W_D the activation energy for hopping arising from disorder, when states at adjacent sites have an energy difference. The Debye temperature θ_D is 530 K for TiO₂,^{6,33} such that $\theta_D/4$ is of the order of T_X . Below $\theta_D/4$, conduction takes place in a very narrow polaronic band consisting of localized polaronic states.²⁶ W_D is expected to be very low²⁶ consistent with the weak temperature dependence at low temperatures reported here, i.e., low E_{A2} . Also, the low Hall-mobility is predicted by the theory of small polaron conduction,^{25,26} as mentioned above. Between $\theta_D/2$ and $\theta_D/4$, the activation energy should gradually decrease to $W_D/2$ as the temperature is lowered. For temperatures larger than $\theta_D/2$, a transition to next-neighbour small polaron hopping is expected. Since $\theta_D/2$ is almost at RT for TiO₂, this distinction will not be further discussed here, as the presented data extend to only 300 K. In literature, both types of polaron hopping have been reported for doped and undoped TiO₂.⁵ For anatase, theory suggests non-adiabatic transfer modes.³² The increase of E_{A2} from $T_s = 530^\circ\text{C}$ to 460°C and to 340°C is also consistent within this model, since a higher activation energy is expected for increased structural disorder.

In the high temperature regime between $\theta_D/2$ and $\theta_D/4$, conductivity can also be modelled by a three-dimensional Mott-VRH mechanism³⁴ as an alternative to the thermally activated behavior σ_1 in Eq. (1). The corresponding combined fit model for VRH and small polaron hopping is the second fit equation used in Fig. 3(d). See supplementary material³⁸ for graphs of the other dopants

$$\begin{aligned} \sigma(T) &= \sigma_3 + \sigma_4 \\ &= \sigma_{03} \exp(-(T_0/T)^{1/4}) + \sigma_{04} \exp(-E_A/k_B T), \end{aligned} \quad (4)$$

TABLE I. Fit parameters in Eq. (1) describing the high temperature conductivity (σ_{01} , E_{A1}) and small polaron hopping in the low temperature region (σ_{02} , E_{A2}), see Figs. 3(a)–3(c). T_S is the substrate temperature during PLD growth. T_X denotes the temperature where both terms in Eq. (1) have the same value.

T_S (°C)	Dopant ^a	σ_{01} (Sm ⁻¹)	E_{A1} (meV)	σ_{02} (Sm ⁻¹)	E_{A2} (meV)	T_X (K)	χ^2
530	Nid	$26\,300 \pm 1600$	50.6 ± 1.3	1040 ± 25	0.44 ± 0.11	180	5×10^{-5}
	Ni	$25\,300 \pm 1300$	49.1 ± 0.4	1270 ± 10	1.21 ± 0.04	186	5×10^{-5}
	Cr	$28\,300 \pm 800$	85.8 ± 0.7	230 ± 3	2.94 ± 0.9	198	4×10^{-5}
	W	$13\,500 \pm 500$	53.4 ± 0.8	1105 ± 9	1.68 ± 0.04	240	6×10^{-5}
460	Nid	$43\,900 \pm 3200$	53.5 ± 1.2	245 ± 20	6.18 ± 0.34	105	3×10^{-3}
	Ni	$42\,300 \pm 2200$	40.2 ± 0.9	500 ± 50	6.02 ± 0.43	89	2×10^{-3}
	W	$25\,500 \pm 1100$	58.4 ± 0.8	280 ± 8	4.74 ± 0.18	138	5×10^{-4}
340	Nid	$(1 \pm 0.15) \times 10^5$	57.3 ± 2.6	770 ± 140	16.82 ± 0.69	97	0.02
	Ni	$41\,900 \pm 3900$	65.2 ± 1.9	1322 ± 85	22.01 ± 0.29	143	0.002
	Cr	6200 ± 1500	96.0 ± 4.3	10.5 ± 0.5	35.67 ± 1.12	110	0.034

^aNid stands for not intentionally doped.

where T_0 is the hopping temperature and σ_{03} is a temperature independent prefactor. All fit parameters (σ_{03} , T_0 , σ_{04} , E_A) of the combined VRH-polaron hopping model are given in Table II. T_0 is given in this model as³⁵

$$T_0 = \frac{18}{k_B N(E_F) a^3}, \quad (5)$$

where a is the localization length and $N(E_F)$ the density of states at the Fermi energy. Other important quantities are³⁵

$$\frac{r(T)}{a} = \frac{3}{8} \left(\frac{T_0}{T} \right)^{1/4} \quad (6)$$

and

$$\frac{\varepsilon_0(T)}{k_B T} = \frac{1}{4} \left(\frac{T_0}{T} \right)^{1/4}. \quad (7)$$

r is the average hopping distance and ε_0 the average hopping energy, which decreases with temperature and is, therefore, suited to connect the high- and low-temperature regimes of small polaron hopping, where the hopping activation energy W is to continuously decrease between $\theta_D/2$ and $\theta_D/4$.

See Table S1 in the supplementary material³⁸ for the additionally fitted parameters from Eqs. (5)–(7). The localization radius was assumed as 1.5 nm, equivalent to Bohr's radius in anatase TiO₂.⁹ The calculated values are similar to those reported for undoped TiO₂ films,^{5,6,36} and TiO₂:Ni ceramics.¹⁴ For the applicability of VRH, the requirements $r/a \geq 1$ and $\varepsilon_0/k_B T > 1$ have to be fulfilled, which is given for the fitted temperatures for all films. Furthermore, VRH requires compensated and localized states in the bandgap with a finite density of states. In TiO₂ hopping takes place from Ti³⁺ to Ti⁴⁺ (Ref. 32) with electrons introduced by oxygen vacancies or Ti interstitials. Compensation can arise from cationic defects such as Ti vacancies²⁷ or from doping with acceptors.

It should be noted that the conductivity data for lowest T_S (Fig. 3(c)) could be fitted reasonably well with a single VRH model in the entire temperature range from 300 down to 35 K, in contrast to the more crystalline films grown at higher T_S . This means that the effect of small polaron hopping on the fits with Eq. (4) goes down with decreasing growth temperature. While the fit parameters of the corresponding processes σ_{04} , E_A in Table II, and σ_{02} , E_{A2} in Table I agree reasonably well for the high $T_S = 540$ °C, they diverge increasingly for lower ordering, see Table II. This effect is expressed as well by the decreasing T_X values in

TABLE II. Variable range hopping and thermally activated model parameters according to Eq. (4) for the TiO₂ films grown at various substrate temperatures T_S as indicated, see Fig. 3(d) and supplementary material³⁸ for corresponding fits of all samples. T_X denotes the temperature where both terms in Eq. (4) are equal. The terms have no intersection for the film where no T_X value is presented.

T_S (°C)	Dopant ^a	σ_{03} (Sm ⁻¹)	T_0 (K)	σ_{04} (Sm ⁻¹)	E_A (meV)	T_X (K)	χ^2
530	Nid	$(6.7 \pm 1.8) \times 10^7$	$(2.7 \pm 0.3) \times 10^6$	910 ± 30	0 ± 0.2	172	5×10^{-4}
	Ni	$(3.9 \pm 0.7) \times 10^7$	$(2.1 \pm 0.2) \times 10^6$	1050 ± 30	0.6 ± 0.1	168	2×10^{-4}
	Cr	$(5.3 \pm 2.0) \times 10^9$	$(1.7 \pm 0.2) \times 10^7$	191 ± 9	1.9 ± 0.3	189	4×10^{-4}
	W	$(2.9 \pm 0.6) \times 10^7$	$(2.6 \pm 0.2) \times 10^6$	1000 ± 20	1.4 ± 0.1	226	9×10^{-5}
460	Nid	$(6.6 \pm 2.0) \times 10^8$	$(5.3 \pm 0.5) \times 10^6$	89 ± 15	2.5 ± 0.6	75	3×10^{-3}
	Ni	$(1.2 \pm 0.3) \times 10^8$	$(2.2 \pm 0.3) \times 10^6$	58 ± 30	0 ± 1.6	50	4×10^{-3}
	W	$(3.2 \pm 0.8) \times 10^8$	$(5.4 \pm 0.4) \times 10^6$	180 ± 15	3.1 ± 0.3	116	9×10^{-4}
340	Nid	$(2.9 \pm 0.4) \times 10^9$	$(6.9 \pm 0.3) \times 10^6$	0.7 ± 1.4	0.01 ± 5	29	0.005
	Ni	$(8.9 \pm 4.0) \times 10^8$	$(6.9 \pm 0.9) \times 10^6$	690 ± 120	22.3 ± 0.8	65	0.003
	Cr	$(1.2 \pm 0.3) \times 10^{11}$	$(5.0 \pm 0.2) \times 10^7$	$(0.6 \pm 5) \times 10^{-4}$	0 ± 21	–	0.011

^aNid stands for not intentionally doped.

Table II. This means that due to an increasing disorder or a decrease of grain size, the onset of small polaron hopping is shifted to lower temperatures, whereas the VRH is extended to a wider temperature range, compare.⁶ Only the Ni-doped film grown at 340 °C has a higher transition temperature of 65 K in comparison to the Ni-doped at 460 °C (50 K), see Table II. The hopping temperature T_0 is also increasing with decreasing T_S for all dopants (Table II), since it is inversely proportional to the localization length and the density of states at the Fermi energy. Structural defects are either causing a decrease of the density of states or a stronger localization of the charge carriers. In any case, variations in T_0 demonstrates the significance of crystalline quality on the transport properties of the films.

A decision on the suitability of the models according to Eqs. (1) or (4) can be made by closer inspection of the reduced chi-square (χ^2) values in Tables I and II. χ^2 of the double-activated model in Table I is clearly lower for all dopants and the two higher growth temperatures 540 and 460 °C. For 340 °C, the VRH plus polaron hopping according to Table II describes the experimental behaviour better, again except Ni-doped TiO₂.

It was already mentioned that doping with Ni, Cr, or W does not change the suitability of the different models itself. But, as shown in Tables I and II, for different dopant the characteristics are varied. It is interesting to note that Ni- and W-doping does not change E_A , T_0 , and ε_0 significantly, while Cr-doping increases these parameters (T_0 by about one order of magnitude, Table II). Probably, Cr can generate states in the bandgap^{29,30} leading to a decrease in the density of states at the Fermi energy or a stronger localization due to impurity-caused disorder. In terms of T_0 , doping with Ni and W changes neither the density of states in the band around the Fermi energy nor the localization radius. However, doping should generate states in the bandgap,²⁸ and p-type conduction in TiO₂ was indirectly confirmed for Ni-doping.^{11,12} Recently, a change from n- to p-type conductivity in N-doped TiO₂ was claimed by substitution of O by N based on anomalous Hall effect measurements.³⁷

In summary, we compared suitability of the double thermally activated model and the VRH plus small polaron hopping to describe the temperature dependent conductivity of epitaxial undoped and Ni-, Cr-, and W-doped TiO₂ anatase thin films. Using reduced χ^2 values, the double-activated model is superior for films with good crystallinity. With decreasing crystalline order, VRH plus polaron hopping describes the high-temperature data increasingly better. On this way, the transition temperature from VRH to the polaron process decreases remarkably with decreasing crystalline order of the films, from about 175 K down to about 45 K.

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