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Modeling the electric 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 In2-xSnxO3 and ZnO.2 Furthermore, TiO2:Nb is commonly used as n-type metal oxide semiconductor in next 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 Tₜ = 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 mm² 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 (Tₜ) 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.
peaks (not shown). In addition, minor peaks of the rutile phase of TiO$_2$ 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 x 10$^{-5}$ millibar up to 0.02 millibar were electrically highly insulating ($R > 10^{10}$ Ω) and any conductivity measurement failed (cf. Refs. 4 and 21). Hence, we only consider films grown at the lowest oxygen partial pressure of 6 x 10$^{-5}$ millibar. Undoped TiO$_2$ (anatase) has a wide bandgap of 3.2 eV. 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 TiO$_2$. The Cr-doped films have a wide bandgap of 3.2 eV. 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 TiO$_2$. This could explain the decrease in conductivity for the Cr$_2$O$_3$ films by compensation of donors. However, the assignment of dopant type of Ni and Cr defects in TiO$_2$ is controversially discussed in density functional theory calculations. W should behave as a donor as W$^{5+}$ or W$^{6+}$ when built in at a Ti site.

The measured conductivities vary by almost five orders of magnitude from 10$^9$ to 10$^5$ 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 TiO$_2$-lattice,$^{27}$ Ni and Cr could act as acceptors$^{28}$ when built in at the Ti site, i.e., Ni in the Ni$^{2+}$ state, and Cr in the Cr$^{3+}$ or Cr$^{5+}$ state. This could explain the decrease in conductivity for the Cr$_2$O$_3$ films by compensation of donors. However, the assignment of dopant type of Ni and Cr defects in TiO$_2$ 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 at 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...


\[ r(T) = \sum_i r_0^i \exp \left( -\frac{E_{A_i}}{k_B T} \right). \]

Another activation energy. Therefore, the experimental conductivity was fitted first with a model of two thermally activated functions, \( \sigma(T) = \sigma_1 + \sigma_2 = \sigma_{01} \exp \left( -\frac{E_{A1}}{k_B T} \right) + \sigma_{02} \exp \left( -\frac{E_{A2}}{k_B T} \right) \).

The low temperature regime can be explained by the theory of small polarons\textsuperscript{26,31} with identical temperature dependence as in Eq. (1). Since in TiO\textsubscript{2} electrons and phonons are strongly interacting, the formation of polarons is possible and has been predicted theoretically\textsuperscript{22,32} and shown experimentally.\textsuperscript{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 TiO\textsubscript{2} 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 \( \exp \left( -\frac{W}{k_B T} \right) \) with different regimes:

\[ W = W_H + W_D/2 \quad \text{for} \quad T > \theta_D/2 \quad \text{and} \quad W = W_D/2 \quad \text{for} \quad T < \theta_D/4, \]

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 \( \theta_D \) is 530 K for TiO\textsubscript{2},\textsuperscript{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.\textsuperscript{26} \( W_D \) is expected to be very low,\textsuperscript{26} 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,\textsuperscript{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 TiO\textsubscript{2}, 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 TiO\textsubscript{2}.\textsuperscript{5} For anatase, theory suggests non-adiabatic transfer modes.\textsuperscript{32} The increase of \( E_{A2} \) from \( T_S = 530 \) to 460 \( \text{K} \) and to 340 \( \text{K} \) 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 mechanism\textsuperscript{34} as an alternative to the thermally activated behavior \( \sigma_1 \) 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 material\textsuperscript{38} for graphs of the other dopants.

\[ \sigma(T) = \sigma_3 + \sigma_4 = \sigma_{03} \exp \left( -\frac{T_0}{T^{1/4}} \right) + \sigma_{04} \exp \left( -\frac{E_A}{k_B T} \right), \]

\( \sigma_{0i} \) 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.
TABLE II. Variable range hopping and thermally activated model parameters according to Eq. (4) for the TiO$_2$ films grown at various substrate temperatures $T_S$. $T_X$ denotes the temperature where both terms in Eq. (4) have the same value.

<table>
<thead>
<tr>
<th>$T_S$ (°C)</th>
<th>Dopant$^a$</th>
<th>$\sigma_{03}$ (Sm$^{-1}$)</th>
<th>$E_{A1}$ (meV)</th>
<th>$E_{A2}$ (meV)</th>
<th>$T_X$ (K)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>530</td>
<td>Nid</td>
<td>26.30 ± 1600</td>
<td>50.6 ± 1.3</td>
<td>1040 ± 25</td>
<td>180</td>
<td>5 x 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>25.30 ± 1300</td>
<td>49.1 ± 0.4</td>
<td>1270 ± 10</td>
<td>186</td>
<td>5 x 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>28.30 ± 800</td>
<td>85.8 ± 0.7</td>
<td>230 ± 3</td>
<td>198</td>
<td>4 x 10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>13.50 ± 500</td>
<td>53.4 ± 0.8</td>
<td>1105 ± 9</td>
<td>240</td>
<td>6 x 10$^{-5}$</td>
</tr>
<tr>
<td>460</td>
<td>Nid</td>
<td>43.90 ± 3200</td>
<td>53.5 ± 1.2</td>
<td>245 ± 20</td>
<td>105</td>
<td>3 x 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>42.50 ± 2200</td>
<td>40.2 ± 0.9</td>
<td>500 ± 50</td>
<td>89</td>
<td>2 x 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>25.50 ± 1100</td>
<td>58.4 ± 0.8</td>
<td>280 ± 8</td>
<td>138</td>
<td>5 x 10$^{-4}$</td>
</tr>
<tr>
<td>340</td>
<td>Nid</td>
<td>(1 ± 0.15) x 10$^3$</td>
<td>57.3 ± 2.6</td>
<td>770 ± 140</td>
<td>97</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>41.900 ± 3900</td>
<td>65.2 ± 1.9</td>
<td>1322 ± 85</td>
<td>143</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>6200 ± 1500</td>
<td>96.0 ± 4.3</td>
<td>10.5 ± 0.5</td>
<td>110</td>
<td>0.034</td>
</tr>
</tbody>
</table>

$^a$Nid stands for not intentionally doped.

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

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

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

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

and

$$\frac{\ell_0(T)}{k_B T} = \frac{1}{4} \left( \frac{T}{T_0} \right)^{1/4}.$$
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. 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 \( T_3 \) 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 \( (\chi^2) \) values in Tables I and II. \( \chi^2 \) 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 TiO\(_2\).

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 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 TiO\(_2\).

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 TiO\(_2\) anatase thin films. Using reduced \( \chi^2 \) 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 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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