Dielectric and conductivity investigations of Rutile Titanium dioxide single crystals

M. Ben Omar and A. Matoussi

Laboratory of Composites, Ceramics and Polymers Materials (LaMaCoP), Faculty of Sciences, University of Sfax BP 805, 3018 Tunisia.
E-mail: matouss_adel@yahoo.fr

Abstract- This paper reports dielectric characterizations of Titanium dioxide (TiO$_2$) oriented with three Rutile crystallographic orientations (100), (001) and (110). The dielectric properties and electrical conductivity were studied at various frequencies (0.1Hz to 10 MHz) and temperatures (100-500 K). The dielectric loss and permittivity constant for all the samples were observed to decrease with the increase of frequency. Electric modulus has been analyzed to identify the dielectric relaxation process. At low frequency, it reveals the interfacial MWS relaxation whereas the dipolar and ionic polarizations were dominated at high frequency. The electrical conductivity has been also discussed in detail. The ac conductivity showed strong temperature behaviors for high frequency. These results were related to crystallographic orientation and microstructure quality of TiO$_2$ samples which play considerable roles in conduction and trapping of electric charges. The trapping phenomena of these samples were under investigations.

I. INTRODUCTION

Titanium dioxide is one of the promising materials used in wide range applications due to its optical and electronic properties. It is used as implant material for dental and orthopaedic applications [1], as white pigment in paints [2], and as semiconductors in the photocatalysis of organic compounds [3-4] and molecules gas sensors [5-6].

Electrodes made of TiO$_2$ are used in electrochromic devices [7] and dye-sensitized solar cells [8]. Titanium oxide has three known structures under ambient conditions: rutile, anatase, and brookite. The rutile structure is the most stable phase and also the most studied [9]. Many recent reviews have shown that electrical and photocatalitic properties depend strongly on crystalline phase, surface structure and chemical composition of TiO$_2$ material [10-12]. Temga et al [13] have reported that the crystallographic orientation and the anisotropy of rutile TiO$_2$ single crystals play significant roles on the conduction and trapping mechanisms of electric charges. They observed that electrons diffuse and are trapped preferentially in the (110) planes than the (001) surface.

In this work, we are interested in investigating the influence of crystallographic orientation of TiO$_2$ on dielectric properties and electric conduction mechanisms.

II. EXPERIMENTAL

The studied single crystals of TiO$_2$ were purchased from the SurfaceNet GmbH (Germany). AFM analyses show that these samples have one-polished face with a RMS roughness lower than 4 nm. The second faces are roughly covered by high density of grains having different shapes and sizes. The samples were grown in Rutile structure along three crystallographic orientations (100), (001) and (110). Impedance spectroscopy measurements were performed using NOVOCONTROL system for dielectric and electrical characterizations of the samples in the frequency range from 0.1 Hz to 1 MHz. TiO$_2$ samples were placed between two Gold parallel plate electrodes (“sandwich geometry”). Amplitude of the sinusoidal voltage was 1000 mV.

For all samples, isothermal frequency scans were conducted from -80°C to 200°C with a temperature step of 20 °C.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the variation of real part of the dielectric constant ($\varepsilon'$) with frequency at various temperatures of TiO$_2$ in three crystallographic orientations. In low frequency, $\varepsilon'(\omega)$ increases with increasing temperature. This result can be explained by an increase in the mobility of charges under the effect of temperature. With increasing the frequency, $\varepsilon'(\omega)$ decreased, which is likely due to the high periodic reversal of the field at the interfaces.

Consequently, the contribution of charge carriers to the dielectric constant was reduced. Also, one can see that for (110) sample the values of dielectric constant are more enhanced about five order of magnitude than those for the (100) orientation. This improvement of dielectric properties can be related to higher atomic density of (110) planes and to negative charge polarity of its surfaces [14]. According to refs [13,14], the (100) and (001) surfaces are neutral and not polar. On the other hand, this can be explained by the highest degree of permittivity anisotropy for (110) sample compared to that for oriented (100) and (001) TiO$_2$ samples.

Fig. 2 presents the variation of tanδ versus frequency of three crystallographic orientations. It is seen that the dielectric loss depends on crystallographic orientations.
Over all ranges of temperatures and frequencies, we observe the similar decrease of dielectric losses from orientation (100), then (001) to (110) one. This result confirms that the (110) sample has the best dielectric properties.

As reported in fig. 3, the frequency dependence of imaginary part of the electrical modulus of the TiO₂ (110) show two distinguished relaxation peaks below a frequency of 1000 Hz. The first peak corresponds to space charges polarization of the titan ions Ti⁺³ and Ti⁺⁴. However, the second peak observed at low frequency is associated to the interfacial Maxwell-Wagner-Sillar (MWS) relaxation can be caused by the presence of extended defects in the bulk of material such as grains and dislocations boundaries [14,15]. Also, the electrode-sample interface can contribute to the interfacial relaxation due to accumulation of electric charges and migration of oxygen vacancies [16-17].

From the frequency maximum of each peak, we have determined the evolution of its relaxation times (τ) with the reciprocal temperature, which follows the Arrhenius law:

$$\tau = \tau_0 e^{\frac{-E_a}{k_B T}}$$  \hspace{1cm} (1)

Where τ₀ is the Debye relaxation time, Eₐ is the activation energy, and k_B is the Boltzmann constant. From the slope of fitted straight lines, the activation energy is determined and results are reported in table 1. Values about 0.25-0.33eV are obtained, for the first peak, which are relatively consistent with the reported value of 0.252 eV for the charge carries hopping between Ti⁺³ and Ti⁺⁴ [18]. This implies that the above relaxation can be attributed to the hopping process.
According to refs [19,20], the activation energy value 1.2 eV is attributed to oxygen vacancies formed in rutile ceramics. Fig. 4 shows that the frequency dependence of the electric conductivity ($\sigma'$) of two TiO$_2$ samples. It reveals two regimes of conduction below and above a frequency of 1 KHz.

Table 1

<table>
<thead>
<tr>
<th>Type</th>
<th>Activation energy (eV) 1st peak</th>
<th>Activation energy (eV) 2nd peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (100)</td>
<td>0.33</td>
<td>1.2</td>
</tr>
<tr>
<td>TiO$_2$ (110)</td>
<td>0.252</td>
<td>1.3</td>
</tr>
<tr>
<td>TiO$_2$ (001)</td>
<td>0.25</td>
<td>0.82</td>
</tr>
</tbody>
</table>

At low frequencies and high temperatures, there appears an independent frequency plateau of conductivity. In general, the ac conductivity of dielectric materials can be calculated by the following equation: 

$$\sigma_{ac} = A(T)\omega^s$$

(2)

Where A is the temperature dependent constant, $\omega$ is the angular frequency and s is the exponent of conduction. We believe that impurities and defects play dominant roles in the ac conduction process at a low frequency range due to their heavy mass. Therefore, as the frequency is increases, the ac conductivity increases more rapidly.

In the case of the first regime, we have determined an energy Ea=0.03 eV, similar to that reported by F. Yakuphanoglu et al [21]. They suggest that the conduction mechanism is mainly caused by hopping of thermally activated carriers into the band tails. In fact, the migration of oxygen vacancies is dominating at second regime. Fig. 5 reports the variation of exponent coefficient (s) as function of inverse of temperature. For all studied samples, the value of exponent tends to decrease as the temperature increases.

Table 2

<table>
<thead>
<tr>
<th>Type</th>
<th>Values of activation energies for ac conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ea (eV)</td>
</tr>
<tr>
<td></td>
<td>1st Regime</td>
</tr>
<tr>
<td>TiO$_2$ (100)</td>
<td>0.03</td>
</tr>
<tr>
<td>TiO$_2$ (110)</td>
<td>0.03</td>
</tr>
<tr>
<td>TiO$_2$ (001)</td>
<td>0.029</td>
</tr>
<tr>
<td></td>
<td>2nd Regime</td>
</tr>
<tr>
<td>TiO$_2$ (100)</td>
<td>1.02</td>
</tr>
<tr>
<td>TiO$_2$ (110)</td>
<td>1.05</td>
</tr>
<tr>
<td>TiO$_2$ (001)</td>
<td>0.77</td>
</tr>
</tbody>
</table>

This behavior indicates a dominant correlated barrier-hopping (CBH) mechanism of conduction [21,22]. In this model, the
charge carrier hops between the sites over the potential barrier separating them. For the orientation (100), the s values are temperature dependent and are increased with increasing temperature between 250K and 350K. This agrees well with the small polaron tunneling conduction model.

Fig. 6 shows the frequency dependence of real and imaginary parts of TiO$_2$(110) impedance at fixed temperature 190°C. Best fitting results are obtained by simulation of the experimental data with an equivalent scheme shown in the inset to Fig 6. Resistors $R_1$ and $R_2$ describe the resistance of the interfacial effects (grain boundaries, electrodes) and the sample bulk, respectively. The used constant phase elements (CPE) take into account spread in values of the resistance and capacitance in the bulk and at surfaces. This electric compound considers all kinds of chemical and structural capacitance of bulk imperfections.

From the linear slopes of circuit times ($\tau_1=R_1C_{PE1}$ and $\tau_2=R_2C_{PE2}$), we have found similar activation energies about 1.05eV for $\tau_1$ and 0.26 eV for $\tau_2$. These values are very closer to that obtained in table 1. This results confirm that $R_1$ and $C_{PE1}$ represent the contribution of interfaces (surface defects and electrodes), whereas $R_2$ and $C_{PE2}$ represent the resistance and capacitance of bulk imperfections.

IV. CONCLUSION

The effect of crystallographic orientation on dielectric and electrical properties of Rutile single crystals TiO$_2$ has been studied. Dielectric analysis shows that the (110) sample has the lowest loss tangent and the highest value of dielectric constant which can reach 1200 at 200°C. The frequency dependence of electric modulus shows two relaxations peaks attributed to interfacial MWS process and space charges polarization. The electrical conductivity is found to be dominated by thermally activated charges carriers over variable range hopping barriers. Activation energies about 0.3 eV and 1.2 eV are determined that can be associated to points defects such as oxygen vacancy. On the basis of impedance spectra, we have proposed equivalent circuits containing resistances and constant phase elements CPE for all the samples.

V. REFERENCES