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The contribution of grain boundary barriers to the electrical conductivity of titanium oxide thin films

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Titanium oxide thin films were prepared by reactive magnetron sputtering. The reactive gas pulsing process was implemented to control the oxygen injection in the deposition process and, consequently, to tune the oxygen concentration in the films from pure titanium to stoichiometric TiO_2, maintaining a homogeneous in-depth concentration. The electrical conductivity of the films was investigated as a function of the oxygen injection time, the metalloid concentration and temperature, in the range 90–600 K. The curved Arrhenius plots of the conductivity were examined taking into account the grain boundary limited transport model of Werner (J. H. Werner [Solid State Phenom. **37–38**, 213 (1994)]). The grain barrier heights were found to depend significantly on the oxygen supplied into the deposition process and thus, on the oxygen-to-titanium atomic ratio in the films. The analysis as a function of temperature showed that the conduction mechanism in the coatings was not solely limited by the oxygen-to-titanium atomic ratio, but also by the grain boundary scattering. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2970034]

The conductivity of polycrystalline films is sensitively related to the potential barriers and space charge regions that are built up around grain boundaries.[1] A strong temperature dependence of the electrical conductivity is commonly observed in metallic and semiconducting films. Furthermore, it is shown that the grain boundaries of polycrystalline semiconductors have a significant influence on the electronic properties. According to the grain boundary model of Seto,[2] if trap states in the intergranular region are present, the capture of the free carriers occurs and thus, the films' conductivity changes. These charged states create potential barriers space charge regions that are built up around the grain boundaries, which then increase the resistance between two neighboring grains. This letter demonstrates that the Werner's theory[3] can be applied to the electrical conductivity behavior versus temperature of titanium oxide thin films. Experimental results showed that for the conduction mechanism, and beyond the oxygen-to-titanium atomic ratio, the transition from metallic- to semiconducting-type behavior of titanium oxide, TiO_x thin films (with x varying from 0 to 2.0) has also an important contribution from the grain boundary scattering.

The TiO_x films were deposited on glass and (100) Si substrates by dc reactive magnetron sputtering from a titanium metallic target (purity 99.6%) in an Ar+O_2 gas mixture. The titanium target was sputtered with a constant current density $J=100$ A m^{-2} while the substrates were grounded and kept at room temperature. Argon mass flow rate was set constant in order to reach an Ar partial pressure of 0.25 Pa. Oxygen was introduced using a rectangular modulation pattern of the mass flow rate by means of a reactive gas pulsing process.[4–7] A constant pulsing period $P=45$ s was used, whereas the time of injection t_{ON} of the oxygen gas was systematically changed from 0% to 100% of the period P. The maximum oxygen flow rate was 0.80 SCCM (SCCM denotes cubic centimeter per minute at STP) during the t_{ON} time whereas the minimum flow was 0 SCCM during the t_{OFF} time (oxygen injection completely stopped). The deposition time was adjusted in order to deposit thin films with a constant thickness close to 400 nm. The crystallographic structure was investigated by x-ray diffraction (XRD) using monochromatic Cu K_α radiation at a grazing angle $\theta=1°$. The chemical composition of the films deposited on silicon wafer (100) was determined by Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA). The electrical conductivity of the films deposited on glass substrates was measured in the Van der Pauw geometry for temperatures ranging from 90 to 600 K.

Werner's theory assumes that the fluctuating barrier heights are described by a Gaussian probability distribution,[3]

$$P(\phi) = \frac{1}{\sigma_\phi \sqrt{2\pi}} e^{(\bar{\phi} - \phi)^2/2\sigma_\phi^2}, \tag{1}$$

where $\bar{\phi}$ denotes the mean barrier height and σ_ϕ denotes its standard deviation. The current across the spatially inhomogeneous grain barriers is limited by the lowest barrier in the Gaussian distribution. In addition, Werner's theory shows that the slopes of the Arrhenius plots of conductivities are curved upward with decreasing the reverse temperature values. The curved behavior of the plots $\ln(\sigma/T)$ is well fitted by a parabola, following:

$$\ln\left(\frac{\sigma}{T}\right) = \frac{a}{T^2} - \frac{b}{T} - c. \tag{2}$$

The mean barrier height $\bar{\phi}$ and the standard deviation σ_ϕ are

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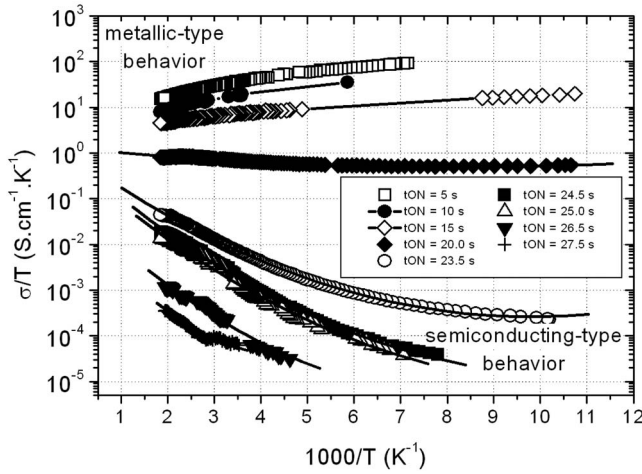
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FIG. 1. Temperature dependence of the electrical conductivity of TiO$_x$ films sputter deposited by the reactive gas pulsing process using various times of injection of the oxygen gas.

$$\sigma_\phi = \sqrt{\frac{2ak^2}{q^2}}, \qquad (3)$$

$$\bar{\phi} = \frac{bk}{q}, \qquad (4)$$

where $k = 1.38 \times 10^{-23}$ J K^{-1} and $q = 1.6 \times 10^{-19}$ A s.

Figure 1 illustrates the temperature dependent conductivity $\ln(\sigma/T)$ for sputtered TiO$_x$ thin films in the temperature range 90 to 600 K. The obtained results can be separated in two groups. The first one concerns TiO$_x$ thin films sputter deposited with t_{ON} injection times up to 15 s. Electrical conductivity at room temperature ranges from $\sigma_{293\ K} = 1.10 \times 10^4$ to 2.14×10^3 S m^{-1}, which corresponds to conventional metallic TiO$_x$ thin film values.[8] For coatings deposited with $t_{ON} = 5$ and 10 s, a typical metallic behavior is observed as a function of temperature. The temperature coefficient of resistance (TCR$_{293\ K}$) calculated at 293 K is reduced from 1.33×10^{-3} to 6.80×10^{-4} K^{-1} (Table I). It becomes negative for $t_{ON} = 15$ s (TCR$_{293\ K} = -1.01 \times 10^{-3}$ K^{-1}). Such a decrease of TCR with O/Ti ratio is in agreement with Banakh *et al.*[8] investigations focused on TiO metallic films. Negative TCR values tend to appear in TiO$_x$ thin films where the low free carrier concentration results in a less efficient screening of the point defects. Understanding electrical transport in such TiO$_x$ metallic systems (point defect concentration reaches several at. %) is still an open question. However, the decrease of TCR versus O/Ti ratio and its negative value reached for $t_{ON} = 15$ s can be related to the Mooij criterion (at

room temperature, resistivity of 150 $\mu\Omega$ cm is an universal criterion for the sign of TCR; if the room temperature resistivity of a sample is larger than this value, it is likely to have a negative TCR).[9] Such a criterion applied in a large number of amorphous or disordered metal conductors remains one of the most criteria applied to explain the negative TCR values in metallic compounds.[10] Similarly, Riess *et al.*[1] explained the change of sign of the calculated TCR from positive to negative values taking into account the number of grain boundaries per electron mean free path. For our results, an increase of the t_{ON} injection time obviously leads to an oxygen enrichment of TiO$_x$ films, but specially the long range order is reduced (from XRD, metallic crystallite size calculated from Scherrer's method reduces from 30 to 5 nm as t_{ON} changes from 5 to 15 s). Thus, assuming the same electron mean free path for all TiO$_x$ films exhibiting metallic behaviors ($t_{ON} = 5-15$ s), the number of grain boundaries is enhanced and a negative TCR value can be expected, although the electrical conductivity decreases versus temperature.

The second group of samples involves TiO$_x$ thin films prepared with t_{ON} injection times higher than 20 s. Conductivity at room temperature is continuously decreasing from $\sigma_{293\ K} = 2.53 \times 10^2$ to 2.86×10^{-2} S m^{-1} as t_{ON} increases from 20 to 27.5 s. For this kind of films, a characteristic semiconducting behavior is measured as a function of temperature. For semiconductors, the Arrhenius plot of the conductivity versus the reverse of the temperature usually exhibits a linear evolution for temperatures higher than the room temperature. The activation energy E_a, which gives evidence that the conduction mechanism is thermally activated can be then calculated. Table I shows that the calculated value for the energy E_a increase from 30 to 190 meV as the t_{ON} time increases. It tends to that of stoichiometric TiO$_2$ compound [$E_a = 650$ meV (Ref. 11)], which correlates with O/Ti ratios determined by RBS and NRA. As the temperature range extends (from 90 to 600 K), Arrhenius plots become curved (Fig. 1) and Werner's theory is relevant to determine the mean heights of the barrier potential $\bar{\phi}$ and the standard deviation σ_ϕ following Eqs. (3) and (4). Measured conductivities of TiO$_x$ thin films deposited at high t_{ON} times are well described by parabola in agreement with Eq. (2). Parameters $\bar{\phi}$ and σ_ϕ have been calculated from conductivity measurements versus temperature in Fig. 1 and for rising t_{ON} injection times (Fig. 2). Both parameters increase with t_{ON} injection time. The mean barrier height changes from 8 to 113 meV and the standard deviation from 9 to 40 meV as the t_{ON} time increases from 20 to 27.5 s. Werner[3] also proposed a homogeneity coefficient H defined as the ratio of

TABLE I. Chemical composition, electrical behaviors, and structure of TiO$_x$ thin films as a function of the t_{ON} time. am. denotes amorphous and N. A. denotes not applicable.

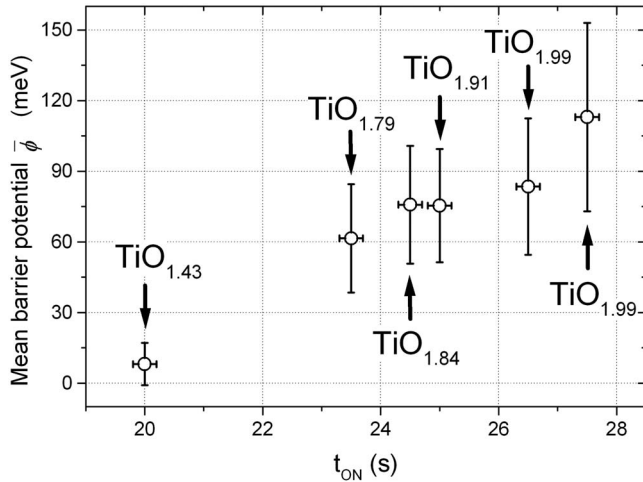| t_{ON} (s)	5.0	10.0	15.0	20.0	23.5	24.5	25.0	26.5	27.5
[O] (at. %)	9.8	33.7	51.3	58.9	64.1	64.8	65.6	66.6	66.6
O/Ti ratio	0.11	0.51	1.05	1.43	1.79	1.84	1.91	1.99	1.99
$\sigma_{293\ K}$ (S m^{-1})	1.10×10^4	5.13×10^3	2.14×10^3	2.53×10^2	4.30	1.62	1.27	1.12×10^{-1}	2.86×10^{-2}
Behaviors		$\leftarrow$ metallic $\rightarrow$				$\leftarrow$ semiconducting $\rightarrow$			
TCR$_{293\ K}$ (K$^{-1} \times 10^3$)	1.33	0.68	−1.01			N.A.			
E_a (meV)		N.A.		30	140	160	150	190	160
Structure by XRD	$\leftarrow$Ti$\rightarrow$	$\leftarrow$am.+fcc TiO $\rightarrow$			$\leftarrow$am.+TiO$_2$ anatase and rutile $\rightarrow$				

FIG. 2. Mean height of the barrier potential $\bar{\phi}$ vs t_{ON} injection time of the oxygen gas. Composition of the TiO$_x$ films is also indicated. Error bars of the energy axis represent the standard deviation σ_ϕ.

$\bar{\phi}$ to σ_ϕ. The larger the H, the more homogeneous is the film. For our TiO$_x$ thin films, the H coefficient is enhanced from 0.88 to 3.1 with the t_{ON} injection time, which are typical values previously reported for other semiconducting compounds.[12–14]

In undoped and substoichiometric TiO$_2$ thin films, it is commonly admitted that the conductivity change is closely linked to the mobile charge carriers.[15] Their concentration originates from point defects, i.e., mainly oxygen vacancies rather than interstitial titanium atoms. The contribution of the oxygen vacancies to the conductivity mechanism predominates for titanium oxide thin films exhibiting semiconducting behaviors and prepared with low t_{ON} times (e.g., O/Ti ratio=1.43–1.91). In addition, the mean heights of the barrier potential are the lowest for the corresponding range of the t_{ON} time ($\bar{\phi}$=8 meV for t_{ON}=20 s), which correlates with a conductivity behavior determined by the oxygen vacancies. For the highest t_{ON} times, O/Ti ratio tends to the stoichiometric TiO$_2$ compounds. The oxygen vacancies concentration is reduced whereas the mean height of the barrier potential is higher than 110 meV. As a result, conductivity is mainly influenced by grain boundary effects and prevails on the point defects.

Summarizing, we have produced TiO$_x$ thin films by reactive sputtering using a pulsed injection of the oxygen gas (reactive gas pulsing process). A systematic change of the t_{ON} injection time of the reactive gas leads to tunable electrical properties of titanium oxides, in agreement with investigations involving other deposition techniques.[16–18] For O/Ti atomic ratios close to or lower than one, a metallic behavior is clearly observed with positive and negative TCR values closely linked to the number of grain boundaries per electron mean free path. Titanium oxide semiconducting films are prepared for longer t_{ON} injection times. Conductivity behaviors are found to be not solely ruled by the oxygen vacancies, but also by the potential at the grain boundaries. Point defects prevail for oxygen-deficient titanium dioxide, whereas the heights of the barrier potential become predominant for thin films tending to the stoichiometric TiO$_2$ compound.

[1] G. Reiss, J. Vancea, and H. Hoffman, Phys. Rev. Lett. **56**, 2100 (1986).
[2] J. Y. W. Seto, J. Appl. Phys. **46**, 5247 (1975).
[3] J. H. Werner, Solid State Phenom. **37**, 213 (1994).
[4] N. Martin, A. R. Bally, P. Hones, R. Sanjinès, and F. Lévy, Thin Solid Films **377**, 550 (2000).
[5] N. Martin, J. Lintymer, J. Gavoille, J. M. Chappé, F. Sthal, J. Takadoum, F. Vaz, and L. Rebouta, Surf. Coat. Technol. **201**, 7720 (2007).
[6] N. Martin, J. Lintymer, J. Gavoille, J. M. Chappé, F. Sthal, J. Takadoum, F. Vaz, and L. Rebouta, Surf. Coat. Technol. **201**, 7727 (2007).
[7] N. Martin, J. Lintymer, J. Gavoille, J. M. Chappé, F. Sthal, J. Takadoum, F. Vaz, and L. Rebouta, Surf. Coat. Technol. **201**, 7733 (2007).
[8] O. Banakh, P. E. Schmid, R. Sanjinès, and F. Lévy, Surf. Coat. Technol. **151**, 272 (2002).
[9] J. H. Mooij, Phys. Status Solidi A **17**, 521 (1973).
[10] D. S. MacLachlan, Phys. Rev. B **25**, 2285 (1982).
[11] A. R. Bally, E. N. Korobeinikova, P. E. Schmid, F. Lévy, and F. Bussy, J. Phys. D: Appl. Phys. **31**, 1149 (1998).
[12] S. Seeger, R. Mientus, J. Röhrich, E. Strub, W. Bohne, and K. Ellmer, Surf. Coat. Technol. **200**, 218 (2005).
[13] B. Ouertani, J. Ouerfelli, M. Saadoun, B. Bessaïs, H. Ezzaouia, J. C. Bernède, Mater. Charact. **54**, 431 (2005).
[14] J. R. Ares, A. Pascual, I. J. Ferrer, and C. R. Sanchez, Thin Solid Films **451**, 233 (2004).
[15] H. Tang, K. Prasad, R. Sanjinès, P. E. Schmid, and F. Lévy, J. Appl. Phys. **74**, 2042 (1994).
[16] D. Mercs, F. Lapostolle, F. Perry, A. Billard, and C. Frantz, Surf. Coat. Technol. **116**, 916 (1999).
[17] E. K. Kim, M. H. Son, S. K. Min, Y. K. Han, C. H. Wang, and S. S. Yom, J. Appl. Phys. **79**, 4459 (1996).
[18] H. Tang, F. Lévy, H. Berger, and P. E. Schmid, Phys. Rev. B **52**, 7771 (1995).