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The interdependence of structural and electrical properties in TiO$_2$/TiO/Ti periodic multilayers

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Abstract
Multilayered structures with 14 to 50 nm periods composed of titanium and two different titanium oxides, TiO and TiO$_2$, were accurately produced by DC magnetron sputtering using the reactive gas pulsing process (RGPP). Structure and composition of these periodic TiO$_2$/TiO/Ti stacks were investigated by X-ray diffraction (XRD) and transmission electronic microscope (TEM) techniques. Two crystalline phases hcp-Ti and fcc-TiO were identified in the metallic-rich sub-layers whereas the oxygen-rich ones were made of a mixture of amorphous TiO$_2$ and rutile phase. DC electrical resistivity $\rho$ measured for temperatures ranking from 300 to 500 K exhibited a metallic-like behaviour ($\rho_{473K} = 1.05 \times 10^{-5}$ to $1.45 \times 10^{-6}$ $\Omega$ m) with a temperature coefficient of resistance (TCR) ranging from $1.20 \times 10^{-3}$ K$^{-1}$ for the highest period $\Lambda = 50.0$ nm down to
negative values close to $-4.97 \times 10^{-4} \text{ K}^{-1}$ for the smallest one $A = 14.0 \text{ nm}$. A relationship between the dimensions of periodic layers and their collective electrical resistivity is proposed where the resistivity does not solely depend on the total thickness of the film, but also on the chemical composition and thickness of each sub-layer. Charge carrier mobility and concentration measured by Hall effect were both influenced by the dimension of TiO$_2$/TiO/Ti periods and the density of ionized scattering centres connected to the titanium concentration in the metallic sub-layers.

**Keywords**

Multilayers, titanium oxides, HRTEM, periodic structure, electrical properties

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Highlights

TiO_2/TiO/Ti periodic multilayers are deposited by reactive sputtering.

Nanometric periods from 14 to 50 nm are precisely produced by gas pulsing.

Hcp-Ti and fcc-TiO phases are found in the metallic sub-layers whereas amorphous and rutile compounds are detected in the TiO_2 sub-layers.

TCR of films exhibiting metallic-like behaviour can be tuned from positive to negative.

Carrier mobility and concentration are connected to the density of ionized scattering centres.
1. Introduction

For many decades, metal oxide thin films, especially titanium-based coatings, have attracted much attention in various fields because of their remarkable physical, chemical and biological properties. They are largely involved in a wide range of applications such as antireflective coatings, gas sensors, biomedical devices, photocatalysts, etc [1-8]. In addition to the intrinsic properties of titanium oxide films (metal, semiconductor, insulator according to the oxygen content), some of their behaviours can also be tailored playing on the nanostructure. It becomes of particular interest when the structuration is performed throughout the whole thickness of the film which may be accomplished in periodic metal/oxide multilayers. The resulting properties (especially the electronic conductivity) can be strongly influenced by the dimensions and the quality of the metal/oxide periods and interfaces. Consequently, structural and interfacial characteristics have to be taken into account to understand the electronic transport properties.

First of all, the fabrication of regular and periodic alternations appears as a relevant challenge, especially with periodic multilayers involving titanium because of its strong reactivity towards oxygen. Many deposition methods have been developed to prepare titanium oxide films [9-15]. However, few deposition processes allow the preparation of metal/oxides nanometric multilayers with abrupt and well-controlled interfaces [16-18]. Among these methods, the reactive sputtering may be an attractive approach to prepare periodic structures at the nanometric scale. However, the reactive sputtering technique normally exhibits hysteresis effects, which makes it difficult to operate the process to obtain certain film compositions [19-22]. Some well-tested approaches like high pumping speeds, feedback control systems or more specific devices were developed to overcome the problems associated with such instabilities [23-26]. Such improvements
have made it possible to prepare metal oxide thin films with tuneable chemical compositions.

In a previous work [27], the combination of DC magnetron sputtering and the reactive gas pulsing process (RGPP) resulted in an accurate and reproducible structuration of titanium oxide multilayers at the nanometric scale. Although these performances, the idea is also to turn a sensitive material into a directly applicative and simple device for gas sensors by melding electrical properties of a metal and an insulator sub-layers. Many methods of gas detection can be found [28], but the simplest and the most frequently used in the field of sensors is an electrical characterization by performing a resistivity measurement [29]. The resistivity of a material depends among others, on the temperature (this dependence is specific to the material) and is characterized by a temperature coefficient of resistivity for metals. In order to obtain a temperature invariant resistivity, the addition of dopant in the material is sometime required but sometime leads to significant manufacture over costs. Thus, the changes of resistivity could only be due to the electrical contribution of some gaseous species adsorbed at the air/film interface. In TiO$_2$/TiO/Ti thin periodic multilayers, only the TiO$_2$ compound has been employed as gas sensor [30]. This compound exhibits semiconducting-like behaviours [31] since its resistivity exponentially decreases as a function of the temperature. On the other hand, hcp-Ti and fcc-TiO are metallic phases and their electrical resistivity linearly increases versus the temperature (positive temperature coefficient of resistance).

In this article, the structural parameters of multilayered periodic TiO$_2$/TiO/Ti thin films including the internal nanostructure evolution are investigated. These periodic stacks are sputter deposited by reactive sputtering using the reactive gas pulsing process (RGPP) [32]. Period of the multilayers is systematically changed from 14.0 to 50.0 nm. A study
of the resistivity versus temperature is performed in order to understand the relationship between the electronic transport properties and the structural characteristics of the films. The thickness of each sub-layer associated to the well-controlled nanometric structuration produce electrical characteristics, which give rise to a metallic-like behaviour with positive and negative temperature coefficients of resistance. A theoretical relationship between resistivity, dimension of the TiO$_2$/TiO/Ti periods and chemical composition is finally proposed. Charge carrier concentrations and mobilities are also investigated so as to better understand their contribution in the electrical conduction characteristics.

2. Experimental details

Multilayers were simultaneously deposited onto (100) Si and glass substrates by DC reactive magnetron sputtering from a titanium metallic target (purity 99.6 at. % and 51 mm diameter) in an Ar + O$_2$ gas mixture. The target was sputtered with a constant current density $J = 100$ A m$^{-2}$. The distance between the target and the unheated substrate was fixed at 65 mm. The gas flow rates were controlled by a homemade system. All depositions were carried out with an argon flow rate of 2 sccm and a constant pumping speed of 13.5 L s$^{-1}$, which produced an argon partial pressure of 0.25 Pa. Oxygen mass flow rate was periodically controlled versus time according to a rectangular signal versus time by the reactive gas pulsing process, namely RGPP [32]. The pulsing period $T_P$ of the oxygen flow rate was varying from 313 to 1000 s. During each period, the flow rate was periodically modulated with a $t_{on}$ injection time which is a fraction of the total period $T_P$. The maximum O$_2$ flow rate was fixed at 4 sccm during the $t_{on}$ injection time. This oxygen flow corresponds to a processing point in compound mode if the flow would be kept constant. Otherwise it was completely stopped (no oxygen injection).
during the \( t_{\text{off}} \) time. The multilayer period thickness \( A \) is expected to be in-between 15 to 50 nm, with \( A = \lambda_{\text{met}} + \lambda_{\text{ox}} \), where \( \lambda_{\text{met}} \) and \( \lambda_{\text{ox}} \) correspond to the thickness of the metal and oxide sub-layers, respectively. As a result, the duty cycle \( \alpha \) defined as the ratio \( t_{\text{on}}/T_{\text{P}} \) takes values from 72 to 90 % in order to tune the \( \lambda_{\text{met}}/\lambda_{\text{ox}} \) ratio. Moreover, the deposition procedure always started with the O-rich sub-layer and finished with the Ti-rich one, the total film thickness \( t_{\text{tot}} \) being close to 400 nm.

The crystalline structure was analyzed by X-ray diffraction (XRD) in \( \theta/2\theta \) configuration using a monochromatized Co K\( \alpha \) radiation. Scans were performed with a step of 0.02° per 0.2 s and a \( 2\theta \) angle ranging from 20 to 80°. Then, for all samples the local structure was characterized by high resolution transmission electron microscopy (HRTEM). The elemental chemical composition was determined by energy-dispersive X-ray spectroscopy (EDX) with a TEM JEOL 2100 FEG operating at 200 kV (scanning probe of 2 nm). The scanning technique of TEM (STEM) was used to get local and precise chemical analyses at the nanometric scale, to discriminate each sub-layer, and to determine their thickness. Moreover, dark field imaging was applied to provide a greater contrast between the different phases.

DC electrical resistivity \( \rho \) of the films deposited on glass substrates was performed versus temperature from 300 to 500 K with a homemade system based on the van der Pauw method. In order to warrant the Ohmic behavior of the four contacts, I-V curves were systematically plotted and the linear evolution was checked for all van der Pauw combinations. Two cycles of measurements were carried out on each sample. The first cycle started at room temperature and sample was heated up to 500 K with a ramp of 2 K min\(^{-1}\) followed by a plateau for 10 min at 500 K. Afterwards, the temperature was decreased with the same ramp down to 300 K and the second cycle continued with the temperature profile as the first cycle. Similarly, charge carrier mobilities and
concentrations were obtained by Hall Effect using the same procedure as resistivity measurements but applying a perpendicular magnetic field of 0.8 Tesla to the sample surface.

3. Results and discussion

3.1 Crystallographic structure by XRD

For all diffractograms (Fig. 1), two main peaks are recorded at $2\theta = 33.3$ and $55.5^\circ$, which are attributed to the silicon (111) and (311) planes, respectively. The presence of this two silicon intense peaks is due to the substrate contribution as the deposit thickness is lower than 450 nm. Two other significant peaks at $2\theta = 40.98$ and $43.25^\circ$ are also detected, but they can not be related to the same crystallographic phase. For the first one, an interplanar distance equal to $d = 0.255$ nm is obtained, which corresponds to the (100) planes of the hexagonal phase of metallic titanium whereas for the second one, the interplanar $d$-spacing is $0.241$ nm. This latter is due to the (111) planes of the fcc-TiO$_2$ phase.

For the shortest period $\Lambda = 14.0$ nm, no diffracted signals are detected. The size of crystalline domains is certainly lower than a couple of nanometers because the growth is periodically disturbed by the pulsing introduction of the oxygen gas. The long range order increases with the period thickness $\Lambda$. An increase of the peak intensity located at $2\theta = 40.98^\circ$ is clearly observed as the period $\Lambda$ rises from 14.0 to 40.0 nm. It is worth noticing the absence of diffracted signals corresponding to the crystalline TiO$_2$ phases, either anatase or rutile, which are the most common phases for such kind of oxide compounds. This could be explained by the weakness of the signal produced by small nanocrystallites of TiO$_2$ (rutile or anatase phase) embedded in an amorphous TiO$_2$ matrix. In order to go further into the microstructure, TEM analyses have been carried
out on different locations of the mainly amorphous TiO₂ matrix and to reveal the
phase(s) in these nanocrystals, as it will be presented in the next paragraph.

3.2 Structure by TEM

TEM observations on the cross-section of the different specimens show that the
alternation of the sub-layers is clearly visible with a regular periodic structure (Fig. 2).
The total thickness $t_{\text{tot}}$ of the films is 345 and 405 nm, respectively (Fig. 2a and 2c).
Similarly, the total thickness $t_{\text{tot}}$, metallic and oxide sub-layers $t_{\text{met}}$ and $t_{\text{ox}}$, respectively,
and the period $\Lambda$ have been measured for all samples as reported in table 1. The sample
references with different periods and the Ti metal concentration are also indicated. These
TEM observations show that the dimension of the period stacks (two sub-layers) is
accurately controlled during the growth and remains constant from the substrate-film to
the film-air interface. TEM micrographs systematically indicate that the interface
between the silicon substrate and the grown multilayers is flat and regular, the thickness
of the native SiO₅ layer being close to 3.0 nm.

In bright field mode (BF in figures 2a and 2c), 23 bright and dark bands alternations are
visible for the sample with $\Lambda = 14.0$ nm, whereas 8 bright and dark bands for the sample
with $\Lambda = 50.0$ nm. These bright and dark bands correspond to the oxide and metallic sub-
layers, respectively whereas in DF mode, it is the opposite. In dark field mode (DF), the
period thickness is accurately measured ($\pm 0.1$ nm) and the difference of sub-layers
crystallinity is evidenced (Fig. 2b and 2d). For the sample with the lowest period $\Lambda =
14.0$ nm, the metallic sub-layer thickness ($t_{\text{met}}$) and the oxide one ($t_{\text{ox}}$) is equal to 6.0 and
8.0 nm, respectively. DF image from the sample with $\Lambda = 50.0$ nm observed with a low
magnification ($\times 15 000$) shows an alternation of wider dark and bright bands, with the
metallic sub-layer $t_{\text{met}} = 35.0$ nm and the oxide one $t_{\text{ox}} = 15.0$ nm. From our operating
conditions and assuming the deposition rates of titanium and titanium oxide, the period $A$
of such multilayers is expected to be in-between 15.0 to 50.0 nm, which is in good
agreement with the TEM measurements.
The crystalline quality of the sub-layers has also been studied in DF mode. The presence
of small bright domains in DF images indicates that the structure is partially
nanocrystalline (Fig. 2b) and that the Ti metallic sub-layer is better crystallized than the
oxide one (Fig. 2d). Moreover, a columnar structure is also pointed out in figure 2d, as
well as the presence of numerous defects close to the crystalline part. Consequently, the
crystallization is not homogeneous through the multilayered structure.
Combining EDX and DF experiments, it is possible to go further through the interface
characteristics between each sub-layer. It is pointed out that the darkest areas correspond
to the mostly amorphous oxide sub-layers ($\lambda_{ox}$), whereas the brightest ones correspond to
crystallized Ti-rich ones ($\lambda_{met}$). In each sample, every oxide sub-layer is composed of a
TiO$_2$ stoichiometric phase from the bottom to the top of the deposit. The titanium
concentration $C_{\lambda_{met}}$ in the metallic sub-layers is kept constant in a given sample but
changes from a sample to another. Then, HRTEM observations confirmed that the
interfaces are distinguishable, and can be very flat in the less crystalline part of the
deposits.

3.3 HRTEM analyses

HRTEM observations indicate that the metal/oxide periodic structure is very regular
through the whole thickness. The sub-layer thicknesses do not change during the growth
process in each period $A$ as typically shown in the HRTEM micrograph for a period $A =
50.0$ nm (Fig. 3a). A magnified area (Fig. 3b) allows a more detailed viewing of the
column going through all the oxide and metallic sub-layers. It also confirms that the
growth continues in spite of the pulsing process. Moreover, if the growth of the metallic sub-layer occurs on a column composed of crystallized TiO$_2$ phase (anatase or rutile), a distortion phenomenon of the metallic sub-layer in the growth direction is observed, which create defects and prevents the deposition of perfectly parallel multilayers to the silicon surface. Selected area electron diffraction patterns (SAED) pointed out a nanocrystalline structure and the presence of significant amounts of titanium-based compounds in all specimens. SAED patterns are more sensitive than XRD measurements to identify the different phases in a material at the nanometre scale. Indeed, this study shows that the occurrence of nanocrystals increases with the thickness of the period $\Lambda$. For each sample, only TiO$_2$ nanocrystals are present in the O-rich sub-layer $\lambda_{\text{ox}}$. The crystallite size increases as function of the sub-layer thickness from $\lambda_{\text{ox}} = 5.0$ to 25.0 nm. The metal sub-layer (Ti-rich) is more crystallized and exhibits two different crystal phases: hcp-Ti and fcc-TiO. Samples with small periods ($\Lambda < 17.0$ nm) are mainly composed by fcc-TiO crystals in the metal sub-layers. For intermediate periods ($17.0 < \Lambda < 35.0$ nm) as well as the largest ($\Lambda > 35.0$ nm) the hcp-Ti crystalline phase appears (for $\lambda_{\text{met}} > 7.0$ nm), which prevails over the fcc-TiO one. This highlights that although the crystallite size increases as a function of the $\Lambda$ period, TiO$_2$ remains the only crystalline phase in the O-rich sub-layer while the hcp-Ti phase becomes predominant compared to the fcc-TiO one as the thickness of the metal sub-layer gradually increases. In order to better understand the nanostructure, each phase and sub-layer are described in more details in the next paragraphs according to some arbitrary outlines (Parts A to E) as presented in figure 3b for a period $\Lambda = 50$ nm.

3.3.1 Poorly crystallized domains – Parts A and B

HRTEM micrographs show that the oxide sub-layers are mainly amorphous (part A). The
entire oxide sub-layer is made of more than 75% of this amorphous part A. The proportion depends on the thickness of the period $\Lambda$. When it increases from $\Lambda = 14.0$ to 45.0 nm, the amorphous part reduces from 95 down to 75% (roughly estimated by HRTEM). This reduction allows the development of a crystalline columnar structure (TiO$_2$ grains) as described later for part C. In this pseudo-crystallization, an interplanar distance $d = 0.350$ nm have been measured, which is close to the theoretical value $d_{101} = 0.352$ nm of the anatase phase. However, this measurement has only been performed for few crystallographic planes and the poor occurrence of this phase is not representative to the part A.

After this oxide sub-layer, the metallic one grows. The latter is mostly crystallized, but two zones can be defined. The first zone contains the part B and is just over the A one. It presents a lower content of crystallized grains than the parts D and E, which are in the second zone of the metallic sub-layer. As previously described from EDS and TEM data, the stacking is homogenous through the thickness $\lambda_{\text{met}}$ of the metallic sub-layer. The crystallinity only differs between the two zones. In the part B, HRTEM points out crystallographic planes parallel to the interface of Si (100). Thus, these planes show a preferential direction of growth. There are two interplanar distances, which appear according to the growth direction. At first, an interplanar distance $d = 0.240$ nm is measured and followed by another at $d = 0.255$ nm, which are close of the fcc-TiO phase ($d_{111} = 0.241$ nm) and hexagonal titanium metal ($d_{100} = 0.255$ nm), respectively. Defects in this sub-layer prevent from accurately locating the interface between these two distances. In most of cases, the size of fcc-TiO grains exhibiting (111) orientation is 4.0 ± 0.5 nm, except for samples with $\Lambda = 14.0$ and 45.0 nm where the thickness of the fcc-TiO grains is higher. However, samples with the metallic sub-layer thickness $\lambda_{\text{met}} > 7.0$ nm exhibit larger titanium grains with $d_{100} = 0.255$ nm (hcp-Ti phase) in the part B.
3.3.2 Crystallized domains – Parts C, D and E

These crystallized parts C, D and E are identified as crystalline columnar structure. The width of these columns can reach 25 nm and be extended through the entire oxide sub-layer thickness $\lambda_{\text{ox}}$. The C part faces the A part previously described (corresponding to the O-rich sub-layer) whereas the D and E parts face the B one (Ti-rich one). Following a column through those sub-layers helps to detail the different phases occurring during the growth from the oxide to the metallic sub-layer. In the complete crystalline part C of the oxide sub-layer (Fig. 4d), [00-1] zone axes are indexed as a rutile-TiO$_2$ phase. The interplanar distance $d_{200} = 0.231$ nm is very close to the theoretical value of 0.230 nm.

The crystallized zone of columns in oxide sub-layers is always composed of a rutile phase, which grows in a preferential direction.

After the rutile TiO$_2$ phase, another crystallized zone is found by HRTEM. This zone includes two parts (D and E). Taking into account the growing direction, zone axes [01-1] of the fcc-TiO phase have been pointed out (part D) in figure 4c. Then, HRTEM picture highlights that the hcp-Ti phase prevails (part E) and grows in the hexagonal conformation with [001] zone axes (Fig. 4b). Thickness of the fcc-TiO phase is always about 4 nm and the remaining thickness corresponds to the hcp-Ti one (except for samples with $\Lambda = 18.0$ and 45.0 nm). Interplanar distances $d_{111}$ and $d_{100}$ (fcc-TiO and hcp-Ti phases, respectively) also exhibit a preferential direction parallel to the substrate surface. Moreover, the selected area electron diffraction pattern acquired in the columnar area confirms that three families of planes grow following a parallel direction to each other, but perpendicular to the growth direction. They are indexed as rutile-TiO$_2$-$d_{200}$, fcc-TiO-$d_{111}$ and hcp-Ti-$d_{100}$, respectively (SAED in Fig. 4a). As a result, we can claim that the multilayered structure is composed of a-TiO$_2$/rutile-TiO$_2$, fcc-TiO and hcp-Ti.
periodic alternations. The formation of a TiO sub-layer between the TiO$_2$ and Ti can, to some extent, be explained by the fact that it takes a certain time to sputter away the oxide layer formed at the target surface. During this time, a TiO film will be grown.

### 3.4 Electrical behaviours

For all samples, the DC electrical resistivity $\rho$ was measured in the van der Pauw configuration in the temperature range $T = 300 – 500$ K (Fig. 5). A linear evolution of $\rho$ versus $T$ was systematically observed for any multilayer with resistivity changing from $\rho = 5.76 \times 10^{-7}$ to $1.22 \times 10^{-5}$ $\Omega$m, which are typical of metallic-like materials. It is worth noting that four samples with the shortest period $\Lambda (\chi' = 0.338$ to $0.464$ defined later from equation (4)) exhibit a negative slope. In addition, resistivity is quasi constant for sample with $\Lambda = 40.5$ nm ($\chi' = 0.523$) whereas the others behave like conventional metals, i.e. an increase of the resistivity as the temperature rises. Since the final deposited sub-layer is titanium, an increase of the period thickness $\Lambda$ leads to a lower resistivity, which tends to that of pure titanium film. For metallic materials, the variation of electrical resistivity $\rho$ is commonly connected to the temperature $T$ using:

$$\rho = \rho_0 \left[1 + \alpha_0 (T - T_0)\right]$$

(1)

with $\rho_0$ is the resistivity measured at $T_0 = 300$ K and $\alpha_0$ is the temperature coefficient of resistance (TCR in K$^{-1}$) defined from the following relationship:

$$\alpha_0 = TCR = \frac{1}{\rho_0} \left[\frac{\partial \rho}{\partial T}\right]_{T = T_0}$$

(2)

As shown in table 1, positive TCR values are measured for periods $\Lambda$ higher than 31.0 nm (except for $\Lambda = 34.5$ nm where TCR is negative). TCR ranges from $2.17 \times 10^{-4}$ to $1.20 \times 10^{-3}$ K$^{-1}$ as the period changes from $\Lambda = 31.0$ to 50.0 nm. Resistivity as well as
TCR shift to the bulk Ti values for the thickest periods ($\rho_{293K} = 3.91 \times 10^{-7}$ $\Omega$m and TCR = $5.5 \times 10^{-3}$ $K^{-1}$ for bulk titanium). However, it significantly deviates from the bulk properties as commonly observed for thin films. This is mainly attributed to the scattering of electrons at the grain boundaries [33]. Thus, the decrease of conductivity can be first related to the increasing number of grain boundaries per electron mean free path. By decreasing the period thickness $\Lambda$, electron scattering is enhanced due to the highest number of interfaces and grain boundaries since the crystallite size decreases from XRD analyses (Fig. 1). It is worth noting that for the shortest periods ($\Lambda < 16.5$ nm), the films become amorphous. No crystallite size can be significantly determined but the interfaces of the periodic TiO$_2$/TiO/Ti alternations are still distinguishable as shown in Fig. 2a and 2b. Thus, one can assume that the scattering effect of electrons is mainly due to interfaces. The electron mean free path (about few tens nanometers in well crystallized films) reduces and is mainly limited by the thickness of the sub-layer periods $\lambda_{ox}$ and $\lambda_{met}$ rather than the grain boundaries. In addition, because of the substantial amount of oxygen in the metallic sub-layer, the defect concentration rises as well, which contributes to the electron scattering and thus, to the high resistivity and low TCR values. The defects can be point defects (vacancies, interstitials), grain boundary discontinuities and 2D defects (dislocations, stacking faults) generated by interfaces of the stacks. In our periodic TiO$_2$/TiO/Ti multilayers, the point defects are mainly oxygen vacancies and titanium interstitials in the metallic sub-layer $\lambda_{met}$. A change of the calculated TCR from $-7.58 \times 10^{-4}$ to $-3.12 \times 10^{-4}$ $K^{-1}$ is even measured for the lowest periods $\Lambda$ although the electrical properties show a metallic-like resistivity. Such negative TCRs correlate with the decrease of the grain size (tending and becoming shorter than the electron mean free path) previously observed from XRD and HRTEM. There variations of resistivity vs. period thickness $\Lambda$ can not be solely explained taking
into account resistivity values of pure Ti and fcc TiO compounds ($\rho_{300K}(\text{Ti}) = 3.9 \times 10^{-7}$ $\Omega m$ and $\rho_{300K}(\text{TiO}) = 2.6 \times 10^{-6}$ $\Omega m$ [34]). Our resistivity measurements showed that $\rho_{300K}$ changes from $1.2 \times 10^{-5}$ down to $5.9 \times 10^{-7}$ $\Omega m$ as the period thickness $\Lambda$ rises from 14.0 to 54.0 nm, i.e. order of magnitude higher than fcc TiO compound for the shortest period $\Lambda$. Thus, the sub-layer dimensions as well as the chemical composition have to be taken into account.

In order to better understand the electrical properties of these multilayers as the period thickness $\Lambda$ changes, we first analyzed the correlation between the resistivity and the $\chi$ parameter. This latter is defined as the metal ($\lambda_{\text{met}}$) to oxide ($\lambda_{\text{ox}}$) thickness ratio in a period $\Lambda$ from:

$$\chi = \frac{\lambda_{\text{met}}}{\lambda_{\text{ox}}}$$ (3)

In table 1, all parameters (especially the composition) are directly linked to the resistivity and their corresponding TCR values. For most of the samples, the resistivity tends to decrease as a function of the metallic sub-layer thickness $\lambda_{\text{met}}$. Assuming a simple mixture rule [35], such a decrease can be assigned to the thickness of the metallic sub-layer in the multilayer period $\Lambda$, i.e. to the $\chi$ parameter. However, the evolution of resistivity at a given temperature (e.g. $\rho_{475K}$ at 475 K as reported in table 1) versus $\chi$ parameter does not exhibit a smooth trend. Multilayers with $\chi = 0.75, 0.69$ and 0.89 ($\Lambda = 14.0, 40.5$ and 42.5 nm, respectively) strongly deviate from a hypothetic simple exponential relationship between resistivity $\rho_{475K}$ and the metal to oxide thickness ratio $\chi$. Such discrepancy can not be due to some variations of the total thickness of the film $t_{tot}$ since all samples are in-between 335 to 435 nm. Therefore, another and more significant parameter than $\chi$ is required to link structure, composition and resistivity. Taking into account EDX analyses samples, which deviates from the hypothetic
exponential relationship between $\rho$ and $\chi$ stated before, titanium concentration $C_{\lambda_{\text{met}}}$ in
the metallic sub-layer versus period $\Lambda$ also exhibits a more or less randomized evolution.

The idea is then to combine the $\chi$ and $C_{\lambda_{\text{met}}}$ parameters so as to get the real part of
titanium in the metallic sub-layer. For the oxide sub-layer, such correction is not relevant
since the chemical composition of this sub-layer is always very close to the TiO$_2$
compound for any oxide sub-layer thickness $\lambda_{\text{ox}}$. Then, the $\chi'$ parameter can be defined
as:

$$
\chi' = \frac{C_{\lambda_{\text{met}}} \times \lambda_{\text{met}}}{\lambda_{\text{ox}}} 
$$

(4)

It was calculated for all samples (Table 1). A regular and monotonous decrease of the
electrical resistivity $\rho$ versus $\chi'$ parameter is then obtained. As a result, period $\Lambda$, sub-
layers thickness $\lambda_{\text{met}}$ and $\lambda_{\text{ox}}$ as well as titanium concentration $C_{\lambda_{\text{met}}}$ in the metallic sub-
layer can be reliably connected to the resistivity. However, the total thickness $t_{\text{tot}}$ of the
sample also plays an important role. Indeed, figure 6 shows a direct relationship, where $\rho$
is a function of $\chi'$ and $t_{\text{tot}}$. For a fixed temperature, resistivity can be expressed as:

$$
\rho = \gamma \exp \left( \frac{\beta t_{\text{total}}}{\chi'} \right) 
$$

(5)

where $\gamma$ and $\beta$ are constants. It is worth noting that $\gamma$ has the dimensions of an electrical
resistivity. Without any multilayer, one can assume that the $\chi'$ parameter approaches
infinity and the film can be considered as pure titanium. Then, the resistivity of the film
becomes that of the bulk titanium and it can be stated that $\gamma$ represents the resistivity $\rho_0$
of pure Ti. From the results presented in figure 6, calculations lead to $\gamma = 5.44 \times 10^{-7}$ $\Omega$ m,
which is very close to the resistivity value measured at room temperature for the Ti pure
sample ($5.80 \times 10^{-7}$ $\Omega$ m). Similarly, $\beta = 2.97 \times 10^{-7}$ $m^{-1}$ has the dimensions of a reciprocal
length. In a manner analogous to the propagation of electromagnetic waves through
matter, its physical meaning can be similar to a virtual linear attenuation coefficient intrinsic to the metal oxide interfaces created by the periodic stacks. We suggest that the \( \beta \) parameter characterizes how easily the charge carriers can penetrate through the interfaces of the multilayered structure.

Goldfarb et al. [36] correlated the rising resistivity in binary transition metal oxide with the increasing oxygen concentration in the films. By increasing the oxygen content, they claim that oxidation causes depletion of the metal d-band charge carriers in favour of the \( \text{O} \, 2p \) valence and so, the carrier concentration decreases. A metal-insulator transition occurs leading to a TCR sign change and an increase of resistivity. In our case, this model cannot be taken into account since the oxygen concentration is not the only parameter which influences the electrical properties of \( \text{TiO}_2/\text{TiO}/\text{Ti} \) multilayers (Table 1). As a result, the resistivity decrease as a function of the \( \chi' \) parameter has to be discussed taking into account mobility and charge carriers concentration.

Hall effect measurements systematically reveal n-type charge carriers for all multilayers. Hall mobility \( \mu \) versus carrier concentration \( n \) is then plotted (Fig. 7). For all samples, \( \log \mu \) decrease as a function of \( \log n \). At first, one can notice that mobility as well as carrier concentration are both influenced by the \( \chi' \) parameter. As \( \chi' \) rises from 0.523 up to 1.623, the carrier concentration changes from \( n = 10^{22} \) to \( 6 \times 10^{22} \, \text{cm}^{-3} \) and the Hall mobility varies from \( \mu = 5 \) to 60 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \). This evolution agrees with the metallic-like behaviour, which is promoted (resistivity tends to that of Ti bulk and positive sign of the TCR) as \( \chi' \) increases (Fig. 5). For bulk metals, electron mobility \( \mu \) is in-between \( 10^2 \) to \( 10^3 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) at 300 K and above room temperature, the temperature dependence follows \( \mu \propto T^{-1} \) [37]. For metallic thin films, electron mobility is lower than those measured for bulks due to electron scattering at the grain boundaries [38], with a film’s thickness dependence, which is related to the nature of the metal. According to Khojier
and Savaloni [39], the mobility vs. thickness of pure titanium films exhibits a low
decrease from $\mu = 1.04 \times 10^3$ down to $1.00 \times 10^3 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ as the thickness rises from 12
up to 40 nm. From the same authors, the effect of the temperature has also been
investigated (from room temperature until 573 K). A decrease of the mobility (10 to 20%
of drop) has been observed with the temperature rising. As a result, period thickness and
temperature variations are in the same order of magnitude in our study. However, the
pure titanium properties can not be taken as the key parameter, which contributes to the
electronic transport properties, even for the thickest period $\Lambda = 50.0$ nm, because Hall
mobility of the periodic TiO$_2$/TiO/Ti multilayers is in-between 5 to 60 cm$^2\text{V}^{-1}\text{s}^{-1}$ (more
than one order of magnitude lower than pure titanium).

It is worth noting that the mobility is even more influenced by the $\chi'$ parameter changes
since Hall mobility exhibits values in-between $\mu = 5$ to 60 cm$^2\text{V}^{-1}\text{s}^{-1}$ as $\chi'$ rises from
0.523 up to 1.623, respectively. Considering the order of magnitude of the carrier
concentration and its evolution as a function of the carrier mobility, the electrical
properties are mainly related to ionized impurity scattering [40]. The theoretical
relationship suggested by Seto [41] for mobility dominated by grain boundary scattering
is negligible. The observed trend can be rather understood by the Brooks-Herring (BH)
theory [42]. In our study, the deposition of TiO$_2$/TiO/Ti periodic alternations generates
several types of defects, which can be point defects, grain boundary discontinuities,
interfacial defects (dislocations, stacking faults) and interfaces due to the multilayered
structure. The point defects are mainly oxygen vacancies and titanium interstitials (self-
interstitial atoms). As a simplifying assumption, it can be firstly assumed that such point
defects act as impurities in the scattering phenomena of the charge carriers. Taking into
account the screening of the ionized impurities, the BH theoretical relationship links
carrier mobility $\mu_{BH}$ $(\text{cm}^2\text{V}^{-1}\text{s}^{-1})$ and carrier concentration $n$ $(\text{cm}^{-3})$ according to the
following equation:

\[ \mu_{BH} = \frac{C_1 T^{3/2}}{N_{II}} \left[ \ln \left( \frac{C_2 T^2}{n} \right) \right]^{-1} \]  

(6)

with \( C_1 \) and \( C_2 \) are constants given by:

\[ C_1 = \frac{128 \sqrt{2\pi \varepsilon^2 k_B^3}}{\sqrt{m_{eff} Z^2 e^3}} \]  

(7)

and

\[ C_2 = \frac{24 m_{eff} \varepsilon k_B^2}{e^2 h^2} \]  

(8)

where \( T \) is the temperature (K), \( k_B \) the Boltzmann constant (1.38×10^{-23} \text{ JK}^{-1}), \( Z \) the charge of the scattering centre, \( \varepsilon \) the permittivity of the material (fixed at 6.25), \( m_{eff} \) the effective mass of electron (2.28×10^{-31} \text{ kg}), \( e \) the elementary charge (1.6×10^{-19} \text{ As}), \( h \) the reduced Planck’s constant (1.055×10^{-34} \text{ Js}) and \( N_{II} \) the ionized impurity concentration (cm^{-3}). For this study, we have \( C_1 = 1.0\times10^{19} \text{ m}^{-1}\text{V}^{-1}\text{s}^{-1}\text{K}^{-3/2} \) and \( C_2 = 1.5\times10^{20} \text{ m}^{-3}\text{K}^{-2} \).

Calculations of \( \mu_{BH} \) vs. \( n \) have been performed for the temperature range 300 – 500 K.

The carrier concentration has been incrementally increased for the studied range \( n = 10^{20} \) - \( 10^{24} \) cm^{-3}. Increment \( I \) has been defined as a function of the carrier concentration range. Hundred increments have been used for each carrier concentration decade (e.g. \( I = 10^{P-2} \) increments with \( P = 21 \) for \( 10^{20} < n < 10^{21} \) cm^{-3}). The ionized impurity concentration \( N_{II} \) was adjusted in order to fit with experimental data as shown in figure 7. It can be seen that \( N_{II} \) increases from 7.30×10^{-3}×n to 4.35×10^{-2}×n cm^{-3} when the \( \chi' \) parameter reduces from 1.623 down to 0.523, respectively. Therefore, the decrease of \( \mu \) versus \( n \) is assumed to be due to an increase of the defects concentration, which act as dominant scattering centres because of the fcc TiO phase occurrence in the metallic sub-layers [43]. This also means that the TiO_2/TiO/Ti periodic multilayers are characterized (supported by
HRTEM observations) by a high stacking fault density in the range of $10^{20}$ cm$^{-3}$. According to McLachlan [44], these stacking faults can mainly be generated by the formation of titanium and oxygen vacancies since both types of defects can coexist over a large chemical composition in the fcc-TiO$_x$ phase (0.8<x<1.3). In addition, since oxygen vacancies exhibit a charge of $Z = 2$, its scattering power is higher than that of single ionized doping elements leading to a reduced mobility and an enhanced carrier concentration.

4. Conclusion

TiO$_2$/TiO/Ti periodic multilayers were successfully prepared by DC reactive magnetron sputtering. The reactive gas pulsing process was used to reach regular periodic alternations with periods $\Lambda$ in-between 14.0 and 50.0 nm. The oxide sub-layers are composed of rutile and amorphous TiO$_2$ phases, whereas the metallic sub-layers are formed by a mixture of hcp-titanium and fcc-TiO phases. The difference of metallic and oxide sub-layers crystallinity was evidenced from TEM and HRTEM observations. It was shown that the TiO$_2$/TiO/Ti periodic structure is partially nanocrystalline with metallic sub-layers, which are better crystallized than the oxide ones. In the metallic sub-layers, the thickness of the fcc-TiO phase was always 4 nm and the remaining corresponded to hcp-Ti. A columnar structure was also pointed out with the occurrence of numerous defects in the crystalline parts. HRTEM investigations confirmed that the columnar growth is maintained in spite of the reactive gas pulses. The chemical composition analyses revealed a homogenous TiO$_2$ stoichiometric compound in the oxide sub-layers while the titanium concentration strongly varied in the metallic sub-layers. The latter must to be taken into account to understand the electronic transport properties. To this aim, a $\chi'$ parameter was defined from the titanium concentration in
the metallic sub-layer as well as the metal ($\lambda_{\text{met}}$) to oxide ($\lambda_{\text{ox}}$) thickness ratio in a single period $\Lambda$. Such $\chi'$ parameter was connected to the DC electrical resistivity using an exponential law. TiO$_2$/TiO/Ti periodic multilayers exhibited a metallic-like behaviour with a TCR sign change and a decrease of resistivity versus $\chi'$. It was mainly assigned to a reduced carrier mobility and an enhanced carrier concentration produced by ionized impurity scattering. The latter was especially favoured by an increase of the defects concentration in the metallic sub-layers. Moreover, the resistivity measurements of these TiO$_2$/TiO/Ti thin multilayers pointed out some tuneable electrical characteristics versus temperature for an optimized $\chi'$ parameter. These results enable some attractive applications of such multilayers, especially for sensors and devices, which often require invariant conduction properties versus temperature.

Acknowledgements

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Table captions

Table 1

Summary of dimensional, compositional and electrical characteristics of TiO$_2$/TiO/Ti periodic multilayer films. $A$ = period of TiO$_2$/TiO/Ti multilayers. $t_{tot}$ = total thickness of the film. $\lambda_{\text{met}}$ = metallic sub-layer thickness. $\lambda_{\text{ox}}$ = oxide sub-layer thickness. $\chi = \lambda_{\text{met}} / \lambda_{\text{ox}}$ as defined from equation (3). $C_{\lambda_{\text{met}}}$ = titanium concentration in the metallic sub-layer. $\chi' = \chi \times C_{\lambda_{\text{met}}}$ as defined from equation (4). TCR = temperature coefficient of resistance calculated from equation (2). $\rho_{473K}$ = DC electrical resistivity at 473 K.
<table>
<thead>
<tr>
<th>( \Lambda ) (± 0.1 nm)</th>
<th>( t_{tot} ) (± 5 nm)</th>
<th>( \lambda_{met} ) (± 0.1 nm)</th>
<th>( \lambda_{ox} ) (± 0.1 nm)</th>
<th>( \chi ) (a.u.)</th>
<th>( C_{\lambda_{met}} ) (± 0.02)</th>
<th>( \chi' ) (a.u.)</th>
<th>TCR (×10^{-4} K^{-1})</th>
<th>( \rho_{475K} ) (×10^{-6} Ωm)</th>
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<tr>
<td>14.0</td>
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<td>0.45</td>
<td>0.338</td>
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<td>10.5</td>
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<td>1.633</td>
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Figure captions

Figure 1
XRD patterns of TiO$_2$/TiO$_x$/Ti multilayered films deposited on (100) silicon wafer for various $\Lambda$ periodic alternations. The $\chi'$ parameter calculated from equation (4) is also indicated. $\bigstar$ = Si substrate; $\bullet$ = fcc-TiO; $\square$ hcp-Ti.

Figure 2
TEM cross-section observations of TiO$_2$/TiO/Ti multilayered films deposited on (100) silicon wafer. a) Low magnification BF and b) DF images of the sample period $\Lambda = 14.0$ nm. The thickness of metallic and oxide sub-layers is $\lambda_{\text{met}} = 6.0$ nm and $\lambda_{\text{ox}} = 8.0$ nm, respectively. The total thickness is $t_{\text{tot}} = 345$ nm. c) Low magnification BF and d) DF images of the sample period $\Lambda = 50.0$ nm with $\lambda_{\text{met}} = 35.0$ nm, $\lambda_{\text{ox}} = 15.0$ nm and $t_{\text{tot}} = 405$ nm.

Figure 3
a) BF micrograph of a multilayer with 8 periods of $\Lambda = 50.0$ nm and a total thickness $t_{\text{tot}} = 405$ nm. b) A magnified part of this multilayer where metallic and oxide sub-layer thicknesses are $\lambda_{\text{met}} = 35.0$ nm and $\lambda_{\text{ox}} = 15.0$ nm, respectively. Poorly crystallized (A and B) and crystallized domains (C, D and E) are shown.

Figure 4
(a) The selected area electron diffraction pattern reveals the epitaxial growth of TiO$_2$/TiO/Ti multilayer, by indication of the three phases.
(b) HRTEM micrograph shows a part of the crystallized domains E of Fig. 3b, with an hcp-Ti structure and a zone axis $ZA = [0001]$. (c) HRTEM micrograph shows a crystalline area of the part D in Fig. 3b with an fcc-TiO structure and a zone axis [01-1]. (d) HRTEM micrograph shows a rutile phase structure with the d-spacing of the (110) and (200) planes, zone axis $ZA = [00-1]$. A white arrow indicates the growth direction.

**Figure 5**

DC electrical resistivity $\rho$ versus temperature $T$ measured on TiO$_2$/TiO/Ti multilayers for period thickness $A$ ranging from 14.0 to 50.0 nm. The $\chi'$ parameter defined from equation (4) is systematically indicated.

**Figure 6**

Linear evolution of the DC electrical resistivity $\rho_{300K}$ at 300 K versus total thickness $t_{tot}/\chi'$ parameter ratio. The $\rho_{300K}$-intercept gives the resistivity of bulk titanium and the slope is related to the capacity of charges carrier to cross through the interfaces of the multilayered structure.

**Figure 7**

Measured Hall mobility $\mu$ as a function of the carrier concentration $n$ of TiO$_2$/TiO/Ti multilayers for various $\chi'$ parameters defined from equation (4). The solid lines represent the $\mu$ versus $n$ evolution calculated from the Brooks-Herring theory assuming that the mobility is dominated by the ionized impurity scattering. The ionized impurity concentration $N_{II}$ is adjusted from the carrier concentration.
Figure 1

\[ \chi' = 1.029 \]
\[ \Lambda = 40.0 \text{ nm} \]

\[ \chi' = 0.911 \]
\[ \Lambda = 31.0 \text{ nm} \]

\[ \chi' = 0.464 \]
\[ \Lambda = 18.0 \text{ nm} \]

\[ \chi' = 0.404 \]
\[ \Lambda = 34.6 \text{ nm} \]

(100) (111)
\[ \chi' = 0.390 \]
\[ \Lambda = 16.5 \text{ nm} \]

(111)
\[ \chi' = 0.338 \]
\[ \Lambda = 14.0 \text{ nm} \]
Figure 4
Figure 5
Figure 6
Figure 7