Anisotropic electrical resistivity during annealing of oriented columnar titanium films

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Abstract

We report on the evolution of anisotropic electrical resistivity versus temperature of titanium thin films. An oriented titanium film (1 µm thick) is sputter deposited by GLancing Angle Deposition (GLAD) using an incident angle α = 80° of the particle flux. Two parallel Ti electrodes cover this GLAD film. We measure the components of the conductivity tensor by the van der Pauw method during an annealing treatment in air ranging from 298 to 873 K. The average DC electrical resistivity ρ changes from 6.03×10^{-6} to more than 2.40×10^{-1} Ωm with the increasing temperature. The anisotropy ratio is A = 1.39 before annealing and reaches 12.4 for the highest temperatures. This enhanced anisotropy is interpreted assuming the oxidation of the porous GLAD titanium film.

Keywords: GLAD, titanium, resistivity, anisotropy, annealing

1. Introduction

DC electrical resistivity of metal and semiconductor thin films can be determined by the van der Pauw (vdP) method [1]. It is a convenient method, which requires only four contacts sufficiently small and located at the circumference of the sample. This powerful method is based on averaging measurements of the potential difference between two electrodes when a known current flows between two other electrodes. One of the strong hypotheses of this method assumes an isotropic conductive medium. However, most thin films produced by vacuum processes, often exhibit anisotropic behaviors. In order to get electronic transport properties in such anisotropic thin films, components of the resistivity tensor have to be determined. For this purpose, the theory of the vdP method has been extended [2-5]. Price [6] showed that the method may be applied to anisotropic materials provided that one of the principal axes of the resistivity tensor is perpendicular to the plane of the sample. Recently, Bierwagen et al. [7] proposed an original procedure to obtain anisotropic transport properties, especially from the results of the vdP measurements. This letter demonstrates that the anisotropic DC electrical resistivity of titanium thin films can be measured from the Bierwagen et al. method during an annealing treatment.

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2. Material and methods

The titanium films were deposited on glass by DC reactive magnetron sputtering from a titanium target (purity 99.6 %) in a pure argon atmosphere using a sputtering pressure P_{sput} = 0.10 Pa. The target was sputtered with a current density J_{Ti} = 100 Am^{-2}. Substrates were grounded and unheated during deposition. A titanium film 1 μm thick was first deposited on the glass substrate by GLancing Angle Deposition (GLAD) [8] using an incident angle α of the particle flux of 80°. An oriented columnar structure was produced with a column angle β close to 40°. The latter is systematically lower than the incident angle because of the shadowing effect produced by the growing columns [8]. Afterwards, two parallel strips extending along the x axis (by means of a mask) of titanium 500 nm thick and separated by 9 mm were deposited by conventional sputtering (α = 0°). Two probes were placed on each titanium strip leading to a square geometry with $L_x = L_y$ = 10 mm (Fig. 1). Then, the vdP configuration was used to measure the average and anisotropic electrical resistivity. The annealing treatment in air was performed following 9 cycles of temperature. The first cycle started from 298 up to 473 K at 5 K min^{-1} followed by a return to 298 K with the same ramp of 5 $Kmin^{-1}$. The second cycle was similar to the previous one up to 523 K (increment of 50 K). The third cycle was up to 573 K and so on until the last cycle (9^{th}) reached 873 K to finally come back to 298 K.

3. Results and discussion

Assuming that the sides of the sample are parallel to the principal axes of the tensor, the conductivity tensor can be expressed in the following form:

$$\sigma = \begin{bmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{yy} \end{bmatrix} \quad (1)$$

Where σ_{xx} (Sm^{-1}) and σ_{yy} (Sm^{-1}) are the principal conductivities in the mutually perpendicular directions x,y of the two-dimensional plane, respectively. In order to get these σ_{xx} and σ_{yy} components, the resistances R_{xx} (Ω) and R_{yy} (Ω) are first measured from:

$$R_{xx} = \frac{R_{14,23} + R_{41,32}}{2} = \frac{\frac{V_{23}}{I_{14}} + \frac{V_{32}}{I_{41}}}{2} \quad \text{and} \quad R_{yy} = \frac{R_{12,43} + R_{21,34}}{2} = \frac{\frac{V_{43}}{I_{12}} + \frac{V_{34}}{I_{21}}}{2} \quad (2)$$

Where V_{23} (V) is the voltage measured across contacts 2 and 3 (inverse for V_{32}) and I_{14} (A) is the current flowing through the contacts 1 and 4 (inverse for I_{41}), and analogously for R_{yy}. The average DC electrical resistivity ρ (Ωm) can be calculated using the classical vdP approach with [1]:

$$\exp\left(\frac{-\pi d R_{xx}}{\rho}\right) + \exp\left(\frac{-\pi d R_{yy}}{\rho}\right) = 1 \quad (3)$$

Where d (m) is the thickness of the sample. The anisotropy in our vdP configuration A_{vdP} is defined as [7,9]:

$$A_{vdP} = \frac{R_{yy}}{R_{xx}} = \frac{\sum_{n=odd^+} \left[n \times \sinh\left(\sqrt{A_{eff}^{-1}}\, \pi\, n \right) \right]^{-1}}{\sum_{n=odd^+} \left[n \times \sinh\left(\sqrt{A_{eff}}\, \pi\, n \right) \right]^{-1}} \quad (4)$$

This equation (4) is used to calculate the effective anisotropy A_{eff}. The anisotropic coefficient A is finally deduced from:

$$A = A_{eff} \times \left(\frac{L_y}{L_x} \right)^2 = \frac{\rho_{yy}}{\rho_{xx}} = \frac{\sigma_{xx}}{\sigma_{yy}} \quad (5)$$

And the σ_{xx} and σ_{yy} components are obtained with:

$$\frac{1}{\sigma_{xx}} = \rho_{xx} = \rho \times \sqrt{A^{-1}} \qquad \text{and} \qquad \frac{1}{\sigma_{yy}} = \rho_{yy} = \rho \times \sqrt{A} \quad (6)$$

Where ρ_{xx} (Ωm) and ρ_{yy} (Ωm) are the resistivities in the mutually perpendicular directions *x,y* of the two-dimensional plane, respectively.

The average DC electrical resistivity ρ was first measured as a function of the annealing treatment (Fig. 2). Before heating, the resistivity at room temperature is $\rho_{298} = 6.03\times10^{-6}$ Ωm, which is more than one order of magnitude of the bulk titanium (ρ_{298} bulk = 3.91×10^{-7} Ωm). It is mainly attributed to the scattering of electrons at the grain boundaries [10]. Due to the high porous structure of the GLAD films [11], scattering is particularly favored at the column interfaces reducing the electronic transport properties. A typical metallic-like behavior is measured as the temperature rises up to $T = 473$ K since ρ_{473} linearly reaches 8.15×10^{-6} Ωm. A linear interpolation of ρ versus T is calculated up to 370 K, leading to a temperature coefficient of resistance (TCR) of 1.19×10^{-3} K^{-1}, which is again lower than that of the bulk value (TCR bulk = 5.50×10^{-3} K^{-1}).

A further increase of the temperature up to 473 K leads to a non linear evolution of the resistivity versus temperature since ρ_{473K} reaches 8.11×10^{-6} Ωm before the temperature drops. For the first cycle, the return to the room temperature gives rise to a linear evolution of ρ versus T and the resistivity is down to $\rho_{298} = 7.24\times10^{-6}$ Ωm before starting the second cycle. This increase of resistivity is mainly attributed to the initial oxidation of the GLAD porous titanium film. Further annealing treatments (2nd to 5th cycles) reduce the metallic-like character of the film since the resistivity reaches $\rho_{298} = 1.83\times10^{-5}$ Ωm at the end of the fifth cycle. In addition, the TCR decreases and finally becomes negative (TCR = -1.07×10^{-4} K^{-1}) due to the emphasized oxidation of the GLAD film. We can suggest that metallic titanium monoxide is produced since negative TCRs are obtained in TiO_x films ($0.80 < x < 1.23$) containing a high concentration of defects [12]. Assuming the Mooij criterion [13], the increasing resistivity vs. annealing cycle is mainly due to a disordering effect (coming from the oxidation), inducing a reduction of the electron mean free path from several to a few interatomic spacings. This trend is even more significant for the 8th and 9th cycles, for

which resistivity values and their evolution as a function of the temperature correspond to a semi-conducting-like behavior. At the end of the final cycle (9^{th}) and as the temperature decreases, ρ_{500} reaches 2.40×10^{-1} Ωm. Below 500 K the film is too resistive to be accurately measured with our vdP system. This last annealing cycle leads to the most important jump of the electrical resistivity since 3 orders of magnitude separate resistivity values measured between the 8^{th} and 9^{th} cycle (axis break in Fig. 2). This smooth metal-to-semiconductor transition has previously been reported for other compounds [14], but rarely for GLAD thin films [15]. It correlates with a change from a low resistivity behavior (metallic-like) of oxygen-rich $TiO_{1+\varepsilon}$ exhibiting a negative TCR [16], to a semiconducting-like behavior observed for oxygen-deficient $TiO_{2-\delta}$ with a low activation energy [17]. In this study, this transition is mainly ascribed to the oxidation of the GLAD porous titanium film, which is emphasized for the 8^{th} cycle, and becomes even more significant at the final annealing treatment. As a result, it can be claimed that an oxygen-deficient titanium dioxide compound is formed. The generalized model of conduction proposed by Goldfarb et al. [18] for amorphous transition-metal oxides is then appropriate to interpret this increase of resistivity vs. annealing treatment. A continuous oxidation causes depletion of the Ti d-band charge carriers in favor of the O 2p valence band, inducing a transition from metallic to hopping conduction, and finally down to the percolation threshold. This oxidation occurs up to a point where the hopping sites tend to be few and so distant from each other that only percolation conduction can take place. In the end, the concentration of hopping sites falls below the threshold for percolation and the resistivity becomes too high to be measured by the vdP technique.

The conduction anisotropy during the annealing treatment has been investigated from calculations of the ρ_{xx} and ρ_{yy} components using equations (1) to (6). Their evolution and the anisotropic coefficient vs. annealing cycle number are measured at 473K (Fig. 3). It is worth noting that the resistivity ρ_{xx} along the x-direction is systematically lower than that of the y-direction ρ_{yy} for any annealing cycle. This difference is mainly related to the GLAD Ti film microstructure. Since a very high porous architecture is especially favored for grazing incident angles of the particle flux ($\alpha > 70°$), the number of electrical pathways available for the free carriers are reduced leading to a decrease of the electron mean free path. In addition, GLAD deposition of columnar films with incident angles close or higher than 60° gives rise to a significant structural and uniaxial anisotropy in the substrate plane induced by the shadowing effect [19]. This effect mainly occurs in the direction of the incident vapor flux. Islands grow with connections to each other by chains perpendicular to the plane of incidence or to the direction of shadowing [20]. Films produce a columnar structure with columns exhibiting an elliptical section versus the incident angle, which is particularly marked for $\alpha \geq 60°$. As a result, $\rho_{xx} = 6.90\times10^{-6}$ Ωm and $\rho_{yy} = 9.62\times10^{-6}$ Ωm are measured with a corresponding anisotropic coefficient $A = 1.39$ for the first cycle. These values seem to be contradictory with results previously obtained by others [21, 22], who reported the lowest resistivity in the particle flux direction (y-direction) for GLAD metallic films. Besides some discrepancies are related to the measurement method and the definition of

the anisotropic coefficient, the authors also reported that the anisotropic transport properties depend on the local microstructure of the films and the nature of deposited materials. However, it should be reminded that our system is composed of Ti stacks where two parallel strips of Ti deposited by conventional sputtering ($\alpha = 0°$) cover the GLAD Ti film ($\alpha = 80°$). Thus, resistivity of our system according to the x-direction is systematically lower than that of the y-direction.

Until the 7th cycle, ρ_{xx} and ρ_{yy} gradually increase up to 1.66×10^{-5} and 2.64×10^{-5} Ωm, respectively and inversely the anisotropic coefficient decreases down to $A = 1.59$. This range of resistivities corresponds to a metallic-like behavior in both x and y directions in spite of a negative TCR value calculated from the average resistivity. The oxidation only occurs on the surface of the conventional Ti film ($\alpha = 0°$) whereas it becomes significant through the thickness of the GLAD Ti film due to its high porous structure [15]. It supports the formation of a $TiO_{1+\varepsilon}$-like compound since the resistivity ρ_{yy} remains in the order of magnitude of metallic compounds.

The sudden increase of the average DC electrical resistivity ρ previously measured from the 8th cycle (Fig. 2) correlates with the beginning of the anisotropy change (Fig. 3). The anisotropic coefficient rises to $A = 12.4$ as the 9th cycle ends and resistivities reach $\rho_{xx} = 6.54\times10^{-2}$ and $\rho_{yy} = 8.13\times10^{-1}$ Ωm. As a result, these last annealing cycles do not solely lead to a smooth metal-to-semiconductor transition. They also emphasize the anisotropy of the electronic transport properties. Oxidation phenomenon proceeds in the GLAD Ti thin film and becomes substantial in the conventional Ti thin film strips. Taking into account the fact that the oxidation kinetics of pure titanium becomes especially significant from about 830 K [23], the conventional Ti film is certainly transformed into a mixture of TiO and TiO_2 compounds since the temperature of the final cycle reaches 873 K. In addition, oxidation strongly depends on the structure of the film, which is especially favored by voids in the GLAD film. For our titanium stack films, this leads to a reinforcement of the anisotropic conductivity as the temperature rises. This trend agrees with the few reports devoted to the role of temperature on the anisotropic electrical transport in thin films [24, 25]. This dependence has been attributed to the anisotropic distribution of the grain boundary (GB) potential barrier heights. A similar approach can be used for our films based on the GB trapping model [26]. Anisotropic growth due to the GLAD process intrinsically leads to the highest GB potential barriers in the y-direction in comparison with the x-ones. The annealing in air enhances this effect, especially in the porous GLAD Ti film which is very sensitive to the oxidation phenomenon.

4. Conclusions

Anisotropic electrical resistivity vs. temperature of titanium thin films has been measured. An extension of the van der Pauw method has been applied to get resistivities ρ_{xx} and ρ_{yy} in the mutually perpendicular directions x,y of the two-dimensional plane and the anisotropic coefficient during incremental annealing cycles in air (from 298 to

873K). As-deposited films exhibit a metallic-like behavior with an average DC resistivity $\rho = 6.03\times10^{-6}$ Ωm and an intrinsic anisotropic coefficient A = 1.39. The metallic character remains as the temperature rises up to 773 K and the anisotropy is slightly enhanced to A = 1.59 assigned to the formation of a TiO compound in the GLAD Ti film. Similarly, the average DC resistivity is close to 2×10^{-5} Ωm and the TCR reduces to become negative (-1.07×10^{-4} K^{-1}). The metallic character remains for this range of temperatures in spite of the oxidation of the GLAD Ti film, which initially occurs because of its highly porous structure. An increase of the temperature up to 800 K and finally 873 K induces a further oxidation of the titanium stack films. Resistivities ρ_{xx} and ρ_{yy} are especially increased from 800 K to show semiconducting-like behaviors with an emphasized anisotropy coefficient A = 12.4. This anisotropic electrical resistivity is attributed to difference of the grain boundary potential barriers in the x and y directions produced by the anisotropic growth of the GLAD process. This effect is promoted by the annealing treatment in air, especially in the porous GLAD Ti film.

Acknowledgements

The authors thank the Region of Franche-Comté for financial support. This work has been supported by the Labex ACTION program (contract ANR-11-LABX-01-01).

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Figure captions

Figure 1

A schematic representation of the titanium stack films and the setup for the DC electrical resistivity measurements. The GLAD Ti film 1 μm thick is deposited by sputtering with an incident angle $\alpha = 80°$ of the particle flux. A cross-section view by scanning electron microscopy exhibits the inclined columnar structure. The two parallel strips of Ti (500 nm thick and separated by 9 mm) are deposited by conventional sputtering ($\alpha = 0°$). The four contacts are set according to a square geometry of size $L_x = L_y = 10$ mm.

Figure 2

Average DC electrical resistivity ρ as a function of the temperature T of the titanium stack films. The annealing treatment in air was performed following 9 cycles of temperature. The first cycle started from 298 up to 473 K followed by a return to 298 K with the same ramp of 5 $Kmin^{-1}$. The second cycle was similar to the previous one up to 523 K (increment of 50 K) and so on until the final cycle (9^{th}) reached 873 K to finally come back to 298 K.

Figure 3

The annealing dependence of orthogonal DC electrical resistivities ρ_{xx} and ρ_{yy} at 473 K and anisotropic coefficient A calculated from equation (5) of titanium stack films. The conduction anisotropy is especially emphasized from the 8^{th} cycle, which corresponds to an annealing temperature close to 800 K.

Figure 1

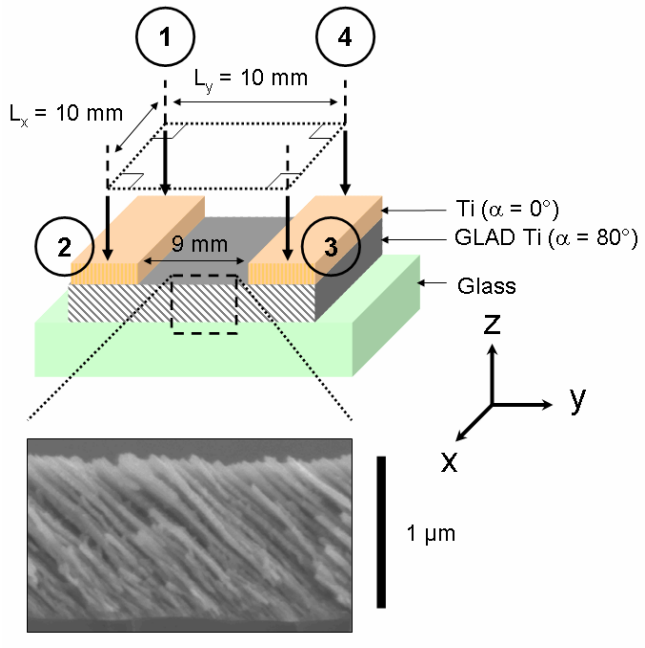

Figure 2

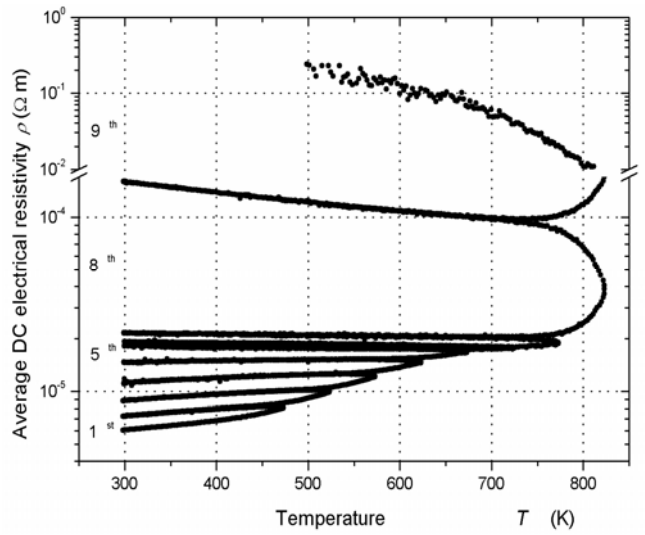

Figure 3