Functional Materials Letters (FML)

Metal-to-dielectric transition induced by annealing of oriented titanium thin films

--Manuscript Draft--

Manuscript Number:	
Full Title:	Metal-to-dielectric transition induced by annealing of oriented titanium thin films
Article Type:	Research Paper
Section/Category:	Prof Jan Van Humbeeck
Keywords:	Sputtering; Thin films; Electrical properties; Metal; Dielectric.
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Abstract:	Titanium thin films were deposited by dc magnetron sputtering. The GLancing Angle Deposition (GLAD) method was implemented to prepare two series of titanium films: perpendicular and oriented columnar structures. The first one was obtained with a conventional incidence angle of the sputtered particles (= 0°), whereas the second one used a grazing incidence angle = 85°. Afterwards, films were annealed in air following 6 incremental cycles of temperatures ranging from 293 to 773 K. Dc electrical conductivity was measured during the annealing treatment. Films deposited by conventional sputtering (= 0°) kept a typical metallic-like behavior versus temperature (300K = 2.0106 S m-1 and TCR293K = 1.5210-3 K-1), whereas those sputtered with = 85° showed a gradual transition from metallic to dielectric material. Such a transition was mainly attributed to the high porous structure, which favors the oxidation of titanium films to tend to the TiO2 compound.
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Author Comments:	Dear Editor of Functional Materials Letters,

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Please find an original article entitled: "Metal-to-dielectric transition induced by annealing of oriented titanium thin films" written by Aurelien BESNARD, Nicolas MARTIN, Fabrice STHAL, Luc CARPENTIER and Jean-Yves RAUCH. Results presented in this letter are original and have never been published. They show a gradual transition from metal to dielectric of titanium thin films sputter deposited by the GLAD (glancing angle deposition) technique. Such transition is produced by an annealing treatment and simultaneously followed by dc electrical measurements. Conventional titanium thin films produced by classical sputtering do not exhibit this kind of transition and are compared to GLAD films. An analysis of the microstructure is discussed taking into account the high porous architecture produced by the GLAD method.

Sincerely,

Pr. Nicolas MARTIN

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Functional Materials Letters
Vol. x, No. x (2xxx) x–x
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METAL-TO-DIELECTRIC TRANSITION INDUCED BY ANNEALING OF ORIENTED TITANIUM THIN FILMS

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Received Day Month Year; Revised Day Month Year

Titanium thin films were deposited by dc magnetron sputtering. The GLancing Angle Deposition (GLAD) method was implemented to prepare two series of titanium films: perpendicular and oriented columnar structures. The first one was obtained with a conventional incidence angle α of the sputtered particles ($\alpha = 0°$), whereas the second one used a grazing incidence angle $\alpha = 85°$. Afterwards, films were annealed in air following 6 incremental cycles of temperatures ranging from 293 to 773 K. Dc electrical conductivity was measured during the annealing treatment. Films deposited by conventional sputtering ($\alpha = 0°$) kept a typical metallic-like behavior versus temperature ($\sigma_{300K} = 2.0\times10^{6}$ S m^{-1} and $TCR_{293K} = 1.52\times10^{-3}$ K^{-1}), whereas those sputtered with $\alpha = 85°$ showed a gradual transition from metallic to dielectric material. Such a transition was mainly attributed to the high porous structure, which favors the oxidation of titanium films to tend to the TiO_2 compound.

Keywords: Sputtering, thin films, electrical properties, metal, dielectric.

Metal-insulator transitions have been investigated for many years [1]. They often arise from variations of the chemical composition, temperature, stress, electric or magnetic field, etc. [2-4]. They correspond to a transformation between states with a dielectric (or semiconductor) and a metallic type of conductivity. Materials exhibiting these phenomena include binary compounds of transition metal oxides. As a result, these transitions have largely been explored for bulk materials like vanadium oxides [5], but few studies have been devoted to such transitions for other materials [6] and to the best of our knowledge, never for thin films exhibiting an oriented columnar structure.

In this work, we report on the effect of an annealing treatment on the micro-structural properties, optical behaviors and dc electrical conductivity of titanium films sputter deposited. Two series of samples were prepared. The first one was conventionally prepared with a normal incidence angle α of the sputtered particles ($\alpha = 0°$). For the second series, the GLancing Angle Deposition (GLAD) was implemented to produce an oriented columnar structure. An incidence angle $\alpha = 85°$ was used to deposit an oriented structure. Both series were heated in air following 6 cycles from 293 to 773 K. Titanium films obtained at normal incidence ($\alpha = 0°$) kept a metallic-like behavior, whereas those deposited by GLAD ($\alpha = 85°$) exhibited a gradual metal-to-dielectric transition. Such a transition comes from the oxidation of the GLAD titanium films due to a high porous structure of the oriented columnar architecture.

Magnetron sputtering was implemented to deposit 300 nm thick titanium thin films. A pure titanium disk (99.8 at. % and 50 mm diameter) was dc sputtered using a constant current density of 100 A m^{-2}. Before introducing argon gas at a sputtering pressure of 10^{-1} Pa (pumping speed of 10 L s^{-1}), the chamber was pumped down to 10^{-5} Pa. Films were deposited on (100) silicon and glass substrates after cleaning in acetone and alcohol. A home made GLAD substrate-holder allowed the preparation of oriented columnar structure by changing the incidence angle α of the particles flux from $\alpha = 0$ to 90° and/or rotating the substrate holder at

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various rotating speeds. In this work, two types of films were prepared without using a rotation of the substrate holder (inclined and fixed substrate only). The first series was deposited using a classical incidence angle α of the particles flux (i.e. $\alpha = 0°$). The second series implemented an incidence angle $\alpha = 85°$. Optical transmittance versus wavelength was measured in the visible range for films deposited on glass substrates with a PerkinElmer Lambda 950 spectrophotometer. Cross-section and surface of the films were observed by Scanning Electron Microscopy (SEM) with a JEOL JSM-6400F. Dc electrical conductivity of the films deposited on glass substrates was measured in the van der Pauw geometry. The home made system allows the conductivity measurements as well as the annealing treatment in air for temperatures ranging from 293 to 773 K. Six cycles were systematically applied for all films. The first cycle started from room temperature up to 523 K at 5 K min^{-1} followed by a return to room temperature at 5 K min^{-1}. The second cycle was similar up to 573 K (increment of 50 K). The third cycle was up to 623 K and so on until the last cycle (6th), which reached 773 K.

A columnar microstructure is produced for any incidence angle of the sputtered titanium atoms (Fig. 1). Columns are poorly defined for films deposited with a conventional incidence angle ($\alpha = 0°$ in Fig. 1c). Films rather exhibit a densely packed structure. Since titanium films have been sputtered with an argon pressure of 10^{-1} Pa and with no external heating of the substrate during deposition, the microstructure corresponds to the T zone of the Thornton's structural zone model [7]. More defined columns are observed for titanium films obtained with an incidence angle $\alpha = 85°$. An inclined columnar structure is clearly achieved with a column angle $\beta = 40°$ (Fig. 1g). As commonly observed with the GLAD technique, such column angle β is below the incidence angle α mainly due to shadowing effect at the atomic scale [8]. In addition, it is below the angle predicted by empirical rules proposed by Nieuwenhuizen and Haanstraa (tangent's rule) [9] or from geometric relationships suggested by Tait et al. [10] because of the sputtered atoms - argon collisions occurring between the target and the substrate. Smooth surface is observed for conventional sputtering (Fig. 1a) whereas films prepared with an incidence angle $\alpha = 85°$ exhibit a more corrugated aspect (Fig. 1e). Tops of the columns are clearly distinguished and the voids surrounding the columns are larger. After annealing cycles (6 incremental cycles up to 773 K), the weakly defined columnar structure is kept for the film deposited at normal incidence $\alpha = 0°$ (Fig. 1d), but more defects can be observed on the surface (bright dots in Fig. 1b). One can suggest that a thin oxide layer (few nanometers thick) is developed on the top of the columns, especially on defects. For annealed films deposited with an incidence angle $\alpha = 85°$, it is worth of noting that the columnar structure is not destroyed (Fig. 1h).

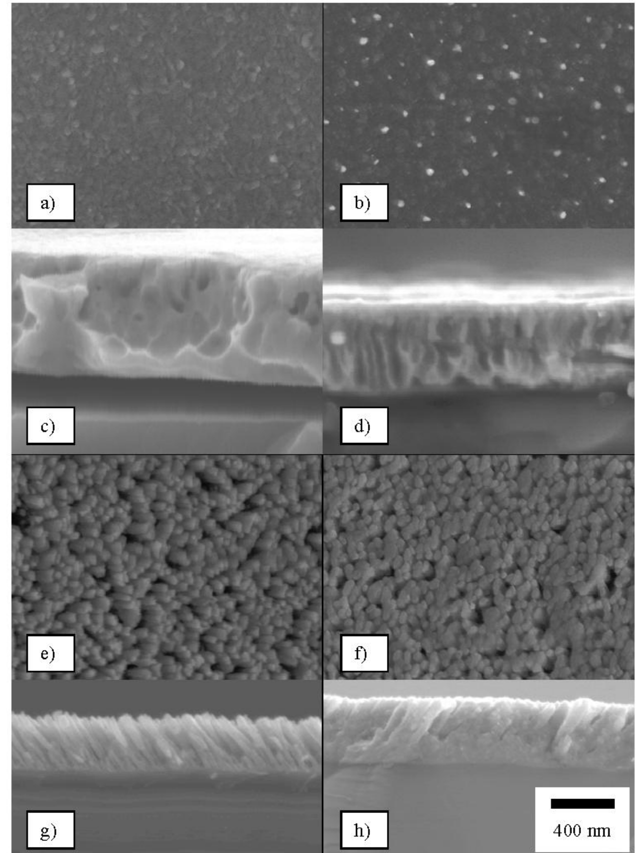

Fig. 1. SEM observations of cross-sections and surfaces of titanium films deposited: a) to d) with a normal incidence angle of the sputtered particles (first series; $\alpha = 0°$); e) to h) by GLAD (second series; $\alpha = 85°$). The columnar microstructure is kept in spite of the annealing treatment as shown in b), d), f) and h) photographs.

The surface morphology previously observed for non-treated titanium films is very similar (Fig. 1e). Regular columns (about 50 nm diameter) separated by voids are clearly observed, which reveals a porous structure (Fig. 1f).

For all annealing cycles, titanium films conventionally deposited ($\alpha = 0°$) exhibit conductivity versus temperature typical of a metallic-like behavior since electrical conductivity is $\sigma_{293K} = 1.22\times10^{6}$ S m^{-1} at 293 K and linearly drops down to $\sigma_{773K} = 7.39\times10^{5}$ S m^{-1} at 773 K (Fig. 2).

A positive temperature coefficient of resistance TCR = 1.52×10^{-3} K^{-1} is obtained. Conductivity as well as TCR are lower than the bulk value ($\sigma_{293K} = 2.56\times10^{6}$ S m^{-1} at 293 K and TCR = 5.50×10^{-3} K^{-1} for bulk titanium). It is commonly observed for metallic thin films and mainly attributed to the scattering of electrons at the grain boundaries [11].

For titanium films prepared with an incidence angle α = 85°, conductivity is strongly modified by the annealing cycles. Before increasing the temperature, conductivity at room temperature is $\sigma_{293K} = 1.56\times10^5$ S m^{-1}. This value is one order of magnitude lower than those previously measured for the titanium film deposited without GLAD ($\sigma_{293K} = 1.22\times10^6$ S m^{-1} for $\alpha = 0°$) [12].

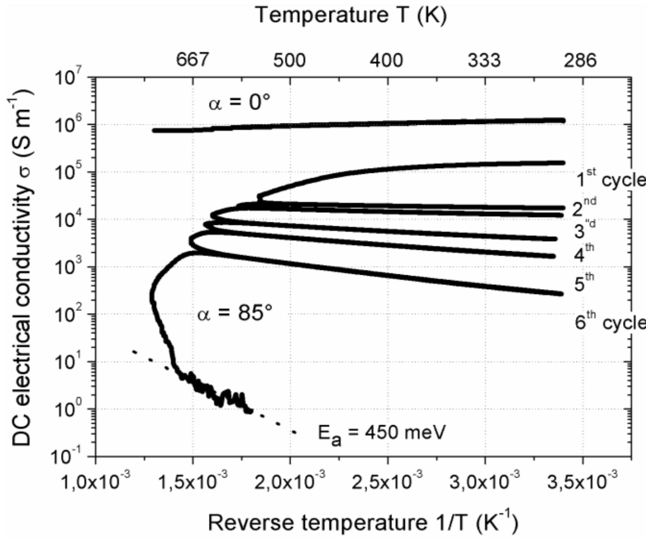

Fig. 2. Dc electrical conductivity as a function of the reverse temperature of titanium films sputter deposited. First series (normal incidence of the sputtered particles, i.e. $\alpha = 0°$) keeps a metallic-like behaviour. Second series (GLAD films at an incidence angle $\alpha = 85°$) exhibits a gradual metal-to-dielectric transition.

As the temperature rises up to 333 K and as expected for metallic compounds, conductivity is linearly reduced. A further increase of temperature up to 523 K leads to a non linear evolution of the conductivity versus temperature and drops down to $\sigma_{523K} = 2.31\times10^4$ S m^{-1}. It is mainly attributed to the oxidation beginning of the titanium film. The return to the room temperature shows a decrease of the electrical conductivity, which is characteristic of either a semiconducting-like behavior observed for oxygen-deficient $TiO_{2-\delta}$ with low activation energy [13], or a metallic-like behavior of oxygen-rich $TiO_{1+\varepsilon}$ with negative TCRs [14]. The additional annealing treatments (2nd to 5th cycles) emphasize the oxidation phenomenon of the films. At the beginning of the 2nd cycle, conductivity is $\sigma_{293K} = 1.73\times10^4$ S m^{-1} and gradually falls down to $\sigma_{293K} = 2.67\times10^2$ S m^{-1} before starting the 6th cycle. In addition, the negative slope of log (σ) versus the reverse temperature becomes more significant. One can suggest that the film is more and more oxidized. The last annealing cycle (from 293 to 773 K) leads to the most important decrease of the conductivity. At 773 K, σ_{773K} is 2.14×10^2 S m^{-1}. Reducing the temperature, conductivity looses again 3 orders of magnitude and reaches $\sigma_{556K} = 8.21\times10^{-1}$ S m^{-1} at 556 K. A further reduction of temperature does not allow conductivity measurements with our van der Pauw system. However, the negative slope obtained between 556 and 717 K suggests a linear behavior in the Arrhenius plot. The activation energy E_a calculated from the log (σ) versus the reverse temperature curve gives rise to E_a = 430 meV. It remains below typical values observed for stoichiometric titanium dioxide thin films (E_a is close to 650 meV [15]), but it is in agreement with previous studies focused on oxygen-deficient TiO_2 compounds exhibiting dielectric properties [16-18].

Optical transmittance versus wavelength supports the dielectric behaviors achieved by titanium films deposited with an incidence angle α = 85° after the annealing treatment (Fig. 3). Films are transparent with an optical transmittance close 60 % at 589 nm. In addition, some interference fringes are clearly viewed. Similarly, TiO_2 thin films 200 nm thick deposited by dc reactive magnetron sputtering (argon + oxygen atmosphere) using a normal incidence of particles ($\alpha = 0°$) and an inclined orientation ($\alpha = 85°$) are shown.

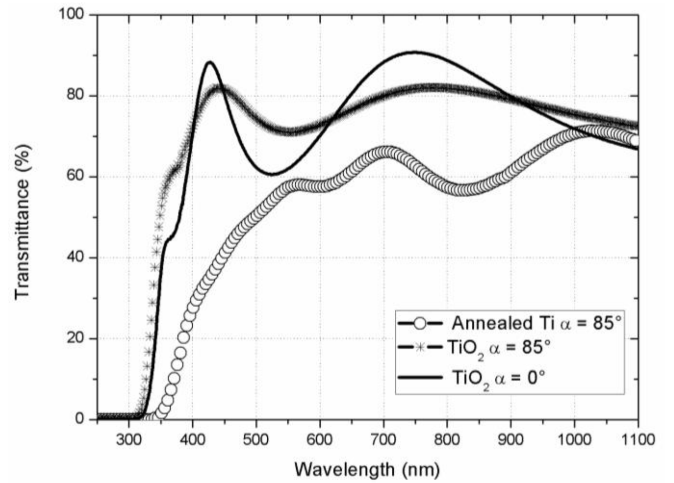

Fig. 3. Optical transmittance spectra versus wavelength in the visible region of GLAD titanium thin films deposited on glass substrates with an incidence angle α = 85° and after the annealing procedure in air up to 773 K. Typical interference fringes are measured and can be compared to those observed for titanium dioxide thin films (thickness 200 nm) produced by classical dc reactive sputtering (Ar + O_2 atmosphere) for an incidence angle α = 0 and 85°.

It is interesting to note that the amplitude of the fringes and thus, refractive indices are strongly influenced by the incidence angle α. Refractive index at 589 nm "n_{589}" was calculated from transmittance spectra by the Swanepoel's method [19]. For normal incidence ($\alpha = 0°$), n_{589} = 2.48 whereas it is lower than 1.93 for α = 85° mainly due to a high porous structure produced for high incidence angles

[20]. For annealed films, n_{589} = 1.84, which is lower than the value of TiO_2 film prepared with α = 85°. As a result, optical transmittance in the visible region support the dielectric characteristics of annealed titanium films deposited by GLAD with an incidence angle α = 85°.

In summary, titanium thin films were sputter deposited using the GLAD method. A conventional incidence angle α of the sputtered particles (α = 0°) was first used, whereas other films were prepared with a grazing incidence angle α = 85°. Films were annealed in air according to 6 cycles of temperatures ranging from 293 to 773 K. Films deposited at normal incidence (α = 0°) kept a metallic-like behavior versus temperature in spite of heating. On the other hand, films obtained with an incidence angle α = 85° exhibited a gradual change of their electrical conductivity. Before annealing, metallic-like properties were observed with a room temperature conductivity higher than $\sigma = 1.22\times10^6$ S m^{-1}. After 6 annealing cycles, conductivity was below 1 S m^{-1} and became too much resistive to be measured by the four probe method. Similarly, optical transmittance as well as refractive index in the visible region exhibited typical optical characteristics close to that of TiO_2 insulating materials. Such a gradual metal-to-dielectric transition solely observed for GLAD titanium films, was mainly related to the oxidation phenomenon of the high porous structure especially favored for grazing incidence angles.

Acknowledgement

The authors thank the Région of Franche-Comté and the city of Besançon for financial supports.

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Figure 1

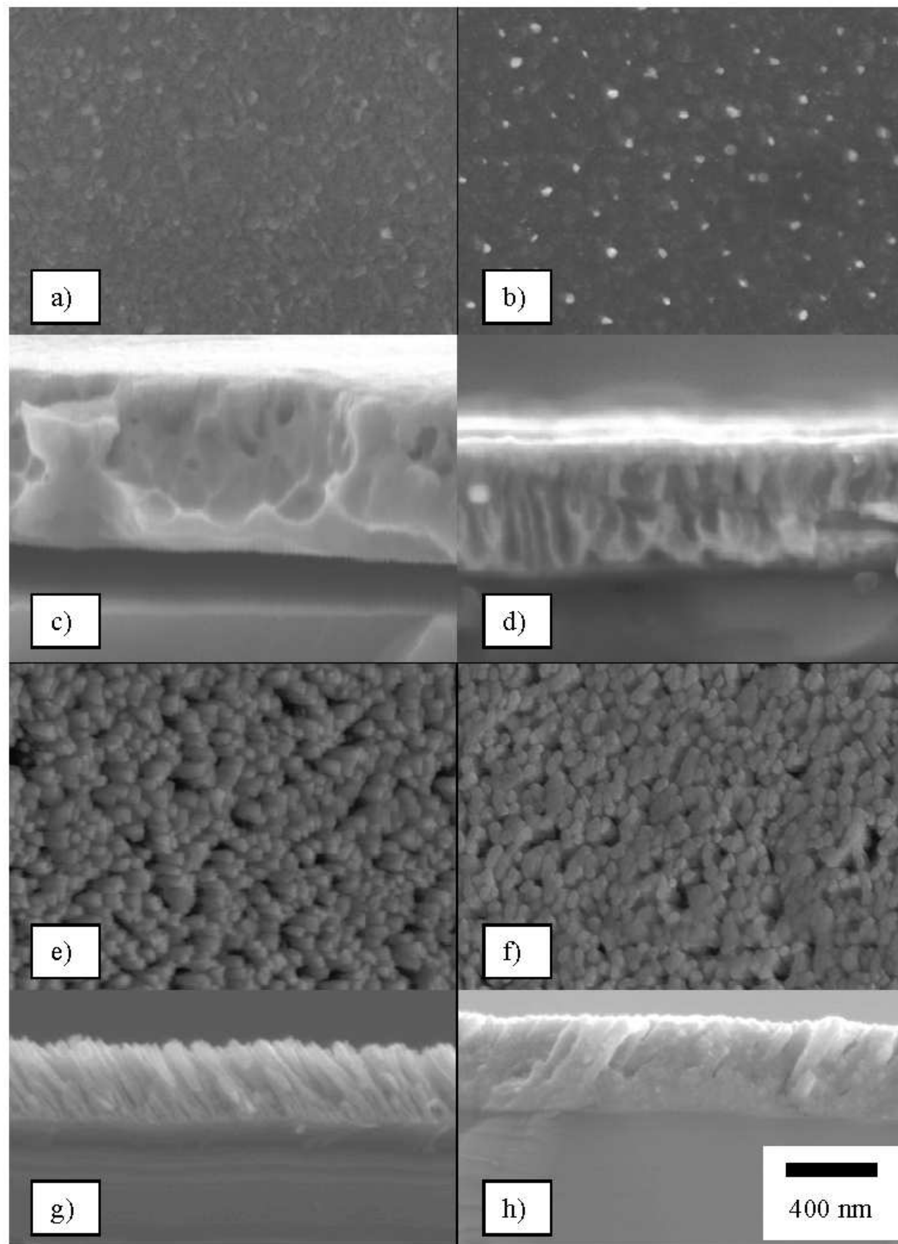

Figure 2

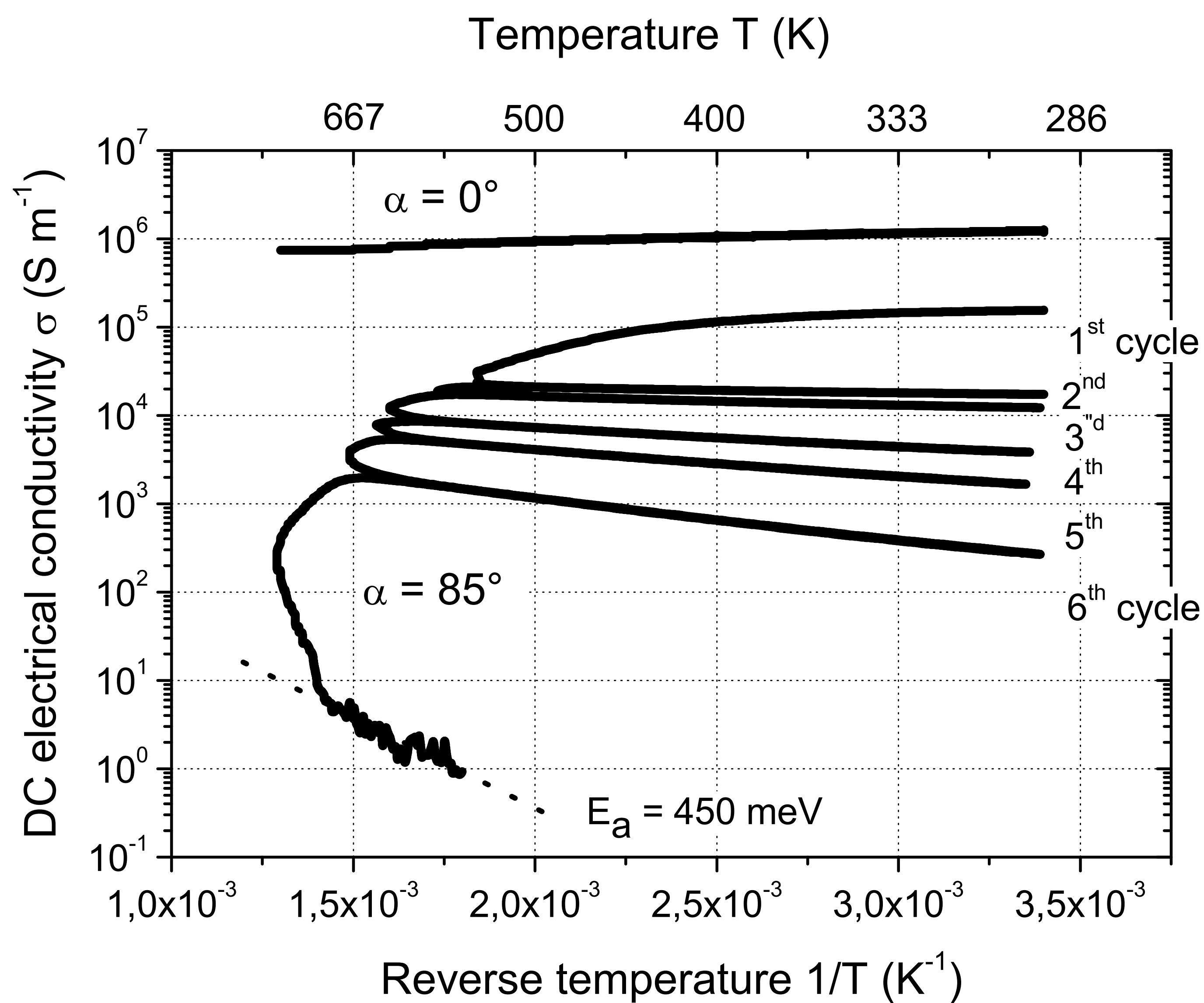

Figure 3