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# Anisotropic and non-heterogeneous continuum percolation in titanium oxynitride thin columnar films

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## Abstract

We report the percolation behaviour of the conductivity of titanium oxynitride films grown by low-pressure metal–organic chemical vapour deposition, composed of  $\text{TiN}_x\text{O}_y$  mixed with  $\text{TiO}_2$ . The usual DC parameters ( $t$ ,  $s$  and  $\Phi_c$ ), obtained from the effective media theory equations, are compared to the universal values ( $s = s_{un}$  while  $t < t_{un}$  because of the film anisotropy). This is the first example of an electrical continuum percolation applied to columnar films with chemically similar conducting and insulating units (non-heterogeneous percolation) whose mixing is based upon the growth temperature during the film growth.

## 1. Introduction

Probing percolation usually requires the random growth of a conducting network within an insulating matrix. This has been achieved for three-dimensional discrete systems such as porous media [1], polymer gel [2] and carbon-black–polymer composite [3]. Also, percolation in thin films was obtained using holes randomly punched into a conducting sheet [4, 5], metal films generated photolithographically from laser speckle patterns [6] and granular metal–insulator mixtures [7–10]. Moreover, continuum systems such as graphite–BN powders [11–13] and porous materials [14] have also been studied. In all these cases, the conducting and the insulating media are very different, leading to heterogeneous percolation. However, the two end-compounds of the percolation process may be chemically very similar in the case of titanium oxynitride thin films where an increased amount of  $\text{TiN}_x\text{O}_y$  content in a  $\text{TiO}_2$  matrix should lead to a percolation behaviour. The aim of this article is to show that such a non-heterogeneous percolation is indeed observed for this original conducting–insulating network where the conducting ratio is *in situ* tunable as a function of the growth parameters.

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Percolation theory allows one to describe with a phenomenological equation the conductivity of a composite medium near the conducting–insulating transition. It has been extensively developed for discrete lattice systems through the following equation [15]:

$$\sigma \propto (\Phi - \Phi_c)^t \quad \text{for } \Phi > \Phi_c \quad (1)$$

where  $\Phi$  is the conducting phase ratio,  $\Phi_c$  the percolation threshold and  $t$  the critical exponent characterizing the conducting region. However, it is also used to describe the conductivity of continuum systems such as cermets (metal–metal oxide) and graphite–polymer mixtures. When the ratio of the conductivities of the two components of a binary insulator–conductor mixture is not very small, i.e.  $\sigma_i/\sigma_c \neq 0$  with  $\sigma_i$  and  $\sigma_c$  the conductivities of the insulating and conducting phases respectively, the conductivity of a continuum medium can be described by an effective medium theory (EMT) [16–19], using the following normalized equations which can fit data in the range  $0 < \Phi < 1$  [20, 21]:

$$\sigma = \sigma_c \left( \frac{\Phi - \Phi_c}{1 - \Phi_c} \right)^t, \quad \text{for } \Phi > \Phi_c \quad (2a)$$

$$\sigma = \sigma_i \left( \frac{\Phi_c - \Phi}{\Phi_c} \right)^{-s}, \quad \text{for } \Phi < \Phi_c \quad (2b)$$

where  $t$  is the critical exponent in the conducting region and  $s$  the critical exponent in the insulating region. It should be pointed out that equations (2a) and (2b) are no longer valid in a range of  $\Phi$  given by the relation [18, 22]

$$|\Phi - \Phi_c| = \delta = \left( \frac{\sigma_i}{\sigma_c} \right)^{1/(t+s)}. \quad (3)$$

In this range, it is possible to use a modification of the general effective medium (GEM) equation, which is an effective medium interpolation formula, proposed by McLachlan [23, 24] and McLachlan *et al* [19]:

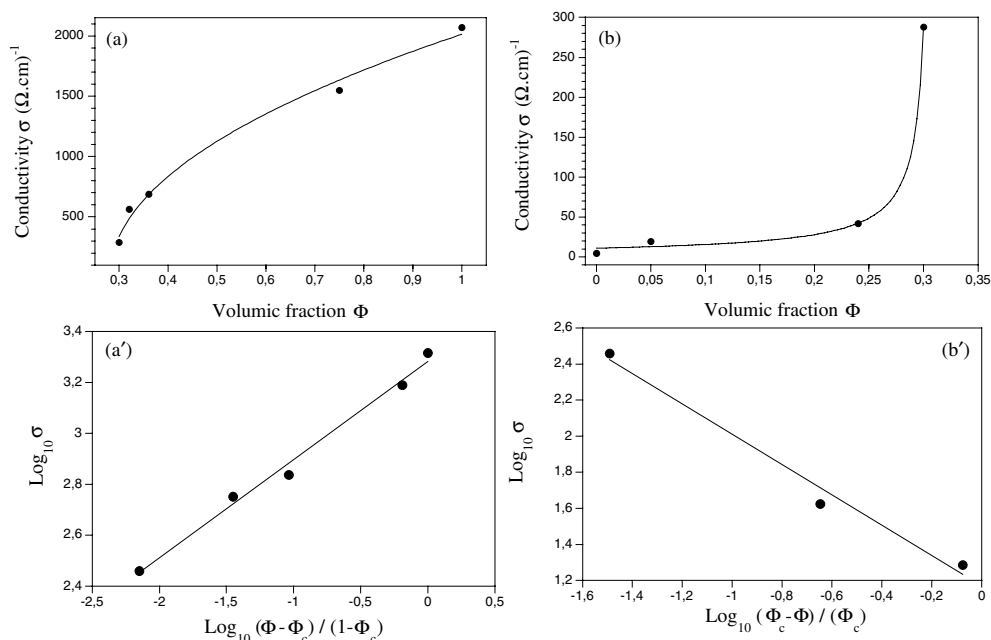
$$(1 - \Phi) \frac{(\sigma_i^{1/s} - \sigma^{1/s})}{(\sigma_i^{1/s} + A\sigma^{1/s})} + \Phi \frac{(\sigma_c^{1/t} - \sigma^{1/t})}{(\sigma_c^{1/t} + A\sigma^{1/t})} = 0 \quad (4)$$

where  $A = (1 - \Phi_c)/\Phi_c$ .

A great number of books [15, 25] and reviews [16, 18, 26] covering percolation aspects have compared results from discrete lattice and continuum systems; until recently, there was general agreement that all these systems should have the same universal values for the critical exponents  $s$  and  $t$ , i.e.  $s_{un} = 0.89$  and  $t_{un} = 2$  in three dimensions [15]. This is the case for the inverse Swiss cheese and potential models which respect the universality of the critical exponents [27, 28]. However, a particular class of continuum systems was found for which the critical exponents  $s$  and  $t$  are higher than the universal ones. One of these unusual models is the Swiss cheese model. In the following, we will compare the values of the critical exponents obtained for this study to the universal values depicted above.

## 2. Results and discussion

Low-pressure metal–organic chemical vapour deposition (LP-MOCVD) is an efficient technique for growing mixed  $\text{TiN}_x\text{O}_y/\text{TiO}_2$  thin films with controlled relative concentrations. Depositions were carried out at 60 Torr in a range of growth temperatures from 450 to 750 °C for 1 h (providing film thicknesses of about 250 nm) on sapphire substrates in order to allow conductivity measurements using a classical van der Pauw four-points method [29]. Figure 1 shows the conductivity of the films plotted as a function of the conducting volumic fraction  $\Phi$

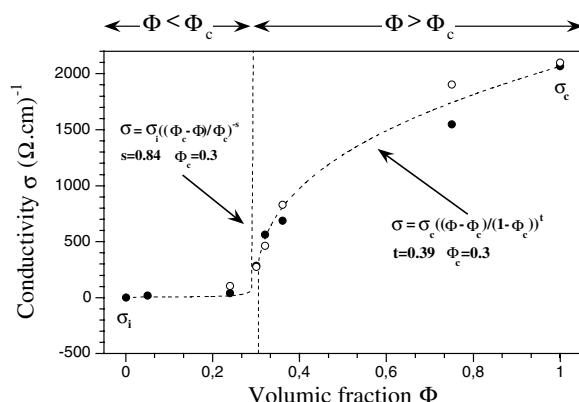


**Figure 1.** Conductivity of  $\text{TiN}_x\text{O}_y$  thin films deposited for 1 h on sapphire as a function of the  $\text{TiN}_x\text{O}_y$  volumic fraction  $\Phi$  for (a)  $\Phi > \Phi_c$  and (b)  $\Phi < \Phi_c$ . The insets (a') and (b') are the log–log plots of the conductivity as a function of  $(\Phi - \Phi_c)/(1 - \Phi_c)$  and  $(\Phi_c - \Phi)/\Phi_c$  respectively. Dots show the experimental data while the solid lines are the result of a fitting according to equation (2a) in (a') and (2b) in (b').

**Table 1.** Volumic fraction  $\Phi$  calculated from XPS analysis, film composition and conductivity as a function of the growth temperature, from [30, 31].

Growth temperature ( $^{\circ}\text{C}$ )	$\Phi$	Composition	Conductivity ( $\Omega^{-1} \text{cm}^{-1}$ )
450	0	Almost $\text{TiO}_2$	4
500	0.05	Almost $\text{TiO}_2$	19
525	0.24	Almost $\text{TiO}_2$	42
550	0.30	$\text{TiO}_2 + \text{TiN}_x\text{O}_y$	288
575	0.32	$\text{TiO}_2 + \text{TiN}_x\text{O}_y$	564
600	0.36	$\text{TiO}_2 + \text{TiN}_x\text{O}_y$	688
650	0.75	$\text{TiO}_2 + \text{TiN}_x\text{O}_y$	1550
700	1	$\text{TiN}_x\text{O}_y$ only	2070
750	1	$\text{TiN}_x\text{O}_y$ only	2110

calculated from XPS analysis in order to separate the  $\text{TiO}_2$  and  $\text{TiN}_x\text{O}_y$  contributions [30, 31]. Table 1 summarizes the conductivity, the film composition and the volumic fraction used in this study as a function of the growth temperature. Table 1 shows that above  $700^{\circ}\text{C}$ , only metallic  $\text{TiN}_x\text{O}_y$  was found to be present in the films, as indicated by  $\Phi = 1$  for both experimental points at  $700$  and  $750^{\circ}\text{C}$ . However, the conductivity increases when the growth temperature increases from  $700$  to  $750^{\circ}\text{C}$ , even if only the metallic phase  $\text{TiN}_x\text{O}_y$  is detected. This trend was previously correlated with an increase of the N/O ratio in the  $\text{TiN}_x\text{O}_y$  phase while increasing the growth temperature [31–33]. Thus, the data point at  $750^{\circ}\text{C}$  was not considered in the percolation study.



**Figure 2.** Conductivity of  $\text{TiN}_x\text{O}_y$  thin films deposited for 1 h (thickness of 250 nm) on sapphire as a function of  $\Phi$  over the whole range  $0 < \Phi < 1$ . Dashed curves are the conductivity calculated from the results of the different fittings, i.e. with  $\Phi_c = 0.3$ ,  $s = 0.85$  and  $t = 0.39$ , and black dots show the experimental data. The conductivity of  $\text{TiN}_x\text{O}_y$  thin films whose thickness is about 50 nm, deposited on sapphire, is also given (white dots), highlighting that they show the same behaviour as the thicker films.

Equations (2a) and (2b) were used since our system is likely to be a continuum one. Indeed, previous works [31, 32] have evidenced  $\text{TiN}_x\text{O}_y$  columns embedded in a amorphous insulating  $\text{TiO}_2$  phase, which should correspond to an inverse Swiss cheese model as regards geometry [27, 28]. Moreover, EELS studies of the films have shown that the  $\text{TiN}_x\text{O}_y$  phase stayed metallic for any growth temperature, through envisaging a plasmonic contribution at about 2 eV [33]. It should also be pointed out that in our system, the conductivity of the conducting phase ( $\sigma_c = 2070 \Omega^{-1} \text{cm}^{-1}$ , from the experimental data at  $\Phi = 1$ ) is not greater than the conductivity of the insulating phase ( $\sigma_i = 4 \Omega^{-1} \text{cm}^{-1}$ , from the experimental data at  $\Phi = 0$ ), i.e.  $\sigma_i/\sigma_c \neq 0$ . Results of the fits were next introduced in log–log plots in order to emphasize the best linearity (see the insets in figure 1) for both insulating ( $\Phi < \Phi_c$ ) and conducting ( $\Phi > \Phi_c$ ) regions. Finally, the values obtained are  $\Phi_c = 0.30 \pm 0.02$ ,  $s = 0.84 \pm 0.05$  and  $t = 0.39 \pm 0.08$ . The percolation threshold  $\Phi_c$  has an intermediate value between those commonly obtained for two dimensions (from 0.35 for a bond percolation in a triangular lattice to 0.7 for a site percolation in an honeycomb lattice [15]) and in three dimensions (from 0.12 in a bond percolation in a fcc lattice to 0.43 in a site percolation in a diamond lattice [15]); the exponent  $s$  exhibits a value in excellent agreement with  $s_{um} = 0.87$  while the exponent  $t$  is very small as compared to  $t_{um} = 2$ . Figure 2 represents the conductivity recalculated from these values, which are in excellent agreement with the experimental data points. This figure also highlights a percolation phenomenon which diverges on both sides of the percolation threshold. Indeed, according to equation (2b), the conductivity tends to diverge as the percolation threshold is reached from below, when it becomes very large on the scale of  $\sigma_i$ . Then, above the percolation threshold, equation (2a) applies and the conductivity approaches 0. Likewise, when the percolation threshold is reached from above, the divergence can be explained by the fact that the conductivity becomes very small on the scale of  $\sigma_c$  as depicted in equation (2a), and then, below the threshold, equation (2b) applies, leading to a huge value of the conductivity.

Concerning the percolation threshold, one could expect an interpretation in terms of dimensional crossover, as previously demonstrated by Clerc *et al* [34], Rappaport *et al* [35] and, more recently, by Ivashchenko *et al* [36], but experiments carried out on thinner films

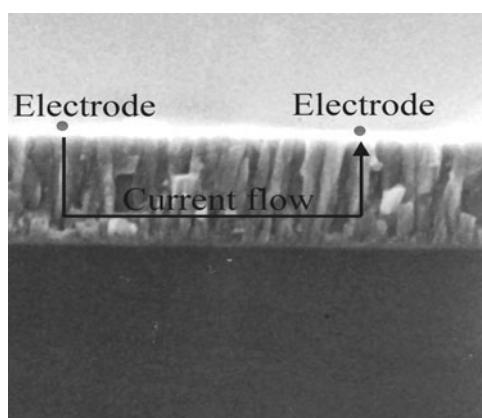
(50 nm instead of 250 nm) exhibited the same value for  $\Phi_c = 0.30$  (figure 2). Besides, it is now well known that the grain structure of the system studied may change the percolation threshold value [19]. Moreover, our value may correspond with the value of 0.32 obtained from the Bruggeman symmetric media theory, as explained by McLachlan *et al* [19]. For example, Shimakawa [37] obtained a percolation threshold of about 0.33 for microcrystalline silicon thin films deposited by the CVD method. Thus the value obtained for the percolation threshold is not unreasonable, all the more so since equations (2a) and (2b) gave the same value of  $\Phi_c$ . Further confirmation came from dynamic studies carried out with impedance spectroscopy which highlighted a crossover from a capacitance behaviour to an inductance one for  $\Phi = 0.30$  [33, 38].

Concerning the critical exponents  $s$  and  $t$ , once their values are obtained, it is possible to calculate the region  $\delta$  where the EMT equations are no longer applicable using equation (3). Taking  $\sigma_i = 4 \Omega^{-1} \text{ cm}^{-1}$ ,  $\sigma_c = 2070 \Omega^{-1} \text{ cm}^{-1}$  from table 1,  $s = 0.84$  and  $t = 0.39$ , the  $\delta$ -value was found to be lower than 0.01, which means that the use of the EMT equations over the whole range  $0 < \Phi < 1$  is reasonable. Moreover, computing the GMT equation (equation (4)) gave satisfactory results only for  $\Phi = \Phi_c$ . It has also been shown [39, 40] that the conductivity at the percolation threshold can be estimated as follows:

$$\sigma_{(\Phi=\Phi_c)} = \sigma_i^{t/(t+s)} \sigma_c^{s/(t+s)}. \quad (5)$$

The experimental point at the percolation threshold  $F_c = 0.30$  is  $\sigma = 288 \Omega^{-1} \text{ cm}^{-1}$ , as shown in table 1. Computing  $\sigma_i = 4 \Omega^{-1} \text{ cm}^{-1}$ ,  $\sigma_c = 2070 \Omega^{-1} \text{ cm}^{-1}$  from table 1,  $s = 0.84$  and  $t = 0.39$  in equation (5) leads to  $\sigma = 285 \Omega^{-1} \text{ cm}^{-1}$  which is in excellent agreement with the experimental value.

Next, concerning the too-small value of the critical exponent  $t$ , it is important to notice that the percolation theory considers perfectly spherical particles for both insulating and conducting materials. As previously found for other materials deposited with the LP-MOCVD technique, the  $\text{TiN}_x\text{O}_y$  films are columnar [31, 32]. Thus, one can assume that this columnar structure may affect the percolation law since the expected sphericity does not occur. Moreover, Smith and Lobb [6] have studied metal films obtained photolithographically from laser speckle patterns, since they were able to control the anisotropy of the conducting phase. They found that the anisotropy had non-trivial and fairly dramatic effects on the critical exponent. Taking  $\alpha$  as the anisotropy coefficient ( $\alpha = l_x/l_y$  with  $l_x$  the dimension in the direction of the overall current,  $l_y$  the other dimension), they obtained a decrease of the critical exponent  $t$  from 1.3 to 0.85 while increasing  $\alpha$  from 1 (isotropic sample) to 5 (a very anisotropic sample stretched in the overall current direction). This decrease of the critical exponent can also be explained by an artificial decrease of the conductance (or an increase of the resistance). Following this result, a model for the current flow in the films can be derived (figure 3). Since the film conductivities were measured using a classical four-probe technique according to the van der Pauw method [29], figure 3 represents a 'cleaved' view of a film obtained by SEM and the two gold electrodes between which the current flows. However, it is important to stress that the electrode surface is actually about  $1 \text{ mm}^2$  and thus one can assume that a great number of columns (whose diameter is about 100 nm) are covered. Starting from one electrode, the current flow first goes through the columns normally to the surface; therefore the layer can be considered as very anisotropic. According to Smith and Lobb [6], a very high value of  $\alpha$  should be applied for this first step, leading to a higher resistance, since the anisotropy and the current flow exhibit the same direction. Next, the current flow crosses the film in a direction parallel to the layer surface, which means that the layer here can be considered as isotropic. Thus, in this region, the resistance stays as it is (i.e. with a low value). Finally, the current flow goes out from the layer normally to the surface, in the same way as in the first step. Therefore, as



**Figure 3.** A schematic drawing of the current flow into the layer. Two of the four electrodes have been drawn schematically; note that the actual size of each electrode is much bigger (the SEM magnification for the film is  $\times 50\,000$ ).

described above, this step induces an increase of the resistance. These three steps of the current path can be considered as serial: the resulting resistance only takes into account the highest resistances, that is to say the anisotropic steps. Then the isotropic path becomes negligible from an electrical point of view, all the more so since there are a lot of anisotropic columns under each electrode for the two anisotropic paths. Thus, this serial model leads to a high value of  $\alpha$ , and therefore to a decrease of the critical exponent. Finally, it is understandable that only  $t$  exhibits a breakdown in universality, since  $s$  is the exponent in the insulating region where the  $\text{TiO}_2$  matrix is amorphous [31, 32], which prevents anisotropy. Moreover, it has previously been shown [31, 32] that the  $\text{TiN}_x\text{O}_y$  conductivity varies with the growth temperature, since the N/O ratio depends upon the growth temperature. Thus, when  $\Phi < \Phi_c$ , this trend has no effect on the conductivity, but once percolated, the conductor becomes dominant and the exponent  $t$  may also be affected by it.

### 3. Conclusions

To summarize, a continuum percolation model has been applied to the conductivity of  $\text{TiN}_x\text{O}_y/\text{TiO}_2$  thin films grown by LP-MOCVD, exhibiting different conducting contents in the films as a function of the growth temperature. Such a conductor–insulator network has never been studied before, and exhibits an original non-heterogeneous chemically similar percolating system. Results of the EMT equations gave  $\Phi_c = 0.3$ ,  $s = s_{un}$  and  $t < t_{un}$ . The model used has been verified through some basic equations near  $\Phi_c$ . An anisotropic model was also introduced for the current flow through the columnar structure in order to explain the low value of the critical exponent. It should be pointed out that the evolution of the N/O ratio as a function of the conducting phase content [31], and also the grain size distribution as a function of the growth temperature [32], could be taken into account in order to make the model developed more precise. Hence, a columnar  $\text{TiN}_x\text{O}_y$  phase embedded in a  $\text{TiO}_2$  matrix which may correspond to an inverse Swiss cheese model, with an *in situ* tunable ratio, as a function of the growth temperature, may lead to a very promising range of materials, but has to be considered as a non-trivial system for an electrical point of view.

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