Influence of the microstructure on the oxidation of Ni thin films

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Article info
Article history:
Received 7 November 2011
Accepted 6 March 2012
Available online 14 March 2012

Keywords:
A. Nickel
A. Sputtered films
C. Oxidation

Abstract
The influence of the initial grain structure on the oxidation of 100 nm thick Ni layers is investigated at 500 °C. Ni films were either formed by fine (diameter < 70 nm) or large grains (diameter < 500 nm) with enhanced Ni(111) crystallite size. The oxide growth rate was determined by gravimetric methodologies. Results of the oxide composition, grain morphology, crystallinity and electrical resistance as a function of the oxidation time are also presented.

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1. Introduction

Oxide-based Resistive Random Access Memories (ReRAM) are a promising candidate for future memory device generation [1]. ReRAM stores information by the electrical resistance state of the oxide material. By applying an external voltage, this resistance state can be reversibly changed between a high and a low value, which effect is called “resistance switching” [2]. We have developed NiO-based ReRAM devices with NiO obtained from the oxidation of Ni films [3,4]. We have observed that NiO resistive switching characteristics strongly depend on the initial oxide resistance, which is determined by the oxidation time [4] and the preparation of the Ni layer prior to the oxidation experiments [3–5]. A detailed characterization of the oxidation kinetics of the Ni films is thus important to relate the microstructure of the oxide formed to their resistance characteristics.

On the one hand, the oxidation of bulk Ni has been extensively investigated [6,7]. At relatively high temperatures the rate limiting step in Ni oxidation is the diffusion of Ni ions and electrons via vacancies and holes, normally present at grain boundaries and dislocations [8]. This transport mechanism has been reported to be affected by the purity of the starting material [7,9–11], pretreatments [7,10,12], crystalline orientation [12], type of oxygen atmosphere [13] and by the thickness and morphology of the oxide scale [7,8,14]. On the other hand, less is known for the case of sub-μm Ni films, where the number of reports is scarce [3,15,16]. In particular, we have already proven that [3], similar to bulk systems, NiO crystalline growth in thin films is strongly dependent on Ni crystallinity. Thin films may be used to produce controllable NiO grain structures, which can help to understand the role of grain boundary texture on the Ni oxidation mechanisms.

This paper extends our previous investigations [3,4] by providing new oxidation kinetics results of the 100 nm thick Ni films obtained via gravimetric techniques. Furthermore, a systematic comparison between the oxide scale characteristics (composition, grain morphology, crystallinity and electrical resistance) and their relation to the Ni structure (grain size and crystallinity) as a function of the oxidation conditions used (500 °C/30–600 s) is also presented.

2. Experimental

2.1. Materials

2.1.1. Substrate

The substrates were 300 mm Si(100) wafers coated with 500 nm SiO2 deposited at 400 °C by chemical vapor deposition. Then, TiN films 40 nm thick were deposited at room temperature onto the SiO2 by reactive sputtering using an Anelva® deposition cluster. The sputtering process is performed in a mixture of Ar and N2 (50 sccm) at 1 kW. These conditions produce N-rich TiN1.3 films, with a cubic crystalline structure [17], resistivity of 200 μΩ cm and formed by fine columnar grains of ~10 nm in diameter.

2.1.2. Ni films: deposition and oxidation

100 nm Ni films were deposited by sputtering at 40 °C. The films were grown at a deposition rate of 0.7 nm s−1, using 0.6 mtorr Ar and 2.5 kW as power setting. The purity of the Ni target was 5N...
(Nikko Materials) with a total amount of metallic impurities of 0.7 ppm (major impurities Co and Cu < 0.1 ppm). The thickness uniformity was $\sim$3% (standard deviation (3σ) obtained from full wafers). After a few days exposed to the atmosphere, the wafer systematically increased their initial weight (right after deposition) in $\sim$0.2 μg cm$^{-2}$. This value would correspond to $\sim$1.3 nm of NiO considering that 1 μg cm$^{-2}$ of oxygen is equivalent to an average NiO thickness of 6.9 nm [18]. The final weight of the Ni films prior to oxidation experiments was 80.8 ± 0.2 μg cm$^{-2}$.

The grain size (GS) of the Ni films was manipulated through an annealing step done after deposition. Ni layers were annealed in an ASM Levitor® 4300 chamber in high purity N$_2$ flow (<0.5 ppb O$_2$; <0.8 ppb H$_2$O) at 500 °C for 10 min. The heating ramp rate was 40 °C s$^{-1}$. In the following we will refer to this step as “preanneal” and the films will be called “Ni–WP” (Ni with preanneal) or “Ni–WOP” (Ni without preanneal). We did not observe any substantial change in the weight of the wafers due to this annealing.

Ni films were oxidized at 500 °C using a Producer® AMAT chamber. The oxidation time ranged between 30 and 600 s. The wafers were annealed with a heating ramp of 16 °C s$^{-1}$ using 3000 sccm O$_2$ flow (H$_2$O < 0.1 ppb) at a total chamber pressure of 4 torr.

2.2. Characterizations

The oxide growth rate determined by the oxygen uptake was obtained by the change in weight of the wafers before and after oxidation. The values given correspond to the average and standard deviation of ten (10) measurements per wafer. The balance has a resolution of 1 μg.

Electron backscattering diffraction (EBSD, taken at $\sim$70° with step sizes of 10 and 20 nm), X-ray diffraction (XRD, CuK$_\alpha$ radiation, $\lambda = 0.15418$ nm) and Raman spectroscopy (RS, 632.8 nm HeNe laser) were used to evaluate the crystallinity of our materials. In the case of XRD, the measurements were carried out in coupled tube-detector ($\theta$–2θ) and grazing incidence detector scan (GI-XRD) configurations. $\theta$–2θ coupled configuration shows the ordering of the film for the crystallographic planes parallel to the substrate. In the case of GI-XRD (detector scan), the scattering vector is continuously changing its orientation during data acquisition. Therefore, GI-XRD provides information regarding the non-oriented (polycrystalline) component of the sample. During GI-XRD the X-ray beam was kept at 1° incidence angle; this low angle also renders high surface sensitivity to this technique. Crystallite sizes (CS) were obtained from the full-width-at-half-maximum (FWHM) of the XRD Bragg reflections and using the Scherrer’s formula [19]. The resolution of our diffractometer is 0.03° equivalent to a CS of $\sim$350 nm (FWHM Si(400) located at 2θ = 69.13°). The quantitative analyzes of the XRD signals were performed using the DIFFRACplus software (background subtraction, peak position and FWHM, relative and integral intensity).

The surface and cross section morphologies of the Ni and the oxide films were characterized by high resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The elemental composition was evaluated by X-ray photoelectron spectroscopy (XPS, Mg Kα emission, 1253.6 eV). Binding energies and oxidation states were obtained from high resolution scans (pass energy 71.55 eV and step size 0.2 eV), calibrating the energy scale by the C1s core level peak position located at 284.8 eV. Bulk composition of the films was determined by elastic recoil detection analysis (ERD, 6 MeV Cl$^{16+}$ ions). The flight path length of the ERD experimental setup was 0.845 m.

The oxidized films were electrically probed in Metal-Oxide-Metal (MIM) and 4-point-probe configurations (sheet resistance, $R_{\text{sheet}}$). MIM top metal layer was defined by Ni dots of 150 μm in diameter deposited through a shadow mask at room temperature by electron beam evaporation. Current density, $J_{\text{Anneal}}$, was obtained from current–voltage (I–V) sweeps using a conventional parameter analysis. Typical I–V curves can be found in [4]. For $R_{\text{sheet}}$ measurements the films were directly contacted by a head already configured with the Van der Pauw 4-point-probe geometry.

3. Results

3.1. Initial Ni thin film characteristics

3.1.1. Crystallinity

Fig. 1 shows the XRD patterns of the initial Ni films. The most significant observation is that while the Ni crystalline planes oriented parallel to the surface of the substrate ($\theta$–2θ scans) clearly differs for both Ni layers tested, the non-oriented component (GI-XRD) is similar among all samples.

Table 1 summarizes the crystallographic characteristics of the initial Ni films as obtained from the $\theta$–2θ XRD patterns (Fig. 1a, 0 s). In general, we observed that Ni films grown on TiN are (111) textured: Ni(200)/Ni(111) intensity ratio is $\sim$14% while for the case of polycrystalline Ni the same ratio is 42% [20]. The effects of the preanneal step on the Ni crystalline characteristics can be summarized as follow (Table 1): (a) Ni CS are at least doubled; (b) Ni(200)/Ni(111) intensity ratio is kept at $\sim$14%, meaning that the high temperature annealing step does not produce any evident crystalline reorientation; (c) Ni lattice parameter was in average 0.352 ± 0.002 nm and it is not influenced by the preanneal step.

In the case of the GI-XRD patterns, Ni(111)/Ni(200) intensity ratio was $\sim$40%, similar to what is found in polycrystalline materials. Ni CS were small, i.e. $\sim$5 nm, and its lattice parameter was comparable to those obtained in the $\theta$–2θ configuration (Table 1, “a” values).

In a phase mixture, the relative amount of each crystalline phase is quantified by the integrated intensity that characterizes each phase. In the same way, we propose that the comparison of the integrated intensities of both $\theta$–2θ and GI-XRD patterns can provide a rough estimation of the relative amount of polycrystalline material that forms the Ni films. These results are shown in Table 2. As expected, the relative amount of polycrystalline material found in the Ni–WOP layers is approximately a factor three larger than the one measured in Ni–WP.

3.1.2. Topography

Fig. 2a–b shows the SEM views of the initial Ni films, Ni–WP and Ni–WOP. The images demonstrate the strong impact of the preanneal in the GS distribution of the Ni films. The change in GS goes together with a thickness reduction of $\sim$10–15% (SEM cross sections not shown), which was also corroborated by $R_{\text{sheet}}$: $R_{\text{sheet}}$ for the Ni–WP and Ni–WP was $\sim$0.9 and 1.0 Ω·cm$^{-2}$, respectively.

A quantitative analysis of the GS distribution was obtained by EBSD (Fig. 2c–d). This analysis was possible only for the case of Ni–WP. Ni–WOP displayed weak EBSD patterns with severe overlap. Standard SEM imaging indicated that the Ni–WOP GS was smaller than 70 nm.

Ni–WP displayed a broad GS distribution, ranging from tens of nm’s to $\sim$450 nm (Fig. 2d). Approximately 30% of the total area is formed by grain diameters smaller than 100 nm, meaning that these samples contain a large amount of high angle grain boundaries (not quantified). The texture component were Ni(111) $\sim$30%, Ni(001) $\sim$12% and Ni(111) $\sim$4%. Large grains are essentially (111) oriented (Fig. 2c).

3.1.3. Surface characteristics

Survey photoelectron spectra of the pristine Ni surface revealed only Ni, O and C. XPS binding energies for O, metallic Ni and Ni
oxides and hydroxides are well established in the literature [21–22]. The Ni2p and O1s high resolution XPS spectra (not shown) displayed the typical features of these two signals [23–24]. Ni2p spectra were formed by the 0, 2+ and 3+ valence state components. Due to the complexity of the Ni2p signal, that requires assigning at least 12 peaks to deconvolute it correctly [22], we have not quantified the amount of each Ni valence state. Alternatively, the analysis of the O1s spectrum showed that the surface of the Ni films are formed by NiO, Ni(OH)2 and water. These are components normally found in the Ni native oxide formed at normal air conditions. NiO/(Ni(OH)2 +H2O) integrated intensity ratio was $C_240.28$ for both initial Ni surfaces, Ni–WP and Ni–WOP. After an erosion with Ar+ ions (at 2 keV and 0.6 mC corresponding to 3 nm removal of SiO2), O and C signals vanished and only Ni was observed. This corroborates the marginal thickness of the native oxide and the high purity of our Ni starting materials.

3.2. Oxidation behavior

In the following, the results related to the oxidation of the Ni films are presented. The microstructure described corresponds to oxide scales thinner than 200 nm.

3.2.1. Oxygen uptake

Fig. 3 shows the oxide growth rate, presented as the change in mass per unit area ($\Delta m/A$) as a function of the oxidation time $t_{\text{oxide}}$. It is assumed that the variation in mass is only due to the incorporation of oxygen into the Ni film. Surprisingly, independent of the Ni preanneal treatment, the oxidation kinetics curves are similar. They can be fitted considering a quadratic relationship, i.e. $(\Delta m/A)^2 \propto t_{\text{oxide}}$ with a parabolic scaling constant of $\sim 2.66(1) \times 10^{-11} \text{g}^2 \text{cm}^{-4} \text{s}$. This value is approximately 3 orders of magnitude higher than what is observed in bulk Ni systems for similar oxidation conditions [8, 25].

3.2.2. Composition

A typical example of the ERD spectra obtained from the oxidized samples is depicted in Fig. 4. ERD only detected H, C, O, Cl and Ni. H and C were located at the surface of the Ni native oxide and their content was below 2 at.%; Cl comes from the ion beam used to perform the ERD experiments. H is related to Ni-hydrides and water and C to C–O (air contamination) as determined by XPS. Ni and O elemental depth profiles comprised two parts (going from the surface toward the TiN): (a) a segment with a rather constant Ni:O ratio followed by (b) an oxygen-graded component. Considering
the average value of the constant-composition part, the films can be described as NiO$_{1-d}$. For the samples oxidized for 30 s, $d$ was $\sim$0.2; for increased times $d$ ranged between $\sim$0.0 and 0.1. NiO$_{1-d}$ compositions did not display any evident tendency as a function of the initial Ni substrate. The decreasing in oxygen content in the oxygen-graded component of the spectra appears to be related to the rough NiO-Ni interface as revealed by SEM and TEM cross sections (Figs. 5 and 6).

For simplicity, in the following we will refer to our oxide as NiO despite the composition aforementioned.

3.2.3. Morphology and thickness

SEM micrographies of Fig. 5 show the evolution of the NiO topography as a function of the oxidation time. The oxide surface morphology was independent of the initial Ni layer characteristics. For samples oxidized for 30 s, NiO was already quite rough, formed by incipient square-like shape grains, which did not seem to cover the whole Ni surface. This structure appeared to be closed only after 180 s where it was possible to observe that NiO was formed by agglomerated platelets, similar to what has been observed during the growth of thick NiO scales, i.e. $>$1 $\mu$m [7,16]. Platelets are indicative of an oriented growth of NiO onto the Ni substrate. Indeed, epitaxial relationships for the growth of NiO onto Ni are well known [26]. In the particular case of platelets, NiO $\{111\}$ planes are reported to grow perpendicular to the Ni textured sample [27,28]. At 600 s, the platelet's microstructure is no longer observed, and NiO grain shapes became diffuse.

NiO–Ni interface was rough (Fig. 5). The cross sections morphologies were sharp only for the samples grown after 300 s or longer oxidation times. At those conditions, NiO columns larger than 100 nm were observed. At the longest oxidation time, i.e. 600 s, Ni was still observed; according to our oxygen uptake measurements and assuming a Ni:O = 1:1 composition ratio (Ni film corresponds to 80.8 $\mu$g/cm$^2$), 47% of the Ni films is still remaining at this condition.

TEM cross sections offer a complementary view to the SEM results (Fig. 6). The cross sections morphologies were sharp only for the samples grown after 300 s or longer oxidation times. At those conditions, NiO columns larger than 100 nm were observed. At the longest oxidation time, i.e. 600 s, Ni was still observed; according to our oxygen uptake measurements and assuming a Ni:O = 1:1 composition ratio (Ni film corresponds to 80.8 $\mu$g/cm$^2$), 47% of the Ni films is still remaining at this condition.

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TEM cross sections offer a complementary view to the SEM results (Fig. 6). The samples investigated were those grown at 180 s oxidation times. TEM showed voids at the NiO–Ni and Ni–TiN interfaces together with holes and cracks within NiO grains. Moreover, it corroborated the SEM results regarding the rough Ni–NiO interface. HRTEM analysis of the non-oxidized part of the Ni layers showed that its main crystalline orientations belonged to the $\{111\}$
family planes. The oxide thickness was in the range of a few tens of nanometres to \(\sim 140\) nm. This range was similar for both initial Ni substrates, Ni–WP and Ni–WOP, given further support to the oxygen uptake results.

3.2.4. Crystallinity

Diffractograms of the oxidized Ni films displayed only the peaks related to FCC NiO \([29]\) (2\(\theta\) positions: NiO(111)\(\sim 37.4^\circ\) and NiO(200)\(\sim 43.7^\circ\)). In the following, only oxide samples grown from 60 s or longer oxidation times will be discussed. The oxide samples grown after 30 s did not provide enough NiO signal in the X-ray patterns.

As evidenced from the \(\theta–2\theta\) diffractograms, NiO grew with a (111) preferential orientation and this texture depended upon the initial preparation of the Ni film (Fig. 1a). Indeed, for all oxidation conditions NiO(111)/NiO(200) intensity ratio of the oxide grown from Ni–WOP was \(\sim 1.6\). For the case of oxidized Ni–WP, the same ratio progressively decreased from 5.6 to \(\sim 1.2\) as the oxidation time increased from 60 to 600 s, respectively.

The amount of NiO crystalline phase was quantified through the integrated intensity of its Bragg reflections. As the oxidation time proceeds, the amount of oxide increases, and this increment depended upon the initial Ni preparation. Fig. 7a shows the oxide integrated intensities normalized to17.9 cps deg, which corresponds to the maximum value measured in Ni–WP films oxidized during 600 s. Until 180 s, the amount of NiO phase is quite similar for both initial Ni substrates; the experimental error is \(\sim 10\%\). However, for longer oxidation times, the quantity of crystalline NiO...
formed from Ni–WP. Qualitatively, this observation demonstrates that NiO obtained from Ni–WOP as compared to that obtained from Ni–WP. Normalization was done dividing by the oxidation time. Both (111) and (200) NiO Bragg reflections were considered for the calculations of the integrated intensity. Normalization was done dividing by 17.9 cps deg, maximum value obtained in the Ni–WP samples oxidized during 600 s. (b) Raman spectra of the Ni films oxidized during 60 s at 500 \(^\circ\)C.

Ni–WP systematically displayed higher \(J_{\text{an}}\) values than those obtained from Ni–WOP. A similar behavior was also observed in the \(R_{\text{sheet}}\) (Fig. 8b). Until 60 s, \(R_{\text{sheet}}\) values are similar for both initial Ni substrates. However, from 180 s on, \(R_{\text{sheet}}\) of the stacks formed by Ni–WOP/NiO were not measurable, i.e. \(R_{\text{sheet}} \geq 10^5\) \(\Omega \cdot \text{cm}^2\). For the stacks with Ni–WP, \(R_{\text{sheet}}\) slightly decreased from 1.5 to 5 \(\Omega \cdot \text{cm}^2\) from 180 s to 600 s oxidation times, respectively.

It is worth mentioning that the evolution of the resistance (Fig. 8) is mainly attributed to changes in the Ni layer and not to the oxidation of the TiN film. Indeed, for the longest oxidation time, XPS charaterizations showed that the Ti2p peak was located at ~454.9 eV, corresponding to TiN; close to the TiN surface, metallic Ni was still present (Ni2p signal at ~852.3 eV), confirming that the Ni film has not been yet fully consumed. We did not observe Ti–O bonds in the bulk of the TiN film.

4. Discussion

On the one hand, the parabolic oxide growth behavior of bulk Ni in the range of 500 to 1000 \(^\circ\)C has been reported to be much dependent on the initial Ni preparation prior to the oxidation treatments [7]. On the other hand, in our case where 100 nm Ni films are oxidized at 500 \(^\circ\)C, the oxidation kinetics obtained from gravimetric techniques did not show any evident dependence with respect to the initial Ni pretreatments. Indeed, in the oxidation time range investigated, i.e. from 30 to 600 s, both initial Ni films, either formed by fine (Ni–WOP) or large grains (Ni–WP), exhibited similar oxygen uptake values (Fig. 3). The larger parabolic scaling constant measured as compared to bulk systems, i.e. \(\sim 2.66(1) \times 10^{-11}\) g/cm\(^2\) s\(^{-1}\), reveals that the oxidation rate in thin films is enhanced. Considering the equivalence between the oxygen uptake and NiO average thickness [18], the estimated diffusion coefficient would correspond to \(D_0 \sim 10^{-15}\) cm\(^2\) s\(^{-1}\). \(D_0\) falls in the upper limit of the reported values for diffusion of Ni in NiO, where the main short circuit paths are grain boundaries and dislocations [8, 32]. In our layers, this diffusion mechanism can be supported by...
the results obtained in the 30 s oxidized samples and the TEM characterization. In the former case, SEM views showed that NiO decorated the boundaries of large Ni grains (Fig. 5); the low amount of oxygen measured for this condition (Fig. 4), i.e. NiO$_{2-8}$, may indicate either the presence of a non-continuous or an extremely non-homogeneous NiO layer. The presence of voids at the Ni–NiO interface observed by TEM (Fig. 6) may be a consequence of the faster Ni outward diffusion through the oxide being formed as compared to the oxygen inward diffusion.

The insensitiveness of the oxygen uptake results against the Ni microstructure may find its cause in the amount of grain boundaries that our initial Ni films contain, pointing out that the pre-anneal treatment is not enough to induce a substantive change in the number of paths available for diffusion. This is clearly evidenced by (a) the large relative amount of the initial nanocrystalline material, which is similar for both Ni layers (Fig. 1b and Table 2) and (b) the large amount of fine grains, i.e. <100 nm in diameter, forming both Ni films (Fig. 2). Moreover, the heating ramp step during the oxidation experiments, that takes ~30 s, also seems to modify the Ni film, leading to similar lateral GS (Fig. 5, top view 30 s sample) and in-plane GS for both initial substrates (Fig. 1a, 0–20 patterns 60 s samples). The similitude in oxidation kinetics was also reflected in the bulk composition and grain topography of the NiO, suggesting that these oxide characteristics are mainly defined by thermally activated processes, similar to what happen with bulk Ni [7], with lesser dependence on the initial Ni preparation. However, the texture and the amount of crystalline NiO phase depended on the initial Ni preparation, what in turn was clearly reflected in the electrical resistance of the oxide films. In the case of the texture, we observed that Ni films formed by large (111) crystallites initially promoted the formation of highly textured NiO(111) materials (Fig. 1a, 60 s). This demonstrates that NiO growth proceeds through an epitaxial relationship with respect to the Ni substrate, hypothesis that is also supported by the presence of the platelet-like grains (Fig. 5). The evolution of the texture in this kind of Ni substrates (Ni–WP) addresses as well the effect that, as the oxidation proceeds, Ni grains are consumed and new crystalline faces are left exposed for oxidation. Consequently, NiO become polycrystalline. Likewise, if Ni is formed by randomly oriented crystallites, they should promote the formation of randomly oriented oxide too, which would be the case of the oxide grown onto the fine-grained Ni films (Ni–WOP).

Regarding the apparent contradiction in the amount of NiO formed when comparing gravimetric (Fig. 3) and crystallographic (Fig. 7) results, we propose that the differences are related to the formation of nanocrystalline material, with characteristics lengths below 3 nm. An estimation of its relative quantity can be provided by the samples oxidized during 300–600 s (Fig. 7a): by XRD the amounts of NiO grown from small (Ni–WOP) and large Ni(111) CS (Ni–WP) were approximately 500 times smaller than the one reported here, i.e. 16°C s$^{-1}$. Similar to the case of nanoparticles [33,34], Ni thin films might be sensitive to the heating ramp used during oxidation experiments. Despite the apparent divergences, our local TEM observations may corroborate that Ni(111) orientation oxidized slower as compared to Ni(200) (Fig. 6). However, this data must be interpreted with caution because Ni(111) CS are larger than Ni(200) CS, thus they would need more time to be consumed by the oxidation process.

5. Summary

We have investigated the role of the grain size and crystallinity in the oxidation at 500°C of 100 nm thick Ni films deposited onto TiN. Ni films were either formed by fine grains or large grains with an enhanced Ni(111) crystallite size. We observed that the oxidation kinetics as obtained from gravimetric methods is insensitive to the initial Ni preparation since similar weight increasing as function of the oxidation time were observed among all initial substrates. The oxide grew with parabolic time dependence, indicating that the rate limiting step is the diffusion through the oxide being formed. The evolution of the oxide bulk composition and its grain morphology were also independent of the Ni pretreatment. However, the crystalline texture and the amount of nanocrystalline oxide did depend on the initial Ni grain characteristic, which in turn was clearly reflected in the oxide electrical properties. We proposed that the nanocrystalline component plays a major role defining the resistance of the oxide since it is related to the amount of grain boundaries present. Our results show that in order to assess correctly the oxidation behavior of thin films, the proper characterization of nanocrystalline (or amorphous) material is of fundamental importance.

Acknowledgments

We acknowledge N. Jossart for process assistance and the partial funding by IMEC’s Industrial Affiliation Program on ReRAM memory. JL and TH would like to thank the financial support of the Chilean Research Council Fondecyt under contract 1090332.

References


[17] Powder Diffraction File TiN card Nr 38–1420, a = 0.4241 nm, FCC structure.


