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Influence of the microstructure on the oxidation of Ni thin films

J.G. Lisoni [a,b,*], L. Goux [a], Th. Hoffmann [b], D.E. Diaz-Droguett [c], M. Jurczak [a]

[a] IMEC, Kapeldreef 75, 3001 Heverlee, Belgium
[b] Physics Department, FCFM, Universidad de Chile, Avenida Blanco Encalada 2008, Santiago, Chile
[c] Physics Department, Facultad de Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile

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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.

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 SiO_2 deposited at 400 °C by chemical vapor deposition. Then, TiN films 40 nm thick were deposited at room temperature onto the SiO_2 by reactive sputtering using an Anelva® deposition cluster. The sputtering process is performed in a mixture of Ar and N_2 (50 sccm) at 1 kW. These conditions produce N-rich $TiN_{1.3}$ 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

* Corresponding author at: IMEC, Kapeldreef 75, 3001 Heverlee, Belgium. Tel.: +32 16 288358; fax: +32 16 281576.
E-mail address: lisonij@imec.be (J.G. Lisoni).

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(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 ~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 ~0.2 μg cm^{-2}. This value would correspond to ~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_2O) 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_2O << 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 ~70° with step sizes of 10 and 20 nm), X-ray diffraction (XRD, CuK_α radiation, λ = 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 (θ–2θ) and grazing incidence detector scan (GI-XRD) configurations. θ–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 Scherreŕs formula [19]. The resolution of our diffractometer is 0.03° equivalent to a CS of ~350 nm (FWHM Si(400) located at 2θ = 69.13°). The quantitative analyzes of the XRD signals were performed using the DIFFRAC^{plus} 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 surface 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^{3+} 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_{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_{MIM}, was obtained from current–voltage (I–V) sweeps using a conventional parameter analysis. Typical I–V curves can be found in [4]. For R_{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 (θ–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 θ–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 ~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 ~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 ~40%, similar to what is found in polycrystalline materials. Ni CS were small, i.e. ~5 nm, and its lattice parameter was comparable to those obtained in the θ–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 θ–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 ~10–15% (SEM cross sections not shown), which was also corroborated by R_{sheet}: R_{sheet} for the Ni–WOP and Ni–WP was ~0.9 and 1.0 Ω/□, 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 ~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) ~30%, Ni(001) ~12% and Ni(011)<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