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Hematite/nickel oxide multilayers characterizations

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Ferrites are known for their magnetic properties and are used for magneto and magneto-optical recording. Recently, some investigations were carried out on different types of mixed valence-defect spinel such as $Mn_xCo_yFe_{(3-x-y)}O_{4+\delta}$. Indeed thin films of these compounds are potential candidates for the next generation of magneto-optical recording media [1]. The principal challenge in recording is to store the information in the less area. Consequently, the coercive field of the material must be the highest. An original way to increase the coercivity of ferrites is to introduce stresses into the material. In case of powders, the stresses can be induced by oxidation processes which generate strong composition gradient inside the material [2–7]. In case of thin films, composition gradient can be obtained from multilayer systems by thermal treatments which allow a partial diffusion of elements in the different layers and therefore induce stresses like the ones caused by oxidation reactions.

The aim of this study was to characterize α-Fe_2O_3/NiO multilayers before and after thermal treatments so as to evidence possible interdiffusion phenomena. The purpose of the present work was first of all to find out experimental tools well suited to the characterization of the chemical compositions of the multilayers in the direction perpendicular to the interfaces at a nanometer scale.

Multilayers were prepared in the LMOV (Versailles, France) using a pulsed laser ablation deposition system. The experimental conditions have been previously described [8]. Samples were deposited on fused quartz substrates which were heated to a fixed temperature ranging from ambient to 500 °C. The elaboration of the NiO/αFe_2O_3 multilayers was achieved by subsequent change of the target exposed to the laser beam. The deposition time can be changed from 10 to 45 min and is chosen equal for depositing each layer. These experimental conditions give global thicknesses ranging from 25 to 200 nm. The results presented here were obtained for three bilayers. The first deposited layer was nickel oxide and the total thickness was in the 100 nm range. The multilayers were annealed during one hour at different temperatures in order to induce interdiffusion phenomena.

Bias cuts were carried out on the multilayers. At first, multilayers were covered with a copper film in order to avoid any breakings during the cut. Copper was deposited in two stages: firstly by ionic bombardment under vacuum and secondly from electrolytic deposition. After this treatment, a rotating abrasive sphere in copper and boron nitride was used to cut the sample. The wheel radius was high enough (15 mm) compared to the characteristic dimensions of the multilayers (about 10^{-4} mm) to induce a bias cut.

Secondary ion mass spectrometry (SIMS) analyses were carried out with the help of a MIQ256 CAMECA apparatus [9]. Both dynamic and static SIMS modes were used in order to obtain on the one hand information on the composition profiles and on the other hand images of the sample after bias cuts. Primary oxygen ions were used with 4 keV energy and a typical ion density in the 10^{14} ions $cm^{-2}\cdot s^{-1}$ range for dynamic SIMS experiments. The iron content was measured from the mass 57 whereas the nickel content was followed using the mass 62. In addition SIMS intensity calibrations were performed by analyses carried out in exactly the same experimental conditions on standards of phases which should be present in the system (α-Fe_2O_3, NiO, Fe_2NiO_4).

Moreover depth calibration was achieved using interference microscopy analysis (micromap) so as to estimate depth and roughness of the craters generated by ion bombardments during SIMS experiments and so to determine the sputtering rates. These experiments were performed with a micromap apparatus with an in-depth resolution better than 1 nm.

The multilayer system has been first of all characterized from a macroscopic point of view by magnetic measurements [8]. The formation of a magnetic compound has been evidenced from the important increase of the magnetic moment after annealing treatments above 350 °C. Hematite (α-Fe_2O_3) and nickel oxide (NiO) being both antiferromagnetic compounds, this increase of the magnetic moment should be due to the formation of the spinel ferrite Fe_2NiO_4 at the interfaces related to interdiffusion processes. However X-ray diffraction analyses did not reveal the formation of new phases: the films being

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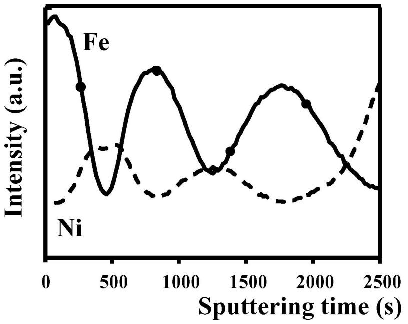
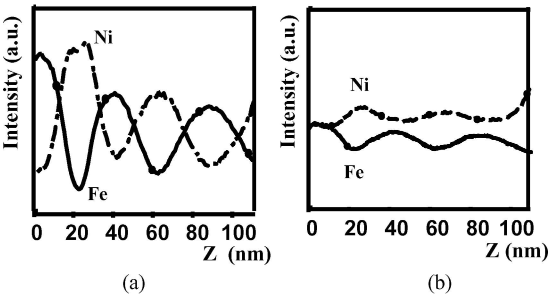


Figure 1 Raw dynamic SIMS results for the room temperature processed sample without subsequent annealing.



(a) (b)

Figure 3 Dynamic SIMS results after intensities and depth calibrations. (a) concerns the sample processed at room temperature without further annealing and (b) the sample annealed at 480 °C.

very thin, it is difficult to detect a new phase at the interface.

In order to obtain microscopic information about the chemical interdiffusion at the SIMS experiments were performed. An example of the SIMS results obtained in dynamic mode for the room temperature processed sample without subsequent annealing are presented in Fig. 1. In these raw results successive maxima of nickel and iron masses can be observed characteristic of a multilayer.

In order to go further in the discussion of the SIMS experimental results, two problems have to be considered, the intensities and the depth calibrations. The first one corresponds to the necessity of correcting the SIMS intensities in order to take into account the differences in the ion yields for iron and nickel. This intensity calibration was performed using a compact Fe_2NiO_4 sample and assuming that the ion yields in the oxides are close to the ion yields in the ferrites. This calibration allows correcting for the low ion yield of nickel [10].

The second problem is to relate the sputtering time with the depth that is to say to know the sputtering yield or the sputtering speed. An interferometric profilometer was used in order to measure the depth of the crater at the end of the SIMS experiment. Several profiles of the hole resulting from the sputtering were performed. An example of an interferometric micro-mapping of the SIMS crater is shown in Fig. 2. The bottom of the crater is quite flat and its depth is about 120 nm. So it is possible to know the sputtering speed (about 3 nm/min in the experimental conditions chosen here) and hence to transform the abscissa from a time scale to a depth scale.

All these calibrations being performed, it is possible to obtain the variations of the ion intensities as functions of z, the depth inside the sample. These results are presented in Fig. 3 for two multilayers, one processed at room temperature without further annealing (Fig. 3a) and the other one annealed at 480 °C (Fig. 3b). On the first one maxima of iron corresponding to nickel minima can be clearly observed: the sample is a multilayer composed of three layers of each oxide, nickel oxide and hematite. When the sample is annealed at higher temperatures (Fig. 3b), this is no longer the case. Although some minima and maxima can be still distinguished the variations are not so important. Oscillations of ion intensities corresponding to nickel and iron become blurred. Moreover it can be observed on Fig. 3b that this phenomenon is even more pronounced for nickel than for iron: diffusion of nickel occurs in the multilayers upon annealing. This conclusion is confirmed by X-ray photoemission spectroscopy (XPS) experiments. Nickel is detected on the surface of a 480 °C annealed sample although its upper layer should be α-Fe_2O_3. This is no more the case for a non-annealed sample.

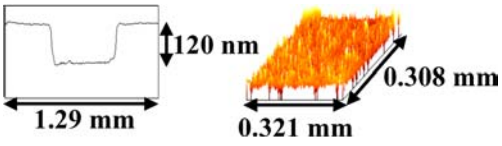
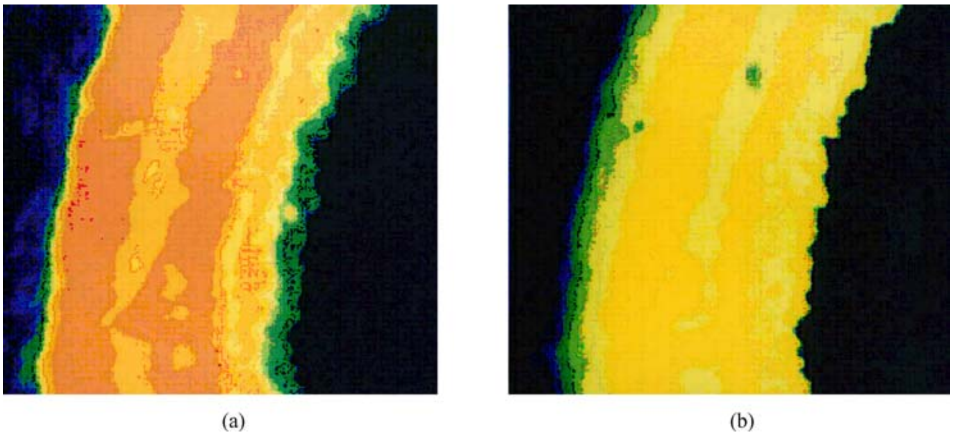


Figure 2 An example of an interferometric micro-mapping of the SIMS crater.

Another way to study phenomena which take place on a scale which is in the nanometer range is to spread the phenomena over much higher dimensions. This was performed by using a bias cut technique. Although a lot of problems occur related to the different hardnesses of the different phases which induce a decohesion between the layers, it is possible using this technique to obtain a sample which exhibits the different layers when observed by optical microscopy or interferometric micromapping. This sample was studied by static SIMS. Images obtained from the iron ion intensity clearly show a succession of iron rich and iron poor layers (Fig. 4a). This is no more clearly evidenced in the case of the nickel image (Fig. 4b): nickel is much more homogeneously distributed in the whole sample than iron. This observation is not due to differences between nickel and iron ion yields but is due to the fact that nickel diffuses in the oxide layers much more easily than iron.

In conclusion, SIMS is widely used in order to study semiconductor multilayers constituting electronic devices but it has been shown in this study that SIMS, either used in a dynamic mode or in a static mode using images, can also provide very useful information concerning interdiffusion in oxide multilayers at a nanometer scale [11, 12]. The non-equivalence of interdiffusion of nickel into iron and iron into nickel is well known notably because it can lead to several effects like the Kirkendall effect [13]. It is evidenced here that a similar effect occurs in the case of nickel/iron oxide systems: nickel diffuses more easily than iron upon annealing



(a) (b)

Figure 4 Static SIMS results after bias cut. (a) concerns iron ion intensity and (b) nickel ion intensity.

treatments in the studied oxide multilayers. This phenomenon induces a specific interfacial reaction which leads to a Fe_2NiO_4 type phase [8]. This result has to be correlated with magnetic measurements.

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