Correlated structural and magnetization reversal studies on epitaxial Ni films grown with molecular beam epitaxy and with sputtering

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We have studied the correlation between film structure and the azimuthal dependence of the magnetization reversal in (001) and (111) epitaxial Ni films grown on MgO substrates using two different deposition techniques: molecular beam epitaxy (MBE) and dc magnetron sputtering. The films were grown and *in situ* annealed under identical conditions. The magnetization reversal was investigated using MOKE. The coercive field in the sputtered (001) Ni films exhibits fourfold azimuthal symmetry as expected for crystalline films of good epitaxial quality, while MBE (001) Ni grown films exhibit an additional uniaxial symmetry superimposed to the fourfold symmetry. We performed high-resolution XRD studies as well as cross sectional TEM studies in order to establish similarities and differences in the structure of the films. Both types of films exhibit epitaxial growth and very good crystalline quality with no indication of strain. The main difference between the films is the different magnetic anisotropy. We postulate that this difference may be due to different interfacial structure and/or morphology due to the possible formation of a NiO interfacial layer only present or highly ordered in the MBE grown films. Polarized neutron reflectivity measurements performed on some of the films are correlated with the interfacial structure and magnetic anisotropy.
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I. INTRODUCTION

Metal–oxide[1,2] interfaces are of growing interest both from a fundamental and industrial point of view. Applications are relevant to many different industrial sectors, such as magnetic storage media and supported catalysts. In the case of epitaxial magnetic films, the magnetic properties, particularly the anisotropy, are known to be dominated by the crystallographic structure of the metal/oxide interface. However, our knowledge of the interface structure is rather limited.

The Ni/MgO interface is a model system for metal/oxide interfaces studies. All previous experimental work[1–12] agrees that the growth of Ni on MgO(001) at room temperature (RT) results in polycrystalline films. From their results, we readily conclude that the differences in the film morphology and the epitaxial orientation relationships are strongly dependent on different processing parameters such as the substrate temperatures, growth rate, etc. Cube on cube (CC) epitaxy combined with a dislocation network, was reported for sputtered films prepared at 580 K and studied by high resolution transmission electron microscopy (HRTEM).[4] Pure CC epitaxy followed by Ni(110) growth was reported for molecular beam epitaxy (MBE) films prepared between 700 and 900 K[3] as well as at RT.[13,14] Interdiffusion and Ni (111) growth were observed at high temperature and high pressure.[5] A detailed study of the local electronic structure by a combination of experiment and theory has not yet been performed for the Ni/MgO interface. Therefore, it is not clear whether a formation of a thin layer of NiO or only a strong hybridization between Ni and O is present at the Ni/MgO interfaces. Also the possibility of a charge transfer across the interface has not yet been discussed.[15]

Since no previous investigations of the Ni/MgO(001) interface were performed on films with pure CC epitaxy, issues at the interface can only be extrapolated. Moreover none of these previous contributions described the structural and morphological evolution at the interface after annealing. We have applied several different techniques to study Ni films grown on different oriented MgO substrates by MBE and sputtering.

II. EXPERIMENT

The Ni films were grown in a MBE VG 80 M system with a background pressure $<5\times10^{-11}$ Torr. Ni was evaporated from a 99.999% pure source. The deposition rate was 0.5 Å/s. The substrates used in the experiment were 0.5 mm thick, $1\times1\ \mathrm{cm}^2$ prepolished high quality MgO(001) and

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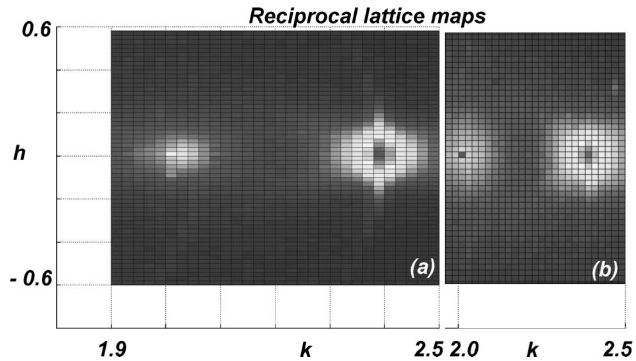


FIG. 1. (a) High resolution XRD reciprocal mesh map obtained for a 30 nm (001) Ni film MBE grown on MgO at 150 °C and annealed *in situ* at 300 °C for 6 h; (b) same map obtained for a 30 nm (001) Ni film sputtered on MgO under similar conditions during growth and *in situ* annealing.

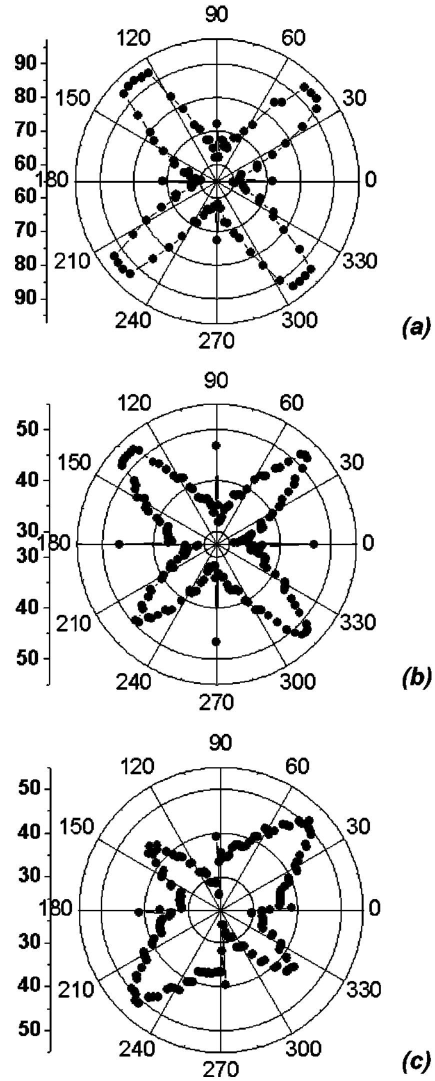


FIG. 2. (a) Azimuthal dependence of the coercive field for an "as-grown" (001) Ni MBE grown film; (b) same dependence for a (001) Ni sputtered film and *in situ* annealed; (c) same dependence for *in situ* annealed (001) Ni MBE grown film. All the films are 30 nm thick. The vertical axis corresponds to the coercive field (Oe).

(111) oriented single crystals, which were heat treated in UHV at 800 °C for 1 h. The UHV heating cycle allowed the surface layers to regain crystalline order evidenced by sharp reflection high-energy electron diffraction (RHEED) patterns. No surface reconstruction of the substrates was observed with RHEED. The combination of flat polished substrates and this *in situ* thermal treatment has been shown to favor growth of single crystal metal films.

Prior to initiating the growth, the substrate temperature was lowered to the appropriate deposition temperature for metal growth [$T \approx 150$ °C for (001) and $T \approx 300$ °C for (111) oriented Ni films].[14,16] Heat transfer was by direct radiation between heater and MgO substrate. The RHEED patterns were recorded continuously during deposition and during subsequent annealing of the films. The surface morphology of the as-deposited and annealed films was determined *in situ* with scanning tunneling microscopy [(STM) RHK model STM 100].[14]

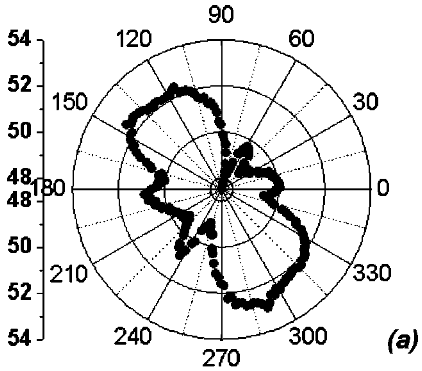
Sputtered films were deposited in a separate chamber with base pressure $< 5 \times 10^{-9}$ Torr. Deposition conditions (substrate temperature, growth rate, annealing temperature, and annealing time) were the same as for the MBE grown films. All films studied were 30 nm thick. Several complementary techniques were correlated to study this system.

III. RESULTS

We performed detailed structural characterization of both types of films using high resolution x-ray diffraction at the Advanced Photon Source (APS), Argonne National Laboratory. Reciprocal space mesh maps indicate epitaxial cube on cube growth in both types films (Fig. 1). From the reciprocal mesh maps we cannot see evidence of strain or texture structure in the Ni films. The x-ray beam was at grazing incidence ($\sim 2°$).

We used longitudinal magneto-optical Kerr effect-(MOKE) to study the anisotropy in the magnetization reversal on the samples. We expected to see the same type of symmetry due to the fcc Ni structure to be reflected in the magnetic properties. That is, we expected to see fourfold in-plane symmetry for (001) films due to the first order magnetocrystalline anisotropy. We note here that for the (111) films we expected to see sixfold symmetry due to the second order magnetocrystalline anisotropy because the first order (threefold) anisotropy collapses in the longitudinal MOKE geometry.[17]

Figure 2 shows the experimental comparison of the azimuthal dependence of the coercivity in (001) Ni films grown by MBE and sputtered under identical conditions. Figure 2(a) (MBE grown film prior *in situ* annealing) and Fig. 2(b) (sputtered film and *in situ* annealed at 300 °C for several hours) show quite similar fourfold symmetry. In order to further smooth the film surface of the MBE grown films, they were *in situ* annealed in UHV at 573 K ($\sim 1/3$ of the Ni melting temperature) for several hours. *In situ* RHEED and STM confirmed surface smoothening.[16] After this treatment we also observed significant changes in the magnetic anisotropy in the MBE grown films [Fig. 2(c)], namely the appear-



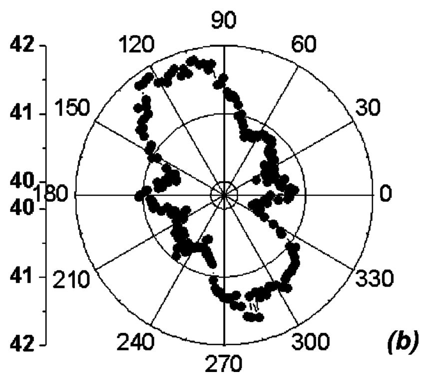


FIG. 3. (a) Azimuthal dependence of the coercive field for an "as-grown" (111) Ni MBE grown film; (b) same dependence for a (111) Ni sputtered film. All the films are 30 nm thick. The vertical axis indicates the coercive field (Oe).

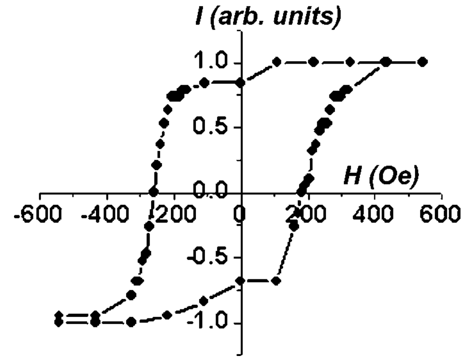


FIG. 4. Hysteresis loop obtained for an exchange biased 30 nm (001) Ni film. This film was *ex situ* annealed at 300 °C and cooled afterwards to ambient temperature under an external field (4 kOe) applied along the [011] crystallographic direction (magnetization easy axis).

ance of an additional uniaxial anisotropy superimposed to the fourfold magnetocrystalline anisotropy.

For (111) Ni films MBE grown and sputtered under identical conditions, we observed the expected sixfold symmetry in the magnetization reversal and also a weak uniaxial anisotropy (Fig. 3). We observed that the coercive field ranges from 48 to 54 Oe for MBE grown samples and from 40 to 42 Oe for sputtered ones, evidencing second order in the anisotropic variations as compared to first order anistropies in (001) oriented films.

IV. DISCUSSION

Based on our observations, we can point out some important features in the samples before and after annealing. Similar (001) films deposited by MBE and sputtering exhibit fourfold symmetry. Similar films sputtered and MBE grown after *in situ* annealing exhibit the same average coercivity. MBE (001) films show additional uniaxial anisotropy after *in situ* annealing at 300 °C. We speculate that this is probably due to the formation of an ordered NiO thin layer at the interface. The Ni (111) films show a weaker uniaxial anisotropy, stronger in the MBE grown sample than in the sputtered one, indicating better crystalline quality in the former compared to the latter. The anisotropy is of second order in the (111) films while is of first order in the (001) ones, as indicated by the range of coercive field values in the azimuthal dependence for each case.

We note here that both MgO substrate and Ni are materials which are face centered cubic, but have large lattice parameter mismatch (16.4%). We observe that although epitaxial films are obtained for this system despite this large mismatch, the epitaxy cannot be simply explained in terms of strained growth. Moreover recent theoretical investigations predict that Ni should strongly interact with MgO(001)[18,19] with large adhesion energy for Ni clusters (0.62 eV/atom) and strong bonding for an isolated Ni atom (1.24 eV). Thus, we believe that the formation of a NiO interfacial layer is favorable and it may also favor epitaxial growth of the Ni film. The lattice constants of MgO and NiO are 4.213 and 4.177 Å, respectively, which has only 0.9% difference, but the constant of Ni is 3.52 Å which has as large as 16.4% of lattice parameter mismatch compared to MgO, so if there exists an intermediate NiO layer exists between Ni and MgO, it may favor the epitaxial growth of the metallic film.

As mentioned above *in situ* annealing at 300 °C induces uniaxial magnetic anisotropy in the [011] direction [Fig. 2(c)]. We note here that a strong uniaxial magnetic anisotropy accompanying a lattice distortion along the [111] direction has been reported in NiO after annealing above its blocking temperature (250 °C) and posterior cooling down to RT.[20] Inhomogeneities in the sample may break the symmetry and the distortion then is along one particular [111] axis. This distortion has a [011] projection on the (001) plane. Thus, our findings suggest the presence of an ordered NiO layer at the interface, that probably grew fcc stabilized by the epitaxy on MgO, and acquired tetragonal distortion after further Ni deposition and posterior *in situ* annealing at 300 °C.

To further establish the existence of this interfacial distorted NiO layer we annealed one (001)Ni sample above the Nèel temperature of NiO and then cooled it down to ambient temperature under an in-plane external field of 4 kOe along the easy axis. We speculate that the lattice distortion of NiO may induce uncompensated spin in the (001) plane in contact with Ni and therefore induce exchange bias on the Ni films. As depicted in Fig. 4, we did observe pinning field along the easy axis. The strength of the pinning field was 39 Oe. Fur-

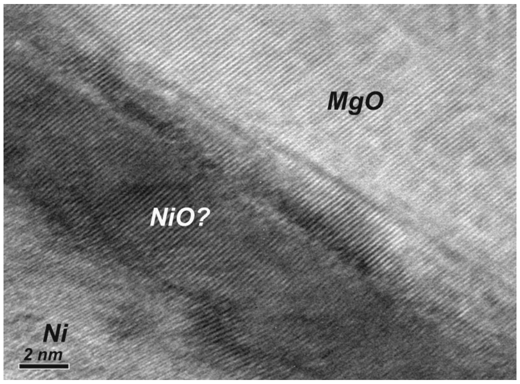


FIG. 5. High-resolution XTEM image of Ni/(001)MgO MBE grown and *in situ* annealed. We note an interfacial ordered layer with very similar lattice constant to that of MgO and appearing with darker contrast in this image. We speculate that this layer may correspond to NiO. The thickness of this layer is ~4 nm.

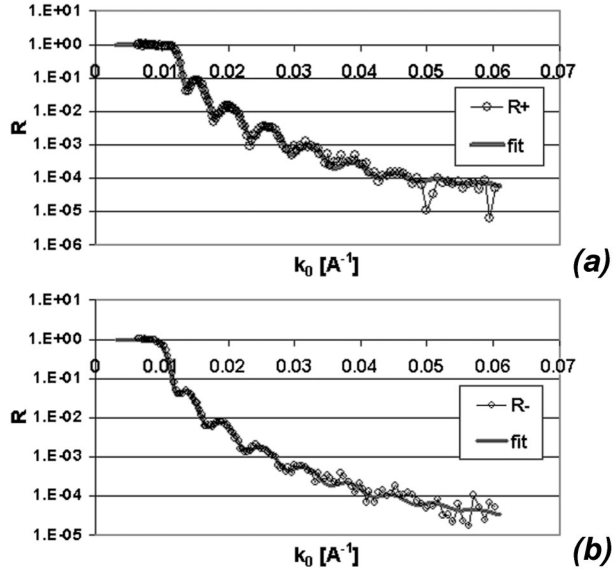


FIG. 6. (a) Reflectivity measured at 1 kOe field and 295 K, along with a fit to the data; (b) reflectivity measured at reversed 1 kOe field and 295 K, along with a fit to the data. The model used to fit the data assumes an interfacial layer 3.8 nm thick and scattering length density of 8.45×10^{-6} Å^{-1}, very close to the value for bulk NiO of 8.72×10^{-6} Å^{-}.

ther tests on the exchange bias of this system are currently in progress to rule out the possibility of exchange bias due to NiO formation on the surface of the films. We also performed high-resolution XTEM studies and an *in situ* annealed MBE grown (001)Ni sample (Fig. 5) exhibited the presence of a dark interfacial layer with lattice constant similar to that of MgO between the Ni and MgO. We suspect that this unknown layer might be NiO. Such layer was not observed in similar films grown with sputtering and *in situ* annealed.

We experimentally found that Ni grows epitaxially on (111) MgO at 300 °C. The epitaxial growth of (111) Ni proceeds cube-on-cube on the MgO substrate from the early stages of growth as indicated by RHEED.[16] We also observed uniaxial anisotropy (Fig. 3) although much weaker than in the (001) case. The origin of this anisotropy is not clear, maybe it stems from surface features (e.g., steps, screw dislocations, etc.), or shape anisotropy. We do not expect to see the effect of the NiO distortion in this configuration because it should be perpendicular to the (111) plane.

Recently, we conducted polarized neutron reflectivity (PNR) studies on some of these samples. Our preliminary PNR measurements on (111) Ni films seem to validate the presence of NiO interfacial layer. Figure 6 shows the reflectivity measured at 1 kG and at 295 K, along with fits to the data. The model produced by the fits contains a layer of about 32 Å between the Ni and MgO, which has a nuclear SLD of 8.45×10^{-6} Å^{-1}, quite close to 8.72×10^{-6} Å^{-1} of NiO further hinting at ordered NiO formation at the interface between Ni and MgO at 300 °C. We note here that the thickness of this interfacial layer predicted by the model is consistent with the thickness of the dark interfacial layer observed in HRTEM images.

V. CONCLUSIONS

From our experimental data we conclude that a different interfacial structure is formed in epitaxial Ni films MBE grown on MgO substrates. The experimental evidence points towards an ordered NiO layer at the interface between Ni and MgO. This layer may be either absent or not highly ordered in similar samples grown with sputtering. Our preliminary studies also indicate a pinning field in (001) Ni films annealed and cooled down to room temperature in the presence of an applied field. PNR data also suggest the presence of an interfacial layer in (111) films. Extensive PNR studies are currently in progress to study the difference between annealed and non-annealed (001) Ni samples. The questions are: Is there a NiO layer formed during growth or after *in-situ* annealing? If it is formed during growth, is the annealing process responsible for the distortion? Extensive studies on the exchange bias in (001) oriented samples are also currently in progress to further establish if the pinning field is due to an interfacial highly ordered and tetragonally distorted NiO layer.

[1]H. Bialas and K. Heneka, Vacuum **45**, 79 (1994).
[2]F. Reniers, M. P. Delplancke, A. Asskali, V. Rooryck, and O. Van Sinay, Appl. Surf. Sci. **92**, 35 (1996).
[3]G. Raatz and J. Woltersdorf, Phys. Status Solidi A **113**, 131 (1989).
[4]H. Nakai, H. Qui, M. Adamik, G. Sáfran, P. B. Barna, and M. Hashimoto, Thin Solid Films **263**, 159 (1995).
[5]R. H. Hoel, J. M. Penisson, and H. U. Habermeier, J. Phys. (Paris), Colloq. **51**, C1 (1990).
[6]H. Sato, R. S. Toth, and R. W. Astrue, J. Appl. Phys. **33**, 1113 (1962).
[7]A. A. Hussain, J. Phys. Chem. Solids **1**, 9833 (1989).
[8]H. Bialas and L.-S. Li, Phys. Status Solidi A **42**, 125 (1977).
[9]N. I. Kiselev, Yu. I. Man'kov, and V. G. Pyn'ko, Sov. Phys. Solid State **31**, 685 (1989).
[10]H. Maruyama, H. Qiu, H. Nakai, and M. Hashimoto, J. Vac. Sci. Technol. A **13**, 2157 (1995).
[11]H. Qiu, A. Kosuge, H. Maruyama, M. Adamik, G. Safran, P. B. Barna, and M. Hashimoto, Thin Solid Films **241**, 9 (1994).
[12]M. R. Fitzsimmons, G. S. Smith, R. Pynn, M. A. Nastasi, and E. Burkel, Physica B **198**, 169 (1994).

[13]A. Barbier, G. Renaud, and O. Robach, J. Appl. Phys. **84**, 8 (1998).
[14]E. B. Svedberg, P. Sandström, J.-E. Sundgren, J. E. Greene, and L. D. Madsen, Surf. Sci. **429**, 206 (1999).
[15]K. Van Benthem, Dissertation University of Stuttgart, Germany, 2002.
[16]R. A. Lukaszew, V. Stoica, C. Uher, and R. Clarke, Mater. Res. Soc. Symp. Proc. **648**, 3.29.1 (2001).
[17]R. A. Lukaszew *et al.*, Phys. Rev. B (to be published).
[18]G. Pacchioni and N. Rösch, J. Chem. Phys. **104**, 7329 (1996).
[19]N. Rösch and G. Pacchioni, in *Chemisorption and Reactivity on Supported Clusters and Thin Films*, edited by R. M. Lambert and G. Pacchioni (Kluwer-Academic, Dordrecht, 1997), p. 353.
[20]R. P. Michel, A. Chaiken, C. T. Wang, and L. E. Johnson, Phys. Rev. B **58**, 8566 (1998).