Available online at www.sciencedirect.com
SCIENCE DIRECT
Applied Surface Science 219 (2003) 74–79
applied surface science
www.elsevier.com/locate/apsusc

Annealing effects on (0 0 1) Ni films grown on MgO

Rosa Alejandra Lukaszew[a,*], Zhengdong Zhang[a], Vladimir Stoica[b], Roy Clarke[b]

[a]Department of Physics and Astronomy, University of Toledo, Toledo, OH, USA
[b]Department of Physics, University of Michigan, Ann Arbor, MI, USA

Received 21 August 2002; accepted 20 January 2003

Abstract

Metal–ceramic interfaces are important in applications as diverse as magnetic storage media and supported catalysts. It is very important to understand how the crystallography and microstructure of metallic films deposited onto ceramic substrates depend on growth and/or annealing conditions so that their physical properties (e.g. magnetic, electronic, etc.) can be tailored for specific applications. To this end, we have studied the epitaxial growth and annealing of (0 0 1) Ni films molecular beam epitaxy (MBE) grown on MgO substrates, where we have observed the evolution of the surface using correlated in situ reflection high-energy-electron diffraction (RHEED) and scanning tunneling microscopy (STM) measurements. We have compared our data with that of (1 1 1) Ni films similarly grown on MgO.

Keywords: Metallic films; Epitaxial growth; MgO

1. Introduction

We have previously shown that *epitaxial* single-crystal magnetic thin films may be used in spin-dependent tunneling applications [1]. In general, the magnetic properties of epitaxial thin films, particularly the anisotropy [2], are dominated by the crystallographic structure of the metal/substrate interface as well as the surface morphology [3]. In addition, for device applications, the roughness at the surface must be very small in order to ensure the integrity of the subsequent layers. Thus, we have considered the growth of magnetic films on MgO substrates, which can be prepared with very smooth surfaces [4].

Theoretical studies have indicated that for Ni films grown on MgO substrates, Ni is expected to strongly interact with MgO [5]. Various researchers have studied the orientation of Ni films on MgO substrates under various growth conditions [6,7], and some reports indicate that Ni forms an epitaxial relationship with Ni[0 0 1]//MgO[0 0 1] and Ni(0 1 0)//MgO(0 1 0) for films deposited using dc sputtering on MgO substrates held at 100 °C [8].

There are also reports on epitaxial growth of *fcc* metals on surfaces with hexagonal surface symmetry such as MgO(1 1 1) [9]. Sandström et al. [10] have shown that at growth temperatures between 300 and 400 °C it is possible to grow smooth ⟨1 1 1⟩ oriented single-domain epitaxial films on MgO substrates, utilizing dc magnetron sputtering in an ultra-high vacuum (UHV) chamber. In the following, we present our studies on the molecular beam epitaxy (MBE)

* Corresponding author. Tel.: +1-419-5302648; fax: +1-419-5302723.
E-mail address: alukasz@physics.utoledo.edu (R.A. Lukaszew).

0169-4332/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0169-4332(03)00634-2

growth/annealing and in situ surface structural characterization of single-domain Ni films grown on (0 0 1) and subsequently annealed in situ and we compare our findings with similar data obtained for (1 1 1) Ni films.

2. Experimental

The Ni films were grown in an MBE VG 80 M system with a background pressure $<5 \times 10^{-11}$ 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 cm $\times$ 1 cm pre-polished MgO(0 0 1) and (1 1 1) oriented single crystals, which were heat-treated in UHV at 800 °C for 1 h. The combination of flat polished substrates and the UHV heating cycle to allow the surface layers to regain crystalline order has been proven to permit growth of single-crystal metal films as well as exhibiting sharp reflection high-energy electron diffraction (RHEED) from the MgO surface.

Ex situ atomic force microscopy (AFM) characterization of the annealed MgO surfaces showed smooth surfaces with a root mean square (rms) surface roughness of 0.2 nm for the (0 0 1) oriented substrates and 0.5 nm for the (1 1 1) oriented ones. Prior to initiating the growth, the substrate temperature was lowered to the appropriate deposition temperature for metal growth ($T \cong 100$ °C for (0 0 1) and $T \cong 300$ °C for (1 1 1) oriented Ni films). Heat transfer was by direct radiation between the heater and MgO substrate. The RHEED patterns were recorded continuously during deposition and during subsequent annealing of the films [11]. The surface morphology of the as-deposited and annealed films was determined in situ with scanning tunneling microscopy (STM).

3. Discussion

3.1. (0 0 1) oriented Ni films

The RHEED pattern of the heat-treated (0 0 1) MgO substrates consisted of long streaks characteristic of a smooth, single-domain surface. Sharp Kikuchi lines indicated long-range lateral coherence. The substrate temperature was lowered to 100 °C for deposition, which was determined to be optimal for single-domain growth [8]. The film's final thickness was in the range of 25–50 nm. During the early stages of growth the RHEED pattern was diffuse showing faint double streaks characteristic of island nucleation and coarsening. After substantial growth (>10 nm) the Ni RHEED pattern evolved from wide and diffuse streaks into sharper and spotty streaks indicating three-dimensional growth (Fig. 1(a)). For films with thickness in the 25 to 50 nm range the RHEED pattern indicated single-domain crystallographic structure in all azimuthal orientations. The typical mounded quality of the surface of metallic thin films [12] was corroborated with in situ STM (Fig. 2(a)). The rms surface roughness of the as-grown films was 0.5 nm. In order to further smoothen the surface, the films were annealed in UHV at 573 K ($\sim$1/3 of the Ni melting temperature) for several hours.

Sharpening of the RHEED pattern during annealing indicated a better crystalline quality as well as smoothing of the surface (Fig. 1(b)). STM imaging of the annealed surface indicated that the relaxation of the surface was dominated by ''turbulent step flow'' due to the presence of defects and dislocations. The rms surface roughness of the annealed films was 0.2 nm. Higher magnification of the annealed surface evidenced a periodic reconstruction (Fig. 2(b and c)) with periodicity of 2.1 nm (Fig. 2(d)).

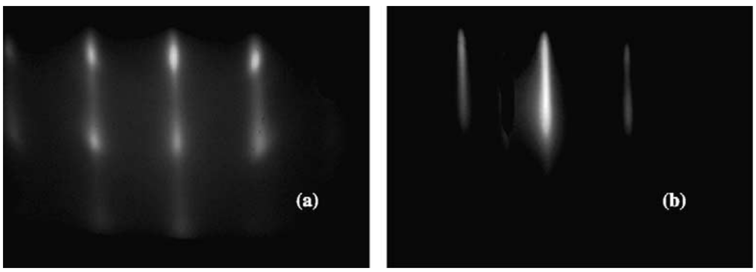

Fig. 1. (a) RHEED pattern of the ''as-grown'' (0 0 1) Ni film, (b) RHEED pattern of the same film after annealing.

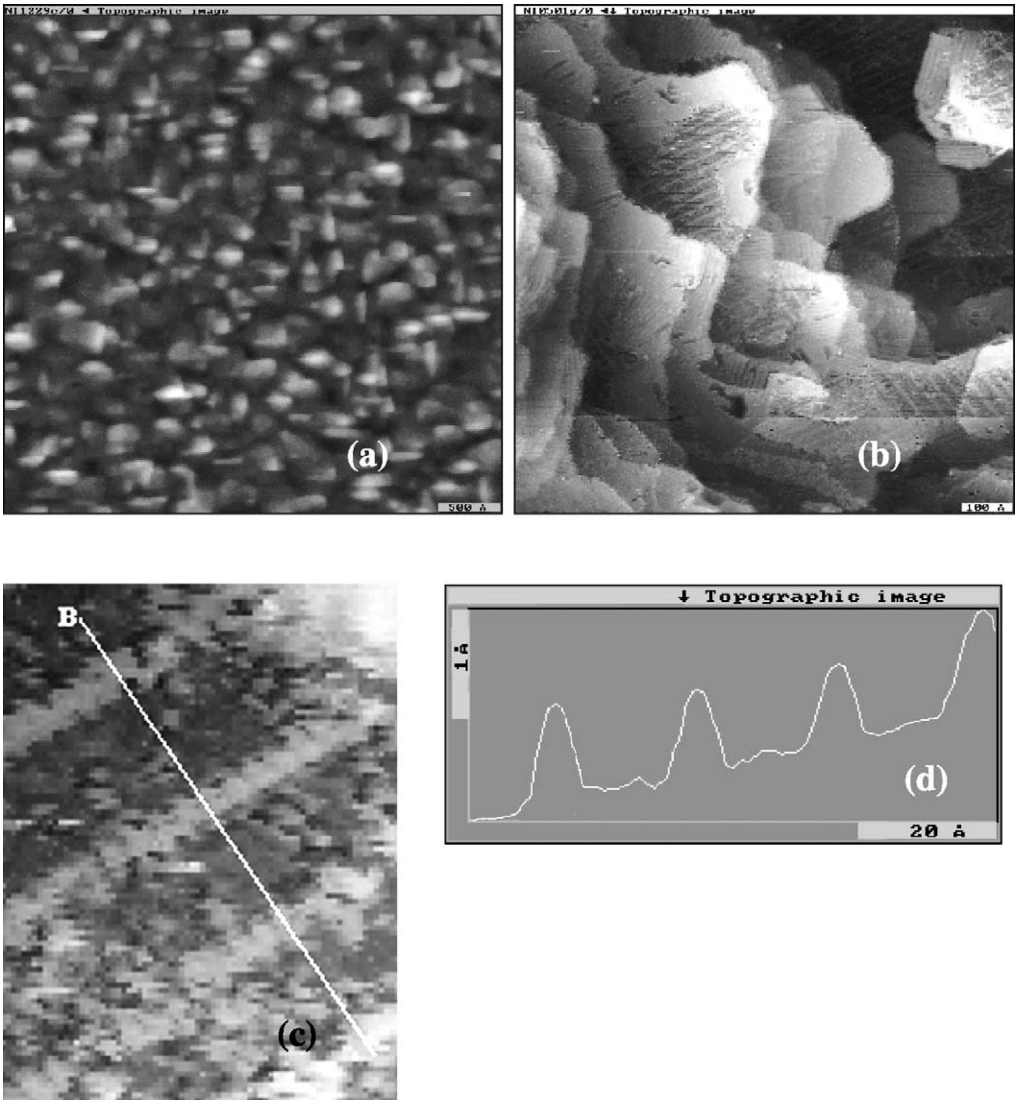

Fig. 2. (a) STM image of a 35 nm ''as-grown'' (0 0 1) Ni film (scale bar = 50 nm), (b) STM image of the same film after annealing (scale bar = 10 nm). Note the stripe configuration on most terraces, (c) magnified section of the previous STM image. The white trace indicates one region where the nano-patterning was measured, (d) line-scan corresponding to the previous image showing a periodicity of 2.1 nm for the nano-patterning.

In order to understand this reconstruction we have considered the possible effect of strain. The lattice misfit between MgO and Ni is 16%. However, it has been postulated [8] that an in-plane super-cell matching (commensuration) between the film and substrate with $a_0(\mathrm{Ni}) \times 6 = 2.0446$ nm and $a_0(\mathrm{MgO}) \times 5 = 2.1066$ nm will reduce the misfit to $\sim$0.8%. The critical thickness needed to relieve such a small strain may be quite large. Still, some authors [13] claim that super-cell matching itself cannot give rise to the formation of single-crystalline Ni layers, as it has been shown that in other cases interfacial periodic reconstructions can exist that allow for single-crystal growth. Our observations seem to support this. Annealing the films may have relaxed the surface evidencing a reconstruction with periodicity related

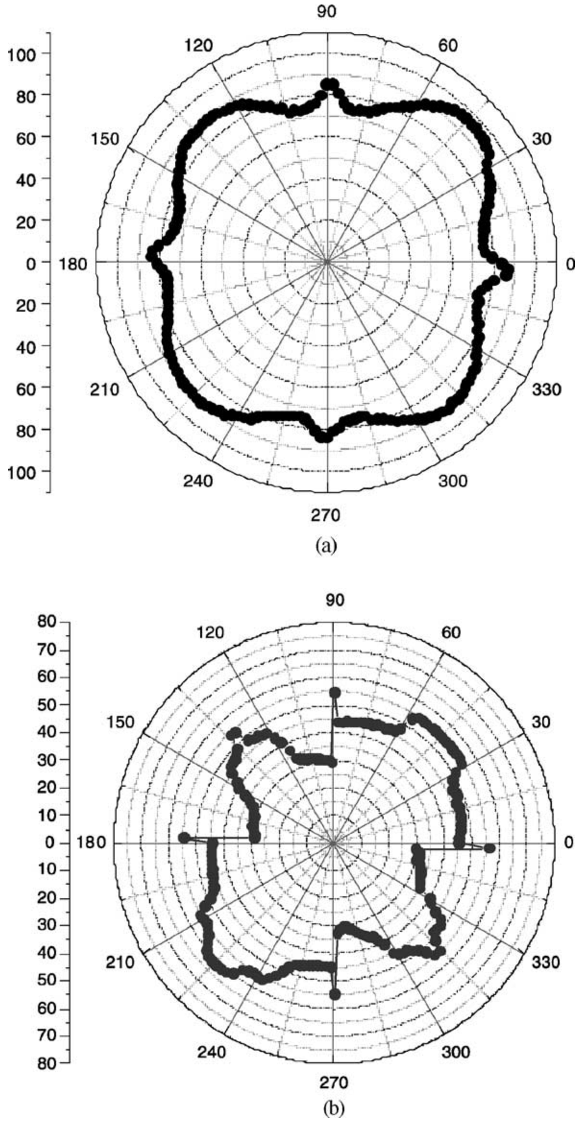

Fig. 3. (a) Azimuthal dependence of the coercive field for a 35 nm (0 0 1) Ni film epitaxially grown on MgO and not annealed. The vertical axis is in Oe. Note the overall four-fold symmetry, (b) the same graph for a 35 nm (0 0 1) Ni film epitaxially grown on MgO and annealed at 573 K. Note the superimposed uniaxial anisotropy.

to the size of the postulated super-cell (i.e. 2.1 nm). Another possibility for the observed reconstruction could be the formation of an asymmetric, coherent tilt boundary [14] as has been observed in other systems or even miss-cut of the MgO surface. Some authors have reported surface nano-patterning with formation of nano-wires attributed to substrate miss-cut when annealing sub-monolayers of Fe epitaxially grown on W substrates [15]. Theoretical modeling of the relaxation of epitaxial films grown on a mismatched surface may shed some light on the actual mechanism behind our observations.

In order to further characterize the films, we have performed azimuthal measurements of the magnetization reversal, using a surface sensitive technique such as longitudinal magneto-optic Kerr effect (MOKE). We have performed measurements on annealed and non-annealed films and as it can be observed in Fig. 3, there is a striking difference in the azimuthal dependence of the coercivity in these films. Both exhibit the typical four-fold symmetry expected for *fcc* epitaxial films dominated by magnetocrystalline anisotropy, with the superposition of a strong uniaxial anisotropy in the case of the annealed films.

As mentioned above, STM studies on the annealed (0 0 1) Ni surface, indicated nano-patterning of the surface through self-assembly of ‘‘stripes’’. Such uniaxial ‘‘stripe’’ reconstructions generally have two types of energetically degenerate domains, rotated by 90° with respect to each other as we also observed in our STM images. If the thin film sample were composed of a 50/50 mixture of stripe domains where the reconstruction is oriented in the two different symmetry directions, a macroscopic sample will show four-fold symmetric magnetic anisotropy. But if one ‘‘stripe’’ domain dominates (e.g. during annealing one domain grew at the expense of the other, or the substrate miss-cut favors one domain orientation over the other), then the net effect will be of a superimposed uniaxial magnetic anisotropy on the four-fold magnetocrystalline anisotropy as indeed we observe. We also expect here that theoretical modeling of the growth and annealing effects on these films will help elucidate the origin of the observed magnetic effect.

3.2. (1 1 1) oriented Ni films

After the UHV thermal pre-treatment, the (1 1 1) MgO substrate temperature was lowered to 300 °C for deposition, the optimal temperature for single-crystal growth [10]. The RHEED pattern indicated that the first two monolayers of growth are strained with a lattice parameter close to that of MgO. The growth proceeds relaxed afterwards with Ni lattice parameter close to the bulk value (Fig. 4(a)). Thus, for this case,

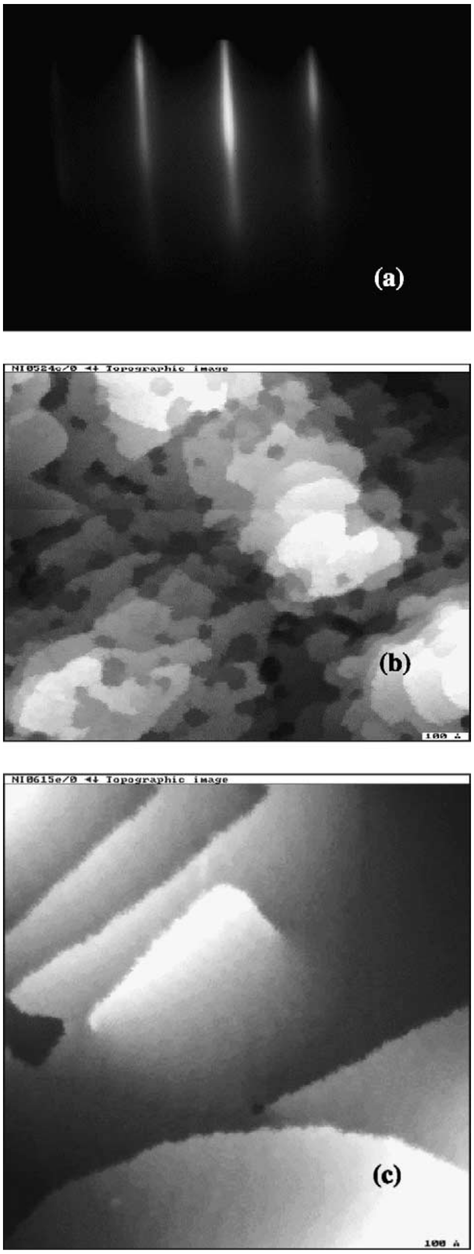

Fig. 4. (a) RHEED pattern after the growth of 25 nm Ni (1 1 1) on MgO, (b) STM image of the surface of the 'as-grown' (1 1 1) Ni film. We notice several islands with vacancies usually associated with screw dislocations, (c) STM after annealing the film shows the presence of a typical screw dislocation on the (1 1 1) Ni film. The scale bar at the bottom right corner corresponds to 10 nm.

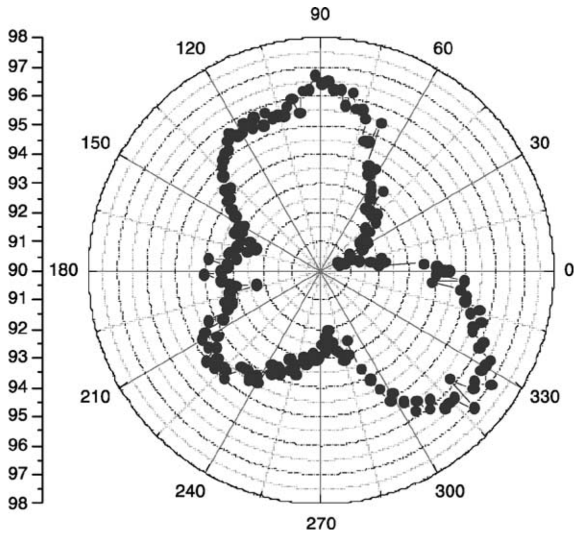

Fig. 5. Azimuthal plot of the coercive field determined from MOKE measurements on the (1 1 1) Ni film grown and annealed on MgO. The vertical axis is in Oe.

as the strained layers are energetically unfavorable, the rapid relaxation may be achieved via formation of a large number of defects and dislocations.

The RHEED pattern confirmed single-domain film during the growth and it is also the same as that of the substrate, indicating that Ni grows with the same stacking sequence (i.e. (1 1 1) oriented *fcc*) as the underlying MgO substrate (Fig. 4(a)). The substrate temperature ensures enough energy and mobility to the subsequent adatoms so that they can find the lowest energy position resulting in a single-domain structure. The STM image of a 25 nm film (Fig. 4(b)) shows large islands with central vacancies associated with dislocations. The rms surface roughness is 0.3 nm. STM after further annealing the film at 300 °C typically showed significant coarsening of the islands and screw dislocations (Fig. 4(c)). Interestingly, the subsequent annealing of these films did not show surface nano-patterning as we observed for the (0 0 1) case, nor any additional magnetic anisotropy (Fig. 5).

4. Conclusions

We have been able to grow epitaxial single-domain smooth Ni films on MgO substrates in both (0 0 1) and (1 1 1) orientations using MBE. Structural characterization of our samples with in situ RHEED confirms the relative crystallographic orientation of the films with respect to the MgO substrate previously reported by other authors for samples grown using sputtering techniques [6–8,10]. We have extended our studies to include the effect of annealing on the structure and magnetic properties of the films. STM imaging of the (0 0 1) annealed Ni surface evidenced formation of a periodic surface nano-patterning. This nano-patterning may be associated with (i) super-cell formation at the interface in order to reduce the lattice misfit with the substrate, (ii) the formation of an asymmetric, coherent tilt boundary, (iii) a slight miss-cut of the MgO substrate or even a combination of (i) and (iii). Detailed cross-sectional transmission electron microscopy studies are currently under way to possibly elucidate the actual relaxation mechanism present during the annealing of the films.

The magnetic anisotropy of the (0 0 1) Ni films is significantly affected by the annealing showing an additional uniaxial anisotropy superimposed to the expected four-fold anisotropy for an *fcc* epitaxial film.

No surface reconstruction was observed for (1 1 1) Ni films grown on MgO substrates and annealed under similar conditions. In addition, for the (1 1 1) case, strain relaxation occurred at the initial stages of the growth via formation of lattice defects and dislocations. No significant difference was observed in the magnetic properties of annealed and non-annealed (1 1 1) Ni films.

Theoretical modeling of relaxation upon annealing of epitaxial Ni films grown on a mismatched substrate may shed some light on the actual mechanisms behind our experimental observations.

References

[1] R.A. Lukaszew, Y. Sheng, C. Uher, R. Clarke, Appl. Phys. Lett. 75 (1999) 1941.
[2] K.B. Hathaway, G. Prinz, Phys. Rev. Let. 47 (1981) 1761; R.A. Lukaszew, E. Smith, R. Naik, C. Uher, R. Clarke, Phys. Rev. Lett., submitted for publication.
[3] A. Moschel, R.A. Hyman, A. Zangwill, Phys. Rev. Lett. 77 (1996) 3653–3656; P. Bruno, J. Appl. Phys. 64 (1988) 3153–3156.
[4] S.S. Perry, P.B. Merrill, Surf. Sci. 383 (1997) 268.
[5] G. Pacchioni, N. Rösch, J. Chem. Phy. 104 (1996) 7329.
[6] H. Qiu, H. Nakai, M. Hashimoto, G. Safran, M. Adamik, P.B. Barna, E. Yagi, J. Vac. Sci. Technol. A 12 (1994) 2855.
[7] J.P. McCaffrey, E.B. Svedberg, J.R. Phillips, L.D. Madsen, J. Cryst. Growth 200 (1999) 498.
[8] E.B. Svedberg, P. Sandström, J.-E. Sundgren, J.E. Greene, L.D. Madsen, Surf. Sci. 429 (1999) 206.
[9] P. Haibach, J. Koble, M. Huth, H. Adrian, Thin Solid Films 336 (1998) 168.
[10] P. Sandström, E.B. Svedberg, J. Birch, J.-E. Sundgren, Surf. Sci. 437 (1999) L767.
[11] D. Barlet, C.W. Snyder, B.G. Orr, R. Clarke, Sci. Instrum. 62 (1991) 1263 (Data Acquisition Using KSA400, k-Space, Assoc. Inc., Ann Arbor, MI 48109).
[12] H. Brune, Surf. Sci. Rep. 31 (1998) 121; J. Amar, Phys. Rev. B 60 (1999) R11317.
[13] A. Zur, T.C. McGill, J. Appl. Phys. 55 (1984) 278.
[14] R. Du, C.P. Flynn, J. Phys: Condens. Matter 2 (1990) 1335.
[15] M. Bode, A. Kubetzka, O. Pietzsch, R. Wiessendanger, Appl. Phys. A 72 (Suppl.) (2001) S149–S153.