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Anisotropic magnetization of epitaxial Ni nanogroove-arrays prepared by reduction of self-organized oxides

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ABSTRACT

A straight and periodic nanogroove-array pattern was formed on the surface of epitaxial Ni (1 1 1) thin films via a unique process, which included self-organization and reduction of oxides. In the formation of the Ni nanopattern, the epitaxial NiO (1 1 1) thin film grown on an α-Al_2O_3 (0 0 0 1) substrate by laser molecular-beam epitaxy (LaserMBE) was used as a starting material. The NiO (1 1 1) films were subsequently subjected to thermal treatment at 700 °C in air for the formation of self-organized nanopatterns, and then at 500 °C in a hydrogen atmosphere for reducing NiO to Ni. The epitaxy and morphology of the Ni (1 1 1) nanogroove array were proved by *exsitu* X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. Anisotropic magnetization behavior of the Ni (1 1 1) nanogroove-array pattern was examined by a *M–H* measurement using a superconducting quantum interference device (SQUID) magnetometer. The *M–H* squareness ratios for the directions parallel and perpendicular to the nanogrooves were about 0.83 and 0.52, respectively. The coercivity along the parallel line was ~0.5 kOe, which was approximately 200% of the value for the other direction. From the magnetization results, the parallel direction was considered as the magnetic easy axis in the in-plane orientation, probably due to the shape effect.

1. Introduction

Recently, nanoscale-integrated structures fabricated using ferromagnetic metal and nonmagnetic or insulative materials have attracted much interest for its applications in spin-controlled electronic devices, such as magnetic-random access memory [1] (MRAM), spin transistors [2], spin filters [3], spin modulators [4], and quantum information devices [5–8], which can be implemented in active control of electron spin dynamics. These spintronics devices utilize the spin-dependent electronic transport, which takes advantage of the electric charge and also the spin degree of freedom of electrons in ferromagnetic materials [9–11]. In spintronics, similar to conventional electronics, the anisotropic property of ferromagnetism, as well as ferroelectricity, piezoelectricity, and optical rotation, may contribute to an increase in the number of material applications that have similar anisotropies.

To apply and enhance ferromagnetic anisotropy in spintronic devices, controlling the crystal orientation and morphology is important. Single crystalline or epitaxial phases of the material are preferred more than amorphous or randomly-oriented polycrystalline phases, because of the decisive influence of the crystallographic anisotropy on the magnetic properties [12]. Some ferromagnetic materials patterned with low-dimensional structures such as nanowires may have uniaxial magnetic anisotropy. This anisotropy inhibits thermal fluctuations that can result in overcoming the critical limit, which makes the ferromagnetic material superparamagnetic in nature. Such features of magnetic nanopatterns improve the stabilization of the recorded elements in high-density devices.

Nickel is a common ferromagnetic transition metal with the ⟨1 1 1⟩ direction as a magnetization easy axis [13], and it is used widely as a matrix of practical Ni-based alloys such as Fe–Ni permalloy. We previously reported on the unique formation of epitaxial Ni (1 1 1) thin film by the oxide epitaxy technique of NiO (1 1 1) and the subsequent H_2-reduction process [14,15]. There have been many reports on the production of epitaxial Ni films directly from the pure metallic source by thermal evaporation [16], electron beam evaporation [17], molecular beam epitaxy (MBE) [18,19], sputtering [16,19], and pulsed laser deposition (PLD) [20], as well as by wet process such as electrodeposition using a toxic

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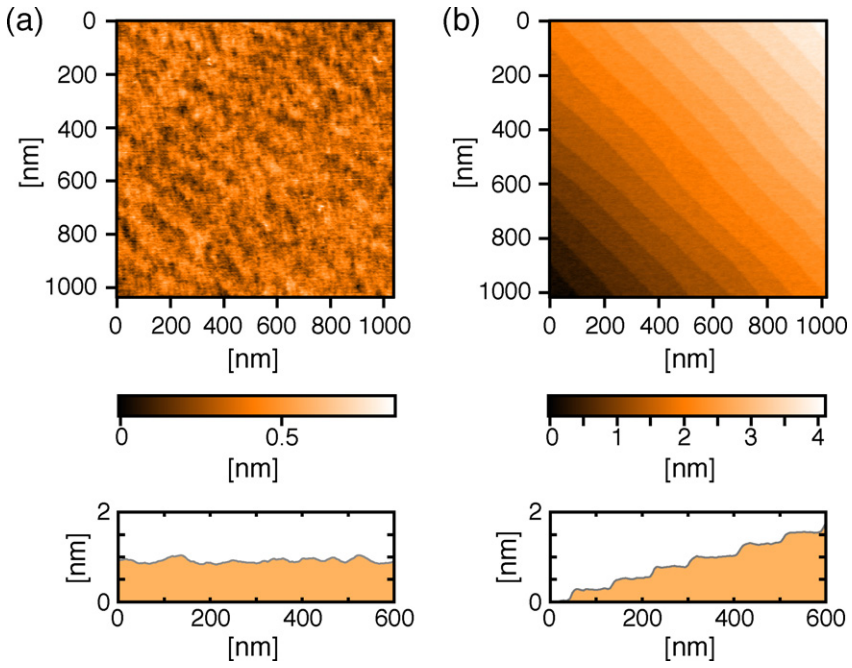

Fig. 1. AFM surface topographies (1 μm × 1 μm) and cross-sectional profiles of sapphire (0 0 0 1) substrates (a) as-received and (b) after thermal treatment at 1000 °C for 3 h in air.

sulfate solution [21]. On the other hand, there are also reports of hydrogen reduction, metallurgical process reacting hydrogen as reduction agent applied to various compounds including oxides to obtain pure phases and alloys of metals such as Fe, Co, Cu, W, and so on [22–25]. We also developed a novel process for fabricating NiO nanopatterns by the self-organization of oxide crystals [26–30]. This nanopatterned NiO can be used as a precursor material for producing Ni nanostructures. Our nanopatterning process using oxides is expected to have features different from other artificial nanoscale patterning methods, such as various lithography techniques [31–34] and graving methods [35,36], which suffer from tradeoffs between high-throughput and fine nanopatterning.

In this study, we prepared a periodic nanogroove array of epitaxial Ni (1 1 1) on an α-Al_2O_3 (0 0 0 1) substrate by a self-organization process, which is a combination of laser molecular-beam epitaxy (LaserMBE) and subsequent thermal treatments in air and a hydrogen atmosphere. The anisotropic magnetization behavior of the nanopatterned Ni film was also characterized.

2. Experimental details

The film was deposited in an ultra-high-vacuum LaserMBE chamber (base pressure: 5×10^{-9} Torr) [37]. A pulsed KrF excimer laser beam (wavelength $\lambda = 248$ nm, pulse duration $s = 20$ ns, frequency = 5 Hz) was focused on a sintered ceramic target of 10 at.%-Li doped NiO (99.9% purity) with an energy density of 3.0 J/cm^2 to deposit the film. An atomically stepped sapphire (α-Al_2O_3 single crystal) (0 0 0 1) substrate obtained by annealing a commercial mirror-polished sapphire wafer at 1000 °C for 3 h in air was employed [38]. The obtained ultrasmooth sapphire substrate exhibited uniformly formed periodic atomic steps, which had a terrace width of 80 nm and a step height of 0.2 nm. A distance of 5 cm was maintained between the substrate and the target during the film growth. The substrate temperature and the atmosphere were fixed as room temperature (20 °C, not heated intentionally) [39] and 1.0×10^{-5} Torr O_2, respectively. The NiO epitaxial thin film was successively annealed at 700 °C in air for 3 h, resulting in the formation of nanogroove stripes on the film surface. The specimens were subsequently annealed in 1 atm of H_2 gas flow at 500 °C for an hour to reduce NiO to Ni. The crystallographic characterization was performed by *exsitu* X-ray diffraction (XRD; Panalytical MRD) using Cu Kα ($\lambda = 1.5418$ Å). Surface observation was performed by atomic-force microscopy (AFM; SII SPI-3700). Magnetization measurements were conducted at liquid He temperature (4.2 K) using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5).

3. Results and discussions

Fig. 1 displays surface morphologies of sapphire (0 0 0 1) substrates before and after artificial modification by heat treatment. Fig. 1(a) is the surface of an as-received substrate that it revealed homogeneous topography without any nanopatterns. Fig. 1(b) shows the surface of the substrate after thermal treatment at 1000 °C for 3 h in air. There were straight, parallel and periodic atomic steps and atomically flat terraces observed on the entire surface. The latter substrates with steps and terraces were utilized for growth of epitaxial films and nanopatterns in this study.

The change in surface morphology of the nanopatterned NiO film after hydrogen reduction was examined by AFM. Fig. 2(a) shows the AFM image of NiO nanogroove arrays, which were observed over the entire substrate. They were obtained by annealing the ultra-smooth epitaxial NiO (1 1 1) thin film at 700 °C in air for 3 h. The nanogrooves were straight and parallel, and each nanogroove had a depth of 20 nm and an open-end width of 50 nm, as detailed in our previous report [27]. Fig. 2(b) shows the topography of the specimen after hydrogen reduction of the NiO nanogroove film at 500 °C for an hour. The AFM image indicates that the nanopattern of the straight grooves remained even after H_2 reduction. However, minimal chipping at the groove edges appeared, which suggests desorption of gases such as O_2 or H_2O from the NiO surface during reduction.

Fig. 3 shows the influence of the thermal treatment in a hydrogen atmosphere on the crystallographic orientation of NiO