Surface modification for epitaxial growth of single crystalline cobalt thin films with uniaxial magnetic anisotropy on GaN(0001)-1 × 1 surfaces

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Abstract. Epitaxial growth and magnetic properties of Co thin films on GaN(0001)-1 × 1 surfaces are studied. The films show degraded saturation magnetization due to the interfacial interaction. On excess-Ga-induced pseudo-1 × 1 surface, 30°-rotation domains in the Co epilayer are inevitable and the films show in-plane magnetic anisotropy. By annealing the starting surface of pseudo-1 × 1 and to achieve a Ga-less 1 × 1 surface, single domain Co epifilms having orientations aligned with the substrate can be grown, which facilitates in-plane uniaxial magnetic anisotropy.

Magnetism in ultrathin transition metal (TM) films has been the subject of intensive study in recent decades [1]. Much attention has been devoted to epitaxial growth on semiconductor substrates, such as Si [2], GaAs [3, 4] and InP [5], for the development of semiconductor-based spintronics. Unfortunately, interfacial reaction between TMs and such substrates usually occurs, impeding effective modulation of the magnetic properties of TM films and their applications. GaN, a wide-bandgap semiconductor that has found many applications in optoelectronics and...
high-temperature, high-power microelectronics, can be an attractive substrate for TM epitaxial growth. The lifetime of spin in GaN has been found to reach $\sim 20$ ns [6], which is three orders of magnitude longer than that in GaAs [7]. GaN-based diluted magnetic semiconductors have been shown to have high Curie temperatures [8]. Therefore, GaN can also be promising for room temperature (RT) spintronic applications [9]. Spin injection at the TM/GaN hetero-interface is also of great interest from both fundamental and application points of view, while magnetism in ultrathin films may display some unique characteristics [1]. The relatively strong chemical bonds of GaN can make it inert to interfacial reaction with the TM deposit [10]. Therefore, it is quite appealing to grow magnetic thin films on GaN for studies of magnetism in ultrathin TM films and the spin properties of TM–semiconductor interfaces.

Some efforts have been made on the growth of TMs on GaN(0001) surfaces, where the behavior and properties of the TM films have been found to depend on the conditions of the starting surfaces of the substrate. For example, when Fe was grown on the thermally annealed GaN(0001) substrate surface, three distinct Fe orientation domains were found, while an in-plane anisotropy along [11$\bar{2}$0] was noted [11]. On the other hand, layer-by-layer growth of a single crystalline Fe film was realized upon an initial modification of the GaN(0001) surface from the pseudo-$'1 \times 1'$ (denoted by ‘$1 \times 1$’ hereafter), characteristic of the excess Ga-covered surface [12], to ($\sqrt{7} \times \sqrt{7}$) by Fe [13]. Perpendicular magnetic anisotropy was observed from such thin Fe layers [13]. As for Ni growth on GaN, however, thermal annealing of the substrate did not seem to promote good epitaxy [14]. There is not much work being reported as yet on Co growth on GaN. Judging from the rather divergent results for the other TMs/GaN systems, it seems necessary to investigate the specific growth and properties of Co-on-GaN(0001) for different surface conditions of the substrate.

In this paper, we present a study of the growth and magnetic properties of epitaxial Co on GaN(0001) by molecular-beam epitaxy (MBE), where the ‘$1 \times 1$’ and GaN(0001)-(1 $\times$ 1) surfaces of the substrate are compared. As documented in the literature, the ‘$1 \times 1$’ surface contains more than two monolayers (MLs) of excess Ga, where the topmost Ga adlayer is fluid-like [12]. The (1 $\times$ 1) surface, which is obtainable by annealing GaN(0001)-‘$1 \times 1$’, contains only 1 ML excess Ga [15]. Single crystalline Co films with perfectly aligned epitaxial relations (i.e. Co(0001)/GaN(0001) and Co[11$\bar{2}$0]/GaN[11$\bar{2}$0]) are obtained only on the annealed surfaces, and the thick films of such show in-plane [10$\bar{1}$0] uniaxial magnetic anisotropy. By comparison, when grown on the ‘$1 \times 1$’ surfaces, domains with the aligned Co[11$\bar{2}$0]/GaN[11$\bar{2}$0] and 30$^\circ$-rotated Co[10$\bar{1}$0]/GaN[11$\bar{2}$0] epitaxial relations are observed, making the in-plane magnetic easy axis isotropic. By annealing the RT-deposited Co films at 600$^\circ$C, we observe an apparent loss in magnetization saturation, which is likely caused by interfacial reaction between Co and GaN substrates by annealing.

The experiments were carried out in a multi-chamber ultrahigh vacuum (UHV) system, which consisted of a radiofrequency (rf) plasma-assisted MBE chamber for III-nitride growth, a surface treatment and Co deposition chamber, analysis chambers equipped with low-energy electron diffraction (LEED) and a scanning tunneling microscope (STM). The rf-MBE was equipped with a conventional effusion cell of Ga and a plasma unit for N flux. The base pressures of all these chambers were below $3 \times 10^{-10}$ mbar. The substrates were commercial GaN grown on 6H-SiC(0001) from TDI, Inc. Both the ‘$1 \times 1$’ and (1 $\times$ 1) surfaces of GaN(0001) were prepared in rf-MBE by growing first a GaN buffer film at $\sim 600$ $^\circ$C under the Ga-rich flux condition. The As-grown surface of the buffer film was of ‘$1 \times 1$’ structure [12], and the root mean square (rms) roughness of this surface was $\sim 2.5$ Å over the area of $1000 \times 1000$ nm$^2$. 

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By carefully annealing such a surface, the \((1 \times 1)\) structured surface results. The two surfaces were easily identified by the LEED measurements, where the former shows satellite diffraction spots surrounding the integer spots of GaN bulk (see figure 1(a)). The \((1 \times 1)\) surface, on the other hand, was characterized by the disappearance of such a satellite spot in LEED, leaving the integer spots with higher intensity (figure 1(d)). The LEED \(I-V\) curve simulation suggested the GaN(0001)-\((1 \times 1)\) surface to be \(\sim 1\) ML Ga-covered GaN(0001), with the Ga adatoms absorbed at the T1 (on-top) sites \([15]\). Subsequent Co deposition on the two surfaces was carried out in the adjacent chamber where the flux of Co was \(\sim 0.01\) ML s\(^{-1}\), as supplied from a water-cooled e-beam cell and measured by a quartz crystal oscillator. All of the Co depositions were done at RT. For some samples, post-growth annealing was carried out \textit{in situ} at 600°C for 20 min. RT LEED and STM experiments were carried out immediately after Co deposition, and, for the latter, the constant-current mode was adopted using a sample bias of +1 V and a tunneling current of 0.1 nA. \textit{Ex situ} characterization of the samples was also conducted by x-ray diffraction (XRD), transmission electron microscopy (TEM) and a vibrating sample magnetometer (VSM) for their structural, interfacial and magnetic properties.

Figures 1(a)–(c) show the evolution of the LEED pattern upon depositing Co at different thicknesses on GaN(0001)-‘\(1 \times 1\)’, while figures 1(d)–(f) show the same when Co is deposited on the GaN(0001)-(\(1 \times 1\)) surface. As described earlier, the starting ‘\(1 \times 1\)’ surface of the substrate contained \(> 2\) MLs excess Ga, where the topmost fluid-like \(4/3\) MLs Ga gave rise to the unique ‘1+\(\frac{1}{6}\)’ diffraction pattern, or the sixfold satellite feature surrounding the integer diffraction spots, in the LEED (see figure 1(a)) \([12]\). After growth of 2 MLs Co (measured in terms of atom areal density of GaN(0001) substrate surface, i.e. 1 ML Co \(\sim 1.13 \times 10^{15}\) atoms/cm\(^2\)), the diffraction spots disappeared with only a diffusive background in the LEED (figure 1(b)), suggesting a disordered or amorphous film of the deposit. After an additional 3 MLs deposition of Co, the LEED pattern remained diffusive, but on a reflection high-energy electron diffraction (RHEED) screen, some vague diffraction features with a measured in-plane lattice spacing close to that of bulk Co became visible (not shown), indicating that the surface was covered by a highly \(c\)-axis textured Co. As the thickness of Co film increased further, the textured film gradually evolved into a more ordered crystalline film, which was manifested by the appearance of two sets of diffraction spots in the LEED, as highlighted by the hexagons in figure 1(c). The corresponding lattice parameters were found to be consistent with those of bulk Co. Compared to the diffraction pattern from GaN, we infer that the set of LEED spots having higher intensity corresponds to a film with the lattices being \(30^\circ\)-rotated with respect to GaN substrate. This may not be surprising, as the lattice misfit can be effectively reduced to \(\sim 9.2\%\) when taking the Co[10\(\bar{1}\)0]/GaN[11\(\bar{2}\)0] or \(30^\circ\)-rotated, epitaxial relation rather than that of the aligned one, where the misfit would amount to about 21.4%. Therefore, the \(30^\circ\)-rotated domains would be dominant in volume over the aligned ones. Quite a different growth behavior was observed when Co was deposited on the GaN(0001)-(\(1 \times 1\)) surface, which contained less excess Ga. Figure 1(d) shows the corresponding LEED pattern of the substrate, where the six-fold satellite diffraction features seen in figure 1(a) disappeared but the integer diffraction spots remained with higher intensity. Upon depositing 3 MLs Co, features corresponding to a strain-relaxed Co film emerged (figure 1(e)), and the aligned epitaxial relation between Co and GaN was also apparent. As the film grew thicker, the diffraction pattern corresponding to Co became stronger and sharper (figure 2(f)), indicating improved crystallinity of the epifilm.
Figure 1. The evolution of the LEED pattern as Co deposition on the GaN(0001)-‘1 × 1’ surface (a–c) or the GaN(0001)-(1 × 1) surface (d–f). Panels (a) and (d) are from the surfaces of GaN(0001) ‘1 × 1’ and (1 × 1) substrates; (b) and (e) are from surfaces after 3 MLs Co deposition and (c) and (f) are from surfaces after 100 MLs growth of Co. (Electron energy in the LEED experiments is $E = 75$ eV for all except (a), which is at 100 eV.) In (a), the small hexagon marks the satellite diffraction feature characteristic of the GaN(0001)-‘1 × 1’ surface, whereas in (c), the solid and dashed hexagons mark the diffraction from the aligned and 30°-rotated domains of epitaxial Co.
Figure 2. STM images showing the surface As-deposited Co films on (a) GaN(0001)-'1 × 1' and (b) GaN(0001)-(1 × 1) surfaces, respectively. In (a), the solid and dashed hexagons mark domains of aligned and 30°-rotated lattices, respectively, with respect to the GaN substrate.

Figure 2 shows STM micrographs of the Co surfaces following ∼ 80 MLs film deposition on GaN(0001)-'1 × 1' (figure 2(a)) and on GaN(0001)-(1 × 1) (figure 2(b)), respectively. In figure 2(a), the surface is seen to contain three-dimensional (3D) islands with their lateral sizes ranging from 10 to 50 nm. The rms roughness of the surface is measured as 12.5 Å over an area of 1000 × 1000 nm². From the orientation of the hexagonal or triangular islands, we may also infer that some are aligned with respect to the lattices of GaN, while others are 30°-rotated, consistent with the LEED observations. Examples of the aligned and rotated islands are circled by the solid and dashed hexagons in figure 2(a). In figure 2(b), on the other hand, the surface appeared more compact and smooth, with a measured rms roughness of ∼ 5 Å over the same area.

To explore the stability of Co/GaN interfaces, in situ annealing at 600 °C for 20 min was carried out for both types of sample. The As-deposited and annealed samples were characterized by XRD and high-resolution TEM. Figure 3 presents the results of the θ–2θ scans of XRD measurements, where the diffraction peaks corresponding to face-centered cubic (fcc) and hexagonal-close-packed (hcp) Co epifilms are identified from all samples. However, from the relative intensity of the fcc versus hcp peaks, we may infer that the As-deposited Co layer on GaN-'1 × 1' is mostly hcp (trace c). After annealing, substantial transformation to fcc stacking takes place, as implied by enhancement of the fcc peak (trace d in figure 3). This is in accordance with the Martensitic phase transition of bulk Co from hcp to fcc at ∼ 400 °C [16]. The situation is more complicated for the Co/GaN-(1 × 1) sample since both the As-deposited and annealed ones show the dominant hcp stacking of the lattices (traces a and b in figure 3). This may result from the stronger interfacial bonding between Co and GaN rather than that of the Co/GaN-'1 × 1' sample, which hinders the Martensitic phase transition at high temperatures. In the XRD measurements, no other diffraction peaks than those from the substrate, fcc- and hcp-Co is observed, suggesting the c-axis epitaxial Co on GaN(0001) for both types of substrates. However, the state of hetero-interface can be different. The inset of figure 3 shows a high-resolution TEM micrograph depicting the presence of a slightly less ordered interfacial layer (between the two dashed lines) for an annealed sample grown on GaN(0001)-'1 × 1'. Regions of the fcc (indicated by arrows pointing to the left) and hcp (indicated by arrows pointing to
Figure 3. XRD $\theta$–$2\theta$ scans of 10 nm thick Co films on GaN(0001)-(1 × 1) (a, b) and ‘1 × 1’ (c, d). Traces (a) and (d) are annealed samples, while (b) and (c) are for As-deposited ones. The dashed rectangle marks the diffraction peaks due to the substrate. Inset: high-resolution TEM micrograph depicting the interfacial layer of an annealed Co/GaN-‘1 × 1’ sample.

the right) phases of Co may also be seen. Although the lattice constant measurements affirm the epitaxial Co films, energy-dispersive x-ray spectroscopy (EDX) experiments detect Ga and N signals in the epilayer. More Ga and N can be detected in the annealed samples. These imply the effect of atoms diffusion from the substrate to the Co epifilm. Given that CoGa is the thermodynamically preferred phase in the Co–Ga–N system [17], we may speculate that there might have been formed a CoGa compound or alloy at the Co/GaN interface, although they are quite disordered in structure and/or small in amount so might not be detected by the XRD measurements.

The magnetic properties of the As-deposited and annealed samples are characterized by VSM at RT. All samples show ferromagnetism, while the saturation magnetization $M_s$, remnant magnetization $M_r$ and coercivity $H_c$ vary depending on the preparation conditions of the samples. Although for bulk hcp- or fcc-Co crystals the easy axis is along [0001] or [111], for epifilms with thicknesses ranging from 80 to 160 MLs studied here, they all exhibited in-plane magnetization. Since the demagnetizing field of Co ($4\pi M_s \sim 17600$ Oe, where $M_s \approx 1400$ emu cc$^{-1}$) is quite large, the dipolar form anisotropy favors magnetic moment alignment parallel to the surface in thin magnetic films [18]. In the preferred direction of magnetization, all samples show excellent ferromagnetic hysteresis loops with the remanence ratio ($M_s/M_r$) reaching a value higher than 86%. For samples grown on GaN(0001)-‘1 × 1’, no obvious in-plane magnetic anisotropy is observed, which is likely related to the presence of rotation domains, as described earlier. Figure 4(a) shows typical in-plane hysteresis loops of such a sample before and after annealing. The saturation magnetization $M_s$ of the As-deposited sample is $\sim 30\%$ less than that of the bulk. After annealing, the saturation magnetization is reduced by $\sim 45\%$ from the bulk $M_s$. The latter may be related to the disordered interfacial layer, as revealed by HRTEM (figure 3, inset), which serves as a magnetic ‘dead’ layer as in Fe/GaAs.

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Figure 4. (a) In-plane magnetic hysteresis loops of Co/GaN(0001)-‘1 × 1’ before and after annealing, where no anisotropy is observed. (b) Hysteresis loops showing in-plane magnetic anisotropy of an As-deposited Co/GaN(0001)-(1 × 1) sample; the external magnetic field was applied along the ⟨1010⟩ and ⟨1120⟩ directions, respectively. The inset shows the same after annealing, indicating the loss of in-plane anisotropy.

Indeed, if the interface layer is made of CoGa alloy, as discussed before, it would be a magnetic spin glass according to Meisel et al [21]. On the other hand, by annealing, the magnetic coercivity seems to be enhanced compared to the As-deposited ones (77.4 Oe versus 49.3 Oe). Interestingly, for samples grown on GaN(0001)-(1 × 1), uniaxial magnetic anisotropy is found with the ⟨1010⟩ preference of $M_s/M_r \sim 89\%$ compared to only $\sim 24\%$ in the [1120] direction (figure 4(b)). Since such a Co film is single crystalline and the Néel effect commonly takes effect within a few atomic layers [22], it is reasonable to attribute such an in-plane anisotropy to the absence of rotation domains and thus improved in-plane crystal symmetry of Co grown on GaN(0001)-(1 × 1). Furthermore, the smaller coercivity...
(~ 16 Oe) of such a sample compared to that grown on GaN-‘1 × 1’ may also be related to the improved crystallinity of the film, where there are fewer pinning centers or defects hindering the domain wall motion and rotation. Annealing such a sample, however, removes the in-plane anisotropy, as is illustrated by the inset of figure 4(b), where the hysteresis loops are found to coincide nearly perfectly when measured along the (1010) and (1020) directions. As in the case of the Co/GaN-‘1 × 1’ sample, annealing makes $M_s$ smaller and $H_c$ higher. Since the anisotropy energy between the Co[1010] and [1120] directions is expectedly small, either interfacial reaction-induced structural defects or diffusive atom-induced compositional variation may have destroyed the anisotropy during annealing.

In summary, very different growth behavior and magnetic characteristics of Co grown on GaN(0001)-‘1 × 1’ versus GaN(0001)-(1 × 1) surfaces are observed. Formation of domains with both aligned and 30°-rotated lattices between Co and GaN is inevitable when using the excess Ga-covered GaN-‘1 × 1’ surface, which leads to in-plane isotropic magnetization. On the less excess Ga-covered GaN-(1 × 1) surface, single domain Co with the aligned epitaxial relation with respect to the substrate is achieved, and the film shows an in-plane uniaxial magnetic anisotropy. Annealing the As-deposited samples causes enhanced interface mixing and/or diffusion of atoms, giving rise to a magnetic ‘dead’ interfacial layer as well as structural/compositional defects, which in turn modify the magnetic behavior of the epifilms.

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