Thermal stability of epitaxial Fe films on GaN(0001)

Cunxu Gao,[a] Oliver Brandt, Hans-Peter Schönherr, Uwe Jahn, Jens Herfort, and Bernd Jenichen
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, D-10117 Berlin, Germany

(Received 10 August 2009; accepted 26 August 2009; published online 14 September 2009)

Epitaxial Fe films are grown on GaN(0001) by molecular beam epitaxy at 50 °C. Several samples of one Fe/GaN structure are subjected to rapid thermal annealing from 300 to 950 °C. Using a variety of experimental techniques, we examine the impact of this annealing step upon the morphological, structural, and magnetic properties of these samples. The results demonstrate that the material system Fe/GaN is thermally stable up to a temperature of 700 °C. © *2009 American Institute of Physics*. [doi:10.1063/1.3230004]

In ferromagnet-semiconductor hybrid structures for spin-injection applications, it is desirable for the ferromagnet to exhibit a high spin polarization as well as a Curie temperature well above 300 K, and for the semiconductor to possess a long spin-relaxation time. In addition, it is imperative to inhibit chemical reactions between the ferromagnet and the semiconductor. These reactions may lead to the formation of nonmagnetic or paramagnetic phases at the interface, which either impede spin injection altogether or realign injected spins.[1–3] For this purpose, one often has to retreat to low temperatures (LTs) during the synthesis of the structure[1,4] and is forced to also avoid any high-temperature (HT) treatment during further processing, which is often impractical. The thermal stability of the materials system under consideration is thus of utmost importance for its use in applications.

In this respect, Fe/GaN is a potentially very attractive ferromagnet-semiconductor hybrid-system, which seems to satisfy the first two criteria defined above.[5–9] In addition, Fe has been shown to grow epitaxially on GaN(0001) (Refs. 10 and 11) analogous to the growth of Fe on both (111) fcc and (0001) hcp crystals.[12–14] However, nothing is currently known about the thermal stability of Fe layers on GaN.

In this letter, we report the growth of epitaxial Fe films on GaN(0001) by molecular beam epitaxy (MBE) at 50 °C and their subsequent annealing at temperatures between 300 and 950 °C. We find that the surface morphology and the saturation magnetization are unaffected up to 700 °C while the crystal quality even improves up to 800 °C. Evidence for secondary (Fe and Ga) phases are observed only at 850 °C and above.

The structures investigated are grown in a custom-built MBE system equipped with solid-source effusion cells for Al, Ga, and Fe. Active nitrogen is provided by a radio-frequency N_2 plasma source. Ga-polar GaN(0001) films are synthesized on AlN-buffered Al_2O_3 substrates. After desorbing the Ga bilayer, the substrate temperature is reduced to 50 °C unless otherwise mentioned, and LT growth of Fe commences at a growth rate of <1 ML/min keeping the chamber pressure at the low 10^{-9} mbar range. Nucleation and growth is monitored *in situ* by reflection high-energy electron diffraction (RHEED). The RHEED patterns (not shown here) evidence a Vollmer–Weber growth mode as well as multiple-domain epitaxy. The actual orientation-relationship between Fe and GaN is clarified by x-ray diffraction (XRD) and electron backscatter diffraction (EBSD). XRD ω-2θ scans are recorded with an analyzer while ϕ scans are taken with open detector. The surface morphology of the films is examined by atomic force microscopy (AFM). The elemental composition of the structure is analyzed by energy dispersive x-ray spectroscopy (EDX) and, at a higher level of sensitivity, by secondary-ion mass spectrometry (SIMS). In-plane hysteresis loops are recorded at 300 K for magnetic fields between ±50 kOe in a superconducting quantum interference device magnetometer (SQUID). All data presented below are corrected for the diamagnetic background of the substrate. Rapid thermal annealing (RTA) of samples cut from a LT wafer is carried out in an N_2 ambient for 1 min at temperatures between 300 and 950 °C.

Figure 1(a) shows the AFM micrograph of an as-grown LT Fe/GaN structure. The total thickness of the Fe film, as measured by x-ray reflectometry and including a surface oxide, is 37.4 nm. The surface exhibits an rms roughness of 1.2 nm over 5×5 μm^2, only slightly larger than typical values for our GaN layers. No obvious changes are observed for this structure annealed at 300 and 650 °C as depicted in Figs. 1(b) and 1(c), respectively. However, Fig. 1(d) shows that annealing at 850 °C induces the formation of grains with a size of hundreds of nanometers. EDX spectra (not shown here) reveal these grains to contain very substantial amounts of both Ga and O in addition to Fe. The presence of O has

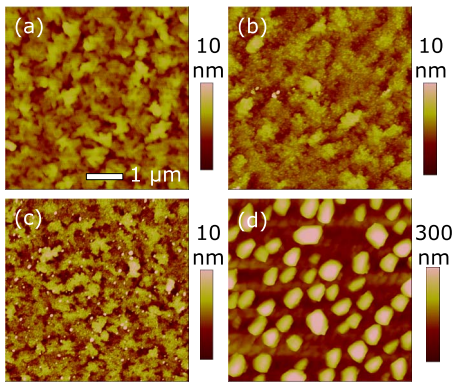

FIG. 1. (Color online) AFM micrographs (5×5 μm^2) of (a) the as-grown LT sample and samples annealed at (b) 300 °C, (c) 650 °C, and (d) 850 °C, respectively.

[a]Electronic mail: gaocunx@pdi-berlin.de.

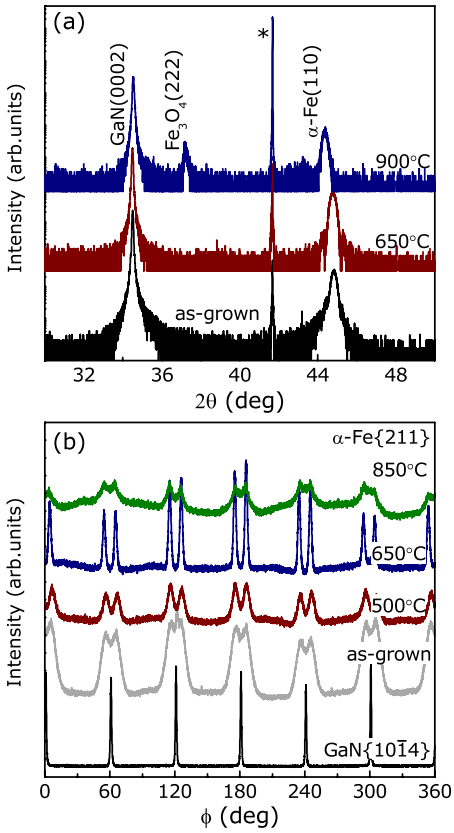

FIG. 2. (Color online) (a) Symmetric x-ray ω-2θ scans of selected samples from the LT structure. The peak labeled with a star is the Al_2O_3(0006) reflection. (b) ϕ scans of the GaN{10$\bar{1}$4} and Fe{211} planes.

basically a technical reason: despite repeated pumping and purging of our RTA system, we cannot get rid of O_2 entirely, but are left with a small but finite O_2 partial pressure.

Symmetric XRD ω-2θ scans are taken within a 2θ range from 10° to 110° for the same samples. Figure 2(a) shows a small portion of these scans. Apart from the (0002) [(0006)] reflections of GaN (Al_2O_3), the (110) reflection of α-Fe can be identified, showing that α-Fe(110)‖GaN(0001). For both the as-grown sample and the sample annealed at 650 °C, no reflections pertinent to a secondary phase can be found. SIMS depth profiles of these two samples (not shown here) demonstrate that there is not even a detectable indiffusion of Fe into GaN. For annealing temperatures higher than 850 °C, an additional reflection appears which coincides with Fe_3O_4(222), in agreement with the EDX analysis mentioned above. In addition, the Fe(110) reflection now evidently occurs at a smaller angle, consistent with incorporation of Ga and the formation of an Fe_xGa_{1-x} compound as revealed by EDX.

Figure 2(b) compares skew-geometry XRD ϕ scans of the GaN{10$\bar{1}$4} (black line) and α-Fe{211} (gray line) planes of the as-grown and annealed LT samples. The GaN(0001) layer exhibits the expected sixfold symmetry, but the Fe(110) film does not show the twofold symmetry of the (110) plane but a sixfold one with two maxima situated ±5° relative to the GaN{10$\bar{1}$4} reflection. This result is consistent with an in-plane orientation-relationship Fe⟨001⟩‖GaN⟨11$\bar{2}$0⟩ occurring in three symmetry-equivalent domains rotated by 120° relative to each other. This particular triple-domain orientation-relationship is known from the

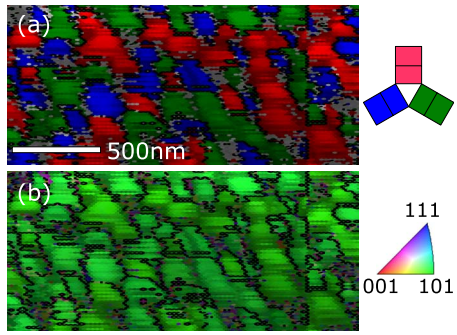

FIG. 3. (Color online) (a) In-plane crystal orientation map (with a 10° tolerance) and (b) inverse pole figure map obtained by EBSD for an Fe/GaN structure grown at HT. Black lines indicate grains boundaries.

field of martensitic transformations as the Nishiyama–Wassermann relation.[10–15]

Most remarkable, however, is the fact that the crystalline quality of the Fe film is greatly improved by annealing as seen by the continuous decrease of the full width at half maximum (FWHM) of the Fe{211} reflections shown in Fig. 2(b). The FWHM finally reaches a value of 1.25° at a temperature of 750 °C, which is basically identical to that measured for the underlying GaN layer. At even higher temperatures, we observe a loss of the in-plane orientation as seen by the drastic broadening of the Fe{211} reflection for 850 °C.

To directly visualize the epitaxial arrangement and, particularly, the domain structure, we investigate the as-grown and annealed LT Fe films by EBSD. However, it turns out that the domain size of all these samples is too small (i.e., <20 nm). We always observe a superposition of all orientations. In contrast, the grain size of an Fe film grown on GaN at a substrate temperature of 600 °C turned out to be well above 100 nm, allowing us to take a EBSD in a straightforward way. Figure 3(a) shows a map of the in-plane crystal orientation of this HT structure, directly evidencing the Nishiyama–Wassermann relation as discussed above and depicted schematically at the right of the figure. Furthermore, Fig. 3(b) shows the inverse pole-figure of this HT grown sample, visualizing its pure (110) out-of-plane crystal orientation.

Figure 4 shows in-plane hysteresis loops for the LT structure measured by SQUID with the magnetic field (H) parallel to the GaN[11$\bar{2}$0] direction at 300 K. The as-grown Fe film exhibits a square hysteresis loop with a coercivity of

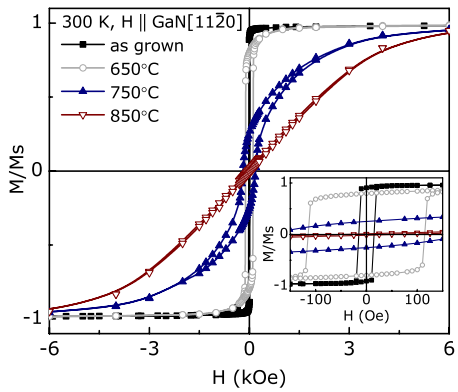

FIG. 4. (Color online) Hysteresis loops obtained at 300 K for selected samples from the LT structure. The inset magnifies the low magnetic field range.

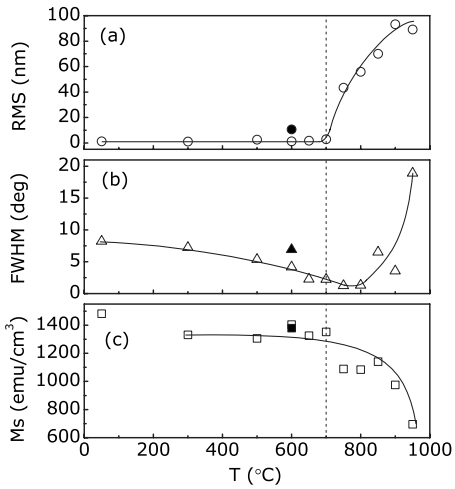

FIG. 5. Dependence of (a) rms roughness, (b) FWHM of Fe{211} reflection, and (c) M_S of the LT samples on RTA temperature. 50 °C is the growth temperature of the as-grown sample. The solid lines are guides to the eyes. The vertical dashed line indicates the temperature limit for keeping connected Fe films with high M_S. Filled symbols indicate results for the HT sample for comparison.

15 Oe and a saturation magnetization M_S of 1480 emu/cm^3. This value is 13.5% smaller than that of bulk Fe, which is mainly due to the difficulty to determine the contribution of the oxide layer to the total thickness of the film. For layers grown on GaN templates, we were able to accurately determine the oxide film thickness, and obtain values for M_S scattering around the value for bulk Fe.

Upon annealing up to a temperature of 700 °C, M_S stays constant with an average value of 1350 emu/cm^3. This drop of 9% with respect to the as-grown film is due to an increase in the oxide thickness, and can be avoided by, for example, capping the Fe layer with Al. Furthermore, we observe a progressive increase in coercivity with increasing annealing temperature. At temperatures above 750 °C, M_S drops rapidly, and the hysteresis loops develop an S-shape. This shape is not related to a change of anisotropy, but coincides with a starting decomposition of the GaN film and a consequent reaction of Ga with the Fe film as detected by EDX. The continuous Fe film then breaks up into isolated (Fe and Ga) grains, changing domain wall motion and thus the shape of the hysteresis.

Figure 5 quantitatively summarizes the results concerning the morphology, crystal quality, and magnetic properties of the films. Evidently, a thermal treatment of these films up to 700 °C is not only not harmful, but even results in a pronounced improvement of crystal quality. Annealing temperatures higher than 700 °C should, however, be avoided, as they lead to the decomposition of the GaN layer and its consequent reaction with the Fe film on top of it.

To summarize and conclude, smooth Fe films were grown epitaxially on GaN(0001) layers using MBE. The epitaxial orientation-relationship is of the Nishiyama–Wassermann type, i.e., α-Fe(110)$\langle 001\rangle \| $GaN(0001)$\langle 11\bar{2}0\rangle$. Upon RTA, the in-plane orientation distribution narrows, implying that grain growth occurs with aligned grains accommodating misaligned ones. Up to a temperature of 700 °C, grain growth proceeds without affecting the morphological, structural, and chemical integrity of the film. When exceeding this temperature, the underlying GaN layer starts to decompose, and the Fe film breaks up into isolated and three-dimensional (Fe and Ga) grains. The thus established temperature limit of 700 °C should, however, already satisfy most requirements for device processing.

We are grateful to Claudia Herrmann and Michael Höricke for expert technical help on AFM, SQUID, and RTA measurements, respectively. Two of us (O.B. and H.P.S.) thank Matthias Wassermeier for his enthusiasm during our initial work on this topic a decade ago.

[1] H.-P. Schönherr, R. Nötzel, W. Q. Ma, and K. H. Ploog, J. Appl. Phys. **89**, 169 (2001).
[2] G. Wastlbauer and J. A. C. Bland, Adv. Phys. **54**, 137 (2005).
[3] M. Ramsteiner, O. Brandt, T. Flissikowski, H. T. Grahn, M. Hashimoto, J. Herfort, and H. Kostial, Phys. Rev. B **78**, 121303(R) (2008).
[4] J. Lu, H. J. Meng, J. J. Deng, P. F. Xu, L. Chen, J. H. Zhao, and Q. J. Jia, J. Appl. Phys. **106**, 013911 (2009).
[5] H. Hasegawa and D. G. Pettifor, Phys. Rev. Lett. **50**, 130 (1983).
[6] R. J. Soulen, Jr., J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry, and J. M. D. Coey, Science **282**, 85 (1998).
[7] B. Beschoten, E. Johnston-Halperin, D. K. Young, M. Poggio, J. E. Grimaldi, S. Keller, S. P. DenBaars, U. K. Mishra, E. L. Hu, and D. D. Awschalom, Phys. Rev. B **63**, 121202(R) (2001).
[8] S. Krishnamurthy, M. Schilfgaarde, and N. Newman, Appl. Phys. Lett. **83**, 1761 (2003).
[9] A. Navarro-Quezada, T. Li, C. Simbrunner, M. Kiecana, G. Hernandez-Sosa, M. Quast, M. Wegscheider, M. Sawicki, T. Dietl, and A. Bonanni, J. Cryst. Growth **310**, 1772 (2008).
[10] R. Meijers, R. Calarco, N. Kaluza, H. Hardtdegen, M. d. Ahe, H. L. Bay, H. Lüth, M. Buchmeier, and D. E. Bürgler, J. Cryst. Growth **283**, 500 (2005).
[11] R. Calarco, R. Meijers, N. Kaluza, V. A. Guzenko, N. Thillosen, Th. Schäpers, H. Lüth, M. Fonin, S. Krzyk, R. Ghadimi, B. Beschoten, and G. Güntherodt, Phys. Status Solidi A **202**, 754 (2005).
[12] S. Andrieu, M. Piecuch, and J. F. Bobo, Phys. Rev. B **46**, 4909 (1992).
[13] A. Biedermann, W. Rupp, M. Schmid, and P. Varga, Phys. Rev. B **73**, 165418 (2006).
[14] M. D. Cropper, T. C. Q. Noakes, M. T. Butterfield, and P. Bailey, Surf. Sci. **594**, 212 (2005).
[15] Y. L. He, S. Godet, and J. J. Jonas, J. Appl. Crystallogr. **39**, 72 (2006).