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Molecular beam epitaxy of ferromagnetic $\gamma'$-Fe$_4$N thin films on LaAlO$_3$(100), SrTiO$_3$(100) and MgO(100) substrates

Keita Ito$^a$, Geun Hyoung Lee$^a$, Hiro Akinaga$^b$, Takashi Suemasu$^a$

$^a$Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennohdai, Tsukuba, Ibaraki 305-8573, Japan

$^b$National Institute of Advanced Industrial Science and Technology (AIST), NIRC, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

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We have attempted to grow $a$-axis-oriented $\gamma'$-Fe$_4$N epitaxial films with smooth surfaces at around 400 °C on LaAlO$_3$ (LAO)(100), SrTiO$_3$ (STO)(100) and MgO(100) substrates by molecular beam epitaxy using solid Fe and a radio-frequency NH$_3$ plasma as the Fe and N sources, respectively. The lattice mismatch of these substrates to $\gamma'$-Fe$_4$N is 0, 3 and 11%, respectively. Epitaxial growth of $\gamma'$-Fe$_4$N films was successfully achieved on the STO(100) and LAO(100) substrates. It was found from reflection high-energy electron diffraction and x-ray diffraction that the $a$-axis orientation of $\gamma'$-Fe$_4$N was degraded with increasing lattice mismatch. High-angle annular dark-field scanning transmission electron microscopy and
electron energy-loss spectroscopy measurements showed that amorphous Al-O layers were present at the $\gamma'$-Fe$_4$N/LAO interface.
1. Introduction

In recent years, spintronics, which is an emerging area of electronics with the potential for new functional devices such as spin random access memory (Spin-RAM) and spin transistors by the creation and control of electron spin, has attracted significant attention. The use of ferromagnetic materials with high spin polarization and low lattice mismatch to Si as effective spin injection electrodes for Si is appropriate. In particular, special attention has been paid to ferromagnetic \(\gamma'\)-Fe\(_4\)N as a spin injection electrode for Si. \(\gamma'\)-Fe\(_4\)N is chemically stable and has a relatively small lattice mismatch of 1.3% to Si(100), and the Curie temperature is reported to be 767 K [1]. Very recently, we have confirmed, from point-contact Andreev reflection measurements, that spin polarization in highly \(a\)-axis-oriented polycrystalline \(\gamma'\)-Fe\(_4\)N thin films grown by molecular beam epitaxy (MBE) is larger than that in \(\alpha\)-Fe [2]. According to Kokado et al., the electrical conductivities of up spins and down spins in \(\gamma'\)-Fe\(_4\)N were theoretically calculated, and spin polarization of the electrical conductivity at the Fermi level is \(-1.0\) [3]. Furthermore, an inverse tunneling magnetoresistance ratio of \(-75\%\) due to negative spin polarization of \(\gamma'\)-Fe\(_4\)N was reported at RT in CoFeB/MgO/\(\gamma'\)-Fe\(_4\)N magnetic tunnel junctions fabricated by sputtering [4]. Therefore, \(\gamma'\)-Fe\(_4\)N is considered to be an appropriate material for application in Si-based spintronics devices [5].

However, the magnetic moments of \(\gamma'\)-Fe\(_4\)N remain unclear from an experimental
Atiq et al. fabricated $\gamma'$-Fe$_4$N films on (100) faces of LaAlO$_3$(LAO), SrTiO$_3$ (STO) and MgO substrates by sputtering, and reported that the saturation magnetization per unit volume ($M_s$) in $\gamma'$-Fe$_4$N increases with decreasing lattice mismatch between $\gamma'$-Fe$_4$N and the substrate used. The lattice mismatch was approximately 0, 3 and 11%, respectively, for the three substrates [6]. We believe high-quality $\gamma'$-Fe$_4$N epitaxial films should be employed to confirm this experimental result, and also to investigate their applicability as spin injection electrodes. There have been many reports on the growth of $\gamma'$-Fe$_4$N thin films on MgO(100) [6-8], STO (100) [6,9], LAO (100) [6], Cu(100) [10] and Si(100) [11] substrates by MBE, sputtering, chemical vapor deposition etc. However, there are few papers on epitaxial growth of $\gamma'$-Fe$_4$N thin films [6-10]. There are no reports so far on the epitaxial growth of $\gamma'$-Fe$_4$N thin films on LAO and STO by MBE. The purpose of this work is to achieve epitaxial growth of $\gamma'$-Fe$_4$N thin films on LAO(100), STO(100) and MgO(100) substrates by MBE. Very thin films of LAO and STO can be utilized as a tunnel barrier layer between $\gamma'$-Fe$_4$N and Si(100) due to their small lattice mismatch to both $\gamma'$-Fe$_4$N and Si(100).

2. Experimental procedures

An ion-pumped MBE system equipped with a high-temperature Knudsen cell for 5N-Fe and a radio-frequency (RF) NH$_3$ plasma for N was used. Thin films of $\gamma'$-Fe$_4$N (samples A–I) were grown on LAO(100), STO(100) and MgO(100) substrates by supplying
Fe and N simultaneously in a stoichiometric proportion. Prior to the fabrication of the $\gamma'$-Fe$_4$N layers, the three substrates were processed differently. STO(100) substrates were dipped into a buffered HF (HF = 5 wt%, NH$_4$F = 35 wt%) solution and heated at 900 °C for 30 min under an oxygen partial pressure of $5 \times 10^{-6}$ Torr, in order to get an atomically flat surface [12,13]. MgO(001) substrates were heated at 900 °C for 30 min in an ultrahigh vacuum. In contrast, for LAO(100) substrates, such a high temperature pre-annealing was not performed, in order to prevent crack formation. The substrate temperature during the growth was optimized in order to get good crystallization and flat surfaces. After several trials, we determined that 375, 400 and 415 °C were suitable temperature for $\gamma'$-Fe$_4$N layer growth on LAO (samples A and G), STO (samples B and H) and MgO (samples C and I), respectively. Table 1 summarizes the growth conditions used for the samples and substrates. The crystalline quality of the $\gamma'$-Fe$_4$N was evaluated from reflection high-energy electron diffraction (RHEED) measurements, x-ray diffraction (XRD) measurements, and atomic force microscopy (AFM). For samples G–I, the $\gamma'$-Fe$_4$N films were capped with a 3-nm-thick Au layer to prevent oxidation on the surface, and cross-sectional transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and electron energy-loss spectroscopy (EELS) measurements were carried out.

3. Results and discussion
Fig. 1(a-c) show typical examples of RHEED patterns observed for samples A-C. Streaky patterns were observed for samples A and B with $\gamma'$-Fe$_4$N layers grown on LAO(100) and STO(100) substrates, respectively. On the other hand, $\gamma'$-Fe$_4$N layers on MgO(100), sample C, showed a spotty pattern together with a ring structure, meaning that the $\gamma'$-Fe$_4$N rotates along the surface normal. The $\theta$-2$\theta$ XRD patterns from samples A-C are shown in Fig. 2(a-c). No diffraction peaks corresponding to $\alpha$-Fe and iron nitrides, other than $\gamma'$-Fe$_4$N, were observed in the samples. Due to the very close lattice constant values between LAO and $\gamma'$-Fe$_4$N as well as the $a$-axis orientation of $\gamma'$-Fe$_4$N, the diffraction peaks due to $\gamma'$-Fe$_4$N overlap the (100)-oriented diffraction peaks of the LAO substrate. Intense diffraction peaks of (100)-oriented $\gamma'$-Fe$_4$N such as (200) and (400) are clearly seen for sample B with the STO(100) substrate. In contrast to $\gamma'$-Fe$_4$N/STO(100), the peak intensity of $\gamma'$-Fe$_4$N(200) for sample C, grown on the MgO(001) substrate, is significantly smaller.

The surfaces of samples A-C were relatively smooth. Fig. 3(a–c) show AFM images of samples A–C. The root-mean-square (RMS) values of the surface roughness were found to be approximately 0.25 nm for each sample. Step and terrace structures were observed for the $\gamma'$-Fe$_4$N surface in sample A with the LAO(100) substrate, as seen in Fig. 3(a). On the basis of these results, we conclude that epitaxial (100)-oriented $\gamma'$-Fe$_4$N films with smooth surfaces were successfully grown on LAO(100) and STO(100) substrates.

We next consider the influence of lattice mismatch on the $a$-axis orientation of
\( \gamma'\)-Fe\(_4\)N and the strain within the \( \gamma'\)-Fe\(_4\)N layers. Fig. 4(a-c) show x-ray rocking curves for the \( \gamma'\)-Fe\(_4\)N(200) plane in samples D-F. Ge(220) single crystals were used to make the incident x-rays parallel in the XRD equipment. The full width at half maximum (FWHM) for 14-nm-thick \( \gamma'\)-Fe\(_4\)N layers, sample D, grown on an MgO(100) substrate was more than 10°. This implies that the a-axis of the \( \gamma'\)-Fe\(_4\)N layers on MgO(100) tilted significantly with respect to the surface normal. In contrast, the FWHM for 12-nm-thick \( \gamma'\)-Fe\(_4\)N layers on STO(100), sample E, was approximately 2°, and the FWHM value decreased further to 0.99° with increasing \( \gamma'\)-Fe\(_4\)N layer thickness to 30 nm in sample F. These results show that the a-axis orientation of \( \gamma'\)-Fe\(_4\)N degraded with increasing lattice mismatch between \( \gamma'\)-Fe\(_4\)N and the substrate used. Fig. 5(a) and (b) show x-ray reciprocal lattice mappings for a 12-nm-thick \( \gamma'\)-Fe\(_4\)N layer, sample E, and a 30-nm-thick \( \gamma'\)-Fe\(_4\)N layer, sample F, on STO(100). Considering that the \( \gamma'\)-Fe\(_4\)N layers are epitaxially grown on STO(100) with the a-axis normal to the sample surface, the \( \gamma'\)-Fe\(_4\)N (113) and STO(113) spots should be on the same vertical line if the lattice constants \( b \) and \( c \) of \( \gamma'\)-Fe\(_4\)N in the lateral direction are equal to those of STO(100). However, as seen in Fig. 5(a) and (b), the \( \gamma'\)-Fe\(_4\)N (113) and STO(113) spots are not on the vertical broken line, but rather on the inclined broken line which crosses the origin of the reciprocal lattice. This indicates that the \( \gamma'\)-Fe\(_4\)N layers in samples E and F are not strained but are fully relaxed.

Fig. 6(a-c) show cross-sectional TEM images of samples G-I. The \( \gamma'\)-Fe\(_4\)N layers in
these samples were covered with 3-nm-thick Au capping layers. As shown in Fig. 6(a), we can clearly see a very thin interfacial layer between the γ'-Fe₄N layers and the LAO(100) substrate in sample G. Fig. 7(a) and (b) show HAADF-STEM images of sample G at low magnification and at high magnification, respectively. In HAADF-STEM images, it is well known that heavy atoms such as La and Fe appear brighter. In the present work, we can see clear lattice images inside the γ'-Fe₄N layers and the LAO substrate, but not around the interface, as shown in Fig. 7(b). Furthermore, around the interface the image is darker than the other areas, indicating that the interfacial layers are amorphous and probably consist of light atoms such as Al. Fig. 7(c) shows EELS depth profiles of Fe, N, La and O atoms observed for sample G. An EELS line scan was performed along the white line shown in Fig. 7(a). From comparison of the profile of O atoms with that of La atoms, it was found that O atoms diffused slightly into the γ'-Fe₄N layers from the LAO substrate. From the HAADF-STEM and EELS analyses results for sample G, we can say that amorphous Al-O layers are likely present at the γ'-Fe₄N/LAO(100) interface. We should also note that the Fe atoms were not uniform in the γ'-Fe₄N layers near the interface. We believe that the diffusion of O atoms into the γ'-Fe₄N layers may affect the profile of the Fe atoms. On the basis of all experimental results in this work, we conclude that γ'-Fe₄N thin films grown on a STO(100) substrate have better crystalline quality than those grown on LAO(100) and MgO(100) substrates.
4. Conclusions

We have succeeded in growing $a$-axis-oriented $\gamma'$-Fe$_4$N films epitaxially on LAO(100) and STO(100) substrates by MBE using 5N-Fe and RF-NH$_3$ as Fe and N sources respectively. In contrast, RHEED and XRD patterns revealed that it was difficult to grow $\gamma'$-Fe$_4$N films epitaxially on MgO(100) substrates. These results imply that the $a$-axis orientation of $\gamma'$-Fe$_4$N was degraded with increasing lattice mismatch. From reciprocal lattice mappings for 14-nm-thick and 30-nm-thick $\gamma'$-Fe$_4$N thin films grown on STO(001) substrates, the $\gamma'$-Fe$_4$N films were found not to be strained. HAADF-STEM and EELS spectroscopy measurements indicated that amorphous Al-O layers were present at the $\gamma'$-Fe$_4$N/LAO interface.

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N. Ota and Prof. K. Asakawa of the Tsukuba Nano-Tech Human Resource Development Program at the University of Tsukuba for useful discussions.
References


Fig. 1. RHEED patterns from samples (a) A, (b) B and (c) C taken from the [100] azimuth of \( \gamma' \)-Fe\(_4\)N.

Fig. 2. \( \theta \)-2\( \theta \) XRD patterns for samples (a) A, (b) B and (c) C.

Fig. 3. AFM images of samples (a) A, (b) B and (c) C. RMS values of surface roughness were 0.24, 0.26 and 0.26 nm, respectively.

Fig. 4. X-ray rocking curves for samples (a) D, (b) E and (c) F for \( \gamma' \)-Fe\(_4\)N(200).

Fig. 5. X-ray reciprocal lattice mappings for samples (a) E and (b) F.

Fig. 6. Cross-sectional TEM images of samples (a) G, (b) H and (c) I. The electron beam was incident along the [100] azimuth of \( \gamma' \)-Fe\(_4\)N.

Fig. 7. Cross-sectional HAADF-STEM images of sample G at (a) low magnification and (b) high magnification. The electron beam was incident along the \( \gamma' \)-Fe\(_4\)N [100] azimuth. Heavy atoms appear brighter than light atoms. (c) EELS depth profiles of Fe, N, La and O atoms observed for sample G along the white line.
Table 1 Growth conditions used for the samples. Samples A and G were grown on LAO substrates. Samples B, E, F and H were grown on STO substrates. Samples C and I were grown on MgO substrates. In samples G-I, γ'-Fe₄N layers were covered with Au capping layers.

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Fig. 1
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