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<tr>
<td>Citation</td>
<td>Scientific reports, 7: 7009</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2017-08-01</td>
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<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/67151">http://hdl.handle.net/2115/67151</a></td>
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<td>File Information</td>
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Fabrication of Epitaxial Fe₃O₄ Film on a Si(111) Substrate

Nozomi Takahashi¹, Teodor Huminicu², Yuta Yamamoto¹, Takashi Yanase³, Toshihiro Shimada³, Atsufumi Hirohata² & Taro Nagahama³

The application of magnetic oxides in spintronics has recently attracted much attention. The epitaxial growth of magnetic oxide on Si could be the first step of new functional spintronics devices with semiconductors. However, epitaxial spinel ferrite films are generally grown on oxide substrates, not on semiconductors. To combine oxide spintronics and semiconductor technology, we fabricated Fe₃O₄ films through epitaxial growth on a Si(111) substrate by inserting a γ-Al₂O₃ buffer layer. Both of γ-Al₂O₃ and Fe₃O₄ layer grew epitaxially on Si and the films exhibited the magnetic and electronic properties as same as bulk. Furthermore, we also found the buffer layer dependence of crystal structure of Fe₃O₄ by X-ray diffraction and high-resolution transmission electron microscope. The Fe₃O₄ films on an amorphous-Al₂O₃ buffer layer grown at room temperature grew uniaxially in the (111) orientation and had a textured structure in the plane. When Fe₃O₄ was deposited on Si(111) directly, the poly-crystal Fe₃O₄ films were obtained due to SiO₂ on Si substrate. The epitaxial Fe₃O₄ layer on Si substrates enable us the integration of highly functional spintoronic devices with Si technology.

In the field of spintronics, spin injection and transport phenomena have attracted much attention owing to the possibility of producing novel functional devices¹⁻³. In particular, the combination of spintronics and semiconductors is a promising technology for the development of the next stage of spintronic devices, e.g., spin-FET or logic devices⁴⁻⁵. The spin injection technique, in which the spin-polarized currents are injected from ferromagnetic metals into conventional semiconductor materials⁶⁻⁻¹⁰, has been intensely investigated for the preparation of spintronic devices. As a result, researchers have succeeded in nonlocal detection¹¹ or the observation of the Hanle effect¹², which demonstrates the spin state in the semiconductor; thus, the behavior of the spin current in the semiconductor can be determined¹³. Recently, graphene has also been the subject of spin injection because the spin diffusion length in such light elements is expected to be long owing to small spin–orbit interaction⁹,¹⁰.

The source of the spin current plays an important role in obtaining high-efficiency spin injection. Magnetic oxides are one of the most promising spin source candidates. However, ferromagnetic metals have been used so far because of convenience during fabrication. Magnetic oxides possess unique properties¹¹⁻¹⁴: Fe₃O₄ or (LaSr) MnO₃ have a half-metallic state, which provides highly spin polarized current¹⁵, and NiFe₂O₄ or CoFe₂O₄ are magnetic insulators, which means that they could work as a spin filter tunnel barrier¹⁶⁻¹⁸. γ-Fe₂O₃ is another candidate as the spin filter barrier. It is the spinel type ferrimagnetic insulator that is obtained by over oxidation of Fe₃O₄¹⁹. Recently, NiCo₂O₄ with spinel structure was discovered to exhibit large magnetoresistance effects²⁰. Therefore, the combination of magnetic oxides and semiconductors enables us to produce new functional devices. Some research groups fabricated the magnetic oxide on oxide semiconductor, Nb: SrTiO₃²¹, and investigated the transport characteristics including spin transport of the junctions¹⁹,²¹. However, epitaxial growth of magnetic oxide on Si, which is the most important semiconductor, has not been established because the surface of Si is easily oxidized by the oxygen atmosphere during the evaporation of the magnetic oxides²².

In this study, we grew Fe₃O₄ epitaxially on a Si(111) substrate by the insertion of an ultrathin γ-Al₂O₃ buffer layer. Fe₃O₄ is the ferrimagnetic conducting oxide with spinel crystal structure. At 120 K, Fe₃O₄ shows phase transition called Verwey transition, at which the electric resistivity decreases drastically and the crystal symmetry decreases from face-centered cubic to monoclinic²³⁻²⁵. Fe₃O₄ is expected to be half-metallic theoretically, meaning to have a spin polarization of 100%¹⁶, and a spin polarization of more than 80% was observed experimentally using a spin-resolved photoemission spectroscopy²⁶. An ultrathin γ-Al₂O₃ layer was inserted to prevent surface
oxidation of Si during the Fe3O4 growth. γ-Al2O3 is an aluminum oxide with the same spinel structure as Fe3O4
and the lattice constant of γ-Al2O3 is 7.91 Å, which is three halves of that of Si with lattice mismatch of −2.9%27.
From the viewpoint of the crystal structure, Fe3O4 and γ-Al2O3 seems to grow on Si epitaxially.

γ-Al2O3 (111) epitaxial growth on Si(111) was reported by two research groups recently. Jung et al. formed a
γ-Al2O3 (111) layer by annealing an Al layer on protective Si oxide, which was carefully oxidized to be reduced
by the Al layer28. Merckling et al. fabricated γ-Al2O3 (111) by the deposition of an Al2O3 source under ultra-high
vacuum29. In the former method, it is difficult to optimize the oxidation of the Si layer and the thickness of Al
film. In contrast, the latter method is simple if an ultra-high vacuum system is accessible.

In this study, the epitaxial γ-Al2O3 buffer layers were prepared using an ultra-high vacuum system and the
Fe3O4 layer was fabricated by reactive molecular beam epitaxy. We investigated the crystal structure, magnetic
and electric properties of the Fe3O4 layer on Si(111) with an epitaxial γ-Al2O3 buffer layer, an amorphous-Al2O3
buffer layer, and without a buffer layer. We succeeded in the fabrication of high quality Fe3O4 films on Si(111)
substrates. The buffer layer had a significant effect on the crystal structure of the Fe3O4 layers.

Results and Discussion

Epitaxial growth. The γ-Al2O3 and Fe3O4 layers were grown by molecular beam epitaxy method. The struc-
tures of the samples were (a) Si(111)/γ-Al2O3 2.4 nm/Fe3O4 50 nm/amorphous-Al2O3 2.0 nm, (b) Si(111)/amor-
phous-Al2O3 2.4 nm/Fe3O4 50 nm/amorphous-Al2O3 2.0 nm and (c) Si(111)/Fe3O4 50 nm/amorphous-Al2O3
2.0 nm, as shown in Fig. 1 (hereafter referred to as (a) EPI, (b) AMO and (c) W/O), respectively. After treatment
of the Si substrate, we confirmed that the in-situ reflection high energy electron diffraction (RHEED) pattern of
the Si substrate had a (7 × 7) streak pattern (Supplementary Fig. S1). This means that the surface of Si was clean
and flat. Figure 2(a) and (b) show the RHEED pattern of γ-Al2O3 and Fe3O4 in EPI. The direction of the incident
electron beam was [11-2]. The RHEED patterns of γ-Al2O3 and Fe3O4 were clear streak patterns indicating that
γ-Al2O3 and Fe3O4 grew epitaxially. Therefore, the γ-Al2O3 film was considered to play a role of a buffer layer for
epitaxial growth of Fe3O4. The surface roughness of γ-Al2O3 and Fe3O4 was estimated to be very small in value by
atomic force microscope (AFM) (shown in Supplementary Fig. S2).

Figure 2(c) and (d) show the RHEED pattern of amorphous-Al2O3 and Fe3O4 in AMO. The amorphous-Al2O3
layer was deposited at room temperature. After the deposition of Al2O3, as shown in Fig. 2(c), the Si (7 × 7) streak
pattern turned into a halo pattern, which indicated that the Al2O3 layer was amorphous. Figure 2(d) shows the
RHEED pattern of Fe3O4 on the amorphous-Al2O3. A ring and streak pattern was observed, which implied the
presence of a polycrystalline surface. Thus, the epitaxial γ-Al2O3 played a crucial role in the formation of epitaxial
Fe3O4 on the Si substrate.

Figure 2(e) and (f) show the RHEED pattern of the Si substrate and Fe3O4 in W/O. The surface of the Si sub-
strate exhibited a diffused streak pattern owing to the introduction of oxygen gas, which oxidized the Si surface.
In Fig. 2(f), the RHEED pattern of Fe3O4 on SiO2 shows a halo pattern, which indicated that spinel-type Fe3O4
was not formed.
X-ray diffraction. To confirm the crystallization, the $\theta$–2$\theta$ X-ray diffraction (XRD) measurements were carried out on three samples, as shown in Fig. 3(a). The diffraction pattern of Fe$_3$O$_4$ on an $\gamma$-Al$_2$O$_3$ buffer layer in EPI (red line) exhibited four peaks (18.3°, 37.2°, 57.2°, 79.4°), which were in agreement with the diffraction patterns of Fe$_3$O$_4$ (111), (222), (333) and (444) planes. This indicated that the Fe$_3$O$_4$ film was (111)-oriented without other orientations or phases. The lattice constant measured by XRD was estimated to be 8.39 Å. The lattice constant of the in-plane direction was estimated to be 8.23 Å (Supplementary Fig. S3), which is smaller than the bulk lattice parameter. Therefore, the Fe$_3$O$_4$ was considered to be compressed in-plane.

To investigate the in-plane epitaxial relationship, we conducted $\phi$-scan measurements of Si(311) and Fe$_3$O$_4$(4-40), as shown in Fig. 3(b). The six peaks of Fe$_3$O$_4$(4-40) appeared at 60° intervals, indicating the presence of two 180° rotated domains in the Fe$_3$O$_4$ layer. The epitaxial relationships were [11-2]Fe$_3$O$_4$(111) and [-1-12]Fe$_3$O$_4$(111) parallel to [11-2]Si(111), as exhibited in Fig. 3(c). In addition, the peaks of the Fe$_3$O$_4$ film were broader than that of the Si substrate. There was a lattice mismatch of 5.7% at $\gamma$-Al$_2$O$_3$/Fe$_3$O$_4$.

The $\theta$–2$\theta$ XRD diffraction pattern of Fe$_3$O$_4$ in AMO (blue line) exhibited four peaks, which was identical with the diffraction pattern of Fe$_3$O$_4$ in EPI. Therefore, the Fe$_3$O$_4$ in AMO was also (111)-oriented. However, the RHEED pattern in Fig. 1(d) implied the presence of a polycrystalline structure. Furthermore, the Fe$_3$O$_4$(4-40) diffraction peak was not observed in the $\phi$-scan measurement. Therefore, we concluded that the Fe$_3$O$_4$ had a textured structure and the growth direction was (111).

The $\theta$–2$\theta$ XRD diffraction pattern of Fe$_3$O$_4$ in W/O (green line) exhibited small peaks related to Fe$_3$O$_4$(311), (400), (422) and unknown peaks. In a previous study, the XRD of Fe$_3$O$_4$ on SiO$_2$ indicated that the Fe$_3$O$_4$ layer was polycrystalline and contained other phases.
To investigate the crystallinity of the Fe₃O₄ layer in detail, we carried out X-ray reciprocal space mapping around the symmetric (222) diffraction for Fe₃O₄ in EPI and AMO (Fig. 3(d)). The symmetrical scan showed that the Fe₃O₄(222) spot on amorphous-Al₂O₃ was larger than the Fe₃O₄ spot on γ-Al₂O₃, which means that the Fe₃O₄ in AMO had an angle distribution in the growth directions. Although the reason for the (111) oriented Fe₃O₄ growth on amorphous-Al₂O₃/Si(111) was unclear, two possibilities exist that could explain this growth. The first is a reduction in the total anisotropy energy related to the surface energy and interface energy. The difference between AMO and W/O could be attributed to the difference of the surface and interface energy of amo-Al₂O₃.
and amo-SiO. The second possibility is that the amo-Al2O3 maintains a crystal structure of Si locally because the amo-Al2O3 layer was very thin. Fe3O4 could utilize such a microcrystal-like region as a growth nucleus.

Transmission electron microscope observation. We conducted cross-sectional transition electron microscopy (TEM) analysis to confirm the crystallinity and compositions of the materials. Figure 4 shows the cross-section TEM images in which the electron beams were incident along the Si [1-10] zone axis. In Fig. 4(a), the TEM image shows that the Fe atoms of Fe3O4 were orderly aligned; thus, the Fe3O4 film was epitaxial. The electron diffraction (ED) of Fe3O4 in EPI shown in Fig. 4(b) was in good agreement with the simulation of spinel structure. The left side in Fig. 4(a) shows the epitaxial relationship on [11-2]Fe3O4(111)/[11-2]Si(111), whereas the center of image shows the epitaxial relationship on [-1-12]Fe3O4(111)/[11-2]Si(111), which were consistent with the results of the φ-scan measurements in the XRD. In addition, the spacing of the (111) planes were estimated at 4.87 Å from the high angle annular dark-field scanning (HAADF) image (Supplementary Fig. S4(c)), which were almost the same as the out-of-plane lattice constant (4.84 Å) determined by XRD in Fig. 3(a) and that of bulk Fe3O4 (4.85 Å). In contrast, the TEM image of Fe3O4 in AMO shown in Fig. 4(c) demonstrated that the structure was polycrystalline and grain boundaries were clearly observed. The ED image in Fig. 4(d) consisted of the diffraction from the grains with some crystal orientations. In the low magnification TEM image (supplementary Fig. S4(b)), some grains with a size of 15–30 nm appeared.

With respect to the buffer layer, the thickness of γ-Al2O3 was estimated from the HRTEM image (Fig. 4(a)) to be approximately 1 nm, which was thinner than the nominal value measured by the crystal oscillator in the chamber. The reason for this difference in thickness was unclear; however, it could be due to the fluctuation of the crystal oscillator or re-evaporation of Al2O3 because the γ-Al2O3 was grown at a high temperature (900°C). We could see the amorphous layer under the γ-Al2O3 layer, which was determined to be a SiOx layer by HAADF and Energy dispersive X-ray spectroscopy (EDS) mapping images (Fig. 5). The SiOx layer was considered to form during the growth of Fe3O4 because the Fe3O4 was grown in 4 × 10⁻⁴ Pa O2 gas. It was reported that Si was oxidized through the γ-Al2O3 layer of less than 2.0 nm by introducing oxygen (>10⁻³ Pa)32. To confirm that, we fabricated a γ-Al2O3 (7.5 nm) film on Si(111), and carried out XRD and TEM observations (supplementary Fig. S5(a) and (b)). The γ-Al2O3 grew epitaxially on Si and we found no amorphous layer at the Si(111)/γ-Al2O3(7.5 nm) interface.

Figure 4. TEM observation: (a) Cross-section TEM image and (b) electron diffraction pattern of Si(111)/γ-Al2O3/Fe3O4 in EPI taken along the [1-10] axis zone, (c) Cross-section TEM image and (d) electron diffraction of Si(111)/amo-Al2O3/Fe3O4 in AMO taken along the [1-10] axis zone.
Magnetic characteristics. The magnetic character of Fe$_3$O$_4$ is one of its fundamental properties. The magnetization curves at room temperature for the Fe$_3$O$_4$ films on γ-Al$_2$O$_3$ layer are shown in Fig. 6(a). The directions of the magnetic field were in-plane [11-2], in-plane [1-10] and out-of-plane [111]. The hysteresis curve along [11-2] was the same as that along [1-10] and the Fe$_3$O$_4$ film had in-plane magnetization. The saturation magnetization ($M_s$) was 480 emu/cm$^3$ for all magnetic field directions. The remanent magnetization ($M_r$), the coercive field ($H_c$), and the remanent ratio ($M_r/M_s$) in the in-plane field were 280 emu/cm$^3$, 500 Oe, and 0.48, respectively, and those for the out-of-plane field were 47 emu/cm$^3$, 225 Oe, and 0.08, respectively. The hysteresis loops for Fe$_3$O$_4$ in EPI, AMO, and W/O are illustrated in Fig. 6(b). Fe$_3$O$_4$ in EPI had the largest $H_c$ and $M_s$ among the three samples. The $M_s$ of Fe$_3$O$_4$ in EPI was the same as the value of bulk Fe$_3$O$_4$. Although the reason for small magnetization for AMO and W/O has not been clear so far, the antiphase boundary or disordered structure at grain boundary could be responsible for it$^{33,34}$.

Transport characteristics. Figure 7 shows that the dependence of the resistance on temperature for the Fe$_3$O$_4$ film in EPI. As is well-known, Fe$_3$O$_4$ is an electric conductor at room temperature and the resistivity increases exponentially with decreasing temperature. The resistivity of the film at 300 K was $2.5 \times 10^{-4} \Omega$cm, which is lower than the bulk value ($5 \times 10^{-3} \Omega$cm$^{35}$). The $d\log R/dT$ plots (inset) show a valley at approximately 120 K. This anomaly corresponds to a Verwey transition$^{36}$, which is a famous phase transition in Fe$_3$O$_4$. The Verwey transition has been reported to sharply change the resistivity by approximately one digit$^{37}$; however, the transition is easily disappeared by impurities or structure defects$^{34,38}$. As the Fe$_3$O$_4$ in EPI possessed magnetic and electric characteristics that were comparable to bulk Fe$_3$O$_4$, the Fe$_3$O$_4$ on γ-Al$_2$O$_3$ buffer layer was very good quality.
Conclusions
We fabricated an epitaxial Fe₃O₄ film on a Si substrate by inserting a γ-Al₂O₃ buffer layer. From the XRD measurement and TEM observation, the γ-Al₂O₃ buffer layer contributed to the growth of epitaxial Fe₃O₄(111) on Si(111). In contrast, the Fe₃O₄ film on an amo-Al₂O₃ buffer layer had an (111)-orientation with a textured structure. The Fe₃O₄ on γ-Al₂O₃ had magnetic properties corresponding to the bulk Fe₃O₄, furthermore the resistivity exhibited a Verwey transition at 120 K. The results indicate that the heterostructure of Si substrate/γ-Al₂O₃/Fe₃O₄ could be used as a part of magnetic tunnel junctions or spin injection devices and will allow us to integrate spintronic devices including Fe₃O₄ electrode, e.g., spin-FET or magnetic tunnel junctions, on Si.

Methods
Preparation of the samples. Before deposition, the Si substrate was cleaned by a standard Radio Corporation of America clean and hydrofluoric (HF) acid solution and annealed at 900 °C under a vacuum of <10⁻⁶ Pa. The γ-Al₂O₃ buffer layer was formed by evaporating the Al₂O₃ source material at 900 °C and annealing at 900 °C for 30 minutes. In previous reports, γ-Al₂O₃ was grown at >850 °C and under a vacuum of <10⁻⁴ Pa. The growth conditions we used for γ-Al₂O₃ were in the range of the report. In Si(111)/amo-Al₂O₃/Fe₃O₄, the amo-Al₂O₃ was grown at room temperature under a vacuum of <3 × 10⁻⁶ Pa. Then, the Fe₃O₄ film was formed by reactive deposition at 300 °C under a O₂ atmosphere of 4.0 × 10⁻⁴ Pa. All the samples were fabricated under the same growth conditions to investigate the dependence of the quality of Fe₃O₄ films on the buffer layer.

Measurements.
The epitaxial growth and crystal structure were confirmed by RHEED, XRD (Rigaku SmartLab (9 kW)), and TEM (FEI Titan3 G2 60-300). Cross-sectional samples for TEM were prepared by using conventional mechanical polishing and dimpling techniques. The magnetic properties of Fe₃O₄ were measured by vibrating sample magnetometer (VSM) and the electrical properties were measured by direct current (DC) measurements.

References

**Acknowledgements**

We would like to express our gratitude to Prof. Yamamoto’s group, Prof. Tokeshi’s group for their cooperation in the microfabrication. We especially thank Prof. Sakaguchi for his advice and helpful suggestions. This work was partly supported by JSPS KAKENHI Grant Numbers 15H05702, 23686006, the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant 2016–57), and the OPEN FACILITY, Hokkaido University Sousei Hall and Nanotechnology Collaborative Research in Hokkaido University. TH and AH are supported by EU-FP7 HAFIR project (NMP3-SL-2013-604398).

**Author Contributions**

N.T. and T.N. conceived and designed the experiments using the help of other authors. N.T., T.N., Y.Y., T.Y. and T.S. performed the sample preparation, XRD measurements, magnetic and electrical measurements. T.H., A.H., N.T. and T.N. performed TEM observations. All the authors contributed to analysing and interpreting the data, and to writing the manuscript.

**Additional Information**

**Supplementary information** accompanies this paper at doi:10.1038/s41598-017-07104-z

**Competing Interests:** The authors declare that they have no competing interests.

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