

Thin Magnetite Films on an Oxidized Silicon Surface: Raman Spectroscopy Study

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Abstract—Polycrystalline films of magnetite (Fe_3O_4) formed by the reactive sputtering of iron in oxygen on Si(001) substrates covered by thin (1.4 nm) or thick (1200 nm) SiO_2 layers have been studied by Raman spectroscopy. It is established that (i) the $\alpha\text{-Fe}_2\text{O}_3$ phase is formed due to the laser-induced heating in magnetite films synthesized on thick SiO_2 layers and (ii) the formation of $\alpha\text{-Fe}_2\text{O}_3$ phase depends on the thickness of the buffer SiO_2 layer.

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Raman spectroscopy is known to be an informative method for investigation of the structure and phase composition of materials. However, experiments employing Raman spectroscopy must take into account the density of the probing laser radiation power, since an intense primary beam can produce degradation of a sample [1]. In particular, this is valid for magnetite (Fe_3O_4), since this compound contains divalent iron and, hence, can readily be oxidized in atmosphere at elevated temperatures. It was reported in [2] that the laser-induced heating of bulk Fe_3O_4 samples in air leads to the formation of other iron oxide phases—in particular, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). This conversion was accompanied by a significant displacement of the characteristic spectral peaks toward lower frequencies, which complicated correct interpretation of the Raman spectra.

The present Letter shows that analogous effects can also be manifested in Raman spectroscopy measurements of thin Fe_3O_4 films synthesized on an oxidized surface of silicon. We have established that the phase transformation of magnetite is not only determined by the density of laser radiation power, but also depends on the thickness of a silicon oxide layer and its thermal conductivity.

The substrates were cut from *n*-type (001)-oriented Si wafers with a resistivity of 4.5 Ω cm, on which a thick (1200 nm) SiO_2 layer was formed by thermal oxidation. Substrates with a thin (1.4 nm) SiO_2 layer were prepared by removal of the initial thick SiO_2 film from half of the surface area, followed by wet chemical treatment in nitric acid (HNO_3) for 5 min. Then, iron oxide films were formed simultaneously on both sides of the substrate using reactive sputtering of iron in oxy-

gen. This process was effected in an ultra-high-vacuum setup at a constant pressure of oxygen (1.0×10^{-6} Torr) and a constant substrate temperature (300°C). Two series of samples were prepared on substrates with thin (series 1) and thick (series 2) SiO_2 layers, in which the iron oxide thicknesses were 33, 66, and 96 nm. The experimental procedure has been described in more detail elsewhere [3].

In the course of iron oxide film growth, the samples were studied by the method of reflection high-energy electron diffraction (RHEED). RHEED measurements were performed under identical conditions for both series of samples. Figure 1a shows the typical RHEED pattern observed in both series, which displays the Debye rings that are characteristic of textured polycrystalline films. Calculations showed that the radii of these diffraction rings are consistent with the inverse values of the interplanar spacing for a spinel crystal lattice with a [100] texture [3]. As the iron oxide film grows, the sharpness of the Debye rings increases, which is indicative of an increase in the grain size. These data agree with the results of atomic force microscopy (AFM) measurements (Fig. 1b) performed on a SOLVER-P47 instrument (NT-MDT Co.). In both series of samples, the surface exhibited an array of iron oxide grains. As the film thickness increased from 33 to 96 nm, the average grain size increased from 15 to 22 nm.

The observed RHEED patterns do not exclude the presence of another iron oxide phase—maghemite ($\gamma\text{-Fe}_2\text{O}_3$)—in the film, since the two phases have close values of the lattice parameter: 0.834 nm ($\gamma\text{-Fe}_2\text{O}_3$) versus 0.839 nm (Fe_3O_4) [4]. On the other hand, these iron oxide phases are well distinguished by the method of Raman spectroscopy. According to

Verbe [5], single-crystalline Fe_3O_4 is characterized by the following active Raman modes: A_{1g} ($\omega = 669 \text{ cm}^{-1}$), E_g ($\omega = 410 \text{ cm}^{-1}$), and $2T_{2g}$ (T_{2g}^1 , T_{2g}^2 , and T_{2g}^3 with $\omega = 193, 540$, and 300 cm^{-1} , respectively). In contrast, the Raman spectrum of $\gamma\text{-Fe}_2\text{O}_3$ exhibits three active modes at frequencies 350, 500, and 700 cm^{-1} [6]. For this reason, we have identified the phase compositions of obtained iron oxide films by Raman spectroscopy.

The Raman spectra in the spectral range of 200–800 cm^{-1} were measured on an NTEGRA Spectra instrument (NT-MDT) using Ar^+ laser excitation at a wavelength of 488 nm. The laser radiation power on the samples surface could be changed using a neutral optical filter of variable density. The laser spot size on the sample surface amounted to $0.5 \mu\text{m}$ and the exposure time was $30 \times 10 \text{ s}$. All measurements were performed in ambient air at room temperature.

Figure 2 shows the typical Raman spectra of iron oxide films with various thicknesses synthesized on substrates covered by thin (series 1) and thick (series 2) silicon oxide layers. The measurements for both series 1 (Fig. 2a) and series 2 (Fig. 2b) were performed at a laser power of $P = 8 \text{ mW}$. The spectra of samples in series 1 display peaks at 303 and 520 cm^{-1} belonging to the silicon substrate and an intense peak at 669 cm^{-1} that is characteristic of Fe_3O_4 . Figure 2a shows that an increase in the thickness of a Fe_3O_4 film leads to growth in intensity of the A_{1g} mode peak and the appearance of a shoulder at $\omega = 540 \text{ cm}^{-1}$ for the peak of silicon. The E_g , T_{2g}^1 , and T_{2g}^3 modes of magnetite were not observed because of their relatively low intensity and overlap with the characteristic modes of silicon. Raman modes corresponding to $\gamma\text{-Fe}_2\text{O}_3$ were also not found.

For the samples of series 2, only the Raman spectrum of a sample with the minimum thickness of the iron oxide film corresponds to magnetite (Fig. 2b), whereas the spectra of 66- and 96-nm-thick films exhibit a set of intense characteristic peaks of the $\alpha\text{-Fe}_2\text{O}_3$ phase with frequencies of 217, 280, and 392 cm^{-1} [7], the positions of which are shifted toward lower wavenumbers. Peaks of Raman modes of the $\gamma\text{-Fe}_2\text{O}_3$ phase were absent.

Taking into account that (i) the films of iron oxide on both thin and thick SiO_2 layers were formed simultaneously (i.e., under identical conditions) and (ii) the RHEED patterns in both series were also identical and assigned to magnetite, heating of films above 400°C by laser radiation [8], rather than a change in the mechanism of iron oxide growth, is a probable reason for the appearance of $\alpha\text{-Fe}_2\text{O}_3$. In this case, a thicker SiO_2 layer with a relatively low thermal conductivity ($\sim 1.4 \text{ W m}^{-1} \text{ K}^{-1}$ [9]) is an obstacle for the removal of evolved heat. In contrast, Fe_3O_4 films formed on a thin SiO_2 layer are not heated to the indicated high temper-

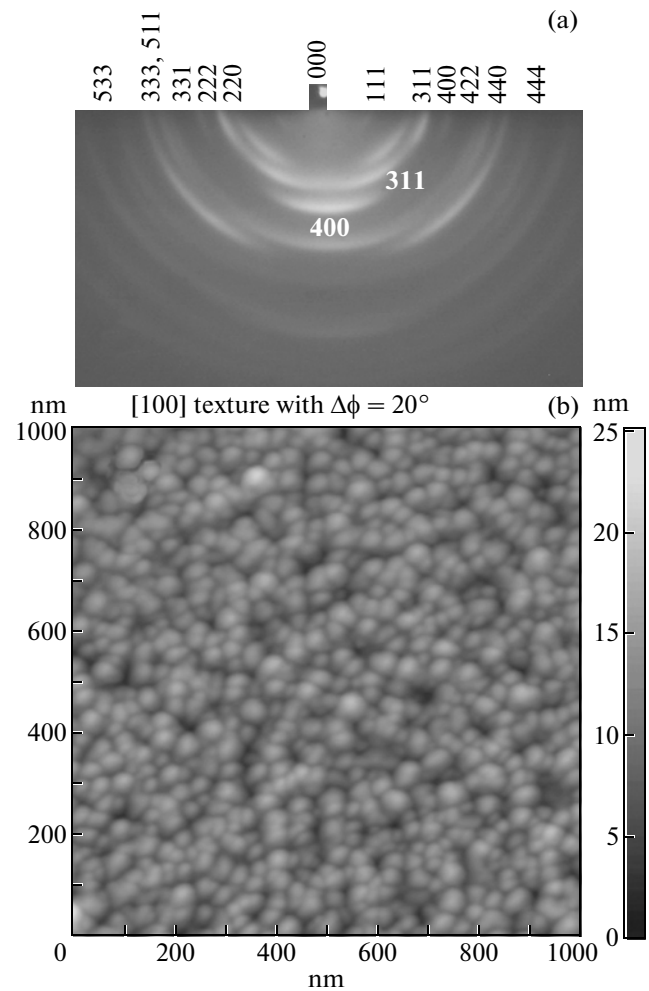


Fig. 1. Typical (a) RHEED pattern and (b) AFM image of a Fe_3O_4 film on $\text{SiO}_2/\text{Si}(001)$ substrate.

ature because the SiO_2/Si interface has rather insignificant heat resistance and the thermal conductivity of silicon is relatively high ($\sim 150 \text{ W m}^{-1} \text{ K}^{-1}$ [9]). Another possible factor decreasing the laser-induced thermal effect in samples with 33-nm-thick Fe_3O_4 films in samples of series 2 may be the discontinuous character of these films (Fig. 1b).

The hypothesis concerning the heating of Fe_3O_4 films by laser radiation was verified on a sample of series 2 with a 66-nm-thick iron oxide film by measuring the Raman spectra at laser radiation powers of 0.8 and 8 mW (Fig. 3). As can be seen, the Raman spectrum recorded with excitation at a laser power of 0.8 mW (Fig. 3, curve 1) almost coincides with the spectrum of a film with $d_{\text{Fe}_3\text{O}_4} = 66 \text{ nm}$ in series 1 (Fig. 2a, curve 2). The measurements of Raman spectra at a laser power of 8 mW leads to the appearance of intense peaks at 216, 281, and 392 cm^{-1} (Fig. 3, curve 2). The observed shift ($\sim 10 \text{ cm}^{-1}$) in the positions of maxima of the characteristic Raman peaks is

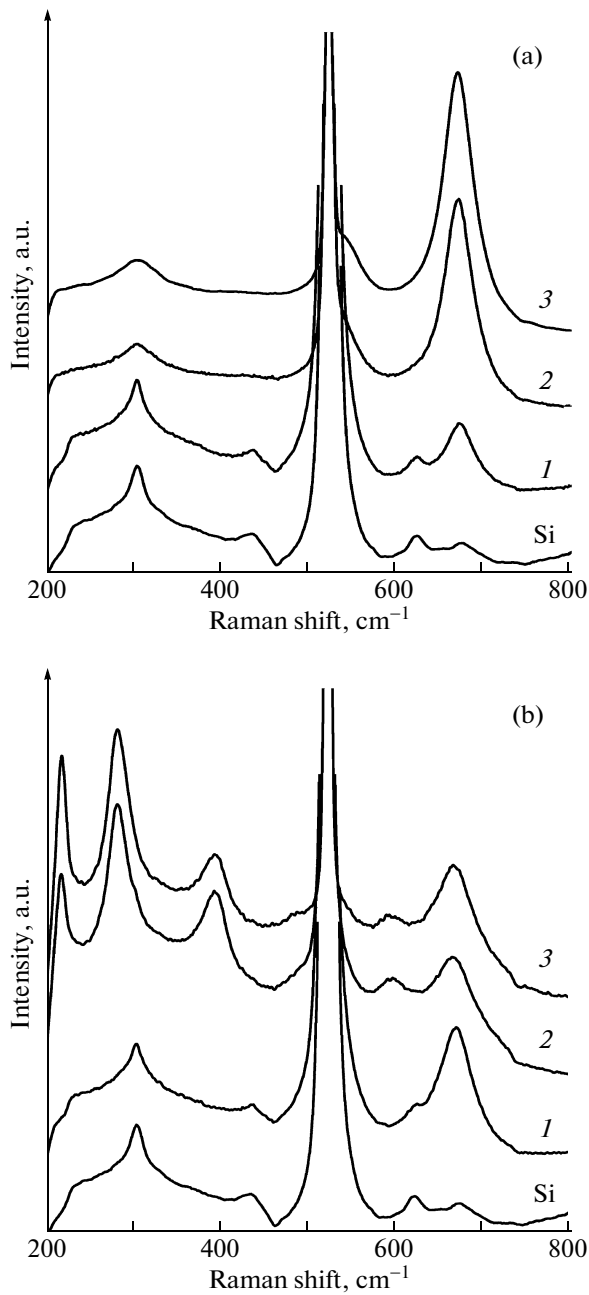


Fig. 2. Raman spectra of silicon (Si) and samples with Fe_3O_4 films of thicknesses (1) 33, (2) 66, and (3) 96 nm formed on (a) thin and (b) thick SiO_2 layers.

also caused by the heating of iron oxide films in the course of measurements of the Raman spectra [10]. The change in the temperature of the sample surface can be estimated using the formula $T = F_0 d \sqrt{\pi} / 2K$, where F_0 is the radiation energy flux density, d is the laser beam diameter, and K is the thermal conductivity. These estimates [11] show that exposure to a laser beam with $P = 8$ mW and $d = 0.25$ μm increases the temperature at the center of the beam spot by $\sim 60^\circ\text{C}$ on the surface of silicon and by $\sim 630^\circ\text{C}$ on the surface

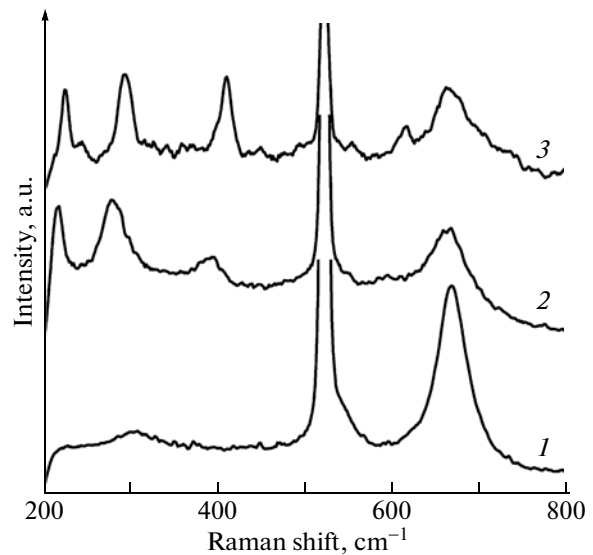


Fig. 3. Raman spectra of samples with 66-nm-thick Fe_3O_4 films formed on a thick SiO_2 layer measured using different powers of probing laser radiation: (1) 0.8 mW; (2) 8 mW; (3) repeated recording at 0.8 mW.

of SiO_2 , which accounts for the appearance of $\alpha\text{-Fe}_2\text{O}_3$. For a repeated measurement of the Raman spectrum at 0.8 mW, the peaks corresponding to $\alpha\text{-Fe}_2\text{O}_3$ were retained, but their positions shifted toward the initial values (Fig. 3, curve 3).

Thus, we have used Raman spectroscopy to study polycrystalline films of magnetite (Fe_3O_4) formed by reactive sputtering of iron in oxygen on silicon substrates covered by thin (1.4 nm) or thick (1200 nm) SiO_2 layers. It is established that measurements of the Raman spectra for magnetite films synthesized on thick SiO_2 buffer layers with low thermal conductivity can lead to the formation of $\alpha\text{-Fe}_2\text{O}_3$ phase due to the laser-induced heating. There exists a minimum thickness of polycrystalline magnetite films at which they do not exhibit such a phase transformation.

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REFERENCES

1. D. L. A. de Faria et al., *J. Raman Spectrosc.* **28**, 873 (1997).
2. O. N. Shebanova and P. Lazor, *J. Raman Spectrosc.* **34**, 845 (2003).
3. V. V. Balashev, V. V. Korobtsov, T. A. Pisarenko, and L. A. Chebotkevich, *Tech. Phys.* **56**, 1501 (2011).

4. R. M. Cornell and U. Schwertmann, *The Iron Oxides: Structure, Properties, Reaction, Occurrences and Uses* (Wiley-VCH, Weinheim, 2003).
5. J. L. Verbe, *Phys. Rev. B* **9**, 5236 (1974).
6. M. Lübke et al., *Surf. Sci.* **604**, 679 (2010).
7. S. J. Oh, D. C. Cook, and H. E. Townsend, *Hyperfine Interact.* **112**, 59 (1998).
8. I. Chamritski and G. Burns, *J. Phys. Chem. B* **109**, 4965 (2005).
9. A. P. Babichev et al., *Physical Quantities (A Reference Book)* (Energoatomizdat, Moscow, 1232) [in Russian].
10. O. N. Shebanova and P. Lazor, *J. Solid State Chem.* **174**, 424 (2003).
11. J. F. Ready, *Effects of High-Power Laser Radiation* (Academic Press, New York, 1971).

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