Lattice deformation in epitaxial Fe_3O_4 films on MgO substrate studied by polarized Raman spectroscopy*

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The lattice structures of epitaxial Fe_3O_4 films deposited on MgO were studied systematically using polarized Raman spectroscopy as a function of film thickness, where interesting phenomena were observed. Firstly, the spectral conflict to the Raman selection rules (RSRs) was observed under cross sectional configuration, which can be attributed to the tetragonal deformation in the growth direction due to the lattice mismatch between Fe_3O_4 and MgO. Secondly, the blue-shift and broadening of Raman peaks evidenced the decrease of the tensile strain in Fe_3O_4 film with decreased thickness. Thirdly, distinct from the other Raman modes, the lowest T_{2g} mode exhibited asymmetric lineshape, which can be interpreted using the spatial correlation model. The increased correlation length introduced in the model can well explain the enhanced peak asymmetry feature with decreasing thickness. These results provide useful information for understanding the lattice structure of epitaxial Fe_3O_4 film.

Keywords: polarized Raman scattering, Fe_3O_4 film, tetragonal deformation, spatial correlation model

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1. Introduction

Iron oxide magnetite (Fe_3O_4), a half-metallic ferromagnet with large spin polarization and high Curie temperature of 858 K, has attracted much attention owing to its intriguing physical properties and potential applications in spintronic devices.^[1-6] The further applications on devices closely rely on the physical properties of Fe_3O_4 films that depend on the type of substrates, thickness and deposition conditions. As we know, the epitaxial Fe_3O_4 films have been grown on a variety of single crystal substrates, e. g. MgO, $\alpha\text{-Al}_2\text{O}_3$, ZnO, Si, and GaAs, by using different methods such as molecular beam epitaxy (MBE), sputtering, and pulse laser

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deposition (PLD).^[3,7-9] Among the substrates mentioned above, MgO is one of the most frequently used because it has a nearly perfect lattice match with Fe₃O₄. The lattice constant of MgO is 4.213 Å, which is nearly the half of Fe₃O₄ (8.3967 Å). Although the lattice mismatch in Fe₃O₄ film on MgO (Fe₃O₄/MgO) is only +0.3%, the prominent changes took place in the magnetic and electronic properties of Fe₃O₄/MgO films due to the tensile strain imposed by MgO substrate.^[10,11] It is already reported that the magnetic properties of Fe₃O₄ films changes significantly with the decreased thickness, which is closely related with the existence of antiphase boundaries (APBs).^[12-14] Revealing the strain effects from substrate and the changes of microstructure with thickness would provide useful information for understanding the magnetic properties of Fe₃O₄ films.

Raman spectroscopy is a powerful tool to probe the microstructure of thin films and its relationship with other physical properties of oxides.^[15,16] In past decades, Raman spectroscopy has been widely employed to study the structure of Fe₃O₄ films.^[8,9,17] Tiwari *et al.* have demonstrated that Raman spectroscopy is a tool to evaluate the APBs in Fe₃O₄ films.^[9] Kumar *et al.* have employed Raman spectroscopy to study the spin-phonon coupling in Fe₃O₄ films at Verwey temperature.^[18] However, most researches were carried by using non-polarized Raman spectroscopy, while polarized Raman study of Fe₃O₄/MgO was rarely reported. With the help of polarized Raman scattering, the symmetry of Raman peaks can be assigned, and the crystallinity and orientation of film can be identified. What is more, the overlapped Raman peaks can be isolated, promising feasible peak fitting and further analysis.

In this work, Fe₃O₄ films were studied systematically as a function of film thickness by polarized Raman spectroscopy. Discrepancy to Raman selection rules (RSRs) observed in the cross sectional geometry was attributed to the tetragonal deformation in the growth direction due to the lattice mismatch between Fe₃O₄ and MgO. Raman peaks were fitted with different numerical functions and got a deeper insight into thickness effects on the structure of Fe₃O₄ film.

2. Experimental details

Epitaxial Fe₃O₄ films were deposited on MgO single crystal substrates using reactive magnetron sputtering. The details of deposition were reported elsewhere.^[19] In this work, Fe₃O₄ films with thickness of 27, 50, 85, 170, 217 nm are used for the Raman study. The epitaxial properties of Fe₃O₄ films have been demonstrated previously using theta-2theta (θ -2 θ) and Φ -scan x-ray diffraction (XRD) experiments. Raman spectra were collected under backscattering geometry using a confocal micro-Raman spectrometer (Horiba/Jobin Yvon Aramis) with a 473 nm laser source. The laser power on the film surface was less than 0.5 mW to prevent laser-induced heating effect on films. Two types of backscattering configurations, including normal and cross sectional scattering configurations were employed in the Raman measurements. The schematic diagrams of these two Raman measurement configurations are shown in Fig. 1, in which the X, Y and Z-axes were the laboratory coordinates. The x and y axes of Fe₃O₄ film were along the [100] and [010] directions of MgO substrate, while the z -axis was the growth direction of the film. In the normal

scattering configuration as illustrated in Fig. 1(a), the x , y and z -axes of films parallel respectively with X , Y and Z -axes. On the other hand, in the cross sectional scattering configuration, the x , y and z -axes of films are respectively along Z , Y and X -axes. As displayed in Fig. 1(b), the incident light propagates along the Z -axis, which corresponds to the x -axis of Fe_3O_4 film. So the incident polarization (P_i) parallel with the z -axis, and the scattered polarization can be along the y (or z)-axes. Cross sectional Raman scattering can provide more information about the stress distribution, domain structure and the crystalline orientation of thin films.^[20-22]

FIG. 1. Schematic drafts for (a) normal and (b) cross sectional scattering configurations. The polarization direction of incident laser is along the X -axis, while the polarization direction of scattered is along X - and Y -axes for parallel (VV) and crossed (VH) scattering geometries, respectively.

3. Results and Discussion

Bulk Fe_3O_4 has a cubic inverse spinel structure with space group $O_h^7(Fd3m)$, which gives rise to five Raman-active modes, $\Gamma_R = A_{1g} + E_g + 3T_{2g}$. Normally, only four peaks are observed in the Raman spectra of Fe_3O_4 , as revealed in previous studies.^[8,9,17] Fig. 2 displays the polarized Raman spectra of 217-nm thick Fe_3O_4 film collected in different scattering configurations. According to the RSRs,^[23] A_{1g} and E_g modes only appear in the VV scattering geometry under the normal scattering configuration, in which P_i is along X -axis as shown in Fig. 1(a), while the T_{2g} modes show up in the VH scattering geometry. In Fig. 2(a), the Raman modes comply with the RSRs in normal backscattering configuration. The peaks at around 307 and 665 cm^{-1} are respectively assigned as the E_g and A_{1g} modes, while the peaks at 193 and 535 cm^{-1} are attributed as the T_{2g} modes.^[17,18,22] The Raman spectra of other thinner films share the similar polarization dependences. The well agreement between our results and RSRs suggests the highly epitaxial characteristics of Fe_3O_4 films. A very weak peak can be seen at A_{1g} position in the VH geometry, which can be attributed to the lattice defects in Fe_3O_4 film. Although Fe_3O_4 films were epitaxially grown, small amount of defects, such as dislocations and vacancies, cannot be excluded. It has been demonstrated by many researchers that the antiphase boundaries (APBs) is the main lattice defects that play a key role in the anomaly properties of epitaxial Fe_3O_4 films.^[11,24,25] APBs are related to the lattice relaxation, formed at the junction of neighboring grains.^[13,26]

FIG. 2. Polarized Raman spectra of Fe_3O_4 film of 217 nm obtained in the normal [(a) and (b)] and cross sectional [(c) and (d)] scattering configuration.

In order to further study the microstructure in Fe_3O_4 films, the cross sectional Raman scattering was carried out. In Fig. 2(c), the remarkable spectral features are observed when P_i parallels with z -axis. The $T_{2g}^{(3)}$ mode appears in the VV geometry which is in contract with the results obtained in the normal Raman scattering configuration. Furthermore, the polarized spectra resemble the features of the normal scattering configuration as the incident polarization is along y -axis (not shown here). The A_{1g} and E_g modes appear in the VV geometry, while the T_{2g} modes are observed in the VH geometry. Such spectral divergence between Figs. 2(a) and 2(c) cannot be attributed to the lattice defects in the films. If the leakage of $T_{2g}^{(3)}$ mode comes from lattice defects, $T_{2g}^{(3)}$ mode should be seen in the VV geometry all the time when the incident polarization parallels with three axes of the film. However, it only turns out when the incident polarization parallels with z -axis. As discussed previously, the crystalline axis $a < b = c$ in Fe_3O_4 films on MgO substrates. The in-plane axes are equal, so the polarized Raman spectra in normal scattering configuration are identical while rotating the incident polarization from x -axis to y -axis. In contrast, the out-of-plane axis is compressed and shorter than the in-plane axes, giving rise to a tetragonal deformation in Fe_3O_4 films. As the lattice constant of Fe_3O_4 is a little smaller than the double of the MgO lattice constant, the in-plane axes of Fe_3O_4 films are elongated in two directions due to the tensile stress in the film. The tetragonal deformation does not only include the elongated in-plane axes, but can also induce the lattice dislocations in the out-of-plane axis in order to release internal stress in the film. The orientation of crystalline axis for Fe_3O_4 film is not strictly along the $\langle 100 \rangle$ directions of the MgO substrate due to the existence of APBs.^[13] Luysberg et al. have demonstrated that the presence of APBs are associated with the formation of misfits dislocations with partial Burgers vectors.^[27] As demonstrated by the selected-area electron diffraction (SAED) patterns, the charge ordering of B-site Fe atoms exists in

the epitaxial Fe_3O_4 films.^[19] The $T_{2g}^{(3)}$ mode originates from the asymmetric bends of oxygen ions with respect to Fe ion, so that it is sensitive to the strain deformation along the crystalline axes.^[28] The tetragonal deformation in film would contribute to the conflicts to RSRs for the $T_{2g}^{(3)}$ mode.^[29] As presented in Fig. 2(b), the $T_{2g}^{(3)}$ mode arises in the VV geometry after rotating the polarization by 45° under the normal incident configuration. According to the RSRs, $T_{2g}^{(3)}$ mode is not zero when the incident and scattered polarizations are parallel to the $[110]$ direction. The VV spectra in the cross-sectional configuration (Fig. 2(c)) exhibits the obvious similarity to the VV spectra under 45° polarization geometry in Fig. 2(b), suggesting the existence of nano-sized areas in which the lattice dislocations are along the $\langle 110 \rangle$ directions. Therefore, the presence of $T_{2g}^{(3)}$ mode in the VV spectra in the cross sectional configuration undoubtedly demonstrated the existence of APBs.

FIG. 3. Thickness dependent peak position and bandwidth (FWHM) of E_g , $T_{2g}^{(2)}$ and A_{1g} modes, respectively.

In order to get a clear insight into the evolution of Raman peaks as a function of film thickness, the Raman spectra were deconvoluted using Lorentz/Gaussian mixed function. Figs. 3(a)-(c) show the thickness dependent peak positions of E_g , $T_{2g}^{(3)}$ and A_{1g} modes. Taking the A_{1g} mode as an example, it shifts from 671.7 to 668 cm^{-1} quickly when the film thickness increases from 27 to 85 nm ($6.4 \times 10^{-2} \text{ cm}^{-1}/\text{nm}$). Similar phenomenon was observed by Tiwari *et al.* in the Fe_3O_4 films thinner than 150 nm.^[9] Then, the peak position of A_{1g} mode varies slowly, with a rate of $5.8 \times 10^{-3} \text{ cm}^{-1}/\text{nm}$, for a thicker film, as exhibited in Fig. 3(c). The other two peaks shift following the same trace as that of A_{1g} mode. As presented in Figs. 3(d)-(f), similar as peak position, bandwidth decreases while film thickness increases from 27 to 85 nm, then keeps at a constant for thicker films. As we know, bandwidth is the reciprocal of phonon lifetime, which decreases while lattice defects increases, so that the broadening of Raman peaks is associated with the increased defects in lattice.^[30, 31] As we know, more lattice defects emerge as a result of the increased density of APBs

while the film thickness is decreasing.^[27,29,32] Thus, the broadening of Raman peaks of Fe_3O_4 films can be attributed to the increased APBs when the film thickness decreases. It is accepted that the lattice relaxation takes place in order to release internal stress while the film thickness increases.^[27,29] At the same time, the grain size in film becomes larger as a result of decreased APBs.^[13] From the Raman spectra, one can see the improvement of Raman signal, such as bandwidth shrinking and frequency softening, as presented in Fig. 3.

Taking a close look at the fitting curves of Raman peaks, it is interesting to find that the lineshapes of Raman peaks are different. One can see that the $T_{2g}^{(1)}$ mode exhibits an asymmetric lineshape with a tail at low frequency, as presented in Fig. 4(a). In sharp contrast, as shown in Figs. 4(b)-(d), the E_g , $T_{2g}^{(3)}$ and A_{1g} modes show the symmetric lineshape, which can be well fitted by Lorentz function, implying the good crystalline quality of Fe_3O_4 films. The asymmetric lineshape comes from the lattice disorder effects, which has been observed in some oxides and semiconductor films.^[33-35] In the ideal single crystal, only phonons near the center of Brillouin zone ($q \sim 0$) contributed to the Raman spectrum. On the other hand, the disorders in film result in the breaking of the translational symmetry, leading to the contribution of $q \neq 0$ phonons to Raman lineshape, which is so-called finite-size effect. Since the Fe_3O_4 films in our hand are highly oriented, the lattice defects are low. As we know, the defects in Fe_3O_4 films mainly from the location shift of Fe ions.^[36] This kind of defects mainly affect the low frequency Raman peaks, so that the $T_{2g}^{(1)}$ mode exhibits an asymmetric lineshape. Furthermore, these high frequency E_g , $T_{2g}^{(2)}$ and A_{1g} modes originating from with Fe-O vibrations, keep the symmetric Lorentz lineshape. The asymmetric lineshape of Raman modes can be described by a spatial correlation model. The assumption of a Gaussian factor $\exp(-q^2 L^2)$, where L is the diameter of the correlation region, is employed in the spectra fitting of mode $T_{2g}^{(1)}$.^[33-35]

The Raman intensity $I(\omega)$ at a frequency ω can be written as

$$I(\omega) \propto \int_0^1 \exp\left(-\frac{q^2 L^2}{4}\right) \frac{4\pi q^2 d^3 q}{[\omega - \omega(q)]^2 + \left(\frac{\gamma(q)}{2}\right)^2},$$

where q is expressed in units of $2\pi/a$, and L is in the unit of a , with a being the lattice constant. L is the correlation length, which reflects the degree of disorder in the film. $\gamma(q)$ is the linewidth of phonon, which is independent on q . For the dispersion curve $\omega(q)$, it can be expressed as $\omega(q) = \omega_0 - Bq^2$,^[34] with $\omega_0 = 196 \text{ cm}^{-1}$ and $B = 29.9 \text{ cm}^{-1}$.

FIG. 4. Different Raman modes and their corresponding numerically fitted curves. Black circles represent the experimental results, the red lines are fitting results.

As shown in Fig. 5(a), the bandwidth increases while film thickness is decreasing, especially for the films thinner than 100 nm. The broadened bandwidth clearly evidences more lattice defects in thinner Fe_3O_4 films. Interestingly, one can see in Fig. 5(b) that L increases with decreasing thickness, following the same trace of bandwidth. As we know, L is the correlation length, which can be used to represent the grain size in film.^[33-35] The results shown in Fig. 5(b) suggest that the correlation length (or grain size) increasing with decreasing film thickness. It has been reported that the asymmetry feature becomes smaller with increasing correlation length. The asymmetry of $T_{2g}^{(1)}$ is calculated using the ratio of half-widths at half maximum of low and high frequency side (Γ_l / Γ_h). As shown in the inset of Fig. 5(b), the asymmetric ratio of $T_{2g}^{(1)}$ becomes smaller in a thinner film, which agrees well with the prediction from the variation of L . It has been demonstrated that the density of APBs in a thin Fe_3O_4 film is higher than that in a thick Fe_3O_4 film. Consequently, the grain size in a thinner Fe_3O_4 film is thought to be smaller. However, as shown in Fig. 5(b), grain size increases in thin Fe_3O_4 film. As we know, L is physically the correlation length for Raman phonons, in which phonons can propagate freely. Our results suggest that APBs are just a kind of lattice defect rather than crystalline boundaries, at least phonons take the adjacent antiphase areas as a whole for propagation.

FIG. 5. (a) bandwidth and (b) correlation length for $T_{2g}^{(1)}$ mode as a function of thickness. The insert figure shows the thickness dependence of the ratio of half-widths at half maximum of low and high frequency side (Γ_l / Γ_h).

4. Conclusion

In this work, polarized Raman spectroscopy was employed to investigate the microstructure of Fe_3O_4 films as a function of film thickness. The Raman spectra in cross sectional configuration clearly imply the tetragonal deformation in the growth direction due to the lattice mismatch between Fe_3O_4 film and MgO substrate. The Raman peak of modes shifting to a higher frequency indicate the decrease of tensile strain with the decreased film thickness, while the broadened peaks imply the increased lattice defects due to the increased APBs density. Moreover, the lowest T_{2g} mode exhibits an asymmetric lineshape, which can be used to monitor the grain size in Fe_3O_4 film. Our results provide a deeper insight into the lattice structure of Fe_3O_4 films on MgO substrates, which are expected to be helpful for the preparation of Fe_3O_4 films and further applications in spintronic devices.

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