Surface Magnetism during Oxygen-Aided Fe Homoepitaxy

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Magnetization-induced optical surface second harmonic generation (SHG) in the longitudinal geometry was used to study magnetism on the $p(1 \times 1)$O/Fe(001) surface during a layer-by-layer Fe growth with surfactant oxygen. Considerable one-monolayer oscillations were observed. Minima of the magnetization-induced contributions to the second order dielectric susceptibility were detected at half-filled monolayers. These contributions were accessed either by measuring a purely magnetic SHG yield, or indirectly from the magnetization dependence of the overall SHG signal, both providing consistent results. The origin of the oscillatory surface magnetism is consistent with the expected oscillating oxygen induced relaxation due to the surface Fe islands.

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It is now well accepted that magnetic properties of ultrathin films, surfaces, and interfaces differ considerably from those of bulk crystals [1]. For example, magnetic moments at flat crystal surfaces are enhanced [2]. In Fe(001) this amounts to about 30% enhancement with respect to the bcc bulk [3–6]. Reducing the coordination of surface atoms by introducing steps, islands, or adatoms can further modify the surface magnetic moments. For the Fe(001) surfaces, first principles calculations predict for step atoms either an enhancement of the magnetic moments by 6% [5], no change [7], or a decrease by 2% [6]. It may be possible to detect such small step-related effects during the epitaxial growth of metals, or they may be overwhelmed by other effects. These could be, for example, island-induced surface relaxation resulting in size-dependent changes of local lattice spacings [8]. There have been no reports estimating relative impact of such effects on magnetism.

Up to now only two experiments [9,10] addressed the changes in surface magnetization during repeated cycles of island nucleation, growth, and coalescence in the layer-by-layer film growth. Both studies found one-monolayer periodic oscillations of the magnetic signal but with an opposite phase. The magnetization-induced surface second harmonic generation (SHG) [11,12] measurements on fcc Co films grown on Cu(001) [9] have shown local maxima in the signal for half-filled monolayers, in accordance with a theoretical prediction [13]. By contrast, experiments employing the spin polarized metastable deexcitation spectroscopy (SPMDS) [14,15] applied on a surfactant-aided growth of Fe on a $p(1 \times 1)$O/Fe(001) surface [10] have shown local minima for the half-filled monolayers.

These studies used surface sensitive techniques, extracting the magnetic information via indirect magnetization-dependent effects. It is then an open question if the half-period shift of the oscillations for the two surfaces is due to their different physical nature or due to an oversimplified interpretation of the experiment. To resolve this contradiction it is important to select one well-defined system and compare these two different techniques.

In this Letter we address this question by performing magnetic SHG measurements on the $p(1 \times 1)$O/Fe(001) surfaces prepared on MgO(001) substrates. We used the direct measurements of purely magnetic SHG intensity for the monitoring of the systematic development of surface magnetism during film growth for the first time. We demonstrate that the pure magnetic SHG results are identical to those obtained in geometries involving also nonmagnetic contributions to the SHG signal. The agreement with the SPMDS data [10] settles the issue of the morphology dependent magnetic properties of the $p(1 \times 1)$O/Fe(001) surface. The present surface morphology analysis provides in addition important structural data for interpretation of the oscillatory surface magnetism. We conclude that the surface morphology in this system controls magnetism mainly by changing strain/stress conditions of the top O/Fe monolayers while the step edges play a minor role.

The $p(1 \times 1)$O/Fe/MgO(001) system offers several advantages. The $p(1 \times 1)$O/Fe(001) surface is not strained due to a lattice misfit and is chemically stable. Relatively thick Fe buffer layers (> 50 nm) obviate any buried interface contributions to SHG [unavoidable for the ultrathin Co on Cu(001) [9]]. The surfactant effect of oxygen [16] results in a complete reproducibility of growth after deposition and subsequent annealing [17].

The SHG experiments were performed in a molecular beam epitaxy apparatus (base pressure $<7 \times 10^{-11}$ mbar). The $p(1 \times 1)$O/Fe(001) surfaces were prepared as follows: Fe films ≈ 50 nm thick were deposited at a pressure $<10^{-10}$ mbar on MgO(001) substrates (polished, annealed in O_2 and after loading into the chamber flashed at $T = 950$ K), with T elevated from 300 to 420 K during the

deposition. Subsequent annealing at 870 K for 30 minutes produced a clean and ordered Fe(001) surface as verified by the medium energy electron diffraction (MEED). This surface was then exposed to ≈ 20 L O_2 (1 langmuir $= 10^{-6}$ Torr s) and annealed at 870 K for 30 min, which resulted in a formation of the $p(1 \times 1)$ oxygen adlayer on the Fe(001) surface [18].

The magnetic SHG was measured in longitudinal geometry (i.e., with the magnetization vector in the film and the optical planes) with ultrashort pulses from a self-made Ti:sapphire laser oscillator (pulse length <10 fs, central wavelength $\lambda \approx 800$ nm, pulse energy ≈ 8 nJ). The experimental setup is depicted in Fig. 1. After setting the incident linear polarization by an achromatic $\lambda/2$ phase plate, the laser beam was focused to a spot ≈ 20 μm lateral size on the surface at 43° angle of incidence. A local surface heating was effectively avoided by raster scanning a surface area of 60 μm $\times$ 60 μm and by rejecting 90% of pulses with a chopper, yielding a very stable SHG signal. The SHG photons entered an analyzer, oriented at an angle α from the s direction, and were detected by photon counting electronics. The Fe film was magnetized along the Fe[100] easy axis by a pulsed field with reversible polarity. Since the magnetization loops were square, the magnetic SHG intensities could be acquired in remanence. The SHG signals were normalized by the SHG reference signal from quartz.

The magnetic SHG signals in the longitudinal geometry are described in the electromagnetic theory using a second order susceptibility tensor $\overleftrightarrow{\chi}^{(2)}_{2\omega}$. For a centrosymmetric solid the SHG fields are, in the electric dipole approximation, generated only at the surface [19]. For a cubic (001) magnetic surface $\overleftrightarrow{\chi}^{(2)}_{2\omega}$ is described, for example, in [20]. Individual tensor elements characterize different interaction channels excited by the incident linear polarization which we indicate as p_{in}, s_{in} (see Fig. 1) or sp_{in} (polarized at $\alpha = 45°$ to s_{in}). The outgoing SHG field has p (i.e., p_{out}) and s (i.e., s_{out}) components [21].

For a given optical geometry one introduces effective susceptibilities which are linear combinations of the tensor elements with an odd symmetry with respect to the magnetization reversal (indicated as χ^{odd}_{eff}) and with an even symmetry (i.e., χ^{even}_{eff}) [21]. Since the inequality $|\chi^{odd}_{eff}|^2 \ll |\chi^{even}_{eff}|^2$ is frequently fulfilled, the expressions for the average SHG intensity I and the magnetic asymmetry A are then given by

$$I(2\omega) = \frac{I^+ + I^-}{2} \propto |\chi^{even}_{eff}|^2 + |\chi^{odd}_{eff}|^2 \approx |\chi^{even}_{eff}|^2, \quad (1)$$

$$A = \frac{I^+ - I^-}{I^+ + I^-} \propto \frac{|\chi^{odd}_{eff}||\chi^{even}_{eff}|}{|\chi^{odd}_{eff}|^2 + |\chi^{even}_{eff}|^2} \cos\Psi \approx \frac{|\chi^{odd}_{eff}|}{|\chi^{even}_{eff}|} \cos\Psi, \quad (2)$$

where Ψ is the phase difference between χ^{odd}_{eff} and χ^{even}_{eff}, and I^+ and I^- are the SHG intensities for the opposite orientations of magnetization.

The thickness-dependent SHG experiments were carried out at 300 K by repeating cycles of depositing a fraction of a monolayer (ML) (at 0.25 ML/ min), and simultaneously measuring the SHG and the specular MEED intensity signals. The high stability of the surface was manifested by a good agreement of the MEED curves which were recorded for stepwise and ''continuous'' depositions.

Typical MEED curves for continuous deposition of Fe are plotted in Fig. 2 for the $p(1 \times 1)$O/Fe(001) and the clean Fe(001) surfaces. The oscillations for the $p(1 \times 1)$O/Fe(001) system confirm the surfactant effect of oxygen [16]. Our scanning tunneling microscopy (STM) measurements gave a lateral size of islands on this system of ≈ 2.5 nm for 0.5 ML of deposited Fe (inset of Fig. 2), and for several successive half-filled monolayers.

As for the SHG, only if the oscillations of χ^{odd}_{eff} are observed irrespective of the optical measurement geometry (involving different odd tensor elements of $\overleftrightarrow{\chi}^{(2)}_{2\omega}$), one can conclude that the surface magnetization is periodically changing during the layer-by-layer growth.

In the p_{in}/s_{out} ($\alpha = 0°$) arrangement $\chi^{even}_{eff} = 0$ and only the tensor elements odd in magnetization, χ_{yxx} and χ_{yzz},

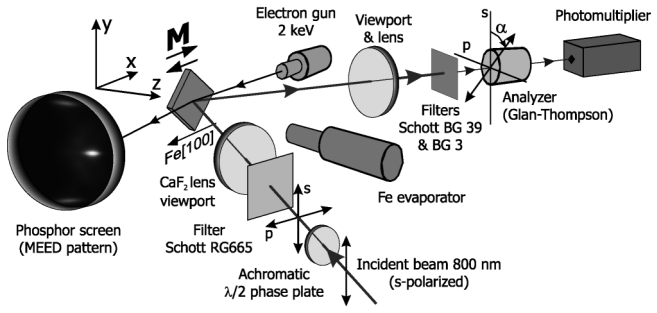

FIG. 1. Schematic drawing of the experimental setup and the geometry employed for the magnetic SHG measurements.

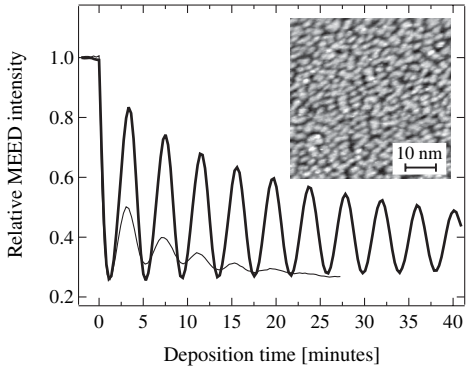

FIG. 2. Specular MEED intensity as a function of deposition time on the annealed surfaces $p(1 \times 1)$O/Fe(001)—thick line, and Fe(001)—thin line, at 300 K. Inset: an STM image of the $p(1 \times 1)$O/Fe(001) surface after deposition of 0.5 ML Fe.

should contribute. According to Eq. (1) the SHG intensity is $I \propto |\chi_{\mathrm{eff}}^{\mathrm{odd}}|^2$. The square root of the intensity is therefore proportional to $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|$. It thus gives *a direct measurement of the magnetization-induced SHG*, while the SHG asymmetry A should be zero by definition [Eq. (2)]. The measured $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|$ in the p_{in}/s_{out} geometry as a function of the deposited Fe thickness is displayed in Fig. 3. It exhibits clear one-monolayer periodic oscillations above 0.5 ML, with minima for the half-filled monolayers. In the experiment a small asymmetry A appears due to thermal drifts of the apparatus and because of a large slope of A close to $\alpha = 0$ (inset of Fig. 3). It was found that the small A does not affect the experimentally measured normalized $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|$ quantity.

In the other "conventional" p_{in}/sp_{out} configuration ($\alpha = 45°$) the even tensor elements χ_{zxx}, χ_{zzz}, χ_{xxz} also contribute in addition to the odd ones (χ_{yxx}, χ_{yzz}). This leads to a large amplification (about 100 ×) of the SHG signal. The mean SHG intensity I and the asymmetry A as a function of the deposited Fe thickness are plotted in the upper panel of Fig. 4. The SHG asymmetry shows periodic oscillations in phase with the p_{in}/s_{out} case while the mean SHG intensity I initially increases and then oscillates with an opposite phase. This is well explained by a periodic creation of islands. Since $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|^2/|\chi_{\mathrm{eff}}^{\mathrm{even}}|^2 < 0.01$, Eqs. (1) and (2) provide $A\sqrt{I} \propto |\chi_{\mathrm{eff}}^{\mathrm{odd}}|\cos\Psi$. The calculated $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|\cos\Psi$ quantity, still showing well-defined oscillations in phase with the p_{in}/s_{out} case, is reported in the lower panel of Fig. 4 (open diamonds). In order to confirm the identity of the effects for the p_{in}/s_{out} and the p_{in}/sp_{out} geometries, any oscillatory behavior of the relative phase Ψ has to be excluded. This was accomplished by introducing an additional 90° phase shift between the odd (s_{out}) and the even (p_{out}) SHG components by means of a $\lambda/4$ phase plate placed in front of the analyzer. Results for this optical configuration with the relative phase $\Psi + 90°$ are plotted in the lower panel of Fig. 4 by the solid diamonds. These two measurements yield $\Psi \approx 57°$ (inset of Fig. 4) and exhibit the same variation with the Fe thickness. A small deviation of the two curves for half-filled monolayers may be explained by a slight difference in concentration of the island nucleation centers for two separate measurements. As a result, any notable influence of the relative phase variation can be ruled out.

Identical oscillatory results are also obtained for the sp_{in}/s_{out} geometry addressing the odd elements χ_{yxx}, χ_{yyy}, χ_{yzz} together with the even element χ_{yyz}. Very similar behavior of the $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|\cos\Psi$ quantity is also seen in the sp_{in}/p_{out} geometry addressing the odd elements χ_{xxy}, χ_{zyz} and the even elements χ_{zxx}, χ_{zyy}, χ_{zzz}, χ_{xxz}. Other experiments carried out with $\lambda \approx 400$ nm excitation light provide almost equal results [22], supporting the independence of the oscillatory effect on the optical excitation mechanism. We therefore conclude that the magnetic contributions to the SHG for this system exhibit local minima for the half-filled monolayers.

The relative magnitude of the magnetic signal oscillation is ≈ 10% to 15%. For the present island size and for a 6% magnetic moment change of the island edge atoms [5]

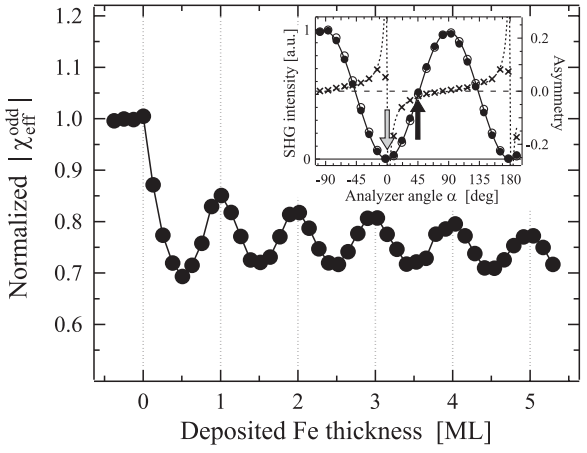

FIG. 3. Normalized $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|$ for the p_{in}/s_{out} geometry as a function of the deposited Fe thickness on the $p(1 \times 1)$O/Fe(001) system. Inset: SHG intensities I^+ (open circles) and I^- (solid circles), and asymmetry A (crosses) as a function of the analyzer angle α for p_{in} fundamental light on the flat $p(1 \times 1)$O/Fe(001) surface. The p_{in}/s_{out} and p_{in}/sp_{out} geometries are indicated, respectively, by the gray and black arrows.

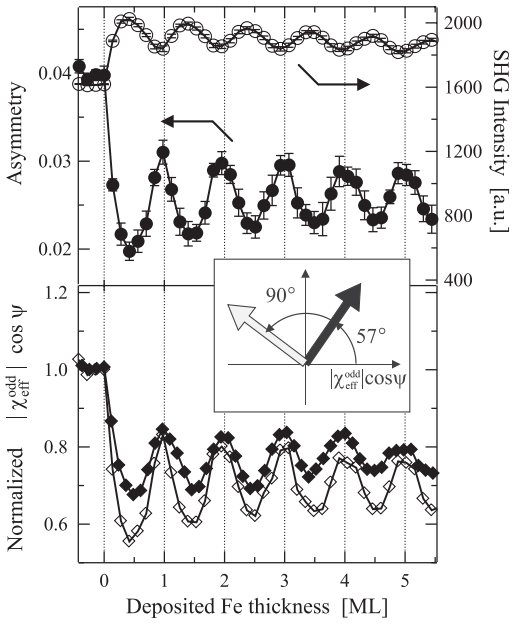

FIG. 4. Upper panel: the SHG intensity (open circles) and asymmetry (solid circles) in the p_{in}/sp_{out} geometry as a function of deposited Fe thickness for the $p(1 \times 1)$O/Fe(001) system. Lower panel: normalized $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|\cos\Psi$ obtained from the data in the upper panel (open diamonds) and from the measurements with a $\lambda/4$ plate in front of the analyzer (solid diamonds). Inset: schematic representation of the effect of the $\lambda/4$ plate on the $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|\cos\Psi$ quantity. See text for details.

the expected oscillation from theory would be only $\approx$ 1.2%. This is much less than observed in our experiments. We should also mention that on clean Fe(001) surfaces no clear oscillations could be resolved for $|\chi_{\mathrm{eff}}^{\mathrm{odd}}|$ despite observing a few damped oscillations in the MEED signals (Fig. 2) and the SHG intensity I. Since for the O/Fe(001) system the average lateral size of the islands at half-filled monolayers is merely 20% smaller than for the homoepitaxy on Fe(001), the large differences in the surface magnetism between the two cases cannot be ascribed to different concentrations of the edge atoms on the surface. We therefore expect that the O-Fe bonds within the surface layer play the key role in determining the observed oscillations for the $p(1 \times 1)$O/Fe(001) system, while the atoms at the step edges can only make a minor (and possibly opposite) contribution. For a flat $p(1 \times 1)$O/Fe(001) surface, an oxygen induced outward relaxation of the topmost Fe atoms (7.5% increase of the surface-to-subsurface Fe-Fe bond length) has been observed [23], and subsequent *ab initio* calculations predicted even much larger (23%) increase [24]. These calculations also found a large sensitivity of the surface Fe magnetic moment upon the O-Fe outward relaxation, with enhancements from 10% to 15% with respect to the clean Fe(001) surface.

Recent studies show that even for homoepitaxial growth on clean surfaces the surface strain for islands is considerably different from atomically flat surfaces [8]. For the O/Fe(001) system with an atomically flat surface the magnetic moments are enhanced with respect to Fe(001). It is plausible that the creation of the islands on O/Fe(001) decreases the outward surface relaxation with respect to the atomically flat surface and consequently also the magnetic moments. The exact mechanism remains an open issue for future studies.

In conclusion, by using the surface SHG we studied magnetism of the $p(1 \times 1)$O/Fe(001) system during the deposition of Fe. These are first systematic measurements of magnetism during the film growth performed in the p_{in}/s_{out} longitudinal geometry where the extremely low SHG intensity is of purely magnetic origin. This obviates an influence of the contributions even in magnetization, which in conventional SHG experiments enhance the SHG intensities but complicate the analysis. Results of these purely magnetic SHG experiments are very coherent with careful measurements in the conventional geometries. This proves a correctness of the purely magnetic SHG measurements. All our experiments show clear one-monolayer periodic oscillations of the surface magnetic response with the local minima for half-filled monolayers. The agreement with the previous SPMDS investigations [10] demonstrates that, despite completely different physical mechanisms, both methods provide compatible results even on the submonolayer level.

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