Periodic Oscillations of the Surface Magnetization during the Growth of Co Films on Cu(001)

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Magnetization induced second harmonic generation is used to investigate the magnetic behavior of fcc Co films growing on Cu(001). An oscillatory behavior of the magnetic asymmetry with one monolayer period is observed. At half filled layers the magnetic signal originating from the surface of the film is enhanced with respect to filled layers. The relation of these results to the magnitude of the magnetic moments of Co atoms at step edges is discussed. [S0031-9007(98)06011-6]

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The influence of the dimensionality on magnetism has been widely studied during the past years. A general trend is that the magnetic moment in ferromagnets like Fe, Co, and Ni is enhanced with reduced coordination number [1]: It was found that the magnetic moment of the free surface is enlarged with respect to that of the bulk [2–5]. From the enhanced moment at rough surfaces on Fe(110) Albrecht *et al.* derived the magnetic moment for atoms at step sites to be larger by roughly $0.5\mu_B$ than for those in the flat surface at $T = 300$ K [6,7]. Recently it has been shown that the morphology of the substrate strongly affects the magnetic anisotropy of the film [8,9]. Weber *et al.* found a one monolayer periodic oscillation in the step induced uniaxial anisotropy [10]. However, no oscillation in the saturation magnetization could be resolved.

During the layer-by-layer growth of ferromagnetic films the average step density periodically oscillates because of the periodic nucleation, growth, and coalescence of islands. For the growth of Co on Cu(001) at room temperature the average island size at half filled layers is of the order of 5 to 10 nm in linear dimensions resulting in a fraction of 10% to 20% of atoms sitting on edge sites [11]. Consequently a periodically oscillating magnetic moment of the topmost layer of the film is expected. To our knowledge this has not yet been observed directly.

It has been shown that magnetization induced second harmonic generation (MSHG) is a highly surface and interface sensitive tool for the investigation of magnetism [12–16]. In materials with inversion symmetry optical second harmonic is generated only at the surface or buried interfaces of these materials within a depth in which the inversion symmetry of the electron density is locally broken. It has been shown now for several cases that this effective interface thickness is of the order of 1 to 2 monolayers (ML) [13,16].

Here we report on the observation of 1 ML period oscillations in the magnetic asymmetry of the MSHG signal from a Co film growing on Cu(001). For a certain geometrical arrangement of sample and optical plane, and polarization of the incident laser light these oscillations appear only in the magnetic signal while the average second harmonic (SH) intensity remains constant giving a strong evidence of periodic changes of the *magnetic* properties during the periodic nucleation, growth, and coalescence of Co islands. The analysis of surface and interface MSHG contributions shows that the magnetization induced component of SHG at the surface is enhanced at half filled layers compared to filled layers.

The Co films were grown on Cu(001) in a molecular beam epitaxy (MBE) apparatus (base pressure $< 4 \times 10^{-11}$ mbar). The Cu substrate was kept at room temperature ($T = 300$ K). p- or s-polarized light of a pulsed Ti:sapphire laser ($\lambda = 840$ nm, 80 fs pulse width) was focused onto the sample in the MBE chamber (spot diameter about 30 μm, pulse energy below 10 nJ). The angle of incidence was $\theta_i = 38°$ and the optical plane was parallel to the $[\bar{1}10]$ azimuthal direction of the Cu crystal. A magnetic field was applied to magnetically saturate the film along directions parallel to the [110] direction, the easy axis of magnetization. The field component parallel to the crystal surface was about 70 Oe. The transversal Kerr geometry was used, i.e., the magnetization direction was perpendicular to the optical plane. Similar to the ordinary Kerr effect in the fundamental light, a change in the SH yield is observed upon reversal of the magnetization. During the growth of the Co film (growth rate about 7 ML/h) the frequency doubled light was recorded for the magnetization in the two opposite directions switched every 5 s. To suppress the background light from the Co oven a shutter in front of the oven was periodically opened and closed ($T_{\mathrm{cycle}} = 20$ s) and the SH intensity was recorded only in the periods of closed shutter.

Figure 1(a) shows the total SH intensity for p-polarized incident light as a function of the Co film thickness d_{Co} for the two opposite magnetization directions. The SH yield from the uncovered Cu surface is much smaller (about 1/30) than that from a Co film. Therefore, at the beginning of the Co deposition the SH intensity increases nearly linearly. The onset of a difference in the SH intensity for ↑ and ↓ magnetization direction at $d_{\mathrm{Co}} = 1.5$ ML indicates the onset of magnetic order.

In Fig. 1(b) the magnetic asymmetry $A = [I_\uparrow(2\omega) - I_\downarrow(2\omega)]/[I_\uparrow(2\omega) + I_\downarrow(2\omega)]$ calculated from the SH intensities in Fig. 1(a) is plotted. For $A \lesssim 0.3$ it is proportional

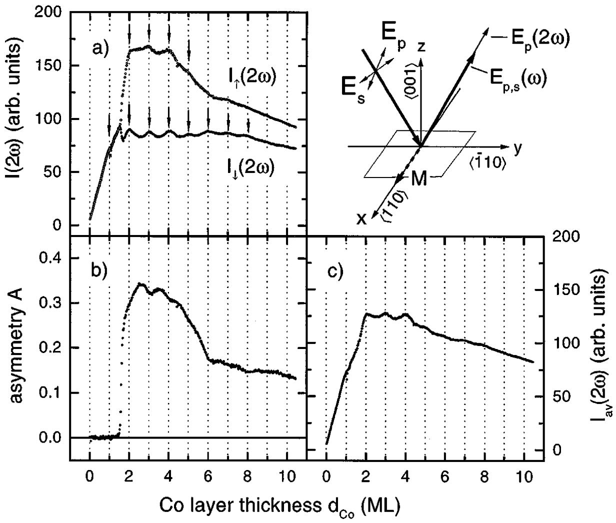

FIG. 1. (a) Measured total SH intensity as a function of the Co film thickness for p-polarized incident light in the transversal Kerr geometry for the magnetization in the ⟨110⟩ direction $[I_\downarrow(2\omega)]$ and in the ⟨$\overline{1}\overline{1}0$⟩ direction $[I_\uparrow(2\omega)]$. The maxima of the 1 ML periodic oscillation in $I_\uparrow(2\omega)$ and $I_\downarrow(2\omega)$ are indicated by arrows. The geometrical setup used in the experiments is drawn in the upper right corner of this figure. (b) The magnetic asymmetry A and (c) the average SH intensity $I_{\text{av}}(2\omega)$ calculated from the SH intensities in (a). The SH intensities were measured during the growth of the Co film.

to the ratio of the magnetic to the nonmagnetic second order susceptibility within 10%. After this fast increase A drops to about 0.15 at 5 to 6 ML. On top of the overall thickness dependence an oscillation with a one monolayer period in the SH intensities $I_\uparrow(2\omega)$ and $I_\downarrow(2\omega)$ is clearly visible up to $d_{\text{Co}} = 7$ to 8 ML. The slowly varying part in the asymmetry is caused by changes in the electronic structure with increasing film thickness and the appearance of quantum size effects in the SHG [12,17,18].

The fact that this asymmetry reaches its maximum value of about 32% already at a thickness of 2.5 ML is a direct proof of the surface/interface sensitivity of MSHG as discussed in Ref. [12]. However, the one ML period oscillations cannot be understood from the abovementioned changes of the electronic structure with Co layer thickness but must be related to the morphology of the surface. It is well known that SHG is quite sensitive to the surface morphology. For example, on a stepped Al surface the enhancement factor varies from 1/4 to more than 10 depending on the step density and step orientation [19]. The enhancement of SHG from this atomic scale roughness is caused by the modified electronic structure at step edges with respect to the electronic structure at the flat surface. Co grows on Cu in a nearly layer-by-layer growth mode [11]. Periodically Co islands nucleate, grow in size, and finally coalesce causing the total length of step edges to oscillate. Therefore, we attribute the observed oscillatory component in the SH intensities $I_\uparrow(2\omega)$ and $I_\downarrow(2\omega)$ to the oscillatory varying step density.

The same periodicity can be found not only in the SH intensities but in the asymmetry A as well. However, since the average SH intensity $I_{\text{av}} = (I_\uparrow + I_\downarrow)/2$ in Fig. 1(c) shows the same oscillation period, a clear separation between electronic and magnetic effects cannot be obtained easily. Therefore we searched for conditions in which the SHG is less sensitive to the surface topological structure. Figure 2 shows the result for s-polarized incident light with otherwise identical conditions as for the measurements in Fig. 1. The SH intensity for this polarization is about 1 order of magnitude lower than for p-polarized incident light. Again, the SH intensities $I_\uparrow(2\omega)$ and $I_\downarrow(2\omega)$ are not constant after the initial strong increase from 0 to 2 ML for reasons discussed above. The average intensity depicted in Fig. 2(c) still shows some variation with the cobalt layer thickness, but at a thickness larger than 5 ML only a very small and smooth variation of I_{av} remains. On the other hand, the asymmetry A shown in Fig. 2(b) exhibits well resolved 1 ML period oscillations from 2 to 8 ML over a slowly varying course. For clarity in Fig. 2(d) the rapidly varying component of A, δA, calculated as the difference of A and its average over 50 points is plotted. The same data treatment is applied to I_{av} and the result, δI_{av}, is plotted in 2(e). Besides the initial oscillation no 1 ML period oscillatory component is observed in δI_{av}. At $d_{\text{Co}} > 5$ ML δI_{av} is completely flat.

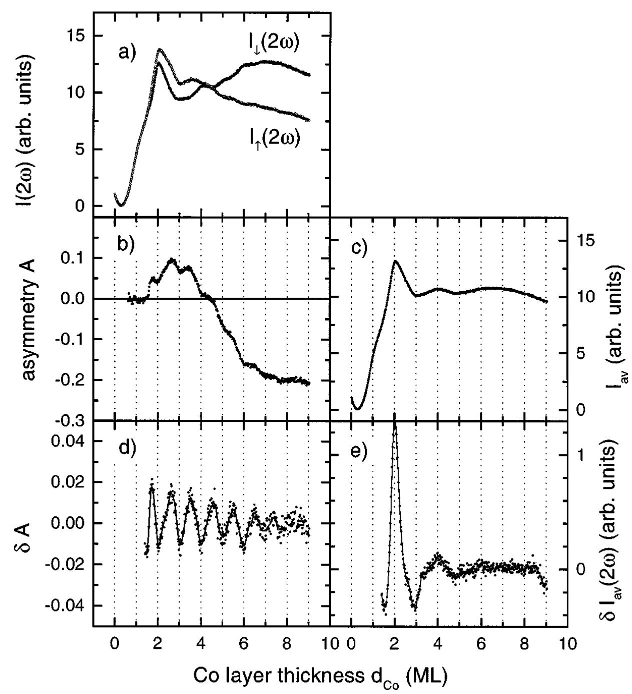

FIG. 2. (a) Measured total SH intensity as a function of the Co film thickness for s-polarized incident light in the transversal Kerr geometry for the magnetization in opposite directions. (b) Magnetic asymmetry and (c) average SH intensity calculated from the SH intensities in (a). In (d) the difference of the magnetic asymmetry and its running average over 50 points is plotted. In (e) the similar difference as in (d) is plotted for the average SH intensity I_{av}.

Initially, the asymmetry in Fig. 2(b) has a relatively small amplitude and even changes sign at around 4 ML thickness. However, this does *not* imply that the magnetization direction has changed. We recall that MSHG is sensitive to the surface *and* the interface magnetization. Therefore, the observed SH intensity is a coherent superposition of the SH light amplitude from the surface and the interface. This fact was used here to increase the sensitivity of MSHG to small changes in the magnetic part of the second order susceptibility. At about 4 ML the magnetic surface contribution is exactly canceled by the interface contribution. For smaller or larger Co layer thickness either the surface contribution becomes larger than the interface contribution or vice versa. Therefore a small change in the magnetic surface second order susceptibility leads to a large relative change in the asymmetry.

Depending whether the surface contribution or the interface contribution is largest an enhancement of the surface contribution leads to an enhanced *or* reduced SH intensity. In general, it is difficult to separate these two contributions for ultrathin films. It can be done by measuring the SH intensity at different incident angles [18]. For only a few ML thick layers, however, the optical phase difference of the light at the surface and the buried interface is very small, so that the difference in weight of surface and interface contributions to the SH intensity is small, too. Therefore we have chosen a different approach: Co grows on Cu pseudomorphically up to a large thickness. It has been shown that at about 16 ML the in-plane lattice constant relaxes partially towards its natural value [20,21] but this does not affect the SH intensities significantly. In agreement with Ref. [20] we found that Co remains in the fcc structure up to large layer thicknesses, in our case up to 150 ML. In Fig. 3 the result from a Co wedge grown onto the Cu substrate ranging from $d_{\mathrm{Co}} = 0$ to 140 ML is depicted. Because of the finite penetration depth of the incident light the Co surface contributes mainly to the SH light at $d_{\mathrm{Co}} > 100$ ML, while with decreasing thickness the contribution from the buried Co/Cu interface becomes more significant. The solid lines in Fig. 3 are fitted curves to the experimental data using the model of infinite thin nonlinear sheets and the theory developed by Sipe [22] and applied to multilayer structures by Wierenga *et al.* [23]. With the exception of $d_{\mathrm{Co}} < 15$ ML the fit reproduces the measured data quite well. The range of very thin layers cannot be described by this model because electronic changes of the film with the cobalt layer thickness are not taken into account.

The calculation confirms that for thicker layers $d_{\mathrm{Co}} > 50$ ML the SH is mainly generated at the surface and the surface magnetization induced SHG leads to *positive* asymmetry. Surface and interface contributions have (nearly) opposite phase. Because of an increasing interface contribution with decreasing d_{Co} a change of sign in the asymmetry occurs at about 50 ML. At $d_{\mathrm{Co}} < 4$ ML, however, the magnetization induced surface contribution is larger than the interface contribution again as indicated by the *positive* asymmetry.

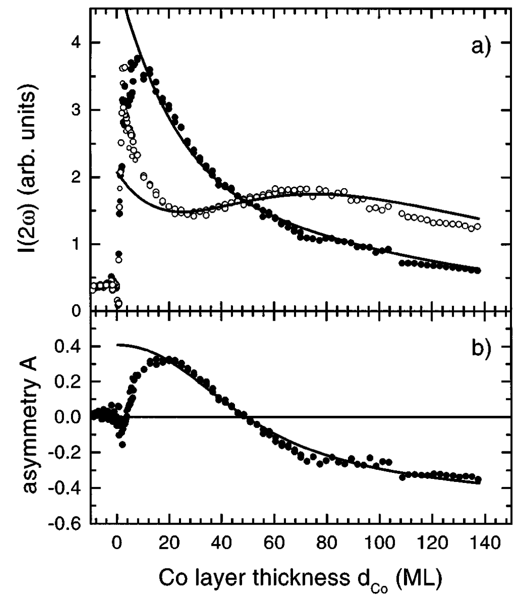

FIG. 3. (a) Total SH intensities from a thick Co wedge for *s*-polarized incident light. Open and solid symbols indicate the measured SH intensities for the magnetization in opposite direction. (b) Magnetic asymmetry: symbols calculated from the measured intensities; solid line calculated from the fit shown in (a) as solid lines.

From the above discussion it is now straightforward to understand the phase of the 1 ML period in Fig. 2. From $d_{\mathrm{Co}} = 0$ to 4 ML the sign of the asymmetry is determined by the surface contribution. At half filled layer this "*surface* asymmetry" is enhanced, and therefore the total asymmetry has a maximum value at half filled layers. Because the average SH intensity does not show the 1 ML periodic oscillation the observed oscillation in the asymmetry is caused by a periodic oscillation of the "magnetic" second order surface susceptibility. As mentioned above, the sign change of the asymmetry at about 4 ML is caused by only the destructive interference of surface magnetization induced SHG and a smoothly increasing interface contribution with increasing d_{Co} resulting from the varying electronic structure of the Co film with the number of (filled) layers. It can be concluded that in the whole investigated thickness range only the magnetic *surface* nonlinearity exhibits the one ML period oscillations, which have their maxima at half filled layers.

As other methods like the linear magneto-optical Kerr effect of Mössbauer spectroscopy, MSHG does not measure magnetization directly. However, it has been shown by Pustogowa *et al.* that the magnetic tensor elements of the second order susceptibility depend linearly on the magnetization to a first approximation [24], and because the amplitude of the periodic part of A is only about 0.02 a linear correlation between the variation of the magnetic surface second order susceptibility or the asymmetry A, respectively, and the variation of the magnetic moment of the surface layer can safely be assumed. Therefore, the observed *increase* of A at half filled layers suggests the *increase* of the magnetic moment of the atoms at step sites as it is expected from the simple argument of reduced coordination number at these sites.

The magnetic moment of bulk fcc Co is about $1.68\mu_B$ (measured) [25] or $1.65\mu_B$ (calculated) [5] per atom. At the surface recent *ab initio* calculations predict an enhanced magnetic spin moment of about $1.83\mu_B$ [5] to $1.79\mu_B$ [4]. The free Co monolayer has a spin moment $\mu_B = 2.09$ [4]. The paper by Smirnov and Bratkovsky [5] gives an enhancement of the magnetic moment at step edges of a 2.5 ML Co film relative to the magnetic moment per atom in the surface plane of a 3 ML film by about 5%. Then, from the average island size of 5 to 10 nm at half filled layers an enhancement of the average magnetic moment of the surface layer by about 0.5% to 1% can be estimated. The measuring amplitude of the oscillatory part of A, δA, is much larger. This large relative oscillation amplitude, however, results from the (partially) destructive interference of surface and interface contribution even making it possible to observe the periodic oscillations. (In the longitudinal geometry with otherwise identical conditions, for example, surface and interface contributions are compensated less and no one ML periodic oscillations in A could be resolved.) From the result of the MSHG measurements from the thick Co wedge we derive a surface asymmetry of $A_s = 0.6$ resulting from the surface nonlinearity alone. Therefore, we take the ratio $\delta A/A_s \approx 0.03$ as an approximate measure of the relative variation of the surface magnetization during the layer-by-layer growth which is a factor of 3 larger than expected from the theoretical calculations mentioned above. However, the asymmetry does not strictly depend linearly on the surface magnetization, and for more quantitative comparison with theory an estimate of the second order susceptibility from theory is needed.

In conclusion, 1 ML period oscillations in the asymmetry of the MSHG signal have been observed, which could be assigned to a periodic change of the magnetic surface susceptibility and therefore to a change of the magnetization of the surface Co layer. This proves the ability of MSHG to detect changes in the magnetic moment at interfaces of the order of $\frac{1}{50}\mu_B$ per atom.

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[1] U. Gradmann, in *Handbook of Magnetic Materials,* edited by K. H. J. Buschow (Elsevier Science Publishers B. V., Amsterdam, 1993), Vol. 7, Chap. 1, p. 1.
[2] C. L. Fu and A. J. Freeman, J. Magn. Magn. Mater. **69**, L1 (1986).
[3] E. Tamura, R. Feder, G. Walker, and U. Gradmann, Phys. Status Solidi (b) **157**, 627 (1990).
[4] O. Hjortstam, J. Trygg, J. M. Willis, B. Johannson, and O. Eriksson, Phys. Rev. B **53**, 9204 (1996).
[5] A. V. Smirnov and A. M. Bratkovsky, Phys. Rev. B **54**, R17 371 (1996).
[6] M. Albrecht, U. Gradmann, T. Furubayashi, and W. A. Harrison, Europhys. Lett. **20**, 65 (1992).
[7] M. Albrecht, T. Furubayashi, U. Gradmann, and W. A. Harrison, J. Magn. Magn. Mater. **104–107**, 1699 (1992).
[8] A. Berger, U. Linke, and H. P. Oepen, Phys. Rev. Lett. **68**, 839 (1992).
[9] P. Krams, F. Lauks, R. L. Stamps, B. Hillebrands, and G. Güntherodt, Phys. Rev. Lett. **69**, 3674 (1992).
[10] W. Weber, C. H. Back, A. Bischof, C. Würsch, and R. Allenspach, Phys. Rev. Lett. **76**, 1940 (1996).
[11] A. K. Schmid and J. Kirschner, Ultramicroscopy **42–44**, 483 (1992).
[12] H. A. Wierenga, W. de Jong, M. W. Prins, Th. Rasing, R. Vollmer, A. Kirilyuk, H. Schwabe, and J. Kirschner, Phys. Rev. Lett. **74**, 1462 (1995).
[13] R. Vollmer, A. Kirilyuk, H. Schwabe, J. Kirschner, H. A. Wierenga, W. de Jong, and Th. Rasing, J. Magn. Magn. Mater. **148**, 295 (1995).
[14] R. Vollmer, M. Straub, and J. Kirschner, Surf. Sci. **352**, 937 (1996).
[15] R. Vollmer, M. Straub, and J. Kirschner, J. Magn. Soc. Jpn. **20**, 29 (1996).
[16] M. Straub, R. Vollmer, and J. Kirschner, Phys. Rev. Lett. **77**, 743 (1996).
[17] T. Luce, W. Hübner, and K. H. Bennemann, Phys. Rev. Lett. **77**, 2810 (1996).
[18] A. Kirilyuk, Th. Rasing, R. Mégy, and P. Beauvillain, Phys. Rev. Lett. **77**, 4608 (1996).
[19] S. Janz, D. J. Bottomley, H. M. van Driel, and R. S. Timsit, Phys. Rev. Lett. **66**, 1201 (1991).
[20] W. Weber, A. Bischof, R. Allenspach, C. Würsch, C. H. Back, and D. Pescia, Phys. Rev. Lett. **76**, 3424 (1996).
[21] W. Schindler, T. Koop, A. Kazimirov, G. Zegenhagen, T. Schulz, R. Feidenhans'l, and J. Kirschner (unpublished).
[22] J. E. Sipe, J. Opt. Spectrosc. Am. B **4**, 481 (1987).
[23] H. A. Wierenga, M. W. J. Prins, and Th. Rasing, Physica (Amsterdam) **204B**, 281 (1995).
[24] U. Pustogowa, W. Hübner, and K.-H. Bennemann, Surf. Sci. **307–309**, 1129 (1994).
[25] X. Liu, M. M. Steiner, R. Sooryakumar, G. A. Prinz, R. F. C. Farrow, and H. Harp, Phys. Rev. B **53**, 12 166 (1996).