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Interface Magnetism and Possible Quantum Well Oscillations in Ultrathin Co/Cu Films Observed by Magnetization Induced Second Harmonic Generation

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fcc Co on Cu(001) and multilayers of Cu/Co/Cu(001) are studied by magnetization induced SHG (MSHG) in combination with linear Kerr measurements, for thicknesses between 1 and 20 monolayers (ML). Interface sensitivity of MSHG is demonstrated by its Co thickness dependency. Aside from a weak modulation, the MSHG signal from Co/Cu is nearly constant for thicknesses between 6 and 20 ML. Very strong oscillations in the MSHG signal are found for the Cu/Co/Cu system as a function of the thickness of the Cu coverlayer, which are possibly related to quantum well states in these thin Cu films.

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The magnetic properties of thin films and multilayer systems containing ferromagnetic material provide a fascinating field of research and are a subject of great current interest [1]. Aside from their technological significance, a number of extraordinary phenomena are observed such as the change of the magnetization from normal to in plane for thin Fe films [2] and a spin behavior at clean surfaces that is different from the bulk [1,3]. In particular, the observed oscillatory exchange coupling through nonmagnetic spacers has stimulated both experimental and theoretical research [4–8]. Very recently, it was shown that quantum well states in the nonmagnetic spacer may act as the mediator for this magnetic coupling [9–11].

So far, experimental observations rely on the use of polarized electrons or the magneto-optical Kerr effect (MOKE). Whereas the first technique is extremely surface sensitive, but cannot probe buried interfaces [12], MOKE has a probing depth of the order of 10 nm, i.e., it represents the bulk magnetization. Recently, it has been shown that the interface sensitive nonlinear optical technique of second harmonic generation is also sensitive to the magnetization [13–16].

In this paper we use magnetization induced second harmonic generation (MSHG) in combination with MOKE to study thin Co films of thicknesses between 1 and 20 monolayers (ML) grown on a Cu(001) substrate. We find that the relative magnetic effect ρ as determined from MSHG reaches a constant value at about 6 ML, in contrast with the MOKE signal that increases linearly with thickness. This different behavior with Co film thickness clearly shows the extreme surface or interface sensitivity of MSHG. This is further proven by the observed changes in ρ due to carbon monoxide adsorption. Between 1 and 6 ML, ρ shows an anomaly that may be related to electronic oscillations (quantum well states). When growing up to 15 ML Cu on top of 10 ML Co/Cu(001), ρ shows very strong oscillatorylike variations in which two periods can be distinguished that are remarkably close to the theoretically predicted and observed quantum well oscillations [6–11].

SHG arises from the nonlinear polarization $\mathbf{P}(2\omega)$ induced by an incident laser field $\mathbf{E}(\omega)$. This polarization can be written as an expansion in $\mathbf{E}(\omega)$:

$$P_j(2\omega) = \chi^{(D)}_{jkl} E_k(\omega) E_l(\omega) + \chi^{(Q)}_{jklm} E_k(\omega) \nabla_l E_m(\omega) + \cdots . \tag{1}$$

The lowest order term describes an electric dipole source. Symmetry considerations show that this contribution is zero in a centrosymmetric medium, thus limiting electric dipole radiation to the interfaces where inversion symmetry is broken. The bulk SH can now be described in terms of the much smaller electric quadrupolelike contributions [second term in Eq. (1)]. We shall verify the negligibility of the latter contributions explicitly.

It has been shown that Co grows pseudomorphic in the fcc structure on Cu(001) [4]. Thus the Co/Cu(001) samples have two (001) magnetic interfaces, the interface between the vacuum and magnetized Co and an interface between Co and the nonmagnetized Cu substrate. Both interfaces have a similar set of nonzero tensor elements. Magnetizing the Co film does not break its inversion symmetry, because the magnetization is an axial vector, so the basic argument for interface sensitivity still holds. The magnetic properties are included by introducing a magnetization dependent nonlinear susceptibility tensor: $\chi^{(D)}_{jkl}(\mathbf{M})$, as was suggested by Pan, Wei, and Shen [17]. We can distinguish tensor elements that are, respectively, even and odd in the magnetization: thus we may write

$$E(2\omega) = [\chi^{(D)}_{\text{even}}(\mathbf{M}) + \chi^{(D)}_{\text{odd}}(\mathbf{M})] E^2(\omega), \tag{2}$$

where $\chi^{(D)}_{\text{even}}(\mathbf{M})$ and $\chi^{(D)}_{\text{odd}}(\mathbf{M})$ are linear combinations of the tensor elements and $E(\omega)$ is the fundamental field at the interface. Changing the sign of $\mathbf{M}$ causes a phase change of 180° between the two contributions in Eq. (2) and leads to a different SH intensity. We now define the relative magnetic effect for MSHG as

$$\rho = \frac{I(2\omega,\mathbf{M}^+) - I(2\omega,\mathbf{M}^-)}{I(2\omega,\mathbf{M}^+) + I(2\omega,\mathbf{M}^-)}, \qquad (3)$$

where $I(2\omega,\mathbf{M}^+)$ and $I(2\omega,\mathbf{M}^-)$ are the SH intensities for opposite directions of the remanent magnetization.

For the SHG experiments we used the 800 nm output of a Ti:sapphire laser operating at a repetition rate of 82 MHz and a pulse width of about 100 fs. The incoming laser light was focused onto the sample, leading to a pulse intensity of about 16 μJ cm^{-2}. At an angle of incidence of 35°, we have studied the *pp* polarization combination (i.e., both fundamental and SH are polarized in the plane of incidence) as well as *sp* (i.e., the fundamental beam is polarized perpendicular to the plane of incidence). No analyzer was needed, because the *s*-polarized SH output was negligible, in accordance with theory [17]. Appropriate filtering was used before the signal was detected by a photomultiplier in combination with a lock-in amplifier. The magnetization was parallel to the (110) direction of the Co film, the easy axis of the film, and perpendicular to the optical plane. The direction of $\mathbf{M}^+$ is parallel to the direction of the vector product of the wave vector of the incoming light and the surface normal. The MOKE hystereses were taken in the longitudinal configuration at an angle of incidence of 45°. The ellipticity changes of the reflected light were measured by modulating the incoming HeNe beam with an acousto-optical modulator.

The samples were prepared in an ultrahigh vacuum system with a base pressure of 7×10^{-11} mbar. Substrate cleaning consisted of several cycles of Ar^+ sputtering followed by annealing at 600 °C. The Co films were grown at a rate of approximately 1 ML/min, while the Cu(001) substrate was kept at a temperature of approximately 100 °C. Epitaxial growth was verified for every film by monitoring the (0,0) medium energy electron diffraction (MEED) spot intensity while depositing [4]. After preparation the film quality was checked by Auger electron spectroscopy (AES); all contaminations were below 1 at. %, except carbon, which was typically 2%–3%. The MSHG and MOKE experiments were done *in situ,* at a pressure of 1×10^{-10} mbar.

Figure 1 shows the MOKE and MSHG hystereses measured on a 15 ML Co film at room temperature. The magnetization induced changes in the SH intensity are very high: $\rho = 48\%$ for the 15 ML Co film. This value is of the same order of magnitude as in previous experiments on other systems [13–15]. We have verified that the SH intensity generated by clean Cu(001) is about 1 order of magnitude lower than the lowest signal from Co/Cu(001) for all Co thicknesses and does not depend on the magnetic field.

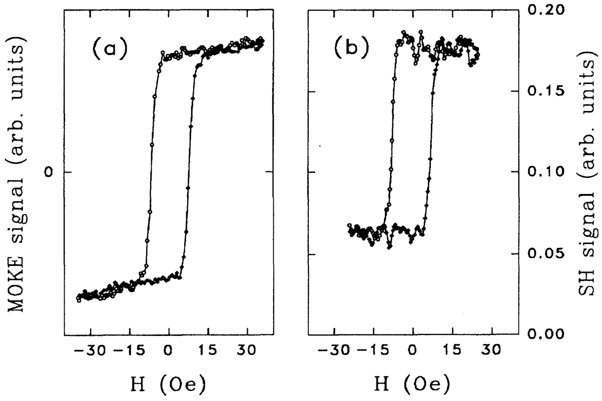

FIG. 1. Hysteresis for 15 ML Co on Cu(001): (a) longitudinal MOKE, (b) *pp* MSHG. Both are the result of averaging over four cycles taking 1 min each. Notice that (b) shows the total SH signal.

Figure 2 shows the amplitude of the MOKE hysteresis (M_r) as a function of the Co film thickness. It is well known that M_r depends linearly on thickness for very thin films. However, deviations from this linear dependence are easily taken into account in a multiple reflection description which includes absorption. We introduce slightly magnetization dependent bulk refractive indices

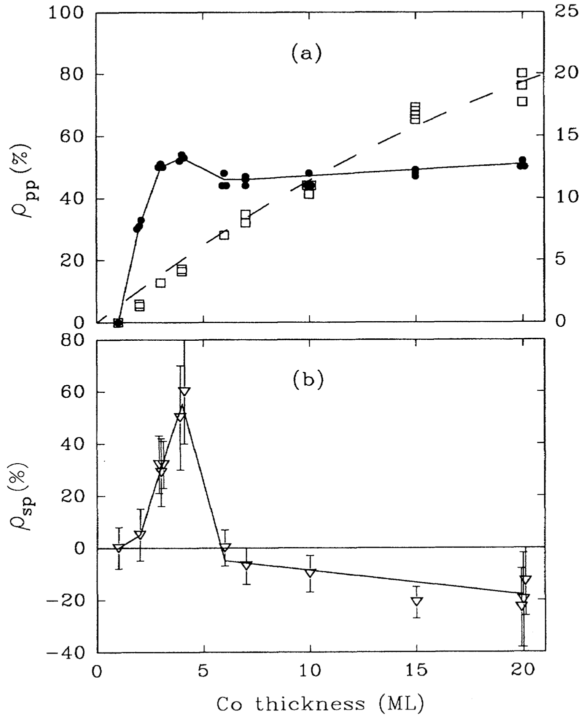

FIG. 2. Thickness dependence of the amplitude of the MOKE hysteresis (M_r) and the relative magnetic effects $\rho(pp)$ and $\rho(sp)$ in MSHG for Co on Cu(001); (a) squares/long dashed line—MOKE data and fit, circles—$\rho(pp)$; (b) triangles—$\rho(sp)$. The solid lines are guides to the eye.

for Co, which is in fact a simplified version of the approach by Gamble and Lissberger [18]. From the close agreement of the calculated curve with the experimental MOKE data, we conclude that the MOKE results are accurately described by bulk refractive indices for Co thicknesses above 3 ML.

The thickness dependence of MSHG is completely different. Figure 2 shows that $\rho(pp)$ changes rapidly up to 3 ML, after which it becomes nearly constant and varies only a few percent for Co layers ranging from 3 to 20 ML. Because we excited with a focused beam, surface inhomogeneities of the substrate cause poor reproducibility of the absolute signals. However, we observed that the variations of the absolute signals were less than a factor of 2 for Co thickness from 3 to 20 ML. The value of $\rho(pp)$, as it represents a relative effect, was reproduced within a few percent. We also observed a rapid increase of $\rho(sp)$ until 4 ML, but in contrast to $\rho(pp)$, $\rho(sp)$ drops down to nearly zero at 6 ML, where it changes sign and remains nearly constant for thicker Co films. The dependence of $\rho(pp)$ and $\rho(sp)$ on the Co film thickness clearly proves that the SH signal is generated only at the interfaces.

The observed SH signal is the superposition of the contributions of the vacuum/Co and the Co/Cu-substrate interface. To determine the relative strength of the SH signal from the two interfaces we measured the SH signal from a Co film on Cu(001) as a function of CO exposure, as gas adsorption is known to strongly reduce the SHG from metal surfaces [19]. We observed that the signals changed until a dosage of 1 langmuir (1 L $=10^{-6}$ torr sec), whereafter they became constant until at least 40 L. The original value of $\rho \sim 45\%$ had increased to $\rho \sim 70\%$. Comparable effects have been observed on adsorbing O_2 and for different Co film thicknesses.

These results can be used to calculate the SH contributions from the two interfaces. Our calculation is based on a multiple reflection model, including nonlinear sources at the interfaces. Details of the method are published in a separate publication [20]. In brief, using the relevant tensor elements and the boundary conditions for a nonlinear source polarization at an interface, the discontinuity of the SH field at the interface is derived. The total SH generated by the sample is calculated by using again multiple reflection theory (now for 2ω) and summing over all interfaces. For both interfaces, we find similar magnitudes of the odd and even tensor components. The calculated $\rho(pp)$ is found to be independent of Co film thickness, and coincides with the experimental results above 6 ML.

The results of the MSHG experiments in the range of 1–6 ML, of course, cannot be explained by simple multiple reflection arguments. We observe a strong peak for *sp*, and for *pp* we measure a small but very reproducible maximum. Although these effects might be caused by strain induced changes of $\chi^{(D)}$, one could speculate on a different origin, namely the appearance of quantum-well-like oscillations in the thin Co film. Their possible existence in Co/Cu(001) was shown by Ortega *et al.* [9]. Plotting their measured photoemission intensity at the Fermi level as a function of Co thickness (Fig. 2, Ref. [9]), one finds one maximum around 3 to 4 ML, in remarkable agreement with the position of the anomalies we observed in our MSHG results. This suggests that the behavior in $\rho(pp)$ and $\rho(sp)$ between 1 and 6 ML is connected with these electronic oscillations in the Co film.

To further investigate this hypothesis, we have studied the Cu/Co(001) system, where quantum well states have been clearly identified [9–11]. For the experiments we used 10 ML Co grown on Cu(001) as a substrate. Figure 3 shows the MSHG results for this Cu/Co/Cu system, as a function of Cu coverage. We observe strong oscillatorylike variations in $\rho(pp)$ with amplitudes up to $\rho = 75\%$. From the simultaneously measured MOKE amplitude we conclude that above 2 ML of Cu, the MOKE results are consistent with a normal multiple reflection analysis, using bulk refractive indices and a *constant* Kerr rotation. In the data of Fig. 3, two interfering periods can be distinguished: one of about 5 ML modulated by a substructure of 2–3 ML. Interestingly, the 5 ML periodicity has been observed by photoemission [9–11], whereas such a short period oscillation has been observed by Johnson *et al.* [8] in MOKE experiments on

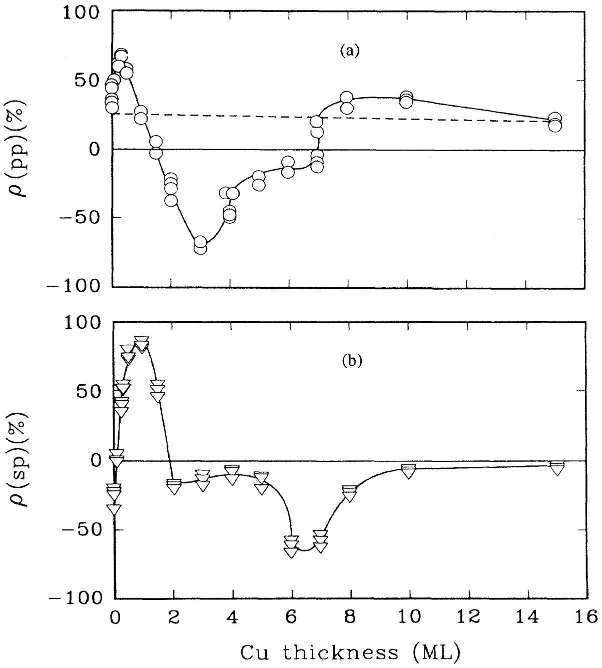

FIG. 3. The relative magnetic effects $\rho(pp)$ and $\rho(sp)$ as a function of Cu coverage on a 10 ML Co film on Cu(001); (a) circles—$\rho(pp)$, dashed line—result of model calculation including optical interference but neglecting quantum well oscillations; (b) triangles—$\rho(sp)$. The solid lines are guides to the eye.

the Co/Cu/Co system. The current idea is that these quantum well states are responsible for the exchange coupling [21], implying the presence of two oscillations with periodicities of 2.6 and 5.9 ML, respectively [6]. The extreme sensitivity of MSHG for these oscillations may be understood from its surface and interface specificity, in combination with results of recent calculations that indicate that these quantum well states primarily affect the density of states at the interfaces [21]. Furthermore, Carbone *et al.* [11] showed that the induced spin polarization in the nonmagnetic material is primarily located at the interfaces.

Assuming a bulklike electronic structure of the Cu films, the Cu thickness dependence of $\rho(pp)$ can be calculated from our multiple reflection model [20] using the values of the various tensor elements as derived from our experiments. The dashed line in Fig. 3(a) shows the result of such a calculation, clearly indicating that classical interference explains by no means the observed strong oscillations.

In conclusion, we have studied epitaxially grown fcc Co films (1–20 ML) on Cu(001) with MOKE and magnetization induced second harmonic generation. MOKE shows the characteristic proportionality to the Co film thickness, but the relative magnetic effect in MSHG is nearly constant for Co films thicker than 6 ML. This proves interface sensitivity of MSHG. The large changes in the SH signal on adsorbing as little as 1 L of CO emphasizes this point.

For the Cu/Co/Cu(001) system where quantum well states are known to exist, huge variations in the relative MSHG signals are observed in which periods can be distinguished that coincide with the expected long and short period quantum well oscillations in thin Cu films. MOKE measurements do not show these oscillations, whereas optical interference also cannot explain the observations.

The MSHG anomaly that is found for Co thicknesses between 1 and 6 ML is possibly also related to a weakly confined quantum well state in the Co film that we can observe because of the extreme surface sensitivity of our technique.

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