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Second harmonic generation study of quantum well states in thin noble metal overlayer films

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Abstract

The nonlinear optical response of a noble metal overlayer on top of a magnetic film shows an oscillatory behaviour dominating the total second harmonic output. The oscillation periods are twice as large as those observed with linear Kerr effect measurements. Spectroscopic studies show that the oscillatory part of the signals comes from the intraband transitions in the overlayer metal.

Keywords: Copper; Gold; Magnetic measurements; Metal–metal magnetic heterostructures; Quantum effects; Second harmonic generation

1. Introduction

In ultrathin films, due to the electronic potential discontinuities at interfaces, the perpendicular component of the wave vector can become quantized giving rise to resonances in the density of states. Those quantum well states (QWS) may act as the mediator for the exchange coupling in magnetic sandwiches leading to a characteristic oscillatory behaviour of the coupling [1]. Photoemission experiments have shown direct evidence of such QWS in thin metal films [2,3]. In addition, these states can become spin polarized even in nonmagnetic metals [4]. As a result, the magnetic properties of a ferromagnetic metal surface will depend on the thickness of the (thin) nonmagnetic overlayer evaporated onto it. For example, magneto-optical Kerr effect (MOKE) measurements demonstrated small oscillatory changes of the Kerr angle as a function of the overlayer film thickness for the Au(111)/Co [5] as well as for the Cu(111)/Co systems [6]. However those oscillations, though measurable, have a very small amplitude. This fact complicates the measurements and explains the small number of the studied systems.

Magnetization induced second harmonic generation (MSHG) is a nonlinear version of the MOKE technique [7,8], with an enhanced sensitivity to the very narrow film interface regions [9,10] and a very large magneto-optical response [11].

In this paper we report the unambiguous observation of QWS in Au(111) and Cu(111) overlayers on Co(0001). The oscillations are found in both the SHG intensity and in the nonlinear magneto-optical Kerr effects measured as a function of the gold or copper overlayer thickness. The very large

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effects in MSHG are in agreement with the interface localization of QWS [12]. For magnetic measurements, we used both polar and transversal configurations, giving rise to polarization rotations and MSHG intensity changes, respectively. The spectral dependencies of the observed signals show that interband transitions in the overlayer metal are responsible for the thickness independent part of the second harmonic intensity which is therefore reduced at longer wavelengths. In contrast, the oscillatory part hardly depends on the photon energy in the low-energy part of the spectrum.

2. Samples and experimental setup

The samples were step-shaped wedges of Au(111) or Cu(111) grown on top of a thin (5–20 monolayers (ML)) Co(0001) film on a thick Au buffer layer on a float glass substrate. The copper wedge was covered by 10 ML of gold for protection. The cobalt films were also grown as steps, with a few different thicknesses (see Fig. 1a). Because of a strong interface-induced perpendicular magnetic anisotropy in this system [13], we had the possibility to use either polar or transversal magneto-optical configurations depending on the cobalt thickness.

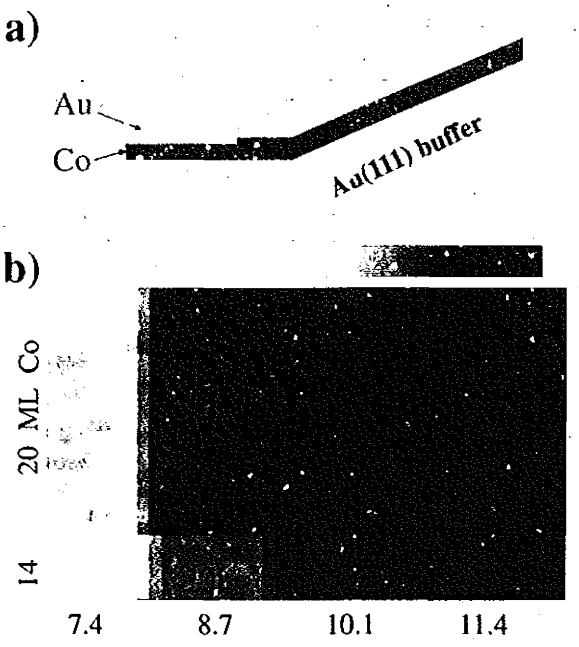

Fig. 1. (a) Au(111)/Co sample structure and (b) second harmonic intensity image ($3.7 \times 1.8\ mm^2$) of a part of the Au(111)/Co sample. Horizontal scale labels indicate the gold thickness in ML.

For the MSHG measurements, the output from a Ti–sapphire laser (100 fs pulse width, repetition rate of 82 MHz) was focused onto the sample while the latter could be moved with the help of a stepping motor in a magnetic field that was either in-plane or perpendicular to the sample. After proper filtering, the outcoming specular second harmonic (SH) light was detected with a photomultiplier. In the polar configuration, a Kerr rotation of the SH polarization was measured similar to what has been described in Ref. [11]. In the transversal configuration, we checked that for both p- and s-incoming light polarizations the SH output was always strictly p-polarized (i.e. in the plane of incidence). As a magnetic signal, we measured the normalized intensity difference for the magnetization up and down.

Fig. 1b shows the second harmonic image of the part of the Au(111) sample. Very strong dependence of SHG on the gold thickness makes the almost monoatomic steps easily visible in second harmonic light. Also one cobalt layer step can be seen.

3. Results and discussion

The second harmonic polarization $P(2\omega)$ of a magnetic medium is generally described by a third rank polar tensor χ^{cr}_{ijk} for the crystallographic contribution and a fourth rank axial tensor χ^{magn}_{ijkl} for the magnetization-induced part:

$$P_i(2\omega) = \chi^{cr}_{ijk} E_j(\omega) E_k(\omega) + \chi^{magn}_{ijkl} E_j(\omega) E_k(\omega) M_l, \quad (1)$$

where $E(\omega)$ is the incoming light field and M is the magnetization of the medium. In centrosymmetric materials, both tensors are nonzero only at surfaces and interfaces, where the inversion symmetry is broken. For a particular magneto-optical configuration, e.g. polar or transversal (and for a

high-symmetry surface), one may consider only one simplified third rank tensor with different components, that are either even in M, describing the crystallographic part, or odd and thus relate to the magnetization-induced contribution [7]. Eq. (1) is then written as:

$$P(2\omega,\pm M)=(\chi_{\mathrm{even}}(\pm M)\pm\chi_{\mathrm{odd}}(\pm M))E^2(\omega), \tag{2}$$

where χ_{even} and χ_{odd} are linear combinations of respectively even and odd tensor elements. In the polar geometry, χ_{even} and χ_{odd} are orthogonal to each other so the vector sum within the brackets results in a SH polarization plane rotation of $\alpha\approx\frac{|\chi_{\mathrm{odd}}|}{|\chi_{\mathrm{even}}|}$. In the transversal geometry, in contrast, both χ_{even} and χ_{odd} act along the same direction, and Eq. (2) shows then a change in the absolute value of $P(2\omega)$, i.e. a change in the SH intensity $I_{\mathrm{SH}}\propto|P(2\omega)|^2$. Then, the magnetization contrast can be defined as:

$$\rho=\frac{I(+M)-I(-M)}{I(+M)+I(-M)}, \tag{3}$$

where $I(\pm M)$ are the SH intensities measured for opposite directions of the sample magnetization.

Figs. 2a and 2b show the SH intensity measured at different wavelengths, for the Au(111) overlayer, displaying a strong oscillatory behaviour as a function of the overlayer thickness. Evidently, these oscillations are a dominating feature of the curves, especially at longer wavelengths. Similar oscillatory behaviour has been found for the MSHG response, both for the polarization rotation in the polar configuration [14] and for the magnetization contrast in the transversal one. All observed thickness dependencies could be fitted with a formula,

$$I_{\mathrm{SH}}=A\exp\left(-\frac{d_{\mathrm{Au,Cu}}}{\delta}\right)\sin\left(2\pi\frac{d_{\mathrm{Au,Cu}}}{\Lambda}+\gamma\right)+B. \tag{4}$$

From Fig. 2 it can be seen that the phase of the oscillations (γ) is wave-length dependent (p-polarization) while the period Λ remains approximately constant. Fig. 3a shows the period Λ for p- and s-incoming polarizations as a function of the second harmonic photon energy.

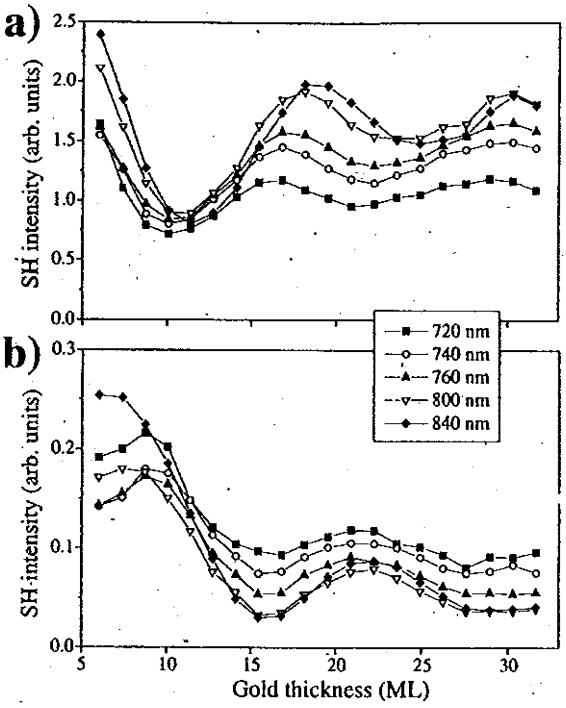

Fig. 2. SHG intensity as a function of the gold overlayer thickness for (a) p-polarization and (b) s-polarization, for different wavelengths.

For both the Au(111) and Cu(111) overlayers the observed period (12–16 ML) is approximately twice the value obtained with linear MOKE. The origin of the observed period doubling is discussed in detail elsewhere [15]. The main difference between the linear MOKE and MSHG is the very different sensitivity to the presence of inversion symmetry. The MSHG response of a perfectly symmetric quantum well should vanish within the dipole approximation. As a result, MSHG is extremely sensitive to the asymmetry of the quantum well states providing the oscillation period which differs from that in linear MOKE. The double period is partly related to the successive odd/even character of the quantum well states. Also interesting is the observation that different light polarizations clearly indicate different periods.

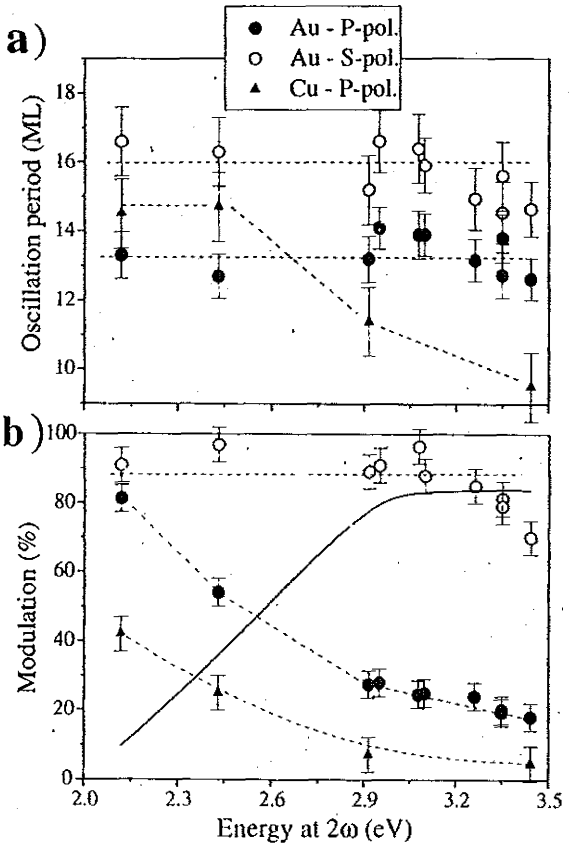

Fig. 3. The fitted values for (a) oscillation periods for s- and p-polarizations and (b) oscilation amplitude relative to the thickness independent background, as a function of the second harmonic photon energy. Dashed lines are guides for the eye. Solid line in (b) shows the absorption in gold (from Ref. [16]).

Fig. 3b shows the dependence of the oscillation amplitude A relative to the background B as a function of the SH photon energy. Also plotted is the optical absorption curve for gold taken from Ref. [16]. While the A/B value for the s-polarized incoming light remains approximately constant (80–90%), for p-polarization this ratio definitely shows a decrease toward higher photon energies. This means that the non-oscillatory part of the signal is considerably reduced at lower energies. This decrease actually coincides with the fundamental absorption edge in gold which strongly suggests optical interband transitions as the origin for the thickness independent part of the SH intensity.

For the Cu(111) overlayer, the periods and amplitudes behave in a way very similar to the case of gold. However, there is one exception: the fundamental absorption edge for copper is shifted to lower energies (2.1 eV instead of 2.5 eV for gold). In other aspects, the band structures of Cu and Au are very similar. Therefore, the observed change in relative amplitude is just shifted to lower energies (Fig. 3b). There is also a considerable change in the oscillation period occuring around 2.7 eV which can possibly be ascribed to the beginning of some type of optical interband transition at this energy.

Thus we can suppose that the strong oscillatory behaviour of SHG at lower photon energies is not related to direct interband transitions. Therefore it is necessary to consider other possibilities, namely (i) the (spin-polarized) band structure of cobalt serves as a source for either initial or final states, or (ii) intraband transitions in gold are responsible for the effect. It has been shown, however, that in the case of transitions between spin-polarized states, the SH intensity should be considerably different for the opposite directions of the sample magnetization [17]. This does not appear to be the case for the considered samples (the relative magnetic effect as defined by Eq. (3), is found to almost always oscillate around zero or very close to it), hence the direct influence of the cobalt band structure can be ruled out.

As for the intraband transitions, they might be of much more importance in very thin films in comparison to the bulk metals. Indeed, for ultrathin films the component of the wave vector perpendicular to the film plane becomes quantized. Therefore the requirement of its conservation is lifted, and the transitions between the subsequent QWS become allowed. Such transitions at low photon energy obviously only take place in the vicinity of the Fermi surface. This fact can naturally explain why the oscillation period does not considerably depend on the photon energy. The only strong change which is observed for the period of the Cu(111) overlayer may therefore be explained by a crossover to interband transitions at higher photon energies.

4. Conclusion

Nonlinear magneto-optics has been demonstrated to be a very powerful tool for the study of (spin-polarized) quantum well states. In the case of (111) oriented noble metal overlayers, oscillations of the MSHG signals as a function of the overlayer thickness persist even at low photon energies, where direct interband transitions are not allowed even for two-photon processes.

Acknowledgements

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