Study of Quantum Well States in Ultrathin Overlayer Films by Magnetization-induced Second Harmonic Generation

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We report a detailed study of the nonlinear magneto-optical response from wedge-shaped (111)-oriented films of noble metals Cu, Au and Ag grown on top of an ultra thin Co film. The spectral dependencies of the oscillatory part of the total optical second harmonic response indicate a dominating role of the free-electron contribution in the optical response from quantum well states.

Keywords: quantum well states, magneto-optics, optical second harmonic generation, ultra thin films, noble metals

1. Introduction

Since the discovery of the oscillatory exchange coupling of magnetic films separated by a nonmagnetic spacer layer from ferromagnetic to antiferromagnetic^{1,2)}, there have been intense efforts to understand these phenomena. It was shown that in ultrathin films, due to the electronic potential discontinuities experienced by electronic states 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) act as the mediator for this magnetic coupling³⁾. Photoemission experiments directly demonstrated oscillations of the electron density of states⁴⁾. Magneto-Optical Kerr Effect (MOKE) measurements have also shown an evidence of such QWS in thin noble metal films on magnetic substrates (Fe and Co)^{5,6)}, and in a bcc Fe(100) layer on Au(100)⁷⁾. Much stronger effects, however, were discovered in nonlinear magneto-optical studies⁸⁻¹⁰⁾.

Due to the fact that optical Magnetization-induced Second Harmonic Generation (MSHG) is known to be surface sensitive on an atomic scale, it seems that MSHG studies might be particularly suitable for improving our knowledge of the electrodynamics of ultrathin metallic films. Though the absolute nonlinear signals are small, the nonlinear magneto-optical effects are very large: compared to the linear Kerr angle, enhancements up to a factor 1000 have been observed¹¹⁾. Little is known however about the real probing depth of the technique. For example, experiments in transition metals seem to limit it to 2-3 ML^{8,12)}, while for the free-electron case it can be considerably larger, of the order of 10-20 ML¹³⁾. Also the very strong influence of QWS in thin noble metal films on MSHG^{8,9)} is in principle an indication that a relatively extended interface region is responsible for the MSHG response.

The magneto-optical studies of QWS are additionally complicated by the strong photon energy dependence, making it more difficult to interpret the observed oscillation periods.

Thus, for any optical study of QWS the question of primary importance is what states are responsible for the signal and what resonant electronic transitions determine the oscillatory behavior.

Clear differences in the MSHG response from QWS in noble and transition metals was related to the participation of the localized d-bands in the latter case. Very steep spectral dependence of the MSHG signal was also in agreement with this conclusion¹⁵⁾.

In the visible spectral range, because of the high value for the interband transition threshold, the behavior of the optical response from noble metals should be considerably affected by the free-electron contribution. In the sequence Cu - Au - Ag, this contribution gradually increases. Till present, however, this free-electron behaviour in quantum wells was never taken into account which may explain, e.g. the poor comparison of theory with the experimental results^{6,9,16)}.

In order to understand the real origin of the observed signal, we performed a thorough study of the (nonlinear) (magneto-) optical response from (111) oriented wedge-shaped films of noble metals. Our results clearly show that also in the absence of any interband transitions, strong oscillatory behaviour is observed as a function of the layer thickness. This demonstrates the importance of the intraband, free-electron like, contributions to the quantum well response.

2. Method and experiments setup

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

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

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 $\mathbf{M}$, describing the crystallographic part, or odd and thus relate to the magnetization-induced contribution¹⁴⁾. Eq. (1) is then written as

$$\mathbf{P}(2\omega, \pm \mathbf{M}) = [\tilde{\chi}_{\text{even}}(\pm \mathbf{M}) \pm \tilde{\chi}_{\text{odd}}(\pm \mathbf{M})] \cdot \mathbf{E}^2(\omega) \quad (2)$$

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

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

where $I^{2\omega}(\pm M)$ are the SH intensities measured for opposite directions of the sample magnetization. Here, in contrast with MOKE, the average intensity I_{SH} is also an important parameter directly representing the electronic structure of an interface or a thin film.

Our samples were step-shaped wedges of Au(111), Cu(111), or Ag(111) epitaxially grown on top of thin (5–20 ML) Co(0001) films on a Au(111) substrate. The copper and silver wedges were covered by 10 ML of gold for protection. The Co films were also grown as steps, with a few different thicknesses. Because of the strong interface-induced perpendicular magnetic anisotropy in this system, we had the possibility to use different (polar or transversal) magneto-optical configurations, depending on the Co thickness.

For the MSHG measurements, a pulsed laser beam from a Ti-sapphire laser (82 MHz $\times$ 100 fs pulses) was focused onto the sample, while the latter could be moved with the help of a stepping motor in a magnetic field either in-plane or perpendicular to the sample. After proper filtering, the outgoing specular second harmonic (SH) light was detected with a photomultiplier. In the polar configuration, the 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_{in} and S_{in} incoming light polarizations, the SH output was always strictly P-polarized (P_{out}), in agreement with theory¹⁴⁾. As a magnetic signal, we measured the magnetic contrast ρ [eq. (3)].

3. Results and discussion

With an addition of a home build optical parametric oscillator, the tuning range of the laser was 720–1170 nm, resulting in the second harmonic photon energies of 2.1–

Figure 1. Oscillation periods (a) and relative oscillation amplitudes (b) of the MSHG response from Cu(111) and Au(111) wedges measured with $P_{\text{in}}P_{\text{out}}$ polarization combination.

3.4 eV. This range allows to make a clear difference between Cu and Au, where interband transitions are allowed in the whole range, and Ag, where they are absent. In the first two metals strong oscillations were reported previously⁹⁾; here we are rather interested in the spectroscopic data (see Fig. 1). The most important feature is the increase of the oscillatory contribution towards the low photon energies. Basically this increase shows up as an inversion of the optical absorption curve (see Fig. 1(b) for Au). For Au(111), the oscillatory period is roughly constant over the whole range of the photon energies, while for Cu(111), it does so at $2\hbar\omega \leq 2.5$ eV but changes at higher energies. Briefly, one can guess from this data that the constant period and the large relative amplitude are the features of low photon energies and free-electron response (virtual electronic transitions) while at higher energies, the changing period (in Cu) and the considerable nonoscillatory background (in both Cu and Au) might be due to interband transitions.

Measurements on a Ag(111) wedge should shed more light on this problem. Indeed, the MSHG response strongly oscillates as a function of the silver layer thickness (Fig. 2), with a very long period. Another observation is the considerable changes in the oscillatory period with changing photon energy (Fig. 3). The linear MOKE measurement also showed small oscillations of the MOKE amplitude (see inset in Fig. 3), with a period

Figure 2. MSHG response from the Ag(111) wedge for different wavelengths.

Figure 3. Oscillation period as a function of the photon energy measured with MSHG on the Ag(111) wedge. Inset shows the oscillations observed with the linear MOKE.

of around 12 ML. As straightforward conclusions from these data, we should mention:

(i) The pronounced oscillatory behaviour in the absence of interband transitions indicates the dominant role of the free-electron behaviour (virtual transitions) also for other noble metals.

(ii) The difference between the periods measured with MOKE and MSHG is consistent with the recently obser-

ved and explained period doubling in nonlinear optics^{9,17)}.

(iii) The strong wavelength dependence of the measured oscillatory periods is however not in line with the data on Cu(111) and Au(111) samples. This fact certainly calls for new developments both in theory (extending Ref.¹⁶⁾) and experiment (such as accurate spectroscopy data in wider range of photon energies).

In conclusion, although neglected till present, free electron behaviour of noble metals strongly affects the QWS-induced part of the (nonlinear) optical response.

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