Magnetization-induced optical second-harmonic generation: A probe for interface magnetism

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The optical second-harmonic intensity generated by magnetic multilayers of cobalt and gold strongly depends on the magnetization. At normal incidence the results are independent of the amount of bulk cobalt and gold, but are accurately described by pure magnetic interface contributions. This represents a way to probe buried interface magnetism using magnetization-induced second-harmonic generation.

The magnetic properties of interfaces in multilayered systems containing ferromagnetic material is a subject of great current interest.[1] It has been shown that the spin behavior at clean surfaces can be very different from the bulk and in general interface magnetism is likely to differ from bulk behavior.[2,3] Systems of alternating layers of magnetic and nonmagnetic materials are of fundamental interest, because of the correlation between the magnetic layers.[4–6] From a practical point of view the switching characteristics of these systems make them very attractive for magnetic data recording.[1] Since interface quality is a major influence, a study of their magnetic properties is desirable.[6]

There exist several techniques (e.g., spin polarized photoemission spectroscopy,[7] spin polarized electron energy loss spectroscopy,[8] and spin polarized low energy electron diffraction[9]) to study the magnetic properties of clean surfaces. Unfortunately (polarized) electrons are difficult to use for studying buried interfaces due to their short mean free path. Since interfaces between thin metallic films are accessible by light, an optical technique would have significant advantage. The magneto-optical Kerr effect (MOKE) is well known and frequently used. This linear optical technique studies the changes in the linear susceptibility as a function of the applied magnetic field. As it is based on the rotation of the polarization of light traveling through a magnetic material, it probes the bulk magnetization. Though very sensitive and even applicable to monolayers, MOKE is not interface specific.

Second-harmonic generation (SHG) is a nonlinear optical technique that derives its interface sensitivity from the breaking of symmetry at boundaries between centrosymmetric media.[10] On theoretical grounds it has been shown that magnetization dependent effects should be detectable with SHG,[11,12] and first experimental indications of magnetization-induced SHG (MSHG) were recently given by Reif *et al.*[13] and Spierings *et al.*[14] In this paper we discuss the influence of the magnetization on the second-harmonic signal from Co/Au multilayers. In order to prove interface sensitivity we vary the number of Co/Au interfaces. Experiments at near normal incidence show that this has a pronounced effect on the observed magnetic field dependence of the second harmonic. The results are interpreted quantitatively in a model that describes the magnetic effects in terms of pure interface contributions, taking into account the multiple reflections between the various interfaces. There is no relation between the amount of bulk Co or Au and the observed effects. This demonstrates that MSHG is a viable tool for probing the magnetic properties of buried interfaces.

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 $\mathbf{E}(\omega)$:

$$P_{\rm i}(2\omega) = \chi^{\rm d}_{\rm ijk} E_{\rm j}(\omega) E_{\rm k}(\omega) + \chi^{\rm q}_{\rm ijkl} E_{\rm j}(\omega) \nabla_{\rm k} E_{\rm l}(\omega) + \cdots . \quad (1)$$

The lowest order term describes an electric dipole source. Symmetry considerations show that these contributions are zero in a centrosymmetric medium, thus limiting electric dipole radiation to the interfaces where inversion symmetry is broken. The bulk second harmonic can now be described in terms of the much smaller electric quadrupolelike contributions [second term in Eq. (1)]. However because of the large volume difference between interface and bulk this does not necessarily mean that the total bulk second harmonic signal is negligible. Interface sensitivity needs to be verified for any given system. Following the treatment of Ru-Pin Pan *et al.*[11] we include the magnetic properties of the material by introducing a magnetization dependent nonlinear susceptibility tensor: $\chi(\mathbf{M})$.

It is important to realize that the inversion symmetry of the bulk is not broken by the magnetization, so the argument for interface sensitivity remains valid. The tensor elements of an "isotropic" magnetic interface are derived from symmetry considerations, taking into account that the magnetization is an axial vector. The interface is defined by the $\hat{x}$-$\hat{y}$ plane, with $\hat{x}$ in the plane of incidence and the magr ization parallel to $\hat{y}$ (see inset in Fig. 1). The symmetry operations are reflection in the $\hat{y}$-$\hat{z}$ plane: $x \to -x, y \to y, z \to z, \mathbf{M} \to -\mathbf{M}$, and reflection in the $\hat{x}$-$\hat{z}$ plane: $x \to x, y \to -y, z \to z, \mathbf{M} \to \mathbf{M}$. We can distinguish two sets of elements, one set is even and the other is odd in the magnetization (see Table I, $\chi_{ijk}=\chi_{ikj}$). Along similar lines we derive the electric quadrupolelike bulk tensor elements of this "isotropic" system with a magnetization along the $\hat{y}$ axis (see Table I, $\chi_{ijkl}=\chi_{ilkj}$).

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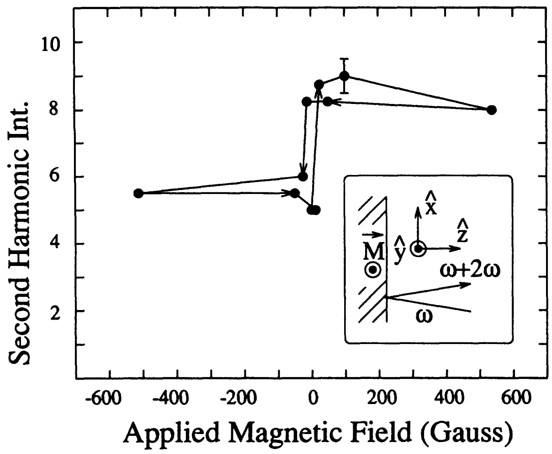

FIG. 1. The $p_{\mathrm{in}}p_{\mathrm{out}}$ second-harmonic intensity (in arbitrary units) as a function of the applied magnetic field for sample A at an angle of incidence of 45°. Inset: The choice of the axis and the magnetization, relative to the plane of incidence.

If we choose an experimental configuration with normal incidence and for both fundamental and second harmonic light a polarization perpendicular to the magnetization (pp-like), there are only two odd tensor element contributing: $\chi^d_{xxx}(\mathbf{M})$ and $\chi^q_{xxzx}(\mathbf{M})$. So we find

$$E_p(2\omega,\mathbf{M}) = C\chi^d_{xxx}(\mathbf{M})E_p^2(\omega) + D\chi^q_{xxzx}(\mathbf{M})E_p(\omega)\nabla_z E_p(\omega), \qquad (2)$$

where C and D are constants. For a multilayered system the amplitude of the fields must be calculated from multiple reflection theory.[15] From Eq. (2) it is clear that a particularly simple situation occurs if we only change the sign of the magnetization, since $E_p(2\omega)$ changes phase by 180°.

For the experiments we used the 532 nm output of a frequency doubled, Q-switched seeded Nd-YAG laser with 8 ns pulse width. The pulse intensity was kept below 7 $\mathrm{mJ\,cm^{-2}}$. The samples were mounted in between the poles of an electromagnet. The applied magnetic field was in the plane of the sample and was perpendicular to the plane of incidence.

The samples consist of thin films of Co and Au, evaporated at a rate of about 2 Å/s, while the substrate was kept at room temperature. The pressure was 5×10^{-7} Torr while evaporating. The substrates were optical quality glass plates, cleaned in ethanol and blown dry with nitrogen. Four systems were studied: sample A has 1 Co/Au-interface: glass+500 Å Co+50 Å Au, sample B has 2 Co/Au interfaces: glass+500 Å Au+50 Å Co+50 Å Au, sample C has 3 Co/Au interfaces: glass+50 Å Co+50 Å Au+50 Å Co+50 Å Au, the fourth sample is a 1500 Å thick Au film. Although the films are polycrystalline, they are isotropic on the scale of the laser beam diameter ($\sim$ 60 $\mathrm{mm^2}$). At this point we would like to emphasize that the precise structure of the interfaces and the choice of the materials is, although of utmost interest for future experiments, at this stage not a real issue. This work is meant to indicate that the technique is not only sensitive to the highly academic clean surfaces,[13] but also to the much more significant buried interfaces. In addition, these systems are suitable candidates for an experimental verification of theories about the oscillatory exchange interaction.[6]

A first indication that we have indeed a proper description of these systems follows from measurements at different polarization combinations. At an angle of incidence of 45° sample A gave negligible second harmonic for $p_{\mathrm{in}}s_{\mathrm{out}}$ and $s_{\mathrm{in}}s_{\mathrm{out}}$ and no magnetic effect. For $p_{\mathrm{in}}p_{\mathrm{out}}$ and $s_{\mathrm{in}}p_{\mathrm{out}}$ we measure a clear dependence on the magnetization. All results are in agreement with the Ru-Pin Pan theory (see Table I). Figure 1 shows the complete hysteresis for $p_{\mathrm{in}}p_{\mathrm{out}}$. The remanent ($\mathbf{H}$=0) MSHG remained constant even after long periods of laser irradiation. If we choose $\mathbf{M} \parallel \hat{x}$, we find no magnetic effects within the experimental accuracy of about 4% for any of these polarization combinations. Although the explanation is beyond the scope of this paper, the results are again in agreement with the theory.[11]

Figure 2 presents the results of experiments on the pure Au film and samples A, B, and C at near normal incidence and pp-like polarization. For each sample we measured the second-harmonic intensities for upward ($\mathbf{M}\uparrow$) and downward ($\mathbf{M}\downarrow$) saturation. As is to be expected, the signal from the Au film is not dependent on the magnetization. The inversion of the $\mathbf{M}\uparrow$ and $\mathbf{M}\downarrow$ levels between samples A and B and between samples B and C is most striking. We believe this is an extremely strong indication that the interfaces play a significant role, especially since qualitatively similar behavior was observed in our experiments at an angle of incidence of 45°.[14] Furthermore we find no correlation between the measured signals and the thicknesses of the Co or Au layers. Sample C gives a larger magnetic effect than sample A, that contains five times more Co. This leads to the reasonable assumption that $\chi^q_{xxzx}(\mathbf{M})$ contributes much

TABLE I. Nonzero tensor elements of the nonlinear susceptibility tensor for a revised 'isotropic' interface and magnetized 'isotropic' bulk.

Interface	Even in **M**	:	xxz, yyz, zyy, zxx, zzz
	Odd in **M**	:	yxy, zxz, xxx, xyy, xzz
Bulk	Even in **M**	:	$xxxx = zzzz, xxyy = zzyy, xxzz = zzxx,$
		:	$xyxy = zyzy, xzxz = zxzx, yxxy = yzzy,$
		:	$yxyx = yzyz, yyyy$
	Odd in **M**	:	$xxxz = -zzzx, xxzx = -zzxz, xyyz = -zyyx,$
		:	$xyzy = -zyxy, xzzz = -zxxx, yxzy = -yzxy$

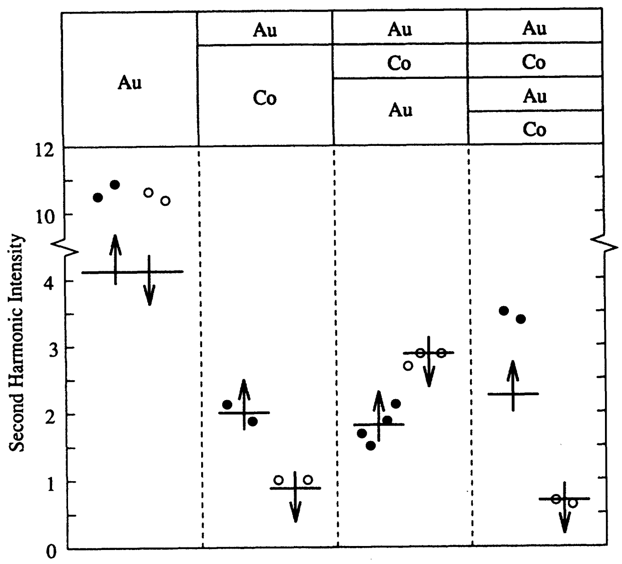

FIG. 2. The second-harmonic signals (in arbitrary units) from the pure Au film and samples A, 1 Co/Au interface; B, 2 Co/Au interfaces; and C, 3 Co/Au interfaces. $\mathbf{M}\uparrow$, film saturated upward; $\mathbf{M}\downarrow$, film saturated downward.

less than $\chi^d_{xxx}(\mathbf{M})$. This assumption is strengthened by MSHG on Co/Cu, where we varied the thickness of the Co film continuously and observed that the magnetic effect, as measured with MSHG, remains constant after a few monolayers.[16] Quantitatively this follows from a model that shows that the results can be described in terms of pure interface contributions.

Figure 3 shows a typical example of the samples under study. The complex coefficients $\hat{\alpha}_n$ are calculated using

$$\hat{\alpha}_n = \frac{\hat{A}_n(\omega)^2}{\hat{S}_n(2\omega)}, \tag{3}$$

where $\hat{A}_n(\omega)$ is the ratio of amplitudes of the fundamental field at interface n and the incoming field outside the sample, and $\hat{S}_n(2\omega)$ is the ratio of the generated second-harmonic field at interface n and the outgoing field. Both $\hat{A}_n(\omega)$ and $\hat{S}_n(2\omega)$ are calculated using multiple reflection theory.

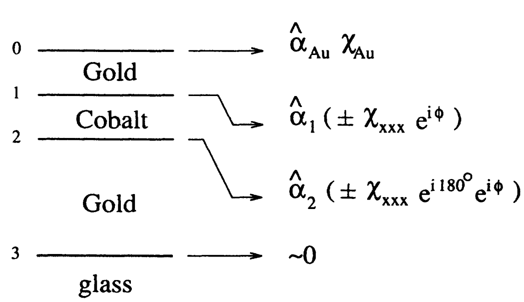

FIG. 3. A schematic example of the samples under study. The relative contributions of the interfaces are indicated.

TABLE II. The α's as calculated from multiple reflection theory. We choose the phase of $\hat{\alpha}_{\mathrm{Au}}$ to be zero.

	$\hat{\alpha}_{\mathrm{Au}}$	$\hat{\alpha}_t$
Pure Au	0.543	
Sample A	0.223	$0.142e^{-i21^\circ}$
Sample B	0.370	$0.112e^{+i18^\circ}$
Sample C	0.257	$0.123e^{-i32^\circ}$

For the air-Au interface there ought to be no second harmonic generation for normal incidence and pp-like polarization, since χ_{xxx} is zero for an isotropic nonmagnetic interface. However the experiments on the pure Au film show significant second-harmonic signal in this configuration. This can be explained by the experimental limitations allowing a minimum angle of incidence of 4°. To first-order approximation we excite χ_{zzz}, χ_{xxz}, and χ_{zxx}. It is important to realize that this limitation is only significant at the first interface. The laser light is refracted to the normal on entering the conducting Au, and extra contributions from the deeper laying interfaces and the bulk need not be considered. We indicate the total contributions of the air-Au interface with χ_{Au}.

Interfaces 1 and 2 in Fig. 3 are boundaries between the same materials. However they differ by a mirror plane parallel to the interface, resulting in a phase difference of 180° between their tensor elements.

The contributions from the Co-glass and the Au-glass interfaces are negligible for samples A and B, because of the thick metal layer between the air-Au and metal-glass interfaces. Furthermore we have measured the contributions of the comparable Co-quartz interface by exiting from the quartz side. We conclude that the contributions of the Co-glass interface in sample C are negligible.

The total second-harmonic signal of the whole system is now described by

$$I(\pm M) = \left| \hat{\alpha}_{\mathrm{Au}}\chi_{\mathrm{Au}} \pm \sum_n (-)^{n-1}\hat{\alpha}_n \chi_{xxx}(M)e^{i\phi} \right|^2, \tag{4}$$

where ϕ is the phase difference between χ_{Au} and $\chi_{xxx}(\mathbf{M})$. The "+" sign refers to $\mathbf{M}\uparrow$, the "−" sign to $\mathbf{M}\downarrow$.

The values of $\hat{\alpha}_{\mathrm{Au}}$ and $\hat{\alpha}_t = \sum_n (-)^{n-1}\hat{\alpha}_n$ for all samples are listed in Table II. We have used the indices of refraction measured by Johnson and Christy.[17] We found that the calculated values for $\hat{\alpha}_{\mathrm{Au}}$ and $\hat{\alpha}_t$ are not critically dependent on the exact thicknesses of the layers. Changing the size of both Co layers in sample C by as much as 10% caused variations of $\hat{\alpha}$ of only a few %.

The results of fitting Eq. (4) to the data for samples A, B, and C are shown in Fig. 2. The values for the fit parameters: $\chi_{xxx}(\mathbf{M})/\chi_{\mathrm{Au}}$ and ϕ, are listed in Table III (χ_{Au} is used as a scaling parameter). Our model clearly

TABLE III. Results of fitting the parameters in Eq. (9) to the data for samples A, B and C.

$\chi_{xxx}(\mathbf{M})/\ \chi_{\mathrm{Au}} = 1.6$	;	$\phi = 88^\circ$

describes the inversion of $I(\mathbf{M}\uparrow)$ and $I(\mathbf{M}\downarrow)$ between samples A and B, and between samples B and C. The calculated value for $I(\mathbf{M}\uparrow)$ of sample C is not in perfect agreement with experiment. However the model does explain that sample C gives a larger magnetic-field-induced second-harmonic effect than sample A. Although surprising and counterintuitive, as C involves deeper interfaces, it is purely the result of multiple reflections in these multilayer systems. The excellent agreement between the observed and theoretically predicted values for the phase difference between the nonmagnetic ($\chi_{\rm Au}$) and magnetic $[\chi_{xxx}(\mathbf{M})]$ contributions is striking. Assuming that both tensor elements are off resonance, time inversion principles predict a phase difference of 90° between odd and even tensor elements,[11] whereas we found 88°. Using the value for $\chi_{\rm Au}$ from the interface fits, we underestimate the second-harmonic signal from the pure Au film by a factor of 3. Since the observed magnetic effects are the result of mixing a magnetic and nonmagnetic contribution [see Eq. (4)], it is not a *priori* clear that this is only a scaling error. However combining the fit values for $\chi_{xxx}(\mathbf{M})/\chi_{\rm Au}$ and ϕ, with $\chi_{\rm Au}$=6 a.u. (the value that follows directly from measurements on the pure Au film), overestimates all results of the multilayer systems by a factor of 2, proving that it is indeed only a scaling problem.

In conclusion, we have shown that the magnetization-induced second-harmonic generation (MSHG) from magnetic-nonmagnetic multilayers is a pure interface effect. To verify interface sensitivity we studied systems containing different numbers of Co/Au interfaces. At near normal incidence we observed that both the number of interfaces and the direction of the magnetization have a pronounced effect on the measured second harmonic signal. The most important result is the inversion of $I(\mathbf{M}\uparrow)$ and $I(\mathbf{M}\downarrow)$ between the samples containing 1 and 2 Co/Au interfaces and again between the samples with 2 and 3 interfaces. This cannot be explained in terms of bulk induced effects. Furthermore we observe no correlation between the bulk amounts of Co or Au and the measured signals. However the results are accurately described in terms of interface contributions and multiple reflections. Because of this sensitivity for the magnetic properties of buried interfaces, MSHG seems extremely promising as a new tool for studying interface magnetism.

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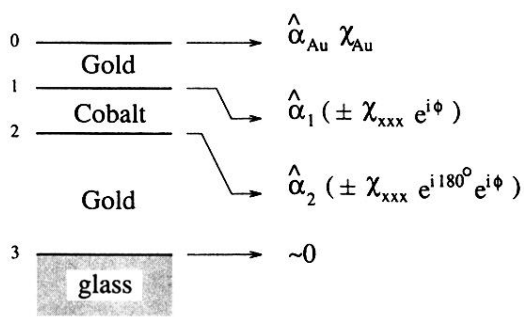

FIG. 3. A schematic example of the samples under study. The relative contributions of the interfaces are indicated.