Effect of photodiode angular response on surface plasmon resonance measurements in the Kretschmann-Raether configuration

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We study the effect of photodiode angular response on the measurement of surface plasmon resonance (SPR) in metallic thin films using the Kretschmann-Raether configuration. The photodiode signal depends not only on the light intensity but also on the incidence angle. This implies that the photodiode sensitivity changes along the SPR curve. Consequently, the measured SPR spectrum is distorted, thus affecting fits and numerical analyses of SPR curves. We analyze the magnitude of this change, determine when it is significant, and develop a calibration method of the experimental setup which corrects for this type of spectral shape distortions. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4748521]

Surface plasmon resonance (SPR), a collective oscillation of conduction electrons at metal-dielectric interface,[1–3] has a very wide range of applications in fields such as sensing,[4,5] biomedicine,[6,7] energy,[8] and light manipulation at the nanoscale.[9,10] In thin films interfaces, the excitation of the surface plasmons may amplify the light electric field up to a factor of 80.[11] Since SPR is scarcely damped in noble metals such as gold or silver, it can be used as a powerful probe for the study of the properties of dielectric films deposited on the metallic film.[11–13]

Among the different experimental set-ups used to study SPR in metal-dielectric interfaces, the attenuated total reflection method in the Kretschmann-Raether configuration, shown in Figure 1, is the most comprehensive.[14,15] A p-polarized laser (intrinsic or obtained using a linear polarizer) is used as the light source. The beam propagates through a semicircular or triangular prism reaching the metallic film at an angle at which it is totally internally reflected. The metallic film may be directly deposited over the prism or over a glass substrate. In the latter case, the glass substrate with the metallic film is attached to the prism with an index matching gel. The prism with the sample is mounted onto a rotation stage, which allows scanning the incidence angle θ. The reflected beam as a function of θ angle is detected with a photodiode used in photocurrent mode (i.e., the current produced by the reflected beam from the inversely-biased photodiode is obtained from the voltage across a load resistor). The typically computer controlled system may have additional optional elements such as a beam-splitter to monitor variations in laser intensity and/or a mechanical beam chopper for use with a lock-in amplifier to improve the signal-to-noise ratio.

As illustrated in Figures 1 and 2, as the stage containing the prism and sample rotates, the beam reflected at the metallic film changes direction. The detection of this reflected beam during the scan is not straightforward and several approaches may be used. For example, the photodetector is mounted onto another independently controlled rotating stage so as to keep the reflected beam at normal incidence with the photodiode surface. Another possibility is to use a fixed large-area photodiode placed close to the sample as shown in Figure 2(a). In the latter approach, although during the scan the reflected beam moves across the photodiode it always falls within its sensing area. As the laser-sample incidence angle (θ) is scanned, the reflected-beam-photodiode angle (β) changes (Figure 2). In particular, for a fixed photodiode, the relationship between β and θ is given by

$$\beta = 2 \cdot (\theta - \theta_0) \tag{1}$$

with θ_0 the incidence angle at which the reflected beam reaches the photodiode at normal incidence (i.e., $\beta = 0$). For the particular geometry of Figure 2(a) at which the photodiode surface is parallel to the incident laser beam, $\theta_0 = 45^\circ$. This is true for semicircular or triangular prisms since the double refraction in triangular prisms produces the same final angle in both cases.

Another possible configuration illustrated in Figure 2(b) consists on fixing the photodiode to the sample rotation stage. In this case, the relationship between the incidence and reflected angles is given as

$$\beta = (\theta - \theta_0). \tag{2}$$

In the third possible configuration, with fixed sample and photodiode, the laser beam incidence direction (Figure 2(c)) is varied. In this case, the relationship between θ and β is also given by Eq. (2).

For all cases illustrated in Figure 2, the reflected beam reaches the photodetector at different positions and with different incidence angles. Since standard photodiode technology exhibits homogeneous sensing areas, the fact that during the scan the reflected beam reaches different photodiode regions should not significantly affect the results. However, the photodiode sensitivity does depend on incident angle.[16–18]

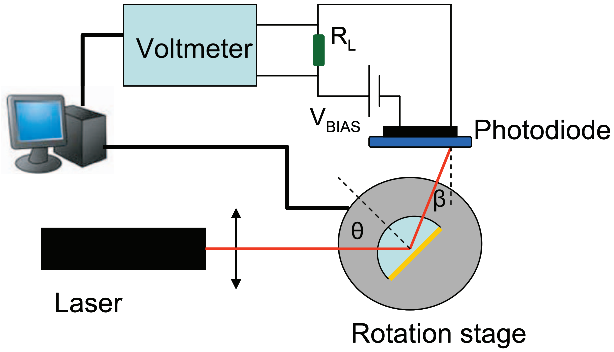

FIG. 1. Schematic of a system used for measuring SPR in the Kretschmann-Raether configuration.

Therefore, the SPR curve profile is affected by changes in the photodiode sensitivity during the scan. In this paper we study the effect of incident beam angular dependence on the photodiode sensitivity and present a correction method when this effect is present. We show that our method produces reliable results which are not affected by these experimental artifacts.

To this purpose we used a device following the geometry depicted in Figure 1 (Kretschmann-Raether configuration). The light source was a HeNe (633 nm) CW 0.5 mW laser. A green HeNe laser (543 nm) CW 0.8 W was also used for comparison purposes. The detector was a Hamamatsu RS Silicon photodiode working in photocurrent mode (V_{BIAS} = −10 V, R_{LOAD} = 5 KΩ). The continuously monitored laser intensity was used to normalize the results and thus correct for intensity fluctuations. The beam was modulated with a mechanical chopper (479 Hz) and the photodiode signal was collected using a lock-in amplifier SRS830 using as reference the chopper signal. The position of the critical angle (at 39.2°) was used to calibrate the absolute angle value, correcting in this way any possible drift of the motor in consecutive spectra. In this fashion the measurements are reproducible within 0.5% error.

Prior to the measurement of SPR spectra, we studied the angular dependence of the photodiode sensitivity. To this purpose we illuminated directly the photodiode with the laser beam recording the signal as a function of incident angle with different wavelengths and polarizations (inset in Figure 3). The photodiode response shows no significant differences for the two laser wavelengths used (543 nm and 633 nm). However, the curves obtained with s and p polarization are appreciably different. For p-polarization we find a minimum at normal incidence and a progressive increase with the incident angle of up to 60° with a latter decay. The maximum difference in sensitivity is approximately 12% (between normal and $\beta = 60°$ incidence). The curve is identical for positive and negative incidence angles and can be fitted to a second degree polynomial function between −40° to +40°. This is a result of several effects such as the effective depletion thickness, p-zone thickness, and photodiode surface reflectivity. The region close to normal incidence exhibits a smaller slope. Thus, this is the region where the photodiode angular response may induce smaller variations in the spectra and may be the preferred one for SPR measurements. For s-polarization, the dependence of the photodiode sensitivity is notably different, with a maximum at normal incidence and decreasing with the incidence angle. At grazing incidence the photodiode sensitivity is about 60% of that at normal incidence. Therefore, any study of the effect of the photodiode angular response must be carried out using proper polarization. This may be particularly important when the SPR curves are measured using a non-polarized light source. In this case, the spectra are commonly presented as the ratio between p and s polarization[19,20] and a different correction must be applied for each polarization. However, we will restrict here to the case of SPR curves measured with a p-polarized light source.

We measured the SPR curves of a 50 nm Au film deposited on sodalime. It is well known that inhomogeneities

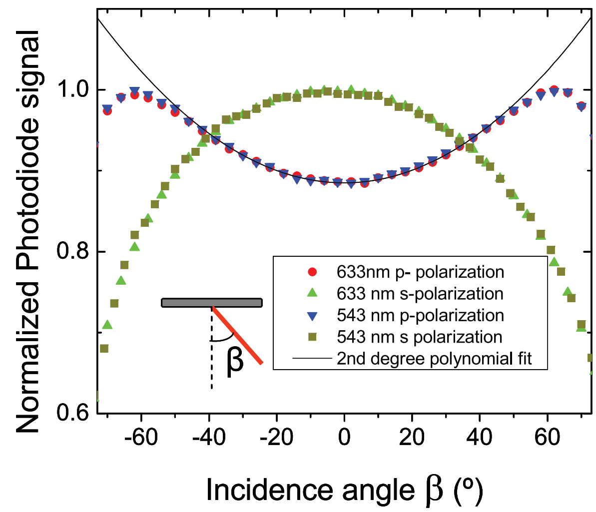

FIG. 3. Photodiode signal (photocurrent mode) obtained by varying the incidence angle for different wavelengths and polarizations and the fit to a second degree polynomial function for the p-polarization curves.

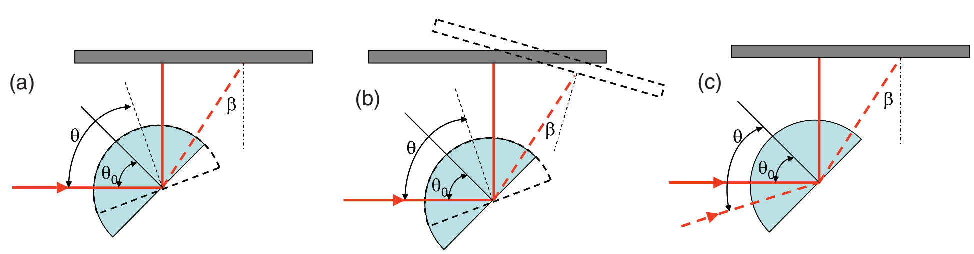

FIG. 2. Variation of the incidence angle of the reflected beam on the photodiode surface for different geometries (a) when the stage with the sample rotates and the photodiode is fixed, (b) when the photodiode rotates with the sample stage, and (c) when the sample stage and the photodiode are fixed and the laser beam changes the incidence direction.

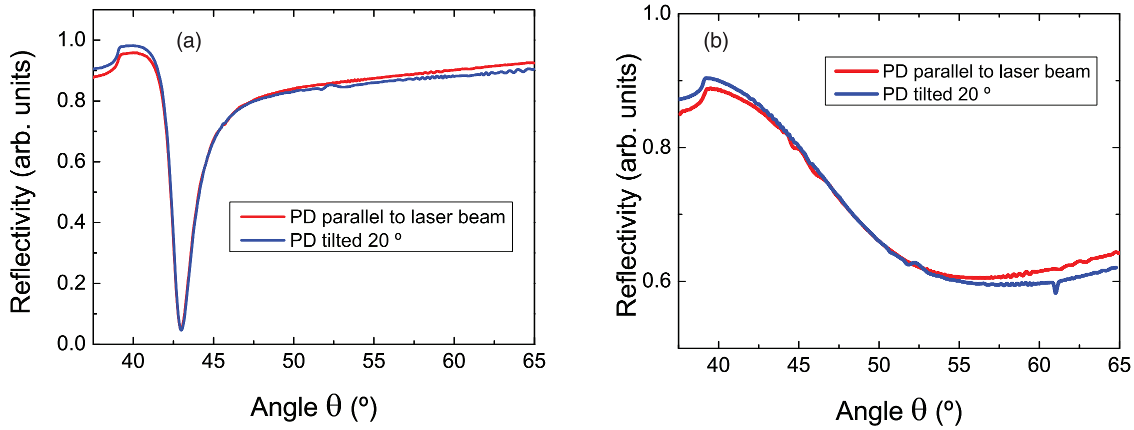

FIG. 4. Average SPR curves for (a) 50 nm Au film and (b) 50 nm Au film + 20 nm Co-phthalocyanine deposited onto sodalime glass obtained with two different orientations of the photodiode. The statistical error is of the same order as the line thickness.

and surface roughness may induce distortions of the SPR spectra.[19–22] Thus, to achieve a minimum roughness and maximum homogeneity, the growth of the gold films was optimized using e-beam evaporator in a vacuum system with a base pressure of 5×10^{-7} torr at a rate of 0.5 Å/s. We measured spectra at 6 different points for each sample. No differences were observed within the experimental resolution of our set-up. The spectra presented in Figure 4 correspond to the average of the 6 spectra obtained from different regions of the sample (line width being the standard deviation). The measured spectra could be fitted assuming a 50 nm Au films[23] onto sodalime glass without roughness effects (the differences between experimental and calculated spectra were of the same order than the experimental resolution). Thus we may exclude significant roughness effects in our measurements.

The spectra were recorded with the photodiode in two different orientations: parallel to the laser beam as shown in Figure 2(a), and tilting the photodiode 20°; hereafter denoted as "parallel" and "tilted" positions, respectively. Thus, for the parallel position $\theta_0 = 45°$ while for the tilted one $\theta_0 = 55°$ (see Figure 2). The results are presented in Figure 4(a).

For low angular incidence, the SPR curve recorded in the parallel geometry exhibits lower reflectivity than in the tilted position, while for large incident angles the situation is reversed. This behavior can be understood in view of the angular dependence of the photodiode sensitivity shown in Figure 3. According to Eq. (1), for an incidence angle $\theta = 37°$, the reflected beam reaches the photodiode surface at $\beta = 16°$ for the parallel position and $\beta = 36°$ for the tilted one. As Figure 3 shows, for p-polarization, with increasing incidence angle the sensitivity of the detector is larger (up to incidence angles $\beta \approx 60°$ that are not reached here) producing an increased photodiode signal. Similarly, for $\theta = 65°$, the light reaches the photodiode at angles of $\beta = 40°$ and $\beta = 20°$ for the photodiode parallel and tilted to the laser beam respectively, explaining the lower signal recorded in the photodiode in the latter case. Nevertheless, we find no significant variations in the resonance peak, with no shift of the resonance position or variation in the resonance width up to our 0.05° resolution limit. Note that in this case the resonance peak width is about $\Delta\theta \sim 3°$, corresponding to $\Delta\beta \sim 6°$. For this range, the variation of the photodiode sensitivity is below 0.5% for both photodiode orientations (see Figure 3).

Figure 4(b) shows the SPR spectra for 50 nm Au with 20 nm Co-phthalocyanine film grown at room temperature and measured with the photodiode in both positions. The homogeneity and roughness of these samples was equivalent to that of the bare Au films. The resonance is attenuated and shifted towards higher angles due to the presence of the phthalocyanine film.[11,24] The detector orientation modifies the spectrum the same as for the bare Au film: the spectrum in the parallel position exhibits lower reflectivity than the tilted one at low incidence angles while the situation reverts for large incidence angles. Contrary to the bare Au film, the photodiode orientation affects significantly the resonance curve of the sample containing the phthalocyanine film. In particular, the resonant angle is $\theta = 55.5°$ for the parallel position and $\theta = 58.5°$ for the tilted one. Moreover, for the tilted position, the resonance attenuation and resonance width are 4% and 10% larger respectively than in the parallel position. These variations are important for interpretations which involve numerical analysis of the resonance curves. A simulation of the SPR curve for the Au-Co-phthalocyanine bilayer (not shown here) revealed that variation of the resonant angle from $\theta = 55.5°$ to $\theta = 58.5°$ would correspond to a change in the real part of the dielectric function of the Co-phthalocyanine from 3.9 to 3.4. Consequently, the photodiode response must be properly taken into account in studies of the dielectric properties of organic molecules, phthalocyanines in particular.

The proper correction of this effect requires determining the sensitivity of the photodiode at each point along the SPR curve. For this, we measure initially the dependence of the photodiode sensitivity with incidence angle (β) as shown in Figure 3. It is important to reemphasize that the photodiode angular response is light-polarization dependent,[16,17] so its sensitivity must be obtained with the same polarization used in the SPR measurements. It is very useful to fit this curve to an analytical expression which for p-polarization is well fitted by a second-degree polynomial function in between −40° and 40° (see Figure 3). Next, the photodiode sensitivity as a

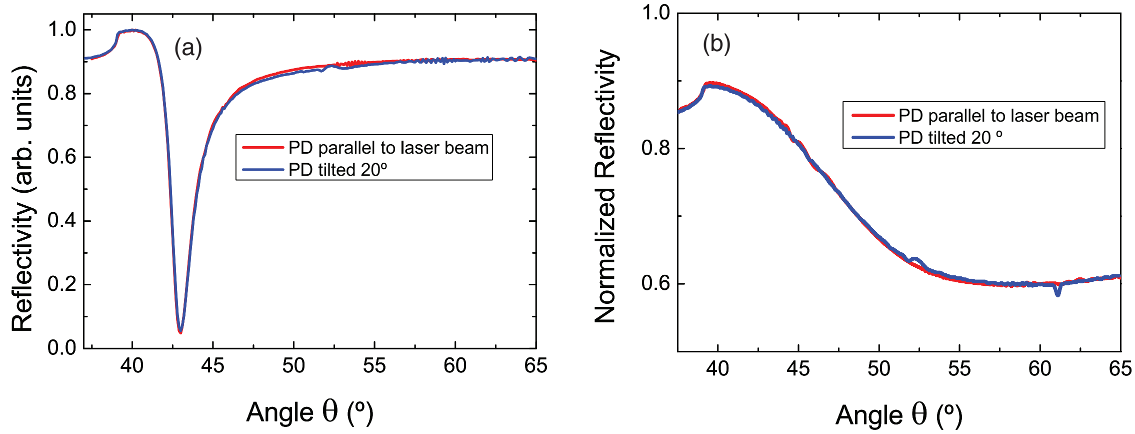

FIG. 5. SPR curve for (a) 50 nm Au and (b) 50 nm Au film + 20 nm Co-phthalocyanine measured with two orientations of the photodiode and corrected by the angular dependence of the photodiode sensitivity. The statistical error is of the same order as the line thickness.

function of the laser-sample incident angle (θ) is obtained using Eqs. (1) or (2) for either geometry. Then, at each incidence angle θ the experimentally measured SPR is corrected by the photodiode sensitivity. The data can either be corrected using experimentally obtained numerical corrections or an analytic expression as obtained before.

To illustrate this procedure, we carried out this correction for the data presented in Figure 4. From the data in Figure 3, the photodiode sensitivity as a function of the incidence angle of incidence of the reflected beam on the photodiode is

$$S(\theta) = 3.84 \cdot 10^{-5}\beta^2 + 1.06 \cdot 10^{-5}\beta + 0.885. \tag{3}$$

With this, Eq. (1) provides the sensitivity of the photodiode as function of incidence angle of the laser on the metallic film for the parallel position

$$S(\theta) = 14.74 \cdot 10^{-5} \cdot (\theta - 45^\circ)^2 + 2.12 \cdot 10^{-5}(\theta - 45^\circ) + 0.885 \tag{4}$$

and for the tilted position

$$S(\theta) = 14.74 \cdot 10^{-5} \cdot (\theta - 55^\circ)^2 + 2.12 \cdot 10^{-5}(\theta - 55^\circ) + 0.885. \tag{5}$$

We used these equations to correct the experimental SPR curves dividing the recorded signal at an incidence angle θ by the sensitivity at that angle.

As Figure 5 shows, with these corrections, the curves match very well. In particular, for the sample with 20 nm of Co-phthalocyanine the position of the resonance angle is now the same (within the experimental error of $\pm 0.3^\circ$).

We analyzed here the situation in which the photodiode is in a fixed position (Figure 2(a)); however the same procedure can be applied to other configurations using the proper equation for the incidence angle of the reflected beam on the photodiode, β, for each point along the SPR curve.

In summary, we showed here that SPR curves in the Kretschmann-Raether configuration are affected by the angular dependence of the photodiode sensitivity. These variations are almost negligible for sharp, narrow resonance such as those present in bare metal films, especially if the resonance position occurs with the reflected beam reaching the photodiode at normal incidence. On the contrary, for highly damped resonances (typical of metallic films with thick overlayers of organic molecules) the curves are significantly modified by the photodiode angular response. This has important effects on the physical results obtained from numerical analyses of the data. These artifacts can be eliminated by measuring the photodiode sensitivity as a function of the incidence angle and correcting properly the SPR data (i.e., dividing the experimental data by the photodiode sensitivity at each point).

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