Polarization dependence of surface plasmon polariton emission

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Surface plasmon polaritons (SPP's) need specific conditions for excitation by photons. In order to fulfill the dispersion relation of the SPP's the photons are required to approach the metal interface from an optically denser medium. For this an attenuated reflection setup (ATR) of a so-called Kretschmann type is used. The excited plasmon may decay by the emission of photons with the same angle with respect to the surface normal. Deliberately using rough metal films the surface plasmon polariton is elastically scattered at the interface. This results in a partial loss of coherence of the reemitted photons. While the angle in respect to the surface normal is conserved, a fraction of the emitted photons leave the plane of incidence, resulting in the so-called ATR cone. Upon analysis of the polarization dependence of light from the ATR cone, an exceptionally clear polarization dependence has been found. The observed behavior is the complete linear polarization of the light in the plane of emission, thus resulting in continuously changed polarization in respect to the polar coordinates within the ATR ring.

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I. INTRODUCTION

Surface plasmon polaritons (SPPs) play an important role in a variety of modern applications, such as surface enhanced Raman scattering[1] (SERS), surface plasmon-coupled emission[2–5] (SPCE), surface plasmon resonance[6–9] (SPR), and subwavelength optics.[10,11] It is therefore expected that progress in the understanding of its mechanism will unlock prospective novel approaches. Here we report on the polarization dependence of the elastically reemitted photons, which permits us to draw important conclusions in conjunction with inelastically re-emitted photons used, e.g., in SPCE.[2–5]

The dispersion relation of a SPP dictates the conditions under which it is excited. One result is that its excitation cannot be achieved by direct irradiation of photons on a metal surface but requires special optical configurations, including those initially proposed by Kretschmann and Raether[12] and Otto.[13] Their common property is that the photons approach from an optically denser medium before impinging on the metal, using an attenuated total reflection (ATR) setup.[12,13] In this paper we use exclusively the Kretschmann configuration.

The use of a semispherical prism, as shown in Fig. 1, has two intrinsic advantages. First, the light path can be used in such a fashion that the incident and outgoing photons are always normal on the prism surface, i.e., refraction at this air glass interface may be neglected. Second, the rotational symmetry of the prism permits unperturbed observation of the scattered light unlike a triangular prism. For SPP's excited by photons with angular frequency ω on thin, smooth metal surfaces, the wavelength-dependent dispersion relation of a SPP is given by the following equation:[14]

$$k_x = \frac{\omega}{c}\sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} = \frac{\omega}{c}\sqrt{\epsilon_3}\sin\alpha \tag{1}$$

with $\epsilon_i = \epsilon_i' + i\epsilon_i''$ complex optical constant of layer i and α photon angle of incidence.

The above equation (1) assigns exactly one unique **k** vector to each wavelength involved in the excitation of a SPP. The photons then need a specific angle of incidence with respect to the surface normal and within the plane of incidence. Furthermore, in order to satisfy the dispersion relation, modification of the **k** vector can only occur if the incident photons are linearly polarized parallel to the plane of incidence. On a perfect, single crystalline, metal surface where scattering events due to imperfections can be considered negligible, the SPP may decay by the emission of photons which are still within the plane of incidence and with the same absolute angle with respect to the surface normal that were needed for their excitation.

On an evaporated and therefore imperfect metal film the propagating surface plasmon polariton is in part elastically scattered from its original direction. This results in a partial loss of coherence of the reemitted photons. While the angle with respect to the surface normal is conserved, most of the emitted photons may no longer be located in the plane of incidence. This results in the so-called ATR cone (Fig. 1). It should be noted that the aperture angle of the reemitted photons is only then unchanged if the total process can be con-

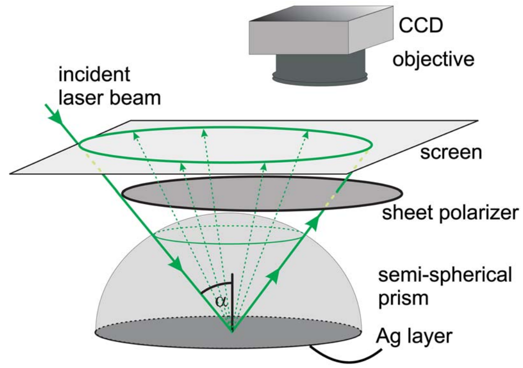

FIG. 1. (Color online) Sketch of the Kretschmann-type ATR setup with a semispherical prism and an additional polarizer.

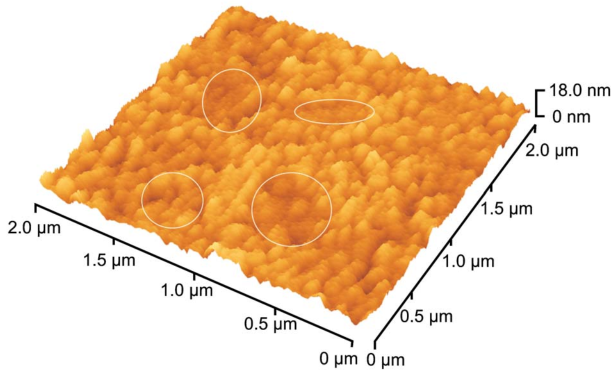

FIG. 2. (Color online) AFM image of the evaporated silver film.

sidered to be elastic. If an inelastic process such as fluorescence or Raman scattering is introduced, the aperture angle of the ATR cone is changed according to the dispersion relation[2–5,15] [see Eq. (1)].

The ratio between the number of reemitted photons situated in the plane of incidence and those detected beyond the plane of incidence is a function of the roughness δ of the metal film.[14,16,17] The roughness also influences the angular position of the reflectivity minimum $\Delta\alpha$ and the ATR curve half-width $\Delta\alpha_{1/2}$ compared to a smooth interface.[14,16,17]

$$\Delta\alpha = \tan(\alpha_{SP})\mathrm{Re}\left[\frac{\Delta k_{SP}}{k'_{SP}}\right] \tag{2}$$

$$\Delta\alpha_{1/2} = -2\tan(\alpha_{SP})\mathrm{Im}\left[\frac{\Delta k_{SP}}{k'_{SP}}\right] \tag{3}$$

with $k'_{SP}=(2\pi/\lambda)\sqrt{\epsilon_3}\sin(\alpha_{SP})$. The quality of the model depends crucially on the definition of Δk_{SP} for which we refer to the literature.[17]

II. EXPERIMENTAL

The excitation of the SPP's was achieved with the green 514.5 nm line of a Coherent Innova 70-4 laser in single line configuration. To prevent distortion of the ATR ring a semispherical prism (BK7, Schott) was used. The prism was cleaned prior to its use by a successive multistep treatment with Ethanol (purity: 99.98% for spectroscopy, Merck), Deconex (Borer Chemie), Neodisher (Dr. Weigert), and Acetone (99.98% pro Analysis, Merck) at 70 °C after finally having dried in a flow of nitrogen (purity: 99.999%, Messer Griesheim). The procedure is explained in greater detail in (Ref. 18). The use of Carot's acid as a standard cleaning procedure for glass surfaces was discontinued due to the irreversible corrosion of the surfaces for some of the chosen glass types. The silver (purity: 99.99%, Goodfellow) was thermally evaporated on the cold prism, in order to increase the roughness of the film. The enhanced roughness gives rise to a very pronounced ATR ring. The degree of roughness was controlled with an AFM (Explorer 2000, Topometrix) and is shown in Fig. 2.

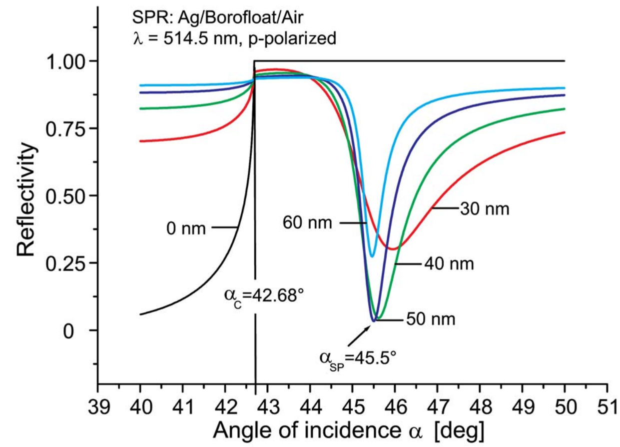

FIG. 3. (Color online) Simulations of reflectivity vs angle of incidence α of a Borofloat-glass/silver/air system with varying silver thicknesses in a Kretschmann-type ATR configuration.

The maximum height deviation in a representative $2\ \mu\text{m}\times 2\ \mu\text{m}$ area, as shown in the AFM scan above, is approximately 18 nm. However, the average roughness δ_{RMS} observed is 2–3 nm. The white circles denote larger depressions in the 50 nm thick layer of typical diameters of 200–400 nm.

III. MEASUREMENTS

The aperture angle of the ATR cone (with best visibility on a rough silver film) is identical to the angle for the maximum SPP excitation which can be found by observing the reflectivity curve. Solving the Fresnel equations by means of a matrix formalism for a multilayered system, with respect to the optical constants,[19] allows the reflectivity with respect to the angle of incidence to be simulated.[20] Figure 3 shows the results of a set of simulations compiled to describe a three-layer Borfloat-glass/silver/air system. The outcome for several different thicknesses of silver coating are also displayed in Fig. 3.

The curve for 0 nm shows the behavior of the system in the absence of a silver coating, where the critical angle α_c specifies the angle at which the total reflection initiates. Furthermore, this graph is lacking an SPP excitation. The remaining four curves (30 nm–60 nm silver thickness) show the excitation of an SPP. This is evident by the clear minima present in their reflectivities located between 45° and 46°. The quality of the excitation can be deduced from the sharpness and depth of the minima. For the above-described system, excited at 514.5 nm, the optimum silver thickness is approximately 50 nm. These results imply that the optimum angle is influenced by the excitation wavelengths, the wavelength-dependent optical constants, and the thickness of the individual layers. This provides an explanation for the highly delicate and extremely sensitive nature of surface plasmon resonance (SPR). In order to fulfill the dispersion relation, only the parallel component k_{par} of the incoming photons can satisfy the inherent conditions of this relation. Therefore, one prerequisite is the sole usage of linearly po-

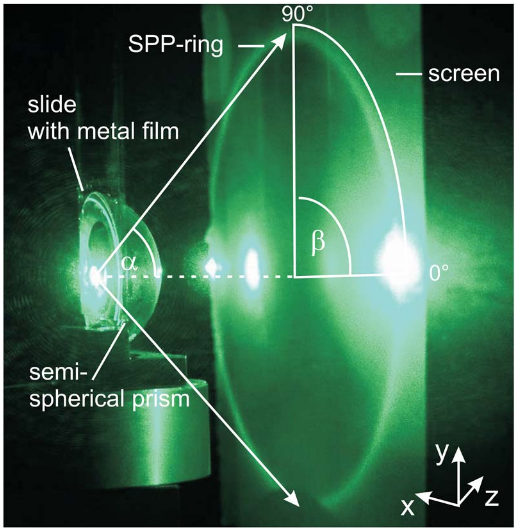

FIG. 4. (Color online) Projection of the ATR cone on a screen.

larized photons within the plane of incidence. The focus of this Brief Report is to analyze the polarization of the light, reemitted directly by the SPP into the ATR cone. An article on the polarization dependence of SPP excited fluorescent emissions (SPCE) has been published by Gryczynski *et al.*[2] An image of the projection of the ATR cone from a semi-spherical prism onto a screen is depicted in Fig. 4.

Due to the symmetry properties of the ATR ring evident in the above image, it is sufficient to confine our analysis to a quarter of the actual ATR ring. Furthermore, it is advantageous to use a reversed gray-scale image in order to show the distribution of light on the projection screen. Please refer also to the notation of the polarization as shown in Fig. 5.

In Fig. 6 a full set of ten measurements is displayed, where the polarization analyzer has been changed from 0° to 90° in consecutive steps of 10°. The light responsible for the excitation and the nonscattered, total reflected light are linearly polarized at 0°.

The result of the analysis is summarized in Fig. 7. It definitively shows that the polarization of the emitted light is not in accordance with the SPP exciting photons, but changes with its origin on the ATR ring. More precisely, the polarization of the light is always perpendicular to the tangent of the ATR ring at this coordinates.

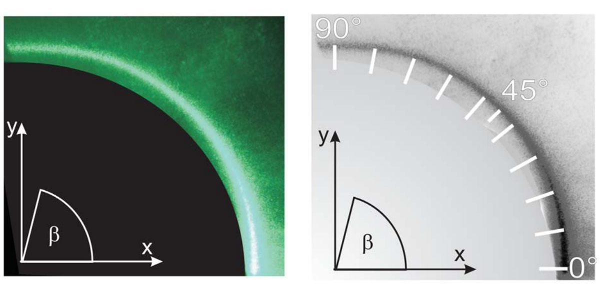

FIG. 5. (Color online) Left: Upper right quarter of the projected ATR cone. Right: Notation of the polarization on an inverted gray-scale image.

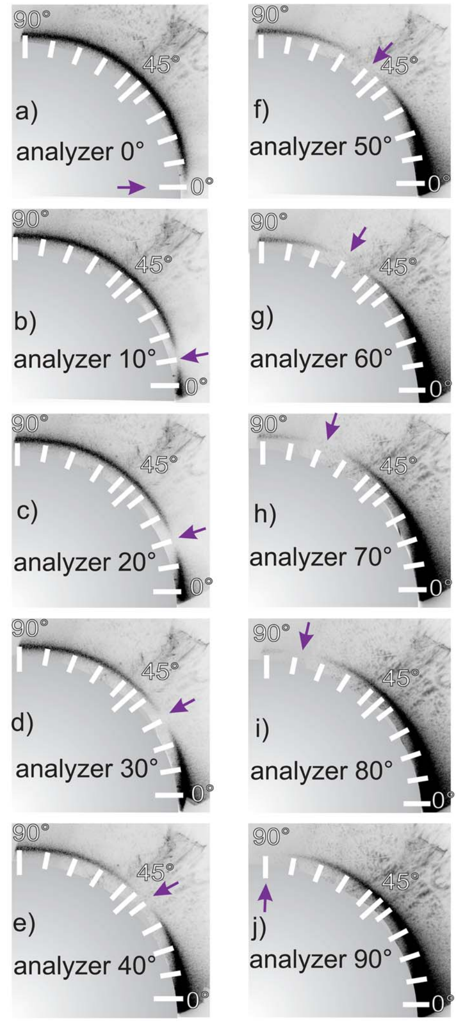

FIG. 6. (Color online) Behavior of the polarization within the ATR ring. The arrows denote the positions of the intensity minima, respectively.

IV. CONCLUSION

The way the orientation of the light vector changes sheds light on the origin of the effect. While a mere reflection would conserve the polarization of light, the changes are clearly due to the effects of the SPP. Following the

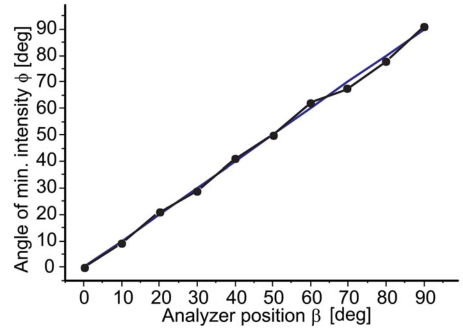

FIG. 7. (Color online) Polarization vs position.

transformation of light into an electron density wave, these propagating electrons are scattered at the imperfections of the metal surface. This changes the direction of propagation. Upon retransformation of the surface plasmon polariton wave into photons, these are emitted with a well-defined angle in the plane between the surface normal and the new electron propagation direction according to the SPP conditions. In order to obey the SPP dispersion relation which has to be valid for the excitation as well as for the deexcitation of the surface plasmon, the polarization of the reemitted light has to be parallel to the above-mentioned new plane and therefore results in the observed effect.

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