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Norbert Kroo [a]; Sándor Varró [a]; Gyz Farkas [a]; Péter Dombi [a]; Dániel Oszetzky [a]; Attila Nagy [a]; Aladár Czitrovszky [a]
[a] Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, Budapest, Hungary

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Nonlinear Plasmonics

Norbert Kroo, Sándor Varró, Győző Farkas, Péter Dombi, Dániel Oszetzky,
Attila Nagy* and Aladár Czitrovszky

Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, Budapest, Hungary

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Theoretical and experimental results on laser light-excited nonlinear surface plasmon (SPO) phenomena are reported. Strongly directional light emission of SPOs was indicated and observed already at relatively low cw laser power. The width of this peaked directional distribution seems to depend on the laser power. Another manifestation of nonlinearity was found by observing a weak squeezing effect in the SPO-emitted fundamental light. At high (pulsed) laser intensity an evanescent (SPO) field enhanced second harmonic emission and a broad metallic luminescent spectrum was found. The second harmonic component is spectrally broader than the fundamental SPO-emitted light. Our simple theoretical model describes all of these observations qualitatively, except for the broad luminescent spectrum.

Keywords: surface plasmons; surface nonlinear optics; femtosecond phenomena

1. Introduction

Surface plasmon polaritons (or surface plasmon oscillations, SPOs) are at the centre of interest within an increasingly broad scientific community because of the unique properties of this collective excitation of conduction electrons on metallic surfaces. These excitations (a 'special type' of light) have dispersion relations significantly different from that of 'ordinary' light; moreover, the diffraction limit does not apply to them, and they may be localized to nanosized metallic irregularities or particles [1]. They may also represent huge electric fields and can be the medium of SPO band gaps, for example, on grated surfaces. These properties imply a broad spectrum of potential applications [2–6].

These special features inspire the study of SPOs. We suggested in a recent paper [7] that from the study of the statistical properties of SPOs by near-field scanning tunnelling microscopy (STM), non-classical properties of these collective oscillations can be deduced. In the same paper a simple model of SPOs was described which we called a double layer potential model. In [7] the linear term of this potential was used.

There is a large number of theoretical papers describing SPO properties (for example, [9–11]) and our findings are in qualitative agreement with these theories. We found, however, that our simple model is more suitable for the generalized description of

*Corresponding author. Email: anagy@szfki.hu

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high-intensity, nonlinear processes. We present here our studies with SPOs excited by high-intensity, femtosecond laser pulses. The second-order term of the double layer potential [7] was also taken into account in another work [8] resulting in nonlinear processes. The detailed description of these theoretical results will be published elsewhere. We use this model in the present paper to interpret the experimental data.

Our theoretical findings are summarized below, followed by a description of the experimental results obtained by cw and high-power picosecond and femtosecond laser excitation of SPOs. In all cases the directional, statistical and spectral properties of the light emitted by the SPOs were analyzed.

2. Theoretical considerations

In our recent work we formulated the basis of a simple model to describe the coupling of light to the assembly of conduction electrons of a metal [7]. In a simple way, this model furnishes the main predictions related to surface plasmon processes on metal surfaces by introducing the so-called 'laser-induced oscillating double layer potential' U_d [7]. We have shown that U_d governs and accounts for all known linear SPO processes, as far as we restrict ourselves to its first approximation term, $U_d^{(1)}$, where we expand U_d according to the displacement of the oscillating electron of the metal. However, to be able to interpret new nonlinear phenomena observed at higher exciting laser fields, we had to generalize the result of [7] by taking the second order term, $U_d^{(2)}$ into consideration in the expansion. This results in $U_d = U_d^{(1)} + U_d^{(2)}$. The detailed description of this generalization will be published elsewhere [8]. Therefore, here we restrict ourselves to the summary of the main predictions of [7] and [8] related to the interpretation of our experimental observations.

The most important statement is that the gradient of U_d (along the metal surface normal) furnishes the 'field enhancement' factor in the evanescent region in the proximity of metal surface as being proportional to ω_p^2/ω^2, where ω_p is the plasma frequency of the metal, and ω is the laser frequency. Because $\omega_p/\omega \sim 10$ for the laser field, the field and the intensity enhancement is 100 and 10,000, respectively, in accordance with other theories.

Furthermore, our model reproduces the results of earlier works [9–11] related to a lobe in the angular distribution of the SPO light (depending on the surface roughness of the metal film). Moreover, it also indicates the intensity dependence of both the angular position of the lobe maximum and of the lobe half-width. A further prediction is that the (surface roughness-dependent) spectral half-width of the observed second harmonic of the SPO light is twice of that of the fundamental SPO light. Both the fundamental and second harmonic light lobes appear on the vacuum side of the Kretschmann geometry.

Finally, we describe the quantization of the {electron} $\otimes$ {laser photon} $\otimes$ {SPO} system by taking into account a linear and a nonlinear term in the joint interaction [8], similarly to the procedure followed in the case of generalizing the potential U_d as described above. The result is a 'phenomenological Hamiltonian' which contains both linear and nonlinear (second order) operator terms which can be interpreted as sources of plasmon squeezing. This result may indicate the possible appearance of squeezing of the SPO-emitted light on a preliminary level. Further details will be presented in [8].

3. Experimental

To support our theoretical findings a set of experiments was carried out with various laser sources.

3.1. *Angular distribution of SPO-emitted light*

We utilized an experimental setup for the measurement of the spatial distribution of the light generated by decaying surface plasmon oscillations. A near-infrared cw diode laser with 808 nm wavelength was used for the excitation of SPOs in a 45 nm-thick gold layer deposited on a right-angle prism. For the SPO coupling setup we used the so-called Kretschmann geometry. To measure the directional power distribution of the light generated by the recombination of SPOs, we placed the gold layer into the centre of a goniometer. A detector (Thorlabs PM 100 with an S-1208 sensor) was also placed on the goniometer which enabled us to measure the power in a 180° angular range. The cw power of the exciting laser was set to 100 mW. Figure 1 shows the measured directional light distribution. The figure also shows that there is a significant peak at around 67.5° with respect to the surface normal for p-polarized exciting light. No signal appeared at s-polarization. At higher laser power (150 mW) the surface was already distorted by the heat due to SPO absorption in the gold film and therefore the data at these laser power values could not be used.

In a subsequent experiment a special long-cavity Ti:sapphire laser oscillator [12,13] pumped by a 7 W solid-state pump source (Laser Quantum's 'finesse' laser) was used to

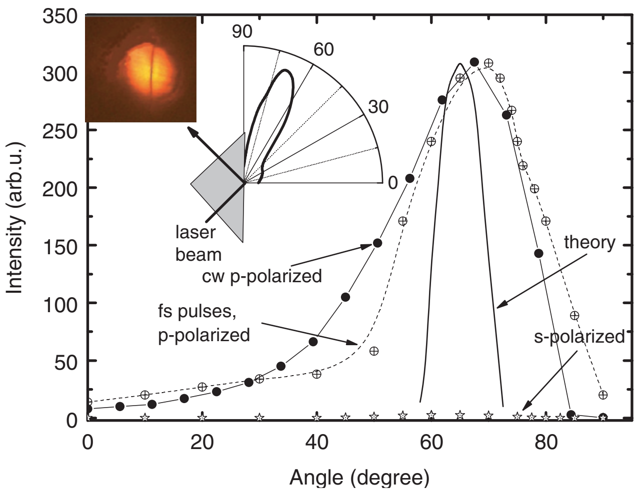

Figure 1. Measured angular distribution of SPO-emitted light. The SPOs were excited by a p-polarized cw diode laser (thin solid line and symbols) and a femtosecond Ti:sapphire laser (dashed line and symbols). S-polarized laser light did not excite SPOs (stars). The thick solid curve shows theoretical data according to the model described in the theoretical considerations section. The inset shows the setup and the angular distribution of femtosecond SPO scattering on a polar plot. The photo image inset shows the laser beam reflected from the surface with the surface plasmon absorption line in the middle. (The colour version of this figure is included in the online version of the journal.)

excite SPOs in the Kretschmann geometry on a 45 nm-thick gold film. The laser delivered either 2 ps-long chirped pulses with ~200 nJ pulse energy directly coming from the long-cavity, positive-dispersion oscillator [12] or 120 fs-long, close to transform-limited pulses with 150 nJ pulse energy after extracavity dispersion compensation with a pair of transmission gratings. The repetition rate was 3.6 MHz. Peak on-target intensities of 10^{11} W/cm^2 and 1.3×10^{12} W/cm^2 were reached with these pulses, respectively. The central wavelength of the laser was 790 nm. After directing the femtosecond beam onto the prism surface, SPOs were coupled out by the irregularities of the gold surface and the light emitted in this way was analyzed.

The first set of experiments with this laser was aimed at measuring the angular distribution of the emitted light. It was performed with a photomultiplier detector behind a monochromator selecting the $\lambda = 790$ nm wavelength. The observed light is p-polarized and there is practically no signal in s polarization, just as in the cw case. The resulting distribution is also shown in Figure 1 together with the cw data. It is seen that the pulsed distribution is somewhat narrower and shifted to larger angles than in the cw case. These angular distribution results are in qualitative agreement with earlier results [9–11] but even more with our model [8], predicting narrower distributions (also presented in Figure 1).

3.2. *Experiments on the potential squeezing of SPO-emitted light*

In our previous experiments [7] the exciting low cw laser power was not sufficient to demonstrate the existence of any nonlinear effects. Here, however, our findings at a higher (100 mW) cw laser power are presented and the statistical parameters of the generated light at this power are analyzed. With a single photon counting module (Perkin-Elmer SPCM-AQR-14) and a data evaluation system (as described in [7] and [14]) the photon statistics have been measured. The measurements were performed for goniometer settings of 0° and 67.5° (the latter being the position of the peak intensity of Figure 1).

Figure 2 shows the photon number distributions of the light generated by plasmons measured at a detection angle of 67.5° (measured from the surface normal). The experiment revealed that the half-width value of the measured laser light distribution is 12.95 ± 0.05 in contrast to the 12.48 ± 0.05 value of the Poissonian (approximately Gaussian) distribution of the SPO-emitted light. Therefore a small (~4%) narrowing compared with the laser distribution is observed, providing another indication of the non-classical behaviour of SPOs. This encourages us to continue this line of research in the future.

3.3. *Spectrum of SPO-emitted light*

In the experiments examining the spectral properties of SPO-emitted light, the same monochromator-photomultiplier system was used as for the angular distribution measurements. Here we used our femtosecond laser only, and the intensity was increased by reducing the beam diameter with a telescope, changing the size of the illuminated spot on the surface of the gold film. The emitted light was observed in the vacuum half-space of the Kretschmann geometry. Firstly, the highly dominant strong SPO-emitted fundamental light, having a narrow spectral width, was easily detected, and its angular distribution is shown in Figure 1. This fundamental light was then filtered out. Upon increasing the power density, the p-polarized second harmonic light showed up first with a quadratic laser power dependence, having a sharp angular distribution around 70°. In Figure 3 we present the measured spectra and relative spectral widths ($\Delta\lambda/\lambda$) of the SPO light emitted

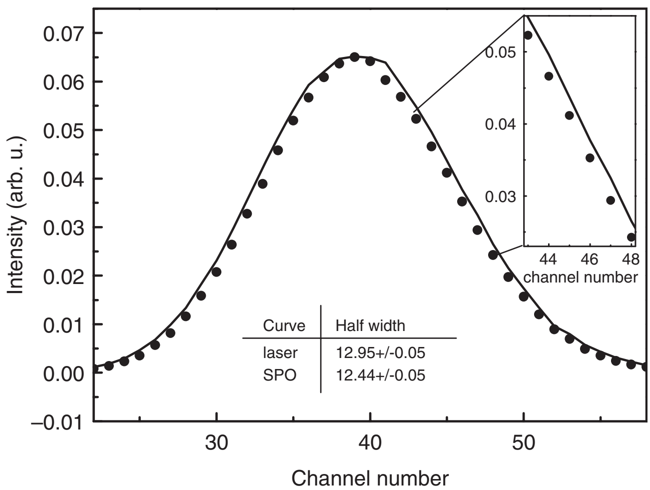

Figure 2. Photon number distribution of the 808 nm 100 mW cw laser (solid line) and of light emitted by SPOs excited by this laser (symbols). The latter is narrower by about 4%. The half-width values of the distributions are the results of fitting Gaussian functions to the experimental data; this can be done since at large numbers the Poissonian distribution turns into a Gaussian.

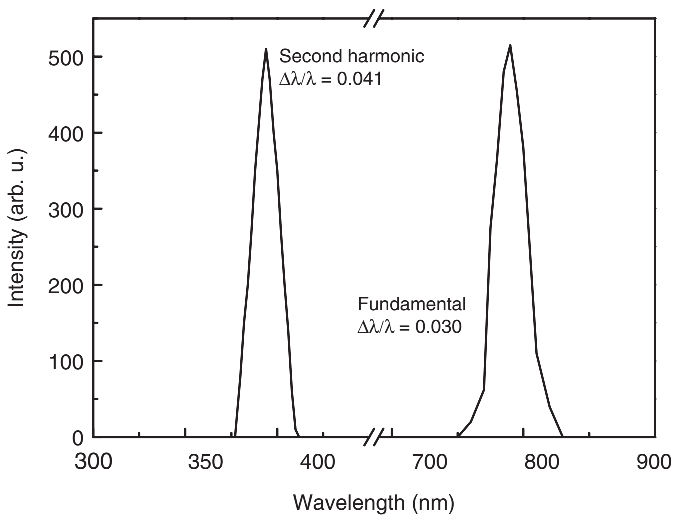

Figure 3. Comparison of the spectrum of the fundamental and the second harmonic light emitted when the plasmons are generated by the femtosecond laser. The change in $\Delta\lambda/\lambda$ at the second harmonic wavelength is in good agreement with the theoretical prediction.

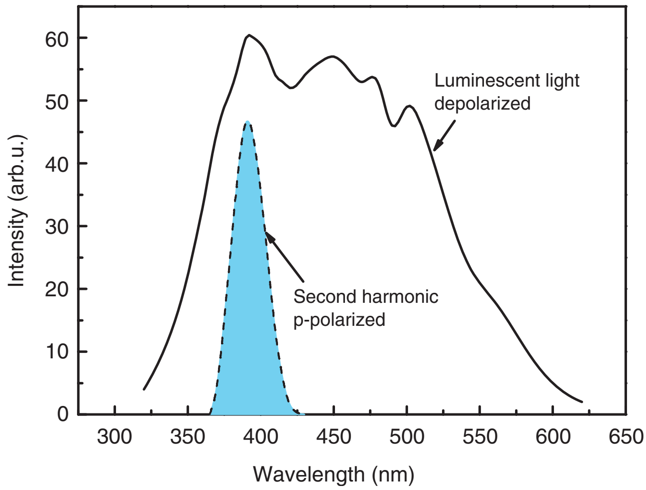

Figure 4. Spectra of the SPO-emitted light induced by femtosecond pulses with a central wavelength of 790 nm. The second harmonic generated at lower intensity (dashed line) and the broad 'luminescence' spectrum at higher intensity (solid line) are plotted. (The colour version of this figure is included in the online version of the journal.)

at the second harmonic wavelength and at the fundamental one. It can be seen that the relative width of the second harmonic is larger than that of the light emitted at the fundamental laser wavelength. This is also in good agreement with our theoretical results [8].

By increasing the intensity of the exciting laser light further, a broadband emission appeared, hiding the second harmonic. This emission had isotropic distribution in space and it was depolarized. The intensity of this light changed with roughly the fourth power of the exciting laser intensity. This spectrum is actually broader than the spectrum shown in Figure 4, since there is a short wavelength instrumental cut-off due to the glass window of the photomultiplier. There is also a long wavelength cut-off resulting from the absorption by a filter put in front of the photomultiplier to block the 790 nm intense SPO-emitted fundamental laser light. The origin of this broad depolarized spectrum is not yet understood. If the origin is not in an inherent but still unknown relation with SPOs, we believe that one of two processes is potentially occurring: it may be (i) the multiphoton-induced (but depolarized) luminescence of the Au metal [15] enhanced by SPOs [16] or (ii) a special Stefan–Boltzmann-type radiation from the Au surface is involved, since the surface is warmed up abruptly by the ultrashort laser irradiation. Subsequently there is an equally fast cooling down of the conduction electrons [17] which, in turn, emit depolarized light with an integrated Planck spectrum [18]. This also explains the fourth order dependence on the laser intensity.

4. Summary

We predicted and observed a sharper peak in the angular distribution of SPO light than that seen previously [9–11]. The observed fundamental wavelength light is p-polarized and it is peaked at around 67.5°, in qualitative agreement with the calculated distribution. This may also indicate the influence of nonlinearity, and eventually the presence of super-radiance may not be excluded, either. Therefore, this phenomenon has to be studied both theoretically and experimentally in more detail. We also observed a broad luminescence spectrum which is depolarized and rather intense. This high intensity could be due to the strong amplification effect of SPOs.

We also demonstrated that second harmonic assisted by SPOs can be generated not only in reflection, as found for example in [19,20], but also from direct decay of SPOs into 'free space', that is, at the vacuum side of the Kretschmann geometry. The second harmonic is spectrally broadened, in qualitative agreement with the predictions of our model.

Our model qualitatively indicates the occurrence of SPO squeezing, when the model is extended by including the nonlinear term into the Hamiltonian. This effect was already presented in [7] as the result of measurements with an SPO near-field scanning tunneling microscope (STM). The analysis of our cw laser excitation measurement supports this conclusion since, for example, at 100 mW laser power a ~4% narrowing of the statistical distribution of SPO-emitted fundamental light was found (when compared with that of the exciting laser).

To sum up, in the present work we demonstrated that in the process of SPO excitation, nonlinear phenomena occur in addition to linear ones. Due to the presence of the strong evanescent electromagnetic field, nearly all linear elementary processes may become more or less nonlinear. This conclusion can be drawn both from our theoretical model and from the experimental data. The simple model presented and the experiments are in good qualitative agreement. Further experiments and calculations are being carried out to clarify the remaining open questions.

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