Surface plasmon polariton - exciton interaction in metal-semiconductor and metal-dye nanostructures

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Abstract. We consider the frequency- and angle-dependent reflectivity of hybrid structures containing metallic components and an optically excitable medium such as organic dyes or semiconductor quantum wells. Clear signatures of a coupling between surface plasmon polaritons and excitons in the excitable medium, in particular avoided crossings with hybridization gaps in the range $\approx 10$-100 meV, are found both experimentally and theoretically.

Electromagnetic excitations at optical frequencies can propagate at metal-dielectric interfaces as surface plasmon polaritons (SPPs), which are mixed modes formed from electromagnetic fields in the dielectric material and plasma oscillations in the electron gas of the metal. SPP wavelengths can be well below optical wavelengths at the same frequency. Therefore, one can expect SPPs to play a major role in future nano-sized devices as a way to guide and manipulate light on a nanometer scale.

The interaction of SPPs with excitons is interesting for at least two reasons. Firstly, one can try to transfer energy from the excitonic into the plasmonic subsystem in order to compensate the large SPP losses that result from metallic absorption and radiative decay \cite{1, 2, 3, 4, 5, 6, 7}. Secondly, novel coupled quantum modes that may be termed exciton plasmon polaritons are expected to be formed in the case of strong SPP-exciton interaction. Only recently, the SPP-exciton interaction was investigated in several hybrid systems combining either a metal and inorganic semiconductors \cite{3, 8} or a metal and a dielectric layer containing organic dyes \cite{9, 10, 11, 12, 13, 14} with geometries similar to those depicted in Fig. 1. Both system classes have their advantages and disadvantages: Excitons in semiconductor quantum wells (QW) show at low temperatures sharp excitation peaks with broadenings in the meV range and high absolute values of the absorption. Excitons in organic dyes, e.g., in Cyanine-based J-aggregates in a PVA matrix as studied in Ref. \cite{14}, are stable at room temperature. They can have very large oscillator strengths, but all resonance features are much broader than in QW spectra. In the present paper, we calculate the coupled SPP-exciton modes in both types of hybrid systems and compare the results with recent experiments. The geometries of the considered systems are sketched in Fig. 1.

First, we discuss the metal-semiconductor hybrid that was investigated in Ref. \cite{3}. It consists of a metal grating which is formed by a periodic arrangement of gold nanowires on top of a typical GaAs/Al\textsubscript{0.3}Ga\textsubscript{0.7}As QW with geometry as specified in Fig. 1(a). We calculate the far-field reflectivity at low temperatures ($T = 10$ K) when this system is illuminated from
The periodically structured metal layer, i.e., the gold nanowire array in panel (a) and the gold reflection grating in panel (b), scatters the incident far-field radiation into SPPs which in turn couple to the dipole moments of the excitons in the semiconductor quantum well (QW) or in dye aggregates. All dimensions are given in nanometers and refer to the GaAs/AlGaAs-QW sample of Ref. [3] (panel (a)) or the sample of Ref. [14] containing Cyanine-based J-aggregates (panel (b)). Red lines indicate the near fields of SPP modes and the near field below the slits.

above by a plane wave with angle of incidence $\theta$ (measured against surface normal). We consider only linear polarization with the electric field in the plane of incidence, which is perpendicular to the nanowires. Maxwell’s equations can be solved for this structure and reflectivities can be calculated once the dielectric function $\varepsilon(\omega)$ is specified for all layers. The complex and frequency-dependent dielectric function for gold is taken from Ref. [15]. For the substrate, the thin buffer layer, and the AlGaAs barriers, we use the real dielectric constants $\varepsilon_{GaAs} = \varepsilon_{GaAs}(\hbar\omega = 1.5 eV) = 13.4$ and $\varepsilon_{AlGaAs} = \varepsilon_{AlGaAs}(\hbar\omega = 1.5 eV) = 13.69$, i.e., we neglect the weak absorption within the substrate and the variation of the bulk dielectric functions over the small energy region around the QW resonances (1.55 eV $\pm$ 20 meV). For low temperatures, the QW dielectric function is dominated by the exciton response, which is calculated via the 2d Elliot-formula [2]. There are heavy hole ($hh$) and light hole ($lh$) resonances in a GaAs QW. The resonances are characterized by the 1s binding energies $E_{b,1s}^{(1s)} = 8.18$ meV, $E_{b,1h}^{(1s)} = 11.64$ meV [16], the band gaps $E_g,1h = 1.552$ eV, $E_g,1h = 1.567$ eV [17], and the anisotropic 1s oscillator strengths $f_{\perp,1h} = 4f_{\parallel,1h} = 89.8 \cdot 10^{-5} \text{Å}^{-2}$, $f_{\parallel,1h} = 53.1 \cdot 10^{-5} \text{Å}^{-2}$, and $f_{\perp,1h} = 0$ [16]. The broadening of the exciton resonances is the only parameter that is fitted to experiment. Good agreement is obtained for $\delta_{hh} = \delta_{lh} = 2$ meV, see Fig. 2 below. Now, all material parameters are specified and Maxwell’s equations can be solved in time or frequency space. Here, we use an approximate frequency space method [2, 18, 19, 20], that is in detail discussed in Ref. [2]. The calculation of the field inside the metals is avoided by enforcing a particular boundary condition (surface impedance boundary condition) at all metal-dielectric (or metal-semiconductor) interfaces [2, 21]. The dominant SPP-related features in the far-field reflectivity are due to SPP modes at the upper grating-air interface, whereas QW excitons couple primarily to SPP modes at the lower metal-semiconductor interface. In order to observe the rather weak signal from SPP-X modes below the grating, we subtract the far-field reflectivity of the free SPP system (no resonance in the QW dielectric function) both from the measured far-field reflectivity of the coupled system and from our calculations. The results are shown in Fig. 2. Good agreement between the calculated and the measured difference spectra is found. The signatures of the $hh$ and the $lh$ excitons are clearly to be seen. For $\theta = 26^\circ$, the resonances are located at the positions of the free exciton resonances, i.e., at $\approx 1.544$ eV and 1.555 eV. This shows that exciton and SPP resonances are decoupled at $26^\circ$. Between $26^\circ$ and $35^\circ$, the exciton resonance energies shift to lower values by $\approx 7$ meV and 11 meV for the $lh$- and $hh$-resonances, respectively. This is a clear sign of SPP-exciton coupling. Furthermore, we
Figure 2. (a) Measured [3] and (b) calculated far-field reflectivity difference spectra (system with SPP-exciton coupling minus free SPP system, color code) as a function of angle of incidence $\theta$ and photon energy for the gold grating-QW system shown in Fig. 1(a).

Figure 3. (a) Measured [14] and (b) calculated far-field reflectivity difference spectra (coupled system minus free dye-contribution, color code) as a function of angle of incidence $\theta$ and photon energy of the metal-dye system that is shown in Fig. 1(b). The inset of panel (a) shows the experimental wavelength-dependent absorption coefficient of a 100-nm-wide dye-containing layer on glass (red symbols) and a fit via Eq. (1) with two Lorentzians (dashed blue line).

We notice a different behavior of the upper and lower branch of the coupled SPP-exciton modes. While clear shifts of the resonance energies can be seen at the low-energy side of the crossing, there are almost no shifts at the high-energy side. The coupling seems to be suppressed for the upper branch. Theory and experiment do not only agree very well qualitatively, but also with respect to resonance energies and resonance angles. The most noticeable difference is only a tiny rigid shift in $\theta$ of $\approx 1^\circ$, which may be caused by the calibration uncertainty of $\pm 1^\circ$.

We find similar good agreement of theory and experiment for a metal-dye system that consists of a gold reflection grating with geometry specified in Fig. 1(b) covered by thin film of $d_{\text{dye}} \approx 60$ nm thickness containing an organic dye [14]. To characterize the dye resonance, the absorption of a $\approx 100$-nm-thick dye-containing PVA film on a glass substrate was measured (see inset Fig. 3(a)). The dielectric function of the dye is modelled in our calculation as a sum of a background contribution and Lorentz-shaped resonant contributions:

$$
\epsilon(\hbar\omega) = \epsilon_{bg} - \sum_n \frac{x_n}{\hbar\omega - \hbar\omega_{\text{res},n} + i\delta_n}.
$$

\[\text{(1)}\]
The refractive index for the PVA matrix material is $n_{bg} = 1.55$. The resonance energies $\omega_{res, n}$, the broadenings $\delta_n$, and the weights $x_n$ of the resonant contributions can be obtained from the measured absorption. The best fit for the dominant resonance is obtained for $\omega_{res} = 1.79$ eV, $\delta = 24.5$ meV and $x \approx 40$ meV. If a second, quite broad Lorentzian is added, the absorption spectra is reproduced almost quantitatively over the full frequency range.

In order to get rid of artefacts resulting from an unwanted frequency dependence of the laser intensity, we subtracted in Ref. [14] the signal of a dye/PVA film of an unstructured metal layer from the reflectivity measured for the coupled SPP-dye system, see Fig. 3(a). The same quantity obtained from our calculations is shown in Fig. 3(b). A strong SPP-exciton interaction with avoided-crossing behavior and a hybridization gap of $\approx 160$ meV is seen in theory as well as in experiment. As in the metal-semiconductor system, the coupled SPP-exciton mode is best pronounced for the low-energy branch. The upper branch is not seen for higher angles in this difference spectrum.

In summary, we studied SPP-exciton coupling in metal-semiconductor and metal-dye systems theoretically. Both systems consist of a periodically structured metal film and a layer of an optically excitable medium. We found SPP-exciton coupling and avoided crossing behavior for both systems, in very good agreement with our recent experiments. The coupling strength is approximately 10 times larger in the dye system, while the modes are much sharper in the QW-system. There is also an interesting, hitherto not completely understood asymmetry between the upper and the lower SPP-exciton branch: While avoided-crossing behavior is seen for the lower branch, the SPP-exciton coupling strength seems to be largely reduced for the upper branch. This suggest that in such hybrid nanostructures excitons are coupled to different surface plasmon polariton and far-field modes and that the interference between all of these modes has to be taken into account when analyzing the optical properties of such nanostructures.

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