Coupling of photoluminescent centers in ZnO to localized and propagating surface plasmons

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A R T I C L E   I N F O

Available online 28 December 2009

Keywords:
ZnO excitons
Ag plasmons
Au plasmons
Exciton-plasmon coupling
Photoluminescence
Photoluminescence decay
Ultrafast pump-probe

A B S T R A C T

The interaction of excitons and other photoluminescent centers in semiconductors with plasmons represents the coupling of the fundamental one-particle, electron-hole excitation with the fundamental many-particle excitation in metals. We describe recent photoluminescence and pump-probe experiments that illustrate both the energetics and the dynamics of this interaction, in a model material incorporating ZnO films separated from a nanostructured plasmonic metal substrate by a variable-thickness spacer layer. We find evidence for different coupling mechanisms for the band-edge exciton and donor–acceptor pair defect luminescence, and discuss the competing roles of localized surface-plasmon resonances and propagating surface-plasmon polaritons. We also present first femtosecond pump-probe lifetime measurements for the band-edge exciton with and without the presence of nearby metal nanostructures.

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1. Introduction

The wide bandgap and large exciton binding energy of zinc oxide (ZnO) have attracted enormous interest in potential electronic and opto-electronic devices [1,2], including nanolasers [3,4]. ZnO has a bandgap of 3.37 eV and exciton binding energy of 60 meV, giving it excellent thermal stability compared, for example, with GaN (binding energy 25 meV). ZnO photoluminescence (PL) spectra exhibit a near-UV band-edge peak in the range 3.24±0.06 eV due to exciton recombination and depending somewhat on impurity concentration and method of crystal preparation, and a yellow-green peak near 2.3 eV. This donor–acceptor pair (DAP) emission is conventionally understood to be a superposition of recombination lines from electrons near the conduction band edge and deep holes on singly ionized oxygen interstitials, Zn anti-site vacancies and oxygen vacancies [2,5].

Plasmons are collective oscillations of conduction electrons in metals observed at the plasma frequency in bulk metals [6]. Metal nanoparticles embedded in transparent dielectrics exhibit a localized surface-plasmon resonance (LSPR) response to illumination by visible light [7]. At nanostructured, especially periodic, surfaces, interactions with light can also create propagating surface-plasmon polaritons (SPPs). Paralleling the world-wide interest in ZnO, there is also a rapidly growing, worldwide research effort aimed at exploiting the unique properties of both LSPRs and SPPs in areas as diverse as biosensing and optical interconnects [8–11].

The coupling of excitons to plasmons in Ag, Au, and Al for spectral control and amplification has attracted particular attention [12–18]. Plasmon–exciton interactions in ZnO-metal composites can amplify the band-edge PL by a factor 10 in Ag–ZnO and Al–ZnO bilayers [12,19,20] and as much as 20 in Au–ZnO nanoparticle composites [21]. PL enhancement in bilayers may result from both coupling of band-edge excitons to SPPs, reflected in an increased Purcell factor [12], and from LSPs that absorb and scatter the ZnO band-edge emission [20]. The band-edge PL enhancement in Au–ZnO nanoparticle composites has been attributed to excitation of LSPs by DAP emission, followed by transfer of hot electrons to the ZnO conduction band [16,22].

In recent experiments, we showed distinctive differences between coupling of light emitted by exciton and donor–acceptor pair recombination to localized vis d vis propagating surface plasmons [23]. That work was motivated by reports of enhanced photoluminescence (PL) efficiency attributed to both localized surface-plasmon resonances (LSPRs) and propagating surface plasmon polaritons (SPPs). However, the existence of ZnO band-edge enhancement due to both charge-transfer mechanisms and local-field mechanisms creates a fundamental problem for studying exciton–plasmon interactions using rough metal films as the source of plasmonic interactions. In such systems, it is difficult to determine whether the PL enhancement or quenching is due to interactions with LSPRs or propagating SPPs.

We addressed this problem by inserting MgO spacer films between the ZnO and Au or Ag films. This expedient enabled us to distinguish PL enhancement due to hot electron transfer from PL enhancement due to...
local-field interactions. Previous authors studying band-edge PL enhancement in ZnO/Au and ZnO/Ag nanocomposites attributed the enhancement to hot electron transfer to the conduction band edge [16,21]. We confirmed this mechanism in a thin-film structure by demonstrating that band-edge PL enhancement disappears when a 10 nm MgO spacer film separates the metal and ZnO films, blocking hot-electron transfer across the metal–ZnO interface. In the same geometry, we showed that the exponential decay of the band-edge enhancement with increasing MgO thickness is consistent with coupling between the ZnO exciton and SPPs propagating on Ag and Au films, while the decay of visible luminescence from intrinsic defect centers in ZnO implies that LSPRs couple to the DAPs via dipole–dipole interactions.

In this review paper, we consider the evidence that photoluminescent centers can interact in distinctive ways with both SPPs and LSPs: Band-edge emission enhancement in Au–ZnO and Ag–ZnO bilayer films arises primarily from SPP–exciton coupling, while visible defect emission is apparently dominated by local-field LSP. Our experiment also confirms that the band-edge emission enhancement for ZnO in contact with thin metal nanoparticulate films is due to electron transfer to the ZnO conduction band edge, as proposed by others. We then describe the latest experiments in which we have measured the time dependence of the PL center coupling to plasmonic surfaces. Relatively little is known about the dynamics of this coupling process. The lifetime of the ZnO band-edge exciton is known to be of order a few ps, but there are no experiments that would give a clue as to how that time scale is affected by the presence of plasmonic metal. In conclusion, we describe other “designer” plasmonic structures that promise to make it substantially easier to characterize quantitatively the dynamics of these interactions.

2. Model materials and experimental procedure

We have demonstrated the potential for separating the interactions of excitons and donor–acceptor pairs (DAPs) in ZnO thin films with localized surface plasmons and surface-plasmon polaritons. By using gold and silver films of varying thicknesses, we were able to vary the surface roughness and thus manipulate the character of the interaction between the ZnO excitons and DAPs and localized or propagating surface plasmons.

Fig. 1 shows schematic and electron micrographs of the samples used in these experiments. Ag and Au films were deposited on 2 cm × 1 cm Si(100) substrates by electron beam evaporation at a pressure of 2.0 μTorr. The deposition rate was maintained at 0.1 Å/s by monitoring the sample in situ using a quartz-crystal microbalance. Before deposition, half of the substrate was masked so that the metal occupied 1 cm × 1 cm squares with thicknesses of 10 nm–60 nm in 5 nm increments. The morphology of the metal films was observed by Rutherford backscattering depth profiling. The metal films shown in Fig. 1 are island-like for deposition thicknesses of 10 nm, but merge to form a nearly continuous film at 30 nm thickness. The thicker films should be rough enough to overcome the photon–plasmon momentum mismatch and support the propagation of SPPs [6]. It should be possible to excite LSPs, on the other hand, on all of the films.

After metal deposition, the masks were removed, and 70 nm of ZnO was deposited by electron beam evaporation onto the full substrate. An equivalent set of samples with 30 nm of Ag and Au was prepared with MgO spacer layers ranging from 10 nm to 60 nm thick in 10 nm increments; these samples were then coated with 70 nm ZnO as before. Variations in the quality of the ZnO film from sample to sample — for example, in the series with varying MgO thickness — were found to lead to shifts of order ± 5% in the photoluminescence peak position. These variations are described in greater detail in Ref. [23], but are not expected to alter the conclusions about the nature of the exciton–plasmon coupling mechanism significantly.

Photoluminescence (PL) measurements were made in reflection using a 200 mW vertically polarized HeCd laser (λ = 325 nm, 3.82 eV) at 45° incidence angle. The ZnO emission was then measured using a monochromator with a thermoelectrically cooled CCD detector and a spectral range of 1.86–3.78 eV, permitting simultaneous monitoring of band-edge and donor–acceptor pair emission. The PL linewidths are relatively broad at this temperature; however, their centroids are consistent with measurements on the best-quality commercially grown crystals.

The PL spectra for 70 nm ZnO films with and without 10 nm island metal undercoatings are shown in Fig. 2a and b. The peak band-edge emission is doubled in the presence of the Au and Ag underlayers, but the enhancement disappears when the 10 nm MgO spacer is introduced. In fact, the metal–ZnO band-edge emission is quenched to half of the ZnO band-edge emission upon introduction of the spacer. In contrast, the metal–ZnO visible emission is enhanced by a factor of roughly 1.5 both with and without the MgO spacer. In

![Fig. 1. Scanning electron micrographs of metal films](image-url)
Reference [23], it is demonstrated that the enhancement of DAP emission in the Ag–ZnO films depends on metal thickness, and also shows that the form of the dependence is the same with an MgO spacer as without. The enhancement is a maximum for 30 nm Ag films with or without a 10 nm MgO film.

To shed further light on the PL enhancement mechanisms for the UV and visible emission, we compared the ratio of ZnO PL emission with a 30 nm metal undercoating to the ZnO PL emission without a metal undercoating for MgO spacer thicknesses of 10–60 nm in Fig. 3. As expected, the enhancement is greater for Ag–ZnO bilayers than for Au–ZnO bilayers over the full spectral range, but similar behavior is observed for both metals. Interestingly, while the band-edge enhancement for both Ag and Au decays to well below 1 as the MgO thickness increases, the enhancement for Ag–ZnO at 2.85 eV increases to a factor 2, and the enhancement for Au–ZnO at 2.5 eV increases to a factor 1.5.

Further insight can be gained by examining the enhancement in band-edge and DAP emission as a function of MgO thickness, illustrated in Fig. 4. Fitting constants for these curves are shown in Table 1. The band-edge luminescence shows a maximum enhancement near 20 nm thickness, while the DAP PL enhancement is monotonically decreasing. The experimental data present us with two sets of observations that bear on the mechanism of exciton–plasmon interactions. Both contact-related effects and local-field effects must be considered to understand the whole picture.

First, there is the band-edge PL enhancement that arises from direct contact with a thin metallic film as seen in Fig. 2a and b for 10 nm metal films. The disappearance of PL enhancement with an MgO spacer layer is caused by direct charge transfer, corroborating the model proposed independently by Lin [21] and Lee [16].

The origin of the hot electrons can be understood as excitation of LSPs in the metal island films. The particles in Fig. 5a and b are roughly 50–80 nm in lateral dimension, so that for both 10 nm Ag and 10 nm Au films, LSP resonances should be supported at photon energies between 1.8 eV and 2.5 eV, depending on the geometry of the nanoparticles (NPs) and the dielectric environment [7]. Mie scattering calculations for spherical particles with a normal size distribution similar to nanoparticles in Fig. 5 predict LSP resonances for Au and Ag of roughly 1.8 eV and 2.05 eV, respectively. The fact that the band-edge emission is quenched when a thin layer of MgO is introduced suggests that the plasmon energy may be preferentially coupling into waveguide modes in the Si substrate when charge transfer to the ZnO is not possible [15,20].

The absence in Fig. 2 of donor–acceptor pair damping cannot be solely attributed to different LSP resonance energies. Instead, because similar DAP enhancement is observed with and without MgO spacers
the enhancement must be a result of dipole–dipole exciton–plasmon interactions. This local-field interaction is seen in exciton interactions with both SPPs and LSPs, and has been understood for GaN-metal quantum wells as arising from evanescent waves creating a perturbative field which affects the exciton recombination rate [17,18]. A recent study of ZnO films in contact with Ag nanoparticles has also attributed enhanced PL to local-field interactions [20].

The exciton recombination rate can be described by the Fermi golden rule, and the Purcell enhancement will increase linearly with the recombination rate [19]:

\[ \Gamma = \frac{2n}{\hbar} | \langle f | H_{int} | g \rangle |^2 \rho(\hbar \omega) . \]  

Here \( \langle f | H_{int} | g \rangle \) is the electron-hole dipole matrix element with a Hamiltonian describing the perturbing plasmon field, and \( \rho(\hbar \omega) \) is the plasmon density of states (PDOS). Both the band-edge enhancement and the Purcell factor have similar temperature dependence, lending further credence to the model of enhanced band-edge emission due to coupling to SPPs [19].

For LSPs, the DOS is maximized near the LSP resonance energy. For SPPs, the PDOS is proportional to \( k (d k/d \omega) \), and so is maximized at energies near the horizontal asymptotes of the dispersion curve, which is plotted in Fig. 5 for Ag and Au at ZnO and MgO interfaces. Fig. 5 demonstrates that the SPP resonance energy and thus the maximum plasmon density of states occurs near 2.9 eV at Ag–ZnO interfaces, 3.2 eV at Ag–MgO interfaces, and 2.4 eV–2.5 eV at Au–ZnO and Au–MgO interfaces. Because the resonance energy for Ag is much closer to the ZnO band edge than that of Au, and because the imaginary component of the silver permittivity is much smaller than the real component, silver SPPs should induce significantly greater band-edge enhancement than Au SPPs.

The SPP exists as an evanescent wave in the dielectric with an exponential decay constant \( z_0 \) given by

\[ z_0 = \frac{\lambda}{2\pi} \text{Im} \sqrt{\frac{\varepsilon_1 + \varepsilon_2}{\varepsilon_2}} . \]  

Evaluating this fringing field depth at the Ag–ZnO and Au–ZnO SPP resonance energies found in Fig. 5, we obtain 27 nm for Au–ZnO, 39 nm for Au–MgO, 21 nm for Ag–ZnO, and 32 nm for Ag–MgO. In Fig. 3b and d, for thicknesses of 50 nm and 60 nm, the ZnO band-edge emission is quenched by roughly 40%, while the emission at the SPP

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**Table 1**

Fitting functions and parameters for the distance dependence of band-edge exciton and donor–acceptor pair emission.

<table>
<thead>
<tr>
<th></th>
<th>Band-edge exciton emission</th>
<th>Donor–acceptor pair emission</th>
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<tbody>
<tr>
<td></td>
<td>( E_{\text{BE}} = (1 + \chi^2) e^{-2x/z_0} )</td>
<td>( E_{\text{DAP}} = A + Bx )</td>
</tr>
<tr>
<td>Au</td>
<td>( A = 9.2 \pm 0.6 )</td>
<td>( A = 0.59 \pm 0.05 )</td>
</tr>
<tr>
<td>Ag</td>
<td>( B = 5.8 \pm 0.4 )</td>
<td>( B = 0.7 \pm 0.1 )</td>
</tr>
<tr>
<td></td>
<td>( R = 0.94 )</td>
<td>( R = 0.96 )</td>
</tr>
<tr>
<td></td>
<td>( \chi^2/\text{DOF} = 0.007 )</td>
<td>( \chi^2/\text{DOF} = 0.005 )</td>
</tr>
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</table>

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**Fig. 4.** Distance dependence of PL enhancement for (a) the band-edge exciton luminescence and (b) the luminescence from donor–acceptor pairs. From Ref. [23].

**Fig. 5.** Dispersion curves for the surface-plasmon polaritons of Au and Ag in MgO and ZnO.
resonance energy is amplified by a factor of 1.4 to 1.5. Evidently when the MgO thickness is much larger than the metal–MgO fringing field depth, SPPs no longer couple to excitons directly; instead they absorb a fraction of the ZnO emission and subsequently scatter that light at the SPP resonance energy.

Detailed analysis of Fig. 4 provides further insight into plasmon–exciton interactions. The Purcell enhancement of the band-edge emission should decay as $\exp(-2z/z_0)$ and the visible enhancement should decay as $1/z^3$ as the MgO thickness increases, but plasmon scattering becomes an increasingly dominant emission source as the MgO thickness increases. However, the best-fit functions for the band-edge and DAP enhancements in Fig. 4 are of the form

$$f_{\text{SPE}}(z) = e^{-2z/z_0} \left(1 + \frac{z^2}{A^2}\right)$$

$$g_{\text{DAP}}(z) = B + \frac{C}{z^3}$$

respectively. We therefore argue that a factor of $z^3$ describes increasing scattering from both SPPs and LSPs, and note that the values of $z_0$ presented in Table 1 for both Ag and Au match the calculated values quite well, confirming the role of SPP–exciton local-field interactions. Indeed, as has been shown on theoretical grounds,
the extra multiplicative factor $z^2$ is expected for the coupling of a point source (such as a dipole emitter) to a two-dimensional plasmonic surface [24].

While the coupling of ZnO excitons and DAPs to LSPs can be understood from Mie theory as a dipole–dipole interaction that leads to scattering of photons, the interaction with SPPs is more complex. SPPs are longitudinal electromagnetic fields that exist at the interface of a metal and a dielectric; they can propagate on the surface of metal films with broken symmetries with wave vector $k_{SPP}$, according to the selection rule

$$k_{SPP} = k_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

where $\varepsilon_m$ and $\varepsilon_d$ are respectively the (complex) dielectric function of the metal and the (real) dielectric constant of the insulator above the metal surface. As Thomas Ebbesen and co-workers demonstrated in 1998 [25], SPPs are also involved in the extraordinary transmission (EOT) effect by “tunneling” light through subwavelength holes in plasmonic metal films at a rate orders of magnitude larger than predicted by conventional diffraction theory [26]. The EOT effect is now generally understood to arise from the coupling of SPPs between an incident photon field on one side of a subwavelength hole array, and scattered photon fields on the other side. We are interested in incorporating this effect into ZnO/MgO/plasmonic metal structures to accomplish the goal of real-time optical or electrical control.

3. Time-resolved pump-probe measurements

While analysis of the PL spectra can provide important clues to the kinetics or energetics of the coupling between luminescent emitters and plasmons, of far greater importance is understanding how the coupling influences the dynamics of energy transfer. We have carried out preliminary studies of the coupling dynamics using the same samples used for the PL studies. Because of the silicon substrate, the degenerate pump-probe geometry we employed differs from the conventional one, as it must be done in reflection. Femtosecond pulses from a Topas optical parametric amplifier at 365 nm were used for both pump and probe. Fig. 6 shows the layout of the experiment. Amplified 800 nm pulses from a regeneratively amplified Ti:sapphire laser (Quantronix Atlas) with nominal 120 fs duration were delivered at a pulse repetition frequency of 1 kHz to a beta-barium borate (BBO) crystal whose orientation with respect to the incident beam was under computer control. In this configuration, an idler beam is produced at 1784 nm and a signal beam at 1460 nm; the signal beam was frequency quadrupled, yielding femtosecond pulses at 365 nm (3.40 eV) with a few μJ energy. This beam was then split in roughly a 90/10 ratio to form the pump and probe beams, respectively.

At 365 nm, the probe excites electrons from near the valence band edge in ZnO to just above the conduction band edge, as shown in the band diagram in Fig. 7. We assume, consistent with other such experiments, that the excited electrons lose energy by electron–phonon collisions and decay at the conduction band edge to the exciton state, located just below the conduction band edge. Since we are probing at the same wavelength, the probe intensity as a function of time is a measure of how much population is in the conduction band as a function of pump–probe delay time, and is thus only an indirect marker for the lifetime of the free-exciton decay or for the coupling to the plasmon. However, as we shall see, the time constants derived from this signal in the case of the ZnO sample is consistent with the ultrafast temporal response of ZnO measured by other researchers; we therefore feel justified in ascribing this decay constant, however indirectly, to the band-edge exciton decay process.

Fig. 8(a) and (b) shows the results for two cases: One for ZnO atop a 10 nm MgO spacer layer, and another for ZnO separated from a 30 nm thick Au film by a 10 nm MgO film. The pump and probe beams were incident on the sample at approximately a 45° angle, as shown in the figure. The delay between pump and probe was set by computer control; the optical delay line had a temporal resolution of less than 2 fs. Recall from Fig. 1 that the Ag film for 30 nm thickness is rough and quasi-continuous, thus can support both surface-plasmon polaritons and localized surface-plasmon resonances; as seen from the previous development, the strongest coupling is between the band-edge exciton and surface-plasmon polaritons.

The time evolution of the probe signal was best fit in both cases by a biexponential function, with a fast decay followed by a longer one. Table 2 shows the fit parameters. We speculate that the initial fast decay may reflect the time required for the electrons generated by the initial above-bandgap excitation to thermalize to the band edge and populate the exciton state. The long-term 1/e decay time of 45 ps for the ZnO/MgO/Si sample is consistent with data from time-resolved studies of high-quality ZnO films [27]. The ZnO/MgO/Ag/Si data are best fit with substantially shorter decay constants, suggesting that both the thermalization and the exciton decay processes are affected by the presence of the metal film.

4. Conclusions and future studies

Multilayer heterostructures comprising doped and undoped ZnO, Au, and Ag plasmonic elements provide a unique workbench for probing and manipulating the coupling of surface plasmons to semiconductor quantum states, with optically active transitions extending from the infrared to the UV, and ZnO has interesting nonlinear optical properties [28]. From the results presented in this paper, it is evident that exciton–plasmon coupling in ZnO heterostructures offers a surprisingly variegated picture of the possible coupling mechanisms, as highlighted in Table 3.

However, it is also clear from the ambiguities in the time-resolved measurements that using plasmonic structures that are designed for specific SPP or LSP interactions is a necessity for future studies. Some of the structures we plan to use in future studies are shown schematically in Fig. 9. In each case, the concept is the same: A ZnO film of well-defined quantum-emitting properties (governed by impurities, defects, and thickness) or ZnO quantum well is separated from a plasmonic nanostructure (nanoparticles, subwavelength holes) by a variable-thickness MgO spacer layer. The optical measurements can be performed either in transmission or reflection, depending on the choice of substrate. Plasmon resonance effects, surface-plasmon polariton propagation and extraordinary optical transmission effects can then be studied both experimentally and computationally under carefully controlled structures, depending on

<table>
<thead>
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<th>Table 2</th>
<th>Biexponential fit parameters for measurements of Fig. 8(a) and (b). In all cases, the ZnO film is 70 nm thick and there is a 10 nm MgO spacer layer, as in the configuration of Fig. 1(e). All times are in ps.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No Ag film</strong></td>
<td><strong>30 nm Ag film</strong></td>
</tr>
<tr>
<td>Rise time</td>
<td>Fall time 1</td>
</tr>
<tr>
<td>1.53</td>
<td>12.0 ± 0.35</td>
</tr>
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</table>

| Table 3 | Categorization of coupling mechanisms between the two types of ZnO photoluminescent centers and possible plasmon mechanisms. |
|---|---|---|
| Proposed mechanisms | Donor–acceptor pair emission | Band-edge exciton emission |
| Particulate (thin) Ag/Au films | LSP–dipole–dipole scattering | LSP and hot-electron tunneling |
| Quasi-continuous Ag/Au films | LSP–dipole–dipole scattering | SPP via Purcell enhancement |
the choice of nanostructure and the specific properties of the ZnO photoluminescence.

Acknowledgements

The authors acknowledge financial support from the National Science Foundation (IGERT graduate student fellowship NSF-DMR-0333302 and NSF-CREST HRD-0420516) and the Office of Science, United States Department of Energy (DE-FG02-01ER45916).

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