Metallic Nanodroplet Induced Coulomb Catalysis for Off-Resonant Plasmonic Enhancement of Photoemission in Semiconductors

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ABSTRACT: The enhancement of light from semiconductors due to surface plasmons coupled resonantly to its emission is limited because of dissipation in the metal and is also restricted by the dielectric characteristics and homogeneity of the metal–semiconductor interface. We report a new mechanism based on electrostatic interactions of carriers and their image charges in metals to generate more photons from optical sources at frequencies that are off-resonant to the localized plasmon frequency. Coulomb catalysis of carrier accumulation resulting from the inhomogeneity of metal nanodroplets on a semiconductor’s surface can result in an enhancement of light that is nondissipative and does not require resonant coupling of plasmons to the emission wavelength. The enhancement occurs because of an increase in the ratio of radiative to nonradiative recombination in the vicinity of metal nanoparticles. It is equally effective with any type of metal and enhances radiation at any frequency, a property that is of principal importance for the realization of widely tunable semiconductor emitters. This fundamental mechanism provides a new perspective for improving the efficiency of light emitters and controlling carrier concentration on the nanoscale. The structural characteristics of the hybrid metal–semiconductor emitters are studied using electron microscopy and atomic force microscopy. We demonstrate the electrostatic mechanism by studying steady-state and transient photoluminescence from two-dimensional semiconductors, such as GaAs/AlGaAs quantum wells, and bulk semiconductors, such as ZnO thin films, emitting in the near-IR and UV wavelength regimes, respectively.

INTRODUCTION

The intensity of light emitted by a semiconductor source is generally determined by the availability of electron–hole (e−h) pairs and by the rate of their spontaneous recombination. However, this rate can be modified by the environment.1 In particular, a metal film deposited on an emitter enhances the rate of radiative spontaneous emission because a photon can be emitted into a surface plasmon channel.2,3 The strongest enhancement is observed at the frequency of plasmonic resonance, ωp. During the last 2 decades, the resonant enhancement of light due to a coupling of the recombining carriers to the surface plasmons has been reported for different emitters, including quantum wells,4,5 quantum dots,5 Si quantum wires,6 distributed Bragg reflectors,7 ionized centers in a diamond,8 and dye lasers.9 A similar plasmonic mechanism leads to a higher recombination rate for emitters in a plasmonic nanocavity10 and organic light emitters.11 Recently, a nonresonant enhancement of radiation from a dipole electro-magnetically coupled to a hyperbolic metal–dielectric metamaterial has also been predicted and detected.12–15 Together, these careful studies demonstrate the enhancement of optical emission for radiation with a frequency near the plasmonic resonance ωp or below the frequency of the topological phase transition (for the case of coupling to a metamaterial). Here, we report the observation that electrostatic interactions between the recombining carriers and the metal also gives rise to a phenomena that increases the intensity of light emitted from optical sources. The nature of the enhancement is akin to the strong Coulomb attraction of an electron that is pulled back by its image charge as it attempts to leave a metal surface. Accordingly, the primary component of the work function in metals is due to attraction between an electron and its image.16
Since the electrostatic force between a charge and its image is always attractive, an isolated metallic nanostructure inclusion within a semiconductor attracts both electrons and holes equally, creating a boundary layer with a higher concentration of carriers. The Coulomb force resulting from the metal thereby catalyzes the modulation of the carrier concentration in the semiconductor. The charge carriers can be localized in a relatively narrow spatial region dependent on the range and dimension of the inhomogeneous field around the metal nanoparticle. Within this enriched layer, the probability of radiative $e^{-}h$ recombination may be orders of magnitude higher than that in the rest of the active zone of the semiconductor emitter.

In most plasmonic-enhanced light emitters, thin films or nanoparticles are deposited on the surface of an emitter. A similar geometry is considered in the present work, but instead of using electrodynamic enhanced light emission due to plasmons, an electrostatic effect resulting from Coulomb interactions in the off-resonant plasmon regime is used for the light emission process. Compared to prior work,17 where nanoparticles were embedded within the active region of the emitter, in the present case the metal nanoparticles are on the surface and separated by a dielectric layer in a two-dimensional quantum well system to demonstrate the image charge effect on surface engineered structures for the first time. This work also shows a direct comparison of the increase in the effect resulting from the electrostatic image charge in the nanoparticles compared to metal thin films. The inhomogeneity due to the random shape and size of the metal nanoparticles accentuates the electrostatic effect compared to that of the metal thin films, where image charge formation is more homogeneous, as shown using a metal–ZnO nanoparticle system.

The width of the enriched layer can be readily estimated. If the carriers can access the region in the vicinity of the metal, then within the layer of thickness $d$ the electrostatic energy of the interaction of a carrier with its image is $\sim \varepsilon^2/ed$, where $\varepsilon$ is the dielectric constant of the semiconductor. This energy must exceed $kT$; otherwise, the electrostatic attraction is dominated by random thermal fluctuations. Assuming that $\varepsilon \approx 10$, one obtains the thickness of the layer $d \approx \varepsilon^2/(\varepsilon kT) \sim 20$ nm at $T = 300$ K, which is comparable to the width of a single active layer in conventional multilayered semiconductor light sources. This limit is valid when $e^{-}h$ plasma is in thermal equilibrium. In a light emitter, the $e^{-}h$ plasma is not in equilibrium. In this case, the enriched layer is formed because of a dynamic balance among the recombinating carriers, carriers created by external excitation, and carriers drifting toward metallic inclusion due to attraction to their images in metal. Because of the drift, the width of the enriched layer may be much greater than 20 nm, extending up to the diffusion length of the carriers.

A high concentration of carriers in the enriched layer increases both the radiative, $\Gamma_r$, and nonradiative, $\Gamma_{nr}$, recombination rates. The most efficient process for radiative recombination in direct-gap semiconductors occurs through a bimolecular mechanism that is quadratic in the carrier concentration, $\Gamma_r = Bn^2$. In contrast, the Shockley–Read–Hall mechanism of nonradiative recombination is characterized by a linear rate, $\Gamma_{nr} = An$. Because $\Gamma_r$ increases more quickly with $n$ than $\Gamma_{nr}$, a higher concentration leads to an increase in the internal quantum efficiency of the system

$$\eta = \frac{\Gamma_r}{\Gamma_r + \Gamma_{nr}} = \frac{Bn}{Bn + A}$$

(1)

Here, we have neglected the $Cn^3$ term for Auger recombination as the carrier concentrations remain low enough compared to the radiative and nonradiative contributions to ignore its contribution. Although the increase in $\eta$ occurs only within a narrow layer near the metal nanoparticle, it is sufficient for a many-fold enhancement of the photoluminescence. The layer is composed partly of carriers generated in situ via photoexcitation and partly of $e^{-}h$ pairs drifting in from distant regions. Many of the pairs that drift in would otherwise have recombined nonradiatively in the absence of the metallic nanoparticle. These carriers comprise a significant portion of the enhanced photoluminescence present in the system.

Frequency matching condition, $\omega = \omega_r$, represents the principal issue for the plasmonic mechanism. For example, the InGaN/GaN quantum well emits blue light ($\omega = 3.05$ eV); therefore, frequency matching occurs for a silver film with $\omega_r \approx 3.0$ eV, leading to a strong plasmonic enhancement.4 The enhancement due to the image charge effect caused by a single inclusion is determined by its size and geometry but not by the type of metal. This universality is well-known in electrostatics, where the field near a conductor is determined by its shape but not conductivity. This insensitivity to the type of metal guarantees a frequency-independent enhancement, which is required for the operation of a wide-band emitter. It is also worth mentioning that gold is the preferred metal in electronics due to its low rate of degradation, as compared to that of other metals. Therefore, it is desirable to use gold in light sources emitting in the visible and UV parts of the spectrum. Although a thin gold film with $\omega_r = 2.36$ eV covering an InGaN/GaN multiquantum well does not lead to a plasmonic enhancement4 because of the frequency mismatch ($\omega_r < \omega$), the gold nanoparticles embedded into the same structure strongly enhance photoluminescence,17 thus providing potential for a technological breakthrough in the design of semiconductor light sources.

The geometry of the metallic component is a very important issue in the electrostatic mechanism. A flat and uniform metal film deposited on a quantum well attracts carriers through their images. Since drift occurs in the direction perpendicular to the metal plane, the $e^{-}h$ pairs are compressed in this direction, but the average in-plane distance between electrons and holes remains unchanged. Increasing the carrier concentration along only a single axis (z axis) leads to a faster recombination of the $e^{-}h$ pairs with the dipole moment oriented along the z axis because these dipoles have a stronger overlap of their $e^{-}h$ wavefunctions. The photons emitted by these dipoles propagate almost parallel to the surface of the quantum well. They can barely escape the structure through the surface because of the total internal reflection. Thus, the fastest $e^{-}h$ recombination processes do not contribute to the emission detected. This leads to a slight decrease in the emission from a GaN quantum well covered by thin gold film.4 Unlike a homogeneous flat film, metallic nanoparticles or metallic objects with sharp edges serve as point attractors. The drift due to Coulomb forces induced by the electrostatic image charge effect leads to the concentration of carriers around a point attractor and is not accompanied by the alignment of the $e^{-}h$ pairs perpendicular to the surface. A local increase in the carrier concentration results in a strong electrostatic enhancement.17

While both the plasmonic and electrostatic mechanisms of enhancement are ineffective for InGaN/GaN QW structures capped with a thin gold film, there is an observable effect of electrostatic attraction. The spectrum of the structure with a
gold covering is blue-shifted with respect to the reference sample, as reported in our earlier work. The blue shift reported in ref 4 remained unexplained. Now, we conclude that it originates from a reduction of the effective width of the quantum well due to the electrostatic attraction of the carriers to the metal film. A stronger confinement of carriers leads to a blue shift in the spectrum. The Stark effect produced by image charges always leads to a blue shift, unlike fields induced by spontaneous polarization and lattice mismatch. These strain-induced electric fields separate electrons and holes, leading to red-shifted emission compared to the quantum well without the internal fields.

RESULTS AND DISCUSSION

Enhancement of IR Light from GaAs/AlGaAs Quantum Wells. To best demonstrate nonresonant enhancement, the resonant (plasmonic) mechanism of enhancement has to be avoided by using metallic inclusions with a plasmon frequency lying well below the frequency of light emission, \( \omega_1 < \omega \). We used a GaAs/AlGaAs quantum well, which emits primarily at 1.53 eV. Metal nanodroplets of Ga were deposited on an epitaxially grown GaAs heterostructure (Figure 1A,B). The enhanced and reference photoluminescence spectra from the GaAs/AlGaAs quantum well are shown in Figure 2. In the reference sample, the spectrum exhibits two peaks, at 1.53 and 1.51 eV. At \( T = 11 \) K, these peaks are due to excitons in the GaAs quantum well and in bulk GaAs (the GaAs buffer region pictured in Figure 1A), respectively. The bulk GaAs emission is not significantly affected by the image charges since the buffer layer is far removed from the Ga droplets. The quantum well

Figure 1. Sample structures including metal nanoparticles. (A) TEM image of a GaAs quantum well (width of 10 nm) with a Ga nanodroplet (ND) on the GaAs cap layer. The quantum well is separated from the Ga ND by a cap layer consisting of a 5 nm GaAs and 10 nm AlGaAs barrier layer. The wetting angle is 36°. Note that the quality of the cap layer beneath the droplet is unaffected by the growth of the droplet. (B) AFM image of the same sample showing the distribution of nanodroplets on the surface. Silver (C), nickel (D), and gold (E) clusters/islands covering the surface of bulk ZnO sample.

Figure 2. Photoluminescence spectra of the GaAs quantum well with Ga nanodroplets (red) and reference (black) at \( T = 11 \) K. Here, the enhancement is observed in the near-IR region, and the blue shift is about 25 meV. The left-most peak represents bulk GaAs emission, which has been used as a reference to normalize the relative intensities of the quantum well peaks. Note the logarithmic scale along the y axis. A CW HeNe laser with 100 mW power at 633 nm was used for the photoluminescence measurements.
emission, however, is enhanced by more than a factor of 20. This enhancement cannot be due to plasmonic coupling. Indeed, for a homogeneous film of Ga deposited on GaAs, $\omega_s = 1.446$ eV, which lies below the emission spectrum in Figure 2. Moreover, for a nanoparticle, the localized plasmon frequency is even lower, depending on its size and shape. For the nanodroplet shown in Figure 1A, the sharp corners produce a strong confinement of the charge distribution, leading to a further decrease of the resonant frequency. It was recently shown that in the vicinity of a corner $\alpha$ the resonant frequency drops as $\sqrt{\pi/\alpha}$. For a nanoparticle with wetting angle $\alpha = 36^\circ$ shown in Figure 1A, this means a decrease by at least 2.23-fold as compared to a homogeneous film. An additional significant feature of the enhanced spectrum is a 25 meV blue shift. This feature, together with the results of time-resolved photoluminescence given below, clearly rules out reflection and scattering at the Ga nanodroplets as reasons for the observed enhancement. At the same time, the electrostatic mechanism offers a natural explanation for these modifications of the spectrum.

In the presence of metal nanoparticles, the carrier concentrations are essentially inhomogeneous. They can be calculated from the coupled nonlinear diffusion equations with the drift terms caused by the electrostatic field $E(r)$

\[
\frac{\partial n_e}{\partial t} = D_e \nabla^2 n_e - \frac{eD_e}{kT} \nabla \cdot (E n_e) - A n_e - B n_e n_h + g
\]

(2)

The equation for holes is obtained by replacing $e$ with $h$. Here, $D_{e,h}$ are the diffusion coefficients for electrons and holes, and $g$ is the density of $e^{-}h^{+}$ pairs produced by the pump light source in 1 s. The electrostatic field $E(r)$ in the drift term in eq 2 is obtained from the Poisson equation

\[
V \cdot (e E) = 4\pi \left[ n_e(r) + n_h'(r) - n_e(r) - n_h'(r) \right]
\]

(3)

where $n_{e,h}(r)$ are the image charge densities of the electrons and holes and $n'_{e,h}(r)$ are the densities of their electrostatic images. These image charges are displaced inside metallic nanostructure inclusions. Equations 2 and 3 form a self-consistent nonlinear set that defines the carrier densities and the distribution of the electric field. Even in the simplest cases, it can be solved only numerically. The strongly inhomogeneous character of the solution is provided by the drift term. In the vicinity of the metallic inclusion, the drift term has a singularity since the field $E$ tends to infinity, independent of the shape of the inclusion. For a plane metal film and a metal sphere, the image of a carrier and the corresponding attractive force can be easily calculated. For a spherical segment in the shape of a cut sphere, shown in Figure 1A, the solution for the electrostatic potential can be well-approximated by the potential produced by a probe charge at a metallic wedge, which is known in electrostatics. Near the edge of the segment, the wedge’s solution is practically exact. For points away from the edge beneath the segment, a solution is given that is practically indistinguishable from the solution for a homogeneous plane. The distribution of the electric field due to an electron near the wedge with angle $\alpha = 36^\circ$ (the wetting angle in Figure 1A) is shown in Figure 6 in the Experimental Section. The attractive force toward the edge of the droplet is provided by the net force, which has two components: in-plane $eE_z$ directed along the radius of the base circle and out-of-plane vertical $E_{z'}$. For a nanodroplet with radius $r = 30$ nm, the in-plane region of attraction extends over 50 nm beyond the edge of the nanodroplet. The typical electrostatic energy $\int_0^\infty eE_z(r)dr$ of a carrier displaced within the region of attraction ($r < 80$ nm) greatly exceeds the thermal energy $kT$ at 11 K, allowing for the formation of a wide enriched layer with a high concentration of carriers.

The attractive out-of-plane component $E_{z'}$ confines the motion of the carriers, thus effectively reducing the width of the quantum well. Since the exciton emission energy increases in a quantum well that is more narrow, we conclude that the blue shift in the enhanced spectrum in Figure 2 is due to the field $E_{z'}$, i.e., the Stark effect induced by image charges. Note that the peak at 1.51 eV is not blue-shifted since it is due to the exciton dynamics, unlike the energy of the excitons in the quantum well.

The luminescence in the GaAs quantum well and bulk ZnO structures is mostly due to the recombination of excitons. Being electrically neutral particles, excitons are attracted to their electrostatic images in metals due to dipole–dipole interactions. The attractive force for such a case is $F = (p \cdot V)E$, where $p = ed$ is the dipole moment of the excitons. In the GaAs/AlGaAs quantum well, the exciton Bohr radius $\lambda_B$ is $>10$ nm, i.e., it is comparable with the quantum well width $D$ and with the size $R$ of the Ga nanodroplets, $\lambda_B \sim D \sim R$. In this situation, the exciton dynamics is not very different from the dynamics of free $e^{-}h^{+}$ pairs since the force of dipole–dipole
interactions $F \sim (e^2\text{e}_0)(E/R) \sim eE \sim \epsilon^2/\lambda_0$ is, by an order of magnitude, the same as the Coulomb attraction $eE \sim \epsilon^2/D$ of a free electron (or hole) to a Ga nanodroplet. Thus, the approximation of plasma of electron–hole pairs is qualitatively valid.

The electrostatic mechanism exhibits a specific power dependence that is not observed for the plasmonic mechanism. Figure 3A shows how the enhancement saturates as the excitation power is increased. Saturation is expected since, in an e–h plasma, the range of electrostatic interactions decreases with increasing carrier concentration (due to Debye screening). Numerical simulations in Figure 3B, based on eqs 2 and 3, show a saturation of the enhancement, at approximately the same level as that observed in the experiment. It is clear that the saturation is due to the presence of metallic nanodroplets since the reference sample shown in Figure 3A,B by black squares exhibits a linear power dependence, thus indicating that Debye screening is still negligible.

One of the distinguishing features of image charge induced light enhancement, compared to plasmon or scattering induced enhancement, is manifested in the behavior of the time-resolved photoluminescence. The coupling of carriers in the quantum well surface to plasmons strongly accelerates the recombination process, decreasing the lifetime of e–h pairs by orders of magnitude.\(^4\) In a sample with a homogeneous distribution of carriers, the e–h lifetime can be extracted directly from the time-resolved experiment because all e–h pairs recombine at the same rate. This is not the case for a sample with distributed metal nanoparticles, where the concentration of e–h pairs is strongly inhomogeneous. In the electrostatic case, the recombination rate induced by Coulomb catalysis within the enriched layer is also significantly increased, whereas the decrease in the lifetime is masked by the continual drift of carriers toward the nanoparticle. The drift draws carriers that would have otherwise recombined nonradiatively into the enriched region, where they instead recombine radiatively (see eq 1). This process continues much longer than the lifetime in the enriched layer since the pairs that have recombined are replaced by those delivered by electrostatic drift. As a result, the time-resolved photoluminescence in Figure 3C shows a slower decay for the quantum well with nanodroplets than in the reference sample. However, this longer decay cannot be attributed to a decrease in the recombination rate, which increases within the enriched layer. Thus, electrostatic attraction not only enhances the intensity of the luminescence but also extends the lifetime due to increased photon recycling. This paradoxical result originates from a strongly inhomogeneous distribution of carriers that, on one hand, locally increases the rate of radiative recombination and, on the other hand, provides more available carriers because of the interplay between drift and diffusion. It can be seen from Figure 3C that the total radiated energy, given by the area under the red curve of slowly decaying intensity, is increased at least by a factor of 2 because of the Ga nanodroplets compared to the energy radiated by the reference sample. This experiment proves that metallic nanostructure inclusions may essentially increase the efficiency of the emitter, thus showing a possible way to conserve energy resources, i.e., to develop techniques that produce more light with the same input power. Numerical simulations based on equations in ref 17 for the regime of time-resolved luminescence in the GaN quantum well with infiltrated gold nanoparticles also clearly demonstrate an increase in the decay time. Comparing the enhancement in the light emission process from a simple molecular or quantum well emitter or a plasmonic emitter, where the light emission is directly proportional to the input pump intensity (as shown by the black squares in Figure 3A), the total emission due to the image charge effect saturates.

The presence of metal does indeed lead to a spatially inhomogeneous population of carriers, which is the main idea of the proposed mechanism of light enhancement. It is true that an inhomogeneous concentration of carriers leads to a coordinate-dependent decay rate, namely, the higher the concentration, the higher the rate of spontaneous emission. Such inhomogeneous decay rates lead, at far field, to a very unusual decay of the photoluminescence, as shown in Figure 3C. This curve is a result of the superposition of incoherent photons emitted with different rates from different parts of the sample. At far field, individual decay rates are undistinguishable. The electrostatic enhancement is sensitive to the concentration of Ga nanodroplets. For too large a concentration, the image charge effect is saturated, whereas for very few droplets on the surface, the Coulomb force is not strong enough to modify the carrier density to enhance the photoemission.

There are other factors that can influence the enhancement in the light emission due to the image charge effect. The scale of the distance of the metal nanodroplets from the emitter with respect to the exciton Bohr radius of the semiconductor quantum well emitter is expected to influence the extent of the light enhancement process, which will be studied in future work. This effect is Coulombic in nature; thereby, the distance of the nanoparticles from the quantum well is also expected to influence the in-plane force due to the inhomogeneity of the nanoparticles. This electrostatic force has a longer range compared to that of the surface plasmonic field that decreases exponentially away from the metal–dielectric interface. However, in a light emitter system where the radiative recombination rate is higher, such as that induced by resonant plasmonic nanoparticles, the influence due to image charge is weaker as the speed of the drift and diffusion toward the metal nanoparticles is significantly slower than the e–h recombination rate.\(^3\)

Enhancement of Near-UV Light Emission from ZnO Bulk Semiconductors. The GaAs quantum well shown in Figure 1A,B represents a particularly “ideal” semiconductor heterostructure with a low concentration of structural defects, high carrier mobility, and well-defined shape of the metallic inclusions. The exciton Bohr radius was comparable to the width of the dimension of the 2D quantum well light emitter. The exciton binding energy is (∼20 meV) comparable to the thermal energy at room temperature, which restricts the enhancement only to low temperatures, where nonradiative recombination is not dominant. However, to demonstrate the universal nature of this effect at room temperature without any quantum confined light emission, the bulk form of a light emitting material system with a stronger exciton binding energy, such as ZnO (∼60 meV), is considered.

The electrostatic mechanism of enhancement is also observed in ZnO, which is a comparatively “nonideal” semiconductor with a higher defect density and lower carrier mobility compared those of GaAs, at room temperature. Here, the emission is due to the recombination of bulk excitons. Since this mechanism leads to an enhancement that is expected to be independent of the type of metal, the samples were coated with silver, nickel, and gold nanostructures (Figure 1C–E). These films were intentionally made nonuniform to avoid the
alignment of image dipoles, which leads to a quenching of the electrostatic enhancement. The observed enhanced spectra are shown in Figure 4A. The strongest enhancement, roughly 10-fold, is observed for silver and gold coatings, and a 2-fold enhancement is observed for the nickel coating. The difference in the level of enhancement is not due to the metals themselves but is instead due to the different morphologies of the films. The size of the Ni nanoparticles is significantly larger, which reduces the inhomogeneous electric field distribution compared to that with the sharp edges or smaller size of the Au or Ag nanoparticles. The enhancement disappears, and the spectra become practically equal in the case of a high-quality uniform coating, as shown in Figure 4B. None of the metals used induce plasmonic enhancement since all three resonant frequencies are below the frequency of emission of a ZnO crystal (see the inset of Figure 4B). Since the emission in ZnO originates from the bulk excitons, the spectra with a metal coating in Figure 4 do not exhibit a blue shift because the image charge fields do not change the binding energy of the bulk excitons.

Although both plasmonics and the image charge effect have a similar end result (enhancement), they are independent and have different physical origins. It is possible that some effects currently attributed to plasmonics might instead arise from electrostatic interactions. For example, the plasmonic mechanism has previously been invoked to explain an enhancement in the UV emission of ZnO due to Au nanoparticles as well as IR emission in Si using Ag nanoparticles. Since the resonant frequency for Au nanoparticles is well below the emission frequency of ZnO and, similarly, that of Ag nanoparticles is well above that of Si light emitters, coupling to surface plasmons should be ruled out as a source of enhancement.

There have been numerous studies of an emission enhancement in ZnO layers due to disordered Ag coatings. In all of these publications (see, e.g., refs 25–27), the obvious frequency mismatch is ignored and the enhancement is unambiguously attributed to plasmonic coupling. Now, we conclude that surface plasmons make a negligible contribution to the enhancement. This is seen from Figure 4B, where a smooth uniform coating by three different metals does not modify the emission spectrum. If plasmons in the Ag film were strongly coupled to the carriers in the ZnO layer, then the blue curve in Figure 4B would be noticeably higher than the others. At low temperatures, nonradiative recombination is reduced and the enhancement in spontaneous emission due to the radiative recombination process exceeds the loss due to the nonradiative process. Moreover, in the backscattered geometry of the photoluminescence measurement, the reflection of the pump laser light due to the Ag film is also expected to enhance the photoluminescence emission from the bulk ZnO.

For disordered islands, the frequency mismatch becomes even stronger since any defect on an ideal plane has a finite curvature that reduces the restoring force, which drives plasma oscillations at the metal surface. A decrease in the plasmonic frequency has been recently demonstrated for a metal wedge. More complicated geometries may lead to a broad-band spectra of plasmonic resonances that, however, always lie below the surface plasmon frequency $\omega_p$, for a plane, see, e.g., refs 28 and 29. The strong enhancement of the intensity of electric field at “hot spots” in disordered metallic aggregates and at sharp corners of plasmonic waveguides does not increase the resonant frequency.

Thus, the enhancement in ZnO samples with a Ag coating cannot be explained by resonant interaction with plasmons. The coupling of excitons in ZnO with surface plasmons requires metallic nanoparticles or islands with resonant frequencies higher than those of silver. Resonant coupling was observed in a ZnO quantum well with deposited aluminum nanodisks. We speculate that the modification of the emission spectrum observed in ref 32 is due to both mechanisms, but it will require a detailed study to separate the contribution of each mechanism. It is also observed from Figure 4A that the spectral width of the emission from ZnO is reduced when the photons are resonantly coupled to the surface plasmon modes in the presence of a Ag thin film because the spontaneous emission from the off-resonant modes does not recombine radiatively as effectively as the resonant modes via the surface plasmon channel. The spectral width of ZnO with Ag and Ni thin films is influenced by a contribution from dissipation due to the interface phonon modes that can lead to inhomogeneous broadening. However, as the areal density of the ZnO surface covered by the metal decreases, as in the case of the metal nanoparticles, the inhomogeneous broadening decreases and the photoluminescence spectral width is comparable to that of the emission from bare ZnO (Figure 4B). Because of the relatively higher concentration of Ni nanoparticles on the
surface of ZnO, as shown in Figure 1d, an increase in the spectral line width is observed.

We have demonstrated a strong spontaneous emission enhancement from semiconductor light emitters that may be explained by the proposed electrostatic mechanism. From the point of view of outgoing energy and the device fabrication process, this mechanism is more efficient than the well-known plasmonic mechanism. It not only enhances the intensity of emission but also extends the time of the enhanced luminescence. The latter property is due to the nondissipative nature of electrostatic interactions. Being universal in the sense that this does not depend on the type of the metal inclusion, it provides a nonresonant enhancement of emission over a wide range of frequencies that makes it very attractive for applications in white-light sources. The enhancement is observed only in systems that exhibit some form of in-plane inhomogeneity in the electric field. The in-plane attractive component of the electric field is responsible for increasing the carrier concentration near the nanoparticle, which produces the enhancement observed. Therefore, a uniform metallic carrier concentration near the nanoparticle, which produces the quantum well result in inhomogeneous charge distribution and hence produces a uniform carrier layer and a 20 nm thick Al$_{0.33}$Ga$_{0.67}$ layer, followed by the deposition of Ga and the formation of Ga droplets at a substrate temperature of 550 °C with the arsenic source being fully closed. The total amount of Ga deposited was equal to an amount that would normally result in 5.0−7.0 monolayers of GaAs growth. After growth, the surface morphology of the QDP samples was characterized using AFM under ambient conditions.$^{33}$

The structural properties of the samples were also characterized by TEM. For TEM, platinum is usually deposited on the surface of the dielectric to achieve a better resolution. Figure 1 merely indicates that the interface is smooth between the Ga droplet and the GaAs cap layer facilitated by the Pt metal. This sample, coated with Pt, was not used for optical characterization. It shows only the structure of the GaAs quantum well with a Ga nanodroplet on the top. Ga nanodroplets are being increasingly used for UV plasmonic material systems.$^{36,37}$ However, there is a long-wavelength IR plasmon mode in bulk Ga metal that can shift further down in energy for Ga droplets$^{38}$ on GaAs. Ga has a low melting point, and the transition temperature is further decreased in the case of nanodroplets. It forms an oil droplet similar to hemispherical droplets due to epitaxial droplet growth, as modeled in this section.

The quantum well samples in our experiments were composed of 33% Al in Ga$_{1-x}$Al$_x$As alloy and are exactly lattice matched to the GaAs substrate over which the entire heterostructure quantum well was grown. The TEM image presented also clearly indicates that the quantum wells are very high quality and does not show the presence of quantum dots. The photoluminescence line width is very narrow compared to

![Figure 5](image1.png) **Figure 5.** Cross-section of the cut sphere and tangent wedge. Polar coordinates of the probe charge $e$ and the observation point are $(\alpha, \gamma)$ and $(R, \theta)$, respectively.

![Figure 6](image2.png) **Figure 6.** Calculated electric field and carrier concentrations near Ga nanodroplets in a GaAs system. (A) Distribution of the out-of-plane, $E_x$, and in-plane, $E_y$, components of the electric field exerted on an electron displaced 15 nm below a metal cut sphere with a radius of 30 nm. The center of the cut sphere is at $r = 0$, and its edge coincides with the dashed vertical line at $r = 30$ nm. Here, we used the analytical solution of the electrostatic problem for a metal wedge.$^{19}$ The dashed lines represent the self-consistent calculations for the reduced electric field due to electrostatic screening used in calculating the concentrations in B. (B) Radial distributions of the carrier concentration at varying temperatures obtained from the diffusion (eq 2) with the image charge field shown in panel A.
that of quantum dots, which suffer from an inhomogeneous dot size distribution, providing another indication that there was no quantum dot formation in this system. As the nucleation of the Ga metal droplet is a top-down process, formed within the molecular beam epitaxy (MBE) system after the GaAs cap layer attains thermal equilibrium, there is no strain modification in the quantum well or on the surface. The interface at the Ga droplet and GaAs is atomically flat and is not expected to suffer from surface recombination or Fermi-pinning effects. The electrostatic enhancement is sensitive to the concentration of Ga nanodroplets. For too large a concentration of the droplets on the surface, the image charge effect is saturated, whereas for very few droplets on the surface, the Coulomb force is not strong enough to modify the carrier density for enhanced photoemission.

ZnO Growth. ZnO thin films were grown by MBE on a sapphire substrate. ZnO growth was carried out at 550 °C following the deposition at 200 °C and annealing up to 650 °C of a low-temperature ZnO buffer layer under oxygen-rich conditions. The homogeneous thin films of Au, Ag, and Al were deposited using thermal vapor deposition on the MBE grown thin film with atomic layer flatness. The Au and Ag metal nanoparticles were formed on the ZnO surface by a combination of thermal evaporation and rapid thermal annealing techniques. To form the droplets, the thin films of metal on ZnO were heated in vacuum at 400 °C for 30 min. As Ni atoms interact with the ZnO lattice at high temperature to form the nonradiative recombination center, the annealing techniques could not be used for the formation of Ni nanoparticles. Ni nanoparticles formed using the rapid thermal annealing technique lead to a quenching of photoluminescence emission. The Ni nanoparticles were instead commercially procured, and the sample was heated at about 130 °C to achieve a better dispersion of the nanoparticles on the surface of ZnO.

Optical Characterization. The GaAs/AlGaAs quantum well has lower exciton binding energy (∼20 meV) and ZnO has a stronger exciton binding energy (∼60 meV) compared to the thermal energy at room temperature (∼26 meV). So that the excitons dissociate at room temperature in the GaAs system, the emission spectra was measured at low temperatures (10–15 K), whereas ZnO was measured at room temperature. For the GaAs/GaAs system, both a 532 nm laser diode and 633 nm HeNe laser were used for excitation. The photoluminescence spectra were collected on a JY Triax 550 spectrometer with a TE-cooled CCD. The temperature was controlled during the temperature-dependent measurement using a closed-cycle liquid He cryostat. For the spectra shown in the figure, photoluminescence was measured using a CW HeNe laser that had an average power of 100 mW at 633 nm. For the UV-based ZnO samples, a HeCd laser was used for excitation. The wavelength of this laser was 325 nm with the power at 45 mW. The photoluminescence from the nanodroplet-covered samples was collected in the forward scattering geometry, where the excitation light provided illumination from the side of the active layer. For ZnO thin films coated with metals, the pump laser was used for excitation from the substrate side to avoid any absorption or reflection of the pump photon by the metal layer. Excitation for the time-resolved measurements was performed using an 80 fs pulse width and an 80 MHz Ti:sapphire laser at 730 nm for Ga/GaAs, which was doubled to 350 nm in the case of Au/InGaN. The excitation power was between 0.06 and 2.92 mW/cm². The decay lifetime was measured using a spectrophotometer-based photon-counting Hamamatsu Streak camera system.

Computational Method. Modeling of geometrical effect of the electrostatic image charge effect in hemispherical nanodroplets on a dielectric:

Solution of the Electrostatic Problem for a Conducting Cut Sphere. The structure of the droplets formed on GaAs was modeled from the TEM images shown in Figure 1A,B. It can be seen that there is a 36° angle that was formed at the interface. Therefore, for the theoretical analysis, the following geometry was used.

The electrostatic field produced by a point probe charge e placed near a conducting cut sphere (spherical segment) in Figure S is approximated by the field of a conducting wedge tangent to the cut sphere. This approximation is valid since the field beneath any conducting flat surface coincides with the field of a homogeneous metal plane away from the edge of the segment. Close to the edge, both objects, the cut sphere and the wedge, induce the same distribution of the electrostatic field, which is determined by the sharpness of angle α. To calculate the electric field, we use the well-known result (see, e.g., ref 19) for the Green function of a conducting wedge. The position of the probe charge e is given by the polar coordinates (α, γ). Then, the electrostatic potential at the observation point with coordinates (R, θ) is determined by the following integral

\[
\Phi(R, \theta) = \frac{e}{(2 \pi - \alpha) \sqrt{2aR}} \int_{\eta}^{\infty} \left[ \frac{\sinh(\pi \zeta/(2 \pi - \alpha))}{\cosh \frac{\pi \zeta}{2a} - \cos \frac{\pi(\theta - \gamma)}{2a}} \right] d\zeta
\]

Here

\[
cosh \eta = \frac{a^2 + R^2}{2aR}, \quad \eta > 0
\]

This potential vanishes at the conducting surfaces θ = 0 and θ = α.

We are interested in the potential at the location of the charge itself, so we let θ = γ and R = a + δ. Since we want to calculate the attractive force eE(α, γ) of charge e to the wedge, we must exclude the potential of the charge itself from eq 4, giving

\[
E(\alpha, \gamma) = -V \Phi' = -\lim_{\delta \to 0} \left[ \Phi(\theta, a + \delta) - \frac{e}{\delta} \right]
\]

Calculating the limits in eq 6, we use the relation δ = Rη, which follows from eq 5. In numerical calculations of the electric field E, we take α = 36°, i.e., the wetting angle measured using the image in Figure 1A. The radius of the base of the cut sphere is 30 nm. The result for the distribution of the radial (in-plane E_r) and vertical (out-of-plane E_z) components of the electric field is shown in Figure 6A for an electron displaced 15 nm below the surface, z = 0. The component E_z, which is the source of the emission enhancement, is different from zero within a wide range, 15 nm < r < 100 nm. It becomes practically zero at r = 0, as it should be for a system with cylindrical symmetry. The vertical component E_z saturates for r < 30 nm, approaching the
value for a homogeneous conducting plane. The reduced field, due to Debye screening, is shown by a dashed line. It was calculated self-consistently using Poisson eq 3 and diffusion eq 2 with \( \frac{\partial n}{\partial t} = 0 \) (continuous wave excitation). For metal inclusion in the form of a cut sphere, the thickness of the enriched layer is different along the vertical and radial directions. Figure 6B shows how carrier concentration increases toward the center, \( r = 0 \). This increase strongly depends on temperature.

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**Notes**
The authors declare no competing financial interest.

### ABBREVIATIONS

QW, quantum well; TEM, transmission electron microscopy; AFM, atomic force microscopy

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