Electrostatic enhancement of light emitted by semiconductor quantum well

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Abstract. Carrier dynamics in metal-semiconductor structures is driven by electrodynamic coupling of carriers to the evanescent field of surface plasmons. Useful modifications in electron and hole dynamics due to presence of metallic inclusions show promise for applications from light emitters to communications. However, this picture does not include contributions from electrostatics. We propose here an electrostatic mechanism for enhancement of light radiated from semiconductor emitter which is comparable in effect to plasmonic mechanism. Arising from Coulomb attraction of e-h pairs to their electrostatic images in metallic nanoparticles, this mechanism produces large carrier concentrations near the nanoparticle. A strong inhomogeneity in the carrier distribution and an increase in the internal quantum efficiency are predicted. In our experiments, this manifests as emission enhancement in InGaN quantum well (QW) radiating in the near-UV region. This fundamental mechanism provides a new perspective for improving the efficiency of broadband light emitters.

1. Introduction

Metallic inclusions in semiconductor structures play the role of environment which may strongly affect the rate of electron-hole recombination. Depending on the final density of photonic states the environment may either decrease or increase the recombination rate. In the former case energy of the radiated photon fits the photonic band gap[1] and in the latter case recombination occurs faster due to Purcell effect [2]. During the last two decades several experimental manifestations of Purcell effect have been observed in semiconductor quantum wells (QW's) covered by thin metallic film [3, 4, 5]. The level of enhancement strongly depends on how exactly the frequency ω of the emitted lights matches the resonant frequency of plasmonic resonance ω_s. If the mismatch between ω and ω_s increases the effect of plasmonic enhancement becomes negligible. This frequency-matching condition limits application of plasmonic mechanism for light enhancement in solid-state light emitters with broadband spectrum. Emitters that radiate blue or near-UV light require coating by silver thin film, since silver exhibits plasmonic resonance in this region of the spectrum. However, because of its fast oxidation silver cannot be widely used in commercial devices. Here gold is relatively immune to corrosion but its resonant frequency lies in the red-IR region. Thus, gold cannot be used in the whole visible spectrum. One more disadvantage of plasmonic mechanism is its relatively high Joule losses which accompany

propagation of surface plasmons in metal. Here we report a new non-resonant and non-dissipative electrostatic mechanism of light enhancement.

The proposed mechanism is based on electrostatic attraction of electrons and holes to their electrostatic images in metallic nano-inclusions. Neutral metal equally attracts electrons and holes, causing the carriers to drift towards, and concentrate near, the nano-inclusion. The rate of e-h recombination depends not only on the density of states but also on the local concentration of carriers, $n(\mathbf{r})$. In the regions with higher concentration the wave functions of electrons and holes strongly overlap that increases the probability of recombination. This, however, does not necessary lead to higher intensity of light if most of the recombination processes are non-radiative. In direct band-gap heterostructures the radiative recombination occurs mostly through the bimolecular mechanism which is quadratic in the carrier concentration, $\Gamma_r = Bn^2$. In contrast, the Shockley-Read-Hall mechanism of non-radiative recombination is characterized by a linear rate, $\Gamma_{nr} = An$ [6]. Thus, faster increase of Γ_r with concentration is beneficial, since it leads to higher internal quantum efficiency of the emitter,

$$\eta = Bn^2/(An + Bn^2). \tag{1}$$

To demonstrate the new mechanism of enhancement we studied photoluminescence from InGaN/Gan multi-QW shown in Figs. 1 and 2. This QW radiates blue light with maximum intensity near $\lambda = 416$ nm. The QW was infiltrated by gold nano-particles. The plasmonic mechanism of enhancement is ruled out since gold nanospheres of diameter from 30 to 35 nm used in our experiment have plasmonic resonance at approximately 2λ.

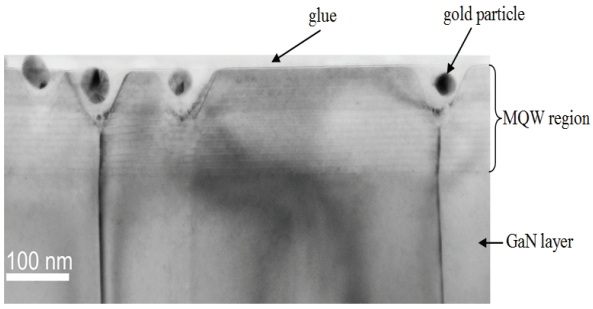

Figure 1. TEM image of InGaN/GaN multi-quantum well with gold particles of $\sim$ 30 size inside the pits.

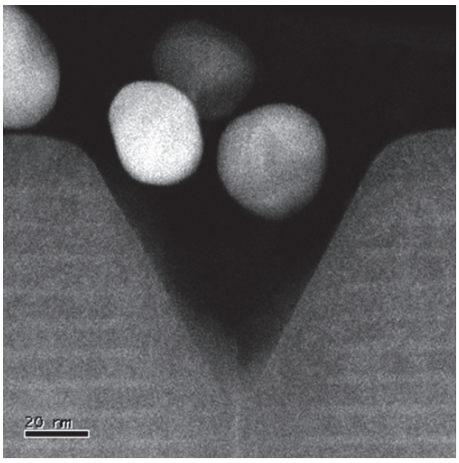

Figure 2. A pit with several gold nanoparticles.

2. Sample preparation and experimental results for the emission spectra

The size of the NP plays a principal role here, determining the level on enhancement. The electrostatic drift of the carriers towards the nanoparticles becomes noticeable if the ratio $\gamma = (e^2/\varepsilon R)/kT$ of electrostatic energy to thermal energy becomes $\gamma \sim 1$. For the effect to be observable at room temperature, this condition requires that the typical size $2R$ of the NP be $2R < 50$ nm given that the dielectric constant of the QW is $\varepsilon \sim 10$.

We measured the PL enhancement from the same material heterostructures of InGaN/GaN which were previously used in Ref. [4, 5] to demonstrate the plasmonic mechanism of enhancement and recently in Ref. [7] to demonstrate the electrostatic mechanism. In nitride

heterostructures threading dislocations end off with inverted pits at the surface provide a natural and invasive way to incorporate metallic nanoparticles inside a QW heterostructure, see Fig. 1.

In order to obtain a pit size of $\sim$ 50 nm, we grew a $In_{0.09}Ga_{0.91}N/Ga$ 14-layer QW with a well thickness of 2.5 nm, barrier thickness of 7.5 nm, and a 15-nm cap layer above the final QW. This light emitting heterostructure was grown by MOCVD under conventional conditions along the (0001) axis without intentional doping [8]. The V-shaped pits act as a potential barrier for non-radiative recombination center. The Au nanoparticles of 30-35 nm suspended in water or DMSO solution were trickled into the pits using a combination of sonication, density of fluid and flow rate. Mechanical contacts between the nanoparticles and the surface of the QW occur randomly at very few points, as it can be seen in Figs. 1 and 2. Near these points of contact a depletion layer may be formed due to Schottky barrier. It repels carriers and in principle may reduce the attraction due to image charges. However, since the area of possible mechanical contacts is negligible as compared to the area of a nanoparticle, the Coulomb attraction remains the dominant force of interaction.

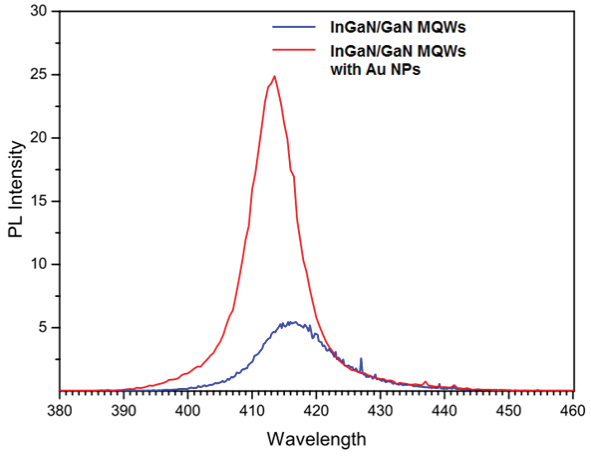

Figure 3. Photoluminescence spectrum of the multi-QW measured at room temperature without (blue curve) and with (red curve) gold nanoparticles.

The PL spectra of the multi-QW with and without gold NPs are shown in Fig. 3 with a maximum photoluminescence intensity at $\lambda = 413$ nm and $\lambda = 416$ nm, respectively. There is roughly a six-fold enhancement in the PL emission with gold at room temperature. As mentioned before, a gold nanoparticle does not serve as plasmonic source of enhancement for an InGaN QW due to having almost two times lower localized surface plasmon energy. Instead, the Coulomb attraction of the free carriers to their image charges in the nanoparticle leads to enhancement. Image charges, being of equal magnitude and opposite sign to the image-inducing carrier, cause both electrons and holes to drift towards the surface of the nanoparticle that increases the electron-hole and exciton recombination rate. Excitons, while being electrically neutral are also attracted to a neutral metal surface. The origin of this electrostatic mechanism is best demonstrated by Thomson's theorem which states that the equilibrium distribution of charges on the surface of an isolated conductor corresponds to the minimum of the potential energy [9]. A direct consequence of this theorem is that a neutral conductor attracts *any* given set of electric charges. Therefore, electron-hole pairs and excitons within the QWs shown in Fig. 1 are attracted towards the metal nanoparticles. The attraction of a single carrier located at a distance r from a neutral metallic sphere of radius R decays fast far away from the sphere, $eE(r) \sim 1/r^5$. However, close to the surface, it grows as $eE(r) \sim 1/(r-R)^2$. This Coulomb force leads to a permanent drift of the carriers. The local concentrations of electrons is obtained from the non-linear diffusion equations in the presence of the electrostatic force $e\mathbf{E}(\mathbf{r})$.

$$\dot{n}_e = D_e \nabla^2 n_e + \frac{eD_e}{kT} \nabla \cdot (\mathbf{E} n_e) - n_e(A - Bn_h) + g. \tag{2}$$

The equation for holes is obtained by replacement $e \Leftrightarrow h$. Here $D_{e,h}$ are the diffusion coefficients for electrons and holes, and g is the density of e-h pairs produced by the pumping laser per second. The electrostatic field **E** in the drift term in Eq. (2) is obtained from the Poisson equation where the real charges and also their electrostatic images in metal must be included.

The strong contribution of the drift term to the e-h kinetics can be demonstrated by an asymptotic steady-state solution if we linearize Eq. (2) in the vicinity of the nanosphere, $r - R \ll R$:

$$n_{e,h}(r) \propto \exp[\gamma R/4(r-R)], \;\; \gamma = (e^2/\varepsilon R)/kT. \tag{3}$$

Here the parameter γ defines the width of the region with higher concentration of carriers. Since it scales as $\gamma \sim 1/T$ the effect of enhancement becomes stronger at lower temperatures. Thus, the electrostatic drift leads to an exponential singularity of the carrier concentration at the surface. This strong non-physical singularity appears since the asymptotic solution (3) is not self-consistent. Once Debye screening, which strongly reduces attraction to the image charges, is taken into account the singularity becomes much weaker. Moreover, Debye screening leads to the effect of saturation of emission enhancement at high pumping power [7]. It is worth mentioning that electrostatic enhancement is not accompanied by Joule losses, unlike the plasmonic enhancement, which inevitably leads to dissipation of energy.

The proposed electrostatic mechanism successfully explains the enhanced spectra in Fig. 3. At the same time the emission spectrum of the QW coated by high-quality gold film does not exhibit enhancement at all [4, 5]. It is obvious that in this case the carriers in the QW are also attracted towards their electrostatic images. However, in the plane geometry this attraction pushes electrons and holes towards the metal film, without changing the average in-plane separation between them. It turns out that the increase of the concentration only along a single coordinate (the one which is perpendicular to the quantum confinement) is not sufficient to produce the effect of enhancement. In this case the image charges may only reduce the effective width of the QW that gives rise to the blue shift of the spectrum, which was not explained in Refs. [4, 5]. Gold nanospheres, being practically point attractors, lead to both effects, therefore the blue shift and emission enhancement are clearly seen in Fig. 3.

3. Conclusions

We propose a mechanism of light emission enhancement from semiconductor heterostructures which is due to attraction of carriers to neutral metallic nano-inclusions. Unlike the well-known plasmonic mechanism, it is free from the frequency-matching condition, thus, is may be used to increase the performance of broad-band solid-state light emitters. Due to its electrostatic nature the new mechanism is non-dissipative and universal, i.e. *any* metal can be used and this does not affect the level of enhancement. Finally, it does not require high-quality coating since any irregularities in the shape of metallic inclusions increase electrostatic image-charge forces.

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