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NANOSTRUCTURE-CONTROLLED PLASMONICS TOWARDS HIGH-EFFICIENCY LIGHT-EMITTING DIODES AND SOLAR CELLS

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Surface plasmon (SP) coupling was applied to increase the emission efficiencies of InGaN/GaN-based quantum wells (QWs) with various emission wavelengths. This technique will provide super bright LEDs which have perfect efficiencies at any wavelength if we can control the SP frequency to obtain the best coupling condition. A huge enhancement of green emission, which has been very difficult to achieve, was observed at certain wavelength and special ranges by controlling the metal nanostructures. Possible device structures of plasmonic LEDs were proposed and discussed. The similar device structures should be useful to develop high-efficiency light-resaving devices, namely, plasmonic solar cells.

Keywords: plasmonics, surface plasmon, nanostructure, light-emitting diode, solar cell

INTRODUCTION

The technique to control and utilize surface plasmon (SP) generated at metal/dielectric interface is called "plasmonics" and has attracted much attention with the recent rapid advance of nanotechnology. The SP can couple to electromagnetic wave at the interface and brings novel optical properties and functions to materials. One futuristic application of plasmonics is the development of high-efficiency light-emitting devices (LEDs). LEDs have been expected to eventually replace traditional fluorescent tubes as new illumination sources. For example, InGaN-based quantum wells (QWs) provide bright light sources, however, their efficiencies are still substantially lower than those of fluorescent lights. The SP coupling technique is one of the most effective methods to increase these efficiencies.

The idea of SP enhanced light emission was proposed since 1990, and it has been applied to increase emission efficiencies of several materials which include InGaN QWs. Gontijo et al. reported the coupling of the emission from InGaN QW into the SP on silver thin firm by using the configuration shown in Fig. 1(a). Unfortunately, they found that the PL intensities dramatically decreased by the SP coupling [1]. By using same sample structure, Neogi et al. confirmed that the recombination rate in an InGaN/GaN QW could be significantly enhanced by the time-resolved PL measurement [2]. However, in these early studies, light could not be extracted efficiently from the metal surface, and the SP coupling has been thought to be a negative factor for LEDs.

Recently, we have reported for the first time large photoluminescence (PL) increases from InGaN/GaN QW material coated with metal thin films by using the configuration shown in Fig. 1(b) [3]. We obtained a 17-fold increase in the luminescence intensity along with a 7-fold increase in the internal quantum efficiency of light emission from InGaN/GaN QWs when nano-structured silver layers were deposited 10 nm above the QWs. We also observed a 32-fold increase in the spontaneous emission rate of InGaN/GaN at 440 nm probed by time-resolved PL measurements. [4]

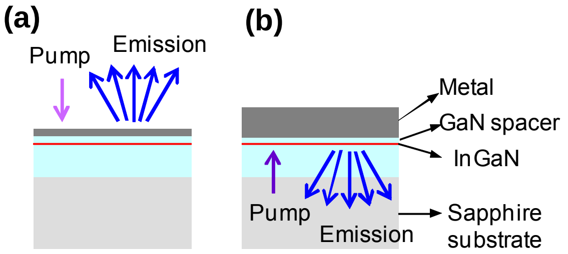

Fig. 1. Sample structure and experimental configuration of previous study reported in Ref. [1-2] (a) and this study (b).

The SP-emitter coupling technique would lead to high-efficiency LEDs that offer realistic alternatives to conventional fluorescent light sources. However, detail mechanism and dynamics of the SP coupling have been still not so clear. We already achieved efficient blue emissions by using this technique. However, it has been still very difficult to obtain highly enhanced green emissions in spite of the importance of applications of the high-efficiency green LEDs. Here, we try to control the SP coupling conditions by employing the metal nanostructures. Further optimizations of nanostructures should bring highly efficient LEDs and also light receiving devices.

EXPERIMENT

InGaN/GaN-based QW wafers were grown on a (0001) oriented sapphire substrate by a metal-organic chemical vapor deposition (MOCVD). The QW heterostructure consists of a GaN (4 μm) buffer layer, an InGaN QW (3 nm) and a GaN cap layer (10 nm). Silver films (50nm) were deposited on top of the surfaces of these wafers by a high vacuum thermal evaporation. The PL measurements were performed by exciting the QW with a 406nm diode laser and detecting

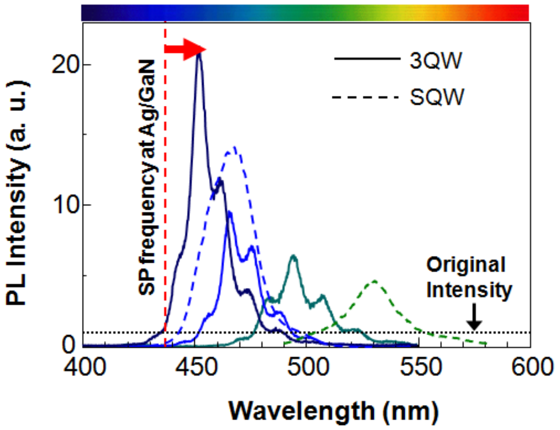

Fig. 2. SP enhanced PL spectra of InGaN/GaN SQW (broken lines) and 3QW (solid lines) coated with Ag. The PL peak intensities of uncoated samples were normalized to 1.

the emission with a multi-channel spectrometer. To perform 3-dimentional finite-difference time-domain (3D-FDTD) simulations, we used commercialized software "Poynting for optics" (Fujitsu Co.).

RESULTS AND DISCUSSIONS

Fig. 2 shows typical PL spectra from an InGaN/GaN QWs separated from Ag films by 10 nm GaN spacers. The PL peak intensities of uncoated samples were normalized to 1 and huge enhancements were observed by Ag coating especially at the shorter wavelength region. The wavelength dependences of the enhanced PL intensities were almost same for single QW and three QWs. These PL enhancements should be attributed to the SP coupling. A possible mechanism of the SP coupling was already proposed elsewhere. [3-5] Electron-hole pairs in the QW couple to plasma oscillation of electrons at the metal/semiconductor interface when the energies of electron-hole pairs and of the SP frequency are similar. Then, electron-hole recombination may produce SPPs instead of photons or phonons, and this new recombination path increases the recombination rate and the internal quantum efficiency. If the metal surface is perfectly flat, the SPP energy would be thermally dissipated. By providing roughness or nanostructure of the metal layers, the SPP energy can be extracted as light. Such roughness allows SPPs of high momentum to scatter, lose momentum, and couple to radiative photon. In order to obtain the high photon extraction efficiencies, the few tens of nanometer sized structures at the metal surfaces were obtained by controlling the evaporation conditions.

The difference between our configuration and that of previous reports [1-2] is direction of photo-pumping and detection. In this study, we photo-pump and detect emission from the backside of the samples through the transparent substrate by polishing the bottom surface [Fig. 1(b)]. By employing such back-side access to the QWs, we can avoid an absorption loss at the metal layer and obtain an effective light extraction from SPP at the interface. Thus we can use very thick metal films. This thickness should be also very important factor to obtain a huge enhanced light emission. If the metal layer is thinner than the penetration depth of SPP, other SPP mode is generated at the air/metal interface of the opposite side of the metal layer. These SPP modes couple each other and form symmetric and anti-symmetric mode of the SPPs. This should modify the SP frequency and coupling condition and make the light extraction very difficult. The thick metal layer is also useful to avoid the oxidation of silver surface. Metal oxidation changes the surface roughness and SP mode. But the oxidation typically is generated only at air/metal interface and not at the metal/semiconductor interface. In this study, SPPs at the metal/semiconductor interface contribute to light emission enhancement. The thickness of metal films (50nm) is large enough to ensure that metal oxidation at air/metal interface does not influence the metal/semiconductor interface. It is very simple solution but the back-side access is the most important trick which enabled us to obtain light enhancements by the SP coupling for the first time.

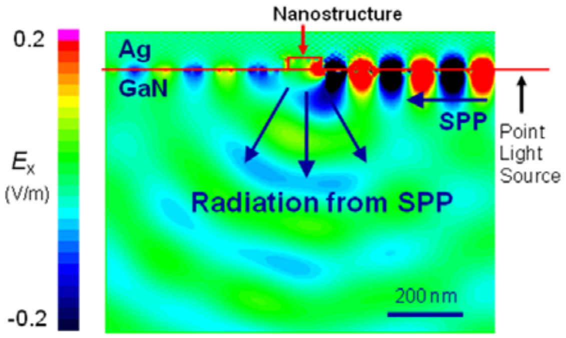

Fig. 3. 3D-FDTD simulations of generation and light extraction of SPPs. SSP was generated from a point light source located on the interface, and it was extracted as light at the gap in the metal layer.

In order to evaluate the SP coupling mechanism we proposed, we employed the 3D-FDTD simulation. Fig. 3 shows the calculated spatial distribution of the electromagnet field around the metal/semiconductor interface. The clear SPP mode appeared and propagated within the interface by the point light source located at the interface. A polarized plane wave with 525 nm wavelength and 1 V/m amplitude was used as a point light source which is as assumption of an electron-hole pair. This result suggests that the SPP mode can be generated easily by direct energy transfer from electron-hole pairs without any special structures. Usually, some special configurations are necessary to generate SPP mode such as a grating coupler or an Attenuated total reflection setting to satisfy a phase matting condition between SPPs and photons. If the light source is located near the metal/dielectric interface within wavelength scale, the SPP mode can be generated regardless of the phase matching condition. Also the light extraction processes can be reproduced by the simulation. The SPP mode can be coupled to photon if there is a nano-sized gap structure at the interface. Then, generated SPP can be extracted as light from the interface, and as a consequence, the emission efficiency is increased. These calculations support our proposed SP coupling model.

Fig. 2 shows that huge enhancements were observed by Ag coating especially at the shorter

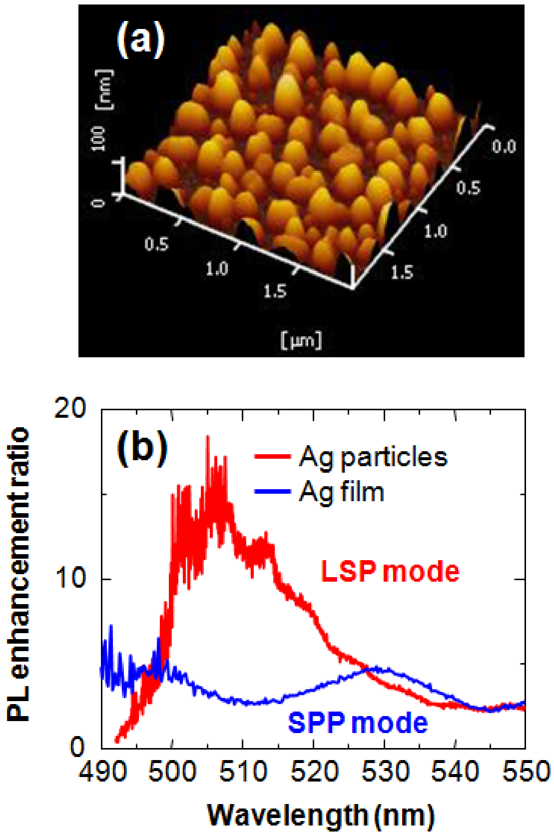

Fig. 4. (a) SPM image of the Ag nanoparticles array structure on InGaN/GaN. (b) PL enhancement ratio plotted against wavelength taken for InGaN/GaN QW with Ag particles and Ag thin film.

wavelength region. The SP coupling effect was remarkable when the emission energy was close to the SP frequency described as dotted line in Fig. 2 at 2.84 eV (437 nm). It was found that the enhancement effect became lower and lower with increasing of wavelength. Our proposed mechanism suggests that very high efficieny may be achievable at any wavelength if we can control the SP frequency and obtain the best matching condition. Tuning of SP coupling should be attainable by choosing the appropriate metal or controlling nanostructures [6]. For example, we try to optimize the SP coupling by employing the metal nanoparticle array structures. Fig. 4(a) shows the Scanning Probe Microscopic (SPM) image of Ag nanoparticle arrays fabricated on InGaN/GaN by a metal deposition and a thermal annealing. The wavelength dependence of the PL enhancement ratios were shown in Fig. 4(b). Remarkable enhancement was observed at 500-520 nm with Ag particles, while the ratios were almost flat with Ag film. This difference should be due to the properties of the localized SP (LSP) mode and the propagated SPP mode. The LSP mode can be tuned by the variations of size and distance of the Ag particles. This result suggests that high efficiency light emitters can be achievable at various wavelength regions by further optimization of nanostructures.

One of the most important targets of this study is device application of the SP coupling. Possible device structures of high-efficiency plasmonic LEDs are shown in Fig. 5 [5]. Fig. 5(a) shows the simplest structure using a usual LED structure with a p-n junction. The metal layer can be used both as an electrical contact and for exciting plasmons. The important point of this structure is that the distance between the metal surface and the InGaN QW must be very close to get a good SP coupling. Therefore, the p-type GaN layer must be thinner than 10 nm. The PL enhancement ratios become exponentially decay with increasing of the thickness of the GaN spacer layer [3, 5]. This feature makes the device application of the SP coupling so difficult. We already fabricated the structure shown in Fig. 5(a) but we were not able to obtain a huge enhancement of emission. There are two reasons; first, p-doping was very difficult into 10 nm thick GaN layer. Second, we could not get a good ohmic contact because the p-GaN layer is too thin. Another possible structure of a plasmonic LED was shown in Fig. 5(b). In this structure, the metal layer for electrode and for SP coupling is different. The SP coupling should happen at the metal particles implanted just above a QW layer in a LED wafer. Fig. 5(c) shows another promising device

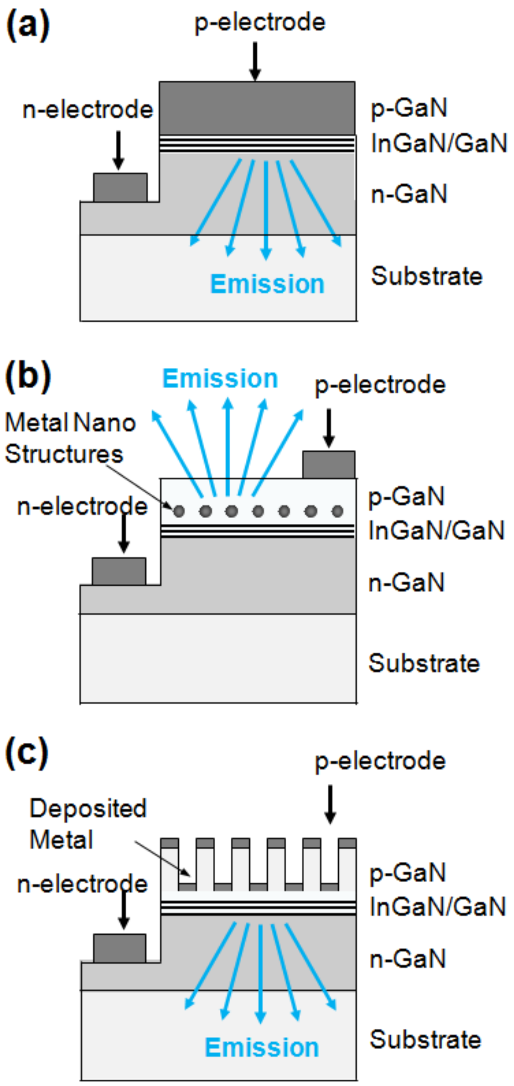

Fig. 5. Possible device structures of high efficient LEDs based on plasmonics with electrical pumping. (a) Metal electrode is located a few nm above the active layer. (b) Metal particles are embedded a few nm above the active layer, (c) p-GaN has 2-dimentional structures.

structure which has a two-dimensional structure fabricated by the lithography and the dry etching processes. By using this structure, the electrons injection and the SP coupling can be well performed at the thick areas and the thin areas, respectively. This should enable both good ohmic contact and SP enhancement effects at the same time. Quite recently a few groups reported about the SP enhanced LEDs based on our technique [7-8], however a high efficient LED structure based on plasmonics is still not yet achieved.

Next very important application of plasmonics is high-efficiency light-resaving devices, namely, solar cells. The SP-exciton and SP-photon coupling processes are reversible processes. Therefore, if the SP coupling increase light emission processes, it should also increase the light receiving processes. The sun-light can couple to the SP at the metal/dielectric interface and generate the excitons in the dielectric materials. The SP coupling make giant electric field at the metal surface by the light-antenna effect of the SP. Therefore, the excitation processes through the SP coupling should be much faster than the direct excitation processes, and increase light absorption efficiencies.

The solar energy is one of the most important renewable energy resources and the photocurrent conversion efficiencies of several kind of solar cells have been rapidly developed. Especially, the crystalline solar cells with silicon or compound semiconductors were well developed and their efficiencies were almost reached to the theoretical limits. The drastic cost reduction is much important for such crystalline solar cells to use for much wider areas. For example, making ultra-thin device structures is required to save the materials. On the other hand, amorphous or organic solar cells are very cheap and easy to treat them but the efficiencies are still very low. The improvements of the efficiencies and device lifetime are most important for such solar cells. The palsmonic solar cells have a potential to apply to high-efficiencies and ultra-thin solar cells, which can overcome the both problems of solar cells of efficiencies and costs. Until now, several types of the plasmonic solar cells have been reported by using random metal particle array structures [9-10] and top-down nanofabricated structures [11]. However these palsmonic solar cells are still far from practical utilizations. Further optimization of the metal nanostructure and tuning of the SP coupling process are required In order to improve the plasmonic solar cell to the practical level.

CONCLUSIONS

The SP coupling is very powerful method to enhance light emission efficiencies of various materials at wider wavelength regions. By using this technique, high-efficiency and high-speed light emission is predicted for optically as well as electrically pumped light-emitting devices, because the SP coupling increases the internal quantum efficiency, and this mechanism is not related to the pumping method. We believe that this method would bring super bright plasmonic LEDs, which become the dominant white light sources as an alternative to conventional fluorescent tubes. Nanostructure-controlled plasmonics has a great potential to develop actual devices of high-efficiency plasmonics LEDs, though the process is still difficult. The similar devices structure should also provide very-thin and high-efficiency plasmonics solar cells in the near future.

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