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Plasmonics for Green Technologies: Toward High-Efficiency LEDs and Solar Cells

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1. Introduction

Nowadays, energy issues became very important problem for us. We spend a lot of energy for illumination at night, so developing high-efficiency light sources is very important to save our energy. Recently, solid-state light-emitting devices have been developed and expected as new-generation light sources because of their advantages such as small, light-weight, long lifetime, easy operation, and saving energy. Since 1993, InGaN quantum wells (QW)-based light-emitting diodes (LEDs) have been continuously improved and commercialized as light sources in the ultraviolet (UV) and visible spectral regions. In 1996, white light LEDs, in which a blue LED is combined with yellow phosphors, have been developed and offer a replacement for conventional incandescent and fluorescent light bulbs. However, these devices have not fulfilled their original promise as solid-state replacements for light bulbs as their light-emission efficiencies have been limited. The most important requirement for competitive LEDs for solid-state lighting is improvement of their quantum efficiencies of light emissions.

Making energy is also very important so much as saving energy. Renewable energies have attracted a great deal of attention as a new energy source instead of fossil resource which is going to be exhausted. 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.

A lot of effort and time have been used to improve the efficiencies of LEDs and solar cells, but still it has been very difficult to achieve dramatic improvements. Here I introduce the unique approach to increase these efficiencies based on "Plasmonics". These studies should bring the new application field of plasmonics for green technologies.

2. Fundamental and application of plasmonics

Conduction electron gas in a metal oscillates collectively and the quantum of this plasma oscillation is called plasmon. A special plasma oscillation mode called surface plasmon (SP) exists at an interface between a metal, which has a negative dielectric-constant, and a positive dielectric material (Raether, 1988). The charge fluctuation of the oscillation of the SP is accompanied by fluctuations of electromagnetic fields, which is called surface plasmon polariton (SPP). Schematic diagram of the SP and the SPP mode generated at metal/dielectric interface were shown in Fig. 1. The SPP can interact with light waves at the interface and it brings novel optical properties and functions to materials. The technique controlling and utilizing the SPP is called "plasmonics" and has attracted much attention with the recent rapid advance of nanotechnology (Barnes et. al., 2003; Atwater et al., 2007).

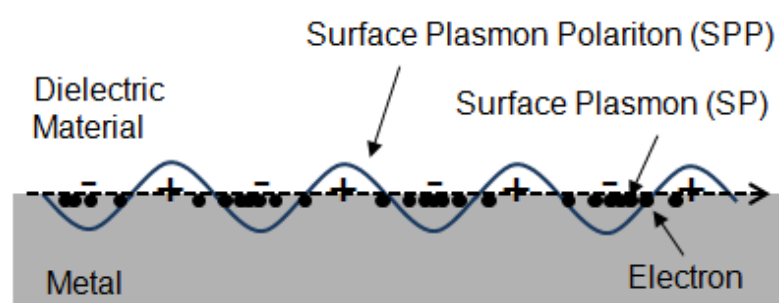


Fig. 1. Schematic diagram of the surface plasmon (SP) and the SP polariton (SPP) generated at the metal/dielectric interface.

The wave vector of the SPP (k_{SP}) parallel to the interface can be written with the following equation when the relative permittivity of the metal is $\epsilon_1 = \epsilon_1' + \epsilon_1''i$ and that of the dielectric material is ϵ_2 .

$$k_{SP}(\omega) = \frac{\omega}{c} \sqrt{\frac{\epsilon_1'(\omega)\epsilon_2(\omega)}{\epsilon_1'(\omega) + \epsilon_2(\omega)}} + \frac{\omega}{c} \left(\frac{\epsilon_1'(\omega)\epsilon_2(\omega)}{\epsilon_1'(\omega) + \epsilon_2(\omega)} \right)^{\frac{3}{2}} \frac{\epsilon_1''(\omega)}{2\epsilon_1'(\omega)^2} i \quad (1)$$

where, ω and C are the frequency of the SPP and the light velocity in vacuum, respectively. The first and second terms of this equation give the dispersion and the damping factor of the SPP. The k_{SP} values are much larger than the wave vector of the light wave propagated in the dielectric media. This fact suggests that the SPP can propagate into nano-spaces much smaller than the wavelength. This enables us to shrink the sizes of waveguides and optical circuits into nano-scale.

Wave vectors of the SPP perpendicular to the interface in a metal or a dielectric material must be an imaginary number because k_{SP} is larger than the light line. This suggests that the electromagnetic fields of the SPP are strongly localized at the interface and it makes giant fields at the interface. This huge field enhancement effect is also one of the most important features of the SPPs. It has been applied to high sensitive sensors using the surface enhanced Raman scattering (SERS), surface plasmon resonance (SPR), and so on.

One futuristic application of plasmonics is the development of high-efficiency LEDs. LEDs have been expected to eventually replace traditional fluorescent tubes as new illumination

sources. For example, InGaN-based QWs provide bright light sources, however, their efficiencies are still substantially lower than those of fluorescent lights. 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 film, however they found that the PL intensities dramatically decreased by the SP coupling (Gontijo, et al., 1999). 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 (Neogi et al., 2002). 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 (Okamoto et al., 2004). 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 (Okamoto et al., 2005). Moreover, we obtained a huge enhancement of light emissions for silicon nanocrystals in silicon dioxide media (Okamoto et al., 2008). Usually the emission efficiencies of such indirect semiconductors are quite low, but by using the SP coupling, it is possible to increase these efficiencies up to values as large as those of direct compound semiconductors.

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. 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, namely, solar cells.

3. Enhancement of photoluminescence of InGaN/GaN

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. 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 the emission with a multi-channel spectrometer.

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 (Okamoto et al., 2005;

Okamoto & Kawakami, 2009). 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.

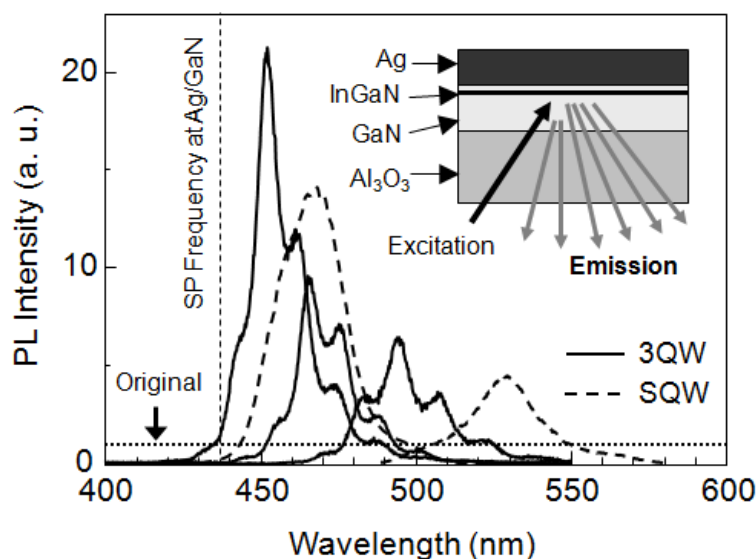


Fig. 2. SP enhanced PL spectra of InGaN/GaN SQW with peak wavelength at 470 and 530 nm (broken lines) and 3QW with peak wavelength at 450, 460, and 500 nm (solid lines) coated with Ag. The PL peak intensity of uncoated sample was normalized to 1. (Inset) Sample structure and excitation/emission configuration.

We photo-pump and detect emission from the backside of the samples through the transparent substrate by polishing the bottom surface. 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. 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.

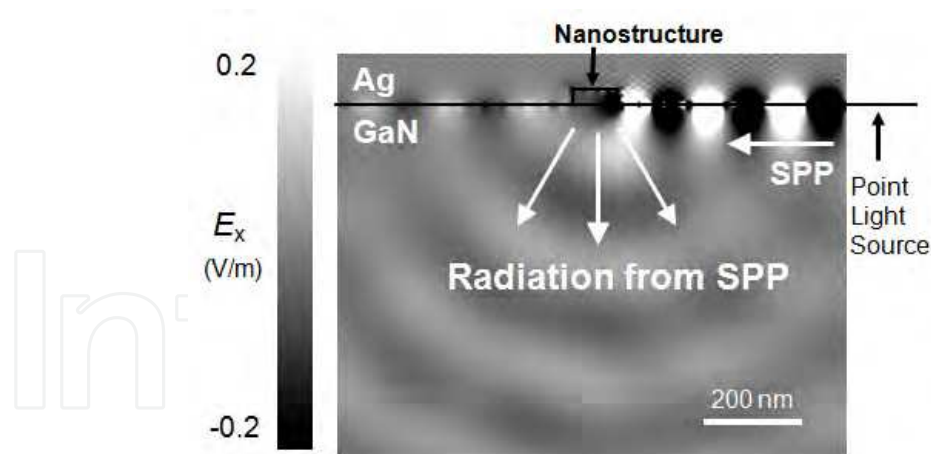


Fig. 3. 3D-FDTD simulations of generation and light extraction of SPPs. SPP was generated from a point light source located on the interface, and it was extracted as light at the gap in the metal layer.

In order to evaluate the SP coupling mechanism we proposed, we employed the 3-dimensional finite-difference time-domain (3D-FDTD) simulation. We used commercialized software "Poynting for optics" (Fujitsu Co.). Fig. 3 shows the calculated spatial distribution of the electromagnetic 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 matching 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.

4. Enhancement of spontaneous emission rate

Fig. 2 shows that huge enhancements were observed by Ag coating especially at the shorter wavelength region. It was found that the enhancement effect became lower and lower with increasing of wavelength. This wavelength dependence of the SP enhancement effect is well correlated to the properties of the SPP. Fig. 4 shows the dispersion diagrams of SPP modes on metal/GaN surfaces calculated by Eq. (1). The SP frequency (ω_{SP}) at GaN/Ag is 2.84 eV (437nm). Thus, Ag is suitable for SP coupling to blue emission, and we attribute the large increases in the PL intensity from Ag-coated samples to such resonant SP excitation. By this reason, the SP coupling becomes remarkable when the energy is near to the SP frequency described as dotted line in Fig. 2. In contrast, ω_{SP} at GaN/Au is 2.462 eV (537 nm), and no measurable enhancement is observed in Au-coated InGaN emitters as the SP and QW energies do not match. In the case of Al, the ω_{SP} is 5.50 eV (225 nm), and the real part of the

dielectric constant is negative over a wide wavelength region for visible light. Thus, a substantial and useful PL enhancement is observed in Al-coated samples, although the energy match is not ideal at 470 nm and a better overlap is expected at shorter wavelengths.

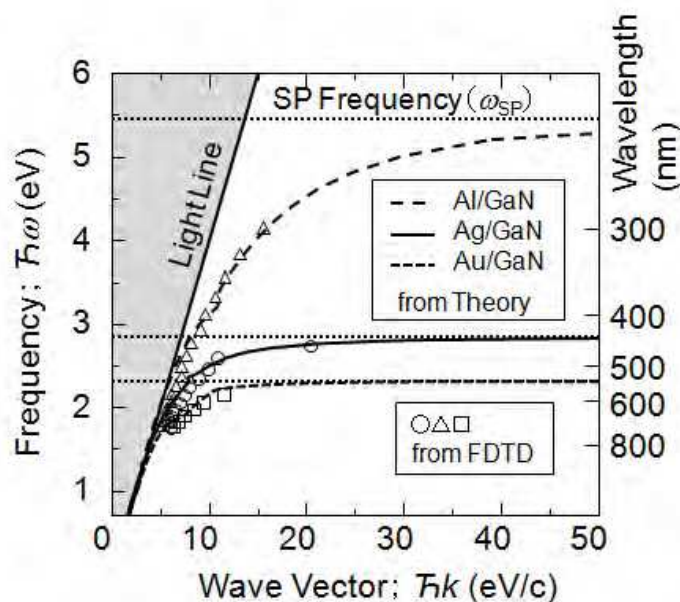


Fig. 4. Dispersion diagrams of the SPP at Al/GaN, Ag/GaN, and Au/GaN interfaces.

The external quantum efficiency (η_{ext}) of LED is given by a product of the light extraction efficiency (C_{ext}) and the internal quantum efficiency (IQE: η_{int}). The original η_{int} value is determined by the ratio of the radiative (k_{rad}) and nonradiative (k_{non}) recombination rates of excitons.

$$\eta_{\text{ext}}(\omega) = C_{\text{ext}}(\omega) \times \eta_{\text{int}}(\omega) = C_{\text{ext}}(\omega) \frac{k_{\text{rad}}(\omega)}{k_{\text{rad}}(\omega) + k_{\text{non}}(\omega)} \quad (2)$$

Under the existence of the SP coupling, the enhanced IQE value (η_{int}^*) can be described as follows,

$$\eta_{\text{int}}^*(\omega) = \frac{k_{\text{rad}}(\omega) + C'_{\text{ext}}(\omega)k_{\text{SPC}}(\omega)}{k_{\text{rad}}(\omega) + k_{\text{non}}(\omega) + k_{\text{SPC}}(\omega)} \approx C'_{\text{ext}}(\omega) \times \eta_{\text{ex-sp}}(\omega) \quad (3)$$

where k_{SPC} is the SP coupling rate and should be very fast because the density of states (DOS) of SPP is much larger than that of the excitons in the QW. C'_{ext} is the probability of photon extraction from the SPPs. C'_{ext} is decided by the ratio of light scattering and dumping of the SPPs through non-radiative loss. C'_{ext} should depend on the roughness and nanostructure of the metal surface. If the SP coupling is much faster ($k_{\text{SPC}} \gg k_{\text{rad}}$), the η_{int}^* is given by the product of C'_{ext} and the exciton-SP coupling efficiency ($\eta_{\text{ex-sp}}$).

The increased emission rates were observed by the TRPL measurement. Fig. 3 (inset) shows the PL decay profiles of uncoated and Ag-coated InGaN/GaN QW samples emitters at 440nm. The PL decay rate (k_{PL}) is attributed to the radiative and nonradiative recombination rate of excitons as $k_{\text{PL}} = k_{\text{rad}} + k_{\text{non}}$. After Ag-coating, k_{PL} values were increased to k_{PL}^* by the SP

coupling rate as $k_{PL}^* = k_{rad} + k_{non} + k_{SPC}$. Usually, k_{SPC} should be much faster than k_{rad} because of the higher DOS of SPP.

Theoretically, the SP coupling rate is given by the Fermi's Golden rule as follows (Gontijo, et al., 1999; Neogi et al., 2002),

$$k_{SPC}(\omega) = \frac{2\pi}{\hbar} |\vec{d} \cdot \vec{E}(\omega)|^2 \rho(\omega) \quad (4)$$

where \hbar is the reduced Plank constant, \vec{d} is the dipole moment of the electron-hole pair, \vec{E} is the electric field of the SPP at the location of the active layer, and ρ is the DOS of the SSP. This equation suggests that the SP coupling rate should be proportional to the DOS.

We defined the enhancement factor (F) of the spontaneous emission rate as follows,

$$F(\omega) = \frac{k_{SPC}(\omega)}{k_{rad}(\omega)} \quad (5)$$

We plotted F value against wavelength in Fig. 5. The solid line in this figure shows slope of the dispersion diagram ($dk/d\omega$), which is proportional to DOS of SPP. We found that F and $dk/d\omega$ are almost same values. This suggests that the enhanced emission rates and IQEs are determined only by the DOS.

Fig. 6 shows the η_{ex-sp} values estimated by

$$\eta_{ex-sp}(\omega) = \frac{k_{spc}(\omega)}{k_{rad}(\omega) + k_{non}(\omega) + k_{spc}(\omega)} \quad (6)$$

The η_{int}^* values can be estimated separately by the temperature dependence of the PL intensities by assuming IQE~100% at low temperature (Okamoto et al., 2004). Obtained η_{int}^* values were also shown in Fig. 6 (broken line). The ratios of η_{int}^* and η_{ex-sp} give the SP-photon coupling efficiency (C'_{ext}) by Eq. (3) and were shown in Fig. 6 (solid line). Fig. 6 shows that all these efficiencies are reached to almost 100% at the shorter wavelength region. This suggests that if we can control the SP frequency and obtain the best SP coupling condition, we can develop super bright LEDs which have perfect efficiencies at any wavelength.

5. Tuning of the SP coupling

Our proposed mechanism suggests that very high efficiency 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. For example, we fabricate several types of metal nanostructures shown in Fig. 7.

Fig. 7(a) shows the Scanning electron microscope (SEM) image of nano grating structure created by electron beam lithography and ion milling. By using this structure, we could enhanced the green emission from InGaN/GaN QW a few times larger. Fig. 7(b) shows the nano grain structure created by control of metal vapour deposition conditions. A few tens

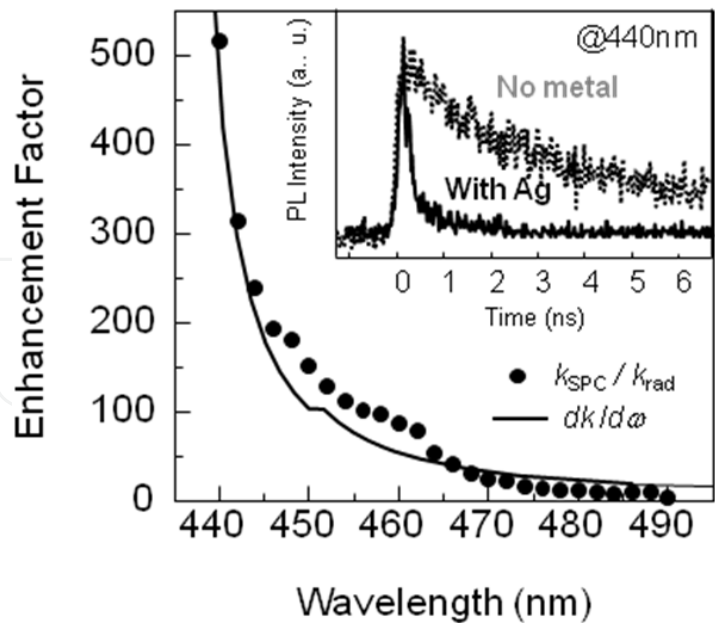


Fig. 5. Enhancement factor of the spontaneous emission obtained by the ratios of surface plasmon coupling rates and radiative recombination rates ($k_{\text{SPC}}/k_{\text{rad}}$). The solid line is $dk/d\omega$ of the SPP at Ag/GaN interface. (Inset) PL decay profiles of uncoated and Ag coated sample at 440nm.

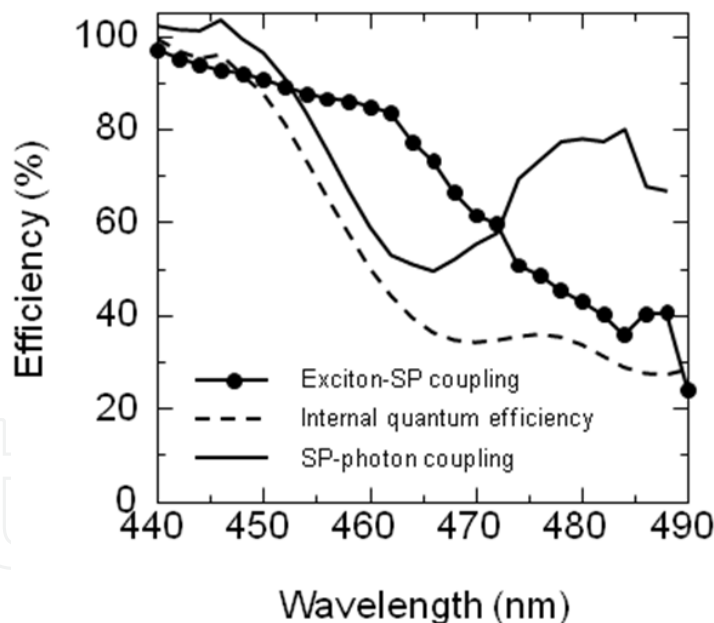


Fig. 6. Wavelength dependences of the exciton-SPP coupling efficiency (marks), the enhanced internal quantum efficiency (broken line), and the SSP-photon coupling efficiency (solid line).

nanometre sized metal grains were generated under the slow deposition rate $\sim 1 \text{ \AA/s}$. This structure is very easy to fabricate and control, so we used this structure for the sample used in Fig. 2. Fig. 7(c) shows the nano particulate array structure created by thermal annealing under nitrogen atmosphere after metal thin film vapour deposition. We can control both the particle size and inter-particle distance independently by initial metal film thickness,

annealing temperature, and annealing temperature. Fig. 7(d) shows the nano particle sheet structure created by the Langmuir-Blodgett (LB) technique at an air-water interface. Quite recently, we succeeded in fabrication of the beautiful periodic nanostructures by the bottom-up technique without E-beam lithography and found very interesting optical properties (Toma et al., 2011).

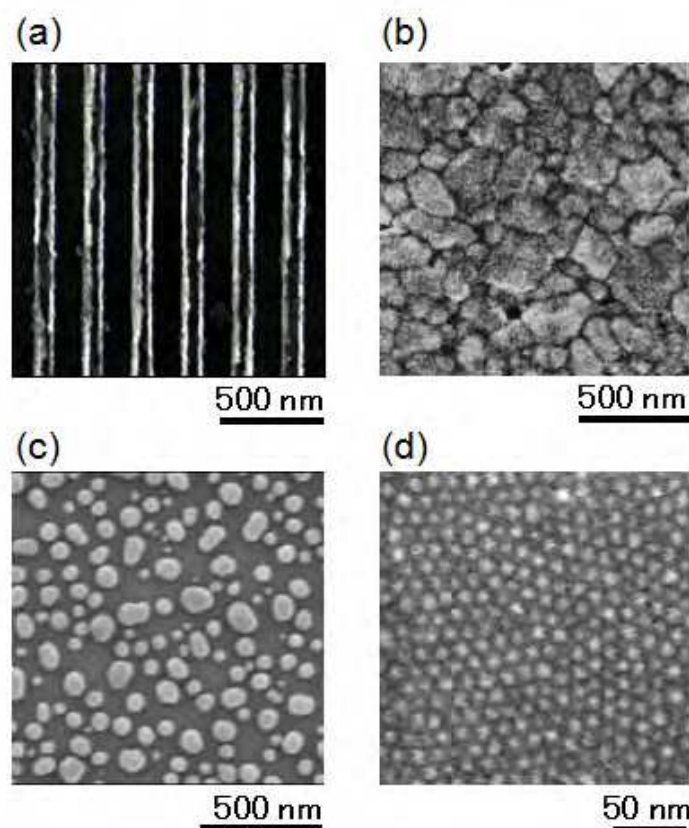


Fig. 7. Scanning electron microscope (SEM) image of various nanostructures of Ag. (a) Nano grating structure created by electron beam lithography and ion milling. (b) Nano grain structure created by control of metal vapour deposition conditions. (c) Nano particulate array structure created by thermal annealing under nitrogen atmosphere after metal thin film vapour deposition. (d) Nano particle sheet structure created by the Langmuir-Blodgett (LB) technique at an air-water interface.

By using the metal nanoparticle structures, we can use the localized surface plasmon (LSP) mode shown in Fig. 8(a). The LSP mode is tenable by the particle size and inter-particle distance. Fig. 8(b) shows the FDTD simulations of the LSP resonance spectra of Ag nanoparticle with various diameters. Inset of Fig. 8(b) show the spatial distributions of the electric field of the LSP mode generated around the Ag nano-particle with 40 nm diameter. The electric fields are strongly localized near the metal particle surface, and the penetration depth is as long as the radii of the particles regardless of the wavelength. The LSP is the non-propagated mode of the electromagnetic field and the localized area is much smaller than the wavelength. Therefore the LSP mode should be applicable to the photonics with nanometer scale, such technology is called plasmonic nanophotonics.

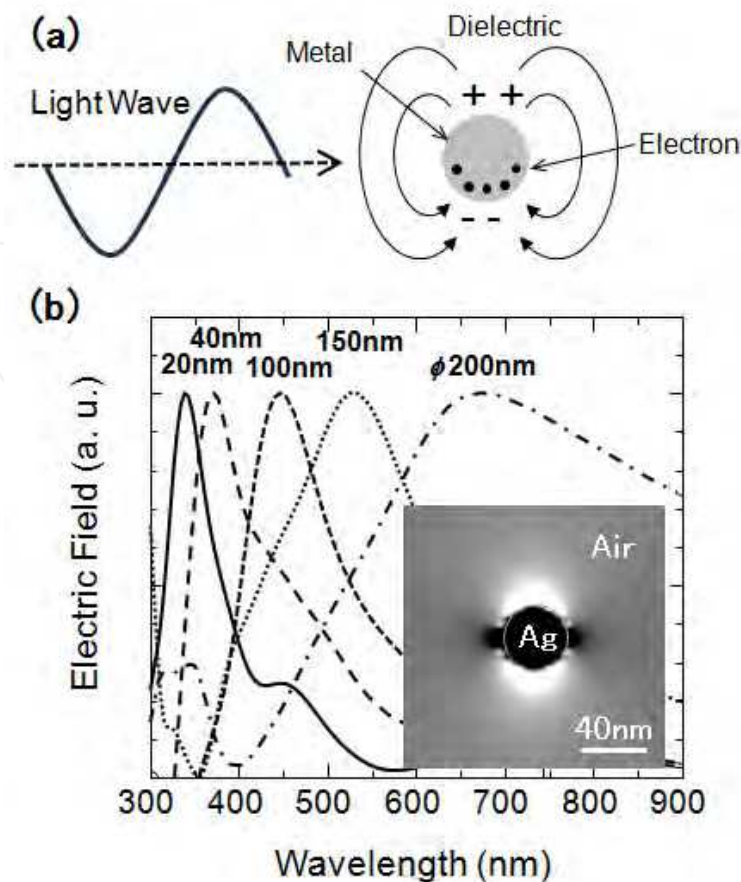


Fig. 8. (a) Schematic diagram of the localized surface plasmon (LSP) mode. (b) The FDTD simulations of resonance spectra of the LSP generated around the Ag nanoparticles with various diameters. (Inset) the spatial distributions of the electric field of the LSP mode.

Fig. 8(b) suggests that the LSP resonance is tunable within whole visible wavelength region by changing the Ag size, and 100~150 nm diameter should be suitable to couple to green light which has been very difficult to enhance. Fig. 9(a) shows the Scanning Probe Microscopic (SPM) image of Ag nanoparticle arrays fabricated on InGaN/GaN by a metal deposition and a thermal annealing. We could fabricate the Ag nano-particle array structure with about 100~150 nm diameter. The wavelength dependence of the PL enhancement ratios were shown in Fig. 9(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 LSP mode and the propagating SPP mode. 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. This result suggests that high efficiency light emitters can be achievable at various wavelength regions by further optimization of nanostructures.

6. Device applications using plasmonics

One of the most important targets of this study is device application of the SP coupling. The SP coupling technique increases IQEs by increasing spontaneous emission rates. This suggests that this should be applicable for electrical pumping because the IQEs do not

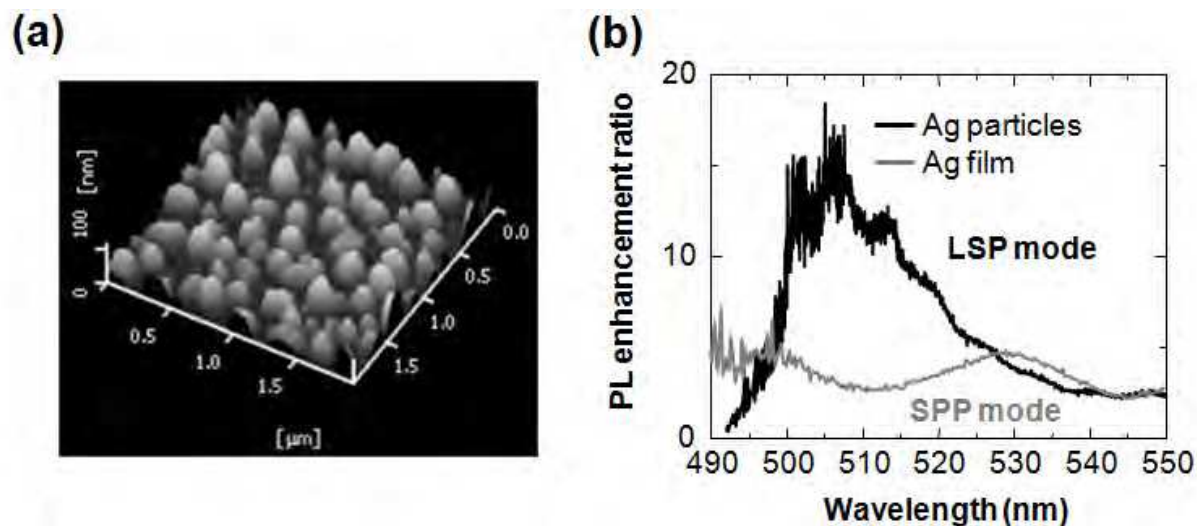


Fig. 9. (a) SPM image of the Ag nanoparticles array structure on InGaN/GaN. (b) PL enhancement ratio plotted against wavelength taken for InGaN/GaN QW with Ag particles and Ag thin film.

depend on the pumping method. So now we try to make super bright plasmonic LEDs by electrical pumping.

Fig. 10 shows the energy conversion scheme of the SP coupling and light emission. The SP-exciton and SP-photon coupling processes provide new emission pathways. The high efficiency LEDs should be achievable if the new emission path through the SP coupling is much faster than the original emission path [(2) + (11) > (3), (4) > (12) in Fig. 10]. By the similar way, plasmonics should be also able to improve high-efficiency solar cells, because the SP-exciton and SP-photon coupling processes are reversible. The sun-light can couple to the SP at the metal/dielectric interface and generate the excitons in the dielectric materials. This process should increase efficiencies of light absorption and photocurrent conversion if (8) > (7), (9) > (12) in Fig. 10.

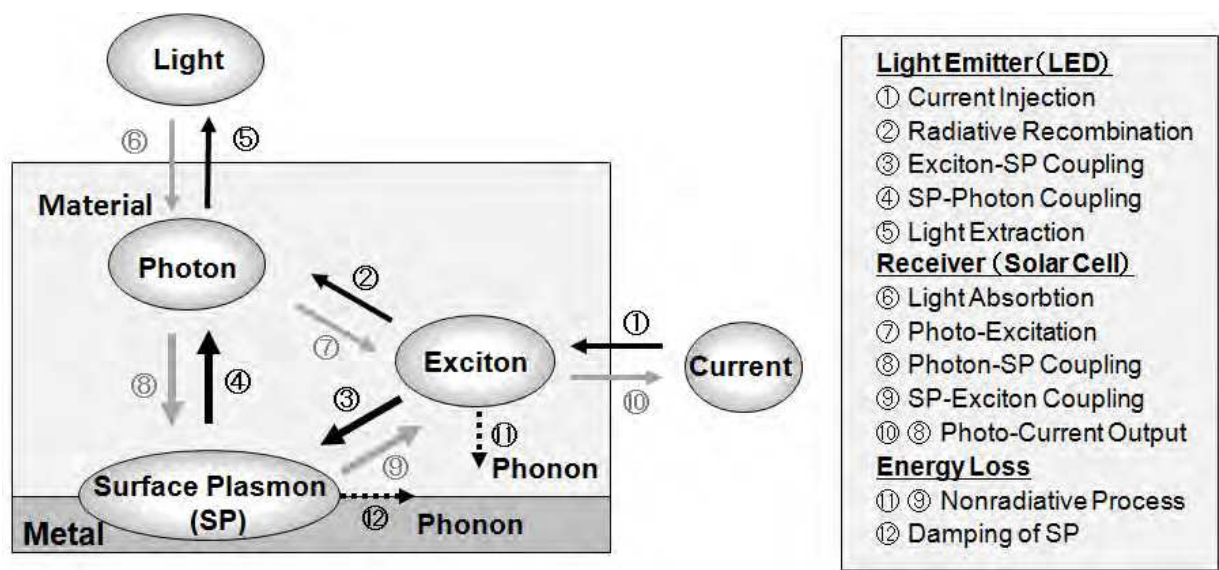


Fig. 10. Energy conversion schemes of the SP enhanced LEDs and solar cells.

Possible device structures of high efficient LEDs are shown in Fig. 11. Fig. 11(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 (Okamoto et al., 2004). This feature makes the device application of the SP coupling so difficult. We already fabricated the structure shown in Fig. 10(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. 11(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. 11(c) shows another promising device 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.

Recently a few groups reported about the SP enhanced LEDs based on our technique. Yeh et al. reported the SP coupling effect in an InGaN/GaN single-QW LED structure (Yeh et al., 2007). Their LED structure has a 10 nm p-type AlGaIn current blocking layer and a 70 nm p-type GaN layer between the metal surface and the InGaIn QW layer. The total distance is 80 nm, which is too far to obtain an effective SP coupling. By this reason, they obtained only 1.5 fold enhancement of the emission. Kwon, et al. also reported a plasmonic LED which has similar structure to Fig. 11(c) (Kwon et al., 2008). They put silver particles on the InGaIn QW layer first, and over grew a GaN layer above the Ag particles. However, a large amount of Ag particles were gone by high temperature of the crystal growth and only 3% particles remained. Therefore, they obtained only 1.3-fold enhancement of the emission. These tiny enhancement ratios should be not good enough for device application. Therefore, a high efficient LED structure based on plasmonics is not yet achieved.

7. Applications to high-efficiency solar cells

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 as shown in Fig. 10. 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 as shown in Fig. 10, and increase light absorption efficiencies.

Plasmonics has the 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 (Stuart et al., 1996; Pillai et al., 2006) and top-down nanofabricated structures

(Atwater & Polman, 2010). 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

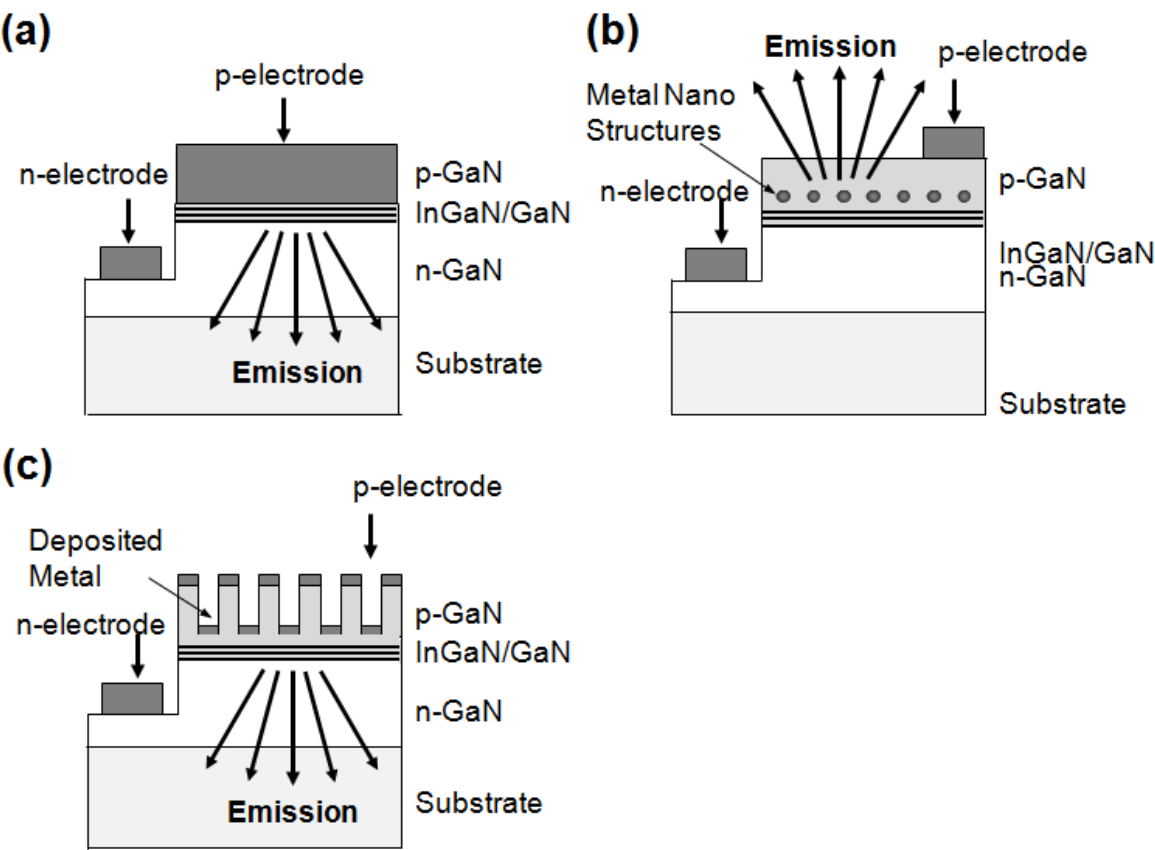


Fig. 11. Possible device structures of high efficient LEDs based on plasmonics with electrical pumping. (a) Metal electrode is located a few nm above the active layer. (b) Metal particles are embedded a few nm above the active layer, (c) p-GaN has 2-dimentional structures.

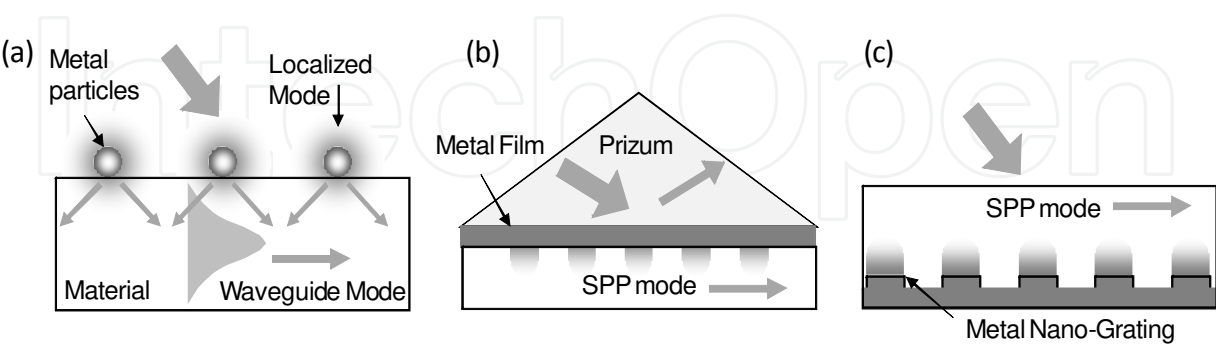


Fig. 12. The previously reported plasmonic solar cell structures based on (a) metal nano particles disposed on the materials, (b) attenuated- total-reflection (ATR) consignation with prism, and (c) nano periodic grating structure.

The previous reported plasmonic solar cells can be classified into three types shown in Fig. 12. Fig. 12(a) show the structure by using the metal nanoparticles, which were simply

dispersed on the top of the solar cells. This structure is very easy to fabricate and useful to any type of the solar cells. But in this case, energy transfer from the LSP mode to material is difficult because the electrical field of the LSP mode is strongly confined around the metal nanoparticle. In many case the LSP mode have to couple to the waveguide mode in the materials. This fact limits the plasmonic enhancement effect, and the device structures must be thicker than the wavelength. On the other hand, the using of propagation SPP modes must be more useful to enhance the efficiency and making ultra-thin structures of solar cells. But the coupling between the light and the SPP is not easy. The wave vectors of the light and the SPP need to be matched in order to be coupled each other. Usually all-reflection setting with prism [Fig. 12(b)] or periodic nano-structures [Fig. 12(c)] are necessary to satisfy the matching condition of the wave vectors. These settings limit the plasmonic enhancement effect into some angle and wavelength of light.

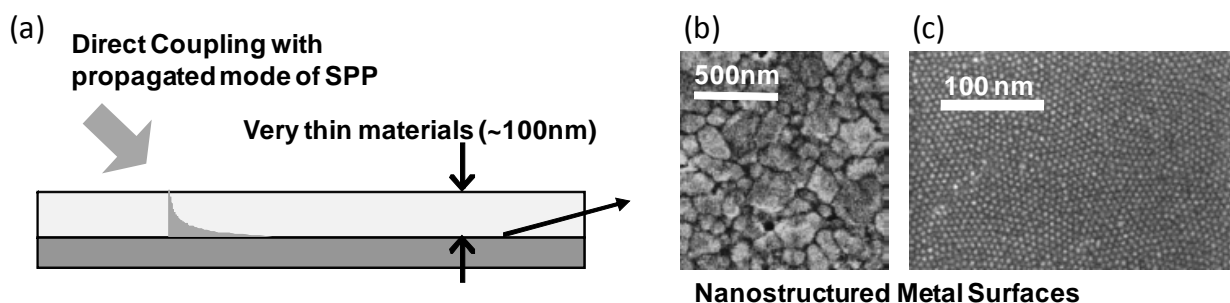


Fig. 13. (a) Our proposed advanced structure of plasmonic solar cells using propagating mode of the SPP. Sunlight can couple to the SPP mode directly by the metall nanostructures at the interface, such as (a) nano metal grain, and (b) metal nano particle sheet structures.

We believe that the structure shown in Fig.13 should be one of the promising device structures for plasmonic solar cells using propagating SPP mode. For the metal nanostructures, random Ag nano-grain structure shown in Fig. 13(a) [same as Fig. 7(b)] should be very useful. We can easily control the Ag nano-grain sizes of the random nanostructures by the metal-deposition conditions. Such structures were already used to extract light emission from the SPP for the light emission enhancements. In section 3, we described that the roughness allows SPPs of high momentum to scatter, lose momentum, and couple to radiative photon. By the opposite way, this structure should enable the direct coupling from sun-light with propagating SPP. Moreover, we can reduce the device thickness lower than 100nm because the SPP propagate within a few tens nm at the metal surface.

The other promising structure is 2D metal nanoparticle sheet structure shown in Fig. 13(c) [same as Fig. 7(d)]. This is high-dense packed structure of the Ag nanoparticles with 5 nm diameter fabricated by the LB technique at an air-water interface (Toma, et al. 2011). This structure enables more flexible tuning of the resonance spectra. Very strong and wide resonance spectra, which is almost overlapped to the solar spectrum, were found for the 2D sheet structure of Ag particles by the FDTD calculations. Moreover it was found that ~99% of the incident light can be confined into the metal nanosheet which is only ~10nm thickness by optical measurements and calculations. This structure should be promising to develop new type of plasmonic solar cells.

8. 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 found that both the exciton-SP and the SP-photon coupling efficiencies were reached almost 100% at the best matched wavelength. This suggests that if we can control the SP frequency and obtain the best SP coupling condition, we can develop super bright LEDs which have perfect efficiencies at any wavelength. It would bring full color devices and natural white LEDs. This technique can be applied not only to InGaN-based materials but also to various materials that suffer from low efficiencies. We believe that the high-efficient plasmonic LEDs should be obtainable by using silicon based materials or other earth-abundant materials. Such LEDs could be very cheap to make and easy to process, and would become widely used light source instead of fluorescent tubes in the near future. Similar plasmonic design should also be applicable to several other optical devices. Especially, the SP coupling technique has been expected to progress solar cell technology. The SP enhanced solar cell have been studied by several groups however such devices have not so far been used practically. We believe that further optimization of nanostructures and controlling the SP coupling would provide high efficient and ultra-thin plasmonics solar cells.

9. Acknowledgements

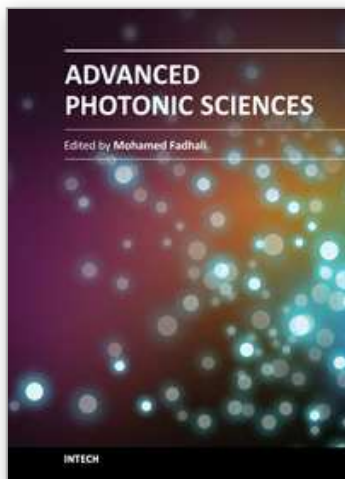
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10. References

- Atwater, H. A. (2007), The promise of plasmonics, *Scientific American*, pp. 56-63.
- Atwater, H. A. & Polman, A. (2010), Plasmonics for improved photovoltaic devices, *Nat. Mater.*, 9, pp. 205-213.
- Barnes, W. L.; Dereux, A. & Ebbesen, T. W. (2001), Surface plasmon subwavelength optics, *Nature*, vol. 424, pp. 824-830.
- Gontijo, I.; Boroditsky, M.; Yablonvitch, E.; Keller, S.; Mishra, U. K. & DenBaars, S. P. (1999), Enhancement of spontaneous recombination rate in a quantum well by resonant surface plasmon coupling, *Phys. Rev. B*, vol. 60, no. 16, pp. 11564 -11567.
- Kwon, M.-K.; Kim, J.-Y.; Kim, B.-H.; Park, I.-K.; Cho, C.-Y.; Byeon, C. C. & Park, S.-J. (2008), Surface-Plasmon-Enhanced Light-Emitting Diodes" *Adv. Mate.* vol. 20, no. 7, pp. 1253-1257.
- Neogi, A.; Lee, C.-W.; Everitt, H. O.; Kuroda, T.; Tackeuchi, A. & Yablonvitch, E. (2002) , Enhancement of spontaneous recombination rate in a quantum well by resonant surface plasmon coupling, *Phys. Rev. B*, vol. 66, 153305.

- Okamoto, K.; Niki, I.; Shvartser, A.; Narukawa, Y.; Mukai, T. & Scherer, A. (2004), Surface-plasmon-enhanced light emitters based on InGaN quantum wells, *Nature Mater.*, vol. 3, pp. 601-605.
- Okamoto, K.; Niki, I.; A. Scherer, Narukawa, Y.; Mukai, T. & Kawakami, Y. (2005), Surface plasmon enhanced spontaneous emission rate of InGaN/GaN quantum wells probed by time-resolved photoluminescence spectroscopy, *Appl. Phys. Lett.* vol. 87, 071102.
- Okamoto, K.; Scherer, A. & Kawakami, Y. (2008), Surface plasmon enhanced light emission from semiconductor materials, *Phys. Stat. Sol. C*, vol. 5, no. 9. pp. 2822-2824.
- Okamoto, K. & Kawakami, Y. (2009), High-Efficiency InGaN/GaN Light Emitters Based on Nanophotonics and Plasmonics, *IEEE J. Select. Top. Quantum Electron.* 15, pp. 1190-1209.
- Pillai, S.; Catchpole, K. R.; Trupke, T. & Green, M. A. (2006), Surface plasmon enhanced silicon solar cells, *J. Appl. Phys.*, 101, 09310.
- Raether, H. (1988), *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer-Verlag.
- Stuart, H. R. & Hall, D. G. (1996), Absorption Enhancement in Silicon-on-Insulator Waveguides using Metal Island Films, *Appl. Phys. Lett.*, 69, pp. 2327-2329.
- Yeh, D.-M.; Huang, C.-F.; Chen, C.-Y.; Lu, Y.-C. & Yang, C. C. (2007), Surface plasmon coupling effect in an InGaN/GaN single-quantum-well light-emitting diode, *Appl. Phys. Lett.* vol. 91, 171103.

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