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Surface plasmon enhanced light emission from semiconductor materials

Koichi Okamoto[*, 1, 2], **Axel Scherer**[3], **and Yoichi Kawakami**[2]

[1] PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan
[2] Department of Electronic Science and Engineering, Kyoto University, Katsura Campus, Nishikyo-ku, Kyoto 615-8510, Japan
[3] Department of Physics, California Institute of Technology, 1200 E. California Blvd., Pasadena, California, 91125, USA

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[*] Corresponding author: e-mail k.okamoto@hy4.ecs.kyoto-u.ac.jp, Phone: +81 75 383 2314, Fax: +81 75 383 2312

Surface plasmon (SP) coupling technique was used to enhance light emissions from semiconductor nanocrystals with evaporated metal layers. We found that the SP coupling can increase the internal quantum efficiencies (IQE) of emission from CdSe-based nanocrystals regardless of the initial efficiencies. This suggests that this technique should be much effective for various materials that suffer from low quantum efficiencies. We also obtained 70-fold enhancement of emission from silicon nanocrystals in silicon dioxide. Obtained IQE value is 38%, which is as large as that of a compound semiconductor with direct transition. The SP coupling technique would bring a great improvement to silicon photonics.

1 Introduction Surface plasmons (SPs) offer the unique ability to localize and enhance electromagnetic fields and have been applied to various optical devices [1]. One futuristic application is the development of super bright light-emitting devices. Semiconductor light-emitting diodes (LEDs) are expected to eventually replace traditional fluorescent tubes as illumination sources. However, their light-emission 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 had been proposed previously but it had been very difficult to enhance visible light emissions [2-4].

Recently, for the first time, we directly obtained significant enhancement of visible light emission from InGaN/GaN quantum wells [5]. 14-fold and 8-fold enhancements of photoluminescence (PL) peak intensities were observed with silver and aluminium coating, respectively. We also observed a 32-fold increase in the spontaneous emission rate of InGaN/GaN at 440 nm probed by time-resolved PL measurements [6]. Likewise, both light emission intensities and rates were enhanced for organic materials [7], polymer light emitters [8], and CdSe-based nanocrystals [9]. These enhancements should be attributed to the SP coupling. Electron-hole pairs generated in the semiconductor materials couple to electron vibrations at the metal/semiconductor interface when the energies of electron-hole pairs and of the metal SP are similar. Then, electron-hole recombination produces SPs instead of photons or phonons, and this new path increases the spontaneous emission rate and the IQE.

This technique would lead the new super bright solid-state light sources. Here we discuss about further possibilities of this method using CdSe and silicon nanocrystals.

2 Experimental CdSe-based quantum dot (QD) nanocrystals (5 nm diameter) were purchased from Evident Technologies. The toluene solutions of the QDs were dispersed on quartz substrates. After the solutions evaporated, a monolayer of the QD nanocrystals remained on the substrates. Silicon nanocrystal QDs were prepared by reactive thermal evaporation of SiO powders in an oxygen atmosphere under vacuum. After rapid thermal annealing, size controlled Si nanocrystals (~3 nm diameter) were formed in SiO_2 by phase separation. This technique was developed by Zacharias et al. and the details had already been published [10]. Metal thin layers (50 nm) were prepared by thermal evaporation.

To perform PL measurements, an InGaN diode laser (405 nm) was used to excite the samples. The PL signal was collected and focused into an optical fiber and subsequently detected with a spectrometer exit with a liquid-nitrogen-cooled CCD camera. Temperature dependence of the PL process was studied within a cryostat capable of cooling the samples from room temperature to ~10 K.

3 Results and discussion First, we measured PL spectra from CdSe-based nanocrystals. We used two types of nanocrystals; one is naked CdSe nanocrystals and other is CdSe core with ZnS shells (CdSe/ZnS). The internal quantum efficiency (IQE) of naked CdSe (~2%) was well increased for CdSe/ZnS structure (~40%) because generated carriers can be well confined into core/shell structures.

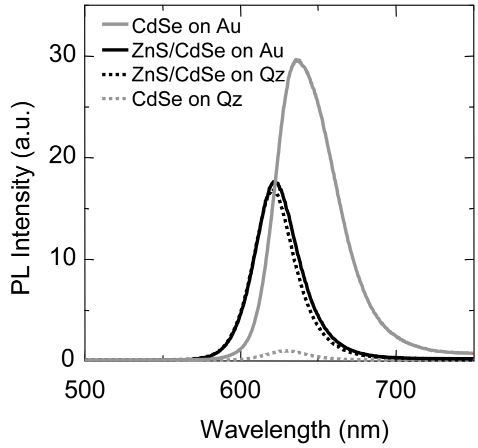

Figure 1 PL spectra for CdSe and CdSe/ZnS nanocrystals on gold (Au) and quartz (Qz).

Figure 1 shows PL spectra of naked CdSe and CdSe/ZnS on gold layers and quartz substrate. A dramatic enhancement in the PL intensity from the QDs on gold layer was very clearly observed for naked CdSe. When the PL peak of the QDs on quartz was normalized to 1, a 30-fold increase of PL intensity was observed. This remarkable PL enhancement should be attributed to strong interaction with SP. The electron-hole pairs in the QDs couple to SPs and be extracted as light at the rough gold surface.

On the other hand, the enhancement of PL intensity of CdSe/ZnS was not remarkable compared with the result of naked CdSe without shells. This fact indicates the merit and demerit of the SP coupling technique for enhancing light emission [9]. By previous studies, we found that the SP coupling increases IQE values by enhancement of spontaneous emission rates [5, 6]. The SP coupling condition is decided by the matching of energies between the SP frequency and emission wavelength. The light extraction is decided by the roughness or nano-structures of the metal/semiconductor interface. Thus, the enhancement condition does not depend on the intrinsic IQE values of materials. This feature suggests that the SP-coupling technique is very effective for increasing the emission efficiency of materials with low intrinsic efficiency like the naked CdSe, but not so effective for high-efficiency materials like the CdSe/ZnS, which were used in this study.

Even though it is not so effective for materials with high emission efficiencies, the SP enhancement technique has further several important advantages. By using this technique, improvement of the efficiency of electrically pumped LED devices should be achievable because IQE is a fundamental property and does not depend on the pumping method. Enhanced spontaneous emission should be useful for high-speed light-emitting devices for the development of communication technology and optical computing. The most important advantage of this technique is that it can be applied to various materials that suffer from low emission efficiencies, which include the indirect semiconductor. Usually the emission efficiencies of such indirect semiconductors are quite low, but it is possible to enhance these efficiencies to values as large as those available from direct compound semiconductors by the SP enhancement. Accordingly, we tried to enhance emissions from silicon-based semiconductors.

Silicon photonics has attracted a great deal of attention in this decade and are expected as light-emitting materials alternative to compound semiconductors. Several nanostructures, such as porous silicon [11], nanocrystals [12], quantum wells [13], and nanowires [14] were fabricated to obtain bright emissions from Si. Here we tried to enhance emission from Si nanocrystals in SiO_2 media with gold thin layers. Figure 2 shows PL spectra for Si nanocrystals. A 70-fold large PL enhancement was observed with gold coating at the wavelength region longer than 650 nm, whereas only 2-fold enhancement was obtained from aluminum-coated sample. This should be reasonable because the SP coupling at Si/Au must be effective at longer wavelength region than 600 nm by dispersion diagram of SP calculated with dielectric functions. On the other hand, SP at Si/Al does not exist around this wavelength region. It exists at much shorter wavelength region.

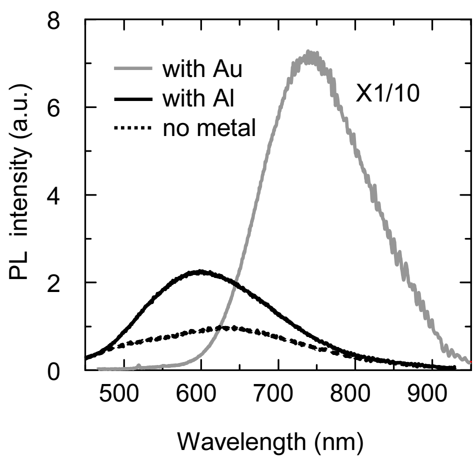

Figure 2 PL spectra for Si nanocrystals in SiO_2 with gold, aluminium, and no metal layer.

After our first report of the SP coupling technique, it was already applied to Si nanocrystals and similar enhancements have been reported at room temperature [15, 16]. In this paper, we measured temperature dependence of PL intensities to estimate the enhanced IQE values.

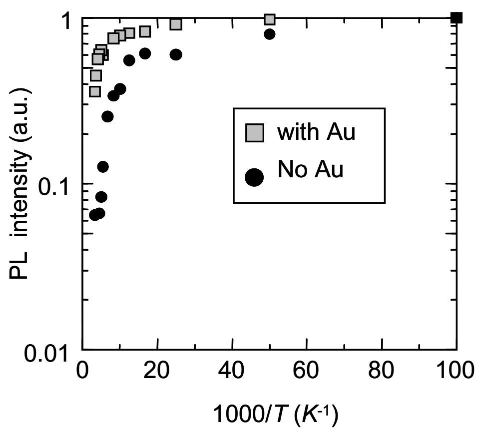

Figure 3 Temperature dependence of PL intensities taken for Si nanocrystals in SiO_2 with/without gold layer.

Figure 3 shows Arrhenius plot of the integrated PL intensities of Si/SiO_2 with/without Au layer. For both samples, the PL intensities reached to a constant value in a quite low temperature region and decreases gradually with increasing temperature. This behavior is similar to the previous reports. In such a case, it can be assumed that IQE is nearly equal to unity at the quite low temperature. IQE value from uncoated Si/SiO_2 was estimated as 6% at room temperature by this assumption. The IQE value increased to 36% after Au coating, explainable by spontaneous emission rate enhancements through SP coupling. This value is as large as that of a compound semiconductor with direct transition. However, the emission intensity of Si/SiO_2 was still much weaker than that of InGaN/GaN or CdSe/ZnS with same IQE value. It was reported that the emission lifetimes of Si/SiO_2 were usually very long (~ms) even though some of Si nanocrystals have very high IQE values (>50%) [17-19]. The SP coupling can enhance the emission rate, but the enhanced emissions still have long lifetimes with millisecond scale [15, 16]. These lifetimes are 1000 times longer than those of InGaN/GaN or CdSe/ZnS which has similar IQE values. The slower emission rates should be reason of weak emission intensities of Si/SiO_2. The excitation densities of nanocrystals become saturated easily and it brings poor carrier injection efficiencies in spite of their high IQE values.

By this reason, so far, silicon-based materials are still not useful for light-emitting materials. We believe that both emission rates and excitation densities of Si nanocrystal can be increased by optimizing the SP coupling condition. Undoubtedly, the SP coupling technique would lead the new super bright semiconductor light sources, which could be very cheap to make, easy to process, and would become commonly used light source instead of fluorescent tubes in the near future.

4 Conclusion The SP coupling is very powerful method technique to enhance light emission efficiencies of semiconductor materials. This technique is very simple and easy, and moreover, can be applicable to various materials that suffer from low quantum efficiencies. So far as we think, the SP coupling may be the only technique with a big possibility of developing the super bright light-emitting devices by use of the silicon-based semiconductors.

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