Surface plasmon polariton mediated photoluminescence from excitons in silicon nanocrystals

Eiji Takeda, Toshihiro Nakamura, Minoru Fujii,[a] Satoru Miura, and Shinji Hayashi
Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

(Received 13 April 2006; accepted 11 July 2006; published online 6 September 2006)

Surface plasmon polaritons (SPPs) of a metal film can efficiently be excited when a light emitter is placed nearby. The excited SPPs are converted to photons by compensating for the momentum mismatch. The authors study SPP-mediated emission from excitons in Si nanocrystals (Si-nc's) by placing an organic grating on a thin Au film placed near Si-nc's. The dispersion relation is obtained from angle-resolved photoluminescence measurements, and all the observed modes are well explained by model calculation. The results indicate that excitons in Si-nc's can efficiently excite SPPs in thin metal films and directed photoluminescence can be realized. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2345261]

Silicon nanocrystals (Si-nc's) exhibit strong visible and near infrared luminescence at room temperature due to the recombination of quantum confined excitons.[1–4] The zero-dimensional quantum confinement effect increases the overlap of electron and hole wave functions in the momentum space resulting in significant enhancement of the radiative recombination rate of excitons. However, even for very small Si-nc's as small as a few nanometers in diameter, the exciton radiative lifetime at room temperature is of the order of 10 μs, which is still longer than that of direct band gap semiconductors. Furthermore, the luminescence quantum efficiency is usually limited to several percent.[5–7] Because of these limitations, Si-nc based light emitting devices are still far from practical applications.

The luminescence intensity of an emitter is known to be strongly enhanced by the proper coupling of the emitter field with surface plasmon polaritons (SPPs) supported by thin metal films.[8–10] SPP is a coupled oscillation of free electrons and electromagnetic field induced by the fluctuation of the electrons. The electromagnetic field decays exponentially away from the surface. When a light emitter is placed very close to a metal surface, SPPs can be excited via efficient nonradiative energy transfer from the emitter. If excited SPPs can be converted to photons with high efficiency, the effective emission rate of the emitter is expected to be enhanced.[11] One of the standard methods to allow SPPs to couple with photons is to introduce a corrugated surface, which allows the compensation of the momentum mismatch between SPPs and photons.[12] The coupling of SPPs with photons by a corrugated surface results in the well-defined directional emission with a characteristic polarization as well as the enhancement of emission rate.

The purpose of this work is to demonstrate the enhancement of photoluminescence (PL) from Si-nc's by the coupling with SPPs. In this work, we employ a one-dimensional grating to couple excited SPPs to photons. The advantage of using a grating is that the modes can be identified unambiguously by analyzing the dispersion relation. We use a simple method to realize Bragg scattering of SPPs, i.e., forming a corrugated organic film on a flat Au film deposited on an active layer containing Si-nc's. We will demonstrate that the corrugated organic layer can scatter SPPs to light efficiently and directed PL is obtained.

We employed a cosputtering method to prepare Si-nc's.[13–15] Si and SiO_2 were simultaneously sputter deposited on a fused-quartz substrate and the deposited film (200 nm in thickness) was annealed in a nitrogen gas atmosphere for 30 min at 1200 °C. By the annealing Si-nc's were grown in thin SiO_2 films (Si-nc:SiO_2). A Au film was then deposited by vacuum evaporation. The thicknesses were 50 and 100 nm for samples A and B, respectively. The light transmittances of Au films with 50 and 100 nm thicknesses are about 3% and 0.3% at 850 nm, respectively. The corrugated surface was obtained by exposing a photoresist (TDMR-AR80 HP, Tokyo Ohka Kogyo) film spin coated on a Au film to an interference pattern produced with a 325 nm line of a He–Cd laser. An atomic force microscope (AFM) image of the sample surface and the schematic illustration of the sample structure are shown in the insets of Figs.1(b) and 1(c), respectively.

In order to measure the angular dependence of PL spectra from the corrugated surface, samples were mounted on a rotating stage and illuminated through the transparent fused-quartz substrate. The excitation source was a 488 nm line of an Ar ion laser. The excitation light was incident normal to the surface, while the collection angle θ was changed from 0° (normal to the surface) to 50°. PL was collected through an aperture (about 1 mm in diameter) from the corrugated side, limiting the angular acceptance to about 1°. PL spectra were measured by using a single grating monochromator with a liquid nitrogen cooled Si charge coupled device. The spectral response of the detection system was calibrated with the aid of a reference spectrum of a standard tungsten lamp.

Figure 1(a) shows the PL spectra of samples A and B collected at $\theta=20°$. The spectra of the samples without organic gratings measured with the same setup are also shown. By the presence of the grating, the shape of PL spectra is strongly modified and several peaks are observed. Polarization-resolved measurements revealed that the strong peaks at 900 and 960 nm in sample A and those at 740, 830, and 970 nm in sample B are transverse magnetic (TM) polarized. At the wavelengths of the highest PL intensity, the

[a]Electronic mail: fujii@eedept.kobe-u.ac.jp

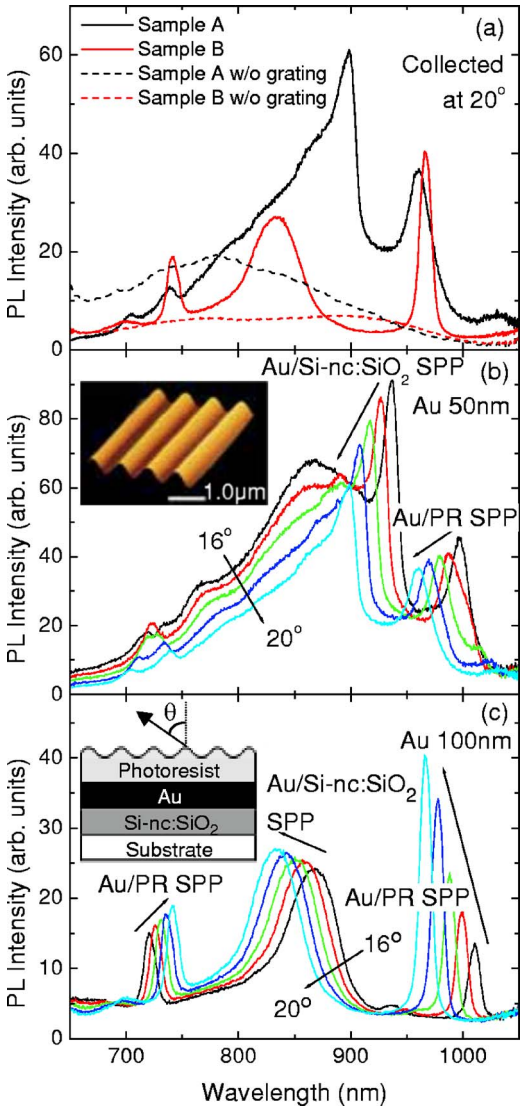

FIG. 1. (Color online) (a) PL spectra of samples A and B collected at a polar emission angle of 20° (solid line) compared with those of the uncorrugated samples (dashed line). Angular dependence of PL spectra of sample A (b) and sample B (c). Au/Si-nc:SiO_2 and Au/PR SPP represent SPP modes associated with the interface between Au and optically active layer and between Au and photoresist layer, respectively. Inset: (b) AFM image of the sample surface; (c) schematic illustration of a sample structure.

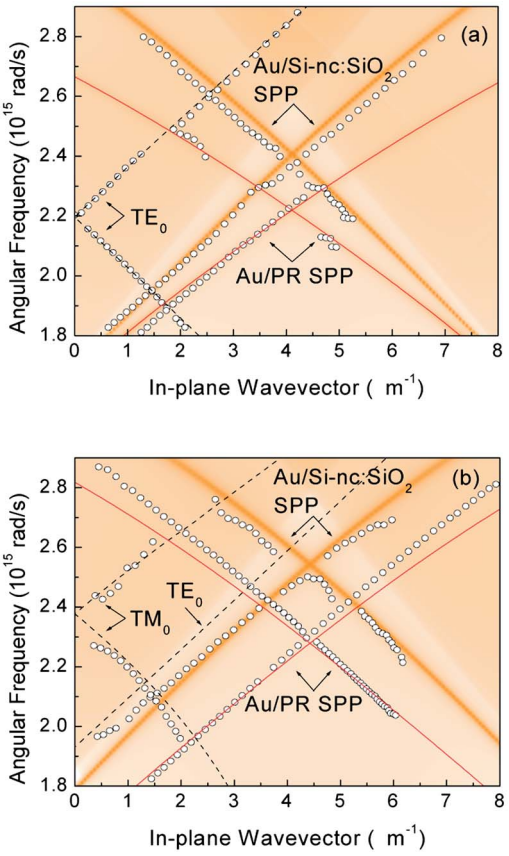

FIG. 2. (Color online) Dispersion relations for sample A (a) and sample B (b). Circles correspond to experimentally obtained data, while color map and curves to those obtained by calculation. The region deeper in color represents larger dissipated power. The modes of which the power dissipation is too small to show by color gradation are represented by curves. Solid curves represent Au/PR SPP modes and dashed ones the lowest order waveguided modes in photoresist layer.

intensities are enhanced by factors of 6.5 for sample A and 10 for sample B. To compare the integrated PL intensities emitted through a thin Au film between the samples with and without a grating, we measured the angle-integrated PL spectra without the aperture. For both samples, the integrated PL intensities are enhanced in the full range of emission wavelength by the presence of a grating. As will be discussed later, the enhancement is due to a better extraction efficiency of the emission for the samples with the corrugated surface. Figures 1(b) and 1(c) show angular dependence of PL spectra for samples A and B, respectively. We can see the shift of the peaks with increasing the collection angle. The shift is due to Bragg scattering of SPPs or the guided modes. From the angular dependence of PL peak wavelengths, the dispersion relations are obtained. The experimentally obtained dispersion relations are shown in Figs. 2(a) and 2(b) for samples A and B, respectively, by open circles.

In order to assign the modes, we calculate the dispersion relations for the five-layer system, i.e., air/photoresist/Au/Si-nc:SiO_2/SiO_2.[16–19] In the calculation, an emitter is regarded as an oscillating electric dipole and the power dissipated from an isotropic dipole positioned at the center of an optically active Si-nc:SiO_2 layer is calculated as a function of in-plane wave vector. For the calculation, the refractive indices of Au, Si, and SiO_2 are taken from literatures[20–22] and that of Si-nc:SiO_2 layer is estimated from the Bruggeman effective medium theory.[23] The wavelength dispersions of the refractive indices of Au, Si, and SiO_2 are taken into account, while that of the photoresist layer is set to 1.68. By the presence of Bragg grating the wave vector of SPPs or the guided modes is augmented or reduced, as $k_{\|}(\omega) = k_0(\omega)\sin\theta = k_m(\omega) \pm nG$, where $k_{\|}(\omega)$ and $k_m(\omega)$ denote the in-plane wave vector of the emitted light and the guided mode, respectively, $k_0(\omega)$ the absolute value of the wave vector of the emitted light, ω the angular frequency, $G = 2\pi/\Lambda$ the grating vector with the grating period Λ, and n an integer meaning the order of the scattering process. In order to reproduce experimentally obtained dispersion relations, we adjusted the values of the grating period and the thickness of the photoresist layer. The best result is obtained when the grating periods and photoresist layer thicknesses are 765 and 189 nm for sample A, and 710 and 360 nm for sample B, respectively. These values are close to the measured ones.

The calculated dispersion relations are shown in Figs. 2(a) and 2(b). The region deeper in color represents larger dissipated power. The modes for which the power dissipation

is too small to show by color gradation are represented by solid curves. In both samples, the strong dissipation shown by color gradients corresponds to the SPP modes propagating at the interface between Au and active layer (Au/Si-nc:SiO_2 SPP), while weak dissipation shown by solid curves to the SPP modes propagating at the interface between Au and photoresist (PR) layer (Au/PR SPP). The calculated dispersion relations of the SPP modes agree well with those of the experimentally obtained ones. We can thus assign the origin of the peaks in Fig. 1. The assignments of the modes are written in Figs. 1(b) and 1(c). The overall agreement implies that the strong PL peaks in Figs. 1(b) and 1(c) arise from the coupling of excitons with SPPs. The slight disagreement between experiments and calculation in Fig. 2 is probably due to the wavelength dispersion of the refractive index of the photoresist layer, which is not taken into account in the calculation.

In Figs. 2(a) and 2(b), the power dissipation of Au/Si-nc:SiO_2 SPP is always much larger than that of Au/PR SPP. This is consistent with Fig. 1(b) where PL intensity of Au/Si-nc:SiO_2 SPP is always larger than that of Au/PR SPP. However, in Fig. 1(c), at particular angles the PL intensity of Au/PR SPP is larger than that of the Au/Si-nc:SiO_2 SPP. This means that larger fraction of power coupled to SPP modes does not always result in larger PL enhancement. The intensity depends also on the penetration depth of evanescent waves associated with SPP modes and the distance to corrugated surface. In sample A, the Au and photoresist layers are thin enough for the Au/Si-nc:SiO_2 SPP mode to efficiently couple to the corrugated surface. On the other hand, in sample B, despite strong coupling with excitons in Si-nc's, the Au/Si-nc:SiO_2 SPP mode cannot efficiently couple to the corrugated surface, resulting in smaller intensity than that of the Au/PR SPP mode.

As described above, the PL enhancement factor is different between samples A and B. This arises mainly from different PL backgrounds between them. The Au layer of sample A is thinner than that of sample B, resulting in higher transmission of the emission light. The transmitted light appears as a background signal, and the larger background results in seemingly smaller PL enhancement.

In addition to the SPP modes, waveguided modes exist in the photoresist layer. The calculated dispersion of the waveguided modes are shown by broken curves in Figs. 2(a) and 2(b). The thickness of the photoresist layer for sample A allows only the zeroth order transverse electric (TE_0) mode to exist. On the other hand, for sample B both the TE_0 and the zeroth order TM (TM_0) modes can exist in the photoresist layer. In Figs. 2(a) and 2(b), experimentally obtained data agree well with the calculated dispersion except for the TE_0 mode in Fig. 2(b) which is not observed experimentally. This is simply due to the existence of the very strong PL peak of the Au/Si-nc:SiO_2 SPP mode nearby.

In conclusion, we observed directional PL from Si-nc's on which a thin Au layer and an organic grating structure are formed. From the angular dependence of the PL spectra, the dispersion relations were obtained. The experimentally obtained dispersion relations agreed well with the calculated ones. The overall agreement allowed us to unambiguously conclude that the directional PL is mediated by SPPs excited by the energy transfer from excitons confined in Si-nc's. The present results suggest that the coupling with SPPs is one of the possible approaches to enhance PL properties of Si-nc's. However, within the present work, i.e., coupling with a one-dimensional grating, the enhancement was not very large. This may be further improved by introducing a two-dimensional grating[24] or matching the effective refractive indices of the media at both sides of metal layer interfaces.[9]

This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] S. Takeoka, M. Fujii, and S. Hayashi, Phys. Rev. B **62**, 16820 (2000).
[3] C. Delerue, M. Lannoo, G. Allan, and E. Martin, Thin Solid Films **255**, 27 (1995).
[4] D. Kovalev, H. Heckler, G. Polisski, and F. Koch, Phys. Status Solidi B **215**, 871 (1999).
[5] W. L. Wilson, P. F. Szajowski, and L. E. Brus, Science **262**, 1242 (1994).
[6] J. C. Vial, A. Bsiesy, F. Gaspard, R. Hérino, M. Ligeon, F. Muller, R. Romestain, and R. M. Macfarlane, Phys. Rev. B **45**, 14171 (1992).
[7] V. A. Skryshevsky, A. Laugier, V. I. Strikha, and V. A. Vikulov, Mater. Sci. Eng., B **40**, 54 (1996).
[8] D. K. Gifford and D. G. Hall, Appl. Phys. Lett. **80**, 3679 (2002).
[9] S. Wedge and W. L. Barnes, Opt. Express **12**, 3673 (2004).
[10] J. Zhang, Y.-H. Ye, X. Wang, P. Rochon, and M. Xiao, Phys. Rev. B **72**, 201306 (2005).
[11] J. Kalkman, H. Gersen, L. Kuipers, and A. Polman, Phys. Rev. B **73**, 075317 (2006).
[12] H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer Tracts in Modern Physics, Vol. 111 (Springer, Berlin, 1988), p. 91.
[13] Y. Kanzawa, T. Kageyama, S. Takeoka, M. Fujii, S. Hayashi, and K. Yamamoto, Solid State Commun. **102**, 553 (1997).
[14] M. Fujii, A. Mimura, S. Hayashi, and K. Yamamoto, Appl. Phys. Lett. **75**, 184 (1999).
[15] M. Fujii, S. Hayashi, and K. Yamamoto, in *Recent Research Development in Applied Physics*, edited by S. G. Pandalai (Transworld, Trivandrum, 1998), Vol. 1, p. 193.
[16] R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. **37**, 1 (1978).
[17] G. W. Ford and W. H. Weber, Phys. Rep. **113**, 195 (1985).
[18] W. L. Barnes, J. Mod. Opt. **45**, 661 (1998).
[19] P. A. Hobson, J. A. E. Wasey, I. Sage, and W. L. Barnes, IEEE J. Sel. Top. Quantum Electron. **8**, 378 (2002).
[20] D. W. Lynch and W. R. Hunter, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, Orlando, 1985), Vol. 1, p. 286.
[21] D. F. Edwards in *Handbook of Optcal Constants of Solids*, edited by E. D. Palik (Academic, Orlando, FL, 1985), Vol. 1, p. 547.
[22] H. R. Philipp in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, Orlando, FL, 1985), Vol. 1, p. 749.
[23] P. A. Snow, E. K. Squire, P. St. J. Russell, and L. T. Canham, J. Appl. Phys. **86**, 1781 (1999).
[24] P. T. Worthing and W. L. Barnes, Appl. Phys. Lett. **79**, 3035 (2001).