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Plasmon Emission from Photoexcited Gold Nanoparticles Embedded in Germano-Silicate Fiber

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Abstract

Light emission at the surface plasmon resonance frequencies from gold nanoparticles embedded in the germano-silicate glass fiber upon Argon laser pumping was observed. The quantum efficiencies at 833nm and 1536nm were estimated to be 5.75×10^{-8} and 2.01×10^{-9} , respectively.

Keywords: Photoluminescence; Surface plasmon resonance; Gold nanoparticles

1. Introduction

Optically excited metal surface show no or very little luminescence. For instance, smooth gold films have photoluminescence (PL) efficiency of $\sim 10^{-10}$ following excitation of electron transitions from the 5d and 6sp bands [1]. In other words, only one photon is emitted each 10^{10} electron-hole pairs excited. One likely reason for this low PL efficiency is known that nonradiative energy relaxation processes of photoexcited carries in metals, such as Coulomb carrier scattering, are much faster than radiative electron-hole recombination, thus quenching the photoluminescence [2].

A unique exception from the rule of low PL yielding in metals is noble metal nanoparticles (NPs). For instance, PL efficiencies on the order of 10^{-4} have been observed in gold nanorods [3]. This is a giant enhancement with respect to $\sim 10^{-10}$ efficiency of smooth gold films. In present study, while remaining relative weak, broadband visible to narrowband infrared PL from gold NPs embedded in the germano-silicate fiber was detected and proven to be measurable at room temperature with the normal optical measurement systems. The optical absorption and PL properties including the quantum efficiencies (QEs) were investigated.

2. Experiments

The fiber incorporated with gold NPs was fabricated in house using the MCVD and solution doping processes, which is detailedly described in Ref. 4 reported by our group.

Due to the boiling temperature as high as 2856° C [5] Au atoms and their clusters can survive from the MCVD process with the temperature up to 2350° C. To confirm the formation and existence of the gold NPs in the core of fiber, the cut-back method to measure the absorption spectrum of the optical fiber becomes almost the only but the most effective indirect way to determine the composition of the dopants existing in the core of the made fiber.



Fig. 1. Schematic diagram of the experiment setup.

To obtain the PL, the fiber was pumped with a 488nm Argon-ion laser at room temperature. As shown in Fig. 1, the 488nm laser beam from Argon-ion laser was reflected by two mirrors and then coupled into one arm of a 3dB coupler by a collimator. At the same time, one power controller was used to measure the feed-back power from the other arm of the given coupler to determine the actual input power into the tested germano-silicate fiber incorporated with gold NPs. In order to get accurate luminescence signal, high sensitive optical spectrum analyzer (OSA) was used as the detector.

3. Results and discussion



Fig. 2. The absorption spectrum of the germano-silicate fiber incorporated with gold nanoparticles

Figure 2 shows the absorption spectrum of the germano-silicate glass fiber incorporated with gold NPs. The absorption peak appeared at 498.4nm (2.48eV), which was due to the SPR of the gold NPs embedded in the fiber core and is the indirect evidence of the existence of gold NPs.



Fig.3. Broadband visible to narrowband infrared photoluminescence of the 30m-long germano-silicate glass fiber incorporated with gold nanoparticles pumping with 488nm Argon-ion laser.

The broadband visible PL in the vicinity of 833nm (1.48eV) to the narrowband infrared PL centering 1536nm (0.81eV) was found to appear when the fiber was pumped with 488nm (2.53eV) Argon-ion laser as shown in Fig. 3. By using the accurately measured input launched power into the fiber and the calculated PL intensities at 833nm (1.48eV) and 1536nm (0.81eV), we confirmed that the averaged QEs were 5.75×10^{-8} and 2.01×10^{-9} , respectively. It is important to note that the visible PL intensity at 833nm was two orders in magnitude larger than that of bulk gold metal [1] and the observation of the infrared PL at 1536nm was the first to report in the field of fiber optics.

Excitation of the gold NPs incorporated germano-silicate glass fiber by the Argon-ion laser at 488nm (2.53eV) may lead to the excitation of d-band electrons into the sp-conduction band (interband transition) and a radiative recombination is followed by an initial electronic relaxation bringing about the visible luminescence. The luminescence between 629nm (1.97eV) and 1200nm (1.03eV) corresponds to the recombination of the excited electron from higher excited states in the sp-band with the hole in the lower lying d-band (interband transition). The lower energy luminescence band in the vicinity of 1536nm (0.81eV) can then be assigned to be the relaxed radiative recombination between the highest occupied (molecular) orbital lowest unoccupied and the orbital (HOMO-LUMO gap) of 1.3eV within the sp-conduction band (intraband transition). The schematic energy transition diagram is shown in Fig. 4, which shows the origin of the two PL bands. The high energy band is proposed to be due to radiative interband recombination between the sp and d-bands while the low energy band is

thought to originate from radiative intraband transitions within the 6sp-band cross the HOMO-LUMO gap. Note that intraband recombination has to involve prior nonradiative recombination of the hole in the 5d-band created after excitation with an (unexcited) electron in the 6sp-band.



Fig. 4. Energy transitions responsible for the two PL bands.

4. Summary

We successfully made germano-silicate glass fiber incorporated with gold NPs. Weak but distinct broadband visible to narrowband infrared PL excited by 488nm Argon-ion laser was found to appear at room temperature. The QEs of the PL fixed at 833nm and 1536nm are confirmed to be 5.75×10^{-8} and 2.01×10^{-9} , respectively. Interband transition between the sp and d-band and intraband transition across the HOMO-LUMO electronic gap inside the gold NPs are responsible for the two bands PL mentioned above.

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