Ultra-fast luminescence of nano-gold film structure

Fang Shen 1, a, Guyu Zhou 2, b
1School of Metallurgy and Environment, Central South University, Changsha, Hunan, 410083, China
2College of Advanced Interdisciplinary Research, National University of Defense Technology, Changsha, Hunan 410073, China
ashenfang@csu.edu.cn
email: fangshen_csu@foxmail.com, bemail: graasure@163.com

Abstract: The Fermi level of gold is not in the band gap, but in the sp band. Therefore, macroscopic gold is usually a non-luminescent material. Unlike gold bulk materials, frequency down-conversion photoluminescence and enhanced photoluminescence from gold nanoparticles have been studied, and the intensity of their photoluminescence is affected by the size, shape and plasmon resonance of the gold nanoparticles. In particular, plasmon resonance helps to increase the photoluminescence intensity by several times than the intensity in the macroscopic gold structure. Gold nanoparticles can also produce photoluminescence including second harmonic and third harmonic under intense photo excitation. Here, in order to study the luminescence properties of gold nanostructures under femtosecond laser, we applied a 5 nm gold film on a Si3N4 substrate by magnetron sputtering. The nano-gold film was excited using a femtosecond laser with an incident peak power density of 2.3 × 10 9 W/cm 2 and 4.5 × 10 9 W/cm 2. We explained that by studying the excitation spectra of nano-gold structures, we can see that SHG occurs at high power density and frequency shift occurs.

1. Introduction
Macroscopic gold structure cannot be used to excite light, but photoluminescence (PL) can be excited by gold nanostructures [1-4]. In 1969, Mooradian achieved the first photoluminescence of gold. He observed a wide range of unpolarized emission spectra with emission peaking around 500 nm. These results are due to the combination of holes in the d-band with the radiation of electrons in the sp-band, with emission quantum efficiencies on the order of 10-10 [1]. Due to the development of nanofabrication technology, it has been able to systematically study photoluminescence from a large number of gold nanostructures [5-9]. For instance, the photoluminescence of gold nanoparticle can be enhanced by plasmons [6], and it has been experimentally demonstrated that thin gold films have photoluminescence properties [7]. These single-particle studies show a close correlation between the PL spectrum and the scattering spectrum and confirm the increase in PL quantum yield compared to bulk gold. Therefore, gold nanostructures have broad application prospects in basic physics theory research and nano-optics, electrical fields, materials fields, and chemical fields. Although nanostructures of gold have been extensively explored, research about the phenomenon and mechanism of interaction between graphene and gold nanostructures have been studied rarely.

In this paper, in order to study the photoluminescence phenomenon of nanostructures, we use a simpler structure, namely island gold film for research. We adjust the power density incident on the
sample by changing the distance of the sample from the femtosecond fiber tip. An ultra-fast photoluminescence of the island-shaped gold film was investigated by plating a 5 nm thick island-shaped gold film on a silicon nitride substrate. We compared the photoluminescence spectra of nanogold films at two different input power densities and analyzed the causes.

2. Ultrafast photoluminescence of island gold film

First, we have grown a 5 nm thick gold film by magnetron sputtering on silicon nitride. Considering that 5nm is very thin, the gold film on silicon nitride is island-shaped. The process schematic is shown in Fig. 1. To investigate the effect of different incident power on the island gold film, we tested the fluorescence spectra of graphene and suspended graphene on the substrate at two different input power densities, 2.3 \times 10^9 \text{ W/cm}^2 and 4.5 \times 10^9 \text{ W/cm}^2, respectively. We use an ultrafast pulsed laser to excite an island-like gold film through a fiber with a tapered end face, as shown in Fig. 2. The center excitation laser has a wavelength of approximately 1.57 \mu m, a pulse width of approximately 130 fs, and a repetition rate of 100 MHz. In order to reduce the dispersion of the transport fibers, the fiber length is reduced to 30 cm. The maximum average output power from the tapered side of the fiber is approximately 10 mW and the focal spot size is approximately 4 \mu m. Photoluminescence from graphene is collected by a lens that couples the light to the fiber and then couples it to a cooled CCD spectrometer (Ideaoptics NOVA, \(-20 \degree C\)) to measure the spectrum.

![Fig. 1 Growth of gold film by magnetron sputtering on silicon nitride.](image)
Femtosecond laser was used to illuminate the nano gold film, and control the incident power density by controlling the distance between the tapered fiber tip and the microdisk. We tested the fluorescence spectra of graphene and suspended graphene on a substrate at two different input power densities of $2.3 \times 10^9$ W/cm$^2$ and $4.5 \times 10^9$ W/cm$^2$, respectively, as shown in Fig. 3.

The photoluminescence from the island gold film was excited by a femtosecond laser, and the input peak power density of the femtosecond laser was the same as that in graphene, which was $2.3 \times 10^9$ W/cm$^2$ and $4.5 \times 10^9$ W/cm$^2$, respectively. As shown in Figure 4, the photon emission at 780 nm corresponds to twice the frequency of the femtosecond laser. This is because the 5 nm island gold film lacks spatial inversion symmetry at the gold/Si$_3$N$_4$ and gold/air interfaces, so it has a non-zero electromagnetic sensitivity $\chi^{(2)}$. Together with SHG, there is also a frequency increase in the intensity of photoluminescence when the peak excitation power is $4.5 \times 10^9$ W/cm$^2$. Previous studies have shown that crystalline gold nanoparticles rarely have upward photoluminescence [10]. Here, our sputtered island gold film is polycrystalline and thinner than gold nanoparticles (40 nm in diameter) (average thickness 5 nm). Therefore, the number of free carriers in the island-shaped gold film is reduced, and the ultra-fast pulse can pump enough free electrons to the excited state. When excited radiation, the excited state of the light-emitting atoms in the role of external radiation field, to the low-energy state or ground state transition, radiation photons. At this time, the energy of the external radiation is exactly the energy difference between the two energy levels of the atom. The frequency, phase, propagation direction and polarization state of the photons emitted by the stimulated radiation and foreign photons are identical. Figure 4 shows the energy band structure of gold. As shown in Fig. 5, the photoluminescence from the island gold film is similar to that of graphene as the excitation intensity increases, and the photoluminescence of the island gold film is mainly concentrated near the emission peak of about 680 nm, which is corresponding. The electron-hole pair recombines near the X point. This is consistent with the electron-hole recombination from the sp band to the d band [11]. In order to eliminate the influence of the substrate on the experimental results, we added a set of control groups to directly implant the femtosecond laser into the substrate so that the input peak power density is $4.5 \times 10^9$ W/cm$^2$, as shown by the solid blue line in Fig. 5. The observed conical fiber optic head was caused by the presence of weak white light in the environment, and there was no white light in the actual measurement.
Fig. 3 Photoluminescence of island gold film under different peak power density light excitation: the input peak power density is (a) $2.3 \times 10^9$ W/cm$^2$ and (b) $4.5 \times 10^9$ W/cm$^2$. (c) Photomicrographs of the structure under the microscope when there is no gold. (d) Schematic diagram of experimental measurement process.

Fig. 4 The energy band structure of gold.
Fig. 5 Photoluminescence of thick 5-nm gold film. The solid black line indicates the radiation when the power density is $4.5 \times 10^5$ W/cm$^2$ on the sample, the solid red line indicates the radiation when the power density is $2.3 \times 10^5$ W/cm$^2$ on the sample, and the solid blue line the radiation without gold. Photoluminescence captured by optical elements to emit a photo CCD camera and all of the emission spectra have the same integration time from the optical spectra analyzer.

3. Summary
In summary, we have grown a 5 nm thick island-like gold film on a silicon nitride substrate by magnetron sputtering, and used a femtosecond laser to study its ultrafast photoluminescence. We control the incident power by changing the distance between the fiber head and the sample. The differences of photoluminescence spectra at different powers are analyzed, which lays a theoretical foundation for the luminescence phenomenon of gold nanostructures.

References
[1] A. Mooradian: Phys. Rev. Lett Vol. 185–187 (1969), p. 22.
[2] J.P. Wilcoxon, J.E. Martin, F. Parsapour, B. Wiedenman and D.F. Kelley: J. Chem. Phys Vol. 9137–9143 (1998), p. 108
[3] O.P. Varnavski, M.B. Mohamed, M.A. El-Sayed and T. Goodson: J. Phys. Chem. B Vol. 3101–3104 (2003), p. 107
[4] O.P Varnavski, T. Goodson, M.B. Mohamed and M.A. El-Sayed: Phys. Rev. B Vol. 235405 (2005), p. 72
[5] H.L. Hu, H.G. Duan, J.K.W. Yang and Z.X. Shen: ACS Nano Vol. 10147–10155 (2012), p. 6
[6] T.V. Shahbazyan: Nano Lett Vol. 194–198(2013), p. 13
[7] W. Ahn, B. Taylor, A.G. Dall’Asén and D.K. Roper: Langmuir Vol. 4174–4184 (2008), p. 24(8)
[8] Y. D. Jin, X. F. Kang, Y. H. Song, B. L. Zhang, G. J. Cheng and S. J. Dong: Anal. Chem. Vol. 2843-2849(2001), p. 13
[9] K. Q. Wang, X Zhao, B Li, K Wang, X Zhang, L. Q. Mao, A. Ewing and Y. Q. Lin: Anal. Chem. Vol. 8683-8688(2017), p. 89 (17)
[10] M. Lippitz, M.A. Van Dijk and M. Orrit: Nano Lett Vol. 799–802 (2005), p. 5(4)
[11] P. Romaniello and P. L. De Boeij: J. Chem. Phys Vol. 164303 (2015), p. 122(16)