Excitation power dependence of lifetime of photoluminescence from gold film in the Kretschmann geometry

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Abstract. We have investigated picosecond-laser-pulse-excited photoluminescence (PL) from an evaporated gold film in the Kretschmann geometry. The total intensity of PL was proportional to the square of continuous wave equivalent laser power for excitation, showing that PL is excited via two-photon optical processes. The lifetime of PL was directly determined as a function of excitation laser power by use of a streak camera. We found that the lifetime is inversely proportional to excitation laser power, indicating that the lifetime of d-band holes created by the two-photon optical processes is inversely proportional to their density.

1. Introduction

Intensive studies of photoluminescence (PL) of gold (Au) have been motivated not only by fundamental interests but also by industrial applications, such as plasmonic materials \cite{1}. PL from Au was first reported by Mooradian in 1969 \cite{2}. Boyd et al. measured excitation power dependence of PL of Au films, and investigated single- and multi-photon excitation processes in PL \cite{3}. Although the dynamics in PL has been intensively investigated for Au, reported lifetimes of PL have ranged from several tens of femtoseconds to a few nanoseconds, showing that the underlying mechanism is complex and has not been fully understood yet \cite{4-6}.

We reported light emission from the W tip-Au sample gap of a scanning tunneling microscope irradiated with picosecond (ps) laser pulses in previous paper \cite{7, 8}. The emission consisted of two components; the first component is excited by the laser-induced electron tunneling whose duration is identical to that of the incident laser pulse and the second component is directly excited by the laser pulse. The duration of the second component was a few hundred ps. This value is much longer than that of the laser pulse used for the excitation.

The second component disappeared when the tip was retracted from the sample surface by a macroscopic distance, showing that this emission is assisted by the presence of the tip. Its spectrum was successfully reproduced by an electromagnetic theory taking into account the presence of the tip which breaks the translational symmetry in the sample surface. We concluded from the experimental

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and theoretical knowledge that the second component is radiated by surface plasmon polaritons (SPP) through the breakdown of the translational symmetry in the sample surface by the presence of the tip. However, one may notice that the lifetime observed here is quite longer than the lifetime of SPP reported in the past [9].

We have carried out one step further experiment on the second component. In the present experiments, instead of the tip in an STM, the Kretschmann geometry was adopted for making SPP radiative. In this geometry, an Au thin film is deposited on the bottom of a hemispherical glass prism. Since the light propagating in the glass has a wavevector whose magnitude is larger than that of SPP localized at the Au film surface, its wavevector component parallel to the surface can be matched to that of SPP by adjusting the propagation angle of the light. In this manner, SPP becomes radiative with the adjusted angle on the prism side without the tip. We already reported that PL radiated in this adjusted angle has the spectra consistent with those of SPP emission through the prism [10]. In this paper, we report about excitation power dependence of the lifetime of PL.

2. Experimental
The sample was an Au film evaporated on the bottom of a hemispherical glass (BK7) prism in a high vacuum of 5.0×10^{-6} Torr. The mass thickness of the film was 40 nm. The dielectric function of the film measured by ellipsometry was consistent with that of bulk Au [11], showing that the film is continuous. In fact, a continuous grain structure was seen in an atomic force microscope image of the sample. Figure 1 shows the schematic of the experimental setup. Optical measurements were performed in the adjusted angle, which is 45° from the surface normal, under atmospheric conditions. The sample was irradiated with a mode-locked Ti:sapphire laser from the air side to excite PL. The pulse width and the repetition rate of the laser were 2 ps and 80 MHz, respectively. The wavelength of the laser was tuned at the wavelength of 920 nm, which corresponds to a photon energy of 1.35 eV. PL emitted in the direction of 45° from the surface normal through the prism was collimated by a first lens and was focused onto the entrance slit of a spectrograph by a second lens. The spectra were analyzed in the photon energy range from 1.5 to 2.4 eV with the streak camera attached to the spectrograph. The temporal resolution of the streak camera was better than 2 ps in the operation mode used in the present experiments.
3. Results and Discussion

Figure 2 shows the continuous wave (cw) equivalent excitation laser power dependence of temporal- and wavelength-integrated (total hereafter) intensity of PL. This graph shows that the total intensity is proportional to the square of excitation laser power. Thus, PL is excited via two-photon optical processes [10].

Figures 3(a) and (b) show temporal waveforms (i.e., wavelength-integrated spectra) of PL for cw equivalent excitation laser powers of 20 mW and 7.2 mW, respectively. The temporal profile of the laser pulse is shown in (c).

Figure 2. Excitation power dependence of intensity of PL from the Au film.

Figure 3. Temporal waveforms of PL from the Au film for excitation laser powers of (a) 20 mW and (b) 7.2 mW, respectively. The temporal profile of the laser pulse is shown in (c).

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Figures 3(a) and (b) show temporal waveforms (i.e., wavelength-integrated spectra) of PL for cw equivalent excitation laser powers of 20 mW and 7.3 mW, respectively. Figure 3(c) is the temporal evolution of the laser pulse. The lifetimes of PL read from Figs. 3(a) and (b) are 3 ps and 8 ps, respectively.
The lifetime becomes shorter as the excitation laser power increases. By taking temporal waveforms as shown in Fig. 3 for various values of excitation laser power, we obtained the relationship between the lifetime and the excitation laser power as shown in Fig. 4. From this relation, we see that the lifetime is inversely proportional to the excitation laser power. As mentioned in the introductory section, various lifetimes have been reported so far. The values reported by Beversluis et al. are in the range of several picoseconds for Au [5]. Those by Imura et al. are from 0.8 ns to 2 ns. Their samples are Au nanorods and are excited by a two-photon optical process. While the lifetime of PL varies in this manner, it is commonly claimed that PL from Au is excited via the recombination of electrons in the sp conduction band and holes created in the d-band by the incident laser. This means that the intensity of PL from Au must be proportional to the number of holes created. In other word, Fig. 4 shows that the lifetime of the holes decreases with the increase of their density. This dependence implies that the density of holes affects their relaxation process through thermally increased electron-electron and electron-phonon scatterings. A decrease of lifetime of PL with an increase of excitation laser power is observed for semiconductors [12-14], which is similar to that shown in Fig. 4. However, the decrease of the lifetime observed for the semiconductors is caused by the screening of internal electric fields which is accelerated by an increase of incident laser power. Thus, this mechanism cannot directly be applied to the present (i.e., metallic substrate) case.

4. Conclusions

Excitation power dependence of PL from Au film with the thickness of 40 nm was investigated in the Kretschmann geometry. Owing to this geometry, the emission from SPP was selectively observed. The total intensity of the emission was proportional to the square of excitation laser power, showing that the light is excited via the two-photon optical processes. Based on the observed power dependence of the lifetime of the emission, we conclude that the lifetime of the d-band holes created by the two-photon optical processes is inversely proportional to its density.

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