

Observation of electron decay dynamics in Pt nano-structures by femtosecond infrared luminescence

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Abstract. Femtosecond infrared luminescence has been observed in bulk and nano-structured platinum. Very broad spectra ranging from 0.3 to 1.05 eV are ascribed to hot luminescence within metal like continuous states both in bulk and nano-structured Pt. In addition, an excitation power dependent lifetime was found in Pt nano-structures.

1 Introduction

Nanometer-sized metal structures especially those of noble metals are important for catalysts, tracers, plasmonic devices, etc. Among them Au nano-spheres are most well-developed in applications, such as size-tunable luminescent material, luminescent tracer, imaging agent for cancer cells[1] and other biomedical applications[2]. Although Pt is one of the noble metals, the optical properties and electronic processes both in bulk and nano-structures are poorly understood. Recently, a bright luminescence from Pt nano-particles with thiol ligands has been reported [3] and the possibility as a new nanoprobe for labelling and imaging of bio-molecules is discussed. However, basic information such as luminescence mechanism or relaxation dynamics is not available even for bulk Pt. In this report, we present femtosecond luminescence in bulk Pt with a rough surface and Pt nano-structures, and discuss the electron relaxation dynamics.

2 Experimental

The bulk Pt sample is a 0.6mm thick plate with a roughened surface as shown in Fig. 1 (a). The Pt nano-structures were prepared by precipitating Pt metal in mesoporous silica film spread on a Si substrate with a SiO₂ buffer layer as schematically shown in Fig. 1(b). The mesoporous silica consists of regularly arranged tunnel structure. As shown by the TEM image in Fig. 1 (b), it contains wire-like nanostructures with different thicknesses and lengths, typical size being several nano-meters in diameter.

To realize femtosecond time-resolution in luminescence measurements, we used up-conversion technique, which has a sensitivity in the infrared (IR) region from 0.3 to 1.05 eV. As a light source, we employed a mode-locked Yb fiber laser with an amplifier, which

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provides 130 fs pulses (photon energy 1.19 eV) at a repetition rate of 100 MHz with an average power of 600mW. The spot size on the sample was 18 μm .

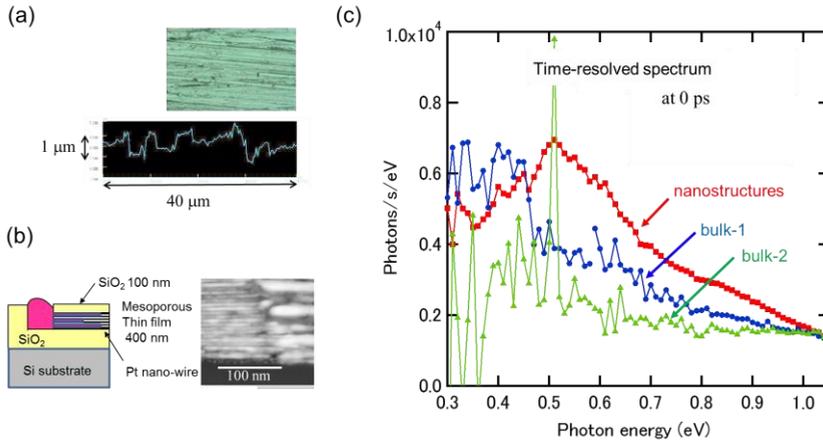


Fig. 1. (a) Surface of the Pt plate roughened by a sand-paper observed with a laser microscope. A typical cross-section of the surface is also shown. (b) Illustration of the device structure containing the Pt nano-structures grown in mesoporous silica. A TEM image of the typical wire structure is shown on the right. (c) Time-resolved luminescence spectra in Pt nano-structures and bulk Pt at 0 ps. Bulk-1 and -2 correspond to different places of the roughened surface.

3 Results and Discussion

3.1 Femtosecond luminescence in bulk Pt

We examined the femtosecond IR luminescence in the bulk Pt. Although the intensity was rather low for the as-purchased Pt plate, we observed a marked increase by roughening the surface. Typical time-resolved spectra at 0 ps are shown in Fig. 1(c) as “bulk-1” and “bulk-2”. In both cases, the spectra extend in the full energy range (0.3-1.05 eV). The intensity and the spectrum shape depend on the position, namely the morphology of the surface. As Pt is chemically stable in air, the luminescence cannot be ascribed to oxide or other Pt compounds. Possibility of white light generation by nonlinear optical effects such as self-phase-modulation (SPM) is also discarded, because the peak intensity has nearly linear power dependence ($\propto I^{1.26}$). Thus the observed IR luminescence is ascribed to an intrinsic property of Pt metal. As far as we know, this is the first observation of luminescence in bulk Pt. The broadness of the spectra (factor 3.5 in energy) suggests that the origin of the luminescence is the carrier recombination within a continuous states spreading below and above E_F (Fermi energy), as is expected in metals (see Fig. 2(b)). In the relevant photon energy range of excitation and emission, both inter- and intra-band transitions are possible around X point. A similar situation holds near the L-point.

The decay profiles at 0.9 eV are shown in Fig. 2(a) with exponential fittings. The lifetime in bulk Pt is relatively insensitive to the surface condition and to the luminescence photon energy between 0.6 and 0.9 eV. The latter property is very different from semiconductors or Dirac electron systems [4], where the lifetime clearly increases at lower energy. This is also understood as a consequence of the continuous DOS near E_F .

The lifetime in Pt is very short in contrast to those observed in bulk 1B-group elements (Au, Ag and Cu) [5]. This is ascribed to the large DOS near E_F in Pt (see Fig. 2(b)), resulting from a heavy overlapping of the d -bands near E_F . In contrast, in the 1B-group metals, the d -bands are located far below E_F and the dispersion near E_F is very simple, so that the DOS is very small and the relaxation is slow.

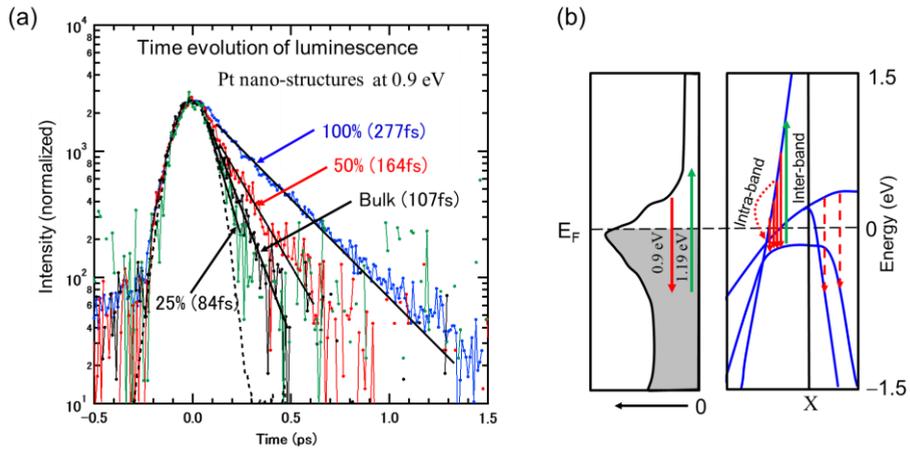


Fig. 2 (a) Excitation power dependence of the luminescence decay profiles taken at 0.9 eV in Pt nano-structures. 100% corresponds to a power of 145 mW on the sample. The decay profile of bulk Pt at 100% excitation is also shown. The straight lines are exponential fittings to each decay curve with time constants shown in the parentheses. The broken curve shows the instrumental function. (b) Density of states and a part of the band structure near X point for bulk Pt.[6] Transitions corresponding to absorption and emission are shown by upward and downward arrows, respectively. The curved dotted arrow shows an intra-band transition.

3.2 Femtosecond luminescence in Pt nano-structures

In the nano-structured Pt (see Fig. 1(b)), we found a very broad luminescence spectrum at 0 ps, as shown in Fig. 1(c). The instantaneous intensity was as high as the hot luminescence (under the same excitation condition) from InAs, which is a direct gap semiconductor. The relatively low intensity at high energy end and a peak structure around 0.5 eV are the features different from the bulk Pt. This might be ascribed to modification of DOS spectrum or the surface plasmon effect in nano-structures, which should be clarified in future.

The most significant difference between bulk and nano-structure is seen in the decay profiles (Fig. 2 (a)). At the lowest excitation power (25% of full power), the lifetime is close to that in bulk Pt, as shown in Fig. 2(a). However, the lifetime increases from 84 fs at 25% to 277 fs at 100%. The slowing down of the decay process is tentatively ascribed to the hot phonon effect. In the nano-meter system, the phonon spectrum becomes sparse and the electron phonon scattering rate will decrease, resulting in slower relaxation.

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6. Rearranged from the figure in Landolt-Boernstein 5.3, 293 (Springer materials).