

Photoluminescence from Au nanoparticles embedded in Au:oxide composite films

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Au:oxide composite multilayer films with Au nanoparticles sandwiched by oxide layers (such as SiO₂, ZnO, and TiO₂) were prepared in a magnetron sputtering system. Their photoluminescence (PL) spectra were investigated by employing a micro-Raman system in which an Argon laser with a wavelength of 514 nm was used as the pumping light. Distinct PL peaks located at a wavelength range between 590 and 680 nm were observed in most of our samples, with Au particle size varying from several to hundreds of nanometers. It was found that the surface plasmon resonance (SPR) in these composites exerted a strong influence on the position of the PL peaks but had little effect on the PL intensity. © 2006 Optical Society of America

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1. INTRODUCTION

Photoluminescence (PL) in metal is very rare owing to its lacking of bandgap. In 1969, Mooradian reported a first observation of optically excited radiation from the metal surfaces of Au and Cu.¹ Mooradian attributed this radiation to the recombination of the electrons in the *s,p* conduction band near the Fermi surface and the holes in the *d* bands generated by optical excitation. However, in this report the quantum efficiency of such an emission was estimated to be only about 10⁻¹⁰, and this value has not changed too much for a long time owing to the samples used in PL measurement, usually in the form of bulk metal or metal films with different surface roughness.² Just recently, very great PL quantum efficiency was achieved in metal nanoparticle systems.³⁻⁹ For example, rather strong (quantum efficiency of 10⁻⁴–10⁻⁵) visible PLs from Au nanorods and nanoclusters smaller than 15 nm have been reported in Refs. 3 and 4, respectively. The PL peaks of noble metals (e.g., Au) were also found to locate in a wide range varying from the visible to the near-infrared region.^{2,3,10-14} Usually the visible photoluminescence was due to the interband transition between the *s,p* conduction bands and the *d* bands, while the infrared one was owing to the intraband transition inside the *sp* conduction band. Relative theoretical studies have also made some progress in dealing with the origins of this PL phenomenon.^{15,16}

Band structure is quite helpful for using better understanding and interpreting the PLs from noble metals. In this paper, we mainly are concerned about Au and its band structure. In the first Brillouin-zone of Au, the energy separation between the Fermi surface and *d* holes near the high-symmetry points X and L is about 1.8 and 2.4 eV, respectively.^{1,13} Both of them are far from the

point where the conduction band and the *d* band overlap. When the energy of the pump light is great enough, the electrons in the upper *d* bands have a probability to be excited if vacant conduction bands exist at that point; then holes are created at *d* bands. However, if the recombination process occurs later, these holes first move closer to the conduction band electrons near the Fermi surface through the intraband scattering; then the interband radiative relaxation happens. That is, PL peak energy is strongly controlled by the energy gap between the Fermi level and the *d* bands. As a result, visible PLs may be generated.¹³ With further enhancement of the energy of the pump light, Mooradian predicted that an emission of photons with energy around 4 eV should occur owing to the excitation of the electrons in the lower *d* bands.¹

Nanoparticles of noble metal-doped dielectric composite materials such as Au, Ag, and Cu have received intense interest on their nonlinear optical properties in recent years due to their very large nonlinear optical susceptibilities that stem from great enhancement of the local field near the surface plasmon resonance (SPR) peak.^{17,18} Such enhancement of the local field could mediate the fluorescence of the materials absorbed on or capped by the metal particles.^{19,20} It was found that two-phonon absorption in noble metals, which then gave visible light emission, was also associated with this enhancement.¹³ However, at present little attention has been paid to the PLs of these composites. We noticed that most of the samples used in the metal PL measurement were bulk metals, metal films with different surface roughness, or nanoparticles supported by a substrate where the SPR effect was not dramatic.

In this paper we report an investigation of PLs generated by the Au nanoparticles embedded in different oxide

matrices (such as SiO_2 , ZnO , and TiO_2). The Au:oxide composite multilayer films were prepared in a magnetron sputtering system in which the Au particles were sandwiched between the oxide layers. Their PLs were studied by employing a micro-Raman system in which an Argon laser with a wavelength of 514 nm was used as the pump light. Distinct PL peaks could be observed in most of our samples. The position of the PL peaks in these composites was found to depend strongly on their SPRs.

2. EXPERIMENTS

The Au:oxide multilayer composite films Au: SiO_2 , Au: ZnO , and Au: TiO_2 were deposited in a multitarget magnetron sputtering system with autocontrolled target switching capability (Denton SJ/24 LL). The targets were 2 in. (5.08 cm) in diameter with their surfaces inclined about 45° toward the substrate and could be controlled by either a dc or an rf power supply. In our experiments, the target SiO_2 , Ti, Zn, and Au with high purity were mounted on the target holders when needed. The substrate holder could rotate around the normal axis in order to obtain a film with uniform thickness and composition. The Au target was controlled by an rf power supply to get a lower deposition rate, whereas the oxide films could be obtained by introducing an oxygen atmosphere (the ratio of $\text{Ar}:\text{O}_2$ was about 8:2 to 9:1) into the chamber during the sputtering of metal or oxide targets. The refractive index of the pure SiO_2 , ZnO , and TiO_2 film prepared in our sputtering condition was 1.5, 1.9, and 2.4, respectively, which was measured by an ellipsometric system at a wavelength of 632 nm. Prior to the multilayer deposition, the growth rate of each component was calibrated by separately sputtering each target under the same deposition condition. The average concentration of metal Au in these composite films could be changed by adjusting the ratio of the layer thicknesses of Au and the oxide.

To create Au nanoparticles, a high-temperature furnace was employed in our experiments to make a thermal treatment on the as-grown composite films. In this furnace, the heating/cooling rate and the annealing duration could be automatically adjusted by changing the program parameters. According to our earlier experience, the annealing temperature of Au: ZnO and Au: TiO_2 composite films should be set to around $600\text{--}700^\circ\text{C}$. At this temperature, the size of both the oxide crystallites and the Au nanoparticles formed during the annealing was not very large and a better dispersion of Au particles inside the composites was obtained. However, the Au: SiO_2 films could stand a relatively high annealing temperature (as high as $950\text{--}1050^\circ\text{C}$). The annealing duration was usually set from 1 s to several hours in order to obtain Au particles with different sizes and shapes. Also, the cross-sectional microstructures of our composite films were investigated by TEM (Philips CM120).

The optical absorption spectra of all the composite films were obtained by using a UV-VIS spectrophotometer (Perkin Elmer, Lambda 20) in a wavelength range between 300 and 1000 nm. Measurement of the PLs of our composite films was carried out in a typical micro-Raman/photoluminescence system (RM3000) in which an Argon laser with a wavelength of 514 nm was applied as the

pumping light and an optical microscope was installed in order to collect more light emitted by the samples.

3. RESULTS AND DISCUSSIONS

Selected cross-sectional TEM pictures of the composite films prepared in our experiments are shown in Fig. 1. It is obvious that the as-grown Au: SiO_2 composite film has an apparent multilayer structure [as shown in Fig. 1(a)] in which very small Au particles connect with each other to form an almost continuous Au film [the thin and dark lines in Fig. 1(a)] and Au layers are well separated by SiO_2 films [the layers with light contrast in Fig. 1(a)]. TEM images of other two kinds of as-grown composite films, Au: ZnO_2 and Au: TiO_2 , will not be displayed here, because they are very similar to that shown in Fig. 1(a). But after thermal treatment, the microstructure of these composite films becomes quite different. The multilayer structure still remains in Au: SiO_2 films annealed at 950°C for 2 h [seen in Fig. 1(c)], while it is completely damaged in Au: ZnO and Au: TiO_2 films annealed only at a temperature of 700°C for 2 h [seen in Figs. 1(b) and 1(d)]. Both the TEM investigation and the x ray diffraction measurement (the results not presented here) revealed that ZnO and TiO_2 films were easily crystallized during the thermal annealing, and this resulted in the formation of holes inside the composites. Therefore, the small Au particles from different layers could go together to form large Au particles. In most of the annealed Au: SiO_2 films, the shape of Au particles was strongly dependent on the thermal annealing conditions and the thickness of Au layers, whereas their size distribution was usually narrow. For example, pancake-like Au particles could appear in the films with a thicker layer of Au or annealed for very short time.²¹ However, the situation was reversed in the other two kinds of films. That is, the Au particles in Au: ZnO and Au: TiO_2 films usually were of the same shape but with a very wide size distribution.

The typical optical absorption spectra of our annealed composite films are displayed in Fig. 2(A). It is clear that

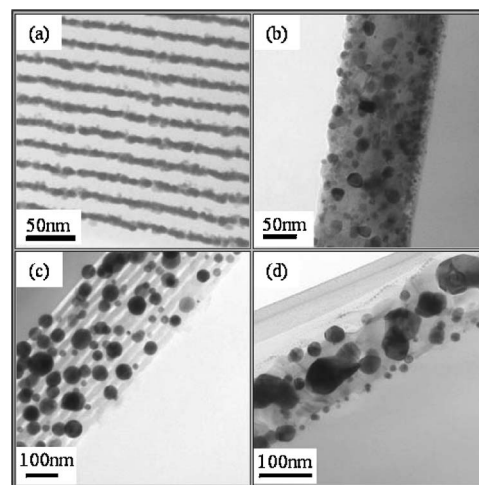


Fig. 1. Selected cross-sectional TEM images of the composite films prepared in our experiment: (a) as-grown Au: SiO_2 film; (b) Au: ZnO film annealed at 700°C for 2 h; (c) Au: SiO_2 film annealed at 950°C for 2 h; (d) Au: TiO_2 film annealed at 700°C for 2 h.

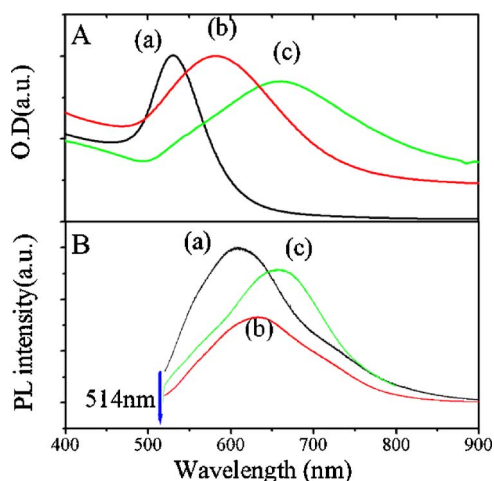


Fig. 2. (Color online) Typical Optical absorption spectra and PL spectra of the Au:oxide composite films. Figure 2(a) is the optical absorption spectra and 2(b) is PL spectra of the composite films: (a) Au:SiO₂, (b) Au:ZnO, and (c) Au:TiO₂.

all these composite films possess dramatic SPR peaks. The SPR peaks of Au:SiO₂, Au:ZnO, and Au:TiO₂ are located at about 530 nm [Fig. 2(A)(a)], 580 nm [Fig. 2(A)(b)], and 660 nm [Fig. 2(A)(c)], respectively. Usually the larger the dielectric constant of the host material is, the more redshifted of the SPR peak of the composite is. In addition, the SPR peaks in Au:SiO₂ films are much narrower than those in the other two kinds of composite films, because in Au:SiO₂ films, there is a more uniform size distribution of the Au particles and a longer decay time of the plasmon excitation owing to the so-called chemical interface damping.²²

When Au:oxide composite films were excited at a laser wavelength of 514 nm, PL spectra with broad peaks located in a wide range were achieved. In our investigation, the shortest wavelength of the PL peak is at about 590 nm, whereas the longest one is at about 680 nm. As mentioned in the Introduction, owing to the special band structure of Au, PLs from these Au:oxide composites could possibly appear in the whole visible region.

Typical profiles of the PL spectra are shown in Fig. 2(B). It is found that all the PL peaks in Au:SiO₂ films have a redshift of more than 70 nm as compared with their SPR peaks. For example, in Fig. 2(B)(a), the PL peak is at about 610 nm. Similar redshift of PL peaks has also been observed in Au:ZnO films [e.g., curve (b) in Fig. 2(B) with a peak at about 630 nm] but with a peak shift a little bit smaller (about 20–50 nm) in comparison with that in Au:SiO₂. However, the PL peaks in Au:TiO₂ films are always quite close to, or make, a blueshift instead of a redshift to their SPR peaks. This is quite different from that in Au:SiO₂ and Au:ZnO films. For example, the curve (c) in Fig. 2(B) has a PL peak around 655 nm, which approaches that of the SPR peak [at about 660 nm in Fig. 2(A)(c)]. Also, Au:TiO₂ films having a PL peak at 640 nm but a SPR peak at 670 nm have been prepared (data is not displayed here). PL spectra of pure SiO₂, ZnO, and TiO₂ films were also investigated by using the same system, but no clear PL peaks were found. This means that the result presented above does not stem from the PL of the matrix materials.

Based on the data plotted in Fig. 2, it is obvious that the PL spectra in these Au:oxide composites are strongly influenced by their SPRs, which intensely depend on the host materials. Otherwise, the PL peak measured in different composites should not change if the PL spectra just reflected the recombination of *d*-band holes and the *s,p* electrons in the Au particles. But it seems that the association between the PL and the SPR spectra was irregular. Further experiments have been undertaken to deal with this subject. We prepared some Au:ZnO composite films with different layer thicknesses of Au but with the same layer thickness of ZnO. After thermal annealing, Au particles in these films were found to be of similar shape but different particle size when we performed a TEM investigation. As listed in Table 1, it is very clear that the variation of the peak position in PL and SPR spectra is very alike. That is, the higher the energy of the SPR, the shorter the wavelength of the PL peak. Furthermore, the PL peaks in the Au:ZnO composite films were always located on the red side of the SPR peaks. Similar results were also found in Au:SiO₂ films with spherical Au particles. The data reported in Ref. 5 was to some extent analogous to ours, in which small Au particles were immersed in the aqueous solutions and the PL peaks were found to follow the SPR peaks (near 525 nm) closely. The separation between the PL and the SPR peaks in Ref. 5 was much smaller than that in our samples. However, such an association between the PL and the SPR peaks has never been observed in Au:TiO₂ films. Therefore, according to the data obtained in our experiments and reported in Ref. 5, we suggest that the PL peak may shift to the red side of the SPR peak only when the SPR energy is high enough, and it may approach more closely to the SPR peak with an increase of energy.

In our investigation, both the as-grown films and films with small Au particles usually have little PL [as shown in Fig. 3(a)]. Only when the Au particles are larger than 20 nm do the PL peaks become remarkable [e.g., Figs. 3(b) and 3(c)]. With a further increase of the particle size to more than several hundreds of nanometers, the intensity of the PL spectrum does not change a lot, but with a shift of the PL peak position [as seen in Fig. 3(d)], the total thickness of Au in samples used in Fig. 3 is the same (about 75 nm). This is quite different from that reported in some references, where only the very small Au particles could generate a distinct PL.^{3,9,10} That is, the PL involving the quantum confinement is to some extent quite different from that involving the SPR. More experiments need to be carried out to deal with such a problem.

On the other hand, it should be noticed that the sample used for Fig. 3(a) had a remarkable SPR peak at 580 nm while there was no SPR peak in sample used for Fig. 3(d).

Table 1. Relationship between the Position of PL Spectra and That of SPR Spectra^a

Peak	Peak Position (nm)				
SPR	578	594	604	608	616
PL	591	610	632	634	641
Difference	13	16	28	26	25

^aSamples used here are Au:ZnO films with different Au particle sizes.

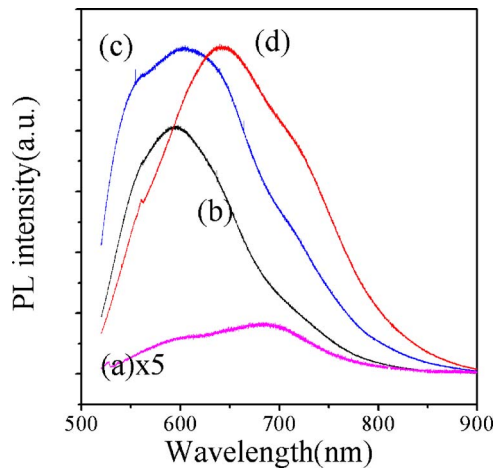


Fig. 3. (Color online) PL spectra of Au:SiO₂ composite films with different sizes of Au particles. The sizes of Au particles are: (a) 15 nm, (b) 36 nm, (c) 78 nm, and (d) more than 200 nm.

Although it was found that the PL peak position in our composites depended strongly on that of the SPR peak, the PL intensity seemed not to be influenced.

4. CONCLUSIONS

We have prepared a set of Au oxide composite multilayer films in a magnetron sputtering system. In these samples, Au nanoparticles were sandwiched by oxide layers (such as SiO₂, ZnO, and TiO₂). Their PL spectra were studied by employing a micro-Raman system in which an Argon laser with a wavelength of 514 nm was used as the pumping light. Distinct PL peaks located at a wavelength range between 590 and 680 nm could be observed in most of our samples, with Au particle size varying from several to hundreds of nanometers. It was found that the SPR in these composites exerted a strong influence on the position of the PL peak but had little effect on the PL intensity.

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