

An approach to achieve significantly faster luminescence decay of thin-film scintillator by surface plasmons

Bo Liu, ^{1,a)} Zhichao Zhu, ¹ Jingtao Zhu, ¹ Shuang Wu, ¹ Hong Chen, ¹ Mu Gu, ¹ Qian Cheng, ² Hong Chen, ² Chuanwei Cheng, ¹ Zhanshan Wang, ¹ Yuping Zhao, ³ and Qingli Zhang³ ¹Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, School of Physics Science and Engineering, Tongji University, Shanghai 200092, People's Republic of China ²Institute of Acoustics, Tongji University, Shanghai 200092, People's Republic of China ³Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

(Received 15 November 2013; accepted 26 January 2014; published online 10 February 2014)

A fast component of 2.2 ns from the LSO thin-film scintillator was achieved through coupling of scintillator with surface plasmons of silver nanoparticles. From the emission spectra, the observed fast component is from the transition of 5d to 4f level of Ce^{3+} in LSO. The fast component is attributed to the enhanced spontaneous recombination rate due to the surface plasmons. The present demonstration provides an interesting approach to improve the timing resolution of scintillator, which is distinguished from these conventional methods. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4864634]

Timing resolution is an important factor in scintillation detection systems for the applications of medical imaging systems, nuclear physics experiments, and high-energy physics experiments.¹ Exploring fast scintillators is currently one of the most important objectives in the field of scintillator. Conventionally, fast scintillators are proposed based on the molecular design for many years. Typical fast scintillators, such as PbWO₄ due to thermal quenching,² BaF₂ due to cross-luminescence,³ Lu₂SiO₅:Ce (LSO) due to the parity allowed electric dipole transition of Ce ion,⁴ achieve fast emission decay processes from luminescence centers in crystals, which depend on the crystal structures and atom components.

In recent years surface plasmons (SPs) have been used to control the spontaneous radiation by the coupling of SPs to the luminescent centers.⁵ Such control is achieved through the change of the recombination rate. SPs are electromagnetic excitations propagating at the interface between a metal and a dielectric, evanescently confined in the perpendicular direction. The overlap of the confined field with luminescence centers leads to the emission into plasmons rather than into free photon modes. Due to the significantly large photonic density of states of SPs at the resonance energy, in accordance with Fermi's golden rule,⁶ the spontaneous recombination transition rate into SPs modes can be greatly enhanced, leading to a very large Purcell factor.⁷ In order to ultimately obtain free photons from SPs modes, the extraction from SPs modes is a key issue.

Using SPs coupling, the luminescence enhancement has been demonstrated in materials with low internal quantum efficiency, such as InGaN quantum well-based light-emitting diodes (LEDs),^{8–10} organic LEDs,^{11–13} semiconductor nanocrystals,^{14,15} Si quantum dot,¹⁶ and amorphous oxidized silicon nitride films.¹⁷ Such enhancement is mainly attributed to the efficient competition from the non-radiative process. For materials with high internal quantum efficiency, however, the total quantum efficiency could not be improved due to the metal loss.⁷

In contrast to the goal of improved luminescence efficiency for most luminescent materials, the purpose of the present work is to demonstrate the improved timing resolution of LSO thin-film scintillator using SPs coupling. The fundamental principle is the increased spontaneous recombination rate through the coupling of SPs, which leads to a faster luminescence decay. LSO scintillator is selected in the present investigation due to its important application in nuclear medical imaging. In this Letter, an approach to control the scintillation decay time is proposed, which is distinguished from the conventional approach based on molecular design.

LSO thin-films on quartz glass substrates were fabricated by sol-gel processing with spin-coating technique with a detailed description in Ref. 18. The thickness of the LSO films was measured to be about 100 nm. In order to excite SPs modes, Ag is a suitable choice for SP coupling to LSO emission. If the metal/dielectric surface was perfectly flat, the SPs could not be extracted into free space because the SPs are by nature guided near the metal layer and are not emitted to air. Therefore, roughness surfaces or nanoparticles are necessary to efficiently scatter SPs into light. In this study, Ag metal films with thickness of 5 nm (sample A) and 10 nm (sample B) were deposited on the surface of the LSO films by magnetron sputtering. After the Ag films were deposited, the samples were subsequently annealed at 400 °C for 10 min in Ar atmosphere to obtain Ag nanoparticles. Atomic force microscopy (AFM) images of Ag nanoparticles deposited on the surface of LSO films are shown in Fig. 1. It is found that after thermal annealing, the Ag form nanoparticles with the RMS roughness of 16.0 and 22.3 nm, the average diameter of 104 and 139 nm, for sample A and sample B, respectively. The shape of these nanoparticles seems to be an oblate sphere. The average size of Ag particles in sample A is smaller than in sample B, which is due to the different

^{a)}Author to whom correspondence should be addressed. Electronic mail: lbo@tongji.edu.cn.



FIG. 1. (a)–(b) Atomic force microscopy (AFM) image of Ag nanoparticles deposited on the surface of LSO film for sample A and sample B. (c)–(d) The depth profile long the dashed line in (a) and (b).

thickness of Ag films deposited. The penetration depth of SP fringing field into the scintillator film is calculated by

$$Z = \frac{\lambda}{2\pi} \sqrt{\frac{(\varepsilon_{LSO}' - \varepsilon_{Ag}')}{\varepsilon_{Ag}'^2}}$$

where ε'_{LSO} and ε'_{Ag} are the real parts of the dielectric constants of the LSO film and metal silver. The penetration depths are calculated to be 40 nm for the emission wavelength at 410 nm. This implies that the effective region of coupling is smaller than the thickness of the prepared samples.

In order to determine the resonance wavelength of SPs, the transmission spectra are shown in Fig. 2. Compared with the reference sample, the obvious dips in transmission spectra of Ag-coated samples suggest the excitation of SPs modes of Ag. It is found that there are one narrow dip band at 355 nm for both sample A and sample B, and one wide band dip at 445 and 500 nm for sample A and sample B, respectively. The origin of the dip band at 355 nm is the normal mode of oscillation across the minor axes.¹⁹ The dip band at the long-wavelength is due to the oscillation along



FIG. 2. Transmission spectra of sample A, sample B, and the reference sample without Ag nanoparticles.



FIG. 3. Time-resolved photoluminescence spectra with emission wavelength at 410 and 440 nm excited by 355 nm for sample A, sample B, and the reference sample. Fitting results are also presented with the solid lines.

the major axes, involving the excitation of both dipole and quadrupole modes of SPs.²⁰ The wavelength of the minimum of dip band is strongly dependent on the size of particle, exhibiting a red-shift with the increasing size.²¹ The overlap of the dip band and the emission spectrum is a necessary condition for the SP-scintillator coupling.

Fig. 3 exhibits the time-resolved spectra with the emission at 410 and 440 nm for the three samples. The decay curves of the reference sample are well fitted by a single exponential decay with the decay time constants of 25.6 and 26.5 ns for 410 and 440 nm, respectively. There are the typical decay time constants of the parity allowed electric dipole transition from 5d to 4f in Ce^{3+} ions. In contrast, it is evident that a new fast component appears in the decay curves of sample A and sample B. The parameters obtained by fitting with a double-exponential decay are presented in Table I. The decay time constant of the slow component is very close to the reference sample. However, the fast components at 410 nm emission have decay time constants of 2.6 and 5.3 ns for sample A and sample B, respectively, which are one order of magnitude shorter than those of the reference sample. The ratio of the fast component reaches 43% and 38% in the total intensity for sample A and sample B, respectively. The fast component is also due to the transition of 5d to 4f level in Ce³⁺ ions. However, the dynamics of luminescence process is significantly accelerated through the SP-scintillator coupling. At the coupling region, the spontaneous recombination rate is significantly enhanced due to the

TABLE I. Summary of the decay time constants and the PL intensity for sample A, sample B, and the reference sample.

Sample	Decay constant at 410 nm (ns)	Decay constant at 440 nm (ns)
Reference	25.6	26.5
	2.6 43%	2.2 49%
Sample A	26.1 57%	26.7 51%
	5.3 38%	3.2 45%
Sample B	25.8 62%	26.8 55%



FIG. 4. Recombination processes involving with SP-scintillator coupling.



enhanced density of states of SP modes at the SP resonance frequency. In fact, since the thickness of layer of scintillator is larger than the penetration depth of SP mentioned above, the layer of scintillator can be divided into two parts. One part of layer close to the Ag particles exhibits SP-scintillator coupling, thus leading to the fast component. It is interesting that the fast component at 440 nm emission exhibits shorter decay time (2.2 and 3.2 ns for samples A and B, respectively) than that of at 410 nm emission. This can be explained by the fact that the 440 nm is more close to the resonance wavelength than 410 nm whereas for the other part of layer beyond the coupling region, the luminescence decay constant keeps nearly unchanged since the distance between the luminescence centers to the Ag particles is so far that the coupling cannot occur.

Without Ag-coating for the reference sample, the radiative and nonradiative recombinations can be described by the recombination rate of k_r and k_{nr} , which depend on the intrinsic electromagnetic characteristic of LSO. The nonradiative recombination with a rate of k_{nr} will give rise to heat by emitting phonons. The corresponding decay time constant can be described as $\tau_0 = \frac{1}{k_r + k_m}$. With Ag-coating with the luminescent layer, the excited states can return to the ground states by exciting SPs modes in Ag nanoparticles due to the SP-scintillator coupling. This is a new recombination channel with a rate of k_{SP} . Thus, the decay time constant can be described as $\tau_1 = \frac{1}{k_r + k_m + k_{SP}}$. The process is illustrated by Fig. 4. Since the k_{SP} is significantly large at resonance wavelength of SPs, the decay time of τ_1 is strongly dependent on k_{SP} .

In order to quantify the increase of spontaneous recombination rate, the Purcell factor as a function of wavelength can be defined as

$$F_p(\lambda) = \frac{k_r(\lambda) + k_{nr}(\lambda) + k_{SP}(\lambda)}{k_r(\lambda) + k_{nr}(\lambda)} = \frac{\tau_0(\lambda)}{\tau_1(\lambda)},$$
 (1)

where λ is the wavelength. From the decay constants, for sample A, the F_p is calculated to be 9.8 and 12.0 at emission of 410 and 440 nm, respectively. For sample B, the F_p is calculated to be 4.8 and 8.3 at emission of 410 and 440 nm, respectively. Larger values of F_p at 440 nm for both samples show that the SP-scintillator coupling is stronger than that at 410 nm, which is consistent with the fact that the resonance

FIG. 5. Photoluminescence spectra for sample A, sample B, and the reference sample. The enhancements of the sample A and the sample B are shown in the inset.

wavelength is close to 440 nm from the transmission spectra in Fig. 2.

The emission spectra with the excitation wavelength at 360 nm are shown in Fig. 5. Compared with the reference sample, the wavelength-integrated emission intensity is decreased by 53% and 49% for sample A and sample B, respectively. At the same time, the ratio of emission intensity to that of reference sample is dependent on the emission wavelength as shown in the inset of Fig. 5. With Ag-coating, the layer of scintillator is composed of the coupling region and out of the coupling region. In the coupling region, the SPs modes in Ag particles could be effectively excited. Subsequently, the decay of SPs modes leads to the reemission of photon and heat which is often called loss of metal. Thus, only part of energy of SPs modes can be extracted into photon due to loss of metal, which can decrease the quantum efficiency of emission. For luminescent materials with very low internal quantum efficiency, the significantly enhanced SP-emitter coupling can lead to increased final quantum efficiency, which is due to the competition from nonradiative combination.⁷ However, for luminescent materials with high internal quantum efficiency such as LSO scintillator, the final quantum efficiency is hard to be improved due to the loss of metal.²²

Beyond the coupling region, taking into account the loss of transmission of Ag nanoparticle layer, the efficiency can be expressed as

$$\eta(\lambda) = \frac{T(\lambda)k_r(\lambda)}{k_r(\lambda) + k_{nr}(\lambda)},$$
(2)

where $T(\lambda)$ is the corresponding transmission.

In the coupling region, the efficiency can be expressed as

$$\eta * (\lambda) = \frac{k_r(\lambda) + C(\lambda)k_{SP}(\lambda)}{k_r(\lambda) + k_{nr}(\lambda) + k_{SP}(\lambda)},$$
(3)

where $C(\lambda)$ is the photon extraction efficiency from the SPs modes.

Assuming that the intrinsic efficiency of LSO is about $\eta_{int} = k_r/(k_r + k_{nr}) = 70\%$ at room temperature,²³ the values

of extraction efficiency $C(\lambda)$ can be determined to be 57% (at 410 nm) and 45% (at 440 nm) for sample A and 65% (at 410 nm) and 55% (at 440 nm) for sample B. The extraction efficiency is dependent on both the size and shape of Ag nanoparticles and the wavelength. The efficient extraction from SPs modes to photons is an important factor, which is the reason why the method of using the SP-scintillator coupling is advantage over the conventional method of pure thermal quenching by increasing the value of k_{nr} in the exploring of scintillator with fast decay time. In other words, this method allows us to obtain the fast decay time of scintillator at the expense of the loss of quantum efficiency as low as possible.

In summary, we have demonstrated an accelerated luminescence decay process for the transition of 5d to 4f level in Ce^{3+} in LSO thin-film scintillator by the SP-scintillator coupling. The decay time constant for the fast component can reach 2.2 ns which is one order of magnitude shorter than that of the sample without SP-scintillator coupling. The enhanced recombination rate due to the significantly increased density of states of SPs is contributed to the very fast component. This method to obtain a fast decay time for the application of scintillator is very distinguished from the conventional method. This demonstration exhibits an important application of accelerated luminescence decay by SPs which has been extensively investigated as a fundamental physical phenomenon for many years.

This work was supported by the National Basic Research Program of China (Grant No. 2011CB922001), the National Science Foundation of China (Grant Nos. 11374229, 11179019, 11375131, and 11234010), and the Shanghai Municipal Science and Technology Commission (Grant No. 11ZR1440500).

- ¹P. Lecoq, IEEE Trans. Nucl. Sci. 59, 2313 (2012).
- ²M. Nikl, P. Bohäcek, K. Nitsch, E. Mihoková, M. Martini, A. Vedda, S. Croci, G. P. Pazzi, P. Fabeni, S. Baccaro, B. Borgia, I. Dafinei, M. Diemoz, G. Organtini, E. Auffray, P. Lecoq, M. Kobayashi, M. Ishii, and Y. Usuki, Appl. Phys. Lett. **71**, 3755 (1997).
- ³A. Myasnikova, E. Radzhabov, and A. Mysovsky, J. Lumin. 129, 1578 (2009).
 ⁴P. D. Rack, J. D. Peak, C. L. Melcher, and J. M. Fitz-Gerald, Appl. Phys. Lett. 91, 244102 (2007).
- ⁵W. L. Barnes, Nature Mater. **3**, 588 (2004).
- ⁶R. Loudon, The Quantum Theory of Light (Oxford Science Publications,
- Clarendon, Oxford, UK, 1973). ⁷A. David, H. Benisty, and C. Weisbuch, Rep. Prog. Phys. **75**, 126501
- ⁸C.-H. Lu, C.-C. Lan, Y.-L. Lai, Y.-L. Li, and C.-P. Liu, Adv. Funct. Mater. **21**, 4719 (2011).
- ⁹K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, and A. Scherer, Nature Mater. **3**, 601 (2004).
- ¹⁰A. A. Toropov, T. V. Shubina, V. N. Jmerik, S. V. Ivanov, Y. Ogawa, and F. Minami, Phys. Rev. Lett. **103**, 037403 (2009).
- ¹¹A. Fujiki, T. Uemura, N. Zettsu, M. Akai-Kasaya, A. Saito, and Y. Kuwahara, Appl. Phys. Lett. 96, 043307 (2010).
- ¹²P. A. Hobson, S. Wedge, J. A. E. Wasey, I. Sage, and W. L. Barnes, Adv. Mater. 14, 1393 (2002).
- ¹³Y. Xiao, J. P. Yang, P. P. Cheng, J. J. Zhu, Z. Q. Xu, Y. H. Deng, S. T. Lee, Y. Q. Li, and J. X. Tang, Appl. Phys. Lett. **100**, 013308 (2012).
- ¹⁴C. Huh, C.-J. Choi, W. Kim, B. K. Kim, B.-J. Park, E.-H. Jang, S.-H. Kim, and G. Y. Sung, Appl. Phys. Lett. **100**, 181108 (2012).
- ¹⁵K. T. Shimizu, W. K. Woo, B. R. Fisher, H. J. Eisler, and M. G. Bawendi, Phys. Rev. Lett. 89, 117401 (2002).
- ¹⁶B.-H. Kim, C.-H. Cho, J.-S. Mun, M.-K. Kwon, T.-Y. Park, J. S. Kim, C. C. Byeon, J. Lee, and S.-J. Park, Adv. Mater. **20**, 3100 (2008).
- ¹⁷Z. Ma, M. Yan, X. Jiang, H. Yang, G. Xia, X. Ni, T. Ling, W. Li, L. Xu, K. Chen, X. Huang, and D. Feng, Appl. Phys. Lett. **101**, 013106 (2012).
- ¹⁸X. Liu, Y. Fan, S. Chen, M. Gu, C. Ni, B. Liu, and S. Huang, Mater. Res. Bull. 48, 2370 (2013).
- ¹⁹P. Royer, J. P. Goudonnet, R. J. Warmack, and T. L. Ferrell, Phys. Rev. B 35, 3753 (1987).
- ²⁰F. Zhou, Z. Li, Y. Liu, and Y. Xia, J. Phys. Chem. C 112, 20233 (2008).
- ²¹M. Rycenga, C. M. Cobley, J. Zeng, W. Li, C. H. Moran, Q. Zhang, D. Qin, and Y. Xia, Chem. Rev. **111**, 3669 (2011).
- ²²H. Mertens and A. Polman, J. Appl. Phys. **105**, 044302 (2009).
- ²³B. Liu, C. Shi, M. Yin, Y. Fu, G. Zhang, and G. Ren, J. Lumin. **117**, 129 (2006).