AIP | Journal of Applied Physics

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Citation: J. Appl. Phys. **114**, 033524 (2013); doi: 10.1063/1.4815939

View online: http://dx.doi.org/10.1063/1.4815939

View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v114/i3

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JOURNAL OF APPLIED PHYSICS **114**, 033524 (2013)

Near infrared photoluminescence from bismuth-doped nanoporous silica thin films

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(Received 14 March 2013; accepted 1 July 2013; published online 19 July 2013)

Photoluminescence (PL) properties of bismuth (Bi) doped porous silica thin films annealed at various temperatures and in different atmospheres were studied. The near infrared (NIR) luminescence depended strongly on the annealing atmosphere and temperature. To reveal the origin of the NIR luminescence, we performed comprehensive PL studies including steady state and time-resolved PL measurements at 8–300 K in wide excitation (250–500 nm) and detection (400–1550 nm) wavelength ranges. It was revealed that multiple Bi luminescence centers, such as Bi^{3+}, Bi^{2+}, Bi^{+}, and Bi dimer, are stabilized in porous silica. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4815939]

I. INTRODUCTION

With the rapid development of computer networks and data-transmitting services, broadband amplifiers and tunable lasers operating in the wavelength range covering the whole optical telecommunication window (1250–1650 nm) have been required. The gain bandwidth of traditional rare earth doped fiber amplifiers is less then 100 nm, due to the restriction of the f-f transition.[1,2] Recently, ultra-broadband near infrared (NIR) emissions from Bi-doped materials have been developed using various host materials.[3–11] Bi-doped optical fiber amplifiers were reported and a broadband and an efficient optical amplification covering the 1.2–1.6 μm region were demonstrated.[12–14] However, the involved luminescence mechanisms and the nature of the Bi NIR emission still remain controversial.

For many years, it is believed that addition of extra elements such as Al is indispensable to obtain NIR emission from Bi-doped bulk glasses.[4,5,12] However, Razdobreev *et al.* recently demonstrated that Bi doped pure silica glass can exhibit NIR luminescence when the silica glass is porous.[8] Furthermore, we have also found that Bi doped oxidized porous Si shows NIR luminescence without additional elements.[15] Oxidized porous Si is a promising material as a host for different kinds of optical centers. Especially, during the past years, Er-doped oxidized porous Si waveguide type amplifiers have been studied and they are considered to be promising for integrated optical filters, amplifiers/modulators, light-emitting diodes, and other optoelectronic devices.[16–18] The broadband NIR luminescence from Bi-doped oxidized porous silica may pave the way for the development of broadband waveguide type optical amplifiers operating in the NIR range. However, the research on Bi-doped oxidized porous silica is still limited and the relation between preparation parameters and photoluminescence (PL) properties is not fully clarified. Furthermore, the origin of the NIR PL is not fully elucidated.

In this paper, we perform comprehensive PL studies of Bi-doped oxidized porous silica thin films annealed in different atmospheres at different temperatures in wide excitation (250–500 nm) and detection (400–1550 nm) wavelength ranges. We also study the temperature dependence of the NIR PL spectra and the lifetime for the NIR PL bands. Based on these results, it is shown that the temperature quenching of the NIR PL is very small, and two different kinds of Bi NIR active centers (Bi^{+} and Bi dimer) co-exist in the Bi-doped porous silica. The ultra-broadband of the NIR luminescence with the lifetime of few hundreds microseconds suggests that the porous Si thin film is a promising material for a Si based waveguide type optical amplifier at optical telecommunication wavelengths.

II. EXPERIMENT

(100) oriented p-type Si wafers with the resistivity of 20 mΩ cm were used as initial substrates for the preparation of porous Si. Porous Si monolayers were prepared by electrochemical anodization in the mixture of hydrofluoric acid (HF) (46 wt. % in water) solution and ethanol (HF:ethanol = 1:1) with the anodic current density of 70 mA/cm^2. At the end of the etching process, a high current pulse (300 mA/cm^2, 1.6 s) was applied to detach the porous Si layer from the substrate. The porosity of the porous Si estimated from the effective refractive index is about 58%.[15,19,20] Porous silica thin films were obtained by oxidizing porous Si at 1000 °C for 1 h in air. For Bi doping, porous silica thin films were soaked in aqueous solution of $Bi(NO_3)_3{\cdot}5H_2O$ for 48 h at room temperature. The pH value of the solution was controlled to be about 3.0 by adding HNO_3 to increase the solubility of $Bi(NO_3)_3{\cdot}5H_2O$. The concentration of $Bi(NO_3)_3{\cdot}5H_2O$ in aqueous solution is 1.5 mM/l. For the activation of Bi, the samples were annealed in air or N_2 gas at the temperatures ranging from 1000 to 1300 °C. Bi concentration in the final products was

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below the detection limit of energy-dispersive x-ray spectroscopy (EDS) measurements (∼0.1 at. %).

NIR PL spectra were measured by using a single grating monochromator equipped with a liquid-nitrogen-cooled InGaAs diode array. Samples were excited at 488 nm using an Ar ion laser. Three dimensional (3D) mappings of the PL intensity versus excitation and emission wavelengths was measured by the spectrophotometer (Horiba Jobin Yvon, Flourolog) equipped with a photomultiplier and an InGaAs photodiode as detectors and a Xe lamp (450 MW) as an excitation source in wide excitation (250–500 nm), and detection (400–1550 nm) wavelength ranges. For all the PL measurements, the spectral response of the detection system was corrected by the reference spectrum of a standard tungsten lamp. The decay time measurements were performed by detecting the modulated luminescence signal with a photomultiplier tube (Hamamatsu, R5509-72), and the signal was analyzed with a photon-counting multichannel scaler. The excitation source for the decay measurements was 488 nm light from an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser. The measurements of NIR PL and decay time were performed in the temperature range of 8–300 K.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows a 3D mapping of the visible to NIR PL intensity of the sample annealed at 1300 °C in N_2 gas. The ordinate is the excitation wavelength and the abscissa is the emission wavelength. Three PL emission bands, one in the visible range and two in the NIR range, can be seen. For the PL emission band around 606 nm, the PL excitation bands appear around 352 and 475 nm. For the NIR PL emission band around 845 and 1410 nm, two PL excitation (PLE) bands are seen around 374 and 420 nm. The PL emission bands around 845 and 1410 nm are similar to those observed for Bi doped pure silica glass fiber preform.[8,13]

In contrast to the sample annealed in N_2 gas, the sample annealed in air at 1300 °C did not show NIR PL (Figure 1(b)). It exhibits a PL emission band around 530 nm with a PL excitation band around 290 nm. Bi-related luminescence is known to be very sensitive to the annealing atmosphere. Recently, Bi doped alkali borosilicate porous silica glass annealed in various atmosphere including oxygen, argon, and hydrogen gases has been reported.[9] It revealed that only the glass annealed in oxygen did not exhibit NIR luminescence. The present results are thus consistent with those in the previous reports.[7,9,21]

For more detailed analysis, normalized PL spectra of the sample annealed in N_2 excited at various wavelengths are shown in Figure 1(c). For comparison, PL spectrum of the sample annealed in air (orange) is also shown. When excitation wavelengths are shorter than 300 nm, both samples show broad PL around 530 nm. The PL and the PL excitation features shown in Figure 1(b) are very similar to those of Bi doped germinate glass and it is in general assigned to Bi^{3+}.[22]

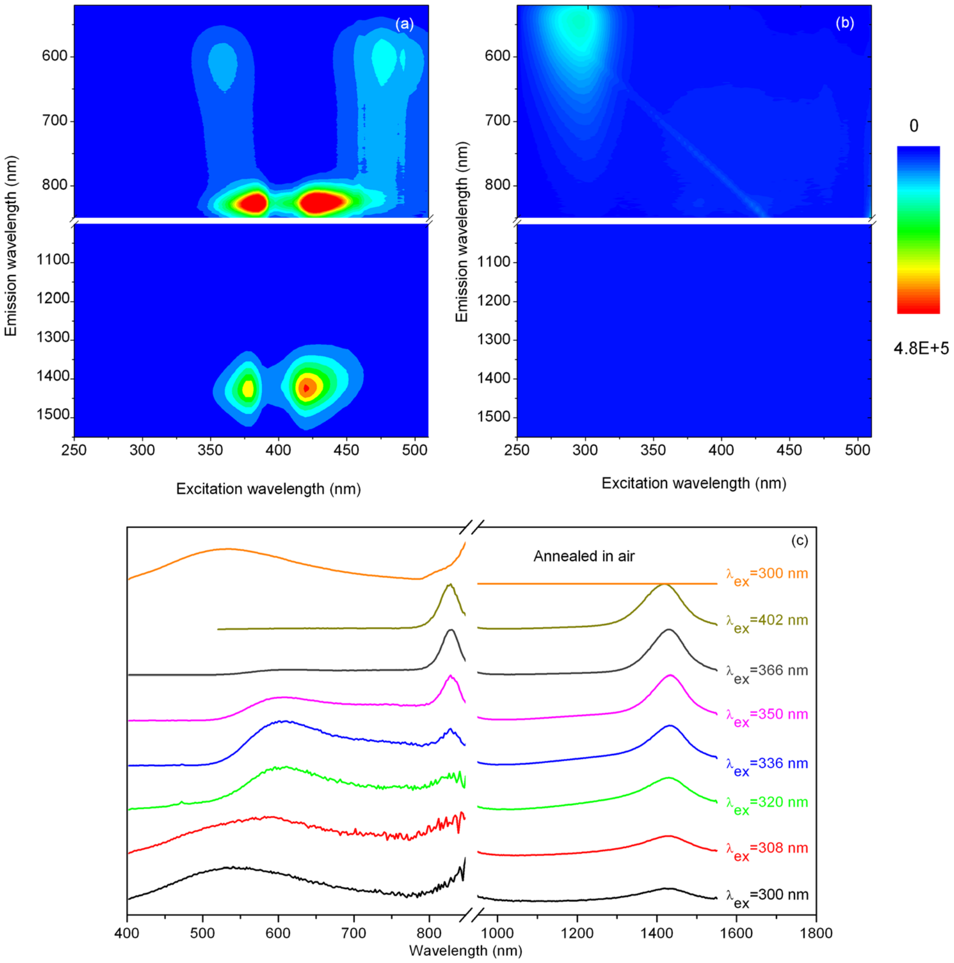

FIG. 1. (a) and (b) are the 3D plots of the PL intensity versus excitation and emission wavelengths of Bi doped porous silica annealed in N_2 and air. (c) Normalized visible to NIR PL spectra of Bi doped porous silica under the various excitation wavelengths.

When the excitation wavelength is 320 nm, a PL peak appears around 606 nm for the sample annealed in N_2 gas. In Figure 1(a), we can see the PL excitation bands around 352 and 475 nm for the PL emission band at 606 nm. This orange emission has been reported for various materials, e.g., SrB_4O_7, and is usually assigned to Bi^{2+}.[23] In addition to these visible PL assigned to Bi^{3+} and Bi^{2+}, the sample annealed in N_2 at 1300 °C exhibits NIR PL around 845 and 1410 nm. These PL emission bands have similar excitation bands around 374 and 420 nm.

To elucidate the mechanism of NIR luminescence, we measured the excitation wavelength dependence of the PL intensity as shown in Figure 2. At the emission wavelength of 1150 nm, we can see two broad PL excitation bands at 500 and 700 nm. This is very similar to those of Bi^+ in multi-component glasses.[5–7,9] On the other hand, at the emission wavelengths of 850 nm and 1450 nm, sharp PL excitation bands at about 374 and 420 nm were observed. These bands are similar to the absorption bands in Bi doped porous silica glass.[8] Very recently, the similar absorption bands were reported in crystals and glasses, in which the absorption was ascribed to Bi dimer.[24,25] Thus, Bi dimer can be considered to be the origin of the PL emission bands at 850 nm and 1450 nm. It should be noted that pure porous silica has been reported to exhibit a PL band around 845 nm with the full width with half maximum of about 150 nm.[26–28] This is very similar to that observed in this work. However, the PL properties of pure porous silica are much different from those of Bi-doped porous silica. Our previous work revealed that the PL intensity of pure porous silica is more than 300 times weaker than that of Bi doped porous silica.[15] In addition, the shape and peak position of the PL from the Bi active center is very insensitive to oxidization conditions of porous silicon. This is in a sharp contrast with that the peak position of PL from porous silica strongly depends on the oxidation condition.[26,28] Thus, the origin of the PL at 845 nm can be ascribed to Bi NIR active center.

Figure 3(a) shows the PL spectra of Bi-doped porous silica annealed in N_2 from 1100 to 1300 °C. The excitation wavelength is 488 nm. We can see two broad PL bands. Both PL bands are strongest when the annealing temperature (Ta.) is 1200 °C. The full width at half maximum of the long wavelength side PL spectra at 1410 nm (annealing temperature is 1300 °C) is comparable to those reported for Bi-doped multi-component bulk glasses.[5,9] Figures 3(b) and 3(c) are the normalized spectra of the two PL bands. It is interesting that the shape of the shorter wavelength PL peak around 850 nm is independent of the annealing temperature, while that the longer wavelength PL peak shifts from 1310 to 1410 nm with increasing the annealing temperature. This result suggests that the PL intensity of Bi^+ (at around 1270 nm) decreases while that of Bi dimer (at around 1420 nm) increases with increasing the annealing temperature. This implies that Bi ions aggregate and becomes Bi dimer when the annealing temperature is high.

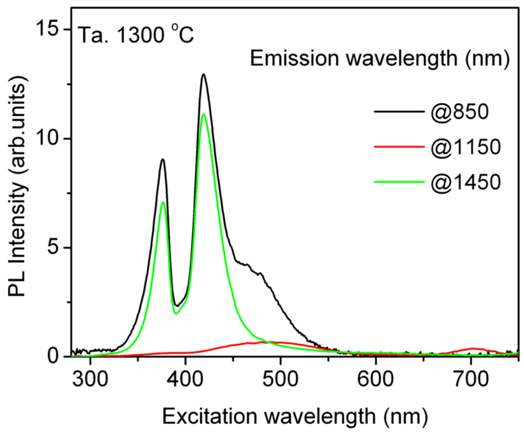

FIG. 2. Excitation wavelengths dependence of PL intensity of the sample annealed in N_2 at 1300 °C. Scale up the intensity of PL for 1150 nm.

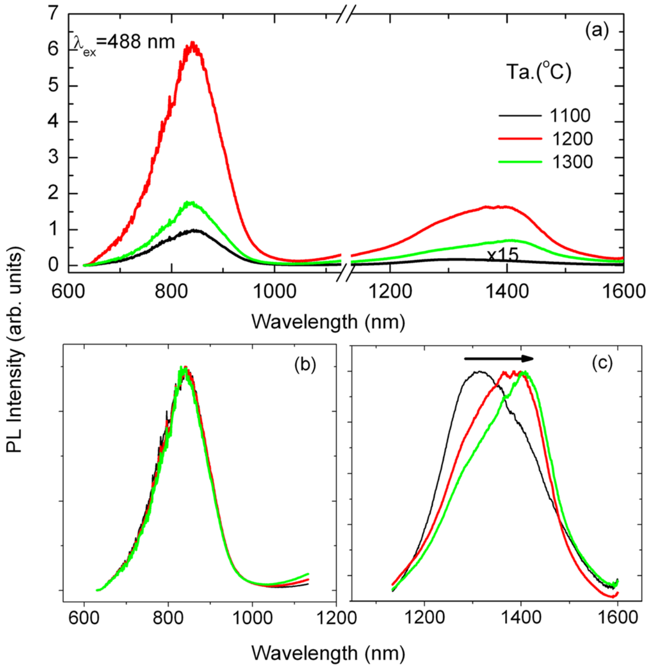

FIG. 3. (a) NIR PL spectra of the sample at various annealing temperatures 1100–1300 °C in N_2 gas. (b) and (c) are the normalized spectra of NIR PL bands.

In order to clarify the valence state of Bi, the X-ray photoelectron spectroscopy (XPS) spectra were measured. Figure 4 shows the XPS spectra of Bi-doped porous silica annealed in N_2 from 1100 to 1300 °C. The samples show Si^{4+} (2s) peak and Bi^{3+} ($4f_{7/2}$) peak, which reveals that 3+ is the dominant valence state of Bi in these samples. Other valence states of Bi were under the detection limit. Unfortunately, due to the low Bi concentration, it is difficult to obtain more information on the valence states of Bi active centers. The XPS intensity of Bi^{3+} peak decreases with increasing the annealing temperature. This is probably due to the evaporation of Bi during the annealing at high temperatures.[7] As shown in Figure 3(a), the PL intensity at 845 and 1450 nm of our samples is the strongest when the annealing temperature is 1200 °C. Probably, this optimum annealing temperature is determined by the trade-off between the activation rate of Bi NIR active centers and evaporation of Bi during the high temperature annealing.

For further study of the NIR PL properties, the NIR PL spectra of the sample annealed at 1300 °C in N_2 atmosphere was measured as a function of temperature. Figure 5(a)

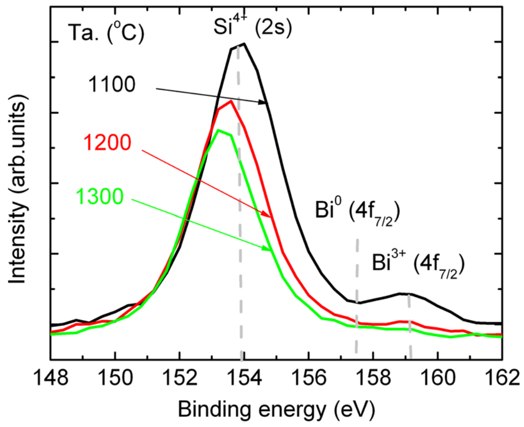

FIG. 4. XPS spectra of Bi doped porous silica annealed in N_2 from 1100 to 1300 °C.

shows the results. For all the temperatures, we can see broad NIR PL spectra. The PL spectra can be decomposed into two Gaussian bands centered at 1270 and 1425 nm. The temperature dependence of the PL intensities of the two PL bands is shown in Figure 5(b). Both the PL intensities first increases and then decreases. Qualitatively similar results were reported in a previous work on the NIR PL from $Bi_4Ge_3O_{12}$ crystal.[29] In that work, the PL intensity increased as the temperature increases from 8 to 100 K, then the intensity dropped by 90% as the temperature raised to 300 K. On the other hand, in our present work, it drops by only 40%. This small temperature quenching is a promising feature for applications such as optical amplifiers at optical telecommunication wavelengths.

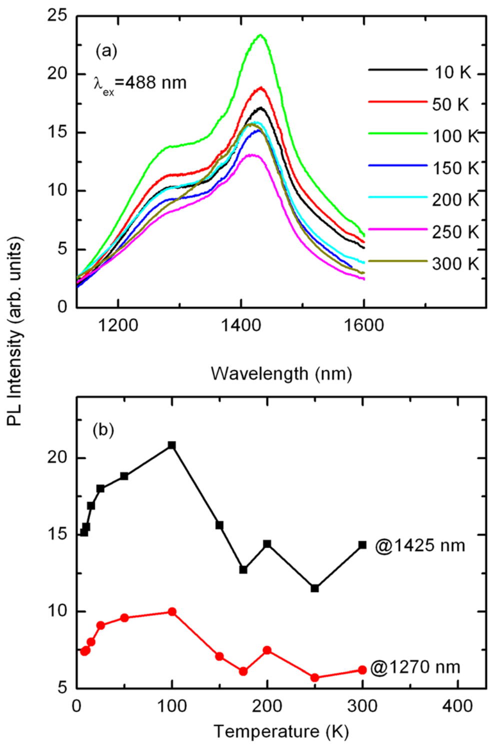

FIG. 5. (a) NIR PL spectra upon photo-excitation with a wavelength of 488 nm at various temperatures 10–300 K of the sample annealed in N_2 at 1300 °C. (b) Temperature dependence of integrated intensity of the two Gaussian peaks at 1270 and 1420 nm in (a).

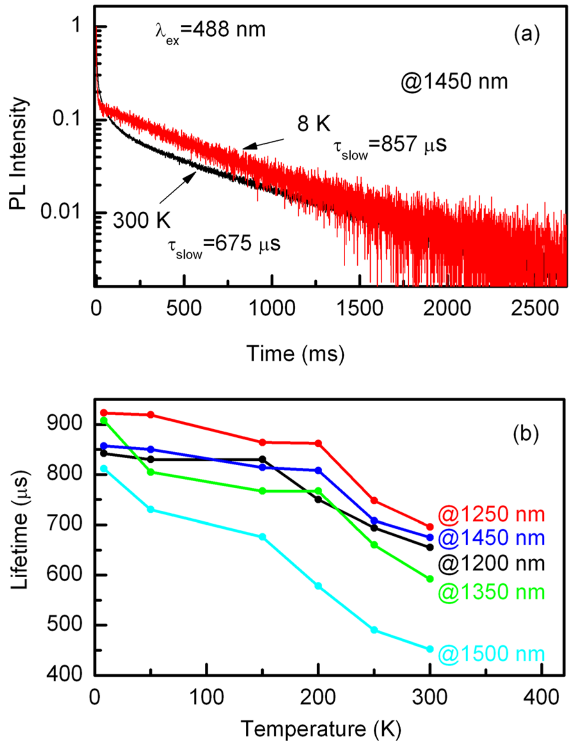

FIG. 6. (a) Decay curves of the sample annealed in N_2 at 1300 °C measured at 8 and 300 k, detection and excitation wavelengths are 1450 and 488 nm, respectively. (b) Temperature dependence of slow component's lifetimes at various detection wavelengths under the excitation wavelength of 488 nm.

To draw more information from the NIR PL properties, time resolved PL is measured as a function of temperature. Figure 6(a) shows decay curves of the sample annealed in N_2 at 1300 °C measured at 8 and 300 K. The detection and excitation wavelengths are 1450 and 488 nm, respectively. The PL decay curves consist of two components, i.e., fast and slow components. The lifetime of the fast components is shorter than 4 μs, which is independent on the detection wavelengths (data were not shown). This component probably arises from defects in porous silica. The lifetime of the slow component at room temperature is 675 μs, which is comparable to those reported for Bi doped glasses and crystals.[3–9] The lifetime increases to 857 μs at low temperature (8 K). In Figure 6(b), the lifetime of the slow component is plotted as a function of the temperature at various detection wavelengths (1200–1550 nm). At all the detection wavelengths, the lifetime decreases gradually with increasing the temperature. The decrease in the lifetime in the temperature range from 8 K to 300 K was about 30%. This value is much smaller than that of $Bi_4Ge_3O_{12}$ crystal, which has been reported to be about 90%.[29] The observed small temperature dependence of the lifetime is consistent with the small temperature quenching of the PL.

IV. CONCLUSION

Bi doped porous silica thin films were annealed at various temperatures in air or N_2 gas atmosphere. NIR PL of these samples was measured as a function of excitation wavelengths. It was found that the annealing in N_2 is necessary for the activating NIR emission from Bi in pure porous silica thin films. The multiple Bi centers would be stabilized in various forms as Bi^{3+}, Bi^{2+}, Bi^{+}, and Bi dimer. Robustness of NIR PL intensity against temperature is shown by measuring the steady state and time-resolved PL at 8 to 300 K.

ACKNOWLEDGMENTS

This work was partly supported by KAKENHI (23310077).

[1] D. Hashimoto and K. Shimizu, J. Opt. Soc. Am. B **28**, 2227 (2011).

[2] J. Wang, E. Vogel, E. Snitzer, J. Jackel, V. da Silva, and Y. Silberberg, J. Non-Cryst. Solids **178**, 109 (1994).

[3] Y. Fujimoto and M. Nakatsuka, Jpn. J. Appl. Phys., Part 2 **40**, L279 (2001).

[4] V. Sokolov, V. Plotnichenko, and E. Dianov, Opt. Lett. **33**, 1488 (2008).

[5] X. Meng, J. Qiu, M. Peng, D. Chen, Q. Zhao, X. Jiang, and C. Zhu, Opt. Express **13**, 1635 (2005).

[6] M. Peng, D. Chen, J. Qiu, X. Jiang, and C. Zhu, Opt. Mater. **29**, 556 (2007).

[7] H. Sun, A. Hosokawa, Y. Miwa, F. Shimaoka, M. Fujii, M. Mizuhata, S. Hayashi, and S. Deki, Adv. Mater. **21**, 3694 (2009).

[8] I. Razdobreev, H. EI Hamzaoui, V. Yu. Ivanov, E. F. Kustov, B. Capoen, and M. Bouazaoui, Opt. Express **35**, 1341 (2010).

[9] S. Zhou, N. Jiang, B. Zhu, H. Yang, S. Ye, G. Lakshminarayana, J. Hao, and J. Qiu, Adv. Funct. Mater. **18**, 1407 (2008).

[10] H. Sun, T. Yonezawa, M. M. Gillet-Kunnath, Y. Sakka, N. Shirahata, Sa chu rong gui, M. Fujii, and S. C. Sevov, J. Mater. Chem. **22**, 20175 (2012).

[11] R. Cao, M. Peng, L. Wondraczek, and J. Qiu, Opt. Express **20**, 2562 (2012).

[12] Y. Fujimoto and M. Nakatsuka, Appl. Phys. Lett. **82**, 3325 (2003).

[13] I. Razdobreev, L. Bigot, V. Pureur, A. Favre, G. Bouwmans, and M. Douay, Appl. Phys. Lett. **90**, 031103-1 (2007).

[14] Y. Arai, T. Suzuki, and Y. Ohishi, Appl. Phys. Lett. **90**, 261110 (2007).

[15] Sa chu rong gui, K. Imakita, M. Fujii, Z. Bai, and S. Hayashi, Opt. Mater. **34**, 1161 (2012).

[16] M. Balucani, V. Bondarenko, G. Lamedica, A. Ferrari, L. Dolgyi, N. Vorozov,V. Yakovtseva, S. Volchek, V. Petrovich, and N. Kazuchits, Thin Solid Films **396**, 202 (2001).

[17] E. Teo, A. Bettiol, P. Yang, M. Breese, G. Mashanovich, W. Headley, and G. Reed, Opt. Lett. **34**, 659 (2009).

[18] L. Luo, X. Zhang, K. Li, K. Cheah, J. Shi, W. Wong, and M. Gong, Adv. Mater. **16**, 1664 (2004).

[19] N. Ishikura, M. Fujii, K. Nishida, S. Hayashi, and J. Diener, Opt. Express **16**, 15531 (2008).

[20] L. Meng, C. MoreiradeSa, and M. Santos, Thin Solid Films **239**, 117 (1994).

[21] V. Truong, L. Bigot, A. Lerouge, M. Douay, and I. Razdobreev, Appl. Phys. Lett. **92**, 041908 (2008).

[22] G. Boulon, B. Moine, and J. Bourcet, Phys. Rev. B **22**, 1163 (1980).

[23] G. Blasse, A. Meuerink, M. Nommes, and J. Zuidema, J. Phys. Chem. Solids **55**, 171 (1994).

[24] L. Su, H. Li, L. Zheng, X. Fan, X. Jiang, H. Tang, G. Ren, J. Xu, W. Ryba-Romanowski, R. Lisiecki, and P. Solarz, Opt. Mater. Express **2**, 757 (2012).

[25] V. Sokolov, V. Plotnichenko, V. Koltashov, and E. Dianow, J. Phys. D: Appl. Phys. **42**, 095410 (2009).

[26] J. C. Vial, S. Billat, A. Bsiesy, G. Fishman, F. Gaspared, R. Herino, M. Ligeon, F. madeore, I. Mihalcescu, F. Muller, and R. Romestain, Physica B **185**, 593 (1993).

[27] D. Xu, G. Guo, L. Gui, and Y. Tang, J. Phys. Chem. B **103**, 5468 (1999).

[28] T. Nakamura, T. Ogawa, N. Hosoya, and S. Adachi, J. Lumin. **130**, 682 (2010).

[29] P. Yu, L. Su, Q. Wang, H. Zhao, X. Guo, Q. Yang, and J. Xu, Nucl. Instrum. Methods Phys. Res. A **631**, 40 (2011).