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Broadband near-infrared emission from bismuth-doped multilayer filmsSatoshi Morimoto,¹ Minoru Fujii,^{1,a)} Hong-Tao Sun,^{2,b)} Yuji Miwa,¹ Kenji Imakita,¹ Jianrong Qiu,³ and Shinji Hayashi¹¹Department of Electrical and Electronic Engineering, Graduate School of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan²International Center for Young Scientists, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan³Institute of Optical Communication Materials, South China University of Technology, Guangzhou 510640, China

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Multilayer structures consisting of bismuth (Bi)-doped silica thin films and different kinds of spacer, i.e., Si, silica, Si-rich silica, layers are grown and the luminescence properties are studied. When samples were annealed at a low temperature, Bi-related near infrared active centers (BRACs) were formed at interfaces between Bi-doped silica and Si-rich silica (or silicon) due to the reduction of Bi³⁺ to BRACs by silicon. On the other hand, films annealed at a high temperature showed similar emission behaviors to bulk glasses. The results demonstrated here establish a new strategy for the control of BRACs and building peculiar Bi activated film structures. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4757579>]

I. INTRODUCTION

Bi, with the electronic configuration of (Xe)4f¹⁴5d¹⁰6s²6p³, is one of the most thoroughly investigated main group elements, which has been known as “the wonder metal” owing to the easy involvement in chemical combinations for the electrons in its p orbital.¹ Bi shows a variety of oxidation states such as 0, +1, +2, +3, +5, or even states between 0 and 1, characterized by multi-type electronic structures. Furthermore, it shows a profound propensity to form clusters, which widely exist in molten Lewis acids and molecular crystals.^{1–4} These peculiarities make them as smart optically active centers in diverse host materials. For instance, the emission peaks of Bi²⁺ occurs in the visible range^{5–7} and those of Bi³⁺ in the ultraviolet and visible ranges.^{8,9} It is noteworthy that the subvalent species, of which the average oxidation states are +1 or between 0 and +1, could show smart photophysical behaviors.^{3,4} The reports of the synthesis and photophysical properties of subvalent bismuth date back to half a century ago.^{10,11} However, only in recent years Bi doped materials have been attracting significant attention to achieve broadband near-infrared (NIR) optical amplification in the whole telecommunication window^{12–21} and to realize *in vivo* bioimaging in the optimal biological window,²² although the exact emission mechanisms are still not clear in most material systems owing to the unsuccessful establishment of the structure-property relationships. In contrast to the applications described above, the research on Bi-doped thin films is very limited. Development of NIR luminescent Bi-doped silica thin films allows us to realize waveguide-type broadband optical amplifiers, which can be integrated in Si-based optoelectronic devices.

In a previous work, we demonstrated the growth of thin films consisting of Bi doped multicomponent glass layers and Si-rich silica layers.²³ Very recently, we found that doping of excess Si in Bi-doped pure silica thin films results in efficient NIR photoluminescence (PL).²⁴ Simplicity of Bi-doped Si-rich silica thin films in their compositions, i.e., only Si, Bi, and O, makes it easier to be integrated in Si-based optoelectronic devices. One of the advantages of this system over other Bi doped bulk glasses or fibers is that we could easily tune the excitation/emission behaviors through adjusting Si concentrations and annealing temperatures. We observed that NIR emissions of some films increase monotonously with increasing excitation energy, which suggests that low-cost optical sources such as LEDs can be used as the excitation sources. Further systematic investigation of this material system is of importance not only for maximizing the luminescence efficiency, but also for understanding the formation mechanism of Bi related NIR active centers (BRACs).

In this work, we develop a new structure which consists of thin layers of Bi-doped pure silica and spacer. We found that the interface between Bi-doped pure silica films and spacer films plays an important role in the formation of BRACs. By comparing luminescence properties of samples with different kinds of spacer materials, we investigated possible luminescence mechanism.

II. EXPERIMENTAL PROCEDURE

The structure of the samples is schematically shown in Figure 1. Bi-doped silica layers (6 nm in thickness) and spacer layers (3 nm in thickness) were alternatively sputter-deposited on fused quartz substrates. Bi-doped silica layers are deposited by simultaneously sputtering SiO₂ and Bi-doped silica glass (Bi₂O₃:SiO₂ = 50:50 mol. %) targets.²⁴ As the spacer layer, three different materials, i.e., Si-rich silica (Si:SiO₂ = 16.4:83.6 mol. %), Si, and silica are used. The

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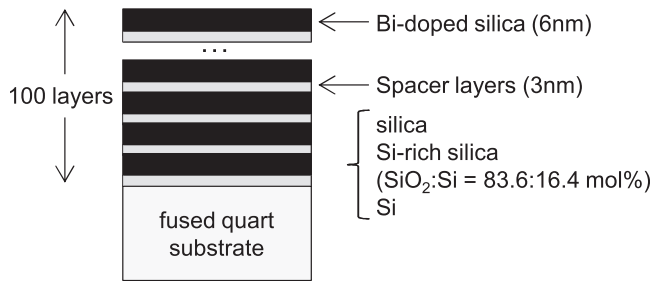


FIG. 1. Schematic illustration of the sample structure. Bi-doped silica (6 nm) and spacer (3 nm) layers are alternatively deposited on fused quartz substrates. The spacer layers are sputter-deposited Si, silica or Si rich silica.

deposition process was repeated until the total number of Bi-layers reaches 100. The total thickness of deposited layer is 300 nm. The as-deposited films were amorphous. The films were then annealed in N₂ gas at 1100 or 1300 °C for 30 min. With these annealing conditions, Si nanoclusters are grown in films.²⁴

For PL and PL excitation (PLE) measurements, several light sources, i.e., He-Cd laser (325.0 nm), Ar ion laser (457.9, 476.5, 488.0, 496.5, 501.7, and 514.5 nm), Ti:sapphire laser (700–800 nm), and diode lasers (403 and 641 nm) were used as the excitation sources. The PL was detected by a liquid N₂ cooled InGaAs diode array (Roper Scientific: OMA-V-SE). The spectral response of the detection system was corrected with a reference spectrum of a standard halogen lamp. Photoluminescence decay curves were measured using a near infrared photomultiplier tube (R5509-72, Hamamatsu Photonics) and a multi-channel scaler (SR430, Stanford Research). All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the PL spectra of the Bi-doped silica multilayer films with spacer layers composed of three different materials. All samples were annealed at 1100 °C. As a reference, the spectrum of a Bi-doped Si-rich silica single layer film with a thickness of 300 nm is shown.²⁴ Note that the thickness of the single layer sample is the same as the

total thickness of Bi-doped silica layers in multilayer samples (6 nm × 50). The single layer sample shows a broad PL peak around 1100 nm, which can be attributed to BRACs.²⁴ In the multilayer samples, the spectra depend strongly on the spacer materials. It is found that when the spacer layer is pure silica (Bi-doped silica (BDS)/silica in Fig. 2(a)), the sample does not show any emission, indicating that BRACs are not activated in Bi-doped silica. On the other hand, when the spacer layer is Si-rich silica (Bi-doped silica/Si-rich silica (BDS/SRS)), a broad emission originating from BRACs occurs. Since Bi is not doped in the Si-rich silica layer, BRACs are considered to be activated at the interface between Bi-doped silica and Si-rich silica. Probably, excess Si in Si-rich silica acts as reducing agents to convert Bi³⁺ into BRACs at the interface. When the spacer layer is Si (BDS/Si), a broad and weak emission apparently different from BRACs is observed around 950 nm. It should be stressed here that, without Bi doping, Si nanoclusters do not show PL around 1100 nm.

Figure 2(b) shows PL spectra of the samples annealed at 1300 °C. When the spacer layer is pure silica, the PL is again not observed. Other three samples exhibit PL with the maximum around 1150 nm. The spectral shape of the sample with the Si-rich silica spacer is very similar to that of the Bi-doped Si-rich silica single layer. When the spacer layer is Si, in contrast to the sample annealed at 1100 °C, Bi-related PL can clearly be observed at 1150 nm in addition to an unknown PL around 1000 nm. The result of decomposition of the spectrum into two Gaussian components is shown in Fig. 2(b) by dotted curves. The intensity of the 1150 nm PL estimated after the decomposition is comparable to that of the Bi-doped Si-rich silica single layer. When the annealing temperature is 1300 °C, the multilayer structure is considered to be almost destroyed. The difference in the spacer layers in BDS/SRS and BDS/Si systems appears as different amounts of excess Si in the whole films. Probably, the total amount of excess Si in the sample with the Si-rich silica spacer layer is not enough to activate all Bi ions into BRACs, resulting in a weaker PL intensity than other samples.

Figure 3(a) shows PL decay curves of the Bi-doped Si-rich silica single layer sample and the multilayer sample

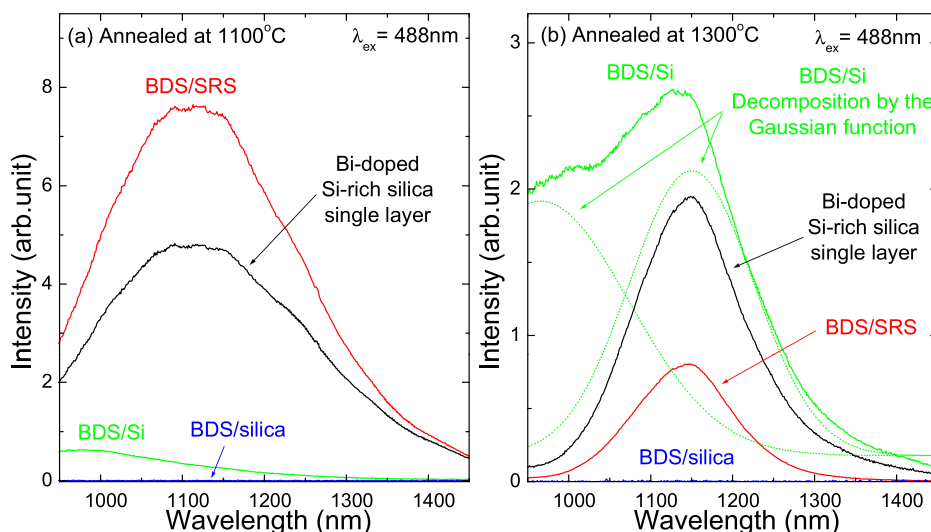


FIG. 2. PL spectra of BDS/SRS, BDS/Si, and BDS/silica multilayer samples, and Bi-doped Si-rich silica single layer sample annealed at (a) 1100 and (b) 1300 °C. The dotted curves in (b) are the result of decomposition of the spectrum of the BDS/Si sample into two Gaussian functions.

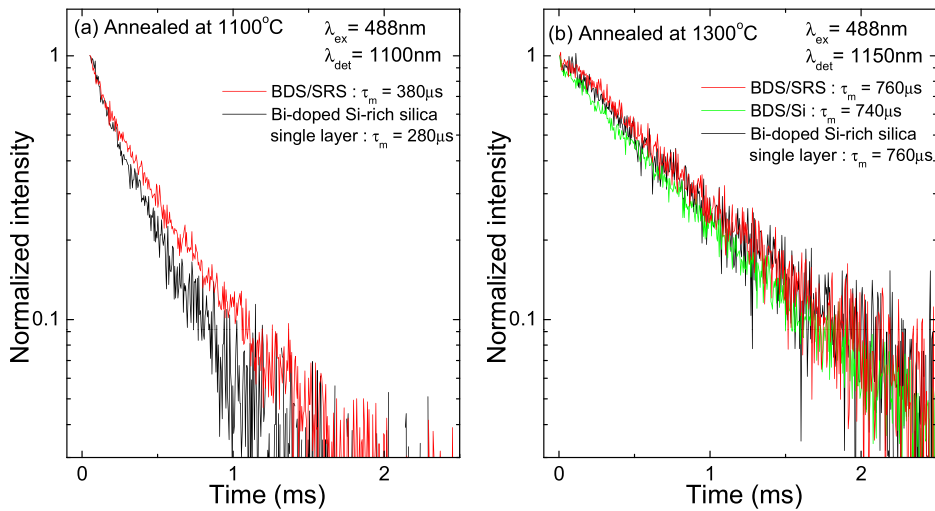


FIG. 3. (a) PL decay curves of BDS/SRS multilayer and Bi-doped Si-rich silica single layer samples annealed at 1100 °C. The excitation wavelength is 488 nm and the detection wavelength is 1100 nm. (b) PL decay curves of BDS/SRS and BDS/Si multilayer samples and Bi-doped Si-rich silica single layer sample annealed at 1300 °C. The detection wavelength is 1150 nm. The decay times estimated by fitting the curves by stretched exponential functions are shown in the figure.

with Si-rich silica spacer annealed at 1100 °C. The excitation and detection wavelengths are 488 and 1100 nm, respectively. The decay curves are not a single exponential function, suggesting that the local environment of BRACs is distributed in a wide range. The PL mean lifetimes (τ_m) are calculated from following equation, $\tau_m = \int_0^{\infty} [I(t)/I_0]d(t)$, where $I(t)$ is the luminescence intensity as a function of time t . I_0 is the initial intensity of $I(t)$ at t_0 . The values of τ_m are calculated as 380 μs for the multilayer sample and 280 μs for the single layer sample. The longer lifetime of the multilayer sample is consistent with the stronger PL intensity (Fig. 2(a)). When the annealing temperature is 1300 °C (Fig. 3(b)), the decay curves become single exponential. The lifetimes become longer, and exceed 700 μs for all the samples. Since this value is comparable to those of Bi-doped multi-component glasses,^{12–18,22–24} it is considered to be an intrinsic lifetime of BRACs. As we described above, the multilayer structures are almost destroyed when they were annealed at 1300 °C. The similar PL lifetimes of the samples in Fig. 3(b) indicates that the local environments of BRACs are almost identical for these samples even though the initial structure and excess Si concentrations are different. This

supports the previous conclusion that the intensity difference in Fig. 2(b) is due to different amounts of the centers.

In Figure 4(a), the intensities of the PL maxima are plotted as a function of the excitation wavelength for Bi-doped silica/Si-rich silica (BDS/SRS) multilayer and Bi-doped Si-rich silica single layer samples annealed at 1100 °C. In both cases, the spectra increase almost monotonously to shorter wavelengths, although there are small bumps around 500 and 700 nm. The broad background in Fig. 4(a) is similar to those reported for Er doped Si-rich silica.²⁵ In that case, 4f electrons of Er^{3+} are excited by the energy transfer from Si nanoclusters. The similarity in spectral shape suggests that the excitation of BRACs is also governed by indirect excitation by Si nanoclusters in Si-rich silica via energy transfer.^{23,24} Figure 4(b) shows the spectra of the samples annealed at 1300 °C. The spectra have two distinctive peaks at 500 and 700 nm due to direct absorption by BRACs, as revealed in aluminosilicate^{12,17,18,23} and aluminogermanate glasses.²¹ The contribution of the indirect absorption is very small. These results confirm that the multilayer structures are almost destroyed and Si nanoclusters were not formed in the films.

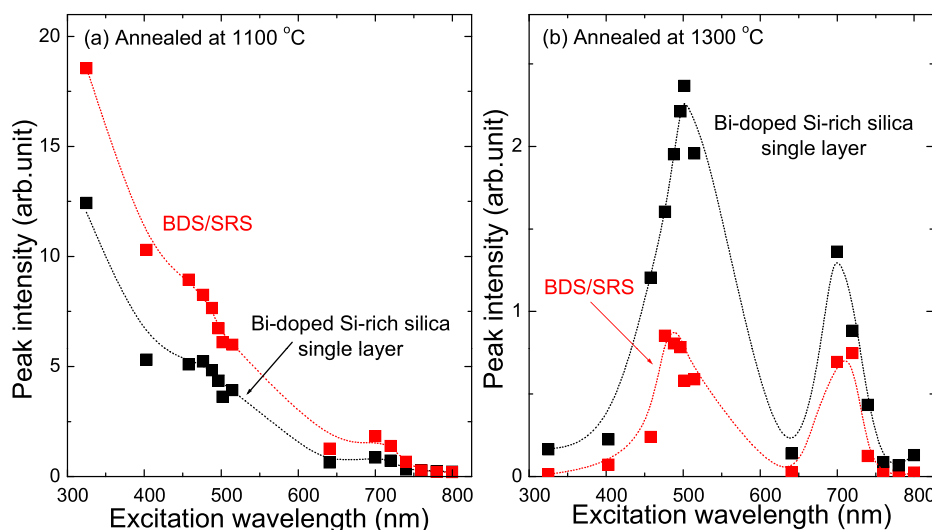


FIG. 4. PL peak intensity as a function of excitation wavelength for BDS/SRS multilayer and Bi-doped Si-rich silica single layer samples annealed at (a) 1100 and (b) 1300 °C. The curves are drawn for the guide to the eyes.

IV. CONCLUSION

We study PL properties of multilayer films consisting of Bi-doped silica and different kinds of spacer layers, i.e., Si, silica, Si-rich silica layers. We demonstrate that, when the annealing temperature is relatively low, Bi-related NIR PL is obtained only when Si-rich silica is used as a spacer. This suggests that BRACs are formed at the interface between Bi-doped silica and spacer when the amounts of Bi, Si, and O at the interface are in an optimum range. The Si-rich silica layers act also as sensitizer for the excitation of BRACs via energy transfer from Si nanoclusters. The sensitization significantly extends the excitation band of BRACs.

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