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Ultrafast nonlinear optical responses of bismuth doped silicon-rich silica films

Kenji Imakita,[1,a)] Yuya Tsuchihashi,[1] Ryo Naruiwa,[1] Minoru Fujii,[1] Hong-Tao Sun,[2] Jianrong Qiu,[3] and Shinji Hayashi[1]
[1]*Department of Electrical and Electronic Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan*
[2]*Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan*
[3]*Institute of Optical Communication Materials, South China University of Technology, Guangzhou 510640, China*

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Nonlinear optical responses of bismuth (Bi) doped silicon-rich silicon dioxide (Si-rich SiO_2) films were studied by a z-scan and an optical Kerr gate method under femtosecond excitation around 800 nm. It was found that the Bi-doping enhances the nonlinear optical response of Si-rich SiO_2 films by several orders of magnitudes. The nonlinear refractive index was of the order of 10^{-11} cm^2/W and the response time was shorter than our time resolution of 100 fs. The nonlinear refractive index was independent of the wavelength in the range from 750 to 835 nm, suggesting that virtual transitions are involved in the nonlinear optical processes. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4766269]

During past decades, silicon-rich silicon dioxide (Si-rich SiO_2) has attracted great attention.[1,2] This material, consisting of silicon quantum dots (Si-QDs) embedded in silicon dioxide (SiO_2), shows much larger nonlinear optical response in the near infrared region than that of bulk-silicon (bulk-Si), owing to their quantum and surface effects.[3,4] The response time of the optical nonlinearity is less than 100 fs, which is short enough for a future high-bit-rate optical telecommunication system.[5] Furthermore, Si-rich SiO_2 is highly compatible with conventional complementary metal oxide semiconductor (CMOS) technologies, enabling low-cost mass-productions of nonlinear photonic devices which can be hybridized with conventional electronic devices.[5]

Impurity-doping in Si-QDs is an important approach to further enhance the nonlinear optical response of Si-rich SiO_2. A localization of an electron or a hole at the impurity site can cause breakdown of the momentum conservation rules in Si-QDs, and enhances the oscillator strength of the interband transition.[6,7] Consequently, the nonlinear optical response of Si-QDs (and hence that of Si-rich SiO_2) is expected to be enhanced. In fact in our previous work, we found that the nonlinear optical response of Si-rich SiO_2 can be enhanced several times by phosphorus (P)- and/or boron (B)-doping.[8–11] The response time was found to be shorter than our time resolution of 100 fs. Thus, impurity doping is expected to be a promising tool in designing a Si-QDs-based material toward the potential application in nonlinear photonics.

In this work, we focus on bismuth (Bi) as an impurity atom. Bi is known to be a n-type impurity for bulk-Si and possesses the largest ionization energy and the smallest Bohr radius among group-V donors.[12] We demonstrate that Bi-doping dramatically enhances the nonlinear optical response of Si-rich SiO_2 and that the nonlinear optical response is faster than 100 fs. The results suggest that Bi-doping is much more effective than P- or B-doping for the enhancement of the nonlinear optical response in Si-rich SiO_2.

Bi-doped Si-rich SiO_2 was prepared by a co-sputtering method.[13] Si, SiO_2, and Bi-doped SiO_2 [$SiO_2 : Bi_2O_3 = 50 : 50$(mol%)] were simultaneously sputter-deposited in Ar gas on a quartz substrate (350 nm in thickness) by using a multi-target sputtering apparatus. The concentrations of Si, O, and Bi were controlled by changing the sputtering rates of each gun. After the deposition, the films were annealed in a N_2 gas atmosphere for 30 min at temperatures from 950 to 1250 °C. The linear refractive index in the near infrared region, measured by spectroscopic ellipsometry, strongly depends on the excess Si concentration and ranges from 1.45 to 1.63 in the present samples. The nonlinear optical responses were evaluated by a z-scan and an optical Kerr gate (OKG) methods.[11] For both measurements, the excitation source was a mode-locked Ti:sapphire femtosecond laser with the pulse width of about 100 fs and the repetition frequency of 82 MHz. The wavelength (λ) is changed from 750 to 835 nm. In the z-scan measurement, the beam waist and diffraction length determined by a knife edge method were 15 μm and 1 mm, respectively. In an OKG measurement, the laser beam was divided into a pump and a probe beams with 10:1 intensity ratio by a beam splitter. The probe beam passed through a time-delay device. The polarization of the probe beam was set to 45° with respect to that of the pump beam by a half wave plate. The pump and probe beams were focused onto the samples by a lens with 80-mm focal length. The incident angle difference between the pump and the probe beams is less than 10°. The beam waist and the diffraction length of these beams were 25 μm and 1.8 mm, respectively. Samples were placed between a half wave plate and a polarizer in a cross-Nicol configuration. The probe beam was detected by a photodiode connected to a lock-in

[a)]Author to whom correspondence should be addressed. Electronic mail: imakita@eedept.kobe-u.ac.jp.

amplifier. The linear absorption spectra were measured by conventional spectrophotometer. The contribution of Fresnel reflection loss was eliminated by using experimentally obtained reflectance spectra.

Figure 1(a) demonstrates a typical result of a closed-aperture z-scan measurement. The excess Si concentration is fixed at 13.6 mol. %, and the Bi_2O_3 concentration is changed from 0 to 1.15 mol. %. Note that the signal of the undoped sample is below our detection limit. We can see the signal increase with increasing the Bi_2O_3 concentration, suggesting that the nonlinear optical response of Si-rich SiO_2 is significantly enhanced by Bi-doping. The Bi-doped samples show symmetric signals of a valley-to-peak structure. This means that the nonlinear optical response is mainly refractive and the contribution of two photon absorption is negligible. In fact, open-aperture z-scan signals of these samples were below our detection limit. The solid curves represent results of fittings by a common model used for the analysis of a z-scan measurement.[14] The results are well-fitted by the model and thus the nonlinear refractive index (n_2) can be obtained with high accuracy. Figure 1(b) plots n_2 as a function of the Bi_2O_3 concentration. The data for the Bi_2O_3 concentration of 0 mol. % are obtained for the samples 20 times thicker than others. The excess Si concentration is fixed at 13.6 mol. % for the Bi-doped samples, and changed from 4.8 to 20.2 mol. % for the undoped samples. It is clear that n_2 increases with increasing Bi_2O_3 concentration. With reference to the undoped samples, the enhancement factor of n_2 by Bi-doping reaches a maximum of 54, indicating that Bi-doping can effectively enhance the nonlinear optical response of Si-rich SiO_2. For all the samples, no signal was detected in the open-aperture z-scan measurements. In the present experimental setup, this indicates that the two photon absorption coefficient (β) is smaller than 2×10^{-8} cm/W. The nonlinear figure of merit ($n_2/\beta\lambda$) is thus larger than 7 for the samples with the highest Bi_2O_3 concentration.

In order to obtain the information on the time response of the nonlinear optical response, we performed OKG measurements. Figure 2 represents the results. The excess Si concentration is fixed to 13.6 mol. %. The signal of the undoped sample is below our detection limit. On the other hand, we can see a signal around zero time delay for the sample with the Bi_2O_3 concentration of 1.15 mol. %. The solid curve is a result of fitting by the Lorentzian function. The signal is symmetric about the zero time delay indicating that the response time is comparable to or faster than our laser pulse width (100 fs). The inset of Fig. 2 shows a result obtained for a carbon disulfide (CS_2) reference sample. The response curve within a few picoseconds is consistent with previous reports.[16] The magnitudes of n_2 of our samples can be estimated by comparing their OKG signal amplitude with that of CS_2 using the following equation:

$$n_2^s = (I_s/I_r)^{0.5} n_2^r (L_r/L_s), \quad (1)$$

where the subscripts s and r represent the sample and the reference, I and L represent the absolute magnitude of OKG signals and the effective sample thickness, respectively.[17] Since the CS_2 sample is rather thick (1 cm), the diffraction length of the pump beam (1.8 mm) was used for L_r, assuming a collinear approximation.[18] By using 1.5×10^{-14} cm^2/W as the n_2 of CS_2,[19] the n_2 of Bi-doped Si-rich silica film was found to be 2.5×10^{-11} cm^2/W. This value is consistent with the value obtained from the z-scan measurement, implying that the optical nonlinearity observed in the z-scan and the OKG measurements arises from the same origin. The ultrafast response in the femtosecond order suggests that virtual, rather than real, transitions are responsible for the optical nonlinearity of Bi-doped Si-rich SiO_2. This is important

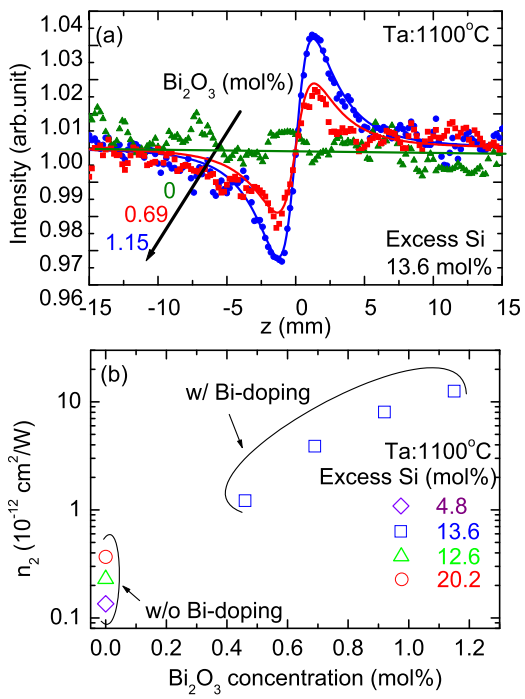

FIG. 1. (a) Bi_2O_3 concentration dependence of a closed-aperture Z-scan spectra for Bi-doped Si-rich SiO_2 films. (b)Bi_2O_3 concentration dependence of n_2 estimated from the Z-scan signals. The data for the Bi_2O_3 concentration of 0 mol. % are the same as those in our previous work on Si-rich SiO_2.[15]

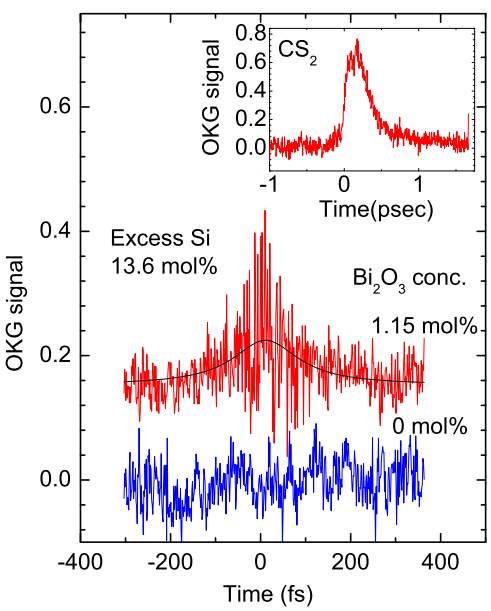

FIG. 2. The result of OKG measurements for Bi-doped and undoped Si-rich SiO_2 films. The inset shows the result for a CS_2 reference sample.

because virtual-transition-related nonlinear optical processes show the fastest response among all kinds of nonlinear optical processes. In addition, the virtual processes ensure the small wavelength dependence of the optical nonlinearity, implying that this material has potential applications in a wide range of wavelengths, including the whole telecommunication windows.

Figure 3 shows the wavelength dependence of n_2. The wavelength ranges from 750 to 835 nm. The data of the undoped sample are the same as those obtained in our previous report.[15] For all the samples, we can see very weak wavelength dependences. For example, when the Bi_2O_3 concentration is 1.15 mol. %, the wavelength dependence is only within 10% fluctuations. This small wavelength dependence indicates that the optical nonlinearity arises from virtual-transition-related processes. Thus, the large enhancement of n_2 by Bi-doping can be expected even in telecommunication wavelengths.

In order to discuss the origin of the nonlinear optical response, we investigated n_2 as a function of a wide range of sample preparation parameters. Figure 4(a) shows excess Si concentration dependences of n_2 for the samples annealed at different temperatures. The Bi_2O_3 concentration is fixed at 0.7 mol. %. With increasing the excess Si concentration, n_2 increases, while it does not depend strongly on the annealing temperature. When the excess Si concentration was zero, the z-scan signals were below our detection limit. Figure 4(b) shows Bi_2O_3 concentration dependences of n_2 for the samples annealed at different temperatures. The excess Si concentration is fixed at 13.6 mol. %. With increasing the Bi_2O_3 concentration, n_2 increases systematically. For all the annealing temperatures, the signals of the undoped samples were below our detection limit. Based on these results, we can conclude that both excess Si and doped Bi play an important role in enhancing the nonlinear optical response of Bi-doped Si-rich SiO_2 films. Probably, Bi atoms modify the electronic configuration of Si-QDs and cause the enhancement of the optical nonlinearity.

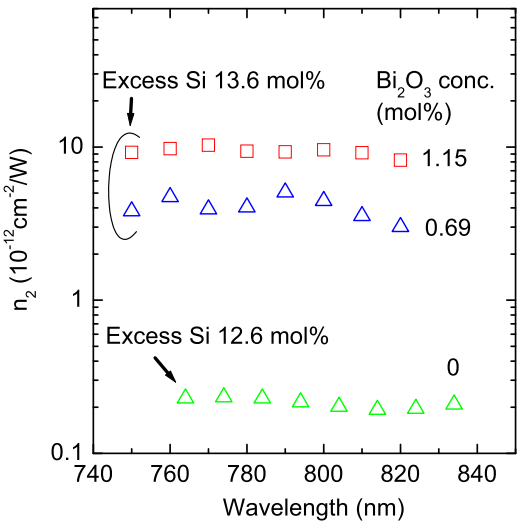

FIG. 3. Wavelength dependence of n_2 of Bi-doped Si-rich SiO_2 estimated by Z-scan measurements. Bi_2O_3 concentration is changed from 0 to 1.15 mol. %. The data for the Bi_2O_3 concentration of 0 mol. % are the same as those in our previous work on Si-rich SiO_2.[15]

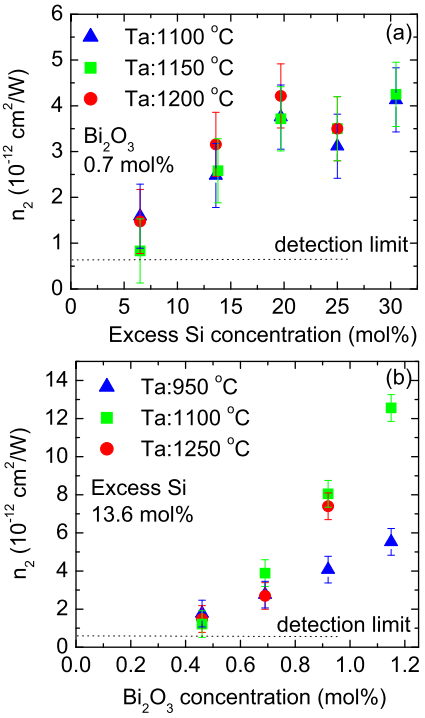

FIG. 4. (a) Excess Si concentration dependence and (b) Bi_2O_3 concentration dependence of n_2 for the samples annealed at different temperatures.

It should be mentioned here that there are two other possibilities for the enhancement of the optical nonlinearity. The first one is Bi_2O_3 in the SiO_2 matrix glass. If Bi_2O_3 is doped into the SiO_2 matrix glass, it can increase the linear refractive index of the matrix glass and consequently enhances the nonlinear optical response, according to the Miller's rule.[20] However, this possibility can be ruled out by considering the fact that n_2 of Bi_2O_3 doped glass is 2 orders of magnitude smaller than that found in the present work, despite the much higher Bi_2O_3 concentration (>50 mol. %).[21] The second possibility is the formation of Bi metal nano particles (Bi-nps). If Si acts as a reducing agent for Bi_2O_3, Bi-nps can be formed in our samples, and as a result, the nonlinear optical response can be enhanced. Indeed, Bi-nps doped glasses have been reported to show strong nonlinear optical response under femtosecond excitation at 800 nm.[22] However, in our samples, no Bi-nps were found by transmission electron microscope (TEM) observation. Probably, as discussed by Park *et al.*,[23] high temperature annealing (>900 °C) is not favorable for the formation of the Bi-nps in amorphous oxide glass because of the low melting temperature of Bi metal (~271 °C).

In fact, our samples show much different absorption spectra from those of Bi_2O_3 or Bi-nps doped glasses. Figure 5 shows the Bi_2O_3 concentration dependence of the absorption spectra. We can see that the absorption is strongly enhanced by Bi-doping in the visible region. The absorption coefficient in the visible region for the most heavily doped sample is of the order of $10^3\ cm^{-1}$, which is two orders of magnitudes larger than that of a Bi_2O_3 doped glass.[24] The absorption spectra have no distinct peaks in the ultraviolet region. This is significantly different from that of Bi-nps, which show a distinct absorption peak around 240 nm arising from the surface plasmon resonance.[23] The enhancement of

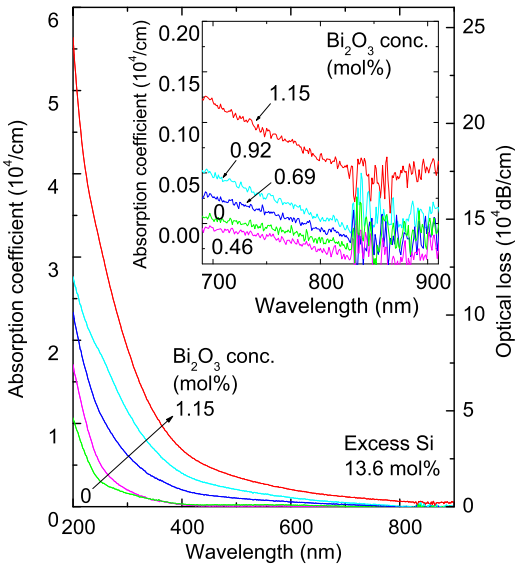

FIG. 5. (a) Bi_2O_3 concentration dependence of absorption spectra of Bi-doped Si-rich SiO_2. The inset shows the expansion around 800 nm.

the absorption by Bi-doping is also considered to originate from the modification of the electronic configuration of Si-QDs caused by Bi-doping.

It is interesting to note here that there is no clear correlation between the optical nonlinearity and the linear absorption in the present work. The inset of Fig. 5 shows the absorption spectra around 800 nm. The absorbance of Bi-doped Si-rich SiO_2 decreases with increasing the wavelength. On the other hand, as shown in Fig. 3, the n_2 does not depend on the wavelength. This contradiction is a clear evidence for the involvement of virtual transitions in the nonlinear optical processes of this material.

In conclusion, we have succeeded in observing a major enhancement of ultrafast nonlinear optical response of Si-rich SiO_2 by Bi-doping. The enhancement factor of n_2 by Bi-doping reaches 54. The response time was shorter than our time resolution of 100 fs. n_2 was shown to be independent of the wavelength in the range from 750 to 835 nm. These results indicate that Bi-doping is a promising approach in designing a Si-QDs-based material toward the application in nonlinear photonics.

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