APPLIED PHYSICS LETTERS VOLUME 85, NUMBER 13 27 SEPTEMBER 2004

The thermo-optic effect of Si nanocrystals in silicon-rich silicon oxide thin films

Se-Young Seo,[a] Jinku Lee, and Jung H. Shin
Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejon, Korea

Eun-Seok Kang and Byeong-Soo Bae
Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejon, Korea

(Received 25 February 2004; accepted 28 July 2004)

The thermo-optic effect of Si nanocrystals in silicon-rich silicon oxide (SRSO) thin films at 1530 nm is investigated. SRSO thin films, which consist of nanocrystal Si (nc-Si) embedded inside the SiO_2 matrix, were prepared by electron-cyclotron-resonance plasma-enhanced chemical vapor deposition of SiH_4 and O_2 followed by a 30 min anneal at 1150 °C. The refractive indices of all SRSO films increased with increasing temperature, with the thermo-optic coefficient increasing from 1.0 to 6.6×10^{-5} K^{-1} as the Si content is increased from 37 to 45 at. %. The thermo-optic coeffecients of nc-Si, obtained by correcting for the volume fraction of nc-Si, also increased with increasing Si content from 1 to 2.5×10^{-4} K^{-1}. The results indicate that the thermo-optic effect of nc-Si is size-dependent, and that it must be taken into account when interpreting the luminescence data from SRSO films with high density of nc-Si. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1798395]

The quantum confinement effects in nanocrystal Si (nc-Si) can increase both the band-gap energy and the recombination probability of electron–hole pairs, inducing efficient visible luminescence even at room temperature.[1] This has led to intense investigations of nc-Si with the hope of developing a Si-based photonic material compatible with Si integration techniques.[2] By now, efficient light emitting diodes[3] as well as optical gain from nc-Si[4,5] have been reported.

Many of the investigations have focused on the luminescence properties of nc-Si. For both practical application and fundamental understanding of nc-Si, however, detailed examination of other optical properties of nc-Si is needed as well. In fact, even though many studies about optical properties of nc-Si have been done, most works have focused on the refractive indices or absorption of nc-Si in the visible range,[6,7] the thermo-optic effects (TOE) of nc-Si at infrared range, which hold the importance for optical communication, have not been investigated. The refractive index is a critical parameter that determines the operational properties of a photonic device, and knowing its dependence on temperature is crucial not only for designing photonic devices, but also to screen out spurious effects that can arise under strong excitation conditions in which the temperature profile of the sample can vary significantly. Finally, as the TOE of a material is dependent on its electronic structure, investigation of the TOE of nc-Si can serve as an independent investigation of the electronic structure of nc-Si.

This letter reports on the thermo-optic effects of silicon-rich silicon oxide (SRSO), which consist of nc-Si embedded inside a SiO_2 matrix. We find that the refractive indices of SRSO films increase as the temperature is raised from 300 to 370 K, and that the thermo-optic coefficient increases from 1 to 6.6×10^{-5} K^{-1} as the Si content is increased from 37 to 45 at. %. The thermo-optic coeffecients of nc-Si, obtained by correcting for the volume fraction of nc-Si, also increased from 1 to 2.5×10^{-4} K^{-1} with the increasing Si content, indicating that the thermo-optic effect of nc-Si is size-dependent. Finally, we discuss the implications of the result on interpreting luminescence data from SRSO.

4-μm-thick SRSO thin films with Si content of 34, 37, 42, and 45 at. % were deposited on 10-μm-thick thermal oxide by electron cyclotron resonance plasma enhanced chemical vapor deposition of SiH_4 and O_2 with Ar plasma. The film thickness and composition was determined by scanning electron microscopy and Rutherford backscattering spectroscopy. Henceforth, they will be referred to as SiXX films, with XX referring to the silicon content in at. %. After deposition, the films were annealed for 30 min at 1150 °C under Ar environment in order to precipitate nc-Si, and hydrogenated by a further 1 h anneal at 700 °C in forming gas (10% H_2 and 90% N_2) in order to passivate defects and to optimize nc-Si photoluminescence. The photoluminescence (PL) spectra were measured using the 477 nm line of an Ar laser at 200 mW pump power, a monochromator, an InGaAs:Cs photomultiplier tube, and the lock-in technique. All PL spectra were corrected for the system response and measured at room temperature. The refractive indices of SRSO films were measured using a prism coupler equipped with an autocontrolled hot stage. The temperature was varied from 300 to 370 K and a 1530 nm light from a laser diode was used as the propagation light source. The detailed measurement procedure and the schematic description of the prism coupling setup can be found in Ref. 8.

Figure 1 shows the normalized room temperature PL spectra of the films. Gaussian-shaped PL peaks in the 1.3–1.6 eV range typical of nc-Si can be observed. The sigmoidal oscillations in the PL intensity are optical artifacts due to multiple reflections. No discernible PL could be ob-

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[a] Electronic mail: seyoungseo@kaist.ac.kr

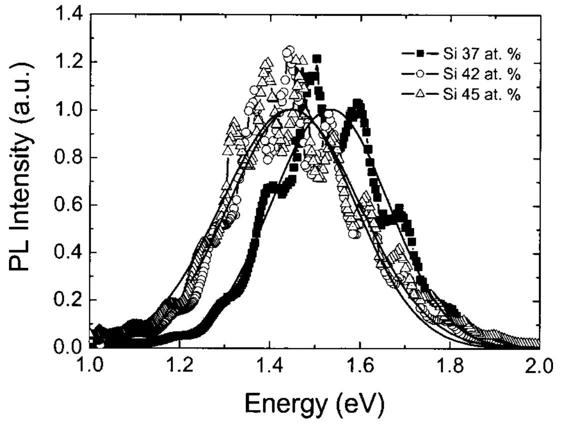

FIG. 1. Photoluminescence spectra from annealed and hydrogenated SRSO films. The symbols are the experimental data, and the solid lines are the Gaussian fits.

served from the Si34 film, and is not shown. A clear redshift of the PL peak from 1.55 to 1.4 eV with increasing Si content can also be observed, indicating increase in the nc-Si size with increasing Si content.[9]

Figure 2 shows the temperature dependence of the refractive indices of SRSO films between 300 and 370 K. The symbols are experimental data, and the lines are linear fits to the data. The refractive index of the Si34 film remains at $1.4568 \pm 5 \times 10^{-4}$ at all temperatures investigated. On the other hand, the refractive indices of Si37, Si42, and Si45 films increase with increasing temperature. The amount of the increase is dependent on the Si content. The refractive index of the Si37, Si42, and Si45 films increase from 1.6230 to 1.6237, from 1.7685 to 1.7694, and from 1.855 to 1.8605, respectively, corresponding to thermo-optic coefficients of $1 \times 10^{-5} \pm 1 \times 10^{-6}$ K^{-1}, $1.2 \times 10^{-5} \pm 4 \times 10^{-7}$ K^{-1}, and $6.6 \times 10^{-5} \pm 1 \times 10^{-6}$ K^{-1}, respectively.

A SRSO can be regarded as a completely phase separated nc-Si/SiO$_2$ nano-composite material. In fact, some suboxided nc-Si/SiO$_2$ interfaces, which is known to be possible origin of nc-Si luminescence,[10] still exist in spite of a complete phase separation. Due to the uncertainty of suboxide-phase fraction, the exact determination of optical properties such as refractive index and the comparison of optical properties between our films and results by others are difficult. However, it is still worth to discuss the TOC of nc-Si neglecting sub-oxide phase since TOC is relative values with temperature. SiO$_2$ has a refractive index 1.44 and a negligible TOC at 1.53 μm, while Si has a refractive index of 3.44 and TOC of 2-2.4$\times 10^{-4}$ K^{-1} at 1.53 μm.[11] Thus, SRSO films have refractive indices and TOCs that are between that of SiO$_2$ and Si. In case of the Si34 film, the excess Si content is too little to have a measurable effect on the TOC, even though it is sufficient to increase the refractive index slightly.

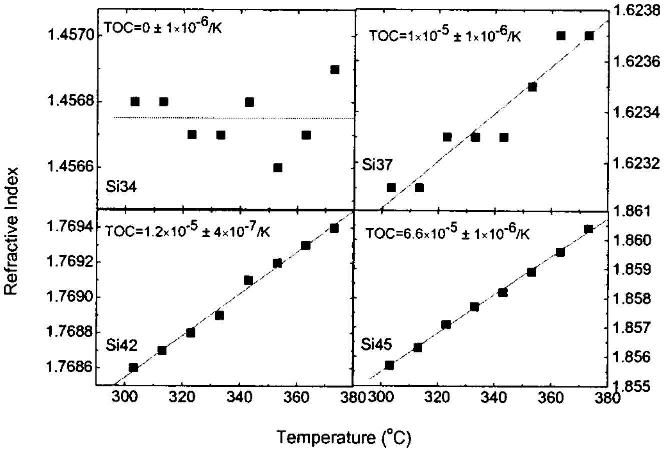

FIG. 2. The refractive indices as a function of the temperature in the range of 303–373 K. The symbols are the experimental data, and the lines are the linear fits to the data. The slope of the line gives the thermo-optic coefficient, and is indicated.

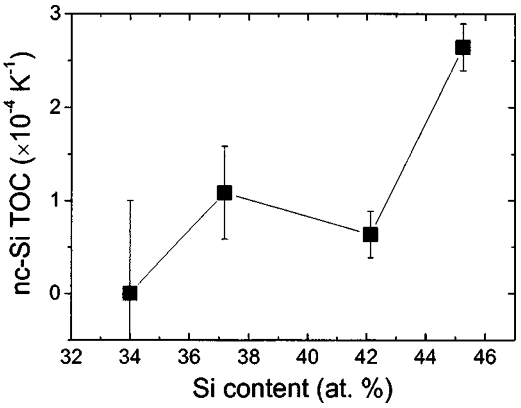

FIG. 3. The thermo-optic coefficients of nc-Si, estimated by correcting the SRSO TOC in Fig. 2 by the nc-Si volume fraction, assuming a complete phase separation of Si and SiO$_2$.

Note, however, that the TOC of Si45 film is nearly seven times that of Si42 film even though the excess Si content volume fraction of precipitated Si increases from 18% to 24% only, indicating that there are factors other than the excess Si content that affect SRSO TOC. This is demonstrated more clearly in Fig. 3, which shows the nc-Si TOC obtained by normalizing the SRSO TOC by the volume fraction of the nc-Si clusters, assuming that the film is fully separated into stoichiometric Si and SiO$_2$. We find that the nc-Si TOCs from the Si37 and Si42 films are only about half of the bulk Si value at $\sim 1 \times 10^{-4}$ K^{-1}. Increasing the Si content to 45 at. % increases the the nc-Si TOC to 2.6 $\times 10^{-4}$ K^{-1}, close to the bulk value.

Such reduced TOC for nc-Si is consistent with theories that relate the TOC of a material with its band gap. In the model derived by Ghosh, TOC is given by[11]

$$\frac{dn}{dT} = \frac{n^2-1}{2n}\left(-3\alpha R - \frac{1}{E_{eg}}\frac{dE_{eg}}{dT}R^2\right), \qquad (1)$$

where α is the thermal expansion coefficient, E_{eg} is the excitonic band gap (3.38 eV for bulk Si), and $R=\lambda^2/(\lambda^2-\lambda_{ig}^2)$ where λ_{ig} is the wavelength corresponding to the isentropic bandgap (0.333 μm for bulk Si). In the present case where λ is 1.53 μm, R is very close to unity. Furthermore, due to the small values of thermal expansion coefficients of both Si and SiO$_2$ ($\sim 10^{-6}$), the second term dominates over the first term. Since the refractive index of Si is much greater than 1, Eq. (1) can thus be reduced to the same form as the Moss rule,[12] which in its differential form is written as

$$4\Delta n/n = -\Delta E_g/E_g, \qquad (2)$$

where E_g is the band gap.

Note that in both cases, the thermo-optic coefficient is inversely proportional to the band gap of the material. Thus, the reduction of the nc-Si TOC is consistent with the increased band gap of nc-Si due to the quantum confinement effect. The actual value of the band gap is difficult to obtain since the value of dE_g/dT for nc-Si is not known. The Varshni relation can well describe temperature dependence of energy band gap and has been successfully used for deduction of TOC of Si-based materials.[13] Even though some fraction of amorphous Si is still present in high temperature annealed films,[14,15] the values of dimension parameters characterizing materials in the Varshni relation are similar between bulk Si and hydrogenated amorphous Si.[13] We thus used bulk Si dimension parameters instead of amorphous Si remaining nc-Si band gap at 0 K to be fitting parameter. In fact, nearly no difference in results was found when amorphous Si dimension parameters were used. Thus we can estimate from Eq. (2) the band gap of the nc-Si in Si37 film to be about 2.2 eV. This is much higher than 1.5 eV, the energy of the nc-Si luminescence peak shown in Fig. 1. However, it is in a good agreement with the calculated and measured absorption band gap of nc-Si luminescent at 1.5 eV,[16] and provides an independent confirmation of the strong Stokes shift predicted for oxide-passivated nc-Si.[10]

We note that an incomplete phase separation of Si and SiO_2 from the original SiO_x may also result in reduced TOC. However, several points indicate that incomplete phase separation does not play a major role in the reduction of the nc-Si TOC. First, it has been reported that a complete phase separation of Si and SiO_2 occurs near 1100 °C, even though the SiO_2 remains defective.[17] Second, from the measured values of refractive index, we can estimate the Si volume fraction. Using the values of 3.44 and 1.44 for refractive index of nc-Si and SiO_2, respectively, we obtain the nc-Si volume fraction Si37, Si42, and Si45 films to be 9%, 16%, and 21%, respectively, which agree quite well with 8%, 18%, and 24% calculated from the film composition and used in Fig. 3.

In addition, the effect of nc-Si/SiO_2 interfaces on TOE has to be considered also. We do not however believe that the interfaces can dominantly contribute for TOE of nc-Si, because Si34 film, which has nearly no nc-Si and its TOE is attributed mainly to suboxided phase, shows complete lack of TOE. On the contrary, such interface can lead to the uncertainty of determination of active Si fraction making it difficult to evaluate exact nc-Si optical properties including TOC as well.[18] A accurate interface model has not been introduced, and will be of much help in clarifying the explanation of nc-Si optical properties.

Finally, it should be pointed out that the positive and non-negligible TOC of SRSO imply that high pump power densities can lead to significant thermal gradient and formation of unwanted waveguides or cavities. For example, if the pump beam is focused into a narrow stripe, the temperature gradient induced by the pump beam itself can form a waveguide. When a 0.1-μm-thick SRSO film with 45 at. % Si on SiO_2 is pumped with 10-μm-wide light source, ΔT of mere 5 K (corresponding the Δn of 0.0003) is found to be sufficient for formation of a multimode waveguide under the pump beam, as shown in Fig. 4. Figure 4 is a graphical solution of the eigenvalue problem for TE modes of waveguide. For calculation, such thermal induced waveguide was regarded as symmetric slab waveguide with thickness w of 10 μm by using the effective index method. In fact we considered for guided light of 0.8 μm, which is the center wavelength of nc-Si luminescence of Si45 film and is different from the wavelength we discussed. However, since refractive indices and TOC of crystalline silicon at $\lambda = 0.8$ μm are higher than those at 1.530 μm,[11] we thus believe that the exact value of such pump beam induced thermal gradient will be larger than our prediction.

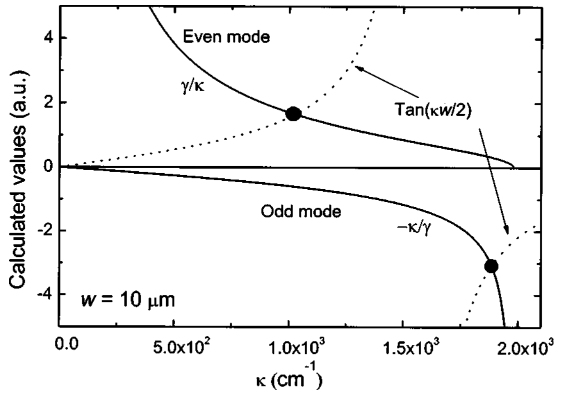

FIG. 4. The graphic solution to the waveguide eigenvalues problem for a 0.1-μm-thick Si45 film with a 10-μm-wide strip with a ΔT of 5 K. κ and γ are the transverse wave vector and attenuation coefficient of waveguide, respectively. We observe two solutions (closed circles), indicating emergence of multimode waveguiding.

In conclusion, we have investigated the thermo-optic effect of silicon-rich silicon oxide. We find that while the overall property can be understood as a mixture of the properties of Si and SiO_2, the thermo-optic coefficients of nc-Si display size-dependence consistent with the enlarged band gap of nc-Si. The results also indicate that thermo-optic effect may play a significant role during optical measurements of SRSO thin films.

This work was supported in part by NRL Project from MOST and BK 21 Project.

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