Photoluminescence and self-interference in germanium-doped silica films

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(Received 10 December 2006; accepted 27 February 2007; published online 2 May 2007)

Germanium-doped silica films were prepared by magnetron cosputtering and postannealing. The photoluminescence properties and their dependence on the Ge contents and annealing temperature were investigated. Our experiments indicate that the observed light emission originates from the neutral oxygen vacancy defects. The substructures in the luminescence bands of the films were found to result from multiple-beam interferences of the emission in the optical cavity formed by the transparent films. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721784]

I. INTRODUCTION

Germanium-doped silica (Ge:SiO$_2$) glass has been intensively investigated due to their interesting optical properties such as optical nonlinearity, strong photosensitivity, and luminescence associated with defects. It is now the main constituent in optical fibers. Ge:SiO$_2$ glass can be fabricated by several methods such as Ge ion implantation, Ge-SiO$_2$ cosputtering, sol-gel preparation, and chemical vapor deposition. Among the abundant defects in Ge:SiO$_2$ glass, the Ge-related neutral oxygen vacancy (≡Ge-Ge≡ or ≡Ge-Si≡) is especially important due to its influence on strong photosensitivity and luminescence. This defect has been referred to as GeO color center or twofold coordinated Ge atom (≡Ge;) in the literature. This defect usually produces two absorption bands, a strong band at ~240 nm and a weak band at ~330 nm, as well as two luminescence bands, a weak band at ~290 nm and a strong band at ~390 nm. In addition to the ultraviolet and violet luminescence bands, a green-yellow luminescent band at 550–600 nm (Refs. 7–11) and another red-infrared one at 650–840 nm (Refs. 7, 9, 11, and 12) have been observed from the materials. However, interpretation of the results and mechanism has been inconsistent and the origins of the green-yellow and red-infrared bands are still unclear. Furthermore, the sample preparation affects the formation of the luminescence centers.

In this work, we examined the photoluminescence (PL) of Ge:SiO$_2$ films prepared by magnetron cosputtering and postannealing. Three PL bands at ~290, 390, and 470 nm originating from the neutral oxygen vacancy defects were observed. The influence of the dosage and annealing temperature on the emission was studied in order to optimize the deposition parameters. The substructures in the PL bands were found to stem from self-interference of the emission, which can in turn be used to determine the thickness and refractive index of the transparent films and to modulate the luminescence spectra.

II. EXPERIMENTAL DETAILS

SiO$_2$/Ge:SiO$_2$/SiO$_2$ sandwich films were fabricated on Si(100) substrates by radio frequency magnetron sputtering. The Ge:SiO$_2$ interlayer was prepared by cosputtering of a SiO$_2$ target (50 mm in diameter) and some Ge chips with the area ratios AR=AGe/ASiO$_2$ ranging from 0.2% to 4.0%. The thickness of the interlayer was measured by optical interference microscopy to be 0.72 μm. The top and bottom SiO$_2$ layers, both ~30 nm thick, were deposited to restrain Ge from leaving the film during annealing. Sputtering was conducted in 1 Pa argon using 100 W power at room temperature. The films were subsequently annealed in nitrogen for 30 min at annealing temperatures (Ta) from 500 to 1100 °C. The PL spectra and PL excited (PLE) spectra were acquired on a Jobin-Yvon FluoroMax fluorescence spectrophotometer (with Xe lamp). Raman scattering was performed on a Jobin–Yvon T64000 Raman spectrometer using the 514.5 nm line of an Ar ion laser. All the measurements were conducted at room temperature.

III. RESULTS AND DISCUSSION

The PL spectra of the Ge-SiO$_2$ cosputtered films were examined using 245 nm excitation. Figure 1 depicts the spectra of the samples with different Ge contents annealed at 800 °C. Each spectrum is composed of an ultraviolet (UV) PL band at ~290 nm and a violet (V) PL band at ~390 nm, and the V band is stronger than the UV band by about a factor of 10. The energy- and intensity-characteristics of the PL bands are in accordance with those of the Ge-related defects.
neutral oxygen vacancy. Figure 2 shows the corresponding PLE spectra monitoring the peak positions of the UV and V bands. A common peak at \( \sim 250 \text{ nm} \) (E1) can be seen from the two PLE spectra. Besides the very strong E1 peak, a peak at \( \sim 330 \text{ nm} \) (E2) can be observed from the PLE spectrum of the V band. The characteristics of the PLE spectra further indicate that the observed UV and V bands originate from the intrinsic electronic transition in the Ge-related neutral oxygen vacancy. In accordance with the energy configuration of intrinsic electronic transition in the Ge-related neutral oxygen vacancy, the UV band and the E1 peak arise from the singlet-singlet transition of \( S_0 \leftrightarrow S_1 \) whereas the V band and E2 peak originate from the forbidden singlet-triplet transition of \( S_0 \leftrightarrow T_1 \), activated by the “heavy atom effect.”

It should be mentioned that we have not observed light emission in the wide region of 520–850 nm from all of our samples, even after changing the exciting wavelength. A blue band at \( \sim 470 \text{ nm} \) observed using 300 nm excitation can be ascribed to the emission from the \( \equiv Si-Si \equiv \) defect in the Ge:SiO2 glass. Here, we focus on the Ge-related defects in the Ge-SiO2 cosputtered films but the contribution of the \( \equiv Si-Si \equiv \) defect will not be discussed in detail.

Figure 1 shows that the intensity of the PL spectrum depends on the Ge contents as indicated by the area ratios (AR) in this work. In addition, it has been found that the symmetry and intensity of the PL bands can be changed by the annealing temperature and annealing time. Figure 3 shows the dependence of the integrated intensity of the V band on the preparing parameters of AR and Ta. Based on our experiments, the optimal parameters for strong light emission are of AR=1% and Ta=1000 °C. For the slightly doped samples with AR≤1%, the PL intensity increases with increasing Ta but diminishes at very high temperature. This change is consistent with the observation in other experiments. The reduction in the PL intensity at very high temperature is believed to be due to the instability of the neutral oxygen vacancy. For the heavily doped samples with AR≥2.0%, the PL intensity increases with increasing Ta even at high temperature. The Raman scattering results indicate that Ge nanocrystals form in the heavily doped samples annealed at high temperature. It is reasonable to assume that aggregation of Ge aids the formation of the Ge-related neutral oxygen vacancy because such defects are only slightly oxygen deficient. One may have noted that the PL intensity decreases at high temperature for the heavily Ge⁺-implanted SiO2 layers. This difference may result from differences between ion implantation and sputtering, especially regarding the type of damage introduced by implantation. In addition, thermal grown SiO2 is different from sputtered SiO2 from the viewpoint of the chemical environment of the luminescence centers.

Both the UV and V bands in the spectra displayed in Fig. 1 are asymmetrical and likely composed of three substructures. One possible origin of these substructures is the similar luminescence centers or modification of one luminescence center in the Ge:SiO2 glass. A bimodal behavior have been reported for the V band, but not observed from the UV band. The PL spectra of our samples are sensitive to the excited positions on the sample as indicated in Fig. 4(a) for a film prepared with AR=1.0% and at Ta=1100 °C. The spectra are obtained after capping the sample with metal with a 1 mm wide slot and then moving the slot from one side of the sample to the other. The variations in the UV and V bands with the excited positions are continued and that each PL band indeed comprises three substructures. The variation in the luminescence bands does not appear to result from the change of the particle size, because Raman scattering indicates that nanocrystals are not formed in this sample. It is
also unlikely to be due to the change of the density of defects, because it would not influence the energy of the emission. Instead, the change in the macroscopic characteristics of the film is the most possible reason which has caused the variations in PL bands with changing excited positions on the sample.

We have noted that the thickness of the sputtered film gradually decreases from the center to the side. If the observed variations of the PL bands with the excited positions are indeed due to changes in thickness of the film, the substructures in the PL bands should arise from optical interferences in the thin film and the separation between adjacent substructures ought to decrease with increasing film thickness. To verify this, a thick film with twice the thickness was prepared under the same conditions. The number of substructures in the UV and V bands is observed to increase to six [(a) in Fig. 4(b)]. The optical interference in the films is due to the excellent reflection at the SiO\textsubscript{2}/Si interface. The interference can be easily controlled by depositing the film on transparent unpolished quartz substrate. The PL spectrum of such a sample [(b) in Fig. 4(b)] indicates that the peak positions of the UV and V bands without interference are at \(\sim 292\) and \(385\) nm, respectively.

Interference of the monochromatic exciting light should not lead to fluctuations in luminescence because the emission in our experiments comes from luminescence centers evenly distributed throughout the films rather than from layered nanocrystals as reported in Ref. 16. Multiple-beam interference of the light emission in the optical cavity in the transparent films is suitable for the formation of the substructures in the PL bands here. The interference occurs due to emission from a luminescence center and multiple reflections. The emissions from different luminescence centers do not interfere on account of random polarization and the initial phase. Therefore, interference at a fixed wavelength is a function of the viewing angle. In the case of a fixed viewing angle, the interference fringes are formed due to the continuous emission wavelengths. The electromagnetic emission can be decomposed into the \(s\)-polarized and \(p\)-polarized components and to meet different interferences, the conditions are

\[
2d\sqrt{n_1^2-n_0^2}\sin^2\theta_0 = (k-\frac{1}{2})\lambda \quad (s\text{-polarized})
\]

and

\[
2d\sqrt{n_1^2-n_0^2}\sin^2\theta_0 = k\lambda \quad (p\text{-polarized}),
\]

where \(d\) is the thickness of the film, \(n_1\) and \(n_0\) are the refractive index of the film and air, respectively, \(\theta_0\) is the angle between the normal of the film and the detection direction, \(k\) is the order of the interference, and \(\lambda\) is the emission wavelength. For the \(s\)-polarized component, the reflection phase at the SiO\textsubscript{2}/Si interface has an additional change of \(\pi\).

We check spectrum (a) in Fig. 4(b) using this interference argument. Owing to low reflection (\(\sim 4\%\)) at the film/air interface, only a small part of the PL intensity is contributed by the interference. Figure 4(c) shows the difference spectrum between spectra (a) and (b) after an adjustment to the same integrated intensity. According to the difference spectrum, the energy separation \(\Delta E\) of the two neighboring subpeaks is almost constant, implying that the materials dispersion \(dn_1/d\lambda\) is very small within the PL band.\(^{17}\) In this case, the energy separation has the form of

\[
\Delta E = \frac{hc}{4d\sqrt{n_1^2-n_0^2}\sin^2\theta_0},
\]

where \(h\) is Planck’s constant and \(c\) is the speed of light. In our experiments, \(\theta_0 = 10°\), \(n_1 = 1.5\), and \(n_0 = 1.0\). The thickness of the thick film to obtained to be \(d = 1.34\ \mu\text{m}\) which is in agreement with the result of \(d = 1.31\ \mu\text{m}\) obtained by optical interference microscopy. From the spectra in Fig. 4(a), the thickness of the film is determined to be \(0.70\ \mu\text{m}\) and the change in the thickness from one side of the film to the other (\(\sim 1\ \text{cm}\) in length) is only \(\sim 70\) nm. The \(\Delta E\) value is only half of that reported in Ref. 17. It is because the subpeaks in our spectra are contributed by the interference maxima of the \(s\)- and \(p\)-polarized components. Our work is also different from that reported in Ref. 18 in which the contribution of the \(p\)-polarized component to the experimental spectra of a thermally 1.67 \(\mu\text{m}\) SiO\textsubscript{2} film is very weak resulting from the use of a large \(\theta_0\). Strong violet emission bodes well for the applications of the Ge:SiO\textsubscript{2} materials to optoelectronics. Self-interference of the emission can be applied to significantly enhance the in-

![Image](https://example.com/image.png)
tensity and reduce the width of the luminescence band by depositing the suitable Bragg reflectors up and down the Ge:SiO₂ film.¹⁹

IV. CONCLUSION

We have examined light emission from Ge-SiO₂ cosputtered films after high-temperature annealing. The observed PL bands arise from the neutral oxygen vacancy defects in the films. The influence of Ge contents and annealing temperature on the emission has been studied. The substructures in the PL bands are found to be the interference fringes caused by multiple-beam interference of the emission in the optical cavity formed by the transparent films. The interference effect can be applied to accurately determined the thickness and refractive index of the transparent film and bodes well for commercial applications of Ge:SiO₂ films in Si-based optoelectronics.

ACKNOWLEDGMENTS

Y.M.Y. thanks Professor X. L. Wu of Nanjing University for his guidance and encouragement and G. S. Huang and F. Kong for helpful discussion. The work was supported by City University of Hong Kong Strategic Research Grant No. 7001981.