Enhanced ultraviolet photoluminescence from SiO$_2$/Ge:SiO$_2$/SiO$_2$ sandwiched structure

J. K. Shen, X. L. Wu,$^{a}$ R. K. Yuan, N. Tang, J. P. Zou, Y. F. Mei, C. Tan, and X. M. Bao
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People’s Republic of China

G. G. Siu
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

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SiO$_2$/Ge:SiO$_2$/SiO$_2$ sandwiched structure was fabricated for exploring efficient light emission. After annealed in N$_2$ (O$_2$$<1\%$), this structure shows three photoluminescence (PL) bands at 293, 395, and 780 nm. The intensity of the 395 nm band is largely enhanced in comparison with that from the monolayered Ge:SiO$_2$ film. Spectral analyses suggest that the three PL bands originate from $S_1\rightarrow S_0$, $T_{2\Sigma}(T_{1\Pi})\rightarrow S_0$, and $T_{1\Pi}\rightarrow S_0$ optical transitions in GeO color centers, respectively. The improvement of the GeO density resulting from the confinement on Ge diffusion is responsible for the enhanced ultraviolet PL. This structure is expected to have important applications in optoelectronics.

As a kind of Si-based light-emitting material, Ge-doped SiO$_2$ film has been investigated for a long time. Various wavelength emissions from the material have also successfully been achieved.$^{1-6}$ These emissions are expected to be very useful in all-color display and optoelectronic integration. Among these emissions, the ultraviolet (UV) emission is of important application potentials in optical data storage system.$^7$ However, the UV emission intensity is generally low so far. Therefore, the improvement of the UV emission efficiency has become a subject of current investigation.

In the literature,$^4$ we have reported the 396 nm UV emission from Ge-implanted SiO$_2$ films and found that GeO is an efficient UV light emission center. So the improvement of the GeO density is a possible avenue to enhance the UV emission. In this letter, we report a kind of SiO$_2$/Ge:SiO$_2$/SiO$_2$ sandwiched structure fabricated by radio-frequency (rf) magnetron cosputtering of Ge and SiO$_2$ targets. Spectroscopic investigations indicate that the sandwiched structure is beneficial to the confinement on Ge diffusion. The improvement of the GeO density in the film is responsible for the enhancement of the UV emission intensity.

The sample fabrications are described as follows: First, a layer of SiO$_2$ film with a thickness of 120 nm was formed on Si substrate ($p$-type, (100)-oriented, 5 Ω cm) by thermal oxidation. Second, Ge and SiO$_2$ (their area ratio was 1:10) targets were cosputtered in argon gas under a rf power of 110 W. The distance between the targets and the substrate was about 50 nm. During film deposition, the substrates were not intentionally heated. So a layer of mixed Ge and SiO$_2$ (Ge:SiO$_2$) film was deposited onto the thermal SiO$_2$ film. The thickness of this Ge:SiO$_2$ layer is estimated to be about 100 nm. Third, further rf sputtering of the SiO$_2$ target was carried out to coat a layer of SiO$_2$ with a thickness of 120 nm on the formed Ge:SiO$_2$ film. So a SiO$_2$/Ge:SiO$_2$/SiO$_2$ sandwiched structure (sample A) was fabricated. Finally, the fabricated samples were thermally treated in N$_2$ (O$_2$$<1\%$) at an annealing temperature ($T_a$) varying from 200 to 1100 °C for 30 min. For comparison, a monolayered Ge:SiO$_2$ cosputtered film with a thickness of 100 nm was also directly deposited onto Si substrates (sample B). Photoluminescence (PL) and PL excitation (PLE) spectra were measured on a Hitachi 850 fluorescence spectrophotometer. Fourier-transform infrared absorption (FTIR) spectra were obtained under normal incidence using a Nicolet 170 SX Fourier-transform infrared spectrometer. All measurements were performed at room temperature.

Figures 1(a) and 1(b) show the PL spectra of samples A and B annealed at 900 °C in N$_2$ (O$_2$$<1\%$) for 30 min, respectively, taken under an excitation of the 250 nm line of a xenon lamp.

The inset shows the dependence of the PL intensity on $T_a$.
FIG. 2. A schematic diagram of the electronic states of GeO molecule. The 293 nm PL band: $S_1 \rightarrow S_0$; the 395 nm PL band: $T_2(T_1) \rightarrow S_0$; and the 780 nm PL band: $T_\Pi \rightarrow S_0$.

To reveal the origin of the enhanced 395 nm PL, we examined the FTIR spectra of samples A and B with $T_a = 900 \, ^\circ\text{C}$. The obtained results are shown in Figs. 3(a) and 3(b). The two spectra clearly display five vibration bands at 450, 580, 800, 870, and 1080 cm$^{-1}$. For sample B, an additional vibration band can be observed at 1020 cm$^{-1}$. The band cannot be observed in sample A. Its disappearance cannot be attributed to an enhancement of the 1080 cm$^{-1}$ band in sample A, because the 1080 cm$^{-1}$ band was found to have same linewidth in the two samples. The 450, 800, and 1080 cm$^{-1}$ bands have been attributed to Si–O–Si rocking, bending, and stretching vibrations of stoichiometric SiO$_2$, respectively, while the 1020 cm$^{-1}$ band has been considered to be related to nonstoichiometric SiO$_x$ ($x < 2$). The 580 and 870 cm$^{-1}$ bands are attributed to Ge–O–Ge bending and stretching vibrations, respectively. From Fig. 3, we can find that the intensities of the 580 and 870 cm$^{-1}$ bands are larger in sample A than those in sample B. This implies that the density of Ge oxide (including GeO, Ge$_2$O$_3$, etc.) is higher in sample A than that in sample B. This is understandable, because the two SiO$_2$ layers confine Ge atoms to diffuse into air and the Si substrate. The improvement of the GeO density in the sandwiched structure can be explained as follows. The existence of the thermal SiO$_2$ layer hinders Ge atoms diffusing into Si substrate to form GeSi alloy which has been testified to have no contribution to the 395 nm UV emission. The coated SiO$_2$ film decreases outdiffusion of Ge atoms and thus makes few Ge atoms escaped from the sample surface. The fact that the 1020 cm$^{-1}$ absorption band vanishes in sample A also implies the existence of the diffusion of oxygen atoms from the two SiO$_2$ layers into the Ge:SiO$_2$ layer. The oxygen diffusion not only leads to the formation of stoichiometric SiO$_2$ matrix but also decreases the segregation of Ge atoms in the sandwiched layer. As a result, the GeO density is further improved. Therefore, the designed structure is really beneficial to an enhancement of the GeO density.

In conclusion, a robust structure, SiO$_2$/Ge:SiO$_2$/SiO$_2$ sandwiched structure, has been fabricated. This structure shows three emission bands at 295, 395, and 780 nm related to the GeO color centers. The intensity of the 395 nm band is far greater than those in sample B. This implies that the density of Ge oxide (including GeO, Ge$_2$O$_3$, etc.) is higher in sample A than that in sample B. This result indicates that the $T_\Pi \rightarrow S_0$ optical transition in the GeO color centers, as predicted by Fig. 2. The 580 and 870 cm$^{-1}$ bands are larger in sample A than those in sample B. This implies that the density of Ge oxide (including GeO, Ge$_2$O$_3$, etc.) is higher in sample A than that in sample B. This is understandable, because the two SiO$_2$ layers confine Ge atoms to diffuse into air and the Si substrate. The improvement of the GeO density in the sandwiched structure can be explained as follows. The existence of the thermal SiO$_2$ layer hinders Ge atoms diffusing into Si substrate to form GeSi alloy which has been testified to have no contribution to the 395 nm UV emission. The coated SiO$_2$ film decreases outdiffusion of Ge atoms and thus makes few Ge atoms escaped from the sample surface. The fact that the 1020 cm$^{-1}$ absorption band vanishes in sample A also implies the existence of the diffusion of oxygen atoms from the two SiO$_2$ layers into the Ge:SiO$_2$ layer. The oxygen diffusion not only leads to the formation of stoichiometric SiO$_2$ matrix but also decreases the segregation of Ge atoms in the sandwiched layer. As a result, the GeO density is further improved. Therefore, the designed structure is really beneficial to an enhancement of the GeO density.
larger than that from the monolayered Ge:SiO$_2$ film. Spectral analyses indicate that the existence of the two SiO$_2$ layers leads to a large improvement of the GeO density and thus makes the 395 nm PL intensity largely enhanced. Our experimental results provide a useful way for enhancing the UV PL, which will be very useful in device applications.

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