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Citation: Appl. Phys. Lett. **77**, 3134 (2000); doi: 10.1063/1.1325399
View online: https://doi.org/10.1063/1.1325399
View Table of Contents: http://aip.scitation.org/toc/apl/77/20
Published by the American Institute of Physics

APPLIED PHYSICS LETTERS VOLUME 77, NUMBER 20 13 NOVEMBER 2000

Enhanced ultraviolet photoluminescence from $SiO_2/Ge:SiO_2/SiO_2$ sandwiched structure

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(Received 2 June 2000; accepted for publication 14 September 2000)

$SiO_2/Ge:SiO_2/SiO_2$ 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 $S_1 \rightarrow S_0$, $T_\Sigma(T_\Pi) \rightarrow S_0$, and $T'_\Pi \rightarrow S_0$ 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. © *2000 American Institute of Physics.* [S0003-6951(00)01446-7]

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 Nicole 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

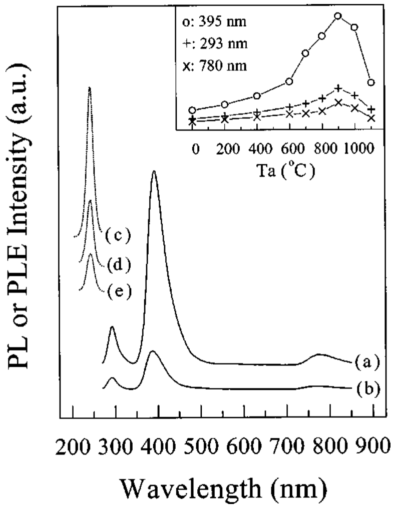

FIG. 1. PL spectra of (a) sample A ($SiO_2/Ge:SiO_2/SiO_2$ sandwiched structure) and (b) sample B (the monolayered Ge:SiO_2 cosputtered film) both annealed at 900 °C in N_2 ($O_2<1\%$) for 30 min, taken under the 250 nm excitation line of a Xe lamp. (c)–(e) PLE spectra of sample A, monitored at 395, 293, and 780 nm, respectively. The inset shows the dependence of the 293, 395, and 780 nm PL intensities on T_a.

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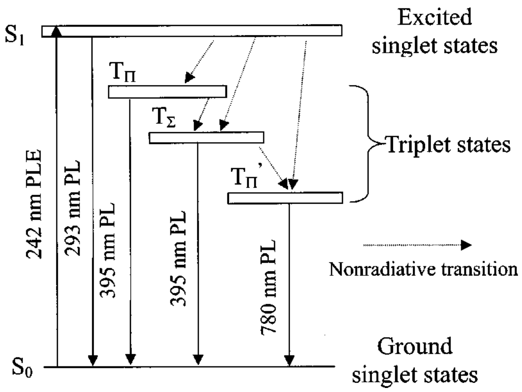

FIG. 2. A schematic diagram of the electronic states of GeO molecule. The 293 nm PL band: $S_1 \rightarrow S_0$; the 395 nm PL band: $T_\Sigma(T_\Pi) \rightarrow S_0$; and the 780 nm PL band: $T'_\Pi \rightarrow S_0$.

Xe lamp. Obviously, three PL bands can be observed at 295, 395, and 780 nm. In contrast, the intensity of the 395 nm PL band from sample A is far larger (more than four times) than that from sample B. This result indicates that the $SiO_2/Ge:SiO_2/SiO_2$ sandwiched structure is beneficial to a large enhancement of the 395 nm PL band intensity. For the samples with different T_a, no emission wavelength shifts were observed. The inset in Fig. 1 shows the dependence of the intensities of the three PL bands from sample A on T_a. We can find from the figure that the PL intensities have similar change tendency. They all reach maximums in the sample annealed at $T_a = 900$ °C. Shown in Figs. 1(c)–1(e) are the corresponding PLE spectra, monitored at 395, 293, and 780 nm luminescence bands, respectively. These PLE spectra display an identical excitation band at 242 nm, indicating that the 293, 395, and 780 nm PL bands have same origin.

The 293 and 395 nm PL bands from Ge-doped SiO_2 have been reported previously.[4,8–10] The common accepted is that the two bands are related to GeO color centers. Figure 2 gives a schematic diagram of the electronic states of GeO molecule.[11–13] A transition from ground (S_0) to the excited singlet (S_1) state gives rise to the 242 nm (5.1 eV) absorption band. A nonradiative transition from S_1 to the triplet state (T_Π or T_Σ) facilitates the 395 nm (3.1 eV) PL. A radiative transition between S_1 and S_0 produces the 293 nm (4.2 eV) PL. Therefore, we can infer that the 295 and 395 nm PL bands obtained from our samples are closely related to the GeO color centers.

To reveal the origin of the enhanced 395 nm PL, we examined the FTIR spectra of samples A and B with $T_a = 900$ °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 $(x<2)$.[14,15] The 580 and 870 cm^{-1} bands are identified to be connected with Ge–O–Ge bending and stretching vibrations,[16] 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_2O_3, etc.) is higher in sample A than that in sample B.[4] 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.[17] The coated SiO_2 film decreases outdiffusion of Ge atoms and thus makes few Ge atoms escaped from the sample surface.[4,17] 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.

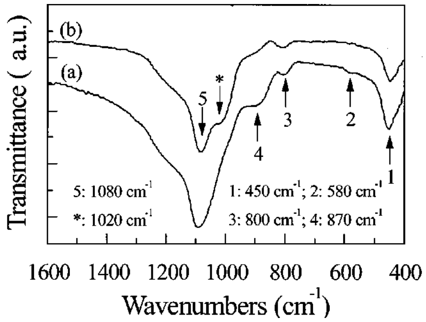

FIG. 3. FTIR spectra of (a) sample A ($SiO_2/Ge:SiO_2/SiO_2$ sandwiched structure) and (b) sample B (the monolayered Ge:SiO_2 cosputtered film) annealed at 900 °C in N_2 ($O_2 < 1\%$) for 30 min.

The origin of the 780 nm PL band is interesting, because this band was frequently observed in various Si and Ge oxides. The constancy of the 780 nm band with T_a does suggest that nucleation and growth of Ge crystals is not a factor. Thus, the infrared PL cannot arise from the quantum confinement on Ge crystallites. In addition, we can rule out the possibility that the PL band comes from two-fold-coordinated Ge or Si[12,18] and Ge or Si neutral oxygen vacancy[9,19] because the PL from these radiative centers should have emission wavelength change with different T_a to some degree.[6] Since the 780 nm PL has similar behavior in SiO_2 and SiO_x matrices, we believe that it cannot also be related to Si oxide. From the consistencies of its PLE feature and the annealing temperature dependence with the 395 nm PL band, we can conclude that the 780 nm PL should originate from $T'_\Pi \rightarrow S_0$ optical transition in the GeO color centers, as predicted by Fig. 2.[12,13] In GeO molecule, all radiative transitions are intramolecular. Thus, the PL bands from the GeO color centers are hardly influenced by the SiO_2 network.

In conclusion, a robust structure, $SiO_2/Ge:SiO_2/SiO_2$ sandwiched film, 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 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.

The authors would like to thank H. Chen for help in PL measurements. This work was supported by the National Natural Science Foundation of China (Nos. 59832100 and 59772038). Partial support was also from the RFDP.

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