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New Photoluminescence Phenomena of Ge/SiO_2 Glass Synthesized by Sol-gel Method

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Abstract: New Ge/ SiO_2 glasses have been synthesized by heating the GeO_2/ SiO_2 dry gels under H_2 gas at 700℃. The resulting fluorescence spectra show that this kind of Ge/ SiO_2 glasses emit strong photoluminescence at 392 nm (3.12 eV), medium strong photoluminescence at 600 nm (2.05 eV) and weak photoluminescence at 770 nm (1.60 eV) respectively. Possible photoluminescence mechanisms are also discussed based on the results of X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS).

Keywords: Ge/ SiO_2 glasses, Ge nanocrystals, photoluminescence, sol-gel method.

Ge-doped SiO_2 glasses have been studied extensively in recent years due to their special significance in microelectronics and optic electronics[1]. Maeda *et al.* prepared Ge micro-crystals embedded in SiO_2 glassy matrices by rf-magnetron cosputtering method [2], and observed 570 nm (2.16 eV) photoluminescence at room temperature. Nagomi *et al.* prepared Ge/SiO_2 glasses by sol-gel method and observed 510-680 nm (2.42-1.81 eV) broad band photoluminescence at 77 K temperature [3]. Min *et al.* prepared Ge crystals embedded in SiO_2 film, and observed 680 nm (1.8 eV) photoluminescence at room temperature[4]. However till so far, there have no reports about Ge/SiO_2 glasses with photoluminescence of more than two colour bands. For this reason, the application of Ge/SiO_2 glasses in light-storage and other fields was limited.

In this paper, we have synthesized a new kind of luminescent Ge/SiO_2 glasses by sol-gel method plus H_2 reduction. When excited by UV light, this material can give off luminescence at three bands. Its property and photoluminescence mechanism based on XRD and XPS results were discussed.

Results and Discussion

GeO_2/SiO_2 dry gels were prepared by method described previously[5]. Then these dry gels were heated at 700°C in a fused silica tube under the flow of 70% H_2 and 30% Ar.

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The gels were held at 700°C for 3 hours to produce Ge/SiO_2 nanometer crystal glasses. The photoluminescence experiment (**Figure 1**) showed that sample A, which was reduced by H_2, emitted three luminescence peaks at 392 nm, 600 nm, and 770 nm respectively. This means that the sample A can produce violet, orange and red light under UV excitation of 246 nm. The unreduced sample B shows no obvious lumenescence peak. Thus, after reduction under H_2, sample A owned a special luminescent property compared with unreduced sample B.

XRD and XPS techniques are always used to study the change of property of the material. In order to analyze the photoluminescence phenomena described above for sample A and B, we employed XRD and XPS to investigate the structure of sample A and B. **Figure 2** shows the XRD experiment results. For sample A (curve A in **Figure 2**), there are obvious crystalline diffraction peaks. The 2θ positions of 27.22°, 45.24°, 53.60°, 72.66°, 83.70° correspond to cubic structure of Ge (111), Ge (220), Ge (311), Ge (331), Ge (422) planes. The 2θ positions of 20.34° and 26.06° correspond to hexagonal structure of GeO_2 (100) and (101) planes. These results indicate there were Ge and GeO_2 crystals in sample A. Also curve B in **Figure 2** shows that sample B are excited mainly as amorphous GeO_2. Even in the heating process, there are very few GeO_2 crystals, corresponding to hexagonal structure of GeO_2 (100) and (101) planes, no Ge crystals existing in the sample B.

Figure 1 The fluorescence spectra of sample A and sample B, the excitation wavelength at 246 nm

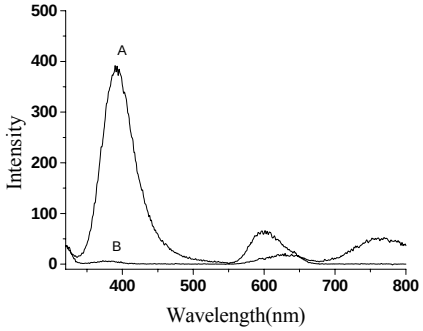
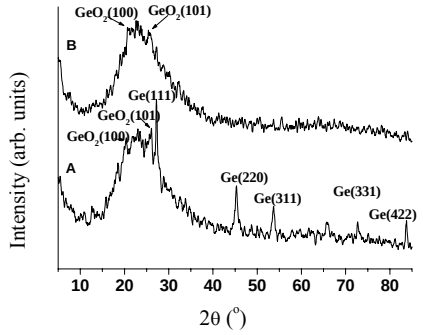


Figure 2 The XRD results of sample A and sample B



The XPS results of sample A are shown in **Figure 3**. After dealing with the results, the spectrum of sample A can be separated to 3 Gaussian peaks centered at 29.24 eV, 31.41 eV and 32.61 eV, corresponding to 3d peaks of Ge, GeOx and GeO_2, and indicate the existence of germanium and germanium oxides in sample A[6], showing some of germanium oxides were reduced to germanium. While for sample B (**Figure 4**), since it was not reduced by H_2, there is only 3d peak of GeO_2, with no indication of the germanium crystal existence. These XPS results are consistent with the XRD results.

The phenomenon observed here that Ge/SiO_2 glasses give off three bands of different color luminescence has never been reported before. We deduce this luminescent property may be due to the existence of Ge nanocrystals in the glass sample[3]. These various-size crystals are under three-dimensional quantum confinement. The relation of their crystal size and the energy corresponding to the luminescence light is $R=\pi h/\sqrt{2m(E-Eg)}$ [7], where m is reduced mass of an electron-hole pair, Eg is an optical band gap of bulk crystalline Ge (which is 0.66 eV here [8]), E is the lowest energy of the electron-hole pair (which corresponds to the energy of the luminescence peak position). From this formula, the crystal sizes of the Ge can be deduced about 10 nm. As a comparison, we found that the samples made in faster H_2 reduction process and bigger crystal sizes did not show this luminescent property.

Figure 3 The XPS results of sample A

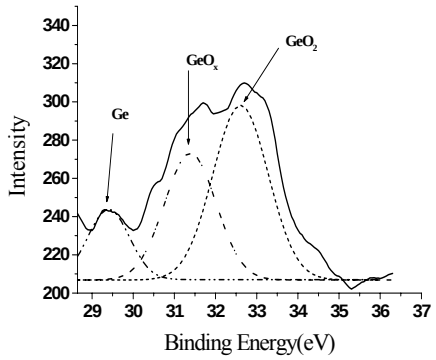
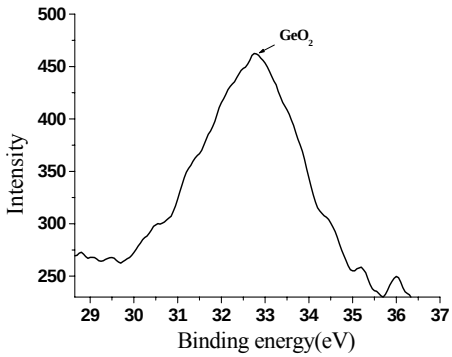


Figure 4 The XPS results of sample B.



On the other hand, the special luminescent property of sample A may be due to the germanium oxygen deficient centers (GODCs) existing in the $Ge_x/Si_x/O_x$ system too [9]. From the results of XRD and XPS experiments, it can be known that the crystals in sample A are Ge, GeO_x and GeO_2, so oxygen in the crystal of sample A is very deficient, causing sample A to emit the photoluminescence with the peak at 392 nm (violet light) which corresponds to GeO indicating that the translated from triplet excited state to singlet ground state, emitting violet light [10]. The photoluminescence with the peak at 600 nm (yellow light) may be caused by the germanium oxide-related defects located at the interface between the germanium nanocrystals and the matrix, which is consistent with the samples made by magnetron cosputtering method [11]. The mechanism for 770 nm (red light) photoluminescence is not very clear yet.

In summary, the Ge/SiO_2 glasses were synthesized by the sol-gel method with H_2 reductione4 and these glasses have a special luminescent property. The results of the fluorescence spectra show that the Ge/ SiO_2 glasses have three luminescent bands with the peaks at 392 nm, 600 nm and 770 nm respectively, that is to say, the Ge/SiO_2 glasses can produce violet, orange and red light at the same time. According to the data of the XRD and XPS, the mechanism of luminescence has been discussed, but the exact reason needs further investigation.

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