Photoluminescence of Silica Made by Sol-gel Method

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Abstract. Photoluminescence of one kind of silica was made by a kind of sol-gel method was investigated. The heat treatment temperature of the obtained gel was 50°C for 2 days and 90°C for 2 hours. Photoluminescence spectra and excitation spectra was investigated and analysed by a Gauss decomposition method. The emission spectra of silica composed of peaks 2.34eV, 2.65 eV and 3.10 eV. The excitation spectrum consisted of 3.1 eV and 5.18 eV. Meanwhile emission of 2.65 eV and 2.34 eV had common excitation peak of 5.18 eV.

1. Introduction
Sol-gel process is a chemical synthesis method, which is mainly based on an inorganic polymerization, initially used for the preparation of inorganic materials such as glasses and ceramics such as SiO2 and so on. The mild characteristic offered by the sol-gel process allow the introduction of organic molecules inside an inorganic network. Thus organics and inorganics and mixed on nanometric scale. So the sol-gel process can tuned with the doped organics to apply at the diverse fields. Sol-gel-derived silica gel was very important on its wide applications in optics, sensors, catalysts and solar acceptors [1-4]. The organic fluorescent molecules doped silica was seen at literatures for photoluminescence [5-8]. Meanwhile there was few literatures refereed the photoluminescence of silica made by sol-gel, because the doped fluorescence dyes had high photoluminescence efficiency and there was big difference between photoluminescence intensities. In this paper, photoluminescence of silica made by a kind of sol-gel method for preparing the fluorescence dyes such as 2,5-bis(5-tert-butyl-2-benzoxazolyl) thiophene (BBOT), perylene derivative(Lumogen red 305) and so on. The emission spectra and excitation spectra of silica were investigated. The emission centers of the silica was discussed in detail.

2. Experimental details
The raw materials included tetraethyoxysiliane (short for TEOS, AR), HCl (AR) and co-solvents dioxane (AR). The molar ratio of TEOS/dioxane/ H2O was chosen to be 3:12:4 only. The sol-gel process in detail was seen at reference [6].The quartz plate(2 cm × 2 cm × 0.1 cm) for silica film were cleaned by detergent solution and swabbed with ethanol firstly, rinsed with deionizer water and washed ultrasonically with acetone, ethanol, and deionizer water. The process of cleaning was done for several times to make the quartz plate very neat. Finally the quartz plate was drying in infrared oven. The silica film was prepared by spin-coating the obtained silica aged sol on the above neat quartz plate. Then the films was dried in a vacuum oven at ~50°C for 2 days and then at 90°C for 2 hrs. The thickness of the film was measured by an Ambios Technology XP-2 surface profiler. Photoluminescence was recorded on a SPEX Fluorolog-3 spectrophotometer while the Ultraviolet-Visible (UV-VIS) absorption spectra violresolution was set at 3 nm. The absorption spectra was measured using a SHIMADZ UV-3101PC
UV-VIS-NIR scanning spectrophotometer. All measurements were performed at ambient conditions. The rotating speed of silica gel was 4000 r/min and the thickness of silica gel was about 350 nm.

3. Results and Discussion

The absorption spectrum of silica was not showed because of the absorption intensity was very weak. Photoluminescence spectra of silica showed the wide band emission spectra in the range of 1.75 eV to 3.8 eV. The typical and the strongest peak centered at 3.1 eV showed in figure 1. The sample of silica mainly was treated at 50°C, so the corresponding sample was labeled P50. In order to assure the emission centers, the spectrum of the emission was decomposed by Gauss function. The decomposition spectrum contained three peaks centered at 2.34 eV, 2.65 eV and 3.10 eV. The full width at half maximum (FWHM) of the corresponding three peaks were 1.0, 0.4 and 1.4 at table 1. The FWHM of peak of 2.65 eV was minimum 0.4. It perhaps coincided with mercury lamp of the Fluorolog-3 spectrophotometer partly, but this influence was relatively small. It did not influence the photoluminescence. The wider emission showed relaxation of the inorganic materials.

The excitation spectrum of the sample P50 inspecting at 2.34 eV was showed at figure 2. The spectrum consisted of two peak 3.2 eV and 5.18 eV. The FWHM of the peaks were 1.9 eV and 2.5 eV. This was just the emission between the energy gaps for the inorganic materials.

At the same time, inspecting the 3.1 eV emission peak also obtained excited peak of 5.1 eV. So the emission of 3.1 eV and 2.35 eV had common the excitation peak of 5.1 eV. Although using energy 4.14 eV excited the sample P50, photoluminescence spectrum showed the whole emission spectrum. This ascribed mainly to the wide energy band emission and wider excitation spectrum.

Emission from silica made by sol-gel mainly was due to inaccurate ratio from Si: O=1: 2. Hence there was some emission between band gaps of SiO₂. This was also from the raw materials ratio of
TEOS/dioxane/H₂O 3:12:4. Obviously the ratio of Si: O was 1:1.3, lower than 2. This was the radical reason for silica emission. Relative to the Si: O=1:2, silica in this paper had more defect states for the photoluminescence and stayed amorphous silica for various films and powders. So photoluminescence of the silica made by the sol-gel method depended on the structure of the silica. The structure of silica depended the raw materials for the preparing and the reaction conditions. The common model of amorphous silica concentrated at Center Force Model (CFM) come out by P. N. Sen, M. F. Thorpe [9]. The confirmation of silica structure mainly was confirmed by the infrared spectrum to disclose the closer distance interaction by CFM. This can be shown at reference [6].

What was the defect states in silica made by this sol-gel method? From the excitation spectrum and emission spectrum, perhaps the same defect emission centers mainly for the emission of 3.1 eV and 2.34 eV. Because the peak of 5.1 eV can excite both 3.1 eV and 2.35 eV and peak of 3.1 eV had bigger ratio in the whole emission spectrum. For the defect states of amorphous silica, there was more viewpoints focused on unpaired electrons defects, such as from $\equiv Si - O\equiv$ to $\equiv Si - O\bullet + \bullet H$ [10]. Meanwhile, emission of 3.16 eV and 4.24 eV for the absorption of 5.0 eV and 7.6 eV, the corresponding the defects for $\equiv Si - Si\equiv$ or $Si_2^0$ [11]. These defects common was called oxygen vacancy mode. In this paper, although the 4.24 eV emission cannot be tested due to the range limit for the fluorescent instrument. But the same for the reference, the emission for 3.1 eV had at the same time the excitation peak of 5.1 eV. So the defects was mainly. The defects was largely named B₂ such as [11].

4. Conclusion

In this paper, absorption spectrum, emission spectrum and excitation spectrum of silica made by a kind of sol-gel method was investigated by UV-VIS and spectrophotometer. Photoluminescence from silica made by a kind of sol-gel method was from the defect states between silica band gaps. Because the non-ideal ratio of Si: O was 1:1.3. So there was wide band emission from the silica. Photoluminescence of silica contained 3.1 eV, 2.67 eV and 2.34 eV, which decomposed by Gauss function. Meanwhile there was the excitation peak of 5.18 eV. Hence the defect state or emission centers was $\equiv Si - Si\equiv$ or $Si_2^0$ for the emission 3.1 eV and 2.34 eV. Further investigation need to confirm.

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