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The influence of metal aluminium on the reduction of the Sm³⁺ doped in aluminosilicate glass films

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Abstract

Sm³⁺-doped glass sol was prepared by a sol–gel method and coated on a bare Si substrate and an Al coated Si substrate (Al/Si). The coated glass films were heat treated in a hydrogen atmosphere or air to reduce the Sm³⁺ to Sm²⁺ and then the optical properties were examined through a photoluminescence (PL) experiment. While the glass films coated on a bare Si substrate or an Al/Si one were well reduced in hydrogen atmosphere, only the glass films coated on the Al/Si substrate were reduced in air. We thus suggest two possible reducing mechanisms related to hydrogen and the metal aluminium and we found that the metal aluminium coated on a Si substrate plays an important role in the reducing process.

1. Introduction

Since Jaaniso and Bill first observed persistent spectral hole burning (PSHB) in materials doped with Sm²⁺ at room temperature [1], the PSHB phenomenon has continually been spotlighted for the possibility of application in high density optical memories and much attention has been paid to the development of new materials for PSHB such as rare earth ion doped crystals [2, 3] or glasses [4], semiconductor doped glasses [5] and organic materials [6]. Rare earth ions, such as Sm and Eu, are known as the best candidates for PSHB guest materials because those ions have unique f–f transition properties in the visible region.

Various kinds of materials are used as host materials. The optical properties of the doped ions strongly depend on the host materials. If the PSHB technique is applied to an optical memory, the optical memory density can be increased by a factor of $\Gamma_{\text{inh}}/\Gamma_{\text{h}}$ (Γ_{inh} :

Table 1. Sample preparation conditions.

Sample	Reduction condition	Substrate
(a)	800 °C, 2 h, H ₂	Bare Si
(b)	800 °C, 2 h, air	Al/Si
(c)	800 °C, 2 h, H ₂	Al/Si
(d)	800 °C, 2 h, air	Bare Si

inhomogeneous linewidth; Γ_h : homogeneous linewidth) [1, 7] compared to the conventional optical memory. Thus, for the development of high density optical memory, one needs to develop new materials having a wide inhomogeneous linewidth with a narrow homogeneous linewidth. A glassy matrix may meet those conditions and many researchers have been paying attention to the development of glass hosts.

In general, two methods, i.e., the traditional melt and quenching method [8] and the sol-gel method [9, 10], are used in the fabrication of rare earth ion doped glasses. While the melt and quenching method needs high temperature, the sol-gel method is carried out at low temperature. In Sm doped glasses, since the hole burning experiment is implemented with f-f transitions of Sm²⁺, one must reduce Sm³⁺ ions to Sm²⁺. There have been several methods for reducing trivalent ions to divalent ions, resulting in increased luminescence efficiency of divalent ions. One of the most common and effective reduction methods is heat treatment at high temperature in hydrogen gas. High intensity laser radiation, such as femtosecond laser pulses [11, 12], or x-rays [13], is also used for the reduction of Sm³⁺ doped materials. Another important factor degrading the luminescence efficiency of divalent ions is dopant clustering. Nogami *et al* overcame this problem by co-doping with Al₂O₃ [14, 15].

In this study, we prepared Sm³⁺ doped aluminosilicate glass sol using a sol-gel method and coated it on two different substrates, i.e., a bare Si substrate and a metal aluminium (Al) coated Si substrate. The Sm³⁺ ions doped in glass were reduced by heat treating the samples at high temperatures in hydrogen or air. The effects of hydrogen and metal Al on the reduction of Sm³⁺ were studied through a photoluminescence (PL) experiment.

2. Experiment

For fabrication of aluminosilicate glass thin films, a sol solution of 1.4 mol% Sm³⁺ doped 10Al₂O₃·90SiO₂ was prepared by using samarium acetate as a Sm precursor (refer to [16] for detailed descriptions). Two kinds of substrates, bare Si(100) plates and metal aluminium coated Si plates, were used for the glass film coating. Metal Al was coated on a Si substrate by the evaporation-deposition method and the deposition thickness was varied by simply controlling the deposition time. The aluminium coated substrates (Al/Si) were subsequently annealed in air at 400 °C for 30 min.

Glass coating was carried out by the spin coating technique. After dropping the sol solution onto a substrate, the substrate was rotated with the speed of 1500 rpm for 10 s; this was followed by a coating at 3000 rpm for 20 s and then the coated film was dried at 200 °C for 10 min. The process of coating and drying was repeated three times, resulting in a three-layered film, and the film was then annealed at 450 °C for 10 min in air. All these processes, i.e., coating, drying and annealing, were again repeated several times in order to get a desired film thickness. Subsequently, the multilayered film was preheated in air at 500 °C for 2 h and finally heated again at 800 °C for 2 h in a hydrogen atmosphere or in air. Four kinds of samples were prepared for this experiment and the preparation conditions are summarized in table 1.

The thickness and the morphologies of the thin film samples were investigated by using a scanning electron microscope (SEM, Hitachi S-800). For the measurement, we made a transverse cut in the glass coated substrates and then took the image of the cross section using the SEM. The thickness of the glass layer was estimated by comparing the layer thickness with the scale given on the image. The thicknesses of the six-layered glass films coated on Al/Si substrates were about 700–800 nm. The PL spectra were measured at room temperature under excitation by 488 nm light from an Ar⁺ ion laser. The PL signal was detected by using a spectrometer (SPEX 1702) equipped with a photomultiplier tube (PMT, Hamamatsu R928) as a detector and then recorded with a computer.

3. Results and discussion

Sm ion is one of the most popular rare earth ions for PSHB use together with the Eu ion and it has sharp emission lines due to the f–f transitions in visible region. As mentioned in the introduction, a glass is a preferred host material for PSHB experiments because it provides a wide inhomogeneous linewidth compared to all other single crystals. However, reducing trivalent Sm ions to divalent ions in glass is not easy. Several researchers showed that this problem could be overcome by incorporating Al₂O₃ in a sol–gel process. Nogami *et al* [14, 15] reported that Al₂O₃ co-doped in silica glass helped with the dispersion of Sm ions in the matrix and increased the Sm²⁺ fluorescence intensity. Jin *et al* [17] also studied the role of Al in sol–gel derived glasses by means of an NMR and x-ray diffraction experiment and showed that the formation of AlO₄ promotes the homogeneous dispersion of Sm and enhances the PL.

In this experiment, we also used 10 mol% of Al₂O₃-containing Sm doped glasses (aluminosilicate). Sm²⁺ has several emission lines originating from the transitions between the first excited states ⁵D_{J'} and the ground states ⁷F_J, where J, J' = 0, 1, 2, ... While almost all the transition lines can be observed for Sm²⁺ doped single crystals, only a few lines are observed for Sm²⁺ doped glasses. Song *et al* [18] interpreted this as follows. In general, the electrons excited by a laser to the 4f5d band of Sm²⁺ rapidly relax to each ⁵D_{J'} level nonradiatively and then radiatively decay to each ⁷F_J level. The energy difference between the 4f5d band and ⁵D_{J'} levels strongly affects the luminescence properties of Sm²⁺ ions. In the case of Sm²⁺ doped single crystals, since the energy of the 4f5d band is close to the ⁵D₂ level, the optically excited electrons in the 4f5d band first relax to the ⁵D₂ level and can then transit to the levels ⁵D₁ and ⁵D₀, cascadingly, through nonradiative decay processes where the electrons again decay radiatively to the ground states, emitting all the relevant fluorescence lines. On the other hand, in the case of Sm²⁺ doped glass matrix, the only observed emission lines were from the level ⁵D₀, i.e., ⁵D₀–⁷F₀, ⁵D₀–⁷F₁, ⁵D₀–⁷F₂ etc, because the energy of the 4f5d band is close to the ⁵D₀ level which makes almost all the electrons excited by optical pumping rapidly decay radiatively via just the level ⁵D₀.

Figure 1 shows the PL spectra of Sm²⁺ doped glass thin films. The labels (a)–(c) denote the PL spectra of the corresponding samples (a)–(c) listed in table 1, respectively. The thin solid curve in spectrum (c) is a fit result which is convoluted with the multiple Gaussian functions shown with six dotted lines. As shown in the figure, three broad peaks originating from the transitions of ⁵D₀–⁷F₀ (denoted by 0–0), ⁵D₀–⁷F₁ (0–1) and ⁵D₀–⁷F₂ (0–2) are clearly observed. In view of the results of Asatsuma *et al* [19], prior to glass coating we coated Al on a Si substrate, expecting the fluorescence efficiency to be enhanced. Although the effect of Al in sol–gel derived glasses, which is doped as Al₂O₃, on the fluorescence efficiency of Sm²⁺ was recently reported [14, 17], there have been no reports concerning the role of metal Al coated on a substrate in a reduction process. However, in this experiment, we observed a big enhancement of the fluorescence efficiency of the Sm²⁺ doped glasses due to the coating of metal Al.

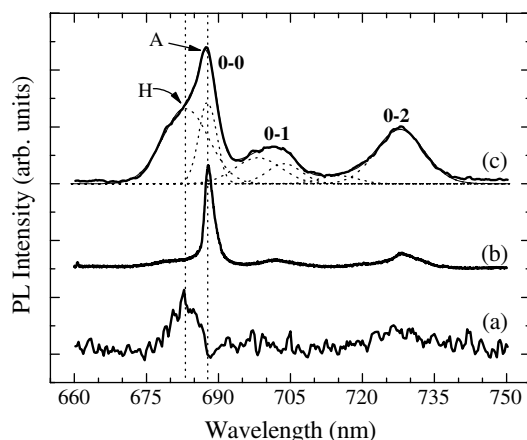


Figure 1. PL spectra of Sm^{2+} doped glass thin films. The glass films were (a) coated on a bare Si substrate and heat treated in a hydrogen atmosphere, (b) coated on a Al/Si substrate and heat treated in air, (c) coated on a Al/Si substrate and heat treated in a hydrogen atmosphere. The thin solid curve in (c) is a curve fitted by multiple Gaussian functions and six dotted lines correspond to Gaussian functions. The two vertical lines are guides for a comparison of peak positions.

In addition to the enhancement of the fluorescence efficiency, we also observed differences in spectral shape and position from the various reduction methods. As can be seen in spectrum (c), the $^5\text{D}_0\text{--}^7\text{F}_0$ transition band can be deconvoluted into two distinct peaks. On the other hand, the spectra of samples (a) and (b) show only one peak. By comparing these three spectra carefully, we found that the positions of all peaks for the samples (a) and (b) coincide with all peaks of the deconvoluted spectrum of (c). This means that the sites at which Sm ions reside preferentially differ for different preparation methods. We assume that the formation of these different environments is due to the two different reduction mechanisms reduced by hydrogen and by the oxidation of metal Al.

The reaction of Sm^{3+} with H_2 can be considered as follows:



It is also possible that Sm^{3+} is reduced to Sm^{2+} concurrently with the oxidation of Al to Al^{3+} . This reduction process is due to the standard reduction potential difference between Al^{3+}/Al and $\text{Sm}^{3+}/\text{Sm}^{2+}$. The standard reduction potential, E^0 , of Al^{3+}/Al is -1.662 V versus SHE (the standard hydrogen electrode), while E^0 for $\text{Sm}^{3+}/\text{Sm}^{2+}$ is -1.55 V versus SHE [20]. The reduction of Sm^{3+} ions by aluminium oxidation proceeds through the following scheme describing the oxidation/reduction process:



As a result, it can be considered that two different environments surrounding Sm^{2+} ions are formed, which results in two 0–0 transition peaks. Thus, we think that the peaks denoted by H and A originate from the sites due to the processes described in equations (1) and (2), respectively. In addition to the different peak positions, the linewidth of the spectrum is also changed with reducing conditions, i.e., the linewidth of sample (b) is much narrower than that of sample (a).

We can clearly see the existence of Sm^{2+} ions from the spectrum (b) in figure 1. The sample (b) was heat treated in air in order to reduce the Sm^{3+} to Sm^{2+} . So far, there has been no report that Sm doped glasses can be reduced in air. Thus, spectrum (b) strongly implies

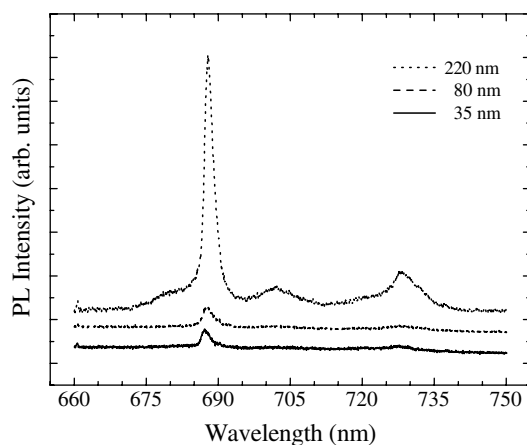


Figure 2. PL spectra of Sm^{2+} doped glass films having different Al thicknesses.

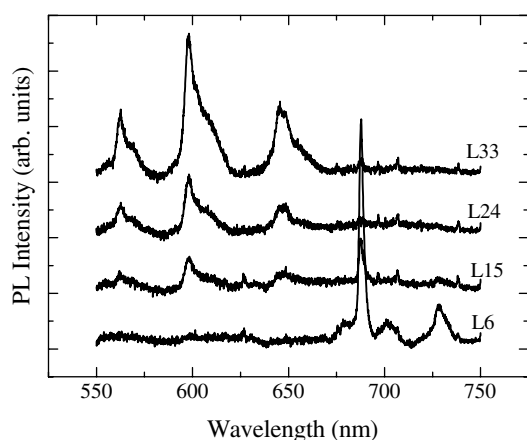


Figure 3. PL spectra of Sm doped glass films measured with different film thicknesses. Al/Si substrates with the Al thickness of 220 nm were used and heat treated in air.

that metal Al coated on a Si substrate played an important role in the reduction of Sm^{3+} . To the best of our knowledge, this result is the first observation of the reduction of Sm^{3+} doped in aluminosilicate glass to Sm^{2+} by heat treatment in air.

Figure 2 shows the variation of the PL intensity depending on the thickness of the Al layer coated on Si substrates. Three samples having different Al layer thicknesses, but with same glass thickness of six layers, were used for the comparison of PL efficiencies. The thicknesses of the Al layers measured from SEM images were about 35, 80, 220 nm. The Sm^{3+} doped glasses coated on Al/Si substrates were heat treated at 800 °C for 2 h in air. As can be seen in the figure, the PL intensity increased with increasing Al thickness. This result also supports our assertion that the metal Al can affect the process of reduction.

We assume that Al can penetrate the glass layer and chemically react with it through the high temperature annealing process. To confirm this assumption, we carried out two experiments. Figure 3 shows PL spectra measured from samples having different glass thicknesses coated on a given Al thickness (220 nm). The numbers in the labels L6, L15, L24, L33 mean the numbers of glass layers coated on the Al/Si substrate. With increasing

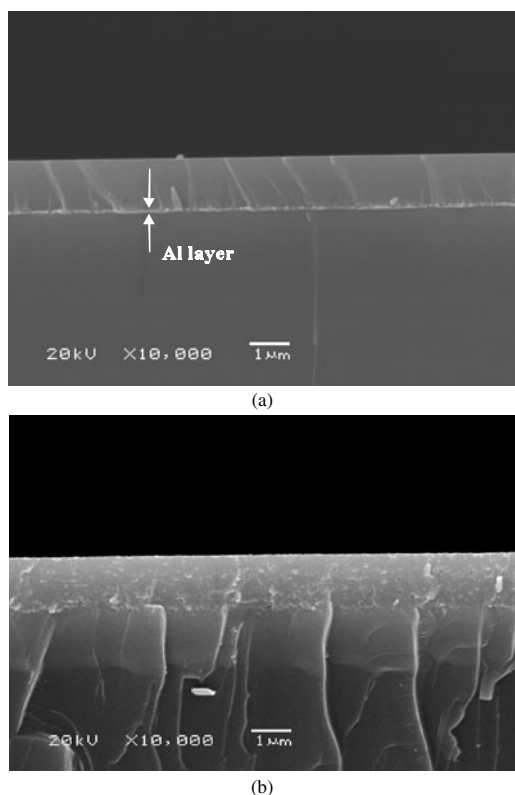


Figure 4. SEM images of the sections of the glass coated Al/Si substrates; (a) before heat treatment; (b) after heat treatment.

glass thickness, new peaks appeared in the short wavelength region. These peaks are due to the emissions of Sm^{3+} ions [21, 22]. Conversely, the PL intensity of the Sm^{2+} ions decreases with increasing glass thickness.

This may be interpreted as follows. As the glass thickness increases for a given Al thickness, the amount of Al becomes insufficient to fully reduce the Sm^{3+} ions in the upper part of the glass; i.e., the upper part of the glass could not be supplied with sufficient Al because Al is already exhausted in the lower part of the glass film. As a result, the Sm^{3+} ions in the upper part of the glass layer remain unreduced and the upper part of the glass layer may prevent the excitation laser from penetrating the lower part of the glass layer or block the fluorescence of Sm^{2+} which comes from the lower part of the glass film. This results in a decrease in Sm^{2+} PL intensity with increasing glass layer thickness. We can see the existence of Sm^{3+} ions from the transition lines in the PL spectrum shown in figure 3.

Figure 4 shows SEM images of a cross section of the glass films. Figures 4(a) and (b) are the images taken before and after the samples were heat treated at high temperature, respectively. In figure 4(a), we can clearly see three separated layers; from bottom to top: Si substrate, an Al coated layer and a glass layer. However, there is no distinct layer which could be regarded as an Al layer in figure 4(b). This might mean that the Al layer is wholly diffused into the glass layer, which makes the physical structure of the Al layer disappear. This may thus support the notion that Al participates and plays an important role in the reduction of Sm^{3+} doped in glasses.

4. Conclusions

Sm³⁺ doped aluminosilicate glass films (10Al₂O₃·90SiO₂) were fabricated by a sol–gel method and coated on bare Si and Al coated Si substrate (Al/Si). The coated glass films were reduced in two different reducing atmospheres, i.e., by heat treating the glass at 800 °C for 2 h in hydrogen or in air. Sm³⁺ doped films were well reduced in a hydrogen atmosphere but not reduced in air without coating Al on the Si substrate. On the other hand, the glass coated on the Al/Si substrate was successfully reduced in air, i.e., without hydrogen gas. The optical properties of Sm ions, such as peak position and bandwidth, depended strongly on the reducing method. In this study, we found that the metal Al coated on a Si substrate plays an important role in the reduction of Sm³⁺ doped aluminosilicate glasses.

Acknowledgment

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