Persistent Spectral Hole Burning in Samarium and Aluminum Codoped Silica Films Prepared by RF Sputtering

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RF スパッタリングにより作製したサマリウム・アルミニウム含有シリカ薄膜の 永続的スペクトルホールバーニング

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We observed persistent spectral hole burning in the excitation spectra of a Sm and Al codoped SiO₂ thin film at 77 and 180 K. The film was prepared from Sm, Al and SiO₂ by RF co-sputtering at a substrate temperature of 300°C. At 77 K, the width of the hole was 2 cm⁻¹ with a depth of 4% of the total intensity, while at 180 K, they were measured at 10 cm⁻¹ and 1% of the total intensity. The optical absorption and photoluminescence properties of the deposited films were changed by the use of elemental Sm and Al instead of Sm₂O₃ and Al₂O₃.

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1. Introduction

Reports of persistent spectral hole burning (PSHB) at room temperature in fluoride single crystals,¹⁾ and then the subsequent discovery of PSHB in glass materials²⁾ have spurred an unprecedented effort by many research groups to explore both the physical mechanism underlying this phenomenon and its technological potential for optical memories. Glasses have the potential to be more suitable for high-density memory device than single crystals because of their wide inhomogeneous width, high transparency and easy mass production. To date, however, these materials have only been prepared in bulk form by conventional glass-melting techniques²⁾ or by sol-gel processes.³⁾⁻⁶⁾ Preparation of thin films of suitable materials is of significant importance. The only report of PSHB in thin films at high temperature was by Asatsuma et al.⁷⁾ who observed it in Sr-halide crystal films. We report on our observation of PSHB in a Sm²⁺-doped amorphous thin film at a temperature of 77 K and above.

2. Experimental

Sm and Al codoped SiO₂ films were prepared using an RF magnetron sputtering apparatus (Anelva, Model SPF-332H) under the conditions listed in Table 1. A Sm chip

(5×5×1 mm³, purity 99.9%) was placed on an Al plate (φ20 mm×1 mm, purity 99.99%) which was placed on a SiO₂ (purity 99.99%) target of 3 inches in diameter. Then the target (Sm+Al+SiO₂) was co-sputtered to deposit films S1-S5, as listed in Table 1. The Sm and Al concentrations of the films were varied by slightly changing the positions of the Sm chip and the Al plate around the center of the SiO₂ target. For comparison, Sm₂O₃ chips (5×5×1 mm³, 3 pcs.) and Al₂O₃ chips (5×5×1 mm³, 6 pcs.) were used for film S6 instead of the Sm chip and the Al plate, respectively.

The structure of the films was determined by X-ray diffraction analysis (Rigaku, Model RINT2100). The composition of the films was determined by X-ray photoelectron spectroscopy (XPS) using monochromatic AlK α radiation (Physical Electronics, Model 5500). Film thickness was measured with a stylus-type instrument (Sloan, Model Dektak3). The optical absorption spectra of the films were measured in the range of 300-800 nm with a spectrometer (Shimadzu, Model UV-3100PC). The photoluminescence (PL) spectra excited by 400-nm light were measured in the range of 550-850 nm with a band-width of 1.5 nm using a spectrophotometer (Shimadzu, Model RF-5300PC) at room temperature. Hole-burning experiments were carried out using an Ar-ion laser pumped DCM dye laser with a linewidth of 1.3 cm⁻¹ at 77, 180 and 300 K. Samples were irradiated using a 683 nm wavelength of the DCM dye laser operating at 640 mW/mm² for 600 s. After irradiation, the excitation spectra were obtained by scanning the output of the DCM dye laser (6 mW/mm²) and monitoring the ⁵D₀→⁷F₂ emission at 725 nm.

3. Results and discussion

All the films deposited in this study were confirmed to be amorphous by X-ray diffraction analysis. The composition and thickness of the deposited films are listed in Table 2. The XPS analysis revealed that the composition of the films

Table 1. Sputtering Condition

Sputtering gas	Ar (purity 99.999%)
Gas pressure	1.0 Pa
RF power	200 W
Substrate material	Fused silica
Substrate temperature	300 °C
Substrate-target distance	50 mm
Target	(Sm + Al + SiO ₂) for S1-S5 or (Sm ₂ O ₃ + Al ₂ O ₃ + SiO ₂) for S-6
Sputtering time	5h

Table 2. Thickness and Composition of the Deposited Films

Film number	Thickness (μm)	Composition (at. %)		
		Sm	Al	Si
S-1	7.58	1.8	7.8	90.4
S-2	5.83	2.1	13.5	84.4
S-3	6.38	2.3	11.5	86.2
S-4	5.45	2.4	11.6	86.0
S-5	5.83	16.5	8.9	77.4
S-6	5.83	16.5	24.5	59.0

S1–S4 was in the range of the reported values for bulk materials.³⁾ The color of these films was clear brown with a slightly reddish tinge. The film S5 was dark brown, while the film S6 was transparent with a faint pink tinge. Figure 1 shows the optical absorption spectra for these films. The strong absorption of the films S1–S5 in the range of 300–600 nm may be due to the $4f^6 \rightarrow 4f^5 5d$ transition of the Sm^{2+} ions or to defects produced by reduction within the Al–Si–O network. No sharp peaks from the $f-f$ transition of Sm^{3+} ions or Sm^{2+} ions were found in these spectra, while two prominent peaks were found in the spectrum of film S6 at 401 and 628 nm, which were attributed to the $^6H_{5/2} \rightarrow ^6P_{3/2}$ transition of Sm^{3+} ions and the $^7F_0 \rightarrow ^5D_1$ transition of Sm^{2+} ions, respectively. These results indicate that reducing conditions are more easily obtained by using elemental Sm and Al rather than Sm_2O_3 and Al_2O_3 .

Sharp peaks were observed in the PL spectra of all films except film S6, as shown in Fig. 2. The PL lines at 683, 700, 725 nm were attributed to $^5D_0 \rightarrow ^7F_{0,1,2}$ transitions of the Sm^{2+} ions, respectively. No PL lines for Sm^{2+} were observed in the spectrum of S6, probably because of a lack of absorption for excitation, although the presence of Sm^{2+} ions was confirmed in the absorption spectrum. On the other hand, weaker peaks were observed for S5, although it had the same Sm concentration as S6. This difference can be attributed to the difference in absorption for excitation. The low PL intensity for S5, compared with those of S1–S4, was due to the absorption of emissions by the $f-d$ transition of Sm^{2+} . S3 had the maximum PL peak intensity at 683 nm, whereas S4 had approximately half the intensity of S3. This result indicates that the PL peak intensity is not dependent on the composition of the films, because both these had roughly the same composition. Further investigations are in

progress to clarify the factors governing the PL intensity.

S3 was used for the PSHB experiments because of its high PL intensity. Figure 3 shows the excitation spectra of Sm^{2+} in the as-deposited film measured at 77, 180 and 300 K after irradiation with a dye laser. The hole depth decreased as temperature increased. The width and depth of the hole at 77 K were 2 cm^{-1} and 4% of the total intensity, respectively. They were approximately 10 cm^{-1} and 1% of the total intensity at 180 K. We could not find a hole clearly at 300 K, because of the small signal to noise ratio in the excitation and hole spectra. Compared with the PSHB of the sol-gel derived Sm^{2+} -doped aluminosilicate glass,³⁾ which was observed to have a depth of 10% and a width of 15–17 cm^{-1} at room temperature, the hole profile of the present film was apparently shallower. For application in the optical data storage at room temperature, deep and narrow holes are required. This difference is the object of the further studies. However, we believe that this PSHB observation is a significant step towards the frequency domain optical

Fig. 2. Photoluminescence spectra, excited at 400 nm, of Sm and Al codoped SiO_2 films. The spectra of S5 and S6 are shown in the insets.

Fig. 1. Optical absorption spectra of Sm and Al codoped SiO_2 films. The spectrum of S5 is multiplied by a factor of 0.2.

Fig. 3. Excitation spectra of S3 measured at 77, 180, 300 K monitored at 725 nm after irradiation at 683 nm.

storage applications and the sputtering method is the most promising method for fabricating them.

4. Conclusions

We observed PSHB at 77 and 180 K, in Sm and Al codoped SiO₂ thin films deposited from Sm, Al and SiO₂ by RF sputtering at a substrate temperature of 300°C. The optical absorption and photoluminescence properties of the deposited films were affected by the use of elemental Sm and Al instead of Sm₂O₃ and Al₂O₃.

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