Preparation Studies of Calcium Sulfide Films for Optical Data Storage

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Abstract- The preparation of CaS films by magnetron sputtering with the requisite properties for optical recording is studied. Sputtering targets are produced from pressed powders permitting rapid investigation of the optimum dopant concentration of the rare earth ions Eu and Sm. The problem of negative ion re-sputtering is addressed but low sputtering rates remain a problem.

Key words: electron trapping optical memory, non-thermal recording mechanisms, CaS optical films

1. Introduction

The goal of the optical recording industry is to achieve areal storage densities of the order of 1Tb/in² by 2010. All current disk-based optical recording technologies employ a thermal recording mechanism. Crucial to the successful operation of the recording process is the strict requirement that the thermal energy deposited in the medium remains localised within the addressed data cell and does not spread laterally to corrupt adjacent cells. Every increase in the storage density challenges the thermal performance of the medium. Alternative non-thermal optical recording technologies are receiving increasing attention. For example media capable of supporting a purely electronic recording mechanism may be produced by introducing application specific energy levels and/or spatially localised impurity centres into the electronic structure of a wide bandgap host material by controlled doping. This concept was first proposed as early as 1988^{1),2)}.

In this recording scheme, shown schematically in its simplest form in Figure 1, the write mechanism involves focussing optical radiation to excite electrons from either the valance band of the host or luminescent centres created by one dopant species (eg. Eu) to electron traps created below the conduction band of the host by the second species (eg. Sm). The optical write energy must therefore be greater than or a substantial fraction of the bandgap and hence write wavelengths in the short visible or near uv are required. To readout the information represented by the 'trapped' electrons it is necessary to eject them from the traps in order that they may register their presence by some means. The process of photo-stimulated luminescence (PSL) achieves this. If the depth of the trap is an eV or so below the conduction band then the stimulating wavelength falls in the infra-red and this mechanism is commonly referred to as infra-red stimulated luminescence (ISL). The presence of recorded information is signalled by the emission of radiation at a

wavelength intermediate between the write and readout wavelengths. Readout is obviously partially destructive of the stored data and data refresh is required.

This report addresses the problem of preparing this type of media in the form of optical quality thin films. The host material selected for study is calcium sulfide ($E_g = 4.8\text{eV}$) since it is the alkaline earth sulfide that has received least attention in this context despite being potentially more stable than SrS. The aim is to produce sputtering targets of this material containing the necessary concentration of dopants in a form that allows the production of films exhibiting the requisite microstructure and optimum levels of Eu and Sm sites to facilitate recording.

Fig.1 Schematic showing one possible Write/Readout process and the part played by Eu and Sm in creating the necessary levels in the host (CaS) bandgap.

2. Experimental details

Initial investigations into basic luminescence and structural properties of CaS doped with Eu and Sm were carried out on powder samples prepared as follows. Calcium sulfide powder (Aldrich 99.9+%) was mixed intimately with various concentrations of Eu₂O₃, Sm₂O₃ (99.99%) and 0.1 weight % of elemental sulfur to provide a sulfurising atmosphere during initial heating. This mixture was loaded into a closed end silica tube of 10mm diameter capped by a similar tube of slightly larger diameter and heated in a tube furnace at 1200 C for 2h under a nitrogen atmosphere, with a trace of H₂S present to remove oxide. During cooling to room temperature a nitrogen atmosphere was maintained in the furnace.

Characterisation of the resulting phosphor samples prior to processing into sputtering targets involved assessment of both phase purity and lattice constant using x-ray diffraction, measurement of luminescence spectra on a Perkin-Elmer LS-50 fluorescence spectrometer and the ISL intensity at 650nm when stimulated at 1200nm using purpose built equipment.

Sputtering targets 100mm in diameter were formed by pressing 6gm of powdered material into a stainless steel die using a pressure of 260kg/cm² maintained for approximately 30minutes. Films were magnetron sputtered from these targets in an atmosphere of pure argon (8mtorr) onto water cooled Vycor[®] substrates using 100W of rf power. To investigate and control the degree of re-sputtering of negative ions, earth shields³⁾ of various depths were arranged to surround the substrate by projecting from the grounded substrate table into the plasma. As deposited the structure of the films was poorly developed. Annealing at 973K for 30minutes in a flowing gas stream of dry nitrogen and hydrogen sulfide rectified this.

3. Results

In the first part of the following discussion Figs 2 through 7 relate to characterisation of the powder samples used to prepare sputtering targets. Figure 2a) shows the emission spectrum of CaS doped only with Sm. This is used to identify the $^4G_{5/2}$ - $^6H_{5/2}$ transition of the Sm³⁺ ion in the spectrum of CaS doped equally with Eu and Sm Fig 2b) where it shows only weakly at around 570nm in the presence of the Eu emission centered on 650nm. The scales in Figs 2a&b) are comparable. The strength of this $^4G_{5/2}$ - $^6H_{5/2}$ transition is then taken as indicative of the number of Sm³⁺ sites produced by a given Sm concentration. Figure 3 shows the intensity of the $^4G_{5/2}$ - $^6H_{5/2}$ emission as a function of Sm concentration increasing smoothly up to a broad peak at about 1000ppm Sm. Using the magnitude of the 570nm peak as a measure of the number of Sm³⁺ sites, Fig 4 shows that the number of such sites created by a given Sm concentration correlates well with the ISL output of the medium as a function of Sm concentration. ISL is produced by the stimulated release of electrons trapped at Sm³⁺ sites, the close correlation observed in Fig 4 confirms the validity of using the 570nm emission peak as a measure of the number of such sites created by a given Sm concentration.

Figure 5 shows the intensity of the broad $4f^65d^1-4f^7$ (650nm) transition of the Eu²⁺ ion as a function of increasing Sm concentration. This shows a linear decrease in emission as the number of trapping sites increases followed by an increased emission above 1000ppm. The peak of the ISL stimulation occurs for wavelengths around 1200nm as shown in Fig.6. Finally Fig.7 shows that CaS:Sm,Eu sputtering target mixtures can be formulated to produce sufficient electron traps which when full can be stimulated by IR to produce an

output (readout) signal at 650nm that is a linear function of the stimulating intensity over more than three orders of magnitude.

Films sputtered from targets prepared as described above are, as deposited, smooth and transparent but have no crystal structure and show no luminescent behaviour. The deposition rate is relatively low (~ 1nm per min.) so that several hours are required to produce the 300nm to 400nm films examined to date.

The luminescent behaviour developed following annealing is shown in Fig. 8. Note the crucial role played by the earth shield surrounding the substrate. Finally, the x-ray spectra shown in Fig.9 confirm the development of crystal structure on annealing.

Fig.2 (a) The emission spectrum of CaS doped only with Sm. Note $^4G_{5/2}$ - $^6H_{5/2}$ transition of Sm³⁺ ion. **(b)** Emission spectrum of CaS doped equally with Eu and Sm.

4. Discussion

The strength of the fluorescence emission from the $^4G_{5/2}$ - $^6H_{5/2}$ transition of Sm³⁺ ion has been shown to be a good indicator of the level of the ISL output for powder samples. It is also demonstrated that the maximum ISL response occurs for dopant concentrations of 1000ppm

Fig.3 Strength of $^4G_{5/2}$ - $^6H_{5/2}$ transition as a function of Sm concentration – Eu concentration 1000ppm.

Fig.4 Correlation of emission strength of $^4G_{5/2}$ - $^6H_{5/2}$ transition (taken as indicative of the number of Sm^{3+} sites) with ISL output as a function of Sm concentration.

Fig.5 Emission intensity of the broad $4f^65d^1-4f^7$ transition of the Eu^{2+} ion as a function of increasing Sm concentration.

Fig.6 ISL stimulation spectrum showing peak response at around 1200nm.

Fig.7 Typical ISL output as a function of incident readout energy at $\lambda=1200nm$ for the powders studied.

and 750ppm of Eu and Sm respectively. In Figure 5 the fluorescence emission intensity at 650nm decreases linearly, as expected, as the number of trapping sites increases up to 750ppm Sm. The increase in emission at 1000ppm Sm and above is unexpected and currently unexplained but could be a consequence of non-uniform dopant distribution in the powder.

Peak ISL emission occurs for a stimulation wavelength of 1200nm, which is believed⁴⁾ associated with the $4f$ to $5d$ transition in Sm^{2+} . The necessity of addressing the problem of negative ion re-sputtering when producing alkaline earth sulfide films is confirmed. The development of good crystal structure in magnetron sputtered CaS requires subsequent thermal processing.

Fig.8 Emission spectra of films re-crystallised by annealing showing the necessity of the substrate earth shield in preventing excessive negative ion re-sputtering.

Fig.9 X-ray diffraction spectra of sputtered films showing how the essentially as deposited amorphous structure is developed into full crystallinity on thermal annealing (R TA).

Whilst the films produced to date appear to have the requisite emission properties for optical storage, the very low sputtering rate employed means they are as yet too thin (300-400nm) for practical application. The scales in Figures 2(b) and 8 are directly comparable but the monochromator slits were set much wider when taking the data for Figure 8. The fluorescence output from the films is thus approximately one twentieth that from the powder samples in reflection. Similar scaling holds for the ISL output from these films. If plotted on Figure 7, which shows the ISL output from a powder sample, the maximum output from a current film would be less than ten units. Their output is therefore insufficient for the sensitivity of the present equipment to permit detailed ISL and other recording studies. These results are however fully consistent with our original estimates based on the ISL output from a cubic micron of film forming the minimum detectable base for optical recording by this process. Assuming the "bit" diameter is determined by wavelength of the infra-red readout beam focussed to the diffraction limit the film thickness required is of the order of a few micron i.e. some ten to twenty times that of the present film samples.

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