Optical properties of magnetron sputtered Tb$^{3+}$ ions containing thin dielectric films for thin film solar cells applications

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Abstract. Results are presented on the deposition and characterization of thin SiO$_2$ and Al$_2$O$_3$ films containing Tb$^{3+}$ ions developed for application as spectral converters. The films are prepared by RF magnetron co-sputtering. The photoluminescence (PL) is measured at room temperature using the 488 nm line of an Ar laser. The dependence is studied of the PL intensity on the Tb concentration in the film. It is found that the intensity exhibits a maximum at about 1 at.%. Annealing studies are performed on SiO$_2$:Tb using two different methods to improve the PL intensity. In both regimes of annealing, the best results are obtained at 650 - 700°C. After treatment at this temperature the Tb PL increases 2.5 - 3 times.

1. Introduction

One of the ways proposed for increasing the efficiency of solar cells is the application of spectral converters [1]. By absorbing light with a shorter wavelength and emitting at a longer wavelength they can transform the solar spectrum to a spectral region better suited to the absorption characteristics of the solar cell materials. For the implementation of this idea, semiconductor nanoparticles [2] or rare earth ions [3] could be used.

Solar cells with glass on the front side have a poor blue and near UV response due to absorption in the glass and in the doped layer. This poor response of so-called superstrate solar cells could be enhanced by spectral conversion of the solar spectrum. Tb$^{3+}$ ions embedded in a transparent film deposited on the front of the glass could convert light from the UV region into the range of 400 – 600 nm [4]. This light would pass through the glass and be utilized by the thin film Si based solar cell deposited on its back.

In this report we present a study of the optical properties of thin films of SiO$_2$ and Al$_2$O$_3$ containing Tb$^{3+}$ ions deposited by magnetron co-sputtering. The dependence was investigated of the
photoluminescence intensity in the above range on the Tb concentration and on heat treatment of the films.

2. Experimental
Thin films were deposited by magnetron co-sputtering using a SiO$_2$ or an Al$_2$O$_3$ target. Pieces of Tb foil of different areas were placed inside the erosion zone of the target. Silica, polished Si and sapphire substrates were used without intentional heating. The substrates were placed in the center of the sample holder, which was parallel to the target at a distance of 12 cm from it. The area of the Tb pieces (i.e., the Tb concentration) and the sputtering power, $P$, (i.e., the deposition rate) were varied. The Tb concentration was measured by Rutherford backscattering spectroscopy (RBS). The thickness of the films was determined by a profilometer.

The photoluminescence (PL) was measured at room temperature by using the 488 nm line of an Ar laser at a power of 2 mW and a nitrogen-cooled CCD camera attached to a single monochromator. Annealing was performed to improve the PL intensity of the SiO$_2$:Tb films employing two different methods: (i) 30 min in vacuum in a tube furnace and (ii) rapid thermal annealing (RTA) for 5 min in nitrogen atmosphere in the temperature interval 600 – 900°C. The PL spectra after the annealing were recorded with a double monochromator and a photomultiplier. The 488 nm laser beam was chopped at 85 Hz and the PL signal was detected by a lock-in amplifier.

3. Results and discussion
The photons of the 488 nm Ar laser line excite the Tb$^{3+}$ ions resonantly from the $^7F_6$ ground state into the $^5D_4$ level [4]. The radiative transitions to the $^7F_{3,4,5}$ levels were recorded. Figure 1 shows a typical PL spectrum of a SiO$_2$:Tb thin film. This spectrum was spectrally corrected for the experimental setup.

![Figure 1. PL spectrum of a 220 nm thin SiO$_2$:Tb film on a Si substrate containing 1.1 at.% Tb.](image-url)

Three characteristic bands were observed and identified as the following 4f-4f transitions: $^5D_4 - ^7F_5$ ($\sim 546$ nm), $^5D_4 - ^7F_4$ ($\sim 586$ nm) and $^5D_4 - ^7F_3$ ($\sim 622$ nm). These emission lines appeared on a broad background which could be related to the luminescence of defects inside the SiO$_2$ matrix.

Different series of samples were sputtered with SiO$_2$ or Al$_2$O$_3$ targets on different kinds of substrates and at two different sputtering powers of 150W and 180W. The intensity of the 542 nm PL band, normalized against the film thickness, is plotted against the area of Tb foil used during the sputtering of the SiO$_2$:Tb films in figure 2, where the different series of samples are shown with different symbols and the substrate and power used are shown. The inset in figure 2 shows the dependence of the Tb concentration on the Tb foil area for most of the same samples, which can be approximated by a linear function. Figure 3 exhibits similar data for the Al$_2$O$_3$:Tb films. In this case all the samples were sputtered at one and the same power of 150 W. The PL intensity, normalized against
the film thickness, exhibits a maximum at about 1 at.% of Tb for the SiO$_2$ and apparently for the Al$_2$O$_3$ matrix. At higher Tb content concentration quenching of the PL sets in [5,6]. It was found that the PL intensity of the thin films on Si substrates was higher than on silica substrates. This could be caused by the different optical properties, which was not considered in the data evaluation. The silica substrates are transparent, whereas the Si substrates lead to interference effects because of the greater refractive index.

Figure 2. Dependence of the PL intensity from thin SiO$_2$:Tb films on the Tb area. The deposition conditions are indicated in the figure. The intensities are normalized against the film thickness. The Tb area corresponds to the Tb concentration in the films (see inset).

Figure 3. Dependence of the PL intensity from thin Al$_2$O$_3$:Tb films on the Tb area. The substrates used are indicated in the figure. The intensities are normalized against the film thickness. The Tb area corresponds to the Tb concentration in the films (see inset).

Further, the dependence was investigated of the PL intensity of the SiO$_2$:Tb samples on the annealing temperature using the two different annealing methods described above. The sample used for the experiment was a 260 nm thin SiO$_2$:Tb film on a Si substrate, which was sputtered with a Tb area of 150 mm$^2$ (Tb concentration of 0.89 at.%). The ratio of the PL intensity in the 542 nm band after the annealing to that before the treatment is given in table 1. The best annealing conditions for thin SiO$_2$:Tb films were found to be in the temperature range 650 – 700°C.

In figure 4 the influence of the two annealing methods is compared for 700°C. Annealing in vacuum for 30 min leads to an increase of the background luminescence, which could be related to defects inside the SiO$_2$ matrix, because of possible outgassing (figure 4 (a)). The samples annealed by
RTA in a nitrogen atmosphere for 5 min did not show this effect (figure 4 (b)). Similar annealing could be used for processing the Tb³⁺ containing films for solar cell applications. After the treatment the substrates with the dielectric film on the front side can be used for depositing thin film solar cells on the back side.

Table 1. Dependence of the PL intensity of the SiO₂:Tb samples on the annealing temperature (T).

| Annealing T [°C] | 600 | 650 | 700 | 800 | 900 |
|------------------|-----|-----|-----|-----|-----|
| PL ratio – vacuum| 2.1 | 2.4 | 2.2 | 1.9 | 1.5 |
| PL ratio - RTA   | 2.4 | 2.5 | 2.7 | 2.5 | 1.8 |

Figure 4. PL spectra of a sample with 260 nm thin SiO₂:Tb film on a Si substrate, sputtered with a Tb area of 150 mm². The sample is annealed (a) in a tube furnace for 30 min in vacuum and (b) by RTA for 5 min in nitrogen both at 700°C.

4. Conclusion
Thin films of SiO₂ and Al₂O₃ containing Tb³⁺ ions were prepared by magnetron co-sputtering. They exhibited photoluminescence in the visible between 500 and 650 nm which makes them suitable for application as spectral converters in thin film silicon based superstrate solar cells. The maximum PL intensity was observed for samples containing about 1 at.% Tb. At higher concentrations quenching sets in.Annealing in vacuum in a tube furnace and by RTA in nitrogen atmosphere was applied in an effort to increase the PL intensity. The RTA at 700°C gave the best results – a close to threefold increase of the PL intensity after annealing and no additional background luminescence. Such treatment could be applied to the substrate with the Tb³⁺ containing film on it before the solar cell deposition.

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