JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 9, September 2009, p. 1335 - 1338

Dependence of the photoluminescence intensity of Tb^{3+} ions in thin films on the deposition conditions♣

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This paper presents results on the deposition and characterization of thin silica and alumina films containing Tb^{3+} ions, prepared by magnetron co-sputtering. The films are intended for applications as spectral converters of the solar spectrum in thin film silicon solar cells. The dependence of the photoluminescence intensity in the films on the deposition parameters and position on the substrate is studied, in order to assess the suitability of this method of preparation for the stated purpose, and to optimize the deposition conditions. At a distance of 7.5 cm between the target and the growing film, strong dependence of the photoluminescence (PL) intensity and film thickness on the substrate radial position is observed. The increased PL intensity over the erosion zone is explained by bombardment of the growing film by particles from the plasma, which causes a better dispersion of Tb ions and less clustering. However, greater distances between the target and substrates should be used for achieving a homogeneous PL intensity and thickness.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Rare earth ions, Photoluminescence, Solar cells, Spectral converters

1. Introduction

The next step in the development of third generation solar cells aims to achieve high efficiency devices, but still to apply thin film deposition methods [1]. One of the ideas in this direction is to extend the spectral sensitivity to shorter wavelengths by conversion of short wavelength photons to longer wavelengths at which the thin film solar cell is most efficient [2]. One possibility to do this is the use of rare earth ions in the front window layer of the cell. Such a rare earth ion is trivalent terbium – Tb^{3+}. It has emission bands in the region 400 - 600 nm, which is convenient for thin film silicon solar cells. This emission can be excited in the ion's f-d and f-f absorption bands situated between 200 and 400 nm. In this contribution, we study thin dielectric films containing Tb deposited by magnetron co-sputtering, with the view to optimize them for application in thin film silicon solar cells.

2. Experimental

SiO_2 and Al_2O_3 targets, with pieces of Tb foil on them, were sputtered in an Ar or Ar + O_2 atmosphere, using rf magnetron sputtering. The pieces of Tb were placed in the erosion zone of the 10 cm target, which was found at about 2 to 3 cm from the centre. The substrates were positioned on a parallel holder at a distance, *r*, above the target of between 7.5 and 14 cm. The deposition parameters, which were varied, are the following: the area of the Tb foil pieces, the Ar partial pressure in the plasma, P_{Ar}, the O_2 partial pressure in the plasma, P_{O2}, the deposition time, *t*, and the sputtering power, *P*. The substrates were not heated during the deposition. Polished Si substrates were used in all cases.

The PL was excited with the 488 nm line of an Ar^+ laser, and recorded using a SPEX 1403 double spectrometer and photomultiplier with a GaAs photocathode in a photon counting mode. The film thickness was measured with a Talystep profilometer, and the Tb and O concentrations by Rutherford Backscattering Spectroscopy (RBS), with an error of 0.05 at. %.

In order to study the dependence of the parameters of the deposited films on their position relative to the erosion zone, a 7.5 cm long Si substrate was placed so that its middle was in the centre of the sample holder, which is directly above the centre of the target. The Tb concentration, thickness and PL intensity of the deposited films were measured at several positions along this substrate.

♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

3. Results

3.1. Influence of the substrate position on the sample holder

A typical example of the RBS spectrum of a sample (deposited with 200 mm^2 Tb on the SiO_2 target, for t = 180 min, at P_{Ar} = 0.5 Pa, P_{O2} = 0 Pa, P = 180W and r = 12 cm) is presented in Fig. 1. The thickness of the sample is d = 600 nm. It can be seen that there is a slight gradient of the Tb concentration, which increases from 0.7 to 1.0 at. % from the surface to the substrate. Similar spectra were measured for the rest of the samples studied by RBS, and the Tb concentration was determined from them.

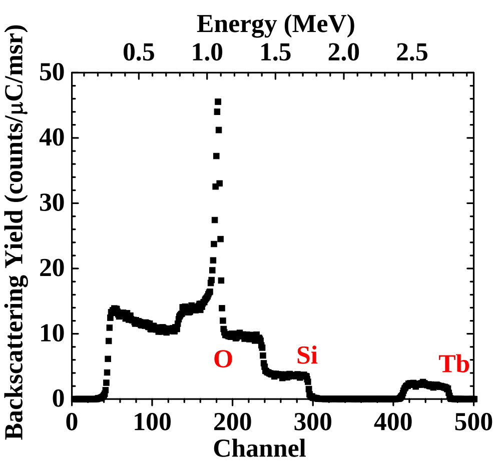

Fig. 1. RBS spectrum of a typical sample.

With the laser line we have used, the Tb^{3+} ions are excited resonantly through the $^7F_6 \rightarrow {^5D_4}$ transition and the PL spectrum consists of three bands due to the $^5D_4 \rightarrow {^7F_5}$ (~ 545 nm), $^5D_4 \rightarrow {^7F_4}$ (~ 590 nm) and $^5D_4 \rightarrow {^7F_3}$ (~ 620 nm) transitions [3]. The most intense of these bands is the first one. An example of it is shown in the inset of Fig. 2. The PL intensity in the maximum of this band at 542 nm, measured under fixed excitation and registration conditions and normalized to the thickness of the sample, will be used as a measure of the PL intensity in the rest of this study.

Fig. 2 shows the PL intensity dependence on the distance from the centre of the sample holder for two different distances r between the target and the substrates, r = 7.5 cm and r = 14 cm. The other deposition conditions were the same for both sets of samples: 440 mm^2 Tb on the SiO_2 target, P_{Ar} = 1 Pa, P_{O2} = 0 Pa, P = 120W, t = 90 min. The figure also shows the data for the thickness of the samples at several positions. As can be seen, the PL intensity passed through a minimum in the middle of the sample holder. In the case of the smaller distance, the PL intensity reached a higher value. However for the larger distance, the PL intensity was more homogeneous between -20 and +20 mm. The thickness was greater, and passed through a maximum in the middle of the sample holder for the smaller distance. For the bigger distance the thickness was much more homogeneous.

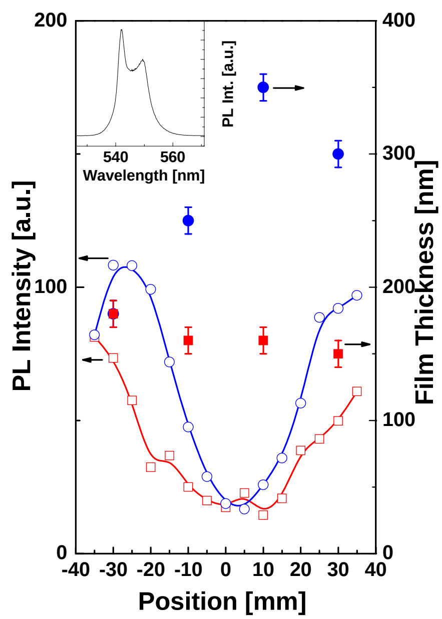

Fig. 2. Dependence of the PL intensity (open symbols) and film thickness (filled symbols) on the position on the sample holder, for distances to the target of: 14 cm (red squares) and 7.5 cm (blue circles). Inset: The most intensive PL band.

In Table 1, the data for the Tb concentration are given for the same conditions of deposition and the two distances to the target. The Tb concentration varied by less than 20% with position and with distance from the target. On the other hand the variation of the PL intensity with the position of the substrate on the sample holder was about a factor of six, between the minimum and the maximum (Fig. 2).

Table 1. Dependence of the Tb concentration on the position on the sample holder, for two distances to the target.

Position [mm]	Tb concentration [at. %]	
	r = 7.5 cm	r = 14 cm
-30	1.9±0.10	1.75±0.05
-10	-	2.1±0.05
10	1.7±0.05	-
30	1.75±0.05	2.05±0.05

3.2. Influence of the argon pressure

Table 2 contains the values of the PL intensity, Tb concentration and sample thickness averaged across the sample holder, for two sets of samples differing only in argon partial pressure in the plasma. The rest of the deposition conditions were the same as above, and *r* was 7.5 cm.

Table 2. Dependence of the mean PL intensity, mean Tb concentration and mean sample thickness on the argon pressure, P_{Ar}

Ar Pressure [Pa]	Mean PL Intensity [a.u.]	Mean Tb Conc. [at.%]	Mean Thickness [nm]
1.0	65	1.8	270
0.5	106	1.85	250

The results show that the thickness and Tb concentration do not depend significantly on the Ar pressure. However the PL intensity exhibits a strong increase with decreasing Ar pressure.

3.3. Influence of the addition of oxygen to the sputtering atmosphere

The rest of the presented data are not averaged, but taken at the centre of the sample holder.

The data presented in the first two rows of Table 3 show a comparison of the thickness, Tb concentration and PL intensity of SiO_2 thin films containing Tb, when P_{O2} = 0 Pa and when P_{O2} = 0.3 Pa. The films were deposited at P_{Ar} = 0.5 Pa and *r* = 12 cm. The addition of oxygen had a weak influence on the Tb concentration - a small increase was observed when oxygen was added. RBS data (not shown) demonstrated that the stoichiometry of the silica matrix did not change with the addition of oxygen in the sputtering gas mixture.

A decrease in thickness resulted from the addition of oxygen. This is not manifested from the data in the table, but becomes obvious when longer deposition times were used.

These data show a small increase in the PL intensity with the addition of oxygen, but further studies of the effect of oxygen in the sputtering gas mixture on the PL intensity are needed.

3.4. Different matrices

Another dielectric matrix, Al_2O_3, was used as a host for Tb^{3+}. The last two rows of Table 3 compare the parameters of two different films - one of SiO_2, the other of Al_2O_3, deposited under the same conditions: 300 mm^2 Tb, P_{Ar} = 0.5 Pa, P_{O2} = 0 Pa, *P* = 150 W, *r* = 12 cm and *t* = 90 min. It is obvious that the deposition rate of Al_2O_3 is much lower. However the concentration of Tb and the PL intensity are comparable in the two films.

Table 3. Dependence of the thickness, Tb concentration and PL intensity on the addition of oxygen in the plasma and on the dielectric matrix. The samples were deposited at P = 150W, t = 90 min.

Sample type	Thickness [nm]		Tb Conc. [at. %]		PL Intensity [a.u.]	
	P_{O2} = 0 Pa	P_{O2} = 0.3 Pa	P_{O2} = 0 Pa	P_{O2} = 0.3 Pa	P_{O2} = 0 Pa	P_{O2} = 0.3 Pa
SiO_2, 200 mm^2 Tb	220	220	1.15	1.2	86	109
SiO_2, 300 mm^2 Tb	240	200	0.9	1.1	75	104
Al_2O_3, 300 mm^2 Tb	140	-	1.15	-	78	-

4. Discussion

From the data presented in this study, a strong variation of the Tb^{3+} PL intensity with deposition conditions is observed, which is greater than the parallel changes in the Tb concentration and sample thickness.

The PL intensity of Tb^{3+} ions is quenched when they are clustered together [4]. Ideally they should be evenly dispersed in the matrix. However, during sputtering, groups of atoms from the target are knocked out and deposited as clusters in the growing film. Bombardment by ionized particles leads to reconstruction of the deposited film. Ion bombardment during deposition has been shown to increase the film density, inhibit the formation of a columnar structure and decrease the average grain size [5]. This process may cause the Tb ions to disperse better in the dielectric film, and consequently increase the luminescent yield. As the areas immediately above the erosion zone on the target get the most intense bombardment, we suppose that this explains the higher PL intensity away from the centre of the substrate holder exhibited in Fig. 1. When the distance between the target and the substrates is greater, this bombardment is much weaker which explains the better homogeneity of the PL intensity of the films deposited at a greater distance *r*.

As the argon pressure in the deposition chamber decreases (Table 2), the energy of the ionized particles reaching the substrate increases. Therefore, the possibility for reconstruction of the deposited film and better dispersion of the Tb^{3+} ions is greater. This could be the reason for the greater PL intensity for a lower argon pressure, while the Tb concentration and film thickness are similar.

Oxygen was added to the plasma in order to counteract the clustering of Tb and achieve higher luminescence yields. This led to a lower deposition rate, but the increase of the PL intensity was small and inconsistent. Further and more detailed study is needed.

The use of Al_2O_3 as a dielectric matrix for the Tb ions does not show any advantages. The Tb concentration and PL intensity are the same for the same conditions of deposition, while the deposition rate is smaller.

5. Conclusions

The dependence of the photoluminescence of dielectric films containing Tb^{3+} ions deposited by rf magnetron sputtering on the deposition conditions was studied. At a distance of 7.5 cm between the target and the growing film, a strong dependence of the PL and film thickness on the substrate radial position was observed. Increased PL intensity over the erosion zone was explained by bombardment of the growing film by particles from the plasma, which caused a better dispersion of Tb ions and less clustering. However, greater distances between the target and substrate should be used, if the aim is a homogeneous PL intensity and thickness. An experiment of adding oxygen to the sputtering gas had a small effect on the PL intensity, and further study in this direction is planned.

Acknowledgements

The study was supported under a contract between CL SENES, Bulgarian Academy of Sciences and IEF-5 Photovoltaics, Research Centre Jülich. The authors are grateful for the use for the Raman measurements of a Coherent Innova 307 laser, bought in the framework of Contract VUF 11/05 with the Bulgarian National Scientific Fund.

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