Green Electroluminescence of Al/Tb/Al/SiO₂ Devices Fabricated by Electron Beam Evaporation

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In this work, the fabrication and the structural, optical and electrical properties of Al-Tb/SiO₂ nanomultilayers have been studied. The nanomultilayers were deposited by means of electron beam evaporation on top of p-type Si substrates. Optical characterization shows a narrow and strong emission in the green spectral range, indicating the optical activation of Tb³⁺ ions. The electrical characterization revealed conduction limited by the electrode, although trapped-assisted mechanisms can also contribute to transport. The electroluminescence analysis revealed also emission from Tb³⁺ ions, a promising result to include this material in future optoelectronics applications as integrated light-emitting devices.

1. Introduction

The invention of LEDs has opened the door for the field of optoelectronics, as the use of semiconductors allows scaling these light sources to the sizes of microelectronic devices employed today. Optoelectronic devices are designed to employ light in combination with (or instead of) electric currents, which introduces many advantages: separation of electronic devices light in combination with (or instead of) electric currents, which requires of Si-based light collectors, transducers between electric and optical signals, light waveguides, and light emitters. For the latter, semiconductor materials doped with rare earth (RE) ions have been widely studied in the last two decades due to their narrow and intense luminescence, as a potential alternative for more efficient devices than LEDs.[4–6]

Rare earth elements have their 4f electronic shell partially filled, and when they are optically active, they usually have an oxidation state +3 due to the loss of one 4f electron and the two 6s electrons. These elements have luminescent properties resulting from the intra-4f transitions (almost independent of the matrix) or 5d-to-4f ones (sensitive to the matrix).[7]

Erbium has been studied as dopant of different films like silica (SiO₂), yielding emissions in the infrared part of the spectrum (≈1535 nm) when in an Er³⁺ oxidation state, which makes it very useful for optical fiber telecommunication systems.[8,9] Other REs have been researched for their emission in the visible range, such as Ce³⁺,[8] Tb³⁺,[10–11] and Eu³⁺,[12] in the blue (460 nm), green (543 nm), and red (615 nm) parts of the spectra, respectively. In the Figure 1, the electronic levels, energies and transitions for a particular RE species (Tb³⁺ ions as it will be later studied in this work[15]) are presented.

Fabrication of these materials has been exploited through many different techniques, such as plasma-enhanced chemical vapor deposition,[11] ion implantation,[14] liquid source chemical vapor deposition,[15] magnetron sputtering,[16] and sol-gel.[17] Some other techniques have also been attempted, but are less commonly employed, like atomic layer deposition.[18]

Following the approach to new RE light emitters, in this work it is described the fabrication and characterization of nanomultilayered (NML) structures composed of SiO₂, Al and Tb³⁺ ions, by means of electron beam evaporation (EBE). In a previous work, different combinations of these layers have been tested aiming at the best layer configuration that exhibits stronger emission.[19] The optical properties of the chosen configuration were studied by photoluminescence (PL) in samples annealed at different temperatures.[20]

The films employed in this work were deposited by using EBE, considering the optimum nanomultilayered structure as Al-Tb/SiO₂, on top of a p-type Si substrate. The films used for the structural and optical characterization consist of 15 × Al/Tb/SiO₂ layers, ending with a SiO₂ layer that serves as protection. For the electrical characterization, 5 × Al/Tb/SiO₂ layers were fabricated, also on a p-type Si substrate, adding a full area bottom electrode of Al and top contact of indium tin oxide (ITO). The ITO contact also allows for electro-optical characterization, as it is a

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssa.201700451.

DOI: 10.1002/pssa.201700451
transparent conducting oxide (TCO). The average composition of the nanomultilayers was assessed by using X-ray photoelectron spectroscopy (XPS). Different techniques were employed to determine the optical properties of the Tb-films, such as PL and cathodoluminescence (CL). The electrical properties were studied through the different $I(V)$ curves obtained. Finally, the electroluminescence (EL) of the NMLs was also measured in the accumulation regime. The results suggest the possibility of employing EBE for the fabrication of RE-doped materials that can be introduced into devices for optoelectronic applications in the future.

2. Experimental Section

Different combinations in nanomultilayer structures for SiO$_2$, Al and Tb were tested in a previous study, in order to achieve the optimal configuration for the optical activation of the Tb$^{3+}$ ions.\[19,20\] All test samples and the ones here employed were fabricated by electron beam evaporation, and deposited on top of p-type Si substrates, which were cleaned with acetone, isopropyl alcohol, ethanol, and de-ionized water, and agitated ultrasonically during each process, before being introduced into the chamber.

The equipment employed for the deposition is a PFEIFFER VACUUM Classic 500 chamber with a Ferrotec GENIUS electron beam controller and a Ferrotec CARRERA high-voltage power supply. The base pressure in the chamber was $1.6 \times 10^{-6}$ mbar and the temperature of the substrate was kept at 100°C. Acceleration voltages were 6 kV for SiO$_2$ and Tb, and 10 kV for Al, with deposition rates of 1.0, 0.2, and 0.2 Å s$^{-1}$, respectively.

The samples for the structural and optical characterization consisted of 15 stacks of Al/Tb/Al/SiO$_2$, with two 10-nm layers of SiO$_2$ before and after them to prevent any atomic diffusion from or to the nanomultilayers. The nominal thickness of the Al, Tb, and SiO$_2$ layers were 0.8, 0.4, and 3 nm, respectively (see Figure 2(a)). After deposition, the samples were submitted to an annealing process at 1100°C in N$_2$ atmosphere for 1 h. An identical sample was also fabricated but with no Al, in order to observe the influence of this element. In the Figure 2(b) the cross-section of the nanomultilayers acquired by transmission electron microscopy (TEM) is shown, where the nanometric structure can be clearly seen: the bright layers with a thickness of 5 nm correspond to SiO$_2$, whereas the dark ones, with a thickness of 3 nm, are a stack of Al-Tb, as demonstrated by electron energy loss spectroscopy.\[20\] As revealed by the TEM image, this stack serves as delta doping system of Tb in a SiO$_2$ matrix, allowing for obtaining nanometric separation between the different Tb layers, while isolating them in the growth direction and thus reducing possible clustering effects.

For the electrical and electro-optical characterization, new samples were fabricated consisting for 5 stacks of Al/Tb/Al/SiO$_2$, also annealed at 1100°C in N$_2$ atmosphere for 1 h. After annealing, indium tin oxide (ITO) electrodes were deposited on top of the multilayers using a shadow mask, with circular shape with a radius of 200 µm, and subsequently annealed at 600°C in N$_2$ atmosphere for 1 h. Finally, a full area Al metallization was performed on the backside of the Si substrate for defining the bottom contact. This structure is schematically shown in Figure 2(c).

To determine the overall composition of the deposited films, XPS measurements were carried out using a PHI 5500 Multitechnique System, thus obtaining information regarding the Al influence on the Tb-related binding formation. Photoluminescence measurements with two different excitation energies were employed for determining the optically active emission from Tb$^{3+}$ ions. The 325-nm line from a HeCd laser or the 488-nm line from an Ar$^+$ laser were used for the excitation of the Tb$^{3+}$ ions. In the case of the HeCd laser, the spectra were analyzed using a Horiba Jobin Yvon LabRAM HR spectrometer, whereas the spectral analysis exciting with the Ar$^+$ laser was done using a GaAs photomultiplier tube (PMT) coupled to a monochromator in a lock-in configuration. For the acquisition of CL spectra, a JEOL JSM-7100F scanning electron microscope coupled to a monochromator and a GaAs PMT was employed. In order to avoid damage on the surface, a defocused electron beam of 80 µA, accelerated at 2 keV, was used for the measurements.

Electrical characterization of the samples was done by two contact measurements with an Agilent B1500 semiconductor device analyzer and a Cascade Microtech Summit 11000 probe station using a Faraday cage. The back-contact was grounded through the chuck, whereas the top ITO-contact was swept from −15 to 15 V, with steps of 50 mV s$^{-1}$.

Emission from the sample obtained through electroluminescence (EL) was collected with a Seiwa 888 L microscope. Whereas the integrated emission was recorded using the same GaAs PMT employed in the PL measurements, the spectral emission was captured by means of Princeton Instruments LN-cooled charge-coupled device via a 1/4m Oriel monochromator.

3. Results and Discussion

Measurements performed by XPS allowed determining the composition and the effect of the presence of Al atoms...
surrounding the Tb ions. In Table 1 we have summarized the obtained results. Whereas the sample with no Al showed stoichiometric SiO₂, the sample containing Al showed an increase of the oxygen content. Thus, this observation implies that, on one hand, the Tb ions in the sample with no Al may be bound to other Tb ions or dangling bonds from SiO₂, and, on the other hand, the sample with Al exhibits an oxygen excess that should be located in the Al/Tb/Al stack (the SiO₂ in the whole sample is stoichiometric). As aluminium is much more chemically reactive than terbium, the oxygen excess in the sample with Al is more likely to be bound to Al forming alumina (Al₂O₃). In order to have a minimum quote of the amount of Tb which is oxidized (i.e., prompt to be optically active), we considered that: (i) all the Si atoms are bound to O atoms, thus forming SiO₂; (ii) all the Al atoms are in the form of alumina (Al₂O₃); and (iii) the remaining O content is bound to Tb atoms. Under these assumptions, and considering the atomic content in the Al/Tb/Al/SiO₂ sample (considering the whole film), we found that at least 45% of the Tb ions are in the form of Tb₂O₃. Thus, the addition of Al contributes to the oxidation of Tb ions, which should also influence their emission properties.[20]

Optical emission of the Al/Tb/Al/SiO₂ structure was first characterized by means of PL. Two different excitation lines were employed: a non-resonant excitation using λ = 325 nm and a resonant excitation with λ = 488 nm (see Figure 3).[12] The spectrum acquired under non-resonant conditions shows peaks at 489, 542, 584, and 621 nm; under resonant excitation, the same emission features were detected but the one at 489 nm, as it is close to the excitation wavelength. These emission bands are a consequence of the intra-4f electronic radiative transitions within Tb³⁺ ions (⁵D₄ → ⁷F_J, with J = 6, 5, 4, and 3).[7,12]

Similar emission to the PL one was obtained when performing CL measurements by exciting the sample with an electron beam of 2 keV, which allows an effective direct excitation of the Tb species by impact excitation. Figure 3 shows the emission spectrum collected with the characteristic peaks of Tb³⁺ at 489, 544, 587, and 624 nm. These emission bands correspond to the ⁵D₄ → ⁷F₃ transitions as previously described. Blue emission bands also appear in the CL spectrum, corresponding to ⁵D₄ → ⁷F₁ (J = 5 and 4) transitions, with peaks at 415 and 437 nm. All these results are in good agreement with others found in the literature (see Ref. [21]).

The most intense emission at 544 nm in both PL and CL spectra corresponds to the green visible range, and it is split into two peaks, as a consequence of the Stark effect due to the local electric field.[7] These results evidence that the employed deposition technique and methodology, that takes advantage of the nanomultilayered deposition of different materials, produce optically active Tb³⁺ species, emitting in the green spectral region.

The electrical properties of the fabricated devices were analyzed by acquiring the I(V) curves, grounding the Al bottom electrode through the chuck whereas the ITO contact on top was swept in two regimes: accumulation (negative bias) and inversion (positive bias). The obtained curves for each regime

| Atomic content (%) | Si | O | Tb | Al |
|-------------------|----|---|----|----|
| Tb/SiO₂           | 33 | 65| 2  | –  |
| Al/Tb/Al/SiO₂     | 24 | 65| 1  | 10 |

Figure 3. Normalized PL and CL measurements of the Al/Tb/Al/SiO₂ structure.
are displayed in Figure 4. The devices can reach intensities in the order of $10^5 \mu\text{A}$ at $-15 \text{ V}$ applied voltage. Higher voltages were not sustained by the ITO contacts as the current increased to mA. The curves show an almost symmetric behavior for both regimes, indicating non-rectifying characteristics.

As shown by structural characterization, the device is composed by layers of SiO$_2$ and Al$_2$O$_3$, for which an insulating behavior, that is, limited movement of charges, is expected. Thus, considering the different transport mechanisms taking place in dielectric materials, we have assessed the electrical conduction of our devices. We found that the best agreement to the experimental data was obtained when considering an electrode-limited conduction mechanism based on Schottky emission. Thermionic emission of electrons is achieved when a potential barrier formed at a metal-insulator (or semiconductor-insulator) interface is overcome. Applying an external electric field the barrier can be lowered, easing the emission. This process can be modeled as:

\[
J_{\text{Schottky}} = \frac{4\pi n e^2 k_B T^2}{\hbar^3} \exp \left(-\frac{\varphi_B}{k_B T} \right) \exp \left(\frac{\beta}{k_B T} E^{1/2} \right),
\]

where $\varphi_B$ is the potential barrier height in (eV), $q$ the elementary charge, $E$ the applied electric field, $k_B T$ the thermal energy, $\hbar$ the Plank’s constant, $m^*$ the effective mass of electrons, and $\beta$ is defined as:

\[
\beta = \sqrt{\frac{q^3}{4\pi\varepsilon_0\varepsilon_r}}.
\]

where $\varepsilon_0$ and $\varepsilon_r$ are the absolute and relative permittivity, respectively.\(^{[22]}\)

The fitting of the experimental $I(V)$ curve to the Schottky emission model yields a relative dielectric constant of the dielectric layer of $\varepsilon_r = 18.86$. However, in general, the obtained permittivity value may differ from the experimentally determined values by means of other optical techniques, due to the heterogeneity of our samples. Actually, Poole–Frenkel mechanism is also in good agreement to the experimental data, however with a large dielectric constant ($\varepsilon_r > 300$). The presence of Al in the structure is the probable cause for the Schottky emission fitting best the data, because electrons must overcome the potential barrier generated by the AlO$_x$ layers, as it has been previously reported.\(^{[23]}\)

The $I(V)$ characteristic of an identical device but without Al (Tb/SiO$_2$ multilayers) has also been analyzed. In Figure 4(c) there is a comparison of the current evolution at different voltages for both kinds of devices, with and without Al. It is evident that similar currents can be achieved for both devices, with and without Al in them, which implies that Al is not strongly influencing the electrical characteristic. Nevertheless, the sample with Al is slightly more resistive than the one with no Al (at high voltages), which could be due to either an increase of the total thickness or the fact that Al layers are presumably fully oxidized and thus become insulating (as we stated before). Another interesting feature is the fact that the slope of the two curves is also slightly different. Checking the conduction mechanisms, both curves follow a Schottky emission model at large voltages, but with a different dielectric constant: the sample without Al presents a dielectric constant of about 8.8, almost half of the one with Al. Consequently, Al is only slightly modifying the $I(V)$ characteristic. Actually, the electrical conduction through the SiO$_2$ barriers should be identical for both devices, just being different through the Al/Tb/Al or Tb layers, which modifies the effective dielectric constant while keeping the conduction mechanism.

The application of an electrical current to the device can also produce the excitation of Tb$^{3+}$ ions, which can be de-excited by emitting their excess of energy in the form of light. No emission (or very weak) was found for the devices with no Al, which is in good agreement with PL measurements (see Refs. [19] and [20]). The total integrated emission collected by the PMT is shown in Figure 5 (a) and 5(b) as a function of the applied voltage and current circulating through the device, respectively. We observed that the threshold voltage for emission to take place is 8.5 V, whereas higher voltages produce an almost exponential increase of the integrated EL. Looking at the behavior of the EL with the injected current, we observe that it increases linearly with a threshold current for emission of $\approx 2 \mu\text{A}$, which establishes a direct relation between impinging electrons and resulting emitted photons. Thus, the linearity of the EL with the injected current at high voltage and injection (i.e., above the excitation threshold) is suggesting that electrons with high kinetic energy are responsible for the excitation of the Tb optical centers. In fact, such electro-optical characteristics are typical of an excitation mechanism governed mainly by direct impact excitation; however, energy transfer mechanisms from the matrix can also be contributing.\(^{[22]}\)

The spectral analysis of the EL is displayed in Figure 6. The spectra were acquired for 30 s, applying $-100 \mu\text{A}$ at $-18 \text{ V}$, in the range of 400–1100 nm. The spectra exhibit peaks at 437, 483, 531, and 576 nm, in a broad low-intensity background. Whereas the former features correspond to $^5\text{D}_4 \rightarrow ^7\text{F}_J$ transitions (with $J = 6, 5, 4,$ and $3$) from Tb$^{3+}$ ions, in good agreement to PL and CL measurements (see Figure 3), the latter band is probably...
originated in the deep defects in either the SiO2 or the ITO contact.

Another interesting observation is the fact that there is an intensity reduction of the Tb emission at successive measurements, reaching total quenching of Tb emission beyond the fifth one (please see spectrum labeled as measurement #6 in Figure 6, where only the background contribution is observed). In order to study this effect, the time evolution of the EL and the applied voltage has been simultaneously monitored at a constant current, this time using a different (i.e., pristine) device (but virtually identical). The results of this particular device are presented in Figure 7. One can observe that the EL emission starts practically simultaneously with the current injection, within the employed time resolution (voltage also increases). Both EL and applied voltage remain constant for about 30 s, immediately after which there is a slight reduction in the voltage, together with a sudden reduction of the EL emission. For longer times, the device becomes even more conductive, inducing the total quenching of the device EL emission. This EL quenching and voltage reduction could be related to some atomic rearrangement after high electron flux is injected. Indeed, it has been observed in oxide matrices that, under certain excitation conditions, a displacement of oxygen atoms takes place.[24,25] This, in turn, induces both the creation of alternative (oxygen vacancies-related) conduction paths and the probable reduction of Tb-O bonds, the latter reducing the concentration of optically active centers. In this frame, an increase of the thermal budget could improve the stability of the Tb2O3 phase, making this material a potential candidate for future optoelectronics applications, in particular as integrated light-emitting devices.

4. Conclusions

Al/Tb/Al/SiO2 nanomultilayers have been fabricated by electron beam evaporation, alternatively depositing each layer. Optical characterization by means of PL and CL showed that Tb3+ ions are optically active. Electrical characterization allowed inferring that the conduction mechanism governing the structure is a Schottky emission model, although thermal activated mechanisms cannot be discarded. The threshold voltage and current for EL to take place were determined by integrated EL measurement. As well, the spectral distribution of EL is related to a combination between Tb3+ ions and matrix defect-related emission. The hereby presented results prove that the combination of electron beam evaporation and nanomultilayer structures are useful to obtain luminescent Al/Tb/Al/SiO2 light-emitting systems.

Acknowledgements

This work was financially supported by the Spanish Ministry of Economy and Competitiveness (TEC2016-76849-C2-1-R and MAT2015-71035-R). O.B. also acknowledges the subprogram “Ayudas para Contratos Predoctorales para la Formación de Doctores” from the Spanish Ministry of Economy and Competitiveness for economical support.

Conflict of Interest

The authors declare no conflict of interest.
Keywords
electron beam evaporation, luminescence, nanomultilayers, rare earth ions, terbium

Received: June 30, 2017
Revised: September 1, 2017
Published online: October 18, 2017

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