



Oxidation and crystallization behavior of calcium europium silicon nitride thin films during rapid thermal processing



M. de Jong^{a,*}, V.E. van Enter^a, E.W. Schuring^b, E. van der Kolk^a

^a Faculty of Applied Science, Delft University of Technology, Mekelweg 15, 2629JB Delft, The Netherlands

^b Energy Center of the Netherlands, Westerduinweg 3, 1755LE Petten, The Netherlands

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ABSTRACT

Luminescent thin films were fabricated on silicon wafers using reactive magnetron sputtering of Ca, Si and Eu in Ar/N₂ atmosphere. In order to activate the luminescence, the as-deposited nitride films were heated to 1100 °C by a rapid thermal processing treatment. X-ray diffraction measurements reveal the crystal phases that form during thermal treatment. By recording scanning electron microscopy images of the surface and the cross-section of the film at different radial locations, the formation of different layers with a thickness depending on the radial position is revealed. Energy dispersive x-ray spectroscopy analysis of these cross-sections reveals the formation of an oxide top layer and a nitride bottom layer. The thickness of the top layer increases as a function of radial position on the substrate and the thickness of the bottom layer decreases accordingly. The observation of different 4f⁶5d¹ → 4f⁷ Eu²⁺ luminescence emission bands at different radial positions correspond to divalent Eu doped Ca₃Si₂O₄N₂, Ca₂SiO₄ and CaSiO₃, which is in agreement with the phases identified by X-ray diffraction analysis. A mechanism for the observed oxidation process of the nitride films is proposed that consists of a stepwise oxidation from the as-deposited amorphous nitride state to crystalline Ca₃Si₂O₄N₂, to Ca₂SiO₄ and finally CaSiO₃. The oxidation rate and final state of oxidation show a strong temperature–time dependency during anneal treatment.

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1. Introduction

The absorption and emission properties of divalent Eu doped calcium silicon oxide [1–3], oxynitride [4–6] and nitride [7] phosphors make them an interesting class of luminescent materials for application in solid state lighting or afterglow. In addition, luminescent materials could enhance the efficiency of photovoltaic devices considerably when applied as spectral shifting or down-conversion thin films [8–10]. Theoretical calculations indicate that luminescent metal silicon oxides and (oxy)nitrides are interesting classes of materials for this application [11]. A possible approach to applying the luminescent materials is by depositing them as thin films on the surface of a photovoltaic device. In order to do so, a more fundamental understanding is required of the thin film deposition and the oxidation and crystallization processes that take place during high temperature anneal of as-deposited films.

Earlier work has shown that thin films typically show low oxygen content after they are extracted from the sputter system. The oxygen content increases strongly when an RTP anneal treatment is performed [12], indicating that the oxidation process is strongly temperature

dependent. In this work the oxidation process of the nitride films is studied in more detail by an ex-situ study of the influence of rapid thermal processing (RTP) on the structure, composition and luminescence characteristics of a thin film that is fabricated by reactive magnetron sputtering of Ca, Si and Eu in an Ar/N₂ atmosphere.

The thin film deposition process, the anneal treatment and the characterization methods are described in the materials and methods section. In the results section, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) analysis and photoluminescence data are presented as a function of the radial position on the film. Identification of different stages of the oxidation reaction, is explained in the discussion section. Finally conclusions are presented on the oxidation and crystallization mechanism and the potential of magnetron sputtering for the formation of luminescent oxide, oxynitride and nitride thin films.

2. Experimental details

Thin film deposition was performed with an AJA Orion 5 magnetron sputtering system. Ca (99.5%), Si (99.999%) and Eu (99.99%) were used as sputtering targets. Preparation and installation of the target materials and the sputtering system are done in a special manner when using Ca and Eu sputter targets, as is described in detail in previous work [12].

* Corresponding author.

E-mail addresses: m.dejong-1@tudelft.nl (M. de Jong), vvanenter@gmail.com (V.E. van Enter), schuring@ecn.nl (E.W. Schuring), e.vanderkolk@tudelft.nl (E. van der Kolk).

First the deposition rates of the targets were roughly estimated based on thickness profiling measurements of SiN_x , EuN_x and $\text{Ca}_x\text{Si}_y\text{N}_z$ thin films deposited on objective glass, using a range of sputter powers for RF sputtered Ca (25–75 W) and Si (50–150 W) and DC sputtered Eu (10–25 W). Since the density of the sputtered films is unknown, these measurements only give a rough estimation of the molar ratio of deposited atoms. Therefore the molar ratio of Ca to Si and Ca to Eu at different sputter powers were calibrated with EDX measurements on the films.

Using the calibrated relations between molar ratios of sputtered materials and different sputter powers, a thin film was deposited on a rotating 5.1 cm round c-Si (111) substrate. The ratio of deposited Ca to Si was calculated to be 1:1. The Eu target was sputtered in order to have an Ca:Eu ratio of 20:1 in the film. This was achieved by sputtering the Ca, Si and Eu targets simultaneously at 75 W, 150 W and 15 W respectively. The intended film thickness was 600 nm and determined after deposition by cross-section SEM images as well as with thickness profiling equipment.

Since Eu sputter rates are typically much higher than those of Ca and Si, the sputter rate of Eu was decreased 10 times by placing a stainless steel cover disc with equally spaced 1 mm diameter holes on top of the chimney of the sputter gun. The sputter rate was checked by sputtering Eu in an Ar atmosphere on a quartz crystal microbalance (QCM) with and without the cover disc. Due to rapid oxidation of Eu thin films in air, this measurement could not be confirmed by profiling measurements. However, the QCM is considered an adequate technique for measuring relative changes in deposition rates.

In order to crystallize the CaN_x , SiN_x and EuN_x materials that are mixed in the as-deposited film, a post-deposition anneal treatment was performed. This was done using a Solaris 150 double-sided illumination RTP system safely 100 °C below the maximum operating temperature of 1200 °C with a ramp rate of 40 °C s⁻¹ while flushing with 6 SLM nitrogen gas containing 7% of the reducing gas H₂ to stimulate the formation of the desired Eu²⁺ valence state instead of the Eu³⁺ valence state. The temperature was measured by placing the back of the substrate on a c-Si thermocouple. The effect of the RTP process on the film was systematically investigated as a function of time during 75 min in steps of 5 min. In between heat treatments, the film was removed from the RTP and photographed under UV illumination between 340 and 360 nm.

XRD measurements were performed at several radial positions by cutting 5–10 mm² diameter pieces containing only the desired areas of the thin film. The pieces were glued on 50 mm diameter c-Si (111) wafers in order to properly align the samples in the Panalytical X'pert Pro MRD system. The incident beam angle was fixed at 19.28°. 1E16 and 2F2 CSH slits were used, resulting in an x-ray beam with 1 mm beam height and 2 mm beam width. Grazing incidence diffraction was performed with a parallel beam geometry. Cu-K α radiation was used, with U = 40 kV and I = 40 mA. Diffraction patterns were recorded between 20° and 70° 2 θ . The step size was 0.02° with a step time of 15 s.

The PL measurements were performed after anneal treatment using an optical fiber connected to an Ocean Optics QE65000 spectrometer. The film was excited at a wavelength of 280 nm at room temperature by using the third harmonic of a 120 fs Ti:sapphire laser.

A HITACHI SU70 Schottky Emission Scanning Electron Microscope with Oxford Aztec EDX-EBSD analyses system and a 50 mm EDX detector were used to record SEM images and measure the elemental composition and distribution with EDX both at 5 kV. The penetration depth of the electron beam was calculated by the authors to be limited to 400 nm at this acceleration voltage as established by Monte Carlo simulations of the mean electron path inside the film. Since the film thickness is calculated at 600 nm, EDX analyses obtained from the surface originate from the thin film only.

It is generally accepted that EDX analyses are limited to qualitative results for O and N, due to physical limitations. This results in a ± 5 weight% error in the measured O and N, provided that a flat sample is used at the correct working distance (both conditions are satisfied in this investigation). For Ca, Si and Eu, a variance typically not higher than ± 0.5 weight% is assumed. Operating parameters, acceleration voltage and beam current were all constant during data acquisition at different positions. This enables for a qualitative comparison of the differences in O and N concentrations as long as they differ more than ± 5 wt%.

Cross-sections of the film were also measured with SEM and EDX, by milling the side of the cut film for 1.5 h using an Hitachi IM4000. Ar⁺ ions are used for milling of the cross sections to prepare a 1–2 mm sample area width for imaging. The sample temperature is limited to 80 °C, hence no effect on element distribution is considered to occur. X-ray mappings are made of the cross sections, resulting in a qualitative indication of the element distribution in the different layers, taking into account that the spatial resolution for EDX mapping lies between 200 and 400 nm.

3. Results

A luminescent circular pattern first appears at the edge of the c-Si wafer as shown in Fig. 1a. This is the result of crystallization of the nitride film by oxidation during the RTP process as will be shown later. Fig. 1 shows that the crystallization and oxidation process at the edge is faster than in the center of the film which effectively causes the luminescent circular patterns to progress radially inward as a function of annealing time.

A change in emission color is observed at the edge of the film from greenish, to white, to yellow with increased RTP time. Formation of additional luminescent areas closer to the center of the film is also observed. The emission color of some of these areas also changes with increasing RTP times. This is demonstrated with photographs of the film that were taken after 10 (a), 30 (b), 55 (c) and 75 (d) minutes of annealing, shown in Fig. 1a–d.

A scale bar is added to Fig. 1d that is drawn from the center of the substrate to the edge at a distance $r = 25$ mm. The positions $r_1 = 0$ mm, $r_2 = 7$ mm, $r_3 = 13$ mm and $r_4 = 23$ mm, represent the inner non-luminescent region and radial patterns (2–4) with distinctly different luminescence colors. These four areas resemble all of the observed luminescent phases.

XRD measurements were performed on positions r_1 – r_4 . The results are found in Fig. 2. The intensities of the XRD peaks in the non-

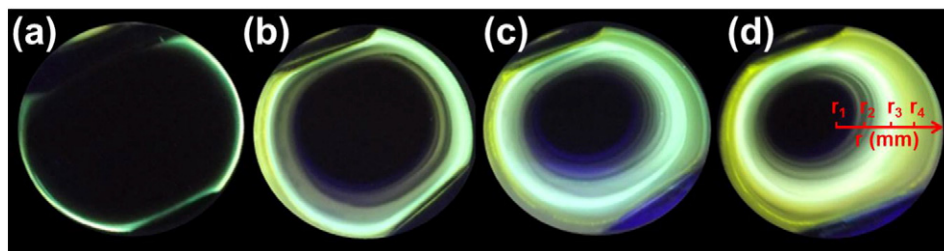


Fig. 1. Photographs of the luminescent thin film under UV illumination after RTP annealing for 10 (a), 30 (b), 55 (c) and 75 (d) minutes. Position numbers 1–4 are at positions $r_1 = 0$ mm, $r_2 = 7$ mm, $r_3 = 13$ mm and $r_4 = 23$ mm respectively.

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