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Er³⁺ and Si luminescence of atomic layer deposited Er-doped Al₂O₃ thin films on Si(100)

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Atomic layer deposition was used to deposit amorphous Er-doped Al₂O₃ films (0.9–6.2 at. % Er) on Si(100). The Er³⁺ photoluminescence (PL), Er³⁺ upconversion luminescence, as well as the Si PL and associated surface passivation properties of the films were studied and related to the structural change of the material during annealing. The PL signals from Er³⁺ and Si were strongly dependent on the annealing temperature ($T = 450$ – 1000 °C), but not directly influenced by the transition from an amorphous to a crystalline phase at $T > 900$ °C. For $T > 650$ °C, broad Er³⁺ PL centered at 1.54 μm ($^4I_{13/2}$) with a full width at half maximum of 55 nm was observed under excitation of 532 nm light. The PL signal reached a maximum for Er concentrations in the range of 2 – 3 at. %. Multiple photon upconversion luminescence was detected at 660 nm ($^4F_{9/2}$), 810 nm ($^4I_{9/2}$), and 980 nm ($^4I_{11/2}$), under excitation of 1480 nm light. The optical activation of Er³⁺ was related to the removal of quenching impurities, such as OH (3 at. % H present initially) as also indicated by thermal effusion experiments. In contrast to the Er³⁺ PL signal, the Si luminescence, and consequently the Si surface passivation, decreased for increasing annealing temperatures. This trade-off between surface passivation quality and Er³⁺ PL can be attributed to an opposite correlation with the decreasing hydrogen content in the films during thermal treatment. © 2011 American Institute of Physics. [doi:10.1063/1.3595691]

I. INTRODUCTION

By virtue of the Er³⁺ emission wavelength at ~ 1.54 μm , Er-doped materials are widely used in optoelectronics.^{1,2} Er³⁺ ions also have the capability of upconverting two or more lower energy photons into one high-energy photon.³ While such upconversion processes represent a loss mechanism for some optoelectronic applications, they are being considered for the enhancement of the energy conversion efficiency of future silicon solar cells.^{4–7} The idea is that by adding an upconversion material to the rear side of a silicon solar cell, a fraction of the sub-bandgap photons ($E_g < 1.1$ eV) that would otherwise be transmitted through the device can now be utilized to create electron-hole pairs in the solar cell. The Er³⁺ photoluminescence (PL) and upconversion luminescence depend strongly on the Er concentration in the film.² Control of the doping profile is, therefore, desirable for the various applications which exploit the optical properties of Er. Many different host materials have been studied in the past decades, including fluorides, sulfides, phosphates, silicates, oxynitrides, and oxides.¹ Al₂O₃ is a particularly interesting host material for Er, as Al₂O₃:Er possesses a relatively high refractive index, which is desirable for waveguide devices, and was shown to exhibit a broad emission spectrum around 1.54 μm . Accordingly, high-gain optical waveguide amplifiers based on Al₂O₃:Er films have been successfully fabricated.^{8,9} In addition, relatively high Er concentrations

can be incorporated in Al₂O₃, as Er₂O₃ exhibits a similar valence and crystal structure.² Er-doped Al₂O₃ has been synthesized using various techniques, including pulsed laser deposition,¹⁰ sputtering of Al₂O₃ and subsequent ion implantation,⁸ co-sputtering of Al₂O₃ and Er₂O₃^{11–14} and plasma-enhanced chemical vapor deposition (CVD).¹⁵

Atomic layer deposition (ALD) is an alternative method that can be used to deposit high-quality and uniform thin films. During a so-called ALD cycle, reactants are sequentially introduced into the reactor, and film growth is governed by self-limiting surface reactions.¹⁶ The self-limiting nature of the growth process allows for precise thickness control with an Ångström level resolution over large area substrates. Consequently, controlled material doping is also possible by alternating the ALD cycles of two or more materials. The dopant profile can be controlled in the vertical (i.e., thickness) direction by changing the ratio between the ALD cycles of the respective materials. In the lateral direction, the separation between the individual dopant atoms is dictated by the growth-per-cycle, which is related, among other variables, to the steric hindrance effect of the specific precursor molecules.¹⁷ Furthermore, the excellent conformality of ALD provides a means for coating high-aspect ratio structures, porous materials, and small particles.

The ALD process for Al₂O₃ is well known and has been extensively researched.^{16,18} As an important emerging application, ALD Al₂O₃ films are very suitable for the passivation of silicon surfaces. A high level of surface passivation is an important prerequisite for obtaining large luminescence quantum efficiencies of Si.¹⁹ The use of Al₂O₃ has, for

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instance, led to a tenfold increase in Si luminescence compared to the use of thermally grown SiO_2 passivation.²⁰ Moreover, considerable interest in Al_2O_3 surface passivation films for silicon photovoltaics has developed over the last few years,^{21,22} which also spurred the development of ALD processes for high-volume manufacturing.^{22,23} For the synthesis of Er_2O_3 by ALD, on the other hand, only a few reports exist. Päiväsaari *et al.* reported an ALD process for Er_2O_3 , using $\text{Er}(\text{thd})_3$ and $\text{Er}(\text{CpMe})_3$ as precursors, in combination with O_3 and H_2O as oxidants, respectively.^{24,25} $\text{Al}_2\text{O}_3/\text{Er}$ waveguides have also been synthesized by ALD,²⁶ but no details on the ALD process were given. In addition, ALD has been used for Er incorporation in Y_2O_3 by alternating the growth of Y_2O_3 and Er_2O_3 layers.^{17,27}

In this study, we used thermal ALD to synthesize amorphous $\text{Al}_2\text{O}_3/\text{Er}$ films on Si wafers. The focus of the paper is the relation between the (structural) changes of the material during annealing and the optical activation of Er^{3+} . In addition, the Si luminescence and the associated surface passivation properties of the films were studied. We show here that post-deposition annealing is essential to optically activate the Er^{3+} ions, resulting in broad photoluminescence (PL) centered around $1.54\ \mu\text{m}$. Two- and three-photon upconversion processes were also detected under excitation of $1.48\ \mu\text{m}$ light. The results show that the removal of OH impurities, which can act as effective quenching centers,^{2,28} played a prominent role in the optical activation, whereas the luminescence properties were not significantly affected by the change from an amorphous to a polycrystalline structure at temperatures $> 900^\circ\text{C}$. In contrast to the Er^{3+} photoluminescence, the surface passivation properties deteriorated at higher annealing temperatures, which can be attributed predominantly to the effusion of hydrogen from the $\text{Al}_2\text{O}_3/\text{Er}$ and the Si interface.

After the description of the experimental details (Sec. II), the ALD process for the synthesis of the Er-doped Al_2O_3 films will be briefly discussed (Sec. III A). Subsequently, the optical properties (Sec. III B) and material properties (Sec. III C) will be reported, with special focus on the influence of post-deposition annealing. In the discussion (Sec. IV), the effect of the structural changes on the Er^{3+} and Si luminescence will be addressed.

II. EXPERIMENTAL DETAILS

The $\text{Al}_2\text{O}_3/\text{Er}$ films were deposited using an Oxford Instruments OpAL reactor at a substrate temperature of $\sim 200^\circ\text{C}$ by thermal ALD. The reactor was operated at a pressure of $\sim 300\ \text{mTorr}$. $\text{Er}(\text{CpMe})_3$ was used as the Er-precursor and stored in a stainless steel bubbler heated to 120°C , well below the decomposition temperature of the precursor. The precursor was introduced into the reactor by a $200\ \text{sccm}$ Ar flow and relatively long dosing times of $30\ \text{s}$ were employed. $\text{Al}(\text{CH}_3)_3$ was the Al-precursor used for the deposition of Al_2O_3 .²⁹ This liquid precursor exhibits a high vapor pressure and was introduced into the reactor vapor-drawn. Dosing times of only $20\ \text{ms}$ were sufficient for achieving saturated growth. For both materials, H_2O served as the oxidant ($20\ \text{ms}$ doses). The ALD films were deposited

on floatzone (FZ) n -type Si(100) wafers. Spectroscopic ellipsometry (SE; J.A. Woollam, M2000) was employed both *in situ* and *ex situ* to monitor the ALD growth process and determine the film thickness and refractive index. Photoluminescence measurements were performed at room temperature using a Nanometrics RPM2000, which had $532\ \text{nm}$ ($50\ \text{mW}$) and $1480\ \text{nm}$ ($250\ \text{mW}$) CW lasers available as pump sources. The corresponding detectors used with these two laser sources were an InGaAs PIN photodiode and a Si CCD detector. The incident spot diameter in both cases was $1\ \text{mm}$ ($7.85 \times 10^{-3}\ \text{cm}^2$). Two scan protocols were employed: (1) Scan from 900 to $1700\ \text{nm}$ using the $532\ \text{nm}$ pump and the InGaAs detector to observe the Si-Si transition at $1.1\ \mu\text{m}$ and the $\text{Er}^{3+}\ ^4I_{13/2}$ to $^4I_{15/2}$ transition at $1.54\ \mu\text{m}$; (2) Scan from 600 to $1100\ \text{nm}$ using $250\ \text{mW}$ $1480\ \text{nm}$ and the Si CCD to detect the 2 photon and 3 photon upconversion transitions in Er^{3+} . For material analyses, X-ray photon spectroscopy (XPS; K-Alpha Thermofisher) and X-ray diffraction (XRD; Panalytical) were used. In addition, Rutherford backscattering spectroscopy (RBS) using $1\text{--}2\ \text{MeV}$ He^{2+} ions and elastic recoil detection (ERD) were used to determine the atomic composition of the film and the hydrogen content (AccTec, Eindhoven). Effusion measurements were performed under ultrahigh vacuum conditions ($10^{-7}\ \text{mbar}$) using a quadrupole mass spectrometer. The effusion of impurities from the sample was monitored as a function of the annealing temperature, $T = 200\text{--}1000^\circ\text{C}$, with a heating rate of $20^\circ\text{C}/\text{min}$.³⁰ The effective lifetime of the minority carriers in Si was measured by the photoconductance decay method (Sinton WCT100). To activate the luminescence, the samples were annealed in a rapid thermal annealing apparatus (ramp up $> 20^\circ\text{C}/\text{s}$) within a N_2 environment.

III. RESULTS AND DISCUSSION

A. Atomic layer deposition of Er-doped Al_2O_3 films

Figure 1 shows a schematic representation of the ALD super-cycle used to deposit the $\text{Al}_2\text{O}_3/\text{Er}$ films. The super-cycle consists of x Er_2O_3 cycles and y Al_2O_3 cycles. Films with various Er concentrations, $[\text{Er}]$, were synthesized by changing the $x:y$ ratio. The two ALD cycles each comprised two half-cycles. In the first half-cycle, the precursor gas was introduced, and in the second half-cycle, H_2O was injected as the oxidant. In between the precursor and oxidant doses,

FIG. 1. (Color online) ALD “super-cycle” for the synthesis of Er-doped Al_2O_3 films.

FIG. 2. (Color online) (a) Film thickness as a function of the number of ALD cycles. (b) Apparent thickness after each ALD half-cycle. In (b), the same optical parameters (Cauchy model with $A_n = 1.64$ and $B_n = 0.005$, representative for Al₂O₃) were used for the Al₂O₃ and Er₂O₃ cycles.

the reactor was purged with Ar to avoid parasitic CVD reactions. Figure 2(a) shows that the thickness of the deposited film increased with the number of ALD cycles. The growth rate was ~ 1 Å/cycle for Al₂O₃ and ~ 0.25 Å/cycle for Er₂O₃, as determined with *in situ* SE. The growth characteristics for this process are illustrated in more detail in Fig. 2(b), where the changes in the surface groups and layer thickness during each half-cycle are reflected by the “apparent thickness.” The apparent thickness was extracted from the ellipsometric parameters (Ψ and Δ) using a simple Cauchy model with fixed optical constants (representative for bulk Al₂O₃).³¹ The increase of the apparent thickness during the Er(CpMe)₃ dosing represents the sticking of the precursor to the growth interface. During the subsequent oxidation step, the apparent thickness decreases by reaction of the adsorbed precursor ligands with H₂O such that the initial surface coverage is restored.¹⁸ The surface reactions in both half-cycles terminated when all surface groups reacted, i.e., the growth is self-limiting. Nonetheless, the relatively low growth-per-cycle for Er₂O₃ is likely to be a result of sub-saturated growth, even with the (optimized) precursor dosing times of 30 s that we applied. Although generally not preferred, a low growth-per-cycle, GPC, can be beneficial for synthesizing films with low Er concentrations. Using the same Er-precursor, Päiväsaari *et al.* reported a higher GPC while using significantly shorter dosing times.²⁵ These shorter dosing times can probably be related to the use of an open crucible rather than a bubbler system as used in this work. The precursor in the bubbler has a comparatively smaller surface area, and, therefore, the influence of the low precursor vapor pressure is more pronounced. For our reactor and precursor injection configuration, a more time-efficient ALD process could be realized when the Er-precursor would combine a relatively high vapor pressure with a high reactivity during the ALD half-reaction at moderate substrate temperatures. Currently, however, the availability of alternative commercially available ALD precursors for Er₂O₃ is still limited. It is interesting to note here that an O₂ plasma was tested as an alternative oxidant for the ALD process for Er₂O₃ in combination with the Er(CpMe)₃ precursor. RBS and infrared absorption measurements indicated a very large fraction of

TABLE I. Properties of as-deposited Er-doped Al₂O₃ samples, determined from the areal atomic densities measured by RBS/ERD. The mass density was calculated from the film composition and the thickness determined by SE.

[Er] (at. %)	[H] (at. %)	O/Al	O/(Al+Er)	ρ_{mass} (g/cm ³)
1.0 ± 0.03	3.0 ± 0.1	1.51 ± 0.08	1.47 ± 0.08	3.6 ± 0.1
2.0 ± 0.1	3.0 ± 0.1	1.59 ± 0.08	1.51 ± 0.08	3.8 ± 0.1
2.7 ± 0.1	-	1.64 ± 0.08	1.51 ± 0.08	3.9 ± 0.1
3.7 ± 0.1	-	1.60 ± 0.08	1.46 ± 0.08	3.8 ± 0.1

- = not measured.

carbon in these plasma ALD films ($[C] > 30$ at. %). The CO_x species, created by plasma-induced oxidation and decomposition of the CpMe ligands, appear to be incorporated into the bulk of the film. This behavior, which is absent for many other plasma ALD processes, is consistent with the tendency of Er (and other lanthanides) to react with CO₂.³² High impurity levels were not observed for thermal ALD Er₂O₃ films.

The thermal ALD process was used to synthesize various Al₂O₃ films with Er concentrations in the range of $[Er] = 0.9$ – 6.2 at. %. Table I lists the material properties of a selection of these samples. The RBS spectrum for the sample with $[Er] = 2.0$ at. % is shown in Fig. 3. The flat Er signal between 1.7 and 1.8 MeV indicates that the Er concentration was relatively constant as a function of film thickness (~ 200 nm) for this sample. All Er-doped films exhibited an O/Al ratio > 1.5 , which is clearly higher than that for stoichiometric Al₂O₃. In addition, the O/(Al+Er) ratio was found to be ~ 1.5 for most of the samples and exhibited no clear trend with $[Er]$. These findings are consistent with the substitution of Al atoms by Er atoms in the Al₂O₃:Er structure. For the range of $[Er]$ between 0.9– 6.2 at. %, the mass density varied between 3.6 ± 0.1 and 4.2 ± 0.1 g/cm³. The two Al₂O₃:Er films that were measured by ERD (Table I) contained the same amount of hydrogen ($[H] \sim 3$ at. %) which was also similar for undoped ALD Al₂O₃ films.²⁹ The hydrogen was present mostly as –OH groups.³³ RBS measurements revealed that the carbon content was below the detection

FIG. 3. (Color online) RBS spectrum of an Er-doped Al₂O₃ film with $[Er] = 2.0$ at. % (1.8×10^{21} atoms cm⁻³). The line is a fit to the data to extract the areal atomic densities.

FIG. 4. (Color online) Photoluminescence spectra of Er-doped Al_2O_3 films ($[\text{Er}] \sim 1.0$ at. %) annealed at various temperatures for an excitation wavelength of 532 nm. (a) PL signal of Si at $1.1 \mu\text{m}$. (b) PL signal corresponding to the first excited state of Er^{3+} ($^4I_{13/2} \rightarrow ^4I_{15/2}$). It was verified that the $1.54 \mu\text{m}$ signal scaled linearly with pump power (1.5–50 mW). The spectrum corresponding to the film annealed at 1000°C was multiplied by a factor of 10 in (a) to show the Er^{3+} emission at $0.98 \mu\text{m}$ ($^4I_{11/2} \rightarrow ^4I_{15/2}$).

limit (< 5 at. %). The impact of annealing on the structural properties will be discussed in more detail in Sec. III C.

B. Optical properties

1. Si luminescence and surface passivation

The luminescence properties of the Er-doped Al_2O_3 films ($[\text{Er}] = 1.0$ at. %) were investigated using an excitation wavelength of 532 nm. The samples were annealed at $T = 450^\circ\text{C}$ and 650°C for 10 min and at 800°C and 1000°C for 1 min. The Si luminescence at $\sim 1.1 \mu\text{m}$ as displayed in Fig. 4(a) is related to the radiative band-band recombination of electrons and holes in Si. This involves the emission of a photon with an energy approximately equal to that of the Si bandgap. Equation (1) gives an expression for the measured PL signal, I_{Si} , and the radiative recombination rate, U_{rad} :

$$I_{\text{Si}} \sim U_{\text{rad}} = B(np - n_i^2) \quad (1)$$

where n , p , and n_i are the electron and hole concentration under illumination and the intrinsic carrier concentration, respectively, and B is a coefficient reflecting the probability of a radiative transition.³⁴ The radiative recombination increases with the density of the generated minority carriers, i.e., holes in the case of n -type Si. The passivation of surface defects by applying the Al_2O_3 film leads to the increase of the excess carrier concentration and, consequently, a relatively enhanced radiative recombination rate. Therefore, the Si PL signal can be regarded as a measure for the surface passivation quality.³⁵ Figure 4(a) shows that the Si luminescence depends strongly on the annealing temperature. The as-deposited sample exhibited a comparatively strong Si PL signal. Annealing at a moderate temperature of 450°C led to

FIG. 5. (Color online) Maximum surface recombination velocity, $S_{\text{eff,max}}$, for (undoped) Al_2O_3 films (~ 30 nm) deposited on Si, as a function of annealing temperature. Annealing was carried out for 1 min at 800 – 1000°C , and for 10 min in other cases. The data for 200°C represents Al_2O_3 in the as-deposited state.

a further increase. However, for higher annealing temperatures, I_{Si} was found to decrease. For the sample annealed at 1000°C , the intensity of the Si PL was very low and comparable to that for Er^{3+} (as discussed below). These results indicate that the application of (Er-doped) Al_2O_3 films in combination with moderate annealing temperatures lead to a significant improvement of the Si luminescence. This was recently also demonstrated for Al_2O_3 -coated Si nanodots.³⁶ The PL data can be compared with the surface recombination velocity, S_{eff} . An upper level of S_{eff} can be determined directly from the effective lifetime (τ_{eff}) of the minority carriers in a FZ Si wafer by assuming that all recombination takes place at the surfaces. The upper level for the surface recombination velocity $S_{\text{eff,max}}$ was extracted at an injection level of $1 \times 10^{15} \text{ cm}^{-3}$ (i.e., significantly lower compared to the injection level during the PL measurements) by the expression:

$$S_{\text{eff,max}} = \frac{W}{2 \times \tau_{\text{eff}}}, \quad (2)$$

where W is the thickness of the silicon wafer ($\sim 280 \mu\text{m}$). Figure 5 shows $S_{\text{eff,max}}$ for a high quality FZ c -Si wafer (n -type, $3.5 \Omega\cdot\text{cm}$) coated on both sides with Al_2O_3 (not Er-doped) annealed at various temperatures. The measured ultra-low values of $S_{\text{eff}} < 2 \text{ cm/s}$ ($\tau_{\text{eff}} = \sim 6 \text{ ms}$) indicate an exceptionally high level of passivation by Al_2O_3 .^{21,22,29} With such low (maximum) surface recombination velocities, the intrinsic (radiative and Auger) recombination is significant in determining the effective lifetime of the minority carriers. The trends of the Si PL signal and S_{eff} were qualitatively in good agreement: S_{eff} decreased by annealing at moderate temperatures, whereas higher temperatures led to a degradation of the passivation performance.^{29,37} The effective lifetime of $\sim 6 \mu\text{s}$ measured after annealing at 1000°C was similar to that obtained for an unpassivated Si

FIG. 6. (Color online) Er^{3+} energy level diagram with the corresponding Russel-Saunders notation for the energy levels.¹ (a) Relevant emission wavelengths observed in this study. (b) 2- and 3-photon upconversion processes. The wavy line indicates phonon relaxation.

wafer. It is interesting to note that in contrast to Al_2O_3 films of Er_2O_3 did not provide a high level of surface passivation after annealing. High Er concentrations may therefore affect the surface passivation performance of doped Al_2O_3 films. However, this can be easily circumvented for potential applications. We have verified that a stack of an ultrathin (~ 5 nm) Al_2O_3 film applied on the Si surface combined with a thick Er-doped Al_2O_3 film on top, resulted in similar passivation properties as a 30 nm undoped Al_2O_3 film.

2. Er^{3+} luminescence

No Er^{3+} photoluminescence could be detected for the $\text{Al}_2\text{O}_3:\text{Er}$ samples in the as-deposited state and after annealing at 450°C . Increasing the annealing temperature to 650°C and above led to the optical activation of Er^{3+} in the material. Figure 4(b) shows the Er^{3+} PL spectrum centered around a wavelength of $1.54 \mu\text{m}$. The emission corresponds to the transition from the first excited state of the Er^{3+} ion to the ground state, i.e., $4I_{13/2} \rightarrow 4I_{15/2}$ (see Fig. 6). It was verified that the luminescence properties were not significantly affected by prolonged annealing of up to 30 min at 650°C . However, a significant increase of the PL signal was observed after annealing at 800°C and 1000°C for 1 min. An increase of the annealing time to 2 min did not lead to a significant further increase. A comparable trend between the Er luminescence and the annealing temperature was reported by Polman *et al.* for sputtered Er-implanted Al_2O_3 .² Also for PECVD-synthesized Er-doped Al_2O_3 films, annealing at 900°C proved to be essential.¹⁵ The PL spectra of the ALD $\text{Al}_2\text{O}_3:\text{Er}$ samples were relatively broad with a full width at half maximum (FWHM) of 55 nm, which is also consistent with earlier reports.^{2,9,15} For the film annealed at 1000°C , an additional luminescence signal at a wavelength of $0.98 \mu\text{m}$ ($4I_{11/2} \rightarrow 4I_{15/2}$) was observed as a shoulder on the Si luminescence.

FIG. 7. (Color online) Upconversion luminescence from Er^{3+} using a laser wavelength of 1480 nm. The Er-doped Al_2O_3 films ($[\text{Er}] \sim 1.0$ at. %) were annealed at 650°C (10 min) and 800°C and 1000°C (1 min). The spectra are off-set for clarity. The inset shows a magnification of the UC PL between 600 and 900 nm of the sample annealed at 1000°C .

3. Upconversion luminescence

The nearly equally spaced energy levels of the Er^{3+} ion in conjunction with the relatively long lifetime of the $4I_{13/2}$ state allow for photon upconversion (UC) processes to occur. Two different UC mechanisms can be discerned: excited-state upconversion (ESA), in which a single Er^{3+} ion is excited stepwise to a higher energy state, and energy transfer upconversion (ETU) where energy is nonradiatively transferred between ions.^{3,13} Here we focus on near-infrared emission through excitation in the infrared with $1.48 \mu\text{m}$ laser light. This excitation wavelength is relevant for upconversion processes for Si photovoltaics.⁴ In addition, this wavelength range can be used to pump optical waveguide amplifiers.⁸ Figure 7 displays the UC luminescence for three $\text{Al}_2\text{O}_3:\text{Er}$ films ($[\text{Er}] \sim 1.0$ at. %) annealed at various temperatures. No upconversion was observed for as-deposited films and for films annealed at 450°C . For higher annealing temperatures, UC luminescence was detected at a wavelength of $0.98 \mu\text{m}$ (FWHM of ~ 28 nm). This two-photon UC process originates from the stepwise excitation to the $4I_{9/2}$ state, subsequent phonon relaxation to the $4I_{11/2}$ state, and successive relaxation to $4I_{13/2}$ by photon emission (Fig. 6). Direct radiative decay from the $4I_{9/2}$ level to the ground state is also observed by the detection of $\sim 0.81 \mu\text{m}$ photons, as displayed in the inset of Fig. 7. In addition, a signal at $\sim 0.66 \mu\text{m}$ ($4F_{9/2}$) was detected, which originates from a three-photon UC process. This $4F_{9/2}$ state can be populated through the $4I_{9/2} \rightarrow 4S_{3/2}$ transition and subsequent relaxation to $4F_{9/2}$, or through direct excitation from $4I_{11/2}$. Note that the measurements provided no direct evidence for the significant population of the $4S_{3/2}$ state, as emission at $0.85 \mu\text{m}$ ($4S_{3/2} \rightarrow 4I_{13/2}$) was not detected, in contrast to observations by van den Hoven *et al.*¹³ Furthermore, the ratio between I_{UC} at 980 and 660 nm of $\sim 10^2$ suggests that the probability of a three-photon UC process is approximately 10^2 smaller compared to UC involving two photons. The upconversion processes appeared to be more strongly

FIG. 8. (Color online) Integrated PL signals as a function of the average Er concentration in the films. (a) The Er^{3+} PL signal centered at $1.54\ \mu\text{m}$ (between 1430–1660 nm) under excitation of 532 nm light and (b) the 980 nm UC PL (between 950–1040 nm) under excitation of $1.48\ \mu\text{m}$ light. The films were all annealed at 1000°C (1 min). The PL signal for each sample was divided by the corresponding film thickness and also corrected for associated (small) differences in reflection of the incoming light, taking into account interference in the film.

dependent on the annealing temperature (800°C – 1000°C) than the Er^{3+} PL signal, as displayed in Fig. 4(b): The UC signal for the sample annealed at a temperature of 800°C was significantly lower than that of the sample annealed at 1000°C . The upconversion processes appear to be very sensitive to the changes in film properties that occur during annealing.

4. Effect of the Er concentration

Apart from the annealing temperature, the Er^{3+} PL and UC signals were found to be strongly dependent on the Er concentration in the films. The effect of $[\text{Er}]$ within the range of 0.9–6.2 at. % on the (integrated) PL and UC signals is displayed in Fig. 8. Despite some scatter in the data, it is evident that the Er^{3+} PL signal exhibited an initial enhancement and subsequent decrease of intensity with increasing $[\text{Er}]$. This decrease at high Er concentrations is also observed for UC. The maximum Er^{3+} luminescence falls in the range of $[\text{Er}]$ of 2.5–3.0 at. %. This range is comparable to that reported for Er-doped Y_2O_3 .³⁸ A maximum upconversion signal was observed for films with lower $[\text{Er}]$ of 0.9–2.5 at. %. The existence of a maximum in the Er^{3+} luminescence can be explained in terms of an increasing density of optically active Er^{3+} ions, which competes with nonradiative relaxation that starts to dominate at higher $[\text{Er}]$. The latter effect is known as concentration quenching, where energy is transferred by Er-Er interactions and coupled to quenching sites such as $-\text{OH}$ groups,^{2,28} as will be discussed in more detail in Sec. IV. Concentration quenching of the $^4I_{11/2}$ state can also be responsible for the observed decrease in UC luminescence at high $[\text{Er}]$. In addition, it is important to note that the population of the $^4I_{9/2}$ state may strongly rely on Er-Er interactions,²⁸ as the ETU process is expected to be the

FIG. 9. (Color online) (a) XPS survey spectrum of Er-doped Al_2O_3 ($[\text{Er}] \sim 1.0$ at. %), (b) Er4d region before and after annealing at 1000°C (1 min). Prior to the measurements the sample surfaces were cleaned by Ar ion irradiation.

prominent UC mechanism for our samples with relatively high $[\text{Er}]$.^{13,39} The mean Er-Er distance can be easily estimated from their concentration when a relatively uniform distribution is assumed. For $[\text{Er}] = 1$ at. %, corresponding to an Er density of $9 \times 10^{20}\ \text{cm}^{-3}$, a mean distance between the ions of $r \sim 1$ nm is obtained. Likewise, an Er concentration of 6.2 at. % corresponds to $r \sim 0.6$ nm between the ions. This suggests that changes of ~ 0.4 nm in the distance between the Er ions can lead to significant changes in the UC and PL efficiency. This observation is in agreement with the strength of the electric dipole-dipole interaction between Er^{3+} ions, which depends on the distance between the ions by r^{-6} .

C. Effect of annealing on structural properties

In this section, the effect of annealing on the structural properties of the Er-doped Al_2O_3 films is reported. First, we briefly address the question of how Er is bonded in the Al_2O_3 film, on the basis of XPS measurements that were performed on a sample before and after annealing at 1000°C . Figure 9(a) shows the XPS survey scan, with peaks related to O (531 eV), Al (75 eV), and Er. Three peaks can be discerned in the binding energy range of Er, with the strongest feature at an energy of 169 eV, as displayed in Fig. 9(b). Compared to bulk Er, which exhibits a doublet at a binding energy of ~ 167 eV, the Er 4d peak is shifted toward higher binding energies.⁴⁰ This is also in good agreement with the value of 169–170 eV for sputtered Er_2O_3 thin films,⁴¹ and indicates that, for our samples, Er is mostly bonded with oxygen. After annealing at 1000°C , the Er 4d peaks were not shifted. However, a relatively stronger signal was observed and the additional features at higher binding energies are better resolved. The XPS signals related to O 1s and Al 2p were not affected. On the other hand, the film thickness was reduced substantially ($\sim 20\%$) after annealing at 1000°C (Table II). In addition, the mass density increased significantly from 3.6 to $4.5\ \text{g/cm}^3$ and the refractive index (at a photon energy of 2 eV) was observed to change accordingly from 1.66 to 1.83.

The data in Table II show that the films were nearly depleted of hydrogen after annealing at 1000°C . To study the effect of the annealing temperature on the removal of hydrogen and other impurities from the $\text{Al}_2\text{O}_3:\text{Er}$ film,

TABLE II. Properties of Er-doped Al_2O_3 films ($[\text{Er}] \sim 1.0$ at. %), as-deposited and after annealing for 1 min at 1000°C , determined by RBS/ERD and SE. The relative change of the parameters is given in the last row of the table.

Parameter	$[\text{H}]$ (10^{21} cm^{-3})	Thickness (nm)	Refractive index	ρ_{mass} (g/cm^3)
as-grown	2.6 ± 0.1	206 ± 2	1.66 ± 0.02	3.6 ± 0.1
1000°C	0.17 ± 0.01	165 ± 2	1.83 ± 0.02	4.5 ± 0.1
change	-95%	-20%	$+10\%$	$+25\%$

thermal effusion measurements ($300\text{--}1000^\circ\text{C}$) were carried out. Figure 10 shows the effusion signals corresponding to various prominent mass-over-charge ratios (m/z) that were detected during these measurements. The $m/z = 2$ signal can be attributed to H_2^+ . The signal at $m/z = 18$ is due to H_2O^+ with $m/z = 17$, OH^+ , a corresponding cracking product of H_2O . The signal $m/z = 44$ can be ascribed to CO_2^+ with $m/z = 12$ being C^+ , a cracking product of CO_2 . Finally, $m/z = 15$ can be attributed to CH_3^+ , which reflects the presence of CH_4 (and possibly other hydrocarbons C_xH_y). The effusion signals can originate from species in the bulk of the Al_2O_3 film as well as on the surface of the sample. The latter can also include (organic) surface contaminants such as adventitious carbon, as corroborated by the XPS measurements. The signals related to CO_2 and CH_x at relatively low temperatures are, therefore, likely to be mainly related to the desorption of surface contaminants. Note that the presence of a significant density of CO_x groups in the bulk of the material would also not be expected for ALD with H_2O as the oxidant, in contrast to plasma ALD where C-O vibrations were detected by infrared absorption spectroscopy.^{33,37,42} On the other hand, it is likely that the CH_x feature at 740°C can be attributed to the removal of carbon impurities that originate from the precursor and were incorporated into the $\text{Al}_2\text{O}_3\text{:Er}$ film during deposition. Maxima in the effusion transients were observed at 700°C for both H_2O and H_2 . In addition, a broad H_2O shoulder is apparent at higher temperatures and also an additional H_2 peak was observed at

FIG. 10. (Color online) Effusion signals measured during annealing an Er-doped Al_2O_3 film ($[\text{Er}] \sim 1.0$ at. %). The heating rate was 20°C/min . The various prominent mass-over-charge ratios are displayed in (a)–(d) and correspond with mainly H_2 , H_2O , CO_2 , and CH_4 (or C_xH_y).

900°C . The effusion features clearly demonstrate that the removal of hydrogen from the Al_2O_3 bulk continues up to high annealing temperatures, where a temperature above 900°C was necessary to deplete the films of hydrogen.

In conjunction with the effusion of impurities from the films, a transition from an amorphous to a polycrystalline phase was observed at high annealing temperatures. Figure 11 shows the XRD signal around an angle of $2\theta = 67^\circ$, which can be assigned to a reflection plane which appears for crystalline Al_2O_3 .⁴³ The Er-doped films ($[\text{Er}] = 1.0$ at. %) were observed to crystallize between annealing temperatures of 900 and 1000°C . In contrast, for undoped Al_2O_3 the onset of crystallization began at lower temperatures of $850\text{--}900^\circ\text{C}$. Therefore, the results indicate that a small fraction of Er in the Al_2O_3 film can change the crystallization properties of the thin film material significantly. This was corroborated by examining films with $[\text{Er}] = 3.7$ and 6.2 at. %, for which the XRD signal at 67° was negligible after annealing at 1000°C (1 min). The large Er atoms in the Al_2O_3 lattice appear to hinder the formation of crystalline grains.

IV. DISCUSSION

The optical activation of Er^{3+} upon annealing the Er-doped Al_2O_3 films can be attributed to the significant structural changes in the films at high temperatures. In principle

FIG. 11. (Color online) XRD spectra, comparing (a) Al_2O_3 films with (b) Er-doped Al_2O_3 ($[\text{Er}] \sim 1.0$ at. %) for various annealing temperatures (1 min, N_2). The film thickness was ~ 200 nm (as-deposited).

two effects can play a role here. First, it may be speculated that the fraction of optically active Er^{3+} ions increases.^{2,44} Second, the influence of nonradiative processes that compete with the luminescence yield can be significantly reduced during annealing. The importance of the second effect was demonstrated for Er_2O_3 and Er-implanted Al_2O_3 films, where a significant enhancement of the lifetime of the $^4I_{13/2}$ level was observed with increasing annealing temperature.^{2,45} Nonradiative relaxation can take place when Er^{3+} ions transfer energy by coupling to the phonon modes of Al_2O_3 (phonon energy of 870 cm^{-1}),² or to impurities in the host material. Al_2O_3 exhibits a relatively high phonon energy compared to, e.g., chlorides and other halides,^{4,5} and, therefore, a relatively high nonradiative recombination rate may be expected.⁴⁶ On the other hand, the transition from an amorphous to polycrystalline Al_2O_3 structure (Fig. 11) is expected to lead to only a slight variation in the phonon energy distribution. As these minor changes only occur for temperatures $>900^\circ\text{C}$, the coupling to phonon modes of Al_2O_3 cannot account for the general trend of increasing luminescence yield upon annealing. As a counter effect, we hypothesize that grain boundaries in the polycrystalline Al_2O_3 constitute additional quenching sites for the Er^{3+} luminescence. Apart from the phonon modes of the host lattice, OH impurities have been identified as prominent quenching sites for Er^{3+} luminescence.^{2,28,47} An important quenching mechanism is concentration quenching, i.e., the transfer of energy between Er^{3+} ions until it is nonradiatively dissipated.¹³ The energy migration between Er^{3+} ions is expected to be effective concerning the relatively high Er concentrations in our films. The broad energy range of the OH stretching vibration around $\sim 3600\text{ cm}^{-1}$ (Ref. 33) matches closely with the energy between $^4I_{11/2} \rightarrow ^4I_{13/2}$ states ($\sim 3670\text{ cm}^{-1}$). Furthermore, the energy of the second harmonic of the OH vibration is relatively close to the energy between the $^4I_{13/2} \rightarrow ^4I_{15/2}$ states ($\sim 6500\text{ cm}^{-1}$). Other impurities, such as CH_x , can also be identified as possible quenching centers. The stretching vibration of CH_3 is located in the infrared absorption spectrum at an energy of $\sim 2945\text{ cm}^{-1}$,^{27,33} which is in the same energy range as that of OH.

The removal of hydrogen from the films during annealing may explain the negative correlation between the Er^{3+} and Si photoluminescence. The normalized Er and Si PL signals are displayed in Fig. 12(a) as a function of annealing temperature, together with the loss of hydrogen from the film in Fig. 12(b). The hydrogen loss was estimated by integrating the $m/z = 2$ effusion signal (H_2) and calibrated by the initial hydrogen content as obtained by ERD. Note here that the effusion of hydrogen from the film in the form of H_2O was not taken into account. Figure 12 reveals that a small fraction of hydrogen can leave the film by effusion into vacuum at moderate temperatures of $\sim 350\text{--}450^\circ\text{C}$. The mobilized hydrogen can also diffuse toward the interface and passivate defects, as was recently demonstrated by a secondary ion mass spectroscopy study on deuterated Al_2O_3 thin films.⁴⁸ Accordingly, very low interface defect densities $\leq 10^{11}\text{ eV}^{-1}\text{ cm}^{-2}$ have been reported for Al_2O_3 thin films annealed at 400°C .²² By increasing the annealing temperature $>450^\circ\text{C}$, significant amounts of OH groups are removed

FIG. 12. (Color online) (a) Normalized PL signals for Si and Er^{3+} (corresponding to Fig. 4). Lines serve as guides to the eye. (b) The hydrogen content in the film as a function of annealing temperature, estimated from the thermal effusion measurements.

from the (Er-doped) Al_2O_3 films. While this represents the removal of quenching centers coinciding with the activation of the Er^{3+} luminescence, the hydrogen loss will also take place at the interface, which leads to a drop of the Si PL and a decreasing level of surface passivation. When the film is depleted of hydrogen ($T \sim 1000^\circ\text{C}$), the Er^{3+} luminescence is activated to the full extent, whereas the surface passivation by the films is lost. These results demonstrate the trade-off between optical activation of Er^{3+} and the silicon surface passivation quality.

Finally it is noted that these results suggest a limited potential of Er-doped Al_2O_3 for silicon technology in combining surface passivation with the upconversion of infrared light. In fact, the most efficient upconversion processes generally occur in host materials with low phonon energies such as $\text{NaY}_{0.8}\text{F}_4$.⁴⁻⁷ Nonetheless, in photovoltaics, technology based on UC processes to harvest sub-bandgap photons has not yet advanced to the point where such devices are practical. Fundamental issues, such as the typically small absorption cross-section of Er ($\sim 10^{-20}\text{ cm}^{-2}$)^{27,49,50} and the strong dependence of the UC efficiency on the light intensity,^{4,13,39} complicate a straightforward solution based on UC for significantly increasing Si solar cell efficiencies.

V. SUMMARY

Atomic layer deposition was used to successfully synthesize Er-doped Al_2O_3 films on Si substrates. Under excitation of 532 nm light, these films exhibited broad Er^{3+} luminescence at $1.54\text{ }\mu\text{m}$ after a high-temperature annealing step. Also 2- and 3-photon upconversion luminescence was detected under excitation of $1.48\text{ }\mu\text{m}$ light. Furthermore, the Er-doped Al_2O_3 films afforded a high level of surface passivation leading to a significantly enhanced Si luminescence (a factor of 60 higher compared with unpassivated Si). A close correlation between the removal of OH impurities during annealing and the increase of Er^{3+} luminescence was demonstrated. A change from amorphous to polycrystalline

Al₂O₃ at annealing temperatures > 900 °C did not play a significant role in the optical activation. In contrast to Er, the Si luminescence decreased at high annealing temperatures, indicating a decreasing level of surface passivation.

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