# Visible luminescence from *a*-SiN films doped with Er and Sm

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Relatively strong and narrow red and green light emission has been achieved from amorphous (*a*-) SiN films independently doped with $Er^{3+}$ and $Sm^{3+}$ ions. The films were deposited by cosputtering a Si target partially covered with small pieces of metallic Er (and Sm) in an atmosphere of pure nitrogen. As a consequence of the deposition method and conditions, the films have an amorphous structure, and contents of Er (and Sm) in the low 0.5 at. %. All characterizations were accomplished on as-deposited samples and at room temperature and included: ion-beam analysis (Rutherford backscattering spectrometry and nuclear reaction analysis) and optical techniques (light absorption, Raman scattering, and photoluminescence and cathodoluminescence). A detailed examination of the experimental results allowed the identification of all luminescence features existing in the films. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1389069]

Since the pioneering work of Ennen *et al.*[1] in the 1980s, the doping of semiconductor hosts with rare-earth (RE) ions has received increasing attention. Tripositive RE ions are known to exhibit sharp and well-defined luminescence which arises mostly from internal transitions between $4f$ levels. Because of the shield provided by the outer $5s^2$ and $5p^6$ shells, the wavelength involved in these intra-$4f$ transitions is temperature insensitive and weakly depends on the host. Moreover, by properly combining different $RE^{3+}$ ions and host matrices it is possible, in principle, to achieve luminescence at wavelengths that span the almost entire infrared-visible–ultraviolet range. As a consequence, RE-doped semiconductors are expected to conceive optoelectronic devices able to exhibit the electronic properties of semiconductors with the unique optical features of $RE^{3+}$ ions. Most of the studies about RE-doped semiconductors have focused on $Er^{3+}$ ions and on light emission in the IR region (at ~1540 nm). In addition to a deeper understanding of the subject, these efforts have provided interesting and renewed possibilities. At present, it is recognized that:[2–4] optically active $Er^{3+}$ ions occur more frequently in an ionic environment than in a covalent one; the efficiency of the $Er^{3+}$ luminescence can be notably improved by proper thermal annealing processes; and the thermal quenching of the luminescence intensity tends to be lower in wide-band-gap compounds. Also, and more recently, visible light emission was observed in Er-doped wide-band-gap materials such as SiN,[5] GaN,[6] and AlN.[7] Actually, visible light emission was achieved from cathodoluminescence experiments[6,8,9] on RE-doped GaN and AlN, pointing out the enormous potential of these compounds for devices such as light-emitting diodes and flat-panel displays, for example.

Considering the above, the present contribution reports a spectroscopic study on Er- and Sm-doped amorphous (*a*-) SiN films.

The present Er- and Sm-doped *a*-SiN films (*a*-SiErN and *a*-SiSmN, respectively) were prepared in a standard radio-frequency (13.56 MHz) sputtering system. During deposition a 99.999% Si target partially covered at random with metallic 99.9% Er (and Sm) platelets and high-purity nitrogen were employed. A nonintentionally doped *a*-SiN film was also deposited for comparison purposes. Polished *p*-type crystalline (*c*-) Si wafers and quartz plates were used as substrates. The films were deposited at 475 K under a power density of approximately 0.85 $W\,cm^{-2}$ and a total pressure of $N_2$ equal to $1.5 \times 10^{-3}$ Torr. The main properties of the doped and undoped *a*-SiN films were investigated by means of: Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), Raman scattering, optical absorption in the 200–2500 nm range, and photoluminescence (PL) and cathodoluminescence (CL) in the visible region.

Typically, the films are ~0.5 $\mu$m thick and the NRA data indicate a nitrogen content of approximately 50 at. %. As a result of such a high [N], the optical band gap of the present films is ~4.5 eV, as determined from optical spectroscopy. The atomic concentration of Er (and Sm) was obtained from RBS and stayed in the low 0.5 at. %. The films deposited on quartz substrates were submitted to Raman scattering measurements, which confirmed their amorphous structure. PL measurements were performed at room temperature by exciting the films with 488.0 nm photons from an $Ar^+$-ion laser. CL experiments were also accomplished at room temperature with a beam current of approximately 10 nA and an electron accelerating voltage of 15 kV.

At this point it is important to stress that contrary to most of the current research on RE-doped nitride compounds (essentially GaN and AlN),[6–9] the present letter corresponds to *a*-SiN films deposited at low temperatures and with no postdeposition treatments.

Figure 1 displays the PL spectra of the films considered in this work. The spectrum of the undoped *a*-SiN film is also represented for comparison. According to Fig. 1, while the
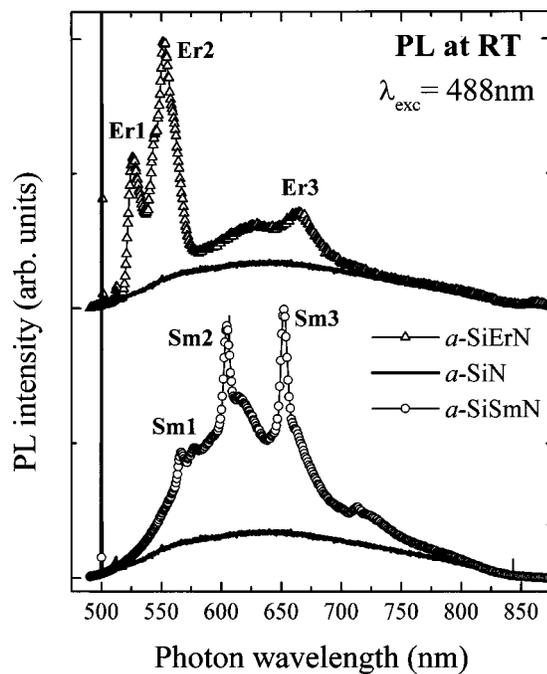
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FIG. 1. Photoluminescence spectra of $a$-SiN, $a$-SiErN, and $a$-SiSmN films prepared under identical deposition conditions. The measurements were performed at room temperature and with 488.0 nm photons. For comparison, the spectra corresponding to the $a$-SiN and $a$-SiErN films have been multiplied by a factor of 5. The very narrow peak at ~500 nm corresponds to the transverse optical phonons of the $c$-Si substrate. The peaks labeled in the figure indicate intra-$4f$ transitions due to the $Er^{3+}$ and $Sm^{3+}$ ions.



FIG. 2. Energy-level diagram of the $Er^{3+}$ and $Sm^{3+}$ ions. Some of the main transitions, and corresponding spectroscopic notation, are denoted in the figure. The transitions near the photon wavelength employed for optical excitation (488.0 nm) were also represented.

undoped $a$-SiN matrix exhibits a very broad and featureless signal, both Er- and Sm-doped films present very well-resolved PL peaks. In addition to the signals due to the $Er^{3+}$ and $Sm^{3+}$ ions (as labeled in Fig. 1), it is also possible to observe some contribution of the $a$-SiN matrix in the doped samples. Since the films are transparent to the 488.0 nm photons employed for excitation, the Raman signal coming from the $c$-Si substrate is also apparent in the spectra of Fig. 1.[10] The disordered nature of the present $a$-SiN films allied with the small energy difference between some $RE^{3+}$ energy levels give rise to new PL features (essentially in the form of shoulders) and will be addressed in a separate report.

The strongest PL signals observed in the $a$-SiErN and $a$-SiSmN films have been properly identified[11] and correspond to the following transitions: Er1 (at ~520 nm) $^2H_{11/2} \rightarrow {}^4I_{15/2}$, Er2 (at ~550 nm) $^4S_{3/2} \rightarrow {}^4I_{15/2}$, Er3 (at ~660 nm) $^4F_{9/2} \rightarrow {}^4I_{15/2}$, Sm1 (at ~560 nm) $^4G_{5/2} \rightarrow {}^6H_{5/2}$, Sm2 (at ~600 nm) $^4G_{5/2} \rightarrow {}^6H_{7/2}$, and Sm3 (at ~650 nm) $^4G_{5/2} \rightarrow {}^6H_{9/2}$, as depicted in Fig. 2. The photon wavelength employed for excitation is also represented in Fig. 2 and resembles very much the $^4I_{15/2} \rightarrow {}^4F_{7/2}$ and $^6H_{5/2} \rightarrow {}^4I_{9/2}$ transitions of the $Er^{3+}$ and $Sm^{3+}$ ions, respectively. It is worth mentioning that both the energy levels and transitions assigned in Fig. 2 correspond to averaged values observed from several different, either crystalline or amorphous, hosts.

Usually, the comparison of different luminescence techniques yields similar results with some possible differences that are associated with the generation of electron–hole ($e$–$h$) pairs and/or to the energy transfer mechanisms.[12] As a result, the combined analysis of PL and CL measurements, of RE-doped $a$-semiconductors, can contribute helpful information towards the understanding of these materials.
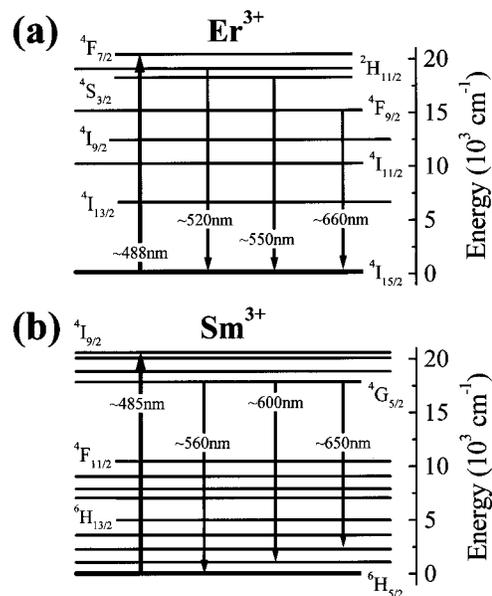
In addition to a high spatial resolution, the CL technique is a convenient and electrodeless method to probe the compatibility of materials for future devices such as electrically pumped light sources, for example.[13] CL depends on the electron interaction volume and is governed by the local density of $e$–$h$ pairs.[12] The $e$–$h$ pair generation, and subsequent CL production, can be approximated[14] by the total primary electron energy-loss profile that maximizes at approximately 0.3 $R_{KO}$, where $R_{KO}$ is the Kanaya–Okayama[15] electron penetration range. Based on these characteristics, a rough evaluation indicates that the maximum electron energy-loss profile is ~0.6 $\mu$m for the present samples. Therefore, most of the CL signals are expected to be produced along the $a$-SiN films, with a small contribution of the $c$-Si substrate.

Figure 3 displays the CL spectra of the present series of $a$-SiN films. At a first glance, the PL and CL spectra resemble each other, with almost the same $Er^{3+}$ and $Sm^{3+}$ optical transitions. In addition to a considerable decrease of the luminescence from the $a$-SiN matrix (Fig. 3) it is important to notice the development of new $Er^{3+}$-related transitions (Er4, at ~390 nm $^4G_{11/2} \rightarrow {}^4I_{15/2}$, and Er5 at ~410 nm $^2H_{9/2} \rightarrow {}^4I_{15/2}$),[11] as well as some features due to the $c$-Si substrate[16] (bulk resonance associated with the lowest direct band gap of $c$-Si at ~370 nm, and transitions involving bonding defects at ~435 and 630 nm). The CL signal at ~550 nm is very similar to that found in $c$-Si after thermal oxidation in a dry atmosphere and most likely comes from the surface of the $c$-Si substrate.[17] Whereas the $Er^{3+}$-related transitions above 488.0 nm and the contribution from the $c$-Si substrate result from the high energy of the electrons, the absence of any CL from the $a$-SiN host needs further consideration. Contrary to crystalline compounds, the threshold energy for electron damage in $a$-semiconductors is considerably smaller, namely, about $10^2$ keV against 1 keV.[13] Moreover, electron irradiation may create defects that are not possible with photons with energies in the visible energy
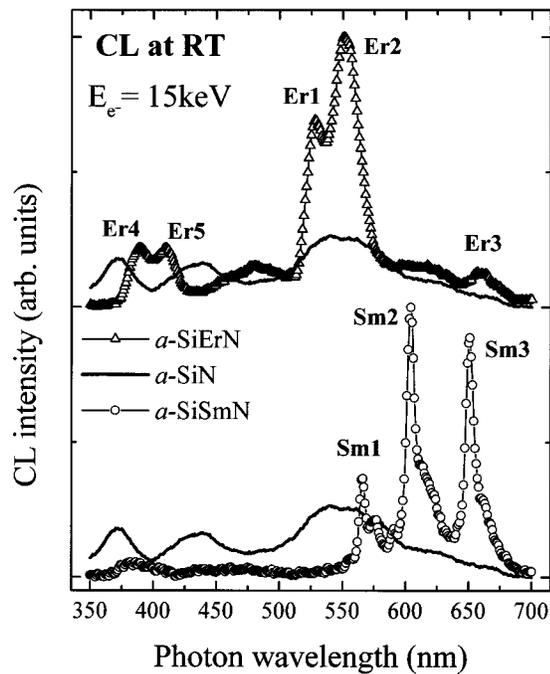
FIG. 3. Cathodoluminescence spectra of $a$-SiN, $a$-SiErN, and $a$-SiSmN measured at room temperature and with electrons of 15 keV. For comparison purposes, the spectra corresponding to the $a$-SiN and $a$-SiErN films have been multiplied by a factor of 2.5. The peaks identified in the figure correspond to intra-4$f$ transitions due to the $Er^{3+}$ and $Sm^{3+}$ ions.

the films stays near 4.5 eV. The light emissions of the films were investigated after excitation with 488.0 nm photons (PL) and 15 keV electrons (CL). Both PL and CL spectra exhibit relatively strong and narrow luminescence peaks that were properly identified and correspond to intra-4$f$ transitions due to $Er^{3+}$ and $Sm^{3+}$ ions. Luminescence from the $a$-SiN host is also observed, but only after photon excitation. Some improvement in the luminescence intensity of the present RE-doped $a$-SiN films is expected to occur after thermal annealing treatments and will be performed in the near future. Furthermore, in association with different spectroscopic techniques, thermal anneals can give insights on the subject. Finally, it is convenient to point out that optoelectronic devices based on the above materials hold several promising qualities which are very attractive for display and lighting. In addition to their entire compatibility with the current (micro)electronics processes, light emission from $RE^{3+}$ ions is spectrally sharp, temperature stable, and requires no color filtering.

range.[18] These additional defects, mainly broken bonds and atomic displacements, act as nonradiative centers that considerably reduce the luminescence efficiency of an $a$-semiconductor and result in a barely detectable (or no) CL signal. Furthermore, $RE^{3+}$ ions are high efficiency recombination centers that effectively compete with other (non)radiative processes taking place in a semiconductor host. As a result, when irradiating the RE-doped $a$-SiN with 15 keV electrons, most of the $e-h$ pairs recombine preferentially through the $RE^{3+}$ ions, which is in perfect agreement with the experimental data of Fig. 3. Luminescence after photon excitation, on the other hand, behaves in a different manner. Despite the almost resonant excitation of the $RE^{3+}$ ions with 488.0 nm photons (Fig. 2), part of the photon energy can also be absorbed by defects in the $a$-SiN matrix giving rise to new $e-h$ pairs.[19] Those $e-h$ pairs that did not experience a nonradiative transition can transfer their energy either to the $RE^{3+}$ ions or to the $a$-SiN host. In this respect, the energy transfer of the photon-generated $e-h$ pairs to the $a$-SiN matrix seems to be more effective in the $a$-SiSmN films where a considerable contribution of the $a$-SiN matrix takes place. The reason for such behavior is not clear at present, but certainly ensues from the disposal of the energy levels of the $Sm^{3+}$ ions and their interaction with the defects of the $a$-SiN host.

In summary, amorphous SiN films independently doped with $Er^{3+}$ and $Sm^{3+}$ ions were deposited by cosputtering at 475 K. All characterizations were performed on as-deposited samples and at room temperature. Raman scattering measurements confirm the disordered nature of the films that are typically constituted of ~50 at. % of nitrogen and [RE] in the low ~0.5 at. %, according to the NRA and RBS data. As a result of such a high nitrogen content, the optical band gap of

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