Effects of Erbium Concentration on the Band Tail States of Er-Doped Hydrogenated Amorphous Silicon

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The effect of erbium-doping on the electrical, optical, and structural properties of hydrogenated amorphous silicon (α-Si:H) is investigated. The electrical conductivity and thermopower measurements show that erbium acts as an n-type dopant in α-Si:H. The photoluminescence measurements show that an optical activity of Er decreases as the Er concentration increases beyond 0.04 at. %, with concurrent Raman and optical absorption measurements showing that erbium induces structural disorder and subsequent increase in the band tail states of α-Si:H. From the temperature dependence of Er³⁺ photoluminescence intensities, we identify competitive carrier capture by these band-tail states as an important factor in determining the overall Er³⁺ photoluminescence intensity. And carbon codoping enhances the Er³⁺ PL intensity and reduces the temperature quenching of the Er³⁺ PL intensity.

Erbium, in its trivalent state, can emit light near 1.54 µm, the wavelength at which the silica-based optical fibers show the minimum absorption, due to transition from the first excited state(⁴I₁₃/₂) to the ground state(⁴I₁₅/₂) of its 4f electrons [1]. Furthermore, Er doped into silicon can be Auger-excited by recombination of optically or electrically generated carriers, most likely trapped at an Er-related level in the bandgap of Si [2], thus making Si-based optoelectronics possible. Because of this potential, Si:Er has been the subject of intense research by many researchers [3,4] since the first work in 1983 [1].

A promising alternative to crystalline silicon (c-Si) is hydrogenated amorphous silicon as it offers several advantages over crystalline silicon for erbium doping such as the possibility of direct and low-cost deposition on optical materials such as glass and higher solubility for Er and codopants such as oxygen, nitrogen, and carbon [5,6]. More importantly, compared to c-Si, α-Si:H has a much wider bandgap (1.5-2 eV depending on the preparation conditions), a factor which has been identified as being crucial for reducing the temperature quenching of Er³⁺ luminescence intensity and obtaining efficient room temperature Er³⁺ luminescence [7,8]. Thus, many researchers have investigated 1.54 µm Er³⁺ luminescence of α-Si:H:Er, and found efficient room temperature photoluminescence [9-12] as well as electroluminescence [13].

However, the properties of α-Si:H are not unique, but depend on preparation conditions as well as on impurities [14,15]. Thus, for α-Si:H:Er to be is imperative to develop an understanding of the effect of erbium doping on the structural and electrical properties of α-Si:H films that are capable of being used in actual devices. In this paper, we report on the effects of erbium doping on the electrical, optical, and structural properties of α-Si:H deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) of SiH₄. ECR-PECVD was shown to be capable of depositing high-quality α-Si:H films for applications such as solar cells [16]. We find that Er is an n-type dopant in α-Si:H. We also find that Er induces structural disorder in the α-Si:H host matrix, and identify this disorder as a serious factor in determining the overall Er³⁺ luminescence intensity.

Er-doped α-Si:H films of varying Er concentrations were deposited on glass substrates (Corning #1737F) using ECR-PECVD of SiH₄ with concurrent sputtering of Er. The details of the deposition methods are given in Ref. [17]. We have previously demonstrated that this method is capable of depositing high-quality α-Si:H:Er films with low concentration of unintentionally doped oxygen or carbon contaminants [18]. The system base pressure was 1 × 10⁻⁶ Torr. The deposition pressure, microwave power, and the deposition temperature were 1 × 10⁻⁴ Torr, 400 W, and 325°C, respectively. The SiH₄ flow rate was 1.5 sccm. Er concentrations as determined by Rutherford backscattering spectroscopy (RBS) were 0.04 ~ 0.57 at. %. The H content in the films was determined by elastic recoil detection (ERD) to be ~ 20 at. %. Raman spectra confirmed that all films were amorphous without any crystalline phase (not shown). The electrical conductivity and Seebeck coefficients were measured.

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using coplanar Al electrodes, all verified to be ohmic. Photoluminescence (PL) spectra and its temperature dependence were measured using the 476.5 nm line of Ar laser with a nominal pump power of 200 mW, a grating monochromator, a thermo-electrically cooled InGaAs detector, the standard lock-in technique, and a closed-cycle helium cryostat. 476.5 nm line of Ar laser was chosen to ensure that all Er$^{3+}$ ions are excited via carriers, as this wavelength does not coincide with any Er$^{3+}$ optical absorption band.

Er$^{3+}$ luminescence is observed from all samples, as is shown in Fig. 1. Only the PL spectra of the 0.04 at. % Er concentration film are shown, but Er$^{3+}$ PL spectra were confirmed to be identical in all samples. The integrated Er$^{3+}$ PL intensities of different films, measured at 25 K and 300 K, are shown in the inset. The 0.04 at. % Er concentration film shows the highest Er$^{3+}$ PL intensity by over an order of magnitude. This is in agreement with other investigators, who have shown that Er$^{3+}$ PL intensity in a-Si:H:Er is greatest near Er concentration of $1 \times 10^{20}$ cm$^{-3}$ [19]. Note the small effect of increasing the temperature on the Er$^{3+}$ PL intensity. This will be discussed more in detail later.

Figure 2 shows the effect of Er doping on the electrical properties of a-Si:H. The electrical conductivity, $\sigma$, increases over several orders of magnitude upon erbium doping, as shown in Fig. 2(a). For comparison, Fig. 2(a) also shows $\sigma$ of intrinsic a-Si:H film without Er deposited under similar deposition conditions. And different from the PL intensity, the room temperature conductivity increases as the Er concentration increases, which means a little correlation between the electrical and optical activity of Er. In Er-doped c-Si, however, the electrical and optical activities are directly correlated [20]. Below the room temperature, $\log_{10} \sigma$ of all films show $T^{-1/4}$ dependence upon temperature, where $T$ is the temperature, indicating that the hopping conduction dominates in this temperature range. Around and above the room temperature, both $\exp(-E_a/kT)$ and $\exp(-(E_a/kT)^{1/4})$ temperature dependence gave equally good fits to the data. The Seebeck coefficient, $S$, of the 0.13 and 1.1 at. % Er concentration films are shown in Fig. 2(b). We observe negative values of -0.2 to -0.6 mV/K like other n-type a-Si:H doped with conventional donor impurities such as P [21]. In c-Si, Er is also an n-type dopant, and creates Er-related states 250-500 meV above the midgap of c-Si [22].

Figure 3 shows the half-width half-maximum(HWHM) of the TO Raman peak of a-Si:H near 480 cm$^{-1}$ on its high wavenumber side and the Tauc gap deduced from the infrared absorption spectra [23]. We observe an increase of the HWHM of the Raman peak and decrease in the Tauc gap as the Er concentration is increased. Unlike c-Si, the overall structure of a-Si:H is not unique. The amount of overall disorder of the a-Si:H matrix, characterized the spread in distribution of the bond angle in a-Si:H, can be affected by extrinsic factors such as im-

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**Fig. 1.** PL spectra of the film with 0.13 at. % Er, measured at 25 and 300 K. An Er$^{3+}$ luminescence peak at 1.537 $\mu$m is observed. The inset shows the integrated Er$^{3+}$ PL intensities of films as a function of the Er content. Note that the scale of the inset is logarithmic.

**Fig. 2.** (a) The dark conductivity $\sigma$ and (b) the seebeck coefficient $s$ as a function of $(1/T)^{1/4}$ and $1/T$ temperature, respectively. The dotted lines serve as a guide to eyes.

**Fig. 3.** HWHM of the TO phonon-mode signal in Raman spectra (closed circles) and the optical bandgap (open circles) of Er-doped films as a function of the Er concentrations.
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Fig. 4. Integrated Er$^{3+}$ PL intensities of Er-doped films. The values are normalized to the value at 25 K.

Band tail states of a-Si:H, as opposed to the midgap states which are associated with point defects such as dangling bonds, are believed to be caused by such structural disorder [21]. There are also strong experimental evidences which correlate the amount of disorder in a-Si:H with the density of the band-tail states as well as the HWHM of the Raman peak [24]. Therefore, Fig. 3 indicates the Er, in addition to creating donor levels, also increases the amount of structural disorder in the a-Si:H matrix, leading to increase in the density of the band-tail states and subsequent reduction of the Tauc gap.

Such band-tail states play an important role in determining the overall Er$^{3+}$ luminescence. This is demonstrated by Fig. 4, which shows the dependence of integrated Er$^{3+}$ PL intensities on the temperature. In all cases, the Er$^{3+}$ luminescence intensity shows very little quenching as the temperature is raised from 25 to 300 K, as is expected given the wide bandgap. However, in case of 0.27 and 0.33 at. % Er concentration films, Er$^{3+}$ PL intensity increases significantly with the initial increase of the temperature before it is quenched. In case of the 0.33 at. % Er concentration film, this initial increase in the Er$^{3+}$ PL intensity is so pronounced that the Er$^{3+}$ PL intensity at 300 K is nearly the same as that at 25 K. Such initial increase of the Er$^{3+}$ PL intensities is consistent with previous results. It indicates that the band-tail states induced by increase in the structural disorder are distinct from the Er-related states that act as a gateway to carrier-mediated excitation of Er, and thus act as competing recombination sites for carriers even though ultimately, they, too, are caused by Er doping. As the temperature is increased, carriers trapped in shallow band tail states are thermalized back into the extended states, thus again becoming available to excite Er.

As it is likely that not all band tail states will be shallow enough for such thermalization to occur, and that not all carriers which have thermalized will excite Er, the fact that Er$^{3+}$ PL intensity is increased by as much as 60 % by increasing temperature indicates that the band tail states capture a significant portion of photogenerated carriers away from Er, and thus play an important role in determining the overall Er$^{3+}$ luminescence. Therefore, it seems that any model for Er$^{3+}$ luminescence in a-Si:H should take the band-tail states and the Er-related levels in the energy gap into consideration, and not focus solely on dangling bonds and midgap states as has been the case so far [7,10,25]. It is worthy to note that it is possible to dope a-Si:H with Er more heavily because of a higher solubility of a-Si:H than one of c-Si, but it does rather decrease the Er$^{3+}$ PL intensity.

In a-Si, alloying, another advantage of a-Si, is possible. This gives us the freedom of engineering the band gap. We, hereby, demonstrate such engineering the band gap of Er-doped a-Si:H from 1.85 to 2.1 eV using carbon co-doping. Carbon co-doping is performed by introducing CH$_4$ during deposition on Corning #7059F with the 300W microwave power, and the carbon concentration is controlled by adjusting the CH$_4$ flow rate from 0 to 0.75 sccm whereas the Er concentration is kept constant. Figure 5(a) shows dependences of the optical band gap and...
carbon concentration on the CH$_4$ flow rate. We observe a monotomic increase in the carbon concentration and the Tauc gap as the CH$_4$ flow rate is increased. As shown in Fig. 5(b), carbon co-doping results in dramatic increase in the Er$^{3+}$ PL intensity more than one order of magnitude, but excessive carbon again results in reduction in the Er$^{3+}$ luminescence intensity. In addition, carbon co-doping increases the band gap of Er-doped a-Si:H so that the Er$^{3+}$ de-excitation is suppresed, thereby reducing the Temperature quenching of Er$^{3+}$ PL intensity, as the inset presented in Fig. 5(b).

In conclusion, we have investigated the effect of Er doping on the electrical, optical, and structural properties of a-Si:H. We find that similar to Er in c-Si, Er in a-Si:H act as n-type dopant, and that a correlation between its electrical and optical activities are absent. In addition, Er doping also causes increase in the structural disorder in a-Si:H and subsequent increase in the density of band-tail states. We identify such band-tail states as playing an important role in determining the overall Er$^{3+}$ luminescence from Er doped a-Si:H. And We observe that carbon co-doping enhances the Er$^{3+}$ PL intensity and reduces the temperature quenching of the Er$^{3+}$ PL intensity.

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REFERENCES