Nd$^{3+}$ photoluminescence and its implication on the excitation mechanisms of Nd$^{3+}$ in Nd doped hydrogenated amorphous silicon alloyed with carbon

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Received 27 November 2002

Abstract

Nd$^{3+}$ photoluminescence from Nd doped, hydrogenated amorphous silicon alloyed with carbon (a-Si:H:C) is investigated. Nd-doped, a-Si:H:C films were deposited using electron cyclotron resonance plasma enhanced chemical vapor deposition of SiH$_4$ and CH$_4$ with concurrent sputtering of Nd. Clear Nd$^{3+}$ luminescence peaks can be observed when excited with 488 nm light, indicating that Nd$^{3+}$ ions in a-Si:H:C are excited via carriers generated in the a-Si:H:C. The energetics of Nd-doped a-Si:H:C rule out defect-related Auger excitation via mid-gap states. Based on the temperature and pump power dependence of Nd$^{3+}$ and intrinsic a-Si:H:C photoluminescence intensities, we identify excitation via Nd-related defects with a strong coupling to Nd$^{3+}$ as a possible excitation mechanism for Nd in a-Si:H:C.

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PACS: 78.66.Jg; 78.55.Ap; 78.30.Ly

1. Introduction

A great interest lies in developing a Si-based light source that could enable realization of compact, low-cost, Si-based integrated photonics as well as optical interchip connections for the next-generation Si integrated circuits. Of the many possible methods, rare earth (RE) doping of Si has attracted a particular attention [1] because of the atomic nature of RE intra-4f luminescence that results in luminescence peaks at well-defined and technologically important wavelengths that are fairly independent of the host and the temperature. Furthermore, when doped into a semiconductor, RE ions can be excited via a non-resonant, Auger-type interaction with carriers generated in the host matrix [2–5].

This increases the effective excitation cross section by several orders of magnitude [6,7], and also allows electrical excitation of RE ions.

Of the many possible Si-based materials, hydrogenated amorphous Si (a-Si:H) and a-Si:H alloyed with carbon (a-Si:H:C) possess the advantages of being mature, widely used semiconductors with the possibility of a direct deposition on other photonic materials such as glass. More importantly, there have been many reports of their promise as the host material for Er$^{3+}$ doping, with high efficiency and much less temperature quenching of RE luminescence than observed in bulk Si [8–13]. By now, light emitting diodes based on Er-doped a-Si:H have been demonstrated [14], and possibility of stimulated emission reported [15].

However, a-Si:H, in contrast to crystalline semiconductors, has localized states at band-tail and near the mid-gap states that allow for many complex carrier-RE interactions. In the case of Er$^{3+}$ doped a-Si:H, this

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has led to several different carrier-Er$^{3+}$ interactions being proposed as the dominant excitation mechanism of Er$^{3+}$ ions in a-Si:H. Fuhs et al. [16] have suggested a Defect-related Auger excitation (DRAE) in which an electron capture by a $D^0$ state Auger-excites Er$^{3+}$. On the other hand, Kühne et al. [13] based on the appearance of a spectral hole and the similarity between the temperature dependence of defect and Er$^{3+}$ luminescence intensities, have suggested a Förster mechanism based on a resonant dipole coupling. Finally, Kim et al. [17] have pointed out the overall similarity between Er-doped a-Si:H and crystalline Si, and have suggested a defect-mediated excitation mechanism similar to that in crystalline Si in which recombination of an exciton trapped at an Er-related defect state Auger-excites Er$^{3+}$. The schematic summary of these different mechanisms are given in Fig. 1.

We note, however, that because the RE elements differ only in the core-level electronic configuration, they have similar characteristics in many different host materials. In fact, many different RE/semiconductor combinations other than Er/Si have been used successfully to obtain RE luminescence. Therefore, by using an RE ion other than Er$^{3+}$, the various models put forth can be tested for their validity and universality.

In this paper, we report on the results of Nd$^{3+}$ doping of hydrogenated amorphous Si alloyed with carbon [18]. Nd$^{3+}$ was chosen because its intra-4f transitions luminescence at $\lambda \approx 0.9 \mu m$ and $\lambda \approx 1.1 \mu m$, well within the range of the intrinsic a-Si:H and a-Si:H:C luminescence. Thus, they can act as a sensitive probe of interaction between localized states and RE ions. Furthermore, these Nd$^{3+}$ luminescence peaks can be detected using Si diodes, raising the possibility of integrating light emission and detection capabilities into one single silicon-based chip. Finally, the $1.1 \mu m$ emission results from a four level energy transition, and therefore facilitates achieving population inversion. a-Si:H:C was chosen because carbon co-doping is well-known to enhance the Er$^{3+}$ luminescence in Si [19,20] without serious degradation of the electronic properties of the film [20,21]. We observe clear luminescence peaks at 0.92, 1.11, and 1.40$\mu m$ corresponding to $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$, and $^4I_{9/2} \rightarrow ^4I_{13/2}$ Nd$^{3+}$ intra-4f transitions, respectively, when excited with 488 nm light, which indicates that Nd$^{3+}$ ions in a-Si:H:C are excited via carriers generated in the a-Si:H:C. The energetics of Nd-doped a-Si:H:C rule out defect-related Auger excitation via mid-gap states. The temperature and pump power dependence of Nd$^{3+}$ and intrinsic a-Si:H:C photoluminescence intensity indicate that a resonant excitation is not likely to be dominant. Finally, we argue that a defect-mediated excitation mechanism similar to that proposed for RE-doped crystalline semiconductors can consistently explain the data.

2. Experimental conditions

Nd-doped a-Si:H:C films were deposited on glass substrates (Corning #7059) using electron cyclotron resonance plasma enhanced chemical vapor deposition of SiH$_4$ and CH$_4$ with concurrent sputtering of Nd. Details of the deposition methods are given in Ref. [11]. The system base pressure was $\sim 1 \times 10^{-6}$Torr. The deposition pressure, microwave power, and deposition temperature were $\sim 1 \times 10^{-4}$Torr, 400 W, and 250°C, respectively. The thickness and the Nd content of the film was deter-

![Fig. 1. Schematic summary of DRAE, Förster mechanism and Auger excitation involving Er-related state.](image-url)
mined by Rutherford Backscattering Spectroscopy (RBS) to be 0.56\(\mu\)m and 0.11at.\%, respectively, and the carbon and hydrogen content was determined by 4.26 MeV carbon resonance and elastic recoil detection (ERD) to be 13at.\% and \(\sim\)20at.\%, respectively (data not shown). The optical band gap was extracted from transmittance measurement using the Tauc relation [22] to be 2.0 eV. For comparison, an Er-doped a-Si:H:C film with similar Er and C content was deposited under identical conditions.

The photoluminescence (PL) spectra were measured using the 488 nm line of Ar laser with a nominal pump power of 200 mW, a grating monochromator, and employing the standard lock-in technique. A Si and InGaAs diode was used for visible and infra-red region, respectively. All PL spectra were corrected for the system response. A a closed-cycle helium cryostat was used for low-temperature measurements. The 488 nm line of Ar laser line was used to ensure that all Nd\(^{3+}\) ions excited via carriers, as this wavelength does not coincide with any of the Nd\(^{3+}\) optical absorption bands. The dark electrical conductivity measurement was done using coplanar Al electrodes, verified to be ohmic.

3. Results and discussion

Fig. 2 shows the PL spectra of intrinsic, Nd-doped, and Er-doped a-Si:H:C, taken at 20 K. We observe a strong, broad luminescence peak from the intrinsic a-Si:H:C film in the 0.6–1.1\(\mu\)m range that is typical of bandtail to bandtail transitions in a-Si:H and related films [24]. The apparent peaks near \(\sim\)0.7 and \(\sim\)0.9\(\mu\)m are optical artifacts due to multiple reflections. Upon Nd-doping, the intrinsic a-Si:H:C luminescence is quenched strongly, and three well-defined peaks appear at 0.92, 1.11, and 1.40\(\mu\)m. Similar quenching of the intrinsic a-Si:H:C luminescence is observed from the Er-doped film as well, which displays a strong luminescence peak at 1.54\(\mu\)m typical of the \(^4I_{13/2} \rightarrow ^4I_{15/2}\) intra-4f transition of Er\(^{3+}\). The inset shows the dependence of the 0.92\(\mu\)m luminescence peak intensity from the Nd-doped a-Si:H:C film upon the pump wavelength. We find that the 0.92\(\mu\)m luminescence intensity is only weakly dependent upon the pump wavelength. Similar behavior is observed from the 1.11\(\mu\)m luminescence peak as well (not shown).

The luminescence peaks at 0.92, 1.11, and 1.40\(\mu\)m coincide well with the known positions of \(^4F_{3/2} \rightarrow ^4I_{9/2}\), \(^4F_{3/2} \rightarrow ^4I_{11/2}\), and \(^4I_{11/2} \rightarrow ^4I_{13/2}\) Nd\(^{3+}\) intra-4f transitions [23]. Furthermore, the shape and the intensity of the peaks compared to the background luminescence intensity indicate clearly that these peaks are due to Nd\(^{3+}\) intra-4f transitions. Furthermore, as the inset shows, the Nd\(^{3+}\) ions are excited via carriers and not through direct optical absorption of the pump beam by the 4f electrons of Nd\(^{3+}\).

The minimum energy required to excite the \(^4F_{3/2} \rightarrow ^4I_{9/2}\) and \(^4F_{3/2} \rightarrow ^4I_{11/2}\) luminescence are 1.35 and 1.12 eV, respectively. An electron capture by a \(D^0\) state, however, is expected to release only about 1 eV, corresponding to half of the optical bandgap due to the mid-gap location of the \(D^0\) states [24]. This is confirmed by the temperature dependence of the dark electrical conductivity, as is shown in Fig. 3. We find that the activation energy for the dark electrical conductivity of the intrinsic a-Si:H:C film, expected to reflect the
energy difference between the conduction band edge and mid-gap states [24], is indeed ~1 eV. Therefore, we conclude that carrier capture by mid-gap states is unlikely to be able to excite the observed Nd$^{3+}$ luminescence. This, in turn, indicates that any mechanisms such as DRAE that specifically involve mid-gap states are unlikely to play a dominant mode in excitation of Nd$^{3+}$ in Nd-doped a-Si:H:C.

On the other hand, both the resonant dipole coupling mechanism and the defect-mediated excitation mechanisms allow interband transitions, and thus can supply enough energy to excite Nd$^{3+}$. Therefore, in order to distinguish between the two mechanisms, the pump power and the temperature dependence of the Nd$^{3+}$ luminescence intensity at 0.92$\mu$m and the intrinsic bandtail-bandtail a-Si:H:C luminescence intensity of Nd-doped a-Si:H:C at 0.92$\mu$m was investigated.

Fig. 4 shows the pump power dependence of the integrated Nd$^{3+}$ luminescence intensity at 0.92$\mu$m and the intrinsic a-Si:H:C luminescence intensity of the Nd-doped a-Si:H:C at 0.92$\mu$m, measured at 20 K. The Nd$^{3+}$ luminescence intensity was obtained by fitting a baseline between 0.86$\mu$m and 0.95$\mu$m, and subtracting the background luminescence. The background luminescence intensity was then taken to be the intrinsic a-Si:H:C luminescence intensity. The inset shows schematically the quantities being measured. We find that the Nd$^{3+}$ luminescence intensity is linearly dependent
upon the pump power up to the highest pump power used. On the other hand, the intrinsic a-Si:H:C luminescence intensity increases sub-linearly, and clearly shows the beginning of saturation at the pump power of 600 mW.  

Fig. 5 shows the temperature dependence of the integrated Nd\(^{3+}\) and intrinsic a-Si:H:C luminescence intensities at 0.92 μm, and we again find differences between them. The Nd\(^{3+}\) luminescence intensity remains nearly constant up to 130 K, and decreases tenfold as the temperature is raised to room temperature. We note, however, that the Nd\(^{3+}\) luminescence remains easily detectable even at room temperature, as is shown in the inset. On the other hand, the intrinsic a-Si:H:C luminescence intensity starts to decrease at temperatures as low as 70 K, and reaches the noise level above 200 K.  

Such discrepancies between behaviors of Nd\(^{3+}\) and intrinsic a-Si:H:C luminescence intensities are difficult to reconcile with the resonant dipole excitation model. Since it treats the intrinsic a-Si:H:C interband transitions as gateways for Nd\(^{3+}\) excitation, it predicts that the Nd\(^{3+}\) and a-Si:H:C luminescence intensities behave similarly. Indeed, a similar temperature dependence of Er\(^{3+}\) and intrinsic a-Si:H luminescence intensities was one of the evidences used to argue for the presence of such resonant dipole excitation in Ref. [13]. Furthermore, given the energetics of Nd\(^{1+}\) intra-4f transitions, a resonant dipole excitation of Nd\(^{3+}\) would have to occur while the carriers are rapidly thermalizing down the bandtail states, and therefore is unlikely to be very effective. Taken together, we believe that for Nd-doped a-Si:H:C, resonant dipole excitation mechanism does not play a significant role in exciting Nd\(^{3+}\) ions.

However, all the data presented here can be explained consistently with the defect-mediated excitation mechanism proposed for RE doped crystalline semiconductors [2–5] in which the recombination of an exciton trapped at an RE-related site Auger-excites the RE ions. In such a case, the interaction is purely electronic, and no resonance is necessary since the excess energy can be dissipated by multiphonon emission [3,25]. This explains the decrease in the overall intrinsic a-Si:H:C luminescence intensity without sharp spectral holes near the optical absorption bands of Nd\(^{3+}\). Furthermore, the coupling between such excitons and RE ions are expected to be very strong [2], with transfer rates reported to be in the \(10^9-10^{11}\) s\(^{-1}\) range [5,26,27] that are much faster than the luminescence lifetimes of intrinsic a-Si:H luminescence (typically in the microsecond range) [24]. Thus, formation of such excitons will effectively remove them from intrinsic a-Si:H:C luminescence, which explains the different pump power and temperature dependence of the Nd\(^{3+}\) and the intrinsic a-Si:H:C luminescence intensities. Finally, we note that this exciton-mediated excitation mechanism has been successful in describing a vast array of RE-doped semiconductors (Er, Nd, and Yb doped Si, GaAs, GaP, and InP) [4–6,28], and it would be reasonable to expect it to apply to RE-doped amorphous semiconductors as well.  

Finally, we note that while DRAE and resonant dipole coupling are unlikely to play a significant role in Nd\(^{3+}\) luminescence from Nd-doped a-Si:H:C, they cannot be ruled out from playing a significant role in Er\(^{3+}\) luminescence from Er-doped a-Si:H. In fact, given a different preparation conditions, they may even play the dominant role. However, the similar intensities of

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Fig. 5. Temperature dependence of Nd\(^{3+}\) and intrinsic a-Si:H:C luminescence intensities at 0.92 μm normalized to the low temperature value. Inset shows room temperature Nd\(^{3+}\) PL spectrum.
Nd\textsuperscript{3+} and Er\textsuperscript{3+} luminescence intensities in Fig. 2 indicate that the efficiency of defect-mediated excitation mechanism is comparable to other mechanisms, and suggest that the defect-mediated excitation mechanism should be included when discussing RE luminescence from RE-doped a-Si:H: and a-Si:H:C.

4. Conclusion

In conclusion, we have investigated the luminescence properties of Nd-doped hydrogenated amorphous Si alloyed with carbon. We observe clear intra-4f luminescence peaks at 0.92, 1.11 and 0.92, 1.11, and 1.40\textmu m from Nd\textsuperscript{3+} ions that are excited via carriers. Based on the energetics of Nd-doped a-Si:H:C, temperature and pump power dependence of Nd\textsuperscript{3+} and intrinsic a-Si:H:C photoluminescence intensities, we argue that a defect-mediated excitation mechanism similar to that proposed for RE-doped crystalline semiconductors is most likely to be the dominant excitation mechanism for Nd\textsuperscript{3+} in Nd-doped a-Si:H:C.

Acknowledgments

It is a pleasure to acknowledge the expert help of Dr J.H. Song with the ion-beam analysis. This work was supported in part by Advanced Photonics Project and National Research Lab project by MOST.

References