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Exponential depletion of neutral dangling bonds density (D^0) by rare-earth doping in amorphous Si films

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ABSTRACT

In this work we study the effect reduction in the density of dangling bond species D^0 states in rare-earth (RE) doped a-Si films as a function concentration for different RE-specimens. The films $a\text{-Si}_{1-x}\text{RE}_x$, $\text{RE}=\text{Y}^{3+}$, Gd^{3+} , Er^{3+} , Lu^{3+}) were prepared by co-sputtering and investigated by electron spin resonance (ESR) and Raman scattering experiments. According to our data the RE-doping reduces the ESR signal intensity of the D^0 states with an exponential dependence on the rare-concentration. Furthermore, the reduction produced by the magnetic rare-earths Gd^{3+} and Er^{3+} is remarkably greater than that caused by Y^{3+} and Lu^{3+} , which led us to suggest an exchange-like coupling between the spin of the magnetic RE^{3+} and the spin of silicon neutral dangling bonds.

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1. Introduction

The a-Si based compounds and their alloys have been of fundamental importance to develop devices for applications in photonic technology such as light sources and spectral data storage [1,2]. These compounds represent a convenient and relatively easy way to produce materials with quite different atomic composition and physical properties. RE-based materials generally have the outermost electronic configuration of the RE and these elements play a decisive role in determining their properties. The RE are known to be highly electropositive and predominantly trivalent, RE^{3+} [3–5]. Much of the current interest in studying RE-doped silicon-based compounds arises from their potential to combine some of the unique characteristics of RE^{3+} ions with the electrical properties of semiconductor hosts [6]. Therefore, we believe that a study involving the effects associated to the interactions between the REs and dangling bonds may be of interest to understand the magnetic properties of the a-Si:RE. In this work, we report experiments of electron spin resonance (ESR) and Raman scattering in amorphous silicon films doped with different RE (a-Si:RE=Y, Gd, Er, and Lu) to explore the structural and electronic RE-doping effects and their interplay with the density of neutral dangling bonds (D^0) present in the a-Si:RE films.

2. Experimental

The amorphous silicon thin films doped with different RE-concentrations were prepared in a high vacuum chamber (base pressure $\sim 2 \times 10^{-6}$ Torr) by radio frequency (13.56 MHz) sputtering using a Si (99.999% pure) target covered at random with small pieces of metallic RE (99.9% pure) elements. Polished crystalline (c-)Si wafers and high-purity quartz plates were used as substrates in every deposition run. During deposition, the substrates were kept at $\sim 70^\circ\text{C}$ under a constant total pressure of $\sim 5 \times 10^{-3}$ Torr of high-purity Ar. For the whole series of films, the nominal RE concentration was estimated by the relative RE-to-Si target area ($A_{\text{RE}}/A_{\text{Si}}$). It is known that Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) are not appropriated for low RE concentration determinations. The ESR experiments were carried out at room- T in a Bruker X-band (9.495 GHz) spectrometer using a room- T TE₁₀₂ cavity. The density of the dangling bonds species D^0 was determined from the ESR intensity as compared to a strong KCl-pitch standard sample. Room- T Raman scattering measurements, using the 488.0 nm line of an Ar^{3+} laser, were also performed and confirmed the amorphous structure of all studied a-Si:RE films.

3. Results and discussion

It has already shown in the literature that for the Gd and Er-doped a-Si:RE films the magnetic susceptibility, $\chi(T)$, follows a Curie–Weiss law at low- T and that from the Curie constant most of the RE species are incorporated into the a-Si:RE films in the RE^{3+} form [7].

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The fitting of the $\chi(T)$ data to a Curie–Weiss law showed that the obtained paramagnetic temperature, θ_p , for the Gd-doped a-Si films is negative, indicating the existence of an antiferromagnetic (AFM) exchange-like interaction between the spins of the Gd^{3+} ions [8].

Fig. 1 presents the room- T Raman scattering spectra for a-Si:RE films doped with (a) $\text{RE}=\text{Y}^{3+}$ and (b) $\text{RE}=\text{Gd}^{3+}$. These data are representative of the behavior found for all RE-doping samples. The Raman spectra in Fig. 1 show a weak and broad peak at $\sim 480\text{ cm}^{-1}$ which corresponds to the transverse-optical like (TO-like) mode of a highly distorted a-Si network [7,9]. This result confirms the amorphous structure of the films for all RE-doping in the studied concentration range.

The room- T D^0 X-Band ESR signal of a-Si and a-Si:RE films doped with magnetic (Gd^{3+} and Er^{3+}) and non-magnetic (Y^{3+} and Lu^{3+}) RE elements are shown in Fig. 2. These films presented the RE concentration of $\sim 0.2\text{ at\%}$. The ESR signal of a quartz substrate is shown for comparison. All samples present a single $g \sim 2$ Lorentzian ESR lines characteristic of the D^0 neutral dangling bonds [7]. According to these data the RE-doping reduces the ESR signal intensity of the D^0 states and the reduction produced by the magnetic rare-earths Gd^{3+} and Er^{3+} is remarkably greater than that caused by Y^{3+} and Lu^{3+} . This is in fact an unexpected result since the doping of a-semiconductors is well known to increase the density of defects and these effects are not obviously dependent on the spin of the dopant [10]. Table 1 summarizes the experimental parameters obtained for representative samples of Fig. 3.

In order to further investigate this effect we study the reduction in the density of D^0 states in our a-Si films as a function

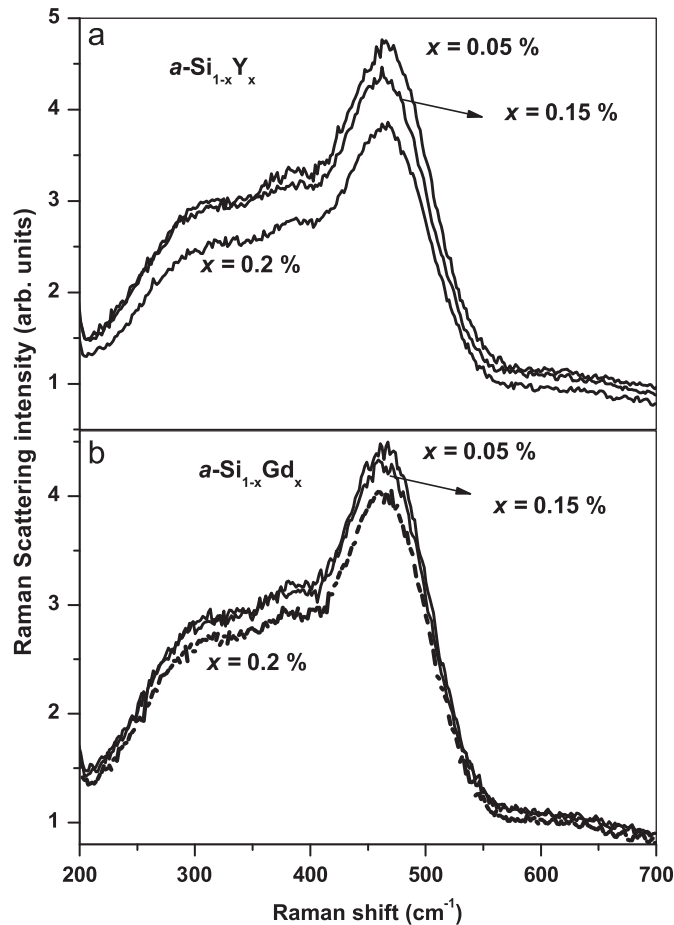


Fig. 1. Room- T Raman scattering spectra for a-Si:RE films doped with (a) $\text{RE}=\text{Y}^{3+}$ and (b) $\text{RE}=\text{Gd}^{3+}$. The weak and broad peak at 480 cm^{-1} is characteristic of highly distorted a-Si networks [7,9].

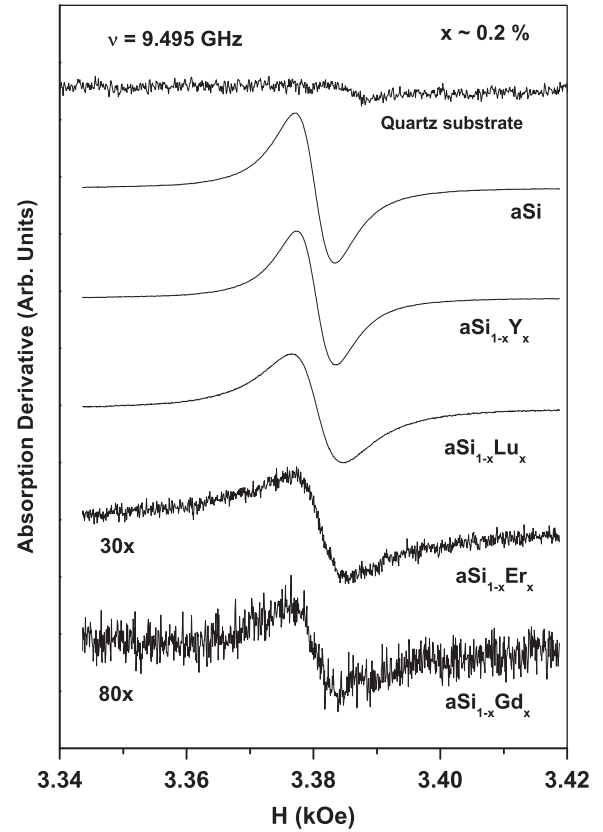


Fig. 2. X-Band ($\nu = 9.495\text{ GHz}$) ESR spectra at 300 K of a-Si films doped with different REs. The spectra of a quartz substrate are also included for comparison.

Table 1

Experimental parameters for representative a-Si:RE films.

Film	RE area (mm ²)	RE concentration (at%)	ΔH_{pp} (Oe)	g	D^0 density (cm ⁻²)
aSi	0	0	7(1)	2.002(2)	$5.2(2) \times 10^{15}$
aSi:Gd	7	0.05(5)	8(1)	2.002(2)	$1.6(2) \times 10^{14}$
aSi:Gd	19	0.2(1)	7(1)	2.002(2)	$4.6(2) \times 10^{13}$
aSi:Er	6	0.05(5)	10(1)	2.004(3)	$1.7(2) \times 10^{15}$
aSi:Er	25	0.2(1)	8(1)	2.004(2)	$2.0(2) \times 10^{14}$
aSi:Lu	5.5	0.05(5)	7(1)	2.004(2)	$5.0(2) \times 10^{15}$
aSi:Lu	84	1.0(3)	9(1)	2.004(3)	$1.8(2) \times 10^{15}$
aSi:Y	5	0.05(5)	7(1)	2.004(2)	$4.8(2) \times 10^{15}$
aSi:Y	97	1.0(3)	6(1)	2.004(2)	$3.8(2) \times 10^{15}$

concentration for different RE species. The number of D^0 states for a given film was determined from the ESR intensity calculated from the double integral of the spectra of Fig. 2 and compared to a strong KCl-pitch standard with a known number of spins. Then the density of the D^0 states were obtained dividing the number of D^0 states by the area of the film.

The room- T density of D^0 states for all the RE-doped a-Si films studied in this work, normalized by its value for pure a-Si ($\text{D}^0_{\text{a-Si}} = 5.2(2) \times 10^5\text{ spin/cm}^2$), are displayed in Fig. 3. Strikingly, according to Fig. 3, we observe that the depletion of D^0 states with RE-doping present an exponential decay as a function of RE concentration. The solid lines are the best fits to the data using the expression $\text{D}^0/\text{D}^0_{\text{a-Si}} = \exp(-x/x_c)$. These fits yield $x_c = 0.014(5)\%$, $x_c = 0.04(1)\%$, $x_c = 0.77(1)\%$ and $x_c = 3.3(1)\%$ for $\text{RE}=\text{Gd}^{3+}$, Er^{3+} , Lu^{3+} and Y^{3+} , respectively.

Interestingly, the data of Fig. 3 reveal some trends regarding the ionic size, difference in ionic charge and spin of the dopant

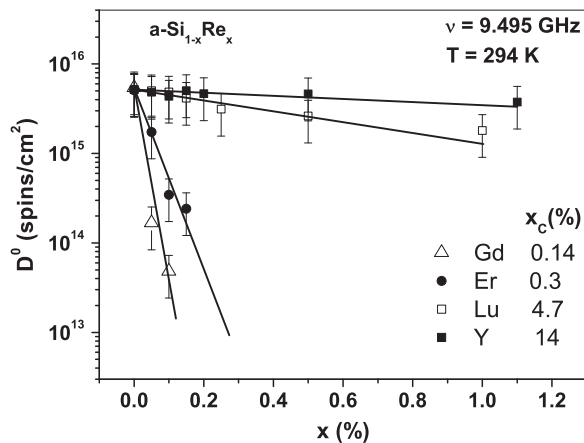


Fig. 3. The room-T density of D^0 states for RE-doped a-Si films. The solid lines are the best linear fits to the data. These linear fits extrapolates to $x_c=0.14(1)\%$, $x_c=0.3(1)\%$, $x_c=4.7(1)\%$ and $x_c=14(1)\%$ for RE= Gd^{3+} , Er^{3+} , Lu^{3+} and Y^{3+} , respectively.

can be deduced from the data in Fig. 3. For instance, comparing the D^0 depletion for the non-magnetic dopants (Y^{3+} and Lu^{3+}), Lu^{3+} doping causes a faster reduction of the D^0 than the Y^{3+} -doping. Y^{3+} has an ionic size closer to the size of Si^0 and therefore these results indicate that the D^0 depletion is partly caused by the local changes induced by size and/or coordination of the RE ions [11]. More importantly, the D^0 depletion is significantly faster for the magnetic REs (Gd^{3+} and Er^{3+}) than for the non-magnetic ones (Y^{3+} and Lu^{3+}).

These results suggest that this “extra” magnetic-depletion efficiency is related to the spin part of the total angular momentum J of the REs and that a Heisenberg exchange-like coupling, $H \sim -J_{RE-DB}S_{RE}S_{DB}$, between the RE^{3+} spin, S_{RE} , and the spin of the D^0 states, S_{DB} , may be the responsible mechanism. This type of coupling is usually governed by the *de Gennes* factor $[(g_J-1)^2J(J+1)]$ in the case that there is no quenching of the RE orbital angular momentum and by the spin factor $S(S+1)$ in the case of quenching of the RE angular momentum. Notice that the *de Gennes* and spin factors assume their highest value at the Gd^{3+} ion ($J=S=7/2$) [7]. The importance of these factors have been already recognized in RE-doped superconductor compounds through the suppression of T_c due to the Cooper-pairs breaking caused by the RE-conduction electron spin exchange interaction

(Abrikosov–Gorkov mechanism) [12,13]. We argue that an exchange coupling, leading to an overlapping of the $4f$ RE^{3+} and D^0 wave functions, may shift and broaden the D^0 ESR line beyond our signal detection limits. These results are also consistent with our recent report on the depletion of neutral dangling bonds, D^0 , by RE doping in a-SiN films [7].

4. Conclusion

We have performed ESR and *Raman* scattering experiments on RE-doped amorphous silicon films grown by co-sputtering. It was found that the RE-ions are incorporated in the a-Si host, predominantly, in the trivalent form and that the a-Si films exhibit D^0 spin densities of $\sim 10^{15}/cm^2$ which are strongly reduced by the RE-doping. The magnetic Gd^{3+} and Er^{3+} ions present a stronger density depletion of D^0 states, which led us to suggest an exchange-like coupling between the spin of the magnetic RE^{3+} and the spin of silicon neutral dangling bonds. Finally, we established that the depletion of D^0 states with RE-doping present an *exponential* decay as a function of RE-concentration. These results suggested the formation of an extremely stable RE-silicon-like complex with a spin-dependent character.

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