Magnetic properties of \textit{a}-Si films doped with rare-earth elements

M. S. Sercheli and C. Rettori

\textit{Instituto de Física “Gleb Wataghin”, UNICAMP, 13083-970, Campinas-SP, Brazil}

A. R. Zanatta

\textit{Instituto de Física de São Carlos, USP, 13560-250, São Carlos-SP, Brazil}

Abstract

Amorphous silicon films doped with Y, La, Gd, Er, and Lu rare-earth elements (\textit{a-Si:RE}) have been prepared by co-sputtering and studied by means of electron spin resonance (ESR), \textit{dc}-magnetization, ion beam analysis, optical transmission, and \textit{Raman} spectroscopy. For comparison the magnetic properties of laser-crystallized and hydrogenated \textit{a-Si:RE} films were also studied. It was found that the rare-earth species are incorporated in the \textit{a-Si:RE} films in the RE$^{3+}$ form and that the RE-doping depletes the neutral dangling bonds (\textit{D}$^{0}$) density. The reduction of \textit{D}$^{0}$ density is significantly larger for the magnetic REs (Gd$^{3+}$ and Er$^{3+}$) than for the non-magnetic ones (Y$^{3+}$, La$^{3+}$, Lu$^{3+}$). These results are interpreted in terms of a strong exchange-like interaction, $J_{RE-DBS_{RE}\Sigma_{DB}}$, between the spin of the magnetic REs and that of the \textit{D}$^{0}$. All our Gd-doped Si films showed basically the same broad ESR Gd$^{3+}$ resonance ($\Delta H_{pp} \approx 850$ Oe) at $g \approx 2.01$, suggesting the formation of a rather stable RE-Si complex in these films.

75.70.-i, 76.30.Kg, 78.66.Jg
I. INTRODUCTION

The outermost electronic configuration of the rare-earth (RE) elements plays a decisive role in determining their properties. These elements are known to be highly electropositive and to exist, predominantly, in the trivalent RE$^{3+}$ form. Moreover, RE$^{3+}$ ions have inner $4f^n$ electrons that are efficiently shielded by the outermost, and completely filled, 5$s^2$ and 5$p^6$ shells. As a consequence, electronic transitions involving the $4f$ orbital usually give rise to narrow and well defined signals that are not, or only weakly, influenced by the local RE$^{3+}$ environment. Anticipating the advantages of these attributes, 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.

Presently, and despite the great advances achieved in the field of RE-doped semiconductor compounds, the topic is still open with lots of challenging questions. Specifically related to the magnetic properties of these compounds, studies on Er-implanted crystalline silicon have concluded that the ESR signal associated with the Er$^{3+}$ ions is absent in samples with no oxygen, which is believed to stabilize sites for the ions. Also, the co-doping with oxygen (or other light impurities) considerably improves the Er-related luminescence signal. Similar research have been conducted on Er-doped hydrogenated amorphous Si-O films and indicated that the photoluminescence intensity depends on the density of neutral Si dangling bonds (D$^0$).

Based on the above scenario, this work presents a systematic study on the magnetic properties of amorphous silicon ($a$-Si) films doped with different RE (Y, La, Gd, Er, and Lu) elements. The samples were prepared by the co-sputtering technique because of its versatility in producing films with quite different, and controllable, atomic compositions. For comparison hydrogenated $a$-Si films doped with RE were also analyzed. Complementary spectroscopic techniques and laser-induced crystallized films were also used in order to achieve further insight.
II. EXPERIMENTAL

This work summarizes and presents part of the data taken from more than 60 films. All films were prepared in a high vacuum chamber (base pressure $\sim 2 \times 10^{-6}$ Torr), by radio frequency (13.56 MHz) sputtering a Si (99.999 %) target covered at random with small pieces of metallic RE (99.9 %) 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 $\sim 70$ °C under a constant total pressure of $\sim 5 \times 10^{-3}$ Torr consisting of high-purity gases (Ar or a mixture of Ar + H$_2$, for the hydrogenated films). For the whole series of films the RE concentration was determined by the relative RE-to-Si target area ($A_{RE}/A_{Si}$). Non-hydrogenated a-Si and hydrogenated a-Si (a-Si:H) films were also deposited for comparison purposes. Laser-induced crystallization treatments, at room atmosphere, were done on some of the RE-doped a-Si and a-Si:H films deposited on quartz substrates. For this treatment, cylindrical lenses and the 532.0 nm line of a Nd-YAG laser (pulse duration of 10 ns, and repetition of 5 Hz) were employed rendering a laser fluence of $\sim 500$ mJ cm$^{-2}$. [8]

The atomic composition of the films were determined mostly from Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA). The optical band gap of the films were investigated through optical transmission in the visible-ultraviolet range in a commercial spectrophotometer. Raman scattering measurements, at room-T and with the 514.5 nm line of an Ar$^+$ laser, were also performed to analyze the atomic structure of the RE-doped a-Si(:H) films.

The electron spin resonance (ESR) experiments were carried out in the 300 – 4 K T-range in a Bruker X-band (9.47 GHz) spectrometer using a room-T TE$_{102}$ cavity. The dc-magnetization measurements were accomplished in the 300 – 2 K T-range using a Quantum Design SQUID magnetometer (RSO mode, 1 T). In addition to the RBS data, the concentration of the magnetic RE species was also determined from the ESR and dc-susceptibility data, $\chi(T)$. In the former, [RE] has been obtained after compari-
son with a Gd$_{1.45}$Ce$_{0.55}$RuSr$_2$Cu$_2$O$_{10+\delta}$ and a strong KCl-pitch standard samples and in
the latter, following a fitting of the low-$T$ dc-susceptibility data to a *Curie-Weiss* law,
$\chi(T) = n g^2 \mu_B^2 J(J+1)/3k(T-\theta_p)$, after subtraction the diamagnetism of a similar undoped
thin film/substrate system.

**III. RESULTS AND DISCUSSION**

Table I displays $P(H_2)$, $A_{RE}/A_{Si}$, and the atomic concentration $[RE]$ (as determined
from RBS, NRA, ESR, and $\chi(T)$ data) of some of the films investigated in this work. For
simplicity laser-crystallized silicon (lc-Si) films are not included in this Table. Notice that
in spite of the quite different methods employed to determine $[RE]$ we always found $[RE]$
$\approx A_{RE}/A_{Si}$. Nevertheless, considerable deviations occur for films deposited in a Ar + H$_2$
atmosphere. This is an expected result since we have adopted a constant total pressure
of $\sim 5 \times 10^{-3}$ Torr in all deposition runs. Thus, taking into account the different sputter
yield due to H$_n^+$ and Ar$^+$ ions, the concentration of REs in the hydrogenated films is
expected to decrease as $P(H_2)$ increases. Table I shows that, within the experimental error,
the magnetic RE contents estimated from ESR and $\chi(T)$ measurements agree with those
obtained from RBS, indicating that most of the RE species are indeed incorporated into
the a-Si(:H) films in the RE$^{3+}$ form. For the Gd$^{3+}$ and Er$^{3+}$-doped a-Si(:H) films the $\chi(T)$
data follow a *Curie – Weiss* law at low-$T$ (not shown). The fitting of the $\chi(T)$ data to a
*Curie – Weiss* law shows that the obtained paramagnetic temperature, $\theta_p$, of the Gd-doped
a-Si(:H) films is negative and larger for films of higher Gd concentration, indicating the
existence of an AFM exchange-like interaction between the Gd$^{3+}$ spins (see Table I). The same behaviour was observed in the Gd$^{3+}$-doped lc-Si films and, also, $\theta_p$ was larger for
the lc-Si than for the corresponding pure a-Si film (not shown).

Figure 1 shows $\chi(T)$ for the undoped films studied in this work. According to these data
both the a-Si and the lc-Si exhibit a low-$T$ paramagnetic behaviour, while the a-Si:H film is
diamagnetic. This is understood based on the nature of the defects present in these films:
i) non-hydrogenated \( a\)-Si and \( lc\)-Si films are known to have, respectively \( \sim10^{20} \) and \( \sim10^{18} \) spins/cm\(^3\), a relatively high density of paramagnetic centers due to singly occupied dangling bond states, \( D^0 \), and ii) hydrogenated \( a\)-Si films, on the contrary, exhibit a high density of diamagnetic dangling bonds (either \( D^+ \) or \( D^- \) states). This interpretation is consistent with the transport properties of the \( a\)-Si and \( a\)-Si:H films. The difference in the density of paramagnetic states is evident in the inset of Fig. 1 that shows the ESR signal of the films being considered. The ESR signal of a quartz substrate is also shown for comparison.

The ESR line width of the \( D^0 \) signal (\( \Delta H_{pp} \)) in the \( a\)-Si and \( lc\)-Si films was measured as a function of \( T \) and the results are displayed in Figure 2. As compared to the \( lc\)-Si films, \( \Delta H_{pp} \) in the \( a\)-Si film presents larger residual width and larger thermal broadening. The larger residual width may be due to an inhomogeneous broadening and the larger thermal broadening to a stronger spin-lattice coupling (shorter spin-lattice relaxation time, \( T_1 \)), and both caused by the larger disorder in the \( a\)-Si films. At the lowest temperature, a small but detectable line broadening is observed in the \( lc\)-Si film which is probably associated with short-range magnetic correlations. The intensity of these signals increases at low-\( T \) and follows approximately a \( T^{-1} \) behaviour which is the typical behaviour of localized spins (see inset of Figure 2). Within the accuracy of our measurements, the \( g \)-values are \( T \)-independent.

Figure 3 shows the \( D^0 \) ESR signal of non-hydrogenated \( a\)-Si films doped with magnetic (\( \text{Gd}^{3+} \) and \( \text{Er}^{3+} \)) and non-magnetic (\( \text{Y}^{3+} \), \( \text{La}^{3+} \), and \( \text{Lu}^{3+} \)) RE elements ([RE] \( \sim \) 2.5 at.%). The ESR signal of a quartz substrate, \( a\)-Si, \( lc\)-Si, and \( a\)-Si:H films are also shown for comparison. According to these data RE-doping reduces the ESR signal intensity of \( D^0 \) states and the reduction produced by \( \text{Gd}^{3+} \) and \( \text{Er}^{3+} \) is remarkably greater than that caused by \( \text{Y}^{3+} \), \( \text{La}^{3+} \), and \( \text{Lu}^{3+} \).

At this point, we shall compare the density reduction of \( D^0 \) states in our \( a\)-Si films due to the different REs. The density of \( D^0 \) states and the \( g \)-value of all the RE-doped \( a\)-Si and \( lc\)-Si films considered in this work are shown in Figure 4. For the present discussion it is important to mention that [RE] \( \sim \) 2.5 at.%, the laser-crystallization treatment, and P[H\(_2\)]
were all similar. Strikingly, and according to Figure 4(a) we observe: i) a depletion of D₀ states with RE-doping. This is an unexpected result since the doping of a-semiconductors is well known to increase the density of defects, [13] and ii) among all studied RE ions, Gd³⁺ and Er³⁺ are the most efficient ones to deplete the density of D₀ states. These results suggest that this phenomenon is partly caused by the size and/or coordination of the RE ions, as exemplified by the density drop of D₀ states by the non-magnetic Y³⁺, La³⁺, and Lu³⁺ ions (see Figure 3). It is interesting to observe that, as far as the suppression of the D₀ states is concerned, the doping with non-magnetic RE ions induces almost the same effect than the laser-crystallization of the a-Si films (see Figure 3). Moreover, the depletion effect is even more pronounced for the magnetic RE ions, Gd³⁺ and Er³⁺, being stronger for Gd³⁺. These results suggest that this ”extra” depletion efficiency should be related to the spin of the magnetic REs and that an exchange-like coupling, \( J_{RE-DBS_{RE}S_{DB}} \), between the RE³⁺ spin, \( S_{RE} \), and the spin of the D₀ states, \( S_{DB} \), may be the responsible mechanism. We argue that such a coupling may shift and broaden the D₀ ESR line beyond our signal detection limits. This coupling is usually governed by the de Gennes factor \( [(gJ - 1)^2J(J + 1)] \) or by the spin factor \( S(S + 1) \). The importance of these factors have been already advised in RE-doped superconductor compounds through the suppression of \( T_c \) caused by the magnetic RE ions. [14] [15] Notice that the de Gennes and spin factors assume their highest value at the Gd³⁺ ion \( (J = S = 7/2) \), which is in agreement with the results of Figure 4(a). These results are also consistent with our recent report on the depletion of neutral dangling bonds, D₀, by RE doping in a-SiN films. [12]

The analysis of the \( g \)-values displayed in Figure 4(b) leads to interesting conclusions. The \( g \)-values of the a-SiRE films are \( \sim 2.0048 \) and those for the lc-SiRE films \( \sim 2.0031 \), which are close to the \( g \)-value of singly charged Si neutral dangling bonds, \( \sim 2.0055 \) (D₀ states). [11] However, the a-SiEr and lc-SiEr films present \( g \)-values of \( \sim 2.0030 \) and \( \sim 2.0005 \), respectively, which are significantly smaller than those of the corresponding series. These small \( g \)-values seem to be intrinsically associated with the Er-doping process itself and suggests that n-type films \( (g \rightarrow 1.998) \) [16] are obtained as a result of the insertion of
Er$^{3+}$ ions. This is in agreement with the results achieved by other authors.\textsuperscript{[3] [4] [16]} The exceptional ability of Er$^{3+}$ to produce $n$-type films may suggest that the Er$^{3+}$ ground state multiplet ($J = 15/2$) lies close to the film’s conduction band. The same trend was also observed for the series of $a$-SiRE:H films (not shown). However, due to the weak D$^0$ ESR signal presented by these films (see Figure 3) it was not possible to accurately determine the $g$-values in these films.

Figure 5 shows a series of $a$-Si films doped with Gd in the $\sim 0 - 7$ at.$\%$ range, as determined from RBS (see Table I). This series was exhaustively studied and for $[\text{Gd}] \gtrsim 0.5$ at.$\%$ the spectra show a broad ($\Delta H_{pp} \approx 850$ Oe) and single resonance ($g \approx 2.01$) associated to a powder-like spectrum of Gd$^{3+}$. Again, the strong reduction effect that the Gd$^{3+}$ ions exert on the D$^0$ ESR intensity can be appreciated in Figure 5. Table I presents the data for a serie of $a$-SiGd:H films where it is observed that the Gd incorporated in the films decreases as $[\text{H}]$ increases. Surprisingly, the $g$-value and line width, $\Delta H_{pp}$, were independent of the Gd$^{3+}$ concentration, chemical environment (amorphous or laser-crystallized), H content, and temperature for $T \gtrsim 30$ K. Hence, these results demonstrate unambiguously that the Gd$^{3+}$ ions form a very stable complex with Si. Films of relatively higher Gd concentrations ($\gtrsim 4$ at.$\%$) present a line broadening for $T \lesssim 30$ K, indicating the existence of Gd$^{3+}$- Gd$^{3+}$ magnetic correlations, in agreement with the large $|\theta_p|$ measured for these films (see Table I). However, in contrast to the work of Hellman \textit{et al.}\textsuperscript{[4]}, low field $0.1 \leq H \leq 0.5$ kOe zero field and field cooled susceptibility measurements in these films did not show any measurable spin glass-like behaviour down to $T \approx 2$ K.

As stated above, hydrogen atoms in $a$-Si are known to considerably reduce the density of D$^0$ states as a result of the passivation of Si dangling bonds.\textsuperscript{[13]} Actually, most of the devices based on $a$-semiconductors correspond to hydrogenated compounds.\textsuperscript{[13]} In addition to the passivation of dangling bonds, the insertion of hydrogen in $a$-Si materials promotes the widening of the optical band gap as a consequence of the recession of the top of the valence band due to the replacement of Si-Si by Si-H bonds. Therefore, the study of the combined effects due to the insertion of RE ions and hydrogen atoms in the $a$-Si host is.
of outmost importance to our discussion. With this purpose we have investigated a series of Gd-doped a-Si:H films. Figure 6 shows the transmission spectra of some Gd-doped a-Si films deposited with increasing hydrogen partial pressures (Table I). According to this figure, films deposited at higher \( P(H_2) \) exhibit a transmission cutoff at higher energies, an indication that the optical band gap is indeed being increased. That is shown in the inset of Figure 6 where the \( E_{04} \) optical band gap (energy corresponding to an absorption coefficient of \( 10^4 \text{ cm}^{-1} \)) is represented as a function of the hydrogen content. The \( E_{04} \) optical band gap of other films investigated in the present study are also displayed for comparison. Usually, films deposited with no hydrogen, and after laser-crystallization, present an \( E_{04} \) optical band gap lower than \( \sim 1.5 \text{ eV} \). Increasing contents of hydrogen widen the optical band gap of these films which is proportional to [H]. The doping of a-Si(:H) films with REs has the opposite effect with \( E_{04} \) values ranging from \( \sim 1.1 \) to 0.7 eV, depending on the [RE]. Laser-crystallization experiments also reduce the optical band gap of the RE-doped a-Si:H films essentially because of the removal of Si-H bonds. [8]

In addition to hydrogenation, different atomic environments may affect the magnetic properties of the RE-doped a-Si films. Thus, it is important to characterize the atomic structure of these films. By means of Raman scattering we have studied the laser-induced crystallized films and the main results are displayed in Figure 7. For simplicity, just the spectra of c-Si and hydrogenated (and Gd-doped) a(lc)-Si films are presented. This figure shows that the spectrum of a-Si:H consists of a weak and broad Raman signal at \( \sim 480 \text{ cm}^{-1} \) that corresponds to the transverse-optical TO-like mode of a highly distorted a-Si network. [7] Moreover, non-hydrogenated a-Si (either RE-doped or not) films exhibit (not shown) an extremely faint and almost featureless signal characteristic of amorphous quasi-metallic compounds. The laser-crystallization processing of the a-SiGd(:H) films gives rise to a relatively strong scattering contribution at \( \sim 515 \text{ cm}^{-1} \) indicating the presence of ordered Si-Si bonds. Based on the position, and line width, of this Raman scattering signal it was possible to infer the size of these so-called crystallites (or crystalline grains) which are \( \sim 50 \text{ Å} \) large. [8] Notice that, despite the appearance of these crystallites, the films still present some
amorphous contribution at 480 cm$^{-1}$ indicating that they were not completely crystallized. The crystallized material was estimated \cite{19} from the ratio between the areas under the Raman peaks due to crystallites and the amorphous tissue, $\rho_c/\rho_a$. The inset of Figure 7 shows $\rho_c/\rho_a$ for various of our studied films. Interestingly, the crystalline fraction $\rho_c/\rho_a$ in the laser-crystallized films depends strongly on the presence of RE species. According to Figure 7, the $lc$-SiGd:H films exhibit an amorphous contribution substantially smaller than the $lc$-Si:H films, suggesting that the RE species may act as crystallization seeds in the a-Si:H network in a similar manner to that verified in other metal-containing a-Si:H films. \cite{20,21} However, the crystallization fraction seems to be weakly dependent on the RE and [RE] (see inset of Figure 7). This result is in agreement with the trends discussed above where the presence of REs diminish the density of D$^0$ states in the films.

Finally, it is opportune to notice that in spite of the great influence exerted by hydrogenation, RE-doping, and laser-crystallization treatment on the optical and structural properties of the studied a-Si films, their magnetic characteristics seem to remain unchanged. One possible reason for such a behaviour could rely on the formation of very stable RE-Si complexes which are almost insensitive to the local environment. This phenomenon is not completely clear at present and more investigations are under way. Because the [O] in our films were found to be smaller than 0.5 at.% (RBS), the formation of any stable RE-Si-O complexes seems to be unlikely.

**IV. CONCLUDING REMARKS**

Rare-earth doped amorphous silicon films were prepared by co-sputtering and investigated by different magnetic and spectroscopic techniques (ESR, dc-susceptibility, ion beam analyses, optical transmission, and Raman scattering). Hydrogenated and laser-crystallized films were also considered in the present study. The main experimental results are: i) RE ions are incorporated in the a-Si(:H) host, predominantly, in the trivalent form,\ ii) a-Si and lc-Si films exhibit D$^0$ spin densities of $\sim 10^{20}$ cm$^{-3}$ and $\sim 10^{18}$ cm$^{-3}$, respectively, which
are strongly reduced by the RE-doping. The magnetic Gd$^{3+}$ and Er$^{3+}$ ions present an even stronger density depletion of D$^0$ states, which led us to suggest an exchange-like coupling between the spin of the magnetic REs$^{3+}$ and the spin of silicon neutral dangling bonds. We should mention that the same behavior has been consistently observed in a series of a-SiN alloys doped with Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, and Lu, giving further support to the assumption of the existence of an exchange-like coupling mechanism, $^{[12]}$ $^{[iii]}$

The Gd$^{3+}$ ESR line shape, line width, and $g$-value does not change with [Gd] or [H], $T$, nor with the local environment (if amorphous or partially crystallized). These results suggested the formation of an extremely stable Gd-silicon-like complex. At the moment more research is under way to elucidate this point, and $^{[iv]}$ The reduction of the D$^0$ $g$-value in both, $a$-SiEr and $lc$-SiEr films, indicates that the Er-doping is more efficient in producing $n$-type films.

V. ACKNOWLEDGMENTS

The authors are indebted to Professor F.C. Marques (UNICAMP) for critical reading of the manuscript. Professor F.L. Freire Jr. (PUC- RJ) and Professor F. Ikawa (UNICAMP) are also acknowledge for the ion beam analyses and for the access to the Raman facilities, respectively. This work has been supported by FAPESP, CAPES, CNPq, NSF, and DMR.
REFERENCES

[1] F.A. Cotton, G. Wilkinson, and P.L. Gaus, in Basic Inorganic Chemistry (John Wiley & Sons, NY, 1987).

[2] For a review on the subject see, for instance, A. Polman, J. Appl. Phys. 82, 1 (1997).

[3] J.H. Castilho, F.C. Marques, G.E. Barberis, C. Rettori, F. Alvarez, and I. Chambouleyron, Phys. Rev. B 39, 2860 (1989).

[4] F. Hellman, D.R. Queen, R.M. Potok, and B.L. Zink, Phys. Rev. Lett. 84, 5411 (2000).

[5] J.D. Carey, J.F. Donegan, R.C. Barklie, F. Priolo, G. Franzo, and S. Coffa, Appl. Phys. Lett. 69, 3854 (1996).

[6] F. Priolo, G. Franzo, S. Coffa, A. Polman, S. Libertino, R. Barklie, and D. Carey, J. Appl. Phys. 78, 3874 (1995).

[7] E.A. Konstantinova, B.V. Kamenev, P.K. Kashkarov, V.Y. Timoshenko, and E.I. Terukov, J. Non-Cryst. Sol. 282, 321 (2001).

[8] M. Bell, L. Nunes, and A.R. Zanatta, J. Appl. Phys. 86, 701 (1999).

[9] See, for example, B. Chapman, in Glow discharge processes, sputtering and plasma etching (John Wiley, NY, 1980).

[10] P.C. Taylor, in Semiconductors and Semimetals, Edited by J.I. Pankove (Academic Press, NY, 1984), Vol. 21C, p. 99.

[11] R.A. Street and D.K. Bielgensen, in The Physics of Hydrogenated Amorphous Silicon II- Topics in Applied Physics, Edited by J.D. Joannopoulos and G. Lucovsky (Springer-Verlag, Berlin, 1984), Vol. 50, p. 195.

[12] M. S. Sercheli, A. R. Zanatta and C. Rettori, Neutral-dangling bond depletion in a-SiN Films caused by magnetic rare-earth elements (submitted to PRB Rapid Communication).
[13] R.A. Street, in Hydrogenated Amorphous Silicon (Cambridge University Press, Cambridge 1991).

[14] M.B. Maple, PhD Thesis (University of California, San Diego, 1969).

[15] K. Gschneider, in Handbook on the Physics and Chemistry of Rare-Earths (Oxford Press, Amsterdam, 1978).

[16] F. Finger, J. Muller, C. Malten, R. Carius, and H. Wagner, J. Non-Cryst. Sol. 266-269, 511 (2000).

[17] J.S. Lannin, in Semiconductors and Semimetals, Ed. J.I. Pankove (Academic, NY, 1984), Vol. 21B, pp. 159-195.

[18] Z. Iqbal and S. Veprek, J. Phys. C: Solid State Phys. 15, 377 (1982).

[19] See, for example, T. Okada, T. Iwaki, H. Kasahara, and K. Yamamoto, Jpn. J. Appl. Phys. 24, 161 (1985).

[20] O. Nast and S.R. Wenham, J. Appl. Phys. 88, 124 (2000), and references there in.

[21] I. Chambouleyron, F. Fajardo, and A.R. Zanatta, Appl. Phys. Lett. 79, 3233 (2001).
FIGURES

FIG. 1. $T$-dependence of the $dc$-susceptibility, $\chi(T)$, for the $a$-Si, $lc$-Si, and $a$-Si:H films. The inset shows the $D^0$ ESR signal at 300 K and 9.47 GHz for the same films.

FIG. 2. $T$-dependence of the $D^0$ ESR line width, $\Delta H_{pp}(T)$, for the $a$-Si and $lc$-Si films. The inset shows the $T$-dependence of the $D^0$ ESR intensity for the same films. The lines are guide to the eye.

FIG. 3. $D^0$ ESR spectra at 300 K of $a$-Si films doped with different REs. The spectra of a $lc$-Si, an $a$-Si:H film and a quartz substrate are also included for comparison.

FIG. 4. Density of $D^0$ states (a) and $g$-value (b) of $a$-Si and $lc$-Si films doped with Y, La, Gd, Er, and Lu. The error bars take into account experimental uncertainties and films with different contents of RE. The lines are guides to the eye.

FIG. 5. ESR spectra of Gd$^{3+}$ in $a$-Si films doped with different concentrations of Gd. The ESR signal from the quartz substrate is also displayed.

FIG. 6. Transmission spectra, as a function of the photon energy, of some Gd-doped $a$-Si:H films deposited under increasing partial pressures of hydrogen. The fringe pattern in the spectra refer to interference effects between the film and the quartz substrate. The inset shows the $E_{04}$ optical band gap as a function of the hydrogen content for some of the films studied in this work. The $E_{04}$ and $[H]$ values typically found for $a$-SiRE and $lc$-SiRE:H films are also represented for comparison.

FIG. 7. Room-temperature Raman scattering spectra for few of our $a$-Si:H films. All curves have been normalized, and the spectra of a non-intentionally doped $a$-Si:H film and of a Si $<111>$wafer are also displayed for comparison. Notice the effect due to the laser-crystallization processing on the Raman spectrum of the $lc$-Si:H and $lc$-SiGd:H films. The scattering signals at $\sim 480$ and $520 \text{ cm}^{-1}$ are due to distorted Si-Si bonds and to the TO mode of Si crystals. The inset shows the crystalline fraction $\rho_c/\rho_a$ in some RE-doped $lc$-Si(:H) films as a function of [RE].
Table I - Deposition parameters and compositional data of the RE-doped α-Si(:H) films. Deposition total pressure (Ar or Ar + H₂) \(\approx 5 \times 10^{-3}\) Torr. Substrate temperature \(\sim 70^\circ C\). \(P(H_2)\), \(A_{RE}/A_{Si}\), \([H]_{NRA}\), and \([RE]_{RBS}\) are the hydrogen partial pressure, relative RE-to-Si target area, hydrogen content determined from NRA, and RE content determined from RBS, respectively. \([RE]_{ESR}\) and \([RE]_{\chi}\) are the RE content determined from ESR and \(\chi(T)\), respectively. \([H]^{*}_{NRA}\) are values estimated from the absorption spectra in the infrared range. \(\theta_p\) is the paramagnetic temperature obtained from a Curie-Weiss law fitting of \(\chi(T)\). n.a. means not available.
| Sample | \( P(H_2) \) | \( \frac{A_{RE}}{A_{Si}} \) | \( [H]_{NRA} \) | \( [RE]_{RBS} \) | \( [RE]_{ESR} \) | \( [RE]_x \) | \( \theta_p \) |
|--------|----------------|--------------------|----------------|----------------|----------------|----------------|----------|
| a-Si   | \(< 2 \times 10^{-6}\) | 0 | \(< 1\) | 0 | 0 | 0 | \(-1.2(4)\) |
| a-Si:H | \(5 \times 10^{-4}\) | 0 | \(\sim 10^*\) | 0 | 0 | 0 | n.a. |
| a-SiY  | \(< 2 \times 10^{-6}\) | \(\sim 5\) | \(< 1\) | 2.5 | n.a. | n.a. | \(-6(2)\) |
| a-SiY:H| \(< 2 \times 10^{-6}\) | \(\sim 7\) | 3.5 | 1.0 | n.a. | n.a. | \(-4(1)\) |
| a-SiLa | \(< 2 \times 10^{-6}\) | \(\sim 5\) | \(< 1\) | n.a. | n.a. | n.a. | \(-2.0(5)\) |
| a-SiGd (1) | \(< 2 \times 10^{-6}\) | \(\sim 10\) | \(< 1\) | 7.5 | 7.6 | 10(2) | \(-12(2)\) |
| a-SiGd (2) | \(< 2 \times 10^{-6}\) | \(\sim 5\) | \(< 1\) | 4.0 | 5.7 | 6(1) | \(-7(2)\) |
| a-SiGd (3) | \(< 2 \times 10^{-6}\) | \(\sim 3\) | \(< 1\) | 2.5 | 3.8 | 5(1) | \(-7(2)\) |
| a-SiGd (4) | \(< 2 \times 10^{-6}\) | \(\sim 2\) | \(< 1\) | 1.5 | 1.4 | 2.0(5) | \(-4(1)\) |
| a-SiGd (5) | \(< 2 \times 10^{-6}\) | \(\sim 1\) | \(< 1\) | 1.0 | 1.5 | 1.5(5) | \(-3(1)\) |
| a-SiGd (6) | \(< 2 \times 10^{-6}\) | \(\sim 0.6\) | \(< 1\) | 0.5 | 1.3 | 0.5(1) | \(-4(1)\) |
| a-SiGd:H (1) | \(< 2 \times 10^{-6}\) | \(\sim 3\) | 1.2 | 2.5 | 4.7 | 5(1) | \(-9(2)\) |
| a-SiGd:H (2) | \(3 \times 10^{-5}\) | \(\sim 3\) | 2.7 | 2.0 | 2.7 | 4(1) | \(-6(2)\) |
| a-SiGd:H (3) | \(1 \times 10^{-4}\) | \(\sim 3\) | 3.7 | 2.3 | 1.1 | 5(1) | \(-6(2)\) |
| a-SiGd:H (4) | \(3 \times 10^{-4}\) | \(\sim 3\) | 7.5 | 1.5 | 1.2 | 2.0(5) | \(-8(2)\) |
| a-SiGd:H (5) | \(3 \times 10^{-3}\) | \(\sim 3\) | 9.0 | 0.4 | n.a. | 0.2(1) | \(-0.4(1)\) |
| a-SiEr  | \(< 2 \times 10^{-6}\) | \(\sim 5\) | \(< 1\) | 2.5 | n.a. | 2.0(5) | \(-4(1)\) |
| a-SiEr:H | \(5 \times 10^{-4}\) | \(\sim 5\) | \(\sim 10^*\) | 0.5 | n.a. | 1.0(5) | \(-4(1)\) |
| a-SiLu  | \(< 2 \times 10^{-6}\) | \(\sim 4\) | \(< 1\) | 2.5 | n.a. | n.a. | \(-5(1)\) |
| a-SiLu:H | \(5 \times 10^{-4}\) | \(\sim 7\) | 5.0 | 0.4 | n.a. | n.a. | \(-5(1)\) |
Figure 1 of 7

Sercheli et al.

\[ \chi \times 10^{-5} \text{ emu/g} \]

Temperature (K)

Abs. Derivative (arb. units)

H (kOe)

\( a\text{-Si} \)

\( lc\text{-Si} \)

\( a\text{-Si:H} \)

quartz substrate

\[ \chi \times 10^{-5} \text{ emu/g} \]
Absorption derivative (arb. units)

Magnetic field (kOe)

- $a$-Si
- $a$-SiY
- $a$-SiLa
- $a$-SiGd
- $a$-SiEr
- $a$-SiLu
- $lc$-Si
- $a$-Si: H
- Quartz substrate
Absorption derivative (arb. units) vs. Magnetic field (kOe)

300 K

$\alpha$ - SiGd $[\text{Gd}^{3+}]$

- 7 at.%
- 4 at.%
- 2 at.%
- 0.5 at.%
- 0 at.%

$D^0$

quartz substrate
