Neutral-dangling bond depletion in $a$-SiN films caused by magnetic rare-earth elements

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Abstract

Amorphous silicon-nitrogen thin films doped with rare-earth elements ($a$-SiN:RE; RE = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, and Lu) have been prepared by co-sputtering and studied by means of electron spin resonance (ESR). It was found that the neutral dangling-bond density [$D^0$] of $a$-SiN films decreases with the presence of magnetic REs and the drop of [$D^0$] approximately scales with the spin and/or the de Gennes factor of each rare-earth element. These results suggest that a strong exchange-like interaction, $\mathcal{H} = J_{RE-D^0} S_{RE} \cdot S_{D^0}$, between the spin of the magnetic REs and $D^0$ may be responsible for this behaviour, similarly to the decrease of $T_c$ in RE-doped superconductors.

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

Taking into account the recent technological advances, and needs of our modern society, the study of the magnetic properties of new materials is of fundamental importance to develop devices for different applications such as, for example, memory structures. In view of their characteristics, amorphous silicon (a-Si) thin films seems to be good candidates for such a purpose. An interesting way of studying the a-Si thin films magnetic response is to focus on the properties of the neutral dangling-bonds (D<sup>0</sup>) present in these materials. Neutral dangling-bonds are paramagnetic centers that are excellent probes for the investigation of a-Si thin films. Moreover, silicon dangling-bonds are charge trapping centers that are more stable under the diamagnetic D<sup>+-</sup>, form. In the present work we have studied the behaviour of the paramagnetic defects D<sup>0</sup> in amorphous silicon nitride thin films doped with various rare-earth elements, a-SiN:RE (RE = rare-earths: Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, and Lu). Depending on the RE dopant, these thin films present a relative strong and narrow light emission, even at room temperature. As a consequence, RE-doped a-SiN thin films are expected to be ideal candidates to develop photonic devices. Towards this end, the study of their magnetic properties will certainly contribute to decide about the potential applications of these materials.

II. EXPERIMENTAL

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 % 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 $\sim 70$ °C under a constant total pressure of $\sim 5 \times 10^{-3}$ Torr consisting of a mixture of high-purity Ar + N<sub>2</sub> gases. The mean thickness of the films was $\sim 500$ nm.
The atomic composition of the $a$-SiN:RE films ($\sim 40\%$ Si, $\sim 59\%$ N, $\sim 0.6\%$ RE) were determined by Rutherford backscattering spectrometry (RBS) in the case of Si and RE and by nuclear reaction analysis (NRA) for N. A non-intentionally amount of hydrogen of $\sim 1-2\%$ H was detected by elastic recoil detection (ERD) analysis in all $a$-SiN:RE films. The density of the films was estimated to be $\sim 8 \times 10^{22}$ at. cm$^{-3}$. The optical bandgap of these films were determined through optical transmission measurements in the visible-ultraviolet range using a commercial spectrophotometer and stays around 5.5 eV. [6] Room-T Raman scattering measurements, using the 488.0 nm line of an Ar$^+$ laser, were also performed and confirmed the amorphous structure of the films.

The electron spin resonance (ESR) experiments were carried out in a Bruker X-band (9.47 GHz) spectrometer using a room-T TE$_{102}$ cavity. All measurements have been taken at room temperature.

### III. RESULTS AND DISCUSSION

This work presents a new approach in the study of the D$_0$ density of $a$-SiN thin films doped with REs. Our main finding was the depletion of the density of D$_0$ in the $a$-SiN matrix caused by the presence of magnetic RE species. We have observed that the insertion of magnetic RE species dramatically suppresses the number of ESR active D$_0$ states and that such a decrease approximately scales with the spin component of the RE magnetic moment.

Table I displays the atomic concentrations [RE], [Si], [N] and [H] as determined from RBS, NRA, and ERD for all the films investigated in this work. From the D$_0$ ESR intensity measurements, and using as standard a KCl-pitch sample, we have estimated the [D$_0$] of each film. The D$_0$ ESR parameters and [D$_0$] are also given in Table I. As can be seen from Table I, the average density of D$_0$ magnetic defects in these films was of, typically, $\sim 2 \times 10^{20}$ cm$^{-3}$.

Figure 1 shows the room-T ESR normalized spectra of D$_0$ in $a$-SiN films doped with
different RE elements (notice the different intensities). From a Lorentzian lineshape fitting of the resonances for all the a-SiN:RE thin films we have obtained approximately the same peak-to-peak linewidth, $\Delta H_{pp} \simeq 18(2)$ G, and field for resonance, $H_R \simeq 3378(1)$ G (corresponding to $g \simeq 2.004(1)$). An early ESR study on undoped a-Si$_3$N$_4$ films pointed out a very weak D$^0$ ESR signal with $g = 2.0054$ and $\Delta H_{pp} = 3.9$ G. A comparison of these data with our larger linewidth and higher [D$^0$] suggests that the present a-SiN:RE films are more disordered. This is probably associated to the higher N/Si ratio ($\geq 1.4$) in our films.

Figure 2 shows [D$^0$] for the various RE elements investigated in this work. It is noted that the magnetic REs cause a dramatic depletion of [D$^0$] and the strongest suppressing effect is found for Gd$^{3+}$, at the middle of the RE-series. Within our experimental accuracy, the non-magnetic RE elements do not cause a systematic change in [D$^0$]. The inset of Fig. 2 presents the drop of [D$^0$], or in another words, the number of inactive ESR D$^0$, $<[D^0(\text{RE}_{nm})]> = [D^0(\text{RE}_m)]$, due to the presence of the magnetic RE$_m$’s relative to the average value for the non-magnetic RE$_{nm}$’s. Notice that the minimum in Fig. 2 correlates quite well with the RE’s de Gennes factor, $(g_J - 1)^2 J(J + 1)$, and/or the $S(S + 1)$ factor.

The striking result of Figure 2 suggests that the mechanism responsible for the depletion of [D$^0$] involves the spin part of the RE magnetic moment and may be attributed to a strong exchange-like coupling, $\mathcal{H} \sim J_{\text{RE-D}^0}\mathbf{s}_{\text{RE}}\cdot\mathbf{s}_{\text{D}^0}$, between the RE$^{3+}$ spin, $\mathbf{s}_{\text{RE}}$, and the spin of the D$^0$, $\mathbf{s}_{\text{D}^0}$. Such a strong exchange coupling may probably shift and/or broaden the D$^0$ resonance beyond the detection limit of our ESR experimental facilities. It is then possible that a coupling of this kind leads to a [D$^0$] decrease involving the de Gennes factor, $(g_J - 1)^2 J(J + 1)$. The existence of this factor has been largely confirmed in RE-doped type II superconductor compounds through the decrease of the superconducting temperature, $T_c$, $(\Delta T_c/\Delta c < 0)$ due to the cooper-pairs breaking property of the RE ions. At this point, we should also mention that the depletion of [D$^0$] could be approximately described by the spin part of the RE-magnetic moment, $S(S + 1)$, that also takes its highest value at the Gd$^{3+}$ ion ($J = S = 7/2$). These two analyses are showed in the inset of Fig. 2.
IV. CONCLUSIONS

Rare-earth doped amorphous silicon-nitrogen films were prepared by co-sputtering and investigated by means of different experimental techniques (ESR, dc-susceptibility, ion-beam analyses, and Raman scattering). The main experimental results can be summarized as: i) a strong depletion in the density of $D^0$ states induced by the presence of magnetic RE ions, and ii) the correspondence between this depletion and the RE’s de Gennes factor, $(g_J - 1)^2 J(J + 1)$, and/or the RE’s $S(S + 1)$ factor. These results led us to propose a mechanism involving a strong exchange-like coupling between the RE$^{3+}$ magnetic moment and the spin of the silicon dangling-bond $D^0$. This strong coupling may cause a large shift and/or broadening of the $D^0$ resonance which are beyond the limit of detection of our ESR spectrometer.

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REFERENCES

[1] V. A. Gritsenko, Y. N. Novikov, A. V. Shaposhnikov, and Y. N. Morokov, Semicond. 35, 997 (2001).

[2] See, for example, R. A. Street, Hydrogenated Amorphous Silicon (Cambridge University Press, Cambridge, 1991).

[3] W. L. Warren, J. Kanicki, J. Robertson, E. H. Poindexter, and P. J. McWhorter, J. Appl. Phys. 74, 4034 (1993).

[4] J. Robertson, W. L. Warren, and J. Kanicki, J. Non-Cryst. Sol. 187, 297 (1995).

[5] A. R. Zanatta, C. T. M. Ribeiro, and U. Jahn, Appl. Phys. Lett. 79, 488 (2001).

[6] A. R. Zanatta, M. J. V. Bell, and L. A. O. Nunes, Phys. Rev. B 59, 10091 (1999).

[7] A. I. Shames, V. A. Gritsenko, R. I. Samoilova, Y. D. Tzvetkov, L. S. Braginsky, and M. Roger, Sol. St. Comm. 118, 129 (2001).

[8] J. Bandet, B. Despax, and M. Caumont, J. Appl. Phys. 85, 7899 (1999).

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

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

[11] A. A. Abrikosov, and L. P. Gorkov, Zh. Eksp. i Teor. Fiz. 39, 1781 (1960); Soviet Phys. JETP 12, 1243 (1961).
FIGURES

FIG. 1. Normalized D⁰ ESR spectra at 300 K and 9.47 GHz for \( \alpha \)-SiN:RE films.

FIG. 2. RE-dependence of the active ESR D⁰ density, \([D^0]\), in the \( \alpha \)-SiN:RE films. The inset shows the drop of \([D^0]\) for each RE doped film; the open and solid symbols correspond to the spin and the de Gennes factors, respectively.

Table I - Atomic composition of the \( \alpha \)-SiN:RE films considered in this work, as determined from RBS (Rutherford backscattering spectrometry) and NRA (nuclear reaction analysis). \( \Delta H_{pp} \), \( H_R \), \( g \), and \([D^0]\) stand for the line-width, resonance field, \( g \)-value, and neutral Si dangling-bond concentration, respectively. “n.a.” means not available and “* ” means minimum detectable value.

| Film    | [Si]_{RBS} | [N]_{NRA} | [RE]_{RBS} | \( \Delta H_{pp} \) (G) | \( H_R \) (G) | \( g \) | \( [D^0] \) (cm\(^{-3}\)) |
|---------|------------|------------|------------|--------------------------|--------------|-------|-----------------|
| \( \alpha \)-SiN  | 40.0       | 58.0       | 0.0        | 16(2) 3378(2) 2.004(1)   | 3.2 \times 10^{20} |
| \( \alpha \)-SiN:Y | 40.0       | 58.0       | 0.7        | 20(2) 3378(2) 2.004(1)   | 4.2 \times 10^{20} |
| \( \alpha \)-SiN:La | 41.0       | 57.6       | 0.4        | 18(2) 3378(2) 2.005(1)   | 2.7 \times 10^{20} |
| \( \alpha \)-SiN:Pr | 40.0       | 58.0       | 0.6        | 16(2) 3379(2) 2.004(1)   | 1.9 \times 10^{20} |
| \( \alpha \)-SiN:Nd | 39.0       | 59.7       | 0.8        | 16(2) 3378(2) 2.005(1)   | 9.6 \times 10^{19} |
| \( \alpha \)-SiN:Sm | 38.0       | 59.2       | 0.8        | 15(2) 3378(2) 2.004(1)   | 9.2 \times 10^{19} |
| \( \alpha \)-SiN:Gd | 39.0       | 59.3       | 0.7        | n.a.         | n.a.         | n.a.  | * 2.5 \times 10^{17} |
| \( \alpha \)-SiN:Tb | 39.0       | 59.3       | 0.7        | 19(2) 3377(2) 2.005(1)   | 1.6 \times 10^{20} |
| \( \alpha \)-SiN:Dy | 38.0       | 59.6       | 0.4        | 17(2) 3377(2) 2.005(1)   | 1.7 \times 10^{20} |
| \( \alpha \)-SiN:Ho | 40.0       | 58.0       | 0.6        | 16(2) 3379(2) 2.004(1)   | 1.7 \times 10^{20} |
| \( \alpha \)-SiN:Er | 38.0       | 59.5       | 0.5        | 16(2) 3379(2) 2.004(1)   | 1.7 \times 10^{20} |
| \( \alpha \)-SiN:Yb | 39.0       | 59.4       | 0.6        | 21(2) 3378(2) 2.004(1)   | 2.4 \times 10^{20} |
| \( \alpha \)-SiN:Lu | 41.0       | 57.7       | 0.3        | 20(2) 3377(2) 2.005(1)   | 4.7 \times 10^{20} |
$a$-SiN:RE

Absorption Derivative

H (Oe)
$D^0 (x 10^{20} \text{ spins/cm}^3)$

$a$-SiN:RE

$\langle D^0(\text{RE}) \rangle - D^0(\text{RE}) (x 10^{20} \text{ spins/cm}^3)$

$S(S + 1)$

$(g_J - 1)^2 J(J + 1)$

RE$^{3+}$