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New paramagnetic center in amorphous silicon doped with rare-earth elements

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A new paramagnetic center associated with rare earths (RE) (La, Ce, Pr, Nd, Gd, Er, and Lu) in amorphous silicon is reported. It is shown that RE impurities are incorporated in *a*-Si and that the density of paramagnetic dangling bonds decreases as a consequence of the presence of these impurities. An interpretation in terms of RE 6*s* orbitals and crystal-field-split 5*d* orbital hybridization suggests that the RE behaves as an acceptor impurity with an associated hole in the *a*-Si valence-band tail, which is responsible for the observed resonance at a *g* value of 2.10 ± 0.01.

In the past it was believed that impurity doping in amorphous (*a*) materials should not contribute to electrically active acceptor or donor levels, because the lack of topological constraints could change the local coordination, saturating all the impurity bonds.[1] However, by use of the cosputtering technique it was shown that in *a*-Si, *a*-Ge,[2-5] and *a*-chalcogenides,[6-8] impurities of low solubility that are deep lying in the corresponding crystalline structures, form localized states near the Fermi level in the amorphous host, causing large hopping-type increase of the conductivity. In the case of *a*-Si and *a*-Ge, it was possible to observe the ESR signal of Mn, Fe, and Ni impurities and the decrease of paramagnetic dangling-bond (D^0) density as the impurity concentration increases.[4,5] Moreover, although Hauser[2] and Chopra and Nath[3] showed that shallow impurities for the crystalline material did not contribute to the conductivity of the amorphous host,[2,3] Spear and Le Comber[9] found that the electrical conductivity of *a*-Si and *a*-Ge prepared by rf glow discharge changed by many orders of magnitude when doped with P and B. Also, light-induced[10-12] and equilibrium[13] ESR experiments in *a*-Si and *a*-S:H doped with P and B showed that negative and positive charged states arose, and that the paramagnetic D^0 density decreased.

Doping of *a* semiconductors with magnetic and nonmagnetic impurities is an interesting area since the effects of the incorporation of impurities on the properties of these structurally and magnetically disordered semiconductors are not completely known and understood. For instance, if it can be unambiguously demonstrated that magnetic impurities can be incorporated in the amorphous host and their semiconducting properties controlled magnetically, amorphous diluted magnetic semiconductors (*a*-DMS) should become an interesting subject to be studied, theoretically and experimentally, from a more microscopic point of view.

ESR has proved to be an important tool to investigate the local environment of paramagnetic impurities in amorphous systems. In this ESR work we show for the first time that by the rf cosputtering technique it is possible to incorporate rare-earths (RE) in *a*-Si, and that these impurities, independent of their 4*f* electronic occupation number, contribute to form a new paramagnetic center which we tentatively associate with loosely localized holes in the *a*-Si valence-band tail.

Amorphous silicon-RE films (a-$Si_{1-x}R_x$) were deposited by the rf sputtering method in a Leybold Heraus Z-400 apparatus. The target was a 3-in. diam, $\frac{1}{4}$-in. thick, 99.999% pure Si disk upon which small metallic wafers of (99.9%) pure RE were placed in an approximately random way. The system was dry-pumped for one hour prior to deposition to base pressure of 10^{-6} Torr. The argon gas was of 99.9995 at.% nominal purity. All samples were prepared under identical deposition conditions. The quartz substrates (3×20 mm^2) were ultrasonically precleaned and kept at 120 °C during the deposition. The target was plasma-etched for several minutes before the beginning of each run. The total pressure was 0.12 Torr in all cases. The nominal RE concentration (of the order of 10^{19} atoms/cm^3 in the reported samples) was estimated from RE target coverage and the sputtering yield of each element. Typical sample thickness was 2–4 μm for a target-substrate distance of 1.5 cm. Details about film texture, optical properties, and precautions concerning oxygen contamination are given elsewhere.[14] The samples being reported are not hydrogenated. The density of D^0 centers and new paramagnetic centers were determined by comparison with a standard *a*-Si sample containing 10^{18} spins/cm^3.

The ESR experiments were carried out in conventional Varian E15 spectrometers using a TE_{102} (100 kHz) and a TE_{011} (1 kHz) room-temperature cavity for *X* band and *Q* band, respectively. The temperature dependence of the *X* band data was obtained with a temperature controller using circulating cold He gas through a cavity quartz insert.

The films were analyzed by x-ray diffraction and Raman scattering, and in all cases the absence of long-range structural ordering, characteristic of amorphous host, was observed.

Figure 1 shows the typical ESR spectra obtained from a-$Si_{1-x}R_x$ films at *X* band. It is also shown there the resonance corresponding to a pure *a*-Si film prepared under the same conditions than those used for the a-$Si_{1-x}R_x$ films. In Table I we give, for each sample at room temperature, the ESR parameters and spin densities corresponding to the paramagnetic D^0 and the new paramagnetic center, which we shall call IFGW-1 (Instituto de Física "Gleb Wataghin").

Figures 2 and 3 show the temperature dependence of the relative resonance intensity and linewidth for both the

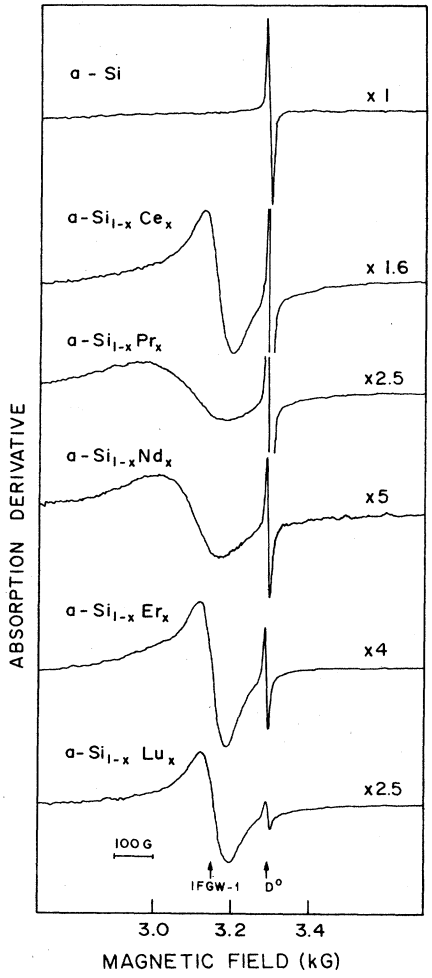

FIG. 1. ESR spectra at X band and room temperature for a-Si and a-$Si_{1-x}R_x$ (R= Ce, Pr, Nd, Er, Lu). The concentrations are indicated in Table I.

D^0 and the IFGW-1 paramagnetic centers, respectively.

The most striking results obtained from these experiments are as follows. (1) All films show the same resonance associated with the presence of the RE in a-Si (IFGW-1 center), independent of the RE $4f$-shell electronic occupation number. For Pr and Nd a larger g value and linewidth were obtained at the X band. (2) The relative resonance intensity for the IFGW-1 center shows a tendency to decrease as the temperature is lowered. (3) The resonance due to the D^0 centers in all samples gives the same g value as in a-Si (g=2.0055) and shows the following features: The D^0 spin density decreases as the RE concentration increases; the linewidth at room temperature is broader the higher the magnetic moment carried by the RE (maximum for Gd $4f^7$); and there is a further linewidth broadening below 30–50 K in the case of magnetic RE impurities. (4) For all samples, except those with Lu and Gd (see below), the nominal RE concentration is of the order of the IFGW-1 spin density and both are larger, by at least an order of magnitude, than that of the D^0 spin density. (5) The Q band data show that the linewidths of the D^0 and IFGW-1 centers are all inhomogeneous, and that for a-$Si_{1-x}Pr_x$ and a-$Si_{1-x}Nd_x$ the g value and the inhomogeneous broadening of the linewidth of the IFGW-1 center were reduced at these frequencies. (6) The absence of structural ordering indicates that the presence of the RE does not contribute to film recrystalization, in spite of the reduction of the paramagnetic D^0 states.

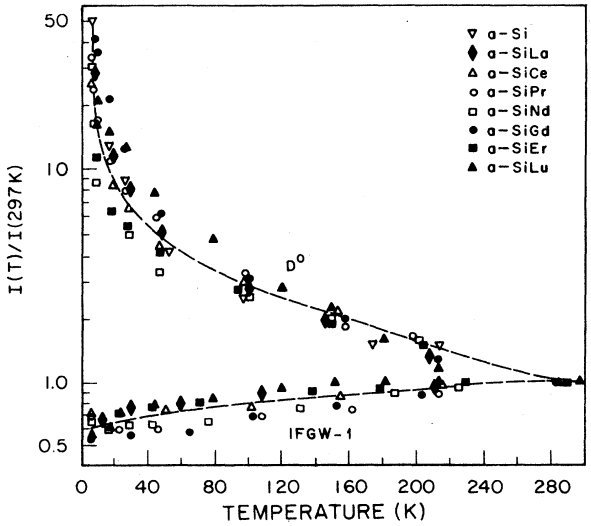

FIG. 2. Temperature dependence of the relative resonance intensity for D^0 and the IFGW-1 center in all measured samples.

Points (1) and (2), together with the fact that the

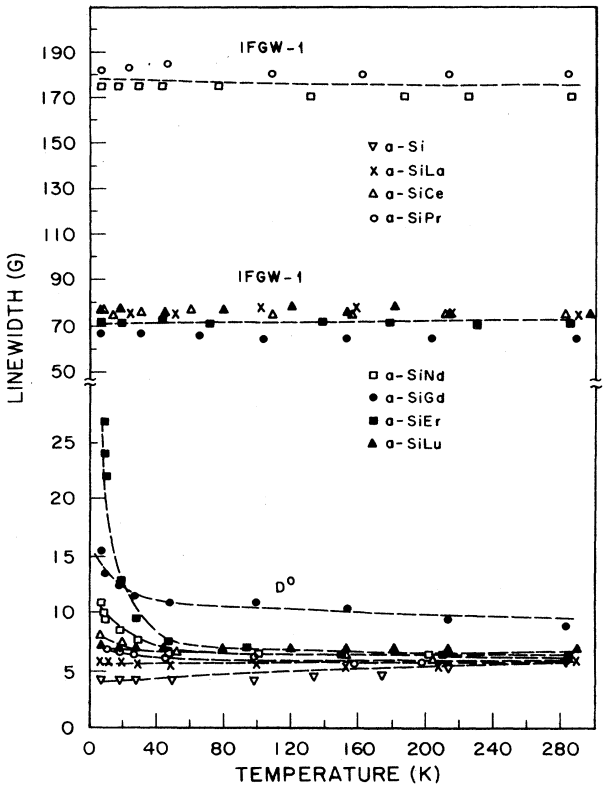

FIG. 3. Temperature dependence of the linewidth for D^0 and the IFGW-1 center in all measured samples.

TABLE I. Room-temperature X and Q band ESR parameters of D^0 and the IFGW-1 center in a-$Si_{1-x}R_x$ ($x=0.001$).

	X band					
	D^0			IFGW-1		
RE	Density[a] (10^{18} spins/cm^3)	g value (± 0.0005)	ΔH (G)	Density[a] (10^{18} spins/cm^3)	g value (± 0.005)	ΔH (G)
None	2.1	2.0054	6.2 ± 1	...	...	...
La	0.9	2.0053	5.5 ± 1	21	2.097	75 ± 10
Ce	1.1	2.0054	6.5 ± 1	35	2.098	75 ± 10
Pr	0.6	2.0054	6.5 ± 1	86	2.137	180 ± 40
Nd	0.3	2.0049	6.5 ± 1	86	2.133	170 ± 40
Gd	0.1	2.0055	9.0 ± 1	2	2.083	65 ± 10
Er	0.5	2.0052	7.5 ± 1	31	2.103	70 ± 10
Lu[b]	0.1	2.0049	7.0 ± 1	16	2.096	75 ± 10

	Q band			
	D^0		IFGW-1	
RE	g value (± 0.0005)	ΔH (G)	g value (± 0.003)	ΔH (G)
None	2.0058	7.5 ± 1	...	...
La	2.0050	13.0 ± 1	2.091	130 ± 20
Ce	2.0055	16.0 ± 2	2.092	140 ± 30
Pr	2.0051	18.0 ± 2	2.099	230 ± 40
Nd	2.0047	20.0 ± 2	2.094	210 ± 40
Gd	2.0053	25.0 ± 2	2.083	95 ± 20
Er	2.0054	22.0 ± 2	2.097	120 ± 20
Lu[b]	2.0051	22.0 ± 2	2.092	130 ± 30

[a] The spin densities are estimated within 50%.

[b] For a-$Si_{1-x}Lu_x$ ($x=0.01$).

IFGW-1 resonance can be observed at room temperature and also with La and Lu impurities, which carry no magnetic moment, give support to the statement that the IFGW-1 paramagnetic center cannot be attributed to the RE localized $4f$ magnetic moment. Therefore, this resonance should be ascribed to a new paramagnetic center associated with the RE but independent of its $4f$ electronic occupation number. In other words, the magnetic levels associated to the total RE angular momentum (J) of the $4f^n$ shell are not affected by this new paramagnetic center, although influences on the g value and linewidth, which within the accuracy of our experiments were not observed, may still be expected.

In order to give a possible mechanism which could account for the observed features and origin of this new paramagnetic center, let us first mention some relevant facts: (a) The RE valence is commonly 3+; thus, it may enter substitutionally in the a-Si at sites with trigonal symmetry (dangling-bond sites). (b) Mandelkorn *et al.*[15] find, that Gd, like B, acts as a acceptor in Si. (c) Hauser[2] observed that impurities with low solubility and at deep levels in the crystalline material form localized states near the Fermi level in amorphous host. Based on these facts a model is proposed, which assumes that for the substitutional RE the local tetrahedral crystal field splits the $5d$ RE orbitals, leading to a triplet ground state (t_2), which could hybridize with the $6s$ RE orbital to form four sd^3 bonds, localized near the Fermi level, three of which may be occupied by the RE valence electrons and the fourth being unoccupied. The four RE bonds formed in this way can be saturated by Si bonds and an extra electron taken from the a-Si valence-band tail, creating near the RE a loosely bound hole responsible for the new paramagnetic center. The presence of a nearby RE may contribute to give a non-s character to the hole orbitals. This in turn, via spin-orbit coupling, could account for the observed inhomogeneous linewidth and large g values ($g=2.10$) of the resonance. This model predicts that the RE acts as an acceptor impurity (R^-) in a-Si, and that the number of holes should increase with temperature, in agreement with the observed increase of the IFGW-1 resonance intensity towards higher temperatures (see Fig. 2). Note that in this model the RE $4f$ electronic occupation number is not relevant. Also the model can give a mechanism for the decrease of the D^0 density in a-$Si_{1-x}R_x$, because the holes at the a-Si valence-band tail may recombine with a nearby electron in a D^0 state, increasing probably the density of D^+ states, which are not paramagnetic. Thus, the actual RE concentration would always be larger than the IFGW-1 center's density and the difference should be given at least in part by the decrease in the D^0 density. It is interesting to note that at least up to concentrations of the order of 10^{10} atoms/cm^3 the RE nominal concentration and IFGW-1 center density are of the same order of magnitude. Thus most of the RE atoms should enter in the a-Si specimen as substitutional dopants, i.e., with tetrahedral coordination. However, in the case of a-$Si_{1-x}Lu_x$ we had to use a nominal concentration of $x=0.01$ ($\simeq 10^{20}$ atoms/cm^3) in order to see the IFGW-1 resonance (see Table I). For a sample with $x=0.001$ only

the resonance corresponding to a reduced D^0 concentration ($\simeq 0.2 \times 10^{18}$ D^0/cm^3) was observed with no observable IFGW-1 resonance. Also for a-$Si_{1-x}Gd_x$ (see Table I) the IFGW-1 and D^0 spin densities are smaller than in other a-$Si_{1-x}R_x$. Therefore, we conclude that a detailed knowledge of the concentration corresponding to different defects, caused by the RE, may strongly depend on the particular RE and film-preparation conditions.

Our model predicts that in crystalline silicon, a-Si:H and in any other tetrahedral semiconductor, the RE may behave as an acceptorlike impurity, i.e., lowering the Fermi level and consequently doping the semiconductor. At this point we would like to call attention to the clear p-type conductivity found for very diluted Er in GaAs (Ref. 16) and Yb in InP.[17] Consequently, we believe that it will be important to do ESR experiments in more doped samples[18] in order to see if the IFGW-1 center can be observed and the RE acceptor character confirmed in these semiconductors. Moreover, Bartkowski *et al.*[19] found a resonance at $g=2$ for Gd in PbTe which was not identified. We suggest that ESR experiments in Lu or La in this rock-salt semiconductor (PbTe) would also be interesting, in order to see if that resonance can be associated to our IFGW-1 paramagnetic center as well. Therefore, Hall effect, thermopower, magnetoresistance, photoluminescence, and resistivity experiments in a-$Si_{1-x}R_x$, a-$Si_{1-x}R_x$:H and their corresponding P- and B-doped and recrystallized samples would be necessary in order to clarify whether impurities can really be considered as acceptor dopants in tetrahedral amorphous and crystalline semiconductors.

Since for our model the magnetic moment, associated to the RE $4f$ shell is not relevant it is possible that by increasing the magnetic RE concentration with the rf sputtering technique, semimagnetic properties could be recognized in these materials. Promising experimental evidence, showing that this may be the case, is the observed low-temperature broadening of the resonance linewidth of the D^0 center for magnetic RE's in a-Si (see Fig. 3). Other evidence that the RE's carry the magnetic moment in a-Si is given by the broad field-independent resonance ($\Delta H \cong 900$ G) recently observed at $g=1.997$ in a-$Si_{1-x}Gs_x$ films, which was attributed to the powder spectra of unresolved crystal-field effects on Gd^{3+} ($4f^7$, $^8S_{7/2}$) ions at low-symmetry sites.[14] In any case susceptibility experiments in the whole series of a-$Si_{1-x}R_x$ will be needed in order to study the magnetic properties of these disordered materials.

Finally, we should mention that the reasons for the reduction of the g value and inhomogeneous broadening of the linewidth observed at the Q band relative to those at the X band for the IFGW-1 center in a-$Si_{1-x}Nd_x$ and a-$Si_{1-x}Pr_x$ (see Table I), are not clear to us at the moment. Probably this could be attributed to the particular position of the RE levels relative to the a-Si bands and Fermi level, and only detailed band calculations, including the RE orbitals, may clear up this point. Also these calculations could show that the properties may depend on the particular RE.

In conclusion, a new paramagnetic center was found, associated with RE impurities in a-Si. According to our interpretation of the experimental results, all RE's may act as acceptor impurities in tetrahedral amorphous and crystalline semiconductors, conserving their magnetic properties. Our model for the origin of this new paramagnetic center is not yet absolutely proved. These results enhance the importance of pursuing more experimental and theoretical studies, in order to characterize and understand the properties of amorphous-diluted magnetic semiconductors. This opens a new area where the semimagnetic properties of a-Si and other tetrahedral-coordinated semiconductors doped with RE's should be investigated.

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