Electron spin resonance in amorphous silicon doped with Gd

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ESR experiments on Gd impurities in amorphous silicon between liquid-He and room temperatures show three resonances which could be ascribed to paramagnetic dangling bonds ($g=2.0055\pm0.0005$), to Gd $^8S_{7/2}$ states ($g=1.997\pm0.005$), and to a new paramagnetic center ($g=2.10\pm0.05$) associated with the presence of Gd atoms. For low-Gd-concentration samples the intensity of the resonance due to dangling bonds decreases as the Gd concentration increases and the intensity of the new paramagnetic center is found to increase with increasing temperature. These results indicate, as we recently found for other rare-earth–element impurities in *a*-Si, that a fraction of the Gd atoms act as acceptor impurities with associated loosely bound holes in the *a*-Si valence-band tail which are responsible for the resonance of the new paramagnetic center observed at a *g* value of 2.10 ± 0.05.

I. INTRODUCTION

Several aspects of the doping of crystalline semiconductors with magnetic $3d$ and $4f$ transition-metal ions have been of considerable interest in the last few years: in particular, the position of the impurities in the lattice, their electronic configuration, and their interaction with the host conduction carriers.[1–6]

The same interest arose when it was chosen that amorphous materials could also be doped.[7–12] In particular, several authors have already reported that $3d$ transition-metal impurities in amorphous materials produce an increase in the electrical conductivity by many orders of magnitude, suggesting that transition-metal impurities form deep localized states in the gap, pinning the Fermi level at their position.[9,10] In order to study these properties, ESR, optical absorption, and conductivity experiments on *a*-Si and *a*-Ge, with Mn, Fe, and Ni impurities were carried out by Kumeda *et al.*[13] and Shimizu *et al.*[14,15] They found that Mn atoms incorporate into the amorphous material in basically two ways, one which contributes to an ESR signal and another which does not. Therefore two different configurations for the Mn atoms may coexist in *a*-Si and *a*-Ge. They also observed that the addition of Mn to these amorphous materials increases the conductivity and decreases the spin density due to paramagnetic dangling bonds (D^0). They have suggested that electron transfer from the transition-metal atoms to D^0 could be the mechanism responsible for the decrease of the D^0 density.

In a recent ESR study of *a*-$Si_{1-x}R_x$ [*R* denotes rare-earth (RE) elements], we reported on a new paramagnetic center with a *g* value of 2.10 (labeled IFGW1) which was observed for several RE's in *a*-Si, independently of the RE $4f$ electronic occupation number. The IFGW1 center was described as the resonance of a hole, loosely bound to a RE negative ion, which enters substitutionally in the *a*-Si lattice.[16] Since the RE ions have a very stable $4f$ inner shell—in particular Gd has seven $4f$ electrons which are normally found in the $^8S_{7/2}$ ground state—we expect that by introducing Gd impurities in *a*-Si it may be possible to observe the resonance corresponding to the Gd $^8S_{7/2}$ state[17] together with that of the D^0 states and the IFGW1 center. Following these ideas, the aim of this work is to incorporate Gd impurities in *a*-Si and to look for the resonance of the localized $4f$ magnetic states of Gd and also to see to what extent Gd behaves like Mn impurities in *a*-Si. In this work we report mainly on ESR, ir, and optical measurements and in a future communication we shall report on the conductivity data of *a*-$Si_{1-x}Gd_x$.

II. EXPERIMENT

Films of amorphous silicon with Gd impurities (*a*-$Si_{1-x}Gd_x$) were prepared by rf cosputtering in 0.12 Torr of 99.9995% argon atmosphere, which was previously pumped out to a base pressure of 4×10^{-6} Torr during 1 h. The textures of the films were rather porous. Films prepared at lower pressure (<0.1 Torr) were more compact, but they did not show the ESR signals which were observed in the films prepared at higher Ar pressure. The nominal Gd concentrations ($0\le x\le0.03$) were determined from the relative area of randomly distributed metallic (99.9%) Gd wafers to that of the plasma-etched (99.999%) Si target, taking into consideration the sputtering yield of each element. The films were deposited on ultrasonically precleaned quartz (3×10 mm^2) substrates and kept at 120 °C at a deposition rate of 1.1 to 1.4 Å sec^{-1} during approximately 1 h, obtaining films with thickness of the order of 2–4 μm for a target-substrate distance of 1.5 cm. The film thicknesses were determined by interferometry and from the interference curves for 100% optical transmission (see below). In order to get a large ESR D^0 signal, no hydrogenation was done in this study. The density of D^0 states obtained in our pure *a*-Si

TABLE I. Room temperature X-band ESR parameters of a-$Si_{1-x}Gd_x$.

	Gd ($^8S_{7/2}$)		IFGW1		D^0	
x	g value	ΔH (G)	g value	ΔH (G)	g value	ΔH (G)
0.03	2.01±0.05	1000±50				
0.016	2.04±0.05	950±50	2.099±0.005	60±5		
0.010	2.01±0.05	860±50				
0.006	2.00±0.05	860±50				
0.004	2.03±0.05	850±50				
0.0023	2.02±0.05	900±50	2.10±0.02	110±20	2.0055±0.0005	13.0±2
0.0010			2.08±0.01	60±5	2.0055±0.0005	9.0±1
0.0005			2.10±0.01	75±5	2.0055±0.0005	8.5±1
0.00					2.0055±0.0005	6.5±1

films, grown under the same conditions, was of the order of 10^{18} spins/cm^3. The films were analyzed by Raman scattering and x-ray diffraction and all of them showed the absence of long-range structural ordering, characteristic of amorphous materials. Infrared experiments, carried out in a JASCO spectrometer, showed that in all our samples there is an absorption band in the region from 9 to 11 μm, typical of Si-O stretching vibrations, indicating the presence of oxygen in our samples. In order to determine the origin of this oxygen, two films of a-$Si_{1-x}Gd_x$ (x=0.016) were prepared at the same time. One of them was covered by 1 μm of pure a-Si film deposited in a pressure of 0.01 Torr of Ar to guarantee a less porous film covering the surface of our sample, and consequently minimizing the oxygen adsorption, when the film was exposed to air. ESR measurements resulted in exactly the same ESR spectra for both samples. The covered film did not show the oxygen ir absorption band, while the uncovered film did. Since the adsorbed oxygen did not affect the resonances at all we conclude that the oxygen adsorption occurs only when porous films are exposed to air, and the oxygen atoms are only inside the films' pores or voids, but not in the bulk. Also for all samples the D^0-state g value was found to be 2.0055±0.0005 (Ref. 18) (see Table I), indicating again that the adsorbed oxygen is not in the bulk.[19] As far as the ESR and ir absorption experiments are concerned, the samples prepared by this method were stable in air during a period of at least one year.

To determine the optical gap, the refraction index, and the thickness of the a-$Si_{1-x}Gd_x$ films, optical transmission experiments were carried out in a Varian spectrometer. Plotting the square root of the absorption coefficient times the photon energy times the refraction index versus the photon energy, and extrapolating to zero transmission, we found that the measured optical gap decreases as the Gd concentration increases (see Fig. 1). The thicknesses and refraction indexes of the films were determined from the 100% transmission curves and are shown in Table II.

For the ESR experiments we used conventional ESR Varian E15 spectrometers at the X and Q bands with room temperature TE_{102} (100 kHz) and TE_{011} (1 kHz) cavities, respectively. At the X band the temperature on the sample was controlled through He or N_2 gas flux circulating in a quartz insert. The spin densities were determined using a standard sample of a-Si with 10^{18} spins/cm^3 (see Table II).

III. RESULTS AND ANALYSIS

The ESR spectra of a-$Si_{1-x}Gd_x$ show three resonances in the temperature range from 4 to 300 K. Samples having low Gd concentration ($x \leq 0.002$) show at room temperature two resonances, one with a g value of 2.0055 with linewidth between 6 and 13 G, and another with g=2.10 and linewidth about 70 G (see Table I). Figure 2 shows the room-temperature spectrum of one of the low

TABLE II. General characteristic of the samples of a-$Si_{1-x}Gd_x$.

x	Thickness (μm)	Optical gap (eV)	n (5200 Å)	D^0 (spin/cm^3)	IFGW1 (spin/cm^3)
0.016					2.2×10^{18}
0.010	3.50±0.18	0.11±0.02			
0.006	3.60±0.18	0.63±0.02	3.06		
0.004	2.65±0.13	0.95±0.02	3.91		
0.0023	3.66±0.18	1.10±0.02	4.26	3.1×10^{16}	3.1×10^{17}
0.001	3.20±0.16	1.20±0.03	3.74	1.3×10^{17}	2.4×10^{18}
0.0005				3.5×10^{17}	2.2×10^{18}
0.0	0.60±0.03	1.18±0.02	4.80	2.1×10^{18}	

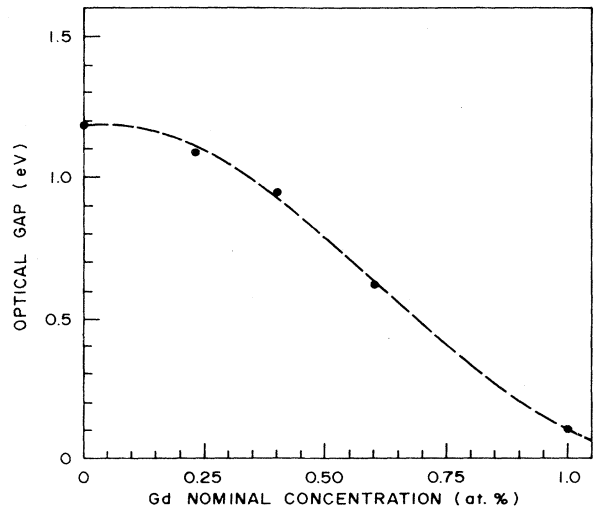

FIG. 1. Gd-concentration dependence of the optical energy gap for a-$Si_{1-x}Gd_x$.

concentration samples ($x=0.001$) where both resonances can be observed clearly. We attribute the narrower resonance to D^0 because the g value, line shape, linewidth, and temperature dependence of the intensity for this resonance are almost identical to those already published[18] and also to those found in our pure ($x=0$) a-Si samples. The broader resonance corresponds to the recently reported IFGW1 center associated to several low-concentration RE impurities in a-Si.[16] The origin of this resonance was attributed to holes in the a-Si valence-band tail associated with the acceptor character of the RE elements, independently of their $4f$ electronic occupation number. Thus in our case this means that the Gd atoms associated with the IFGW1 centers would probably conserve the magnetic properties of their $4f^7$ shell. Then one can argue that, if this actually happens, a resonance near $g=2.0$, from the ground state of the $4f^7$ electrons ($^8S_{7/2}$), should be observed, at least at low temperatures. For low-concentration samples as the temperature is lowered, a third and very broad resonance ($g=2.0$, $\Delta H \cong 900$ G) actually appears below 80 K, whereas for more concentrated samples ($x>0.004$) only this broad resonance can be seen in the range of temperatures. Figure 3 shows the ESR X-band spectra for a-$Si_{1-x}Gd_x$ ($x=0.006$) at liquid-nitrogen temperature. Room-temperature Q-band ESR experiments show that the linewidth of this resonance does not depend on the microwave frequency ($g=1.997\pm0.005$, $\Delta H \simeq 900\pm100$ G). This and the fact that the nominal Gd concentration is always larger than the IFGW1 spin density (see Table II) suggest that this broad unresolved resonance may be the powder spectra of the crystal-field-split $^8S_{7/2}$ ground state of Gd atoms at low-symmetry sites, probably trigonal ones, with their three valence bonds saturated. Furthermore, unlike the temperature dependence of the resonance intensity of the IFGW1 center, which decreases toward low temperature, the intensity of the resonance associated with Gd low-symmetry sites and that of D^0 increases, following approximately a T^{-1} behavior, indicating that these resonances come from a system of highly localized spins.[16] Therefore we conclude that only a fraction of the Gd atoms may be at tetrahedral site acting as an acceptor impurity in a-Si, and being responsible for the observed resonance at a g value of 2.10 (IFGW1 center). The resonance due to the $4f^7$ electrons of these Gd atoms at nearly cubic sites was not observed.

In one of our higher-Gd-concentrated samples ($x=0.016$), two resonances, the IFGW1 center and the broad resonance at $g=2.00$, were observed. The corresponding room-temperature spectrum is shown in Fig. 4. We believe that this was a highly inhomogeneous sample, where regions with different Gd concentrations may have been responsible for the simultaneous observation of these two resonances. From all this discussion we conclude that the actual concentrations corresponding to different Gd defects in a-Si strongly depend on the films preparation conditions and also from the particular RE used.[16]

In Table I we summarize the room-temperature ESR parameters measured from the observed spectra at X-band for all our samples. Within the accuracy of our experiment these parameters were found to be temperature independent, except for the D^0 linewidth which broadens below 30–50 K.[16] This broadening and the increase of

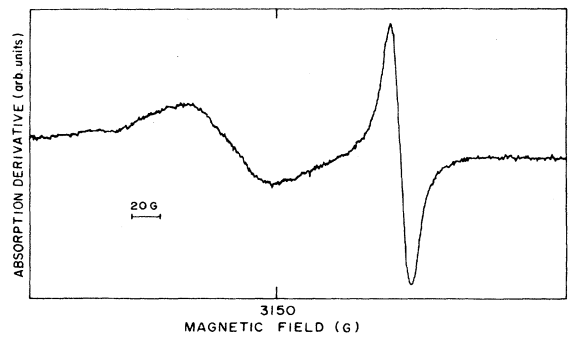

FIG. 2. ESR spectra of a-$Si_{1-x}Gd_x$ ($x=0.0005$) at room temperature. The high field ($g=2.0055\pm0.0005$) and low field ($g=2.08\pm0.03$) resonances correspond to D^0 and the IFGW1 paramagnetic center, respectively.

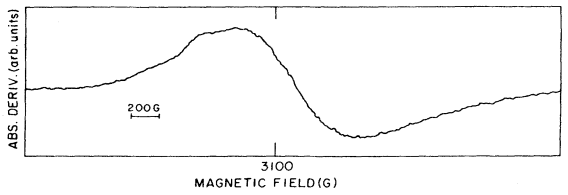

FIG. 3. ESR spectra of a-$Si_{1-x}Gd_x$ ($x=0.006$) at liquid-nitrogen temperature. The broad ($g=2.01\pm0.05$) resonance corresponds to Gd ($^8S_{7/2}$) atoms.

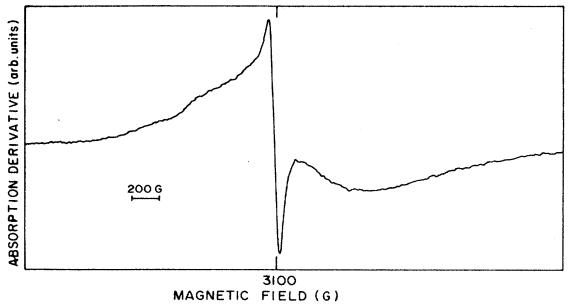

FIG. 4. ESR spectra of a-$Si_{1-x}Gd_x$ ($x=0.016$) at room temperature. The narrow ($g=2.08\pm0.03$) and broad ($g=2.01\pm0.05$) resonances correspond to the IFGW1 center and Gd ($^8S_{7/2}$) atoms, respectively.

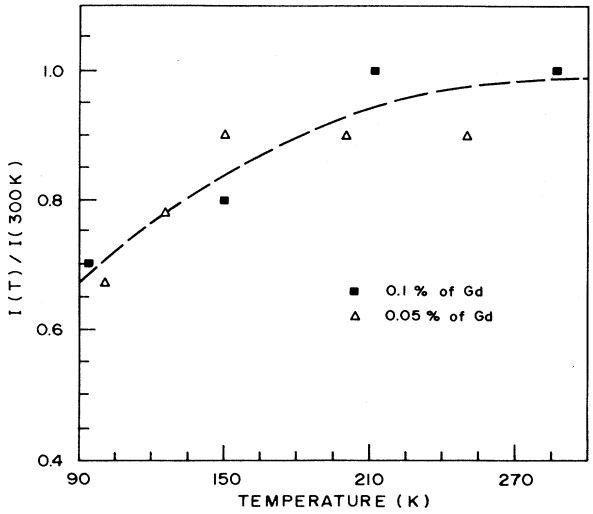

FIG. 5. Temperature dependence of the relative resonance intensity for the IFGW1 center ($g=0.208\pm0.05$).

the D^0 and IFGW1 room-temperature resonance linewidths as the Gd concentration increases (see Table I) suggest that even in low-concentrated samples there may be magnetic interactions probably due to the presence of the Gd magnetic moment which could inhomogeneously contribute to the broadening of these resonances. Q-band experiments[16] confirmed that the D^0 and IFGW1 resonances were both inhomogeneous.

IV. DISCUSSION

The observed decrease of the optical energy gap as the Gd concentration increases (see Fig. 1) suggests that at least part of the Gd atoms may have been substitutionally incorporated in a-Si with tetrahedral coordination, probably forming deep electronic states near the Fermi level.[20–22] These states may act as acceptor levels, creating hole states in the a-Si valence-band tail, which in turn would be responsible for the observed resonance at $g=2.10$ and the decrease of the resonance intensity toward lower temperature (see Fig. 5). A possible mechanism which could account for the Gd atoms becoming acceptor impurities in a-Si, is that the $5d$ Gd atomic orbitals may be split by the cubic crystal field, leaving the triplet (t_2) state lower, which could hybridize the $6s$ Gd orbital to form four bonds which could be saturated by four Si electrons and an extra electron taken from the a-Si valence-band tail. In other words the Gd atom at a tetrahedral site could behave as an acceptor impurity. It is interesting to note that this interpretation could account for the observed decrease in the D^0 concentration by the addition of Gd atoms in a-Si (see Table II), because a hole recombination with an electron from a nearly D^0 could be the reason for the observed decrease in the D^0 density. This model has also been used to explain the resonance observed for other RE elements in a-Si.[16] Since our model for the origin of this new paramagnetic center is not absolutely proved, we decided to label it the IFGW1 center.

V. CONCLUSIONS

Although at the moment it is not clear to us why only films prepared at high residual pressure makes the Gd and IFGW1 resonances observable, we believe that Gd impurities in a-Si are incorporated at least in two ways, one corresponding to Gd at low symmetry sites and the other at substitutional tetrahedral sites giving rise to a new paramagnetic center which we have tentatively associated to diluted acceptors of Gd impurities in a-Si. The resonance due to the $4f^7$ electrons of these acceptor Gd atoms, which should appear as the powder spectra of the $^8S_{7/2}$ ground state at nearly cubic symmetry, may not be easily observed because this resonance should overlap with the broad and more intense resonance coming from the Gd atoms at lower symmetry sites. It is evident that more experimental data such as the Hall effect, light-induced electron spin resonance, conductivity, etc., are needed in order to characterize the RE impurity behavior in a-Si and consequently verify if our interpretations are correct.

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