Spin-lattice relaxation in amorphous silicon. Evidence of anomalous temperature dependences

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Spin-lattice relaxation in amorphous silicon. Evidence of anomalous temperature dependences

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Résumé. — Nous avons étudié la relaxation spin-réseau d'électrons localisés dans des films de silicium amorphe évaporés. Les dépendances du taux de relaxation avec la température et la concentration ont été mesurées dans la gamme 4,2-290 K. Au-dessous de 10 K, un goulot d'étranglement des phonons apparaît. Entre 10 et 100 K, un processus à un seul phonon prédomine. Il peut être interprété en supposant l'existence d'une interaction d'échange appréciable. Au-dessus de 100 K, enfin la relaxation spin-réseau est provoquée par le *hopping*.

Abstract. — We have investigated the spin-lattice relaxation of localized states in evaporated amorphous silicon films. Temperature and concentration dependences of the relaxation rate have been measured in the temperature range 4.2-290 K. Below 10 K a phonon bottleneck is present. Between 10 and 100 K, a single phonon process predominates. It can be accounted for assuming a significant exchange interaction. Above 100 K, spin-lattice relaxation is governed by hopping.

Recently many investigations have been reported, devoted to Electron Spin Resonance (E.S.R.) in amorphous silicon and germanium (a-Si and a-Ge). Brodsky and Title [1] made the first studies on sputtered materials and their results have been confirmed in later studies carried out by Agarwal [2], Connel and Pawlik [3] and Voget-Grote *et al.* [4]. However, in spite of much experimental data, the nature of the defect centres associated with the E.S.R. signal remains somewhat obscure. It is the effect of exchange or motion on E.S.R. spectra that constitutes the major problem [5-9].

In order to determine the role played by exchange, we have developed the measurement of the spin-lattice relaxation time, T_1, in evaporated amorphous silicon films, in the temperature range, 4.2 to 300 K, and for spin concentrations ranging from 6×10^{19} to 1.5×10^{20} cm^{-3}. T_1 was determined by the modulation method [10-12], which is particularly apt for values of T_1 from 10^{-4} to 10^{-10} s. The principle of the method is the following. The microwave field is amplitude modulated. A signal proportional to $\partial M_z/\partial t$ is induced in a coil, placed along the static field and close to the sample. The variations of the signal amplitude with the modulation frequency allow the determination of the relaxation time T_1.

The samples were prepared from very pure cylindrical rods of undoped silicon (including less than 10^{13} impurities/cm^3), which were mounted in a water cooled copper crucible. After outgassing the system at 420 K for several days a pressure of 10^{-9} torr was finally obtained using a 600 l/s ionic pump. An electron gun was used for the evaporation. The deposition rate was varied from 10 to 40 Å/s and the thickness of the films obtained was about 1.5 μm.

The substrates were flexible films of polyimide « Kapton » [13] of size $5 \times 5 \times 0.015$ cm cooled to liquid nitrogen temperature. During evaporation, the pressure was about 10^{-6} torr. The samples were stored in air at room temperature *prior* to the E.S.R. and spin-lattice relaxation (S.L.R.) investigations.

To characterize the samples, we have developed some preliminary E.S.R. studies at room and liquid nitrogen temperatures using an X-band homodyne spectrometer. We have also investigated the influence of anneals on the films. The samples, placed in quartz tubes at atmospheric pressure, were isochronally heated at temperatures increasing from 323 to 973 K. For samples annealed up to 623 K, the E.S.R. line, seen at room and liquid nitrogen temperatures, is symmetrical, Lorentzian and isotropic. Above 623 K, it becomes asymmetrical and intermediate between a Lorentzian and a Gaussian [7]. The influence of the annealing temperature on the spin density of our samples is shown in figure 1. At 900 K, crystalliza-

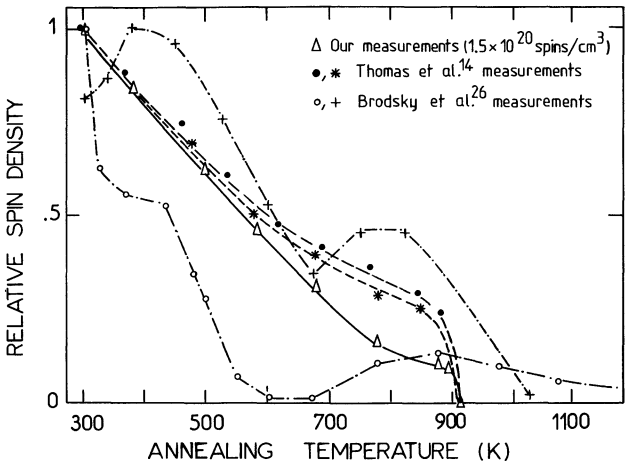

Fig. 1. — Influence of successive isochronal anneals on the number of spins. The initial number of spins is normalized to unity. The results obtained by Thomas *et al.* [14] and Brodsky *et al.* [26] are also given.

tion is effected and a drastic fall in the number of spins is observed (5 $^{o}/_{oo}$ of the initial concentration). These results are in good agreement with Thomas [14] but are very different from those found by Brodsky *et al.* [26] whose annealing curves show a non-zero spin density after crystallization. We think this behaviour can be attributed to the presence of magnetic impurities in their samples. In contrast, our samples are less contaminated, and the E.S.R. signal is due to dangling bonds. The g-values, linewidths and densities of spins that we have observed in a-Si, are shown in table I. The properties of the samples are independent of the deposition rate for rates varying from 10 to 40 Å/s.

The spin-lattice relaxation rate has been measured with an X-band modulation spectrometer, described elsewhere [15, 16]. The E.S.R. line is homogeneously broadened as previously shown by saturation experiments [17]. The variations of the signal amplitude with the modulation frequency are typical of a system with a single time constant. The dependences of the relaxation rate T_1^{-1} on temperature, T, and spin concentration, n, are shown in figure 2 for one unannealed and three annealed samples. At a given temperature, T_1^{-1} is proportional to n^3 (Fig. 3). At a

Table I. — E.S.R. *data obtained on evaporated amorphous silicon films.*

Samples	Spin concentration (cm^{-3})	g-value	ΔH_{pp} (G) 77 K	ΔH_{pp} (G) 300 K	Annealing Temperature (K)
a-Si(1)	1.5×10^{20}	2.0057 ±0.0005	4.5 ±0.2	7.8 ±0.4	unannealed
a-Si(2)	1.1×10^{20}	2.0057 ±0.0005	4.5 ±0.2	6.35 ±0.3	473
a-Si(3)	8.1×10^{19}	2.0057 ±0.0005	4.5 ±0.2	5.45 ±0.3	538
a-Si(4)	6×10^{19}	2.0057 ±0.0005	4.5 ±0.2	4.7 ±0.2	623

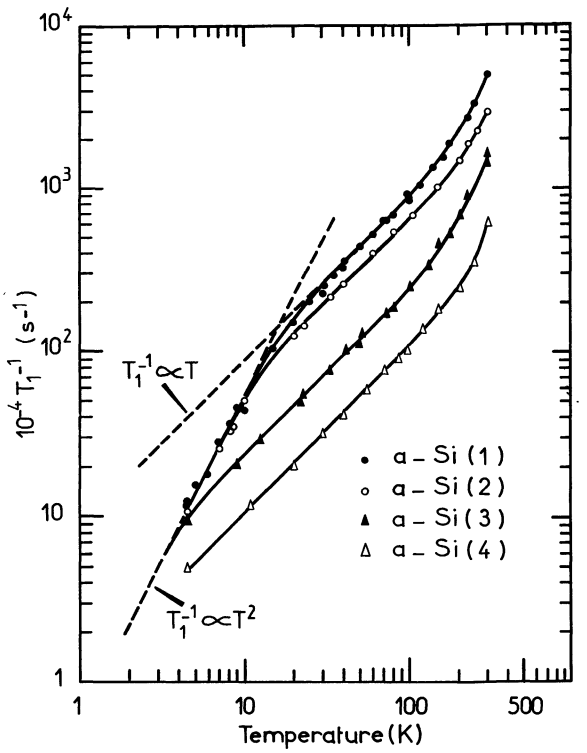

Fig. 2. — The S.L.R. rate measured at 9.4 GHz *versus* temperature for evaporated amorphous silicon films. The spin concentrations and annealing temperatures are shown in table I. The theoretical dependences $T_1^{-1} \propto T$ (direct process) and $T_1^{-1} \propto T^2$ (phonon bottleneck) are drawn with dashed lines.

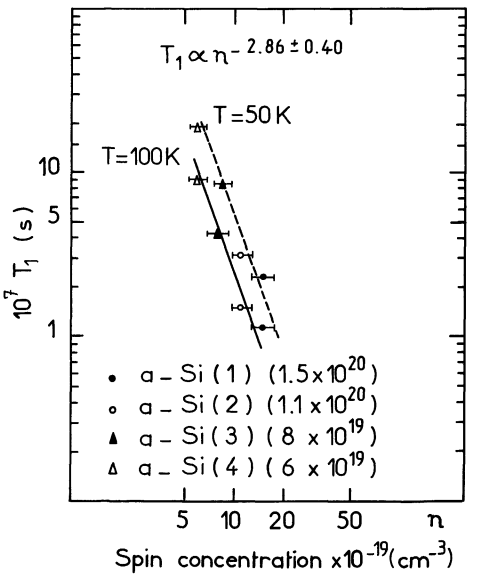

Fig. 3. — Influence of spin concentration on S.L.R. for a-Si films at 50 and 100 K. The slopes of the straight lines indicate that the relaxation time T_1 is proportional to n^{-3}.

given concentration, there are three distinct temperature regimes : (i) below 10 K where $T_1^{-1} \propto T^2$ for the most concentrated sample, (ii) in the range 10 to 100 K where $T_1^{-1} \propto T$, and (iii) above 100 K where the relaxation rate increases more quickly.

In the last case, the line broadening has exactly the same temperature dependence as the S.L.R. rate. The line is thus broadened by S.L.R. However, in amorphous materials, the linewidth is bound to the hopping conductivity [4, 9, 18], which means that S.L.R. is governed by hopping between 100 and 300 K. If hopping is effective, the relaxation rate can be written as $T_1^{-1} = T_{1h}^{-1} + T_{1ph}^{-1}$ where T_1^{-1}, T_{1h}^{-1} and T_{1ph}^{-1} are, respectively, the experimental value, the value due to the hopping process and the value due to the phonon process. Thus, T_{1h}^{-1} should satisfy the equation $T_{1h}^{-1} = K \exp(-T_0/T)^{-1/4}$. The experimental curves of log T_{1h}^{-1} *versus* $T^{-1/4}$ are plotted in figure 4. The value of T_{1ph}^{-1} has been found by extrapolating the temperature dependence of T_1^{-1}, below 100 K. The straight lines in figure 4 confirm that the dependence of T_{1h}^{-1} is characteristic of a hopping process [19]. Furthermore, T_0 can be determined from the slopes of these lines. The values obtained agree well with those found from electrical measurements [18, 20].

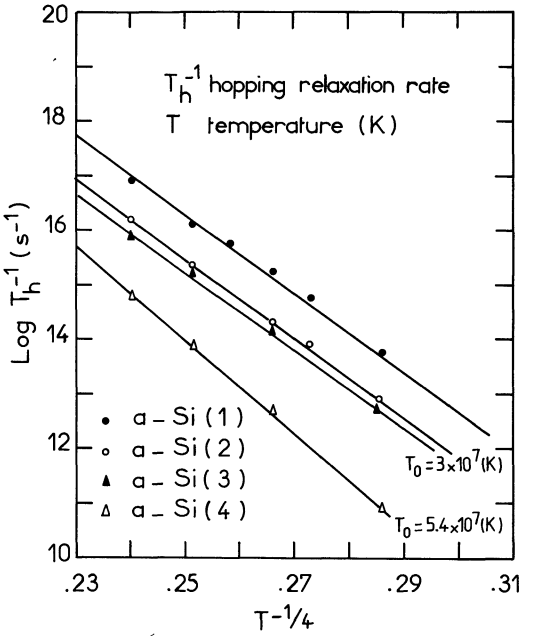

Fig. 4. — Influence of temperature on S.L.R. for a-Si films above 100 K. The relaxation rate T_{1h}^{-1} represents the value due to hopping process ; T is temperature. The straight lines confirm a dependence of T_{1h}^{-1} with temperature, characteristic of hopping

$$(T_{1h}^{-1} \propto \exp(-T_0/T)^{-1/4}).$$

The observation of a relaxation rate proportional to T, between 10 and 100 K, is quite surprising. One feature of the amorphous state seems to be the presence of localized vibrational phonon modes as postulated by Zeller *et al.* [21]. The high energy states being the most localized, the two phonon process becomes inefficient when the spins are placed far from these modes, thus excluding fast dependences such as $T_1^{-1} \propto T^7$ or T^9. To determine the origin of the linear temperature dependence, we note that the S.L.R. rate is concentration-dependent, in the temperature range investigated. Two concentration-dependent mechanisms can be considered. The first, initially proposed by Waller [22], is based upon passage of the Zeeman energy directly to the lattice, *via* the dipolar interaction. It gives $T_1^{-1} \propto n^2$. When applied to a-Si, it leads to values of T_1^{-1} too small by several orders of magnitude. The second mechanism, which strongly depends on concentration, has been developed by Bloembergen and Wang [23] : the Zeeman energy is transmitted to the lattice *via* an exchange interaction. It gives $T_{ZL} = T_{ZE} + T_{EL}$, where T_{ZL}, T_{ZE}, T_{EL} represent respectively the Zeeman-lattice, the Zeeman-exchange and the exchange-lattice relaxation times. We have calculated T_{ZE}^{-1} and T_{EL}^{-1} for a sample of spin concentration, 10^{20} cm^{-3}.

Assuming an exchange energy modulated by lattice vibrations [24], we find :

$$T_{ZE}^{-1} = \frac{\sqrt{2\pi}}{2\hbar^2} g^4 \beta^4 d^{-6} \omega_e^{-1} \exp\left(-\frac{\omega_0^2}{2\omega_e^2}\right),$$

where $\hbar$, g, β are the usual parameters, d is the distance between two neighbouring Si-atoms, ω_e is the exchange frequency and ω_0, the Zeeman frequency. Several authors [5, 6, 7, 9] have found a Curie temperature of about 1 K corresponding to

$$\omega_e \simeq 2 \times 10^{11} \text{ rad.s}^{-1}$$

for a-Si. Assuming $d = 5$ Å, the value for a single crystal, we find for $\omega_0 = 6 \times 10^{10}$ s^{-1},

$$T_{ZE}^{-1} = 2 \times 10^8 \text{ s}^{-1}.$$

The most likely mechanism for the exchange-lattice relaxation is through modulation of exchange by lattice vibrations. From the data of Griffiths [24], we find :

$$T_{EL}^{-1} = \frac{100 \lambda^2 a^2 \omega_e^4 k}{\pi \rho v^5} T$$

λ and a being, respectively, the damping term of the exchange integral and the average distance between adjacent spins. From conductivity measurements we obtain [20] $\lambda \sim 4 \times 10^{+7}$ cm^{-1}. The sound velocity is equal to 3×10^5 cm.s^{-1} and the density is equal to that of monocrystalline silicon $\rho = 2.35$ g.cm^{-3}. From these data we find : $T_{EL}^{-1} = 7.9 \times 10^4 T$ s^{-1}. In the temperature range of interest we have, $T_{EL} \gg T_{ZE}$ and $T_{ZL} \sim T_{EL}$. The calculated T_{ZL}-value agrees satisfactorily with the experimental results ($T_1 \sim 10^{-6}$ s at 10 K).

Finally, $T_{EL}^{-1} \propto a^2 \omega_e^4$ with $a \propto n^{-1/3}$ and $\omega_e = \omega_e^0 \exp(-\lambda a)$. Taking $\lambda \sim 4 \times 10^7$ cm^{-1} and $3 \times 10^{19} < n < 10^{20}$ spins.cm^{-3}, we get $\omega_e \propto n$ which leads to $T_{EL}^{-1} \propto n^{3.3}$. The agreement with the observed dependence $T_1^{-1} \propto n^{2.86 \pm 0.45}$ is acceptable.

Thus, the three-reservoirs-model accounts well for the S.L.R. over the temperature range investigated. Furthermore, the best-fitted value of 1 K for the exchange energy confirms the conclusions drawn by Bachus *et al.* [9] who attribute this high value to the strongly interacting spins within the clusters, whereas an anisotropic exchange responsible for a line broadening of about 10 G could be due to the interactions between clusters.

Below 10 K, the temperature dependence becomes : $T_1^{-1} \propto T^2$. Using the Scott and Jeffries model [25], we have calculated the temperature at which the bottleneck arises for a sample of spin concentration, 10^{20} cm^{-3}. We obtain 10 K in good agreement with experiment. Furthermore, the calculation leads to an increasing bottleneck temperature when n is increased which is also in accordance with experiment.

In summary, we have investigated spin-lattice relaxation in evaporated a-Si. The influence of annealing on the spin-concentration indicates the paramagnetic states are bound to structural defects. An anomalous *high temperature* single phonon process is observed and a significant exchange interaction has to be assumed to account for it. A phonon bottleneck is present at helium temperature. Finally, hopping is considered as being responsible for the fast spin-lattice relaxation observed above 100 K.

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