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ELECTRON PARAMAGNETIC RESONANCE AND RELAXATION OF AMORPHOUS SILICON BELOW 1 K

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Amorphous silicon, generated within crystalline Si by $^{28}Si^{+}$ ion implantation, exhibits an electron spin relaxation rate which varies with temperature as $T^{2.37}$ between 0.3 and 4.2 K. These results exclude the current model of a phonon-limited, direct relaxation mechanism in *a*-Si. A relaxation process, consistent with the known temperature variation, is outlined. EPR signal strengths, relative to a known paramagnet at temperatures near 1.2 and 0.4 K, put limits on an antiferromagnetic Curie–Weiss temperature of $0 \leqslant \theta \leqslant 0.06$ K.

OVER THE PAST eight years several papers have suggested that anomalous behavior is exhibited by the intrinsic dangling bond paramagnetism in *a*-Si [1–4]. One such feature is the possibility that small deviations from a strict Curie law temperature dependence appear in the strength of its electron paramagnetic resonance (EPR) signal. This deviation has been described by a $1/(T+\theta)$ dependence with θ in the range between 0 and 5 K and is sample dependent. A value of 5 K was reported by Fritzsche and Hudgens [1] from bulk susceptibility data. Brodsky and Title [2] measured the EPR signal of *a*-Si generated by glow discharge decomposition of silane gas and reported $\theta = 1.3 \pm 0.4$ K. By contrast, Thomas *et al.* [3] made *in situ* studies on ultra-high vacuum evaporated *a*-Si between 5 and 120 K and found good agreement with a strict Curie law within the accuracy of their temperature determination, which was ± 1 K. Our data are consistent with a value of $0 \leqslant \theta \leqslant 0.06$ K.

Another unusual property of *a*-Si is the temperature dependence of its electron spin–lattice relaxation (SLR) rate, $1/T_1$. Gourdon *et al.* [4] measured it in evaporated *a*-Si films between 4.2 and 290 K and reported a T^2 temperature dependence below 10 K which changed to a T dependence above 30 K in an unannealed sample. They attributed this to a phonon bottleneck [5–8]. A phonon bottleneck requires that the spins be more tightly coupled to the resonant frequency phonons than the latter are coupled to the thermal bath. The degree to which the relaxation is phonon-limited is determined by σ, the bottleneck factor [7]:

$$\sigma = (E_z/T_{1d})/(E_{ph}/T_{ph}), \tag{1}$$

where $E_z = 1/2\hbar\omega N \tanh(\hbar\omega/2kT)$ is the Zeeman energy of the system of N spins; $1/T_{1d}$ is the normal, direct process, spin relaxation rate with a temperature dependence of $R_0 \coth(\hbar\omega/2kT)$; $E_{ph} = 1/2\rho(\hbar\omega)\hbar^2\omega\Delta\omega \coth(\hbar\omega/2kT)$ is the energy of the phonon system at $\hbar\omega$ with an energy bandwidth $\hbar\Delta\omega$ determined by the homogeneous width of the EPR absorption lineshape; and T_{ph} is the phonon relaxation time. In the presence of a phonon bottleneck ($\sigma > 1$) the return of the spin system to thermal equilibrium after a saturating microwave pulse is governed by a pair of coupled non-linear differential equations [6, 7]. Near thermal equilibrium the resulting nonexponential recovery can be approximated as exponential with a time constant $(\sigma + 1)T_{1d}$. The observed (spin-bath) relaxation rate under conditions of a strong bottleneck ($\sigma \gg 1$) is

$$\frac{1}{T_b} = \frac{\rho(\hbar\omega)\hbar\Delta\omega}{NT_{ph}} \coth^2(\hbar\omega/2kT). \tag{2}$$

At high temperatures ($kT > \hbar\omega$) this reduces to the T^2 dependence reported by Gourdon *et al.* [4].

The requisite strong spin–phonon coupling would be unusual for spins with g values near 2.00 because of the small orbital moments. Furthermore, strongly phonon-limited conditions ($\sigma \gg 1$) cannot revert to normal conditions ($\sigma \ll 1$) with a tripling of the temperature since the T dependence of σ is $\tanh(\hbar\omega/2kT)$. Thus, on theoretical grounds, the bottleneck explanation

is unlikely to be correct. Working at 16.5 GHz and at temperatures as low as 0.3 K, we are able to rule out the $\coth^2(\hbar\omega/2kT)$ temperature dependence of a phonon bottleneck in favor of a simple T^n power law.

In this paper we present a discussion of our experimental apparatus, our relaxation data, the anomalous temperature dependence of the SLR rate, evidence against any antiferromagnetic exchange interaction between spins, and suggest a different relaxation mechanism for spins in *a*-Si.

Our Ku-band superheterodyne pulse spectrometer [9] incorporates a He-3 refrigerator as the upper wall of a cylindrical TE_{011} (wave meter) mode cavity which resonates near 16.5 GHz. This wall is thermally isolated from the others by a thin walled cupronickel He-3 pumping line so that temperatures as low as 0.3 K can be obtained. Under these conditions the remaining walls of the cavity are in contact with liquid He-4 at a temperature near 1.2 K, allowing the EPR spectrum of samples at two temperatures to be compared within the same cavity. Samples are inserted through the cavity bottom which is then sealed with an indium O-ring gasket. He-3 gas is liquified in a condenser at 1.2 K which opens via a beryllium-copper needle valve into the evaporation pot where it is pumped with a $150\,l\,s^{-1}$ diffusion pump. Temperatures are measured and controlled to a few millikelvin by a germanium resistance thermometer and a 22.4 Ω heater driven by a negative feedback temperature control system. Calibration of the germanium resistance thermometer between 4.2 and 1.2 K was based upon the vapor pressure of He-4. Below 1.2 K, it was calibrated by comparing the EPR signals from two samples of Nd-doped lanthanum magnesium nitrate $(La_2Mg_3(NO_3)_{12}x24H_2O$, abbreviated LMN:Nd, $g_\perp = 2.702$, $g_\parallel = 0.362$) – one in contact with the He-3 pot, the other at 1.2 K. These double nitrate samples were doped with Nd to 1 at.% to insure accurate thermometry assuming a simple Curie law paramagnetism. This assumption should be valid since magnetically concentrated cerium magnesium nitrate (CMN) is known to exhibit a simple Curie law paramagnetism into the millikelvin regime [10]. All temperatures we report here are corrected for temperature dependent magnetoresistance effects in the germanium resistance thermometer. Microwave power levels were under 50 pW during c.w. experiments.

An amorphous Si layer was produced by implanting 5×10^{15} 250 keV $^{28}Si^+\,cm^{-2}$ into high purity, vacuum float zone grown, crystalline silicon. This method produces very pure amorphous Si with consistent sample characteristics and minimal H, C, and O contamination. This amorphous layer is calculated [11, 12] to extend from the surface to a depth of 4600 Å and gives rise to the amorphous resonance having an isotropic, nearly

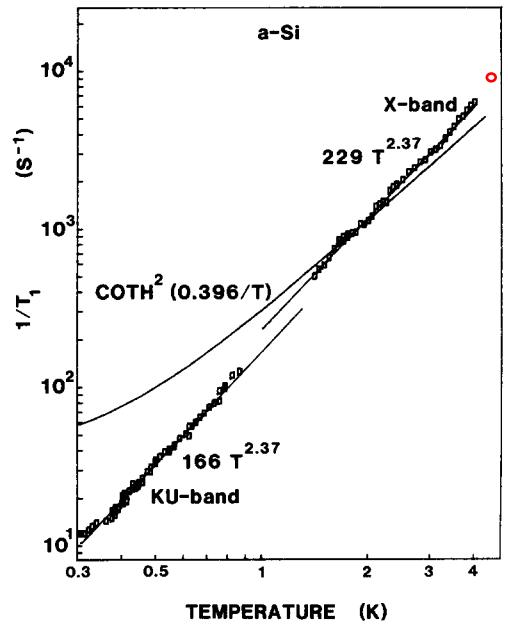

Fig. 1. Electron spin–lattice relaxation rates of the dangling bond paramagnetism in amorphous Si at 16.4985 and 9.489 GHz between $T = 0.3$ and 4.0 K. These pulse saturation-recovery data were constrained to fit the same power law in temperature, but allowed to yield different prefactors. A temperature dependence of $\coth^2(\hbar\omega/2kT)$, corresponding to a phonon-limited relaxation mechanism at Ku-band, is shown for comparison.

Lorentzian lineshape with a peak-to-peak derivative width of 7 G and a *g*-value of 2.0059. The density of these unpaired spins ($S = 1/2$) is $\approx 1 \times 10^{19}\,cm^{-3}$.

Figure 1 shows our combined relaxation data on the same sample of *a*-Si at Ku- and X-band frequencies, 16.4985 and 9.489 GHz, respectively. The X-band spectrometer has been described by Allen *et al.* [13] and is limited to liquid He-4 temperatures. As seen in Fig. 1, the temperature dependence of $1/T_1$ from both sets of data are well fit by a common T^n power law with $n = 2.37 \pm 0.06$. When fit separately the Ku- and X-band data fit best to $n = 2.39 \pm 0.09$ and $n = 2.34 \pm 0.07$, respectively. Shown in Fig. 1 for comparison is the theoretically predicted temperature variation for a phonon bottleneck at 16.5 GHz; that is, a $\coth^2(0.396/T)$ function scaled to meet the extrapolated Ku-band data at 4.0 K. The weak (38%) microwave frequency dependence might reflect a magnetic field dependence but it will be no stronger than $H^{-0.6}$. Our signal recoveries appeared exponential over the last 20–35% of the recovery, depending upon temperature. We believe that the data of Fig. 1 rule out a phonon bottleneck as the dominant relaxation mechanism in *a*-Si at low temperatures.

We made repeated measurements to determine if the

strength of the EPR signal in *a*-Si deviated from a normal $\tanh(\hbar\omega/2kT)$ temperature dependence. In these experiments, ratios in the intensities of the EPR signals from LMN:Nd and *a*-Si samples, both attached to the He-3 pot, were compared at 1.25 and 0.4 K. We found that within experimental error, the ratio of the peak-to-peak derivative heights equaled the ratio of the total areas under the EPR absorption curves. The latter were measured from the absorption derivative curves by mechanically computing the first moment using an Amsler Integrator. Apparent deviations from Curie law paramagnetism could be diminished by reducing the incident microwave power. The results at our lowest operating power (~ 50 pW) correspond to

$$\frac{\text{LMN:Nd (0.400 K)}}{\text{a-Si (0.400 K)}} \times \frac{\text{a-Si (1.25 K)}}{\text{LMN:Nd (1.25 K)}} = 1.02 \pm 0.02. \tag{3}$$

Modeling any deviation of equation (3) from unity in terms of an antiferromagnetic Curie–Weiss temperature, our results are consistent with

$$\tanh(0.396/T + \theta) \quad \text{with} \quad 0 \leqslant \theta \leqslant 0.06\ \text{K}. \tag{4}$$

Finally we wish to suggest once again [14] a mode of SLR which could account for the observed temperature dependence, which according to our data and that of Gourdon *et al.* [4] varies as $T^{2.37}$ at low temperatures and changes to approximately a T dependence between 10 and 30 K. The mechanism we suggest is one proposed originally by Lyo and Orbach [15] to account for the T^2 temperature dependence of the homogeneous optical linewidth in amorphous materials. Their application of this mechanism to electron spin relaxation remains unpublished, but detailed calculations were considered by Kurtz and Stapleton [16]. The relaxation mechanism involves spin coupling to a system of two level energy states (TLS) with energy splittings $E \gg \hbar\omega$ and a density of states $\rho(E)$. The TLS are strongly coupled to the phonons to produce fast TLS relaxation rates

$$\frac{1}{T_{\text{TLS}}} \propto E^3 \coth(E/2kT). \tag{5}$$

The E^3 factor arises from an E^2 density of phonon states and an additional factor of E from the creation or destruction of a phonon of energy E. This strong TLS–phonon coupling preserves thermal equilibrium while the spin system relaxes due to mutual TLS–spin transitions induced by a weak coupling between spins and nearby TLS.

The spin relaxation rate is computed using a mixed second-order perturbation calculation involving $\mathcal{H}_{T-S}$, the TLS–spin Hamiltonian, and $\mathcal{H}_{T-ph}$, the TLS–phonon Hamiltonian. As used here, $\mathcal{H}_{T-ph}$ creates or destroys a phonon of energy E, but leaves the TLS unchanged. $\mathcal{H}_{T-S}$, by contrast, flips both the spin and the TLS. This generates an energy denominator E from the lack of energy conservation in the intermediate state. The average spin relaxation rate (observed due to spin–spin interactions) follows a temperature dependence given by [16, 17]

$$\langle 1/T_1 \rangle_{av} \propto \int_0^{E_{\max}} \frac{E\rho(E)\,\mathrm{d}E}{\sinh(E/kT)}, \tag{6}$$

where $\rho(E)$ is the density of states of the TLS system and $E_{\max}$ is its cutoff value. If $\rho(E) \propto E^{\lambda}$, then equation (6) predicts a $T^{2+\lambda}$ temperature dependence at low temperatures ($T \ll E_{\max}/k$) and a T dependence at high temperatures.

One possible TLS system is tunneling states. A λ value of 0.37 is not unreasonable for tunneling states in amorphous materials. The low temperature heat capacity, thermal conductivity, and dielectric susceptibility of Li, Na and K β-alumina have been explained using a tunneling state density parameterized by $A(E/E_0)^{0.2} + B(E/E_0)^3$, where E_0 is a normalizing energy, $B/A \leqslant 10^{-4}$, and $E_{\max}/k \geqslant 65$ K [18]. Microwave frequency experiments [19], designed to detect the presence of charged tunneling states in our sample of *a*-Si, gave negative results. Nevertheless, of all electron spin relaxation mechanisms known to us, only the mechanism outlined above seems capable of explaining these data.

At this point little can be said concerning the identification of the TLS or their interaction with the paramagnetic electrons in *a*-Si. If $\langle 1/T_1 \rangle_{av}$ is to be nearly independent of magnetic field, $\mathcal{H}_{T-S}$ must be field independent. This rules out any modulation of the electrostatic field as the dominant relaxation mechanism since Kramers' theorem reduces such coupling to zero in the absence of a magnetic field. Hyperfine interactions are too rare (95.3% even–even nuclei) to provide the coupling.

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