

Nature of paramagnetic centers in *a*-Si and *a*-Si:H

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A comparative ESR study has been undertaken of various kinds of *a*-Si and *a*-Si:H. Experiments on sputtered samples reveal that the local configuration of the usual dangling-bond (DB) centers ($g \approx 2.0055$) depends on the details of deposition. The g value may gradually be reduced to values as low as 2.0041 as a result of local-structure change. Regarding the $g = 2.004$ signal originated from conduction-band-tail (CBT) states, it is shown that the effective correlation energy (U_{eff}) is large and the temperature dependence of its spin density is due to the presence of donor levels—not due to a small- U_{eff} effect as has previously been concluded. Related to this, ample evidence is provided, indicating that the $g = 2.004$ signal in P-doped *a*-Si:H and the $g = 2.005$ DB line are in fact variants of the same kind of defect. Systematic analysis identifies the $g = 2.004$ CBT states signal with $T_{\frac{3}{2}}^- - T_{\frac{3}{2}}^+ + e^-$ defect centers thus showing that a great deal of the CBT states are defect states rather than disorder-induced localized states. Regarding the $g = 2.013$ signal in *a*-Si:H, evidence is provided showing that this cannot be associated with valence-band-tail states. Rather it concerns defects positioned at ≈ 0.6 eV above the valence-band mobility edge, whose nature is as yet to be determined. Their presence relates directly or indirectly to H incorporation.

I. INTRODUCTION

The dominant defects in amorphous Si (*a*-Si) and hydrogenated amorphous Si (*a*-Si:H) are believed to be threefold-coordinated Si centers or dangling bonds (DB's) denoted as T_a^0 in Adler's notation;¹ these are observed by dark electron-spin resonance^{2,3} (ESR) in *a*-Si and undoped *a*-Si:H with spectroscopic splitting factor $g \approx 2.0055$. The effective correlation energy U_{eff} is accepted to be⁴ ≈ 0.3 eV. Recently,⁵ however, some doubt has been cast upon the undercoordinated character of the $g = 2.0055$ defect; instead, it has been proposed that most of the ESR-active defects are fivefold-coordinated Si center, labelled as "floating bonds." In addition, two other signals with $g \approx 2.004$ and 2.01 were observed either by dark ESR in, respectively, P-doped and B-doped^{4,6,7} *a*-Si:H or by light-induced ESR (LESR) in^{8,9} intrinsic device-quality *a*-Si:H. These were conventionally^{7,8} attributed to conduction-band-tail (CBT) electrons and valence-band-tail (VBT) holes, respectively. However, little is known about the nature of these localized centers and various difficulties¹⁰ are met with this conventional model. It is clear that more information is desired to clarify all these problems.

The distinction between the DB and $g \approx 2.004$ CBT states line is largely based on the fact that they have unequal g and U_{eff} values and usually, different line shapes too.^{6,7} Also the position of their respective energy levels in the band gap differs.^{6,7} The present article will demonstrate that the g -value difference is not substantial by showing that the DB line may also exhibit a g value of 2.004, depending on the local structure of the DB defects. The value $U_{\text{eff}} = 10$ meV determined before¹¹ for the $g = 2.004$ CBT states line will be shown to be spurious; the actual U_{eff} is much larger. *K*-band (20.9 GHz) ESR experiments on P-doped *a*-Si:H reveal that the line shape

of the $g \approx 2.004$ signal at 77 K is asymmetric similar to the asymmetry of the DB line in ³ *a*-Si:H. These results and other experimental facts favor the identification that the $g \approx 2.004$ line also arises from a DB-type defect which is, as will be shown, in accordance with theoretical predictions. In regards to the $g \approx 2.01$ line we succeeded in observing this signal in a slightly B-doped *a*-Si:H with activation energy $E_a = 0.87$ eV as derived from the dc electrical conductivity measurement. This casts doubt on the conventional model where the $g \approx 2.01$ line is associated with the VBT states.

II. EXPERIMENTAL

Samples fabricated by different methods were studied, viz., intrinsic, P- and B-doped glow-discharge (GD) deposited *a*-Si:H and sputtered *a*-Si and *a*-Si:H. This allows a direct comparison in one spectrometer of the pertinent defect features over various preparation methods. The GD specimens are deposited on Al foil using 5 W of rf power in a capacitively-coupled system filled with pure SiH₄ or PH₃ (1 vol %)/SiH₄ (99 vol %) for intrinsic and P-doped *a*-Si:H, respectively. For ESR measurements, the Al substrate was etched off in a mixture of H₃PO₄, H₂SO₄, and HNO₃ at $T \approx 40^\circ\text{C}$. The slight B doping arose as a result of residual B atoms left in the deposition chamber. As determined by secondary ion mass spectroscopy (SIMS) the B concentration in the *a*-Si:H film is 10 at. ppm. The substrate temperature T_S during deposition was 270°C, 200°C, and 250°C for the intrinsic, P-doped, and B-doped samples, respectively.

Details of the sputtering setup and part of the sputtered materials were described elsewhere.¹² Prior to the sputtering the deposition chamber was pumped to a base pressure $\approx 10^{-6}$ Torr using a turbo molecular pump. Both pure *a*-Si and hydrogenated *a*-Si:H films were

prepared and different deposition rates (r_d) were realized by changing the rf power W from 50 to 180 W; the substrates, held at room temperature (RT) by water cooling, were high-purity ($\geq 99.9999\%$) quartz plates. Some of the sputter deposition parameters are listed in Table I. Samples within one set (i.e., A or S : cf. Table I) were deposited sequentially under identical circumstances apart, of course, from those parameters monitoring r_d . An exception to this is sample A which was fabricated under a somewhat less accurately defined pressure setting. After initial ESR measurements the sputtered films were annealed at $T_A=200^\circ\text{C}$ for 30 min in vacuum (pressure $p \leq 10^{-4}$ Torr).

ESR experiments were carried out in the temperature range $77 \leq T \leq 320$ K using X - (9.0 GHz) and K - (20.9 GHz) band homodyne spectrometers driven in the absorption mode under conditions of adiabatic slow passage. Application of the magnetic-field modulation technique resulted in the detection of absorption-derivative dP_μ/dB spectra; P_μ and B represent the microwave power in the cylindrical TE_{011} cavity ($Q \approx 4000$) and externally-applied magnetic induction, respectively.

III. RESULTS AND INTERPRETATION

A. Intrinsic and P-doped GD a -Si:H

The intrinsic GD a -Si:H exhibits the usual DB line with T -independent $g = 2.0055 \pm 0.0001$. The peak-to-peak width of the absorption-derivative signal $\Delta B_{pp} = 14.0 \pm 0.5$ G at K band and 7.5 ± 0.3 G at X band, revealing the inhomogeneous linewidth broadening. The spin density N_S is about $2 \times 10^{17} \text{ cm}^{-3}$. The line shape was found to be asymmetric exhibiting a nearly Gaussian shape on the high-magnetic-field side and near-Lorentzian shape on the low-field side in agreement with previous results.³

As expected the P-doped GD a -Si:H film exhibits an ESR line with $g = 2.0044 \pm 0.0001$; this g value remains *unaltered* over the whole T range measured ($77 \leq T \leq 320$ K). From dc electrical dark conductivity (σ) measurements the value $E_a = 0.28$ eV was found for the activation energy while $\sigma(295 \text{ K}) \equiv \sigma_{RT} = 1 \times 10^{-4} (\Omega \text{ cm})^{-1}$. This $g = 2.0044$ line has conventionally been ascribed^{7,8} to electrons in the CBT states, and weak bonds are now widely accepted⁴ as the corresponding microscopic origin.

Figure 1 presents a K -band spectrum obtained at 77 K. A new interesting feature is that the line shape is *asym-*

metric; it shows up Lorentzian and nearly Gaussian at the low- and high-field side, respectively. The ratio Y'_L/Y'_H is 0.85, where Y'_L and Y'_H are the amplitudes of the low- and high-field peak, respectively. At X band this asymmetric feature cannot be clearly unveiled although the line shape appears to be asymmetric too. At 77 K $\Delta B_{pp} = 6.3 \pm 0.3$ G at X band and 11.0 ± 0.3 G at K band; both are smaller compared with the DB linewidth of the intrinsic a -Si:H. The line-shape factor, defined as

$$l \equiv \frac{2A}{(Y'_L + Y'_H)\Delta B_{pp}^2}, \quad (1)$$

where A is the area under the absorption curve has also been analyzed. At K band, $l = 2.2 \pm 0.2$ and increases to 2.9 ± 0.2 at X band which is in accordance with the previously reported⁷ value; since the relative importance of the frequency-independent intrinsic linewidth ΔB_{pp}^i increases at lower observational frequency (f), the intrinsic line shape must be roughly Lorentzian. The small deviation from the Gaussian line shape at the high-field side in Fig. 1 is probably due to the contribution of this Lorentzian-like intrinsic line which is more pronounced at X band. It is interesting to note that quite a similar line shape has also been observed³ for the DB ($g = 2.0055$) line in less defective intrinsic material ($N_S \leq 10^{19} \text{ cm}^{-3}$) by dark ESR. Also, such an asymmetric $g = 2.004$ signal has been observed¹³ by LESR in intrinsic a -Si:H. This quite specific asymmetric line shape of the $g = 2.004$ line arises, as pointed¹³ out by Street and Biegelsen for the case of the usual $g = 2.0055$ DB line, because the corresponding defect centers are axially symmetric and g_\perp is expected to be broadened by lattice fluctuations much more than g_\parallel , where $g_\perp > g_\parallel$. From the frequency dependence of ΔB_{pp} , both ΔB_{pp}^i and the g -spectrum width (inhomogeneous broadening) ΔB_{pp}^g can be estimated.⁷ For the $g = 2.0044$ line, our results give $\Delta B_{pp}^i = 2.7$ G and ΔB_{pp}^g (X band) = 3.6 G. Comparing with the characteristics of the DB line,^{7,14} it can be concluded that the $g = 2.004$ line and the DB line have similar ΔB_{pp}^i , but the g spectrum of the former is smaller which is the main reason for the linewidth difference mentioned above. This can be understood as the consequence of a smaller g_\perp value in accordance with the smaller average g value (2.004).

Figure 2 shows the temperature dependence of ΔB_{pp} and l both at X and K band. The linewidth remains constant up to ≈ 150 K and then starts to increase at both frequencies. At ≈ 230 K, the line has turned symmetric with $l \approx 3.6$ at both frequencies. However, as may be

TABLE I. Sample preparation characteristics of the sputtered a -Si and a -Si:H films.

Sample	B1	A1	A2	A3	A4	A5	S1	S2	S3
Ambient	Ar	Ar	Ar	Ar	Ar	97% Ar + 3%H ₂ ^a	Ar	99%Ar + 1%H ₂ ^a	97%Ar + 3%H ₂ ^a
P_a^b (mTorr)	10	12	9	9	9	11	8	10	8
W (watt)	130	180	150	100	50	100	100	100	100
r_d (nms ⁻¹)	0.058	0.061	0.044	0.038	0.015	0.035	0.030	0.024	0.028

^aIn vol %.

^b P_a is ambient pressure during sputtering.

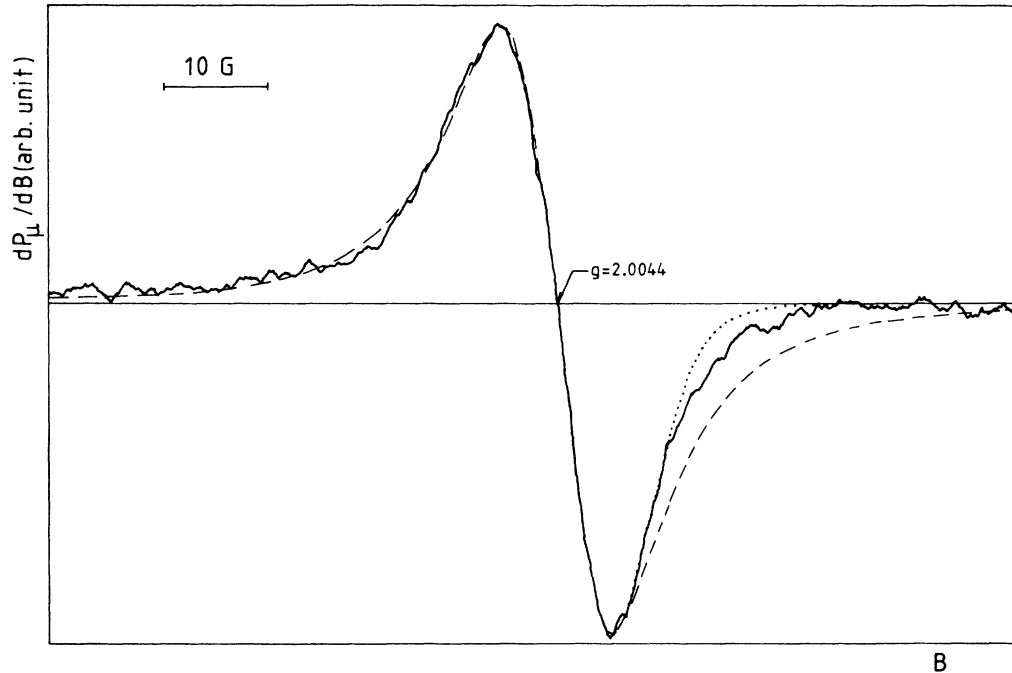


FIG. 1. K-band (20.9 GHz) absorption-derivative ESR spectrum (solid line) measured at 77 K with $P_\mu = -2.4$ dBm on P-doped *a*-Si:H glow-discharge deposited in a PH_3 (1 vol %)/ SiH_4 (99 vol %) ambient. The dashed and dotted lines represent computer-calculated Lorentzian and Gaussian line shapes, respectively, scaled to the experimental curve at the peak positions.

seen from Fig. 2 also, a strong increase of l is noticed above 250 K, which should be very interesting. At 320 K, l reaches a value as high as 8.2 ± 0.7 at K band which is significantly larger than 3.6. Despite all the changes in line shape, the spin density of the 2.0044 line, given as $N_S = (8 \pm 0.8) \times 10^{16} \text{ cm}^{-3}$ and which is obtained by double numerical integration of the dP_μ/dB spectra over a

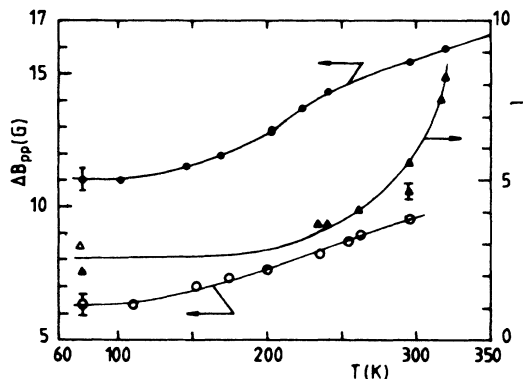


FIG. 2. Observed peak-to-peak linewidth ΔB_{pp} and line-shape factor l vs T of P-doped *a*-Si:H glow-discharge deposited in a PH_3 (1 vol %)/ SiH_4 (99 vol %) ambient. The line-shape factor was calculated along relation (1). The open and solid circles represent data obtained at X band (9.0 GHz) and K band (20.9 GHz), respectively. Notice the strong increase of l above the Lorentz line factor (i.e., 3.6) for $T > 250$ K. The solid curves are only meant to guide the eye.

sufficiently broad range, remains perfectly constant over the whole range $77 \leq T \leq 320$ K. At variance herewith, it has previously been reported^{6,11} that N_S does change with T above ≈ 150 K although the details depend strongly on sample preparation methods and doping levels.

One of the possible explanations for the former N_S change, as suggested before,¹¹ is a small- U_{eff} value of about 10 meV. However, this explanation can hardly be reconciled with the fact that N_S increases nearly a factor of 4 over a small temperature range of barely 40 K whereas it remains constant for $T < 180$ K as reported by Hasegawa, Kasajima, and Shimizu;⁶ the latter authors also showed that the temperature dependence of N_S depends strongly on doping level, a fact that the small- U_{eff} interpretation failed to face up to. In our case when σ reaches the value of $1 \times 10^{-4} (\Omega \text{ cm})^{-1}$ at RT, the corresponding ΔB_{pp} at X band increases about 3 G compared with the low- T value (6.3 G). This σ versus ΔB_{pp} relationship is in perfect agreement with the results¹¹ of Dersch, Stuke, and Beichler, although in their case the conductivity reaches the value of $1 \times 10^{-4} (\Omega \text{ cm})^{-1}$ at a much lower temperature (≈ 195 K) due to the smaller activation energy (0.2 eV). This observation supports the view that the line broadening is strongly correlated with the number of conduction electrons.¹¹ We also noticed that as long as the line broadening at X band is less than about 3 G, the N_S change is not discernible.^{6,11} This is in agreement with our results too, where N_S remains constant even up to 320 K. The latter also directly indicates that U_{eff} is large. It is clear that no specific temperature

can be associated with the starting point of N_S increase as would be expected for the small- U_{eff} effect. This supports the recent suggestion⁴ of Stutzmann *et al.* that the N_S change is simply due to the partial recapture of thermalized donor electrons by the $g=2.004$ centers owing to the differing density of states distribution of donors and $g=2.004$ centers. In support, by comparing the number of electrons in the CBT of P-doped α -Si:H as determined by the sweep-out technique and the number of spins of the 2.004 line measured by ESR at 40 K, Street and Zesch¹⁵ concluded that even at low temperature ESR measures essentially all of the CBT electrons and that the correlation energy U_{eff} cannot be very small.

Another interesting feature which appears in Fig. 2 is that the $g=2.004$ line remains inhomogeneously broadened even at high temperatures. Moreover, a rough estimate shows that the g spectrum is even broader at RT (4.5 G) than at 77 K. It can be easily shown that for an exponential density-of-states distribution with a characteristic temperature¹⁶ T_C of about 300 K, the singly-occupied states distribute at RT over a much broader energy range than at 77 K and energy levels closer to the conduction-band mobility edge E_C become occupied. Hence the conclusion that the g -value distribution of the spin centers closer to E_C is broader than those far from E_C ; consequently, spin centers associated with the flanks of the g spectrum at high temperatures must mainly originate from spin centers closer to E_C . The average g value, however, is temperature independent indicating that the average g value does not vary with energy levels. In addition to the g -spectrum broadening, the intrinsic linewidth ΔB_{pp}^i also increases from ~ 2.7 G at 77 K to about 5 G at RT due to the lifetime broadening via interactions with conduction electrons.¹¹ Since l largely exceeds the Lorentzian line-shape factor 3.6 at high temperatures, there must be a broad distribution in intrinsic linewidth, viz., spin-lattice relaxation time¹⁷ T_1 . Presumably, T_1 is smaller (broader lines) on the flanks of the g spectrum than in its central part at high temperatures, since l is larger at K band than at X band above RT. This can be understood since spins closer to E_C relax more easily via conduction electrons⁴ than those far from E_C , in agreement with the recent suggestion of Stutzmann *et al.* that part of the CBT state electrons closer to E_C cannot be detected by ESR due to rapid spin-lattice relaxation.

B. B-doped α -Si:H

In the B-doped sample, we observed the usual³ DB line with $g=2.0053$ characterized by $\Delta B_{\text{pp}}(K \text{ band}) = 14.0 \pm 0.3$ G, $\Delta B_{\text{pp}}(X \text{ band}) = 7.5 \pm 0.3$ G, and $N_S = 2.5 \times 10^{16} \text{ cm}^{-3}$. All four quantities did not show any temperature dependence from 77 to 300 K. Additionally, we also observed a broad line with K -band characteristics $g=2.013 \pm 0.001$ and $\Delta B_{\text{pp}} = 32$ G staying unaltered from 77 K to RT. The N_S of this broad line is $1.0 \times 10^{16} \text{ cm}^{-3}$. A RT K -band spectrum is shown in Fig. 3. The broad line is computer fitted by a symmetric line

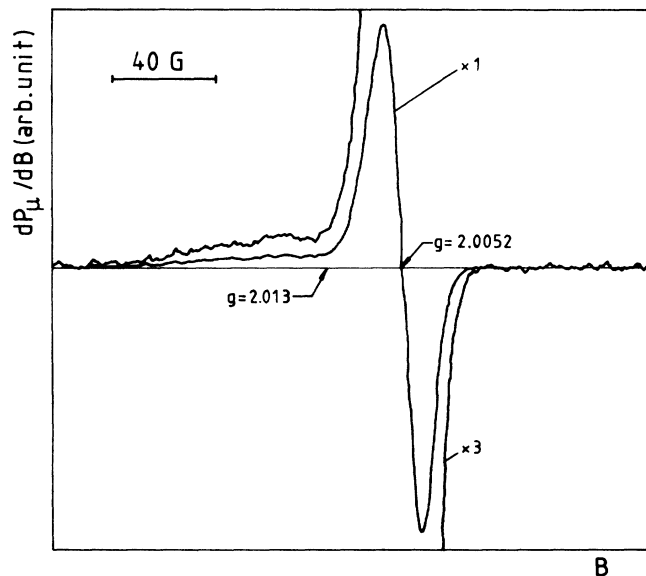


FIG. 3. K band absorption-derivative ESR spectrum measured at 295 K with $P_\mu = 0$ dBm on slightly B-doped α -Si:H ($E_a = 0.87$ eV). From the three-times-expanded curve, the presence of the broad $g=2.013$ signal is clearly recognized. This signal may be computer simulated by a symmetric linewidth $l = 1.8$.

with $l = 1.8$. This line is only observable at K band. At X band, it disappears under the shoulder of the DB line. This signal is undoubtedly the ESR signal conventionally attributed^{7,8} to VBT states. However, the Fermi level is still quite far from E_V as follows from dc conductivity experiments which give an activation energy of 0.87 eV and $\sigma_{\text{RT}} = 6 \times 10^{-12} (\Omega \text{ cm})^{-1}$. Thus, E_F is nearly at midgap, which is a typical result for a slightly B-doped sample.^{18,19}

Time-of-flight¹⁶ and optical absorption experiments²⁰ show that the density of the VBT states distributes exponentially with the characteristic temperature $T_C \approx 487$ to 580 K. With a preexponential factor $g_0 = 3 \times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$ and $T_C = 580$ K it can be shown that maximally (for $U_{\text{eff}} = \infty$) the possible contribution to the observed N_S from this density of states is less than $1 \times 10^{16} \text{ cm}^{-3}$ when $E_F - E_V$ is larger than 0.5 eV. With increasing $E_F - E_V$, the situation gets worse. Since $E_F - E_V$ in our case is about 0.8 eV, we rather feel that it is more reasonable to associate the $g=2.013$ signal with defect states which have a distribution in the lower part of the band gap. Even in this model it is hard to propose a defect-state peak which does not disturb the exponential form of the VBT states significantly while giving a spin density as high as $\approx 1 \times 10^{19} \text{ cm}^{-3}$ as observed in some,^{6,7} but not all,⁴ heavily B-doped samples. This suggests that defects with $g=2.01$ might be rare in undoped material and might be enhanced by B doping. An acceptorlike defect peak with a Gaussian distribution and a standard deviation $\sigma = 0.15$ eV centered at $E_V + 0.6$ eV gives $1 \times 10^{16} \text{ cm}^{-3}$ spins for $E_F - E_V = 0.8$ eV, in agreement with the present observations.

C. Sputtered *a*-Si and *a*-Si:H

The slowly sputtered ($r_d < 0.05$ nm/s) specimens show some unusual but quite interesting features. As reported before¹² an ESR signal with $g \approx 2.0041$ has been observed in slowly-deposited *a*-Si and *a*-Si:H, which is far from the expected DB value ($g = 2.0055$) but quite near to the value $g = 2.0043$ observed in heavily P-doped *a*-Si:H by dark ESR (Refs. 6 and 7) or in intrinsic *a*-Si:H by LESR.⁸

To further investigate the nature of this "low"- g center, a series of films were sputter deposited with gradually decreasing r_d listed as series *A* in Table I. In all *as-deposited* samples of pure *a*-Si a *symmetric* ESR signal (referred to as signal I) with $2.0041 \leq g \leq 2.0051$ independent of observational frequency and temperature has been observed; its line shape is nearly Lorentzian at *X* band. In *a*-Si:H (i.e., *A5*, *S2*), this signal is asymmetric at *K* band with more Lorentzian character at the low-field than at the high-field side. This line-shape change with hydrogenation is identical to the line-shape change of the standard DB line³ ($g = 2.0055$). The susceptibility follows the Curie law between $4 < T \leq 300$ K. From the *A*-series data we notice the *gradual* decrease of g along with decreasing r_d while keeping the Ar pressure constant. No systematic change of N_S and line shape or two-line structure along with g could be observed. Together with the fact that the energy level of the corresponding defect states is near midgap,¹² this suggests that the $g = 2.0041$ ESR signal in our experiments also arises from DB's.

Table II lists various ESR properties of signal I, observed in these samples at $T = 300$ K both before and after annealing at $T_A = 200^\circ\text{C}$. This annealing treatment

does not change g . From the f dependence of ΔB_{pp} and l , it appears that the signal is inhomogeneously broadened. However, owing to the high spin density in some samples the line is exchange narrowed leading to a nearly Lorentzian line shape. With annealing N_S decreases slightly, and the line shape obtains a more Gaussian character accompanied by the decrease of l . The inhomogeneously broadened nature of the low- g signal appears quite clearly from, for example, sample *S1* annealed at 200°C ; both l and ΔB_{pp} depend strongly on observational frequency. These results are typical for the usual ($g \approx 2.0055$) DB line observed on highly defective materials.²¹ Note that ΔB_{pp} of sample *S2* is much broader than for the other samples. In less defective material where exchange narrowing is not significant ΔB_{pp} (*X* band) only amounts to ≈ 7.5 G (cf. the undoped and the B-doped GD *a*-Si:H samples discussed), whereas for sample *S2*, ΔB_{pp} (*X* band) = 11.0 G. Interestingly, the electron diffraction pattern of *S2*, reveals that microcrystallites exist in this sample. The (220) and (311) rings of *c*-Si are clearly seen to lie on the second amorphous ring. Other samples did not show such sharp diffraction rings. The formation of the microcrystalline structure is probably, among others, enhanced by the presence of H atoms during deposition; $(-\text{SiH}_2)_n$ polymers might also be formed. This analysis suggests that ΔB_{pp} of the low- g centers can be broadened by the formation of microcrystallites or $(-\text{SiH}_2)_n$ polymers.²²

Regarding the hydrogenated *a*-Si:H films, similar to the newly-observed ESR signal of $g = 2.012$ (\equiv signal II) in *S2* reported before,¹² a signal with $g = 2.013$ and intensity $I \propto T^{-1}$ was observed in the *as-deposited* sample *A5*.

TABLE II. Summary of *X*- (9.0 GHz) and *K*- (20.9 GHz) band ESR data of signal I obtained at 300 K on sputtered *a*-Si and *a*-Si:H samples in the *as-deposited* state and after annealing at $T_A = 200^\circ\text{C}$ in vacuum for 30 min.

Sample	g (± 0.0001)	N_S^a (cm^{-3}) ^a	ΔB_{pp} (9.0 GHz)	ΔB_{pp} (20.9 GHz)	l (9.0 GHz)	l (20.9 GHz)
<i>B1</i> :AD ^b	2.0051	2.7×10^{18}		8.4 ± 0.3		1.2
<i>A1</i> :AD	2.0047	1.3×10^{20}	4.6	5.4 ± 0.3	3.3 ± 0.3	3.1 ± 0.3
:AN ^b	2.0047	1.1×10^{20}	4.2	5.8 ± 0.3	3.4 ± 0.3	3.3 ± 0.3
<i>A2</i> :AD	2.0046	8.0×10^{19}	4.4 ± 0.3	5.3	3.1	3.1
:AN	2.0046	6.8×10^{19}	4.3 ± 0.3	6.0	2.8	2.3
<i>A3</i> :AD	2.0045	7.0×10^{19}	4.5	5.3	3.3	3.0
:AN	2.0045	3.7×10^{19}	4.7	8.0	2.7	2.4
<i>A4</i> :AD	2.0042	6.5×10^{19}	5.7	7.4	3.0	2.6
:AN	2.0042	2.9×10^{19}	6.2	11.2	2.4 ± 0.3	2.4 ± 0.3
<i>A5</i> :AD	2.0046	8.7×10^{18}	7.0	12.0	2.4	2.1
:AN	2.0046	1×10^{17}		14.5 ± 0.5		
<i>S1</i> :AD	2.0041	1.0×10^{20}	6.7	9.5	3.5	3.6
:AN	2.0041	7.2×10^{19}	7.0	10.2	3.4	2.6
<i>S2</i> :AD	2.0042	1.4×10^{19}	11.0 ± 0.5	17.0 ± 1.0		
:AN	2.0042	8.0×10^{17}	9.0 ± 1.0	16.0 ± 1.0		
<i>S3</i> :AD	2.0042	2.5×10^{19}	6.4	11.3 ± 0.5	3.3	2.6
:AN	2.0042	1.0×10^{19}		10.8		2.0

^aEstimated absolute error 20%; relative error 5%.

^bAD: *as-deposited*. AN: *annealed*.

The linewidth ($\Delta B_{pp} = 28 \pm 3$ G), however, is smaller than the *S2* one. As shown in Table II, N_S (signal I) decreases rapidly with annealing for samples *A5* and *S2*, but not for *S3* from where it is concluded that *B5* and *S2* contain much more hydrogen than *S3*. This suggests that signal II is somehow correlated with H incorporation.²³ We identify²³ this signal II with the broad line observed in the B-doped *a*-Si:H.

As extensively outlined previously,¹² any possible impurity influences on the *g*-value change and the presence of line II could be excluded. Recent quantitative SIMS profiling affirmed former findings, that is to say, no impurity other than Ar was found to be present above the 1% level. Also, the high N_S values of signal I and its slow decrease with annealing in the pure *a*-Si films (cf. Table II) point at a low-*O* contamination.

IV. DISCUSSION

A. The DB nature of the $g = 2.004$ signal in sputtered material

A scan through literature shows that there exists a considerable variation²⁴ in DB *g* value, i.e., $2.0045 \leq g \leq 2.0061$ over the various *a*-Si and *a*-Si:H films studied. Apparently, all these signals were identified with the DB signal without having bothered much about the *g* divergencies. If we further add to this our signal-I results on the gradual decrease of *g* along with r_d in sputtered samples one may conclude that the DB *g* value may vary over a range as substantial as $2.0041 \leq g \leq 2.0061$, depending on the particular preparation method and conditions.

The *g* changes are believed to be related to differences in local configurations.²⁵ *a*-Si and *a*-Si:H lattices are thought to be far from equilibrium because they are not cooled from the melt. Except perhaps the DB's in the highest-quality *a*-Si:H (i.e., very low N_S), which are probably thermally generated,²⁶ most of the DB's are built in during the film growth to relieve strain in the overconstrained network. Therefore, their local configurations are expected to be sensitively dependent on preparation conditions. As the deposition rate changes by varying the rf power, circumstances such as free-surface ion bombardment may alter. Transmission electron microscopy experiments show that our films deposited with high r_d (e.g., *A1*) are more homogeneous than films deposited with low r_d . Although the specific variations in the deposition process with decreasing r_d are not yet fully understood, the influence of the latter on film structure and DB *g* value is clearly revealed by the present experiments.

The DB *g* value has been calculated²⁷ by Ishii, Kumeda, and Shimizu using an extended Hückel theory for a 13-atom cluster. Bond lengths and bond angles are the same as in *c*-Si. For this DB defect, $g = 2.0061$ is found as the average over the principal *g*-tensor values. When the DB-bearing atom was allowed to move vertically towards the plane of the three pyramidally backbonded Si atoms by 0.033 nm the DB *g* value decreased to 2.0045. Compared to our data these results suggest that the DB's in the slowly sputtered samples, influenced (among oth-

ers) by ion bombardment, are backrelaxed in a similar way. It appears that the DB *g* value does not depend sensitively on its energy-level position in the band gap since the *g* value keeps constant over a quite wide range of energies.⁷

B. The DB nature of the $g = 2.004$ signal in P-doped *a*-Si:H

The high resemblance, namely, similar in *g* value, U_{eff} , ΔB_{pp} , and line shape between the DB line and the 2.004 line observed in P-doped *a*-Si:H is striking. The $g = 2.004$ signal appears to behave as a variant of T_3^0 positioned at a different *E* level in the bandgap as suggested by the unequal behavior regarding E_F shifts⁷ (doping). With this respect the electron-nuclear double resonance (ENDOR) and electron-spin-echo envelope-modulation experiments²⁸ are worth mentioning. This report indicates that the wave function extents of the DB centers and the $g = 2.004$ centers of the CBT states are actually quite similar. These researchers suggest that the $g = 2.004$ signal originates from more localized electrons, such as DB centers. This is consistent with our conclusion that U_{eff} of the $g = 2.004$ line is not small. Hence, experimental results suggest that the $g = 2.004$ line in P-doped *a*-Si:H (including the one observed in *a*-Si:H by LESR) also arises from DB-type defects, and in view of the close similarities one is almost forced to associate the $g = 2.004$ signal with the close variant of T_3^0 , i.e., $T_3^+ + e^-$. In case the signal would arise from disorder present in *a*-Si, large variations in *g* and ΔB_{pp} would be expected¹ when the Fermi level changes over about 0.15 eV; the deeper these states are in the bandgap, the larger the disorder they pertain to. However, the $g = 2.004$ line is observed to be identical over this energy range.^{6,7}

Recently, Bar-Yam and Joannopoulos²⁹ (BJ) showed theoretically that U_{eff} of the DB is negative if sufficient lattice relaxation is allowed; however, lattice relaxation might be prevented by a high potential barrier due to highly overconstrained network.³⁰ Interestingly, it becomes now clear that H atoms in *a*-Si:H are distributed inhomogeneously.³¹ In the vicinity of H-rich regions where the network is less constrained, U_{eff} can be negative during film growth. The neutral DB's then transfer to positively- and negatively-charged centers T_3^+ and T_3^- , namely,



concurrent with lattice relaxations.¹ A spatially-close $T_3^+ - T_3^-$ pair will form an intimate charge transfer defect (ICTD) which is energetically more favorable due to the extra Coulomb interaction;¹ the energy reduction by forming such an ICTD compared to the uncorrelated T_3^+ and T_3^- is estimated to be larger than¹ 0.5 eV. Hence, an electron captured by T_3^+ of an ICTD occupies a higher energy level than the usual DB state. The distribution of the density of states for such ICTD is expected¹ to be roughly exponential which is consistent with the observed CBT states distribution. In the H-poor region usual DB's with positive U_{eff} may exist because the lattice is not flexible enough without help of the strain-

relieving H atoms.

When an electron—supplied either by donors (E_F shift) or light excitation—is trapped at T_3^+ of an ICTD, i.e., $T_3^+ + e^- \rightarrow T_3^{*0}$, a DB-type paramagnetic center is formed which is identified with the $g=2.004$ CBT states line. Although a weak local-structure relaxation would accompany such capturing process the local configuration of T_3^{*0} remains much closer to T_3^+ . This is because the Si network is essentially fixed during deposition. According to²⁹ BJ the DB-bearing atom of a T_3^+ defect has moved to the plane of the three backbonded Si atoms over about 0.038 nm compared to the original neutral T_3^0 position, whereas the other atoms remain nearly at the same position. As already cited, along Ref. 27, such backward shift over 0.033 nm decreases g from 2.0061 to 2.0045. Hence, T_3^{*0} should exhibit a lower g value (also a smaller g spectrum) than the usual DB centers in agreement with experiment.

Previously, we concluded that the $g=2.004$ centers in P-doped *a*-Si:H make up a great deal of the CBT states. In view of our identification with $T_3^+ + e^-$ centers, it follows that the main part of the CBT states originates from ICTD centers. Comparing with weak bonds, such ICTD centers have a larger electrical dipole moment and the wave function of the captured electron is more localized. A similar model has also been proposed by Morigaki.³²

C. The $g=2.013$ ESR signal

Less is known about the origin of the $g=2.013$ signal from the present work. Generally, one notices that the observation of this signal relates to the presence of H in *a*-Si, i.e., either weakly- or fully-hydrogenated *a*-Si. Within the model presented, one could feel tempted to associate this signal with a T_3^- defect capturing a hole. Along the theoretical insights²⁷ such a defect would show $g \approx 2.007$. Hence, the observed large shift in g from 2.0055 \rightarrow 2.013 suggests a different origin for this signal. Moreover, the observed spin density of the $g=2.013$ line may reach^{6,7} a value $\approx 10^{19} \text{ cm}^{-3}$ which is orders of magnitude higher than the spin density of the $g=2.004$ line observed in P-doped samples. This is not to be expected if both types of centers, i.e., $T_3^- + \text{hole}$ and $T_3^+ + e^-$, would always be created in equal numbers. As stated previously we believe that the $g=2.013$ line originates from defect states situated in the lower part of the band gap, but not from the VBT states.²³ The existence of a defect band at ≈ 0.6 eV above E_V is also evidenced by deep-level transient spectroscopy and other experiments.³³ Apparently, more study is needed to clarify the microscopic nature of the originating centers.

V. CONCLUSIONS

An experimental comparison has been presented of the various ESR centers observed so far in intrinsic *a*-Si and *a*-Si:H and doped (both B and P) *a*-Si:H. The similarities between the DB line and the CBT states line were emphasized. On experimental grounds, the main conclusions of this work are as follows. (1) Direct experimental evidence has been provided showing that the effective correlation energy of the $g=2.004$ line in P-doped *a*-Si:H is much larger than the previously suggested value of 10 meV. (2) The line shape of the $g=2.004$ line in P-doped *a*-Si:H has been unveiled to be asymmetric with the same specific asymmetry as the usual DB line. (3) From the frequency dependence of the $g=2.004$ line in P-doped *a*-Si:H, the widths of the intrinsic line and the g spectrum have been estimated showing that the former is similar to the one of the DB line but the latter is smaller. Moreover, it was established that the g -value distribution of states closer to E_C is broader than the one far from E_C . (4) The usual DB defects may exhibit significant differences in g value, depending on the local lattice situation. This implies that small differences in g value only cannot be used to distinguish DB's from other type of defects.

Regarding the microscopic modelling of the observed centers, there are two main conclusions. (1) The $T_3^+ + e^-$ defect, where T_3^+ is the positively-charged threefold-coordinated Si center of the ICTD $T_3^+ - T_3^-$, has been proposed as the microscopic model for the $g=2.004$ line in P-doped *a*-Si:H. This model accounts for all the similarities and differences between the usual DB line and the $g=2.004$ line in P-doped *a*-Si:H. This implies that the majority of the CBT states originate from the ICTD centers. (2) There is experimental evidence that the $g=2.013$ line arises from defect states situated in the lower part of the band gap but not from VBT states.

Within this model the characteristic features and the observability of the various signals over the different *a*-Si and *a*-Si:H samples studied both by dark ESR and LESR are consistently explained.

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