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Evidence of $g = 2.013$ defect centers in a-Si:H

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By carrying out ESR measurements at relatively high microwave frequency (20.9 GHz) we have observed an ESR signal with $g=2.013$ in intrinsic sputtered a-Si:H deposited at 300 K. The same signal was also observed in slightly-B-doped device-quality glow-discharge a-Si:H. Calculations of the spin density versus the Fermi-level position show that this signal cannot be a valence-band-tail hole resonance. It is shown that the measured spin density is consistent with association of the signal with a defect band situated 0.6 eV above the valence-band mobility edge E_V. Evidence supporting this defect-band model is summed up and it is suggested that boron doping might create extra defects with $g \sim 2.013$.

I. INTRODUCTION

It is generally believed that the dangling bond (DB) center is the major defect in pure amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H). Indeed, both in a-Si and in intrinsic a-Si:H a *single* electron-spin-resonance (ESR) signal with a g value ~ 2.0055 has been observed[1] which is attributed to DB defects. An interesting question regards the existence of other types of defects. A first indication comes from field-effect (FE) experiments. The density of states $g(E)$ derived from FE data shows[2] a clear defect band 0.6 eV above the valence-band mobility edge E_V in a-Si:H. Also, deep-level transient spectroscopy (DLTS), which has the advantage of being very sensitive to the underlying density of states and which measures essentially the bulk $g(E)$, clearly reveals[3] the presence of a defect band at midgap and one at 0.5 eV above E_V in doped a-Si:H. The midgap feature has been positively identified as arising from doubly occupied DB states.[4] The one at 0.5 eV has not yet been conclusively identified. From photoconductivity and infrared quenching photoconductivity measurements[5] evidence was obtained for the existence of at least two types of defects with one defect band ~ 0.6 eV above E_V in intrinsic a-Si:H, which is different from DB-type defects. All these experiments indicate that in addition to the DB defect band, another defect band situated at ~ 0.6 eV above E_V exists both in intrinsic and in doped a-Si:H.

The present work concerns the study of defects other than DB's by means of ESR: It reports on the first clear observation of an ESR signal with $g = 2.013$ in *intrinsic* a-Si:H prepared by rf sputtering (SP). Moreover, it will be shown that the $g = 2.013$ resonance is also observable in slightly-B-doped device-quality glow-discharge (GD) a-Si:H whose Fermi level is at midgap position. These observations are only achievable by performing ESR at a microwave frequency (K band, 20.9 GHz) higher than the commonly used X band (~ 9.0 GHz). The $g = 2.013$ response observed in both kinds of materials is unambiguously identified as the $g = 2.013$ signal observed by dark ESR in heavily-B-doped a-Si:H; the latter has been attributed to valence-band-tail (VBT) holes.[6,7] A simple calculation shows that associating the $g = 2.013$ resonance with a defect band at 0.6 eV above E_V is consistent with the observed ESR spin density; regarding this, the conventional VBT states model is in failure. Finally, it is evidenced that the $g = 2.013$ defect formation is necessarily assisted by hydrogen incorporation.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Three kinds of samples were studied. Slightly-B-doped glow-discharge a-Si:H was deposited on mica in a capacitively coupled system filled with pure SiH_4; the substrate was kept at 250 °C during deposition. The B doping occurred as a result of the residual B atoms present in the reaction chamber; the B concentration was determined by secondary ion mass spectroscopy (SIMS) as $\sim 10^{17}$ cm^{-3}. The gas flow rate and rf power are 40 standard cm^3 per min and 5 W, respectively. After deposition the a-Si:H film was easily peeled off from the mica whereupon 14.4 mg material was collected in a quartz tube for ESR measurements.

Pure a-Si and a-Si:H films were deposited by rf sputtering onto Al foil or high-purity quartz substrates kept at room temperature (RT) by water cooling. The system is pumped to a base pressure of 1×10^{-6} Torr with a turbo-molecular pump system. The deposition chamber is first cleaned and sputtered with silicon prior to the final film sputtering run to avoid contaminations. Additional details of the sputtering setup have been described elsewhere.[8] Table I contains some deposition parameters. Samples $S1$ to $S3$ have already been studied partially in Ref. 9. Some films of sample $D2$ were deposited on Al foil and some on quartz plates. Those on the Al substrate were etched off in a mixture of 45% H_3PO_4, 13% H_2SO_4, and 6.5% HNO_3 (all wt. %) and distilled H_2O. For ESR measurements the film was collected in a quartz tube.

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TABLE I. Some preparation characteristics of sputter-deposited a-Si and a-Si:H films.

Sample[d]	S1	S2	S3	A5	D1	D2
Ambient	Ar	99% Ar+1% H_2 (vol. %)	97% Ar+3% H_2 (vol. %)	97% Ar+3% H_2 (vol. %)	Ar	90% Ar+10% H_2 (vol. %)
P_a (Torr)[a]	0.008	0.01	0.008	0.011	0.035	0.006
W(W)[b]	100	100	100	100	150	100
r_D (nm/s)	0.030	0.024	0.028	0.035	0.075	0.028
d_{Si} ($\pm$0.02 μm)[c]	0.52	0.75	0.80	0.95	2.0	0.85

[a] P_a is the ambient pressure.
[b] W is the rf power.
[c] d_{Si} is the thickness of the film.
[d] Samples within one set are labeled by equal prefixes (i.e., S, A, or D) to indicate that they have been prepared *sequentially* in the *same* experimental setup. Set (prefix) symbols are consistent with those previously used (see, e.g., Refs. 8 and 9).

B. ESR measurements

ESR experiments were carried out mostly at RT at both X (8.99 GHz) and K bands (20.9 GHz) in homodyne reflection spectrometers driven in the absorption mode under adiabatic slow passage. Modulation of the externally applied magnetic induction field **B** and using phase-sensitive detection resulted in the detection of absorption-derivative spectra dP_μ/dB; P_μ represents the microwave power in the cylindrical TE_{011} ($Q\approx4000$ at K band) cavity. Both spectrometers were foreseen with signal-averaging facilities. The number of spins N_S of the respective signals were determined relative to an Al_2O_3:Cr^{3+} intensity standard by double numerical integration of the dP_μ/dB spectra recorded with nonsaturating P_μ levels. The maximum P_μ levels available are $\sim$50 and 9 mW at X and K bands, respectively. Values of g were determined relative to the g value, i.e., $g_{LiF:Li}=2.002\,29$, of Li particles embedded in neutron-irradiated LiF.

III. RESULTS

A. Sputtered a-Si and a-Si:H

Regarding the SP material, a strong ESR signal (referred to as line I) with $2.0041\leq g\leq2.0051$ was observed in all samples. Previously[8] we have demonstrated that the g value of this signal can be reduced from 2.0051 to 2.0041 by reducing the rf power which led to the decrease of the deposition rate r_d. The ESR characteristics of this signal are listed in Table II. The g values listed were determined at the K band. This signal has been unambiguously identified[9] as the DB line present in all intrinsic a-Si and a-Si:H and will not be discussed any further in the present work.

Instead, attention is paid to a broad signal (line II) with $g\sim2.013$, which is observable in addition to the well-known DB line. This signal is observed in all samples sputtered in H-rich ambient and the deduced ESR properties are summarized in Table II. It has been reported before[8,9] for the slowly deposited intrinsic a-Si:H films [S2 (cf. Ref. 9) and A5 (cf. Ref. 8)]. The broad signal is also observed in sample S3 (containing somewhat less H_2, unlike what *nominal* settings would indicate; cf. later), as may be seen from the K-band spectrum shown in Fig. 1. On the expanded curve, a structure indicated by the arrow is clearly observable which was not reported in our previous work.[9] This spectrum may also be interpreted as a superposition of a broad line with $\Delta B_{pp}\sim30$ G at $g\sim2.01$ and the DB line. The amplitude of the broad line, however, is too weak to allow a reliable estimation of ΔB_{pp} and g. It is important to mention that at the X band there is no indication of its presence. There are two main reasons for this. The first one concerns the difference in g values between the two signals involved. Although both signals contain some inhomogeneous broadening (cf. Table II), a higher resolution is still obtained at the K band because the linewidth of both signals increases more slowly than linearly with microwave frequency f (cf. Table II). Second, the line shape of both

TABLE II. X- and K-band properties of the ESR signals observed at 300 K on sputter-deposited a-Si and a-Si:H and on a slightly-B-doped glow-discharge deposited a-Si:H specimen. All measurements were carried out in the absence of saturation effects.

	g ($\pm$0.0001)		ΔB_{pp} (9.0 GHz) ($\pm$0.3 G)		ΔB_{pp} (20.9 GHz) ($\pm$0.5 G)		N_s[a] (cm^{-3})	
Sample	I	II	I	II	I	II	I	II
S1	2.0041		6.7		9.7		1.0×10^{20}	
S2	2.0042	2.012	11.0$\pm$0.5	40$\pm$3	17$\pm$1	77$\pm$5	1.4×10^{19}	$(1.0\pm0.5)\times10^{19}$
S3	2.0042	2.013$\pm$0.003	6.4		11.0	30$\pm$15	2.5×10^{19}	$\sim3\times10^{17}$
A5	2.0046	2.013	7.0		12.0	28$\pm$3	8.7×10^{18}	$(2.5\pm0.8)\times10^{18}$
D1	2.0050		5.2		8.4		2.4×10^{19}	
D2	2.0048	2.013$\pm$0.001	7.4		12.4	28$\pm$3	2.4×10^{19}	$(1.0\pm0.3)\times10^{18}$
GD1[b]	2.0053	2.013	7.5		14.5	32$\pm$3	2.5×10^{16}	$(1.0\pm0.3)\times10^{16}$

[a] Accuracy estimated to be $\pm$20%.
[b] GD1 refers to the slightly-B-doped a-Si:H sample.

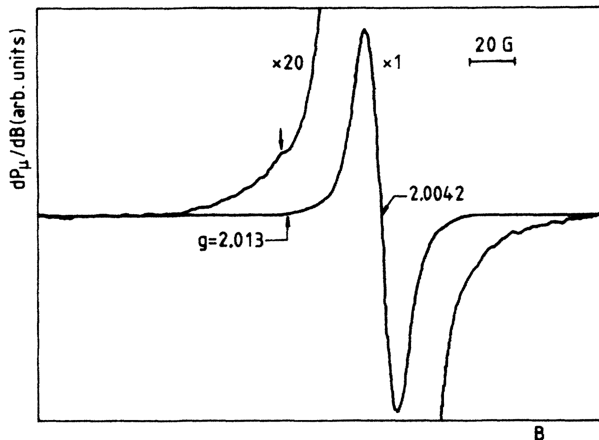

FIG. 1. K-band absorption-derivative ESR spectrum measured at RT with $P_\mu = 0$ dBm on SP a-Si:H film S3. From the 20 times expanded curve, the presence of a broad line is discernible as indicated by the arrow.

signals obtains a more Lorentzian character at the X band (intrinsic Lorentzian linewidth of the order of the Gaussian distribution width); the broader tailing off of signal I is likely to further overshadow signal II. Figure 2 represents a K-band spectrum of sample $D2$. In this case, the broad line is easily discernible and the computer simulation of the spectrum gives $g = 2.013 \pm 0.001$ and $\Delta B_{pp} = 28 \pm 3$ G. The line-shape factor, defined by

$$l = \frac{A}{\frac{1}{2} h_{pp} \Delta B_{pp}^2} \tag{1}$$

is found to be 1.8. Herein, A is the area under the absorption curve and h_{pp} is the peak-to-peak amplitude of the dP_μ/dB curve. Again, the broad line is not observable at the X band. Notice that the g value ($=2.0048$) of signal I in this sample (cf. Table II) is not far from the standard g value[10] ~ 2.0050 for SP material. Hence, it is

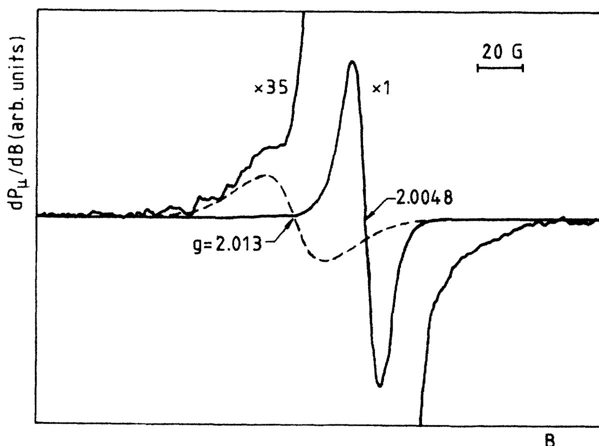

FIG. 2. K-band absorption-derivative ESR spectrum (solid line) measured at RT with $P_\mu = 0$ dBm on SP a-Si:H film $D2$. From the 35 times expanded curve, the presence of the broad line is clearly recognized. Computer fitting of the broad line, which is shown by the dashed line, gives $g = 2.013$, $\Delta B_{pp} = 28$ G, and $l = 1.8$.

concluded that the broad line is present in all SP intrinsic a-Si:H deposited at RT. Although sincere attempts were made, no such signal could be traced in pure a-Si samples, i.e., $S1$ and $D1$.

The estimated $N_S(\mathrm{II})$ of line II is listed in Table II. It would be interesting to relate these values to the H content actually incorporated in the films; unfortunately, the precise hydrogen content is unknown. However, there are indications from annealing experiments. These show that the $S3$ film contains the least amount of H atoms compared to $S2$, $A5$, and $D2$ because the spin density $N_S(\mathrm{I})$ of signal I of all a-Si:H films have been reduced to $\sim 10^{17}$ cm^{-3} upon annealing the films in vacuum ($p \leq 10^{-4}$ Torr) for 30 min at 340 °C—except film $S3$ whose $N_S(\mathrm{I})$ only reduced to 4.5×10^{18} cm^{-3}. Since, the estimated spin density $N_S(\mathrm{II}) \sim 3 \times 10^{17}$ cm^{-3} of film $S2$ is the lowest among the SP samples, it appears reasonable to conclude that the broad line with $g = 2.013$ only appears in a-Si:H and that its intensity $N_S(\mathrm{II})$ increases to some extent with the H concentration. This view is supported by the fact that the broad line is absent in all pure a-Si we have measured (e.g., $S1$).

Of course, the observation of an eventual $g = 2.013$ line in pure a-Si will technically be more difficult because of the increased intensity of signal I. Signal I in pure a-Si deposited at low Ar gas pressure (≤ 10 mTorr) is generally strong, with $N_S(\mathrm{I}) > 5 \times 10^{19}$ cm^{-3} (e.g., sample $S1$) compared to a-Si:H, with $N_S(\mathrm{I}) \lesssim 2 \times 10^{19}$ cm^{-3}. Such an increase in intensity of signal I might suffice to totally mask the broad line. This, however, could not have happened for sample $D1$, which is a pure a-Si film and in which no $g = 2.013$ is discernible. Its spin density $N_S(\mathrm{I})$ is 2.4×10^{19} cm^{-3} which is *comparable* to that of our a-Si:H samples. The reason why $N_S(\mathrm{I})$ of the pure a-Si sample $D1$ is so "low" is because of the high Ar pressure during deposition which is consistent with the literature.[11]

Finally, regarding the annealing treatment at 340 °C, it is worth it to mention that both signal I and II decrease with annealing. Signal II has now even become totally unobservable.

Regarding the origin of signal II, spectroscopic artifacts have been well checked. The possibility that signal II comes from the substrates used has been excluded. This is directly clear from measurements on film $D2$ in which no substrate was involved. Also, any contamination effects can be excluded: SIMS analyses do not show any indication of the dangerous elements such as transition metals which might introduce ESR signals. C, N, and O concentrations are all below 1% (i.e., [O]/[Si] < 1%). These analyses indicate that the $g = 2.013$ line is intrinsic to the a-Si:H.

B. B-doped GD a-Si:H

Figure 3(a) shows a K-band spectrum of the GD a-Si:H:B film. As expected, the DB line with $g = 2.0053 \pm 0.0001$ is observed with ΔB_{pp} (K band) $= 14.5 \pm 0.3$ G and ΔB_{pp} (X band) $= 7.5 \pm 0.3$ G. The spin density $N_S(\mathrm{I})$ is 2.5×10^{16} cm^{-3} which implies a device-quality film. As may be seen from Fig. 3(a), in ad-

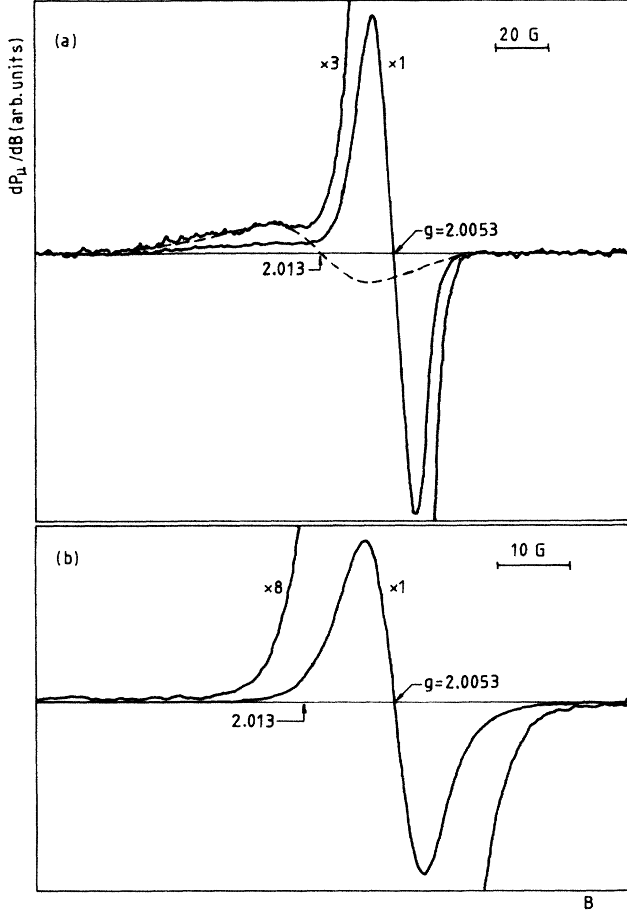

FIG. 3. (a) K-band absorption-derivative ESR spectrum (solid line) measured at RT with $P_\mu=0$ dBm on GD B doped a-Si:H film GD1. From the 3 times expanded curve, the broad line is clearly recognized. Computer simulation of the broad line, shown as the dashed line, gives $g=2.013$, $\Delta B_{pp}=32$ G, and $l=1.8$. (b) is an X-band spectrum observed with $P_\mu=0$ dBm on the same sample, from where it is clear that now the broad line is not observable.

dition to the DB line, a broad line with $g=2.013$, $\Delta B_{pp}=32\pm3$ G, and $l=1.8$ is also present; its spin density $N_S(\mathrm{II})$ is 1×10^{16} cm^{-3}. Figure 3(b) presents an X-band spectrum of this film. Clearly, the broad signal cannot be observed at this frequency, as was the case for the SP samples. The $g=2.013$ line has been observed before by light-induced ESR (Ref. 6) (LESR) in device-quality intrinsic a-Si:H and by dark ESR (Refs. 7 and 12) in heavily-B-doped a-Si:H and has been attributed to VBT holes. dc electrical conductivity (σ) measurements reveal an activated behavior with activation energy $E_a=0.87$ eV and σ at 300 K (σ_{RT})$=6\times10^{-12}$ Ω^{-1}cm^{-1}. The rather low σ_{RT} value and the E_a value imply[13] that the Fermi level E_F in this GD film is exactly at midgap position which is consistent with the fact that the film is slightly B doped. This is the first report of the $g=2.013$ line in a film with E_F at such a deep level. This again must be ascribed to the intrinsic higher resolution of K-band measurements. We should, however, mention that this broad line has already been observed before[7] with E_F at a relatively deep level. A spin density $N_S(\mathrm{II})$ of $\sim1\times10^{16}$ cm^{-3} has been observed[7] in a sample with E_F-$E_V\approx0.65$ eV. Our result may be considered as a convincing extention of this earlier observation in the sense that it unsettles the conventional VBT states model for this signal. It favors the model of deep-level gap states originating this line, as will be outlined later.

IV. DISCUSSION

A. Invalidity of the VBT states model for the $g=2.013$ response

The similarity (cf. Table II) between the broad line observed in SP a-Si:H films and the broad line observed in GD a-Si:H:B films is impressive. They have nearly identical g value and line shape. Only the linewidth is slightly different. Presumably, this is due to the presence of B atoms in the GD film:[7] i.e., ${}^{10}_{5}$B (19.78% natural abundance) and ${}^{11}_{5}$B (80.22% natural abundance) have nuclear spin $I=3$ and $\frac{3}{2}$, respectively. These could lead to unresolved hyperfine broadening. LESR measurements[14] on intrinsic GD a-Si:H at the K band show that the broad line has $\Delta B_{pp}=28\pm3$ G and $g=2.011$. Hence, in all aspects the newly observed broad line in intrinsic SP a-Si:H films and the well-known broad line associated with VBT holes are actually identical regarding their ESR characteristics. Hence the conclusion to assign *a common origin to both signals.*

Supposing that the $g=2.013$ line arises from VBT holes, then it is easy to calculate the density of singly occupied VBT states by holes (n_h) as a function of E_F, which is given by

$$n_h=\int_{E_V}^{\infty} g(E)f_1(E,T)dE \tag{2}$$

with

$$f_1=\frac{2\exp[-(E-E_F-U_{\mathrm{eff}})/kT]}{1+2\exp[-(E-E_F-U_{\mathrm{eff}})/kT]+\exp[-(2E-2E_F-U_{\mathrm{eff}})/kT]} \tag{3}$$

which is the probability function that the state contains one hole. U_{eff} is the effective correlation energy of the VBT holes, k is Boltzmann's constant, and $g(E)$ is the density of VBT states given by[15]

$$g_{VBT}(E)=g_0\exp[-(E-E_V)/kT_c]\ , \tag{4}$$

where $kT_c=0.042$ or 0.05 eV, as given by time-of-flight[15] and optical absorption experiments,[16] respectively. Using $g_0=3\times10^{21}$ eV^{-1}cm^{-3}, $kT_c=0.05$ eV, and $U_{\mathrm{eff}}=\infty$, it

follows that n_h is lower than 1×10^{16} cm^{-3} when E_F is 0.5 eV above E_V. If we still want to keep the VBT model for the $g=2.013$ line (cf. Table II), a roughly constant VBT states density $\sim1\times10^{17}$ eV^{-1}cm^{-3} beyond $E_V+0.5$ eV must be assumed which extends up to the upper half of the band gap, in order to account for the observed spin density N_S(II) in the studied GD a-Si:H:B. It seems more reasonable, however, to associate the $g=2.013$ line with a particular defect band in the lower half of the gap rather than sticking to the VBT states model which denies[2,3,5] the possibility of another type of defect band in the band gap other than DB's.

B. The defect-band model

The defect-band model immediately raises the pertinent question why this signal is generally not observable by dark ESR in intrinsic device-quality GD a-Si:H but becomes stronger with B doping? The reason is that the majority of these defects are doubly occupied by electrons in intrinsic a-Si:H. Two possibilities exist: first, the defect state is spin active when neutral; second, the defect state contains pair electrons when neutral. For the first possibility, the majority of the 2.013 defects receive an electron, thus becoming spin inactive, in intrinsic device quality a-Si:H since no signal of $g=2.013$ is observed in such materials. In principle DB defects might donate electrons to the $g=2.013$ defects. However, in device-quality a-Si:H, the DB concentration N_S(I) is very low ($\sim10^{16}$ cm^{-3}) whereas the concentration of $g=2.013$ defects N_S(II) observed in slightly-B-doped device-quality a-Si:H is at least comparable, usually higher than[7] 10^{16} cm^{-3}. Further, taking into account the Fermi-level position in intrinsic device-quality a-Si:H which is situated[13] in the upper half of the band gap or near the midgap, few DB defects are positively charged since the center[17] of the DB defect band is at the lower half of the band gap (~0.9 eV or ~1.2 eV below the conduction band mobility edge E_c). Thus, it is quite unlikely that the $g=2.013$ defects get negatively charged by accepting electrons from DB defects. Since no other donor candidates are proved to be present, the first possibility is excluded. For the more likely second possibility, it is straightforward to see why no signal of $g=2.013$ is observed in the intrinsic device-quality a-Si:H simply because they are spin inactive when neutral. In B-doped a-Si:H, the Fermi level is shifted to the lower half of the band gap and part of the $g=2.013$ defects become singly occupied. To outline the model, we assume that the DB defect band is given by[17]

$$g_I(E)=3\times10^{16}\frac{1}{\sqrt{2\pi}\sigma}\exp[-(E_D-E)^2/2\sigma^2]\ \text{eV cm}^{-3} \tag{5}$$

with $\sigma=0.1$ eV and $E_D=0.65$ eV above E_V (supposing the mobility gap is 1.8 eV), and the $g=2.013$ defect band is given by

$$g_{\rm II}(E)=g_0\frac{1}{\sqrt{2\pi}\sigma}\exp[-(E_D-E)^2/2\sigma^2] \tag{6}$$

with $g_0=1\times10^{17}$ cm^{-3}eV^{-1}, $\sigma=0.15$ eV, and $E_D=0.6$ eV above E_V. For these density of states the spin densities N_S(I) and N_S(II) of the DB and the $g=2.013$ signals, may be easily calculated as a function of E_F position using

$$N_S({\rm I})=\int_{-\infty}^{+\infty}g_I(E)\frac{2\exp[-(E-E_F)/kT]}{1+2\exp[-(E-E_F)/kT]+\exp[-(2E-2E_F+U_{\rm eff})/kT]}dE \tag{7}$$

for the DB signal and

$$N_S({\rm II})=\int_{-\infty}^{+\infty}g_{\rm II}(E)f_1dE \tag{8}$$

for the $g=2.013$ signal where the singly occupied $g=2.013$ defect state is supposed to be acceptorlike; f_1 is given by expression (3). Both quantities are plotted versus E_F-E_V in Fig. 4 with the solid line presenting N_S(I) and the dashed line presenting N_S(II) for $T=70$ K. The crosses represent N_S(II) at $T=300$ K. It is clear that varying T does not make much difference where the effective correlation energy $U_{\rm eff}=0.4$ eV has been taken for both the DB and $g=2.013$ defects. The calculated N_S(I) and N_S(II) account satisfactorily for the measured spin densities. For $E_F=E_V+0.8$ eV, the calculated N_S(I) and N_S(II) are $\approx2\times10^{16}$ cm^{-3} and $\approx1\times10^{16}$ cm^{-3}, respectively, in agreement with the observations on the B-doped GD film. The dependencies of the calculated N_S(I) and N_S(II) on the Fermi-level position are also in agreement with experiments.[7,18] This model explains the observed N_S(II) increase[7] with B doping initially and the decrease of N_S(II) with B doping when the

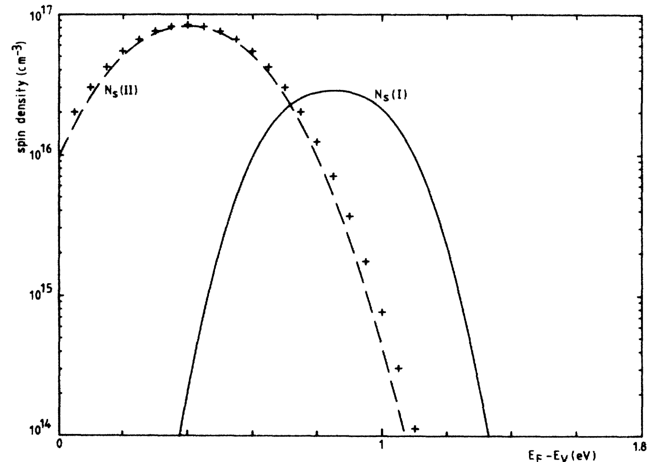

FIG. 4. The calculated spin density N_S(I) of the DB line (solid line) using Eq. (7) and spin density N_S(II) of the $g=2.013$ line (dashed line) using Eq. (8) vs the Fermi-level position at $T=70$ K. The values of the parameters used for the calculations are given in the text. The crosses represent N_S(II) at $T=300$ K.

B concentration is increased over a certain level.[18] However, in heavily-B-doped material,[7] the observed spin density N_S(II) may be as high as $\sim 1\times 10^{19}$ cm^{-3} which is $\sim$100 times stronger than what is reached with the present numbers. We could increase g_0 in Eq. (6) to $\sim 1\times 10^{19}$ cm^{-3} in order to allow the calculated N_S(II) to reach such high values, but this will distort the form of the exponential density of states [cf. Eq. (4)] below $E_V+0.5$ eV significantly which is not consistent with time-of-flight (TOF) experiments[15] in intrinsic and slightly doped a-Si:H. The only way out of this difficulty is to suppose that B doping creates $g=2.013$ defects. Indeed, it has been observed by DLTS that the defect band at 0.6 eV above E_V (the $g=2.013$ defect band in the present model) increases with B doping.[19] Other evidence comes from the hydrogen evolution experiments. It has been shown[15,20] that B doping effects dramatically the hydrogen evolution spectra. It has been demonstrated[20] that B doping introduces voids or internal surfaces into a-Si:H and influences the hydrogen evolution spectra in a similar way as depositing films at low substrate temperatures ($\sim$RT) in many aspects. This result supports the idea that B doping creates $g=2.013$ defects since depositing a-Si:H on RT substrates, which influences the film structure in a similar way[20] as B doping, also introduces $g=2.013$ defects as observed in this work. At this stage, however, we cannot conclude whether H atoms are directly involved in the $g=2.013$ defect. This defect might also arise from internal surfaces, where its formation may need the presence of hydrogen, at least during deposition. Other kinds of microvoids, such as the one present in SP a-Si deposited under high Ar gas pressure[11] (e.g., sample $D1$), do not introduce the $g=2.013$ defects: No 2.013 line is observed in film $D1$ and, in general, none in pure a-Si.

Figure 5 presents the overall density of states [$g(E)$] in the a-Si:H band gap deduced from the present model including the VBT states given by Eq. (4) with $g_0=3\times 10^{21}$ cm^{-3} eV^{-1} and $kT_c=0.05$ eV; the $g=2.013$ defect band given by Eq. (6) with $g_0=1\times 10^{17}$ cm^{-3}eV^{-1}, $\sigma=0.15$ eV, and $E_D=0.6$ eV; the conduction band tail (CBT) states given by

$$g_{\text{CBT}}=3\times 10^{21}\exp[-(1.8-E+E_V)/kT_c]\ \text{eV}^{-1}\text{cm}^{-3} \tag{9}$$

with[15,16] $kT_c=0.0258$ eV; and the DB defect band given by Eq. (5) with $\sigma=0.1$ eV and $E_D=1.0$ eV (instead of 0.65 eV). The latter value is the center position of the distribution of doubly occupied DB states (D^-). This value is taken instead of $E_D=0.65$ eV to allow direct comparison with the DLTS results.[3] These measurements are carried out on P-doped material, i.e., E_F positioned higher up in the band gap. The overall density of states $g(E)$ preserves the feature that it is roughly exponential[21] below $E_V+0.5$ eV in intrinsic and slightly doped a-Si:H as has been claimed by TOF experiments.[15] Also, the presented overall density of states reflects the general features of the density of states observed[3] by DLTS which measures a $g(E)$ distribution in P-doped a-Si:H as pictured in Fig. 5 (i.e., the DB is doubly occupied).

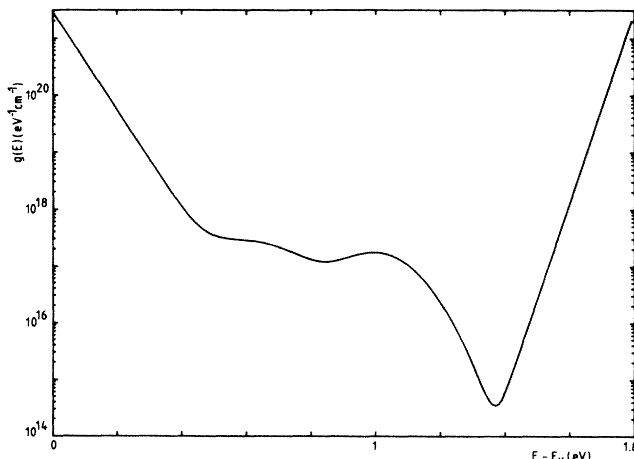

FIG. 5. Proposed distribution of the density of states in the a-Si:H band gap as deduced from the present ESR study. This includes VBT states, the $g=2.013$ defect band, the DB defect band ($g\sim 2.005$), and the CBT states as function of electronic energy E for n-type doped a-Si:H. Note that in this material the majority of the DB's are doubly occupied with a distribution centered at 1.0 eV above E_V.

A final comment concerns the observability of the $g=2.013$ line in our intrinsic SP a-Si:H. The a-Si:H films were deposited at RT. Such films contain a large amount of DB defects and the films are highly constrained. The degree of disorder is higher than device-quality a-Si:H and large potential fluctuations are expected. Therefore, both the DB defect band and the $g=2.013$ defect band are expected to be much broader than in device-quality a-Si:H such as the studied B-doped GD a-Si:H. In such a case, the upper-lying $g=2.013$ defects can loose an electron to lower-lying DB defects and become spin active. Since the DB defect density is *quite high*, it is quite plausible that such charge transfer may proceed into a sufficient extend to make the $g=2.013$ line observable by ESR.

V. CONCLUSIONS

We have reported the first clear observation of an ESR signal with $g=2.013$ in intrinsic sputtered a-Si:H deposited at RT with low Ar gas pressure. The correlation between the spin density of this signal and the H concentration in the film is very strong. However, it is not yet clear whether H atoms are directly involved with the corresponding defects. In any case, no $g=2.013$ line is observed in pure a-Si.

A "broad" line with $g=2.013$ has also been observed in slightly-B-doped GD a-Si:H. The Fermi-level position is precisely midgap, about 0.8 eV above E_V. All ESR characteristics of this signal are identical to the $g=2.013$ signal observed in intrinsic SP a-Si:H. From this, both signals are assigned a common defect origin. Arguments were given that this defect is spin inactive when neutral. A simple calculation shows that the observed spin density of the $g=2.013$ line *cannot be accounted for by the model of the VBT hole line.* It was shown that attributing this signal to a defect band centered at 0.6 eV above E_V is consistent with the observed spin density in slightly-B-

doped a-Si:H. For heavily-B-doped a-Si:H, it is concluded that defect centers with $g=2.013$ can be created as a result of B doping. The density of states derived from the model presented which includes a defect band centered at $E_V+0.6$ eV is in good agreement with DLTS results. The observability of the $g=2.013$ line in intrinsic SP a-Si:H deposited at RT is explained in terms of high disorder, hence large potential fluctuations in such films causing the broadening of both the DB defect band and the $g=2.013$ defect band. Generally, the $g=2.013$ line does arise from a defect band in the gap—not from VBT holes, as assumed in the conventional model.[6,7]

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