Role of interstitial hydrogen and voids in light-induced metastable defect formation in hydrogenated amorphous silicon: A model

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Densities of states of a large set of samples have been measured. Samples were deposited by radio-frequency powered glow discharge under various conditions of temperature, power, gas pressure, and dilution of silane. Density of states was studied in the as-deposited, light-soaked, and annealed states. For all the samples light soaking resulted in an increase of both the deep defect density and of the conduction-band tail states. For samples deposited on the edge of crystallinity and polymorphous materials irreversible modifications of the density of states were observed after light soaking followed by annealing. Since none of the existing models of the metastability can account for this behavior we propose a model. In this model, light induced creation of dangling bonds is mediated by interstitial hydrogen. Hydrogen coming from the breaking of Si-H bonds is trapped into voids or platelets during light soaking and released in the lattice during annealing. This model fully explains our experimental results and also many other experimental observations found in the literature.

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I. INTRODUCTION

Since its discovery in 1977 the Staebler and Wronski[1] (SW) effect has attracted more and more research. The application of hydrogenated amorphous silicon (*a*-Si:H) in thin films solar cells, for which light induced degradation is a major limitation to obtain high stable conversion efficiencies, stimulated this research to understand and eventually to minimize this effect. Many models have been proposed to explain the SW effect and the role of hydrogen is now recognized to be predominant. It is not the purpose of this paper to give a complete review of these models. Such a review can be found in the literature.[2] The fact is that none of the existing models can satisfactorily explain the results of the density-of-states measurements that we have made on a large variety of samples.

For our study, samples have been prepared by rf glow discharge under various conditions of temperature, rf power, gas pressure, and dilution of silane. The density of states of these samples has been studied in the as-deposited, light-soaked, and annealed states. We have obtained two surprising results. First, we observed an enlargement of the conduction-band tail upon light soaking showing that the lattice structure is modified by this process. Second, for some samples, the annealing process, after light soaking, was unable to restore the optoelectronic properties measured in the as-deposited state. In particular, the deep defect density remained higher than that measured in the as-deposited state as if some hydrogen, essential to passivate the dangling bonds, had been trapped and lost during the light soaking or the annealing of the samples. This peculiar behavior, depending on the microstructure of the samples, was mainly observed on polymorphous materials (pm-Si:H) (Ref. 3) and on samples deposited on the edge of crystallinity.[4] This naturally attracted our attention on the available traps for the H atoms removed from the Si-H bonds during light soaking and we wondered also under which form H could be trapped. We speculate that, to be lost, hydrogen must be stored under a form that could not be thermally broken and H_2 molecule is a possible candidate. Since large room is needed to store H_2 molecules they could be trapped in voids or platelets. Surprisingly, despite the large quantity of voids in *a*-Si:H, they have attracted little attention about their possible role in the SW effect.[5]

In this paper, we present a model in which both interstitial H_2 molecules and voids play a major role in the SW effect and that fully account for our results as well as for the results of many other experiments.

In Sec. II, we present the different deposition conditions under which samples have been prepared and the experiments that have been performed on these samples. In Sec. III, we present the evolution of the density of states (DOS) of studied samples that we have observed under light soaking and annealing at different temperatures successively. In Sec. IV, we review some of the recent developments on the role of hydrogen during the light soaking and annealing processes. Then we present our model and compare the expected outcomes with recent results of characterizations performed on various types of hydrogenated amorphous silicon thin films.

II. SAMPLES AND EXPERIMENTS

Many types of samples, prepared under various conditions, have been studied. All the samples were deposited by radio-frequency (13.56 MHz) powered plasma enhanced chemical vapor deposition (rf-PECVD) systems. The gas were either pure silane, or a mixture of silane and helium or argon or hydrogen. The deposition temperature T_d, the dilution ratios, the total gas pressure or the rf power were varied to obtain different series of materials.

All the deposition conditions are summarized in Table I. In this table, we also give some information on the type of the materials (amorphous, polymorphous, or close to microcrystalline), and on the hydrogen content. For instance, concerning the Ar-diluted series, there is a clear evolution of the

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TABLE I. Summary of the deposition conditions, type of material, and hydrogen content of the studied samples measured either by infrared (IR) or ERDA.

	T_d (K)	% SiH_4	Pressure (Pa)	Power Density (mW/cm^2)	Type of material	% H
Standard	423	100	5	11	Amorphous	12–13 (IR)
	523	100	5	5	Amorphous	9–10 (IR)
Ar	523	1	65.8	35.8–122.5	[Amorphous at	16–9 (IR)
Diluted	523	1.5	26.4	20.4–81.6	low power,	9 (IR)
	523	5	26.4	20.4–449	edge of crystal	11–5 (IR)
	523	10	26.4	20.4–353	at high power]	9–13 (IR)
He	523	45	80	33	Amorphous	12–15 (IR)
Diluted	473	3	52–184	79	Polymorphous	14 (ERDA)
H	423	2	78.9–289.5	110	Polymorphous	15–19 (ERDA)
Diluted	423	15	13–52.6	11	Polymorphous	

material from amorphous to microcrystalline structure with increasing power.[4,6]

For all the samples we have followed the same experimental procedure. The samples were first annealed 1 or 2 h at the deposition temperature under vacuum, leading to what we call the as-deposited (AD) state in the following. In the AD state, the DOS above the Fermi level has been measured by means of the modulated photocurrent (MPC) technique[7] and for some samples below the Fermi level using the constant photocurrent method (CPM).[8] The samples were then light soaked (LS), either 2 min or up to full saturation. Light soaking of the samples was achieved at 80 °C under the water-filtered light of a xenon lamp. The light was also filtered by a thin *a*-Si:H layer resulting in a 300-mW/cm^2 red light flux. The light-soaking kinetics was monitored by measuring the photocurrent of the sample at 20 °C regularly during the experiment. The DOS of the samples after LS was estimated by means of MPC and CPM.

Annealing was performed under vacuum first at 420 K for samples deposited at this temperature or at 460 K for samples deposited at higher temperatures. For all the samples deposited at 423 K the annealing at the deposition temperature was followed by an annealing at 460 K because the annealing at 420 K was inefficient to restore the as-deposited DOS.

After each 12 h annealing, we measured the DOS by means of the MPC technique and compared the result to the DOS obtained in the AD state. The annealing procedure was repeated until the DOS in the annealed state and the DOS in the AD state were the same or until no change in the DOS could be obtained. The DOS below the Fermi level was estimated afterward by CPM.

III. RESULTS

A. Light-soaking results

One sample chosen arbitrarily from almost all the series of samples have been light soaked for 2 min only. The DOS was then measured by MPC. After a short annealing (1 or 2 h) the sample was light soaked to saturation. All the samples exhibited almost the same behavior: after 2-min light soaking we noticed an increase of the deep defect density but almost no change in the conduction-band tail (CBT) states. It is worth to say that 2 min is not an unique scale of time to observe such a behavior. Samples presenting a very fast light-soaking kinetics may show a slight increase of the CBT states after 2-min light soaking, and, indeed, it is what we have observed. But still we believe that there exists a sample-dependent time zone in which the deep defect density increases while the CBT remains constant. On the other hand, after full light soaking we observed an increase of both the deep defect density, larger than the increase measured after only 2 min, and the CBT. This behavior was seen on *all* the studied samples (37 samples), and, consequently, we believe that it is rather universal irrespective of the structure of the material. As an illustration, this peculiar behavior is shown in Fig. 1 for a standard sample deposited at 523 K.

We have to underline that an increase of the capture cross section of the probed states could be responsible of the increase of the CBT and DOS measured by MPC. Indeed, the MPC technique does not probe strictly the density of states $N(E)$ but the quantity $N(E)\nu(E)/\mu$, where ν is the attempt to escape frequency of the states and μ is the extended states mobility of the carriers interacting with the localized states. The plots of the DOS are done assuming that the electron

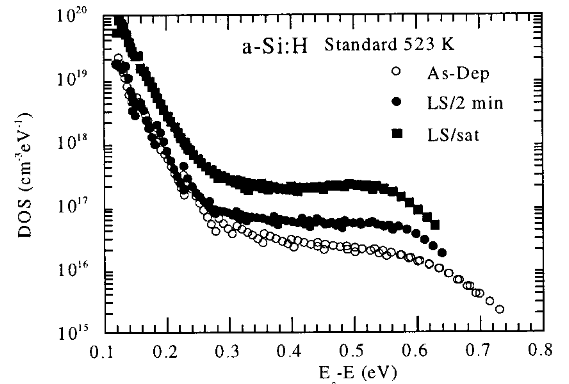


FIG. 1. Evolution of the DOS of a standard sample measured by MPC after 2 min light soaking (LS/2 min) and after saturation (LS/sat) compared to the as-deposited (As-Dep) DOS.

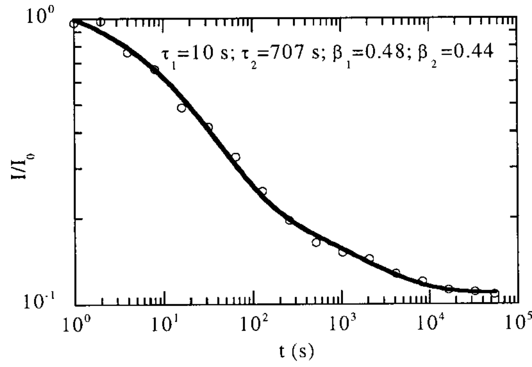


FIG. 2. Evolution of the photocurrent with time measured on the sample of Fig. 1 during light soaking normalized to the value measured in the as-deposited state.

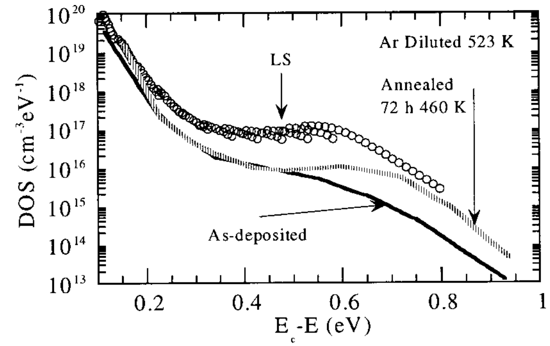


FIG. 3. DOS measured by MPC of an Ar-diluted sample. Only the envelops of the DOS are presented for the measurement in AD (full line) and annealed states (dashed line). In the LS state, only the points obtained at the highest frequencies at which the experiment has been done are displayed. Clearly annealing 72 h at 460 K does not restore the deep states to their AD values.

mobility is of the order of 10 $cm^2 V^{-1} s^{-1}$ and that ν is independent of the energy and equal to 10^{12} s^{-1}, two values that are the most accepted for *a*-Si:H (details are given in Ref. 7). Therefore, an increase of the MPC measured CBT and DOS can be related to an increase of the DOS or an increase of the capture cross section or both. Recently, Meaudre and Meaudre have reported an increase of both the DOS and the capture cross section of states close to the Fermi level upon light soaking (See Ref. 9 and references therein).

In Fig. 2, we present the light soaking evolution of the photocurrent with time normalized to the value before light soaking for the same sample as in Fig. 1.

The full line is a fit of the experimental data using two stretched exponential distributions with the equation

$$\frac{I}{I_0}=\left[\frac{I}{I_0}\right]_0-\left[\frac{I}{I_0}\right]_1\exp\left\{-\left(\frac{t}{\tau_1}\right)^{\beta_1}\right\}-\left[\frac{I}{I_0}\right]_2\exp\left\{-\left(\frac{t}{\tau_2}\right)^{\beta_2}\right\}. \tag{1}$$

The values of τ_1, τ_2, β_1, and β_2 are reported on the figure. We have found this behavior on almost all our samples irrespective of the preparation conditions. Note that we have used this type of equation only to show that a single stretched exponential distribution is not sufficient to fit the experimental data. This two-exponent fit result is consistent with the MPC results given above, both of which indicate that two types of states are sensitive to the light-soaking process: the deep states whose density modifies rapidly and the band tail states whose density increases only after a given amount of time. The question is whether we can assume that the evolutions of these two distributions are independent, and then we can use two stretch exponential distributions to fit the kinetics, or not. Actually, we believe that the increase of deep states density might cause some modifications of the structure that eventually results in an increase of the CBT states. We shall come back to this point later.

B. Annealing results

As far as annealing is concerned, we have observed many different evolutions mainly depending on the deposition parameters.

For samples deposited at 523 K, some samples had their DOS totally restored by the annealing process performed at 460 K, but for many samples, mostly those prepared under Ar dilution, we have observed that even after 72 h annealing the deep states density was still higher than the deep states density measured in the as-deposited state. This behavior is shown in Fig. 3.

However, for deposition temperatures above or equal to 473 K all the samples except two (two among 23) had their conduction-band tail restored as in the as-deposited state. Note that, for the samples for which it was possible to restore the as-deposited DOS, the annealing kinetics of the CBT states was far longer than the annealing kinetics of the deep defect density.[10] This behavior indicates that (i) for some samples hydrogen is probably stored in some place during light soaking from where release of hydrogen and, hence, dangling bond (DB) passivation is not possible by thermal annealing even at 460 K, and (ii) the structural modifications induced by light soaking slowly recover by annealing.

This is not the case for samples deposited at 423 K. Only one sample (1 among 14) prepared at 423 K (pm-Si:H prepared at 263 Pa) shown reversible change of the DOS. Here we have to distinguish between standard samples and polymorphous samples.

For standard samples deposited at 423 K annealing at the deposition temperature leads to a decrease of the deep states toward their as-deposited value but the conduction-band tail remains unchanged. We then annealed these samples at 460 K. The deep defect density was then fully restored but it was impossible to restore the CBT to its AD value (See Fig. 4).

At this point one can wonder if the irreversibility we have observed for the CBT is due to light soaking or annealing at a temperature higher than the deposition temperature. To find an answer, we have studied two layers of standard material deposited in the same run at 423 K. Both layers presented the same DOS in the AD state, as measured by MPC and CPM, and no evolution of DOS upon annealing at 420 K. Then, one layer ($L1$) was light soaked and the other one ($L2$) was annealed 24 h at 460 K. This annealing resulted in a signifi-

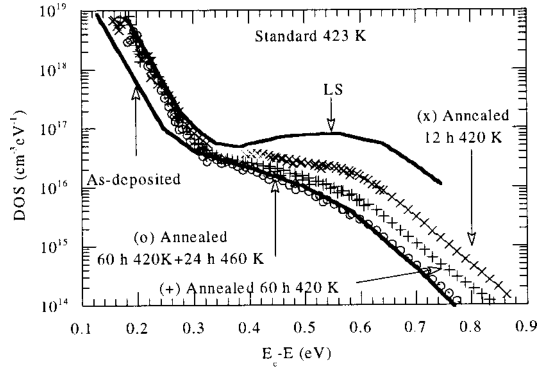


FIG. 4. Evolution with LS and annealing of the DOS measured by MPC of a standard sample deposited at 423 K. After 60 h annealing at 420 K (+) the DOS is not restored to its AD value. Annealing 24 h more at 460 K restores the deep defect density but not the CBT (○).

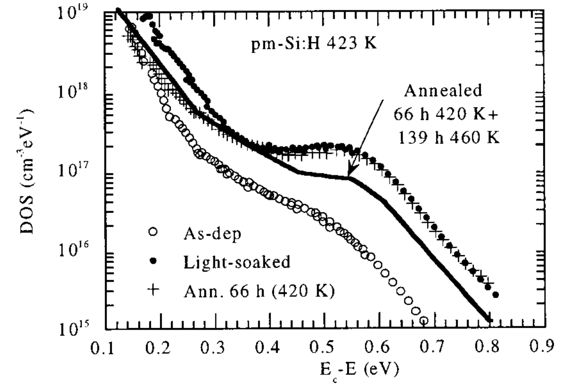


FIG. 5. Evolution with LS and annealing of the DOS measured by MPC of a pm-Si:H sample deposited at 423 K. It can be seen that after annealing at 420 K for 66 h, the annealed DOS (+) is not very different from the LS DOS (●), both being much higher than the AD DOS (○). Annealing at 460 K does not restore the AD DOS either.

cant broadening of the CBT states but less than the one induced in $L1$ by full light soaking.

Annealing of $L1$ for 24 h at 420 K after light soaking could not restore neither the deep states nor the band tail. After another annealing of 24 h at 460 K the deep states came back to their as-deposited value but the conduction-band tail final value was that we had measured on $L2$ after annealing 24 h at 460 K. We have not noticed any change in the valence-band tail by CPM in any cases. This may be due to the fact that the relative increase of the valence-band tail states, if any, is small, the valence-band tail states being already very large in the AD state.

We have also checked that once a 423-K standard sample has been light soaked and annealed at 460 K, further light soaking followed by annealing at 460 K process did not modify the DOS. Thus, we can say that for the 423 K standard samples, for which it was impossible to bring back the CBT to its as-deposited value, structural modifications occurred during first annealing at a higher temperature than T_d, leading to an enlargement of the CBT.

The evolution of DOS of polymorphous materials deposited at 423 K upon light soaking followed by annealing at 460 K is not as simple. First, annealing of all the polymorphous samples at the deposition temperature was almost inefficient even after 66 h (See Fig. 5). Annealing at 460 K was usually more efficient but not enough to restore neither the deep defect density nor the CBT for most of the polymorphous samples except one among ten. For these samples light soaking followed by annealing results in irreversible changes in terms of both passivation by hydrogen and structure of the lattice. Second, the DOS evolves after each further light soaking followed by annealing at 460-K cycle.

The evolution of the CBT and of the deep states of the different types of samples upon annealing is summarized in Table II.

It is not surprising to observe different behaviors between polymorphous materials and standard materials since the first one is believed to be made of nanocrystallites embedded into an amorphous matrix.[3] The presence of these nanocrystallites certainly induces a different microstructure in polymorphous material than in amorphous materials.[11]

From the above behaviors of the different samples upon LS and annealing, it is clear that LS and annealing mechanisms are not simply the opposite processes of the same mechanism. Influence of the annealing process on the DOS depends largely on deposition conditions, that is on the samples microstructure, whereas LS does not depend so much on these conditions.

IV. DISCUSSION

From the annealing results it is seen that the deep defect densities of some samples never recover their AD values. This indicates that some of the hydrogen atoms removed from the breaking of Si—H bonds, are stored in some trap and lost for DB passivation. Of course, we have rejected the possibility of H effusion at the temperatures at which we have performed annealing.

A. H_2 in *c*-Si and *a*-Si:H

The breaking of the Si—H bonds may not be as trivial as the simple abstraction of the H atoms as this process requires 3.6 eV, a quite large value. Indeed, some authors have proposed another mechanism in which the H atom goes into bond-centered position (H-BC) between two Si atoms leaving a DB behind.[12] This mechanism requires only 1.74 eV and could be initiated by carrier recombination from tail states to tail states. The infrared (IR) measurements performed by Darwich *et al.* favor the hypothesis of H-BC creation.[13] They put into evidence that at the beginning of the LS process new absorption lines appear in the spectra that they attributed to an increase of the H-BC population. According to Darwich *et al.* the creation of the H-BC is correlated with a decrease of the Si—H IR absorption. They have also noted that after a few hours of light soaking these new absorption lines disappeared. Thus, H-BC is certainly not a stable configuration and one has to find out a mechanism that results in a further decrease of the H-BC concentration. Here, we can put forward the proposition of Van de Walle and

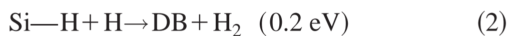
TABLE II. Evolution of the CBT and of the deep states upon annealing after light soaking for the different types of samples.

Samples	T_d (K)	Type of material	Annealing at 420 K		Annealing at 460 K	
			CBT	Deep states	CBT	Deep states
Standard	523	Amorphous			Restored	Restored
Ar diluted	523	Amorphous edge of crystal			[Restored except two samples among 17]	Restored higher than AD
He diluted	523	Amorphous			Restored	Restored
He diluted	473	Polymorphous			Restored	Restored
Standard	423	Amorphous	No influence	Slight decrease	Broader than AD	Restored
H diluted	423	Polymorphous	No influence	No influence	Broader than AD	Higher than AD

Tuttle in which another H atom comes to passivate the newly created DB left by the H atom gone in BC position.[14] This would result in an increase of the Si—H IR absorption. The Si atom turns to be overcoordinated and, according to Van de Walle and Tuttle,[14] the two hydrogen atoms gather under molecular form either H_2, if the molecule is afforded enough room–for instance, in voids or platelets, or H_2 interstitial ($H_2{}^i$), equivalent to $H_2{}^i$ in T sites observed in c-Si, and leave a DB behind (~0.2 eV). Thus, a further decrease of the Si-H IR absorption should be seen. This mechanism of H-BC creation and annihilation at the very beginning of the LS process indicates that H-BC could play the role of the "intermediate precursor" put into evidence by Heck and Branz.[15]

Note that according to Safonov, Lightowlers, and Davies the hydrogen-vacancy-(interstitial) complexes in crystalline silicon (c-Si) could play the role of dimer precursors, providing a mechanism for bringing hydrogen atoms together.[16] We have here another mechanism that would result in creation of H_2 molecules.

Also experimentally it was shown that one of the processes responsible for the aging of MOS devices is the creation of dangling bonds at the c-Si/a-SiO_2 interface via[17]



$$\mathrm{Si—H} + \mathrm{H} \rightarrow \mathrm{DB} + \mathrm{H_2} \quad (0.2\ \mathrm{eV}) \tag{2}$$

All these mechanisms show that $H_2{}^i$ can be generated in amorphous and crystalline silicon materials and we can reasonably assume that $H_2{}^i$ is a possible end product of the light-soaking process. However, one has to wonder about the source of the free H atom that will first passivate the newly created DB and then gather with the H-BC to form a H_2 molecule.

If $H_2{}^i$ can be an end product, we suggest that $H_2{}^i$ may also play an active role during the LS process. According to Chevallier,[17] $H_2{}^i$ in T site and $H_2{}^*$, an equivalent of the $M(\mathrm{Si—H})_2$ of Branz,[2] present roughly the same stability within a few meV in c-Si. The relative stability of these two species is still a matter of discussion. Some authors favor the existence of $H_2{}^*$.[18] In particular, they have shown that interstitial H_2 easily dissociates in close vicinity of a vacancy or a self-interstitial defect and, according to them, it is one of the reason why $H_2{}^i$ is detected only in c-Si containing a high concentration of hydrogen.[16] Note that a high concentration of hydrogen in that case corresponds to 1.5×10^{16} cm^{-3} far below the concentration met in a-Si:H. Taking account of the concentration of hydrogen present in a-Si:H, even in low H content samples prepared by hot-wire (chemical vapor disposition) CVD,[19] it would be very surprising if $H_2{}^i$ was not incorporated in large quantities in this material. Some evidence of this incorporation was given recently by Fedders *et al.*[20] These authors have shown that $H_2{}^i$ was present in large quantity, up to 40% of the total hydrogen present in the material. If according to Ref. 18, $H_2{}^i$ can be easily dissociated in close vicinity of a nonhydrogenated vacancy, we propose that the new dangling bond, created by the migration of the previous H atom toward the BC position, can favor the dissociation of any $H_2{}^i$ located close to it. The dissociation of the $H_2{}^i$ molecule could even be helped by recombination of carriers at the newly created DB.

B. Model for the Staebler-Wronski effect

We then propose the following mechanism for light soaking. In a first step, some Si—H bonds are broken, likely assisted by the energy released from tail to tail recombination of carriers. However, as the breaking of a Si—H bond releasing a free H in the lattice needs a high energy (3.6 eV), we believe that a reaction proposed by Tuttle and Van de Walle is more likely to occur: the H moves from the Si—H bond to a BC position (1.74 eV) or even in the antibonding (AB) position (1.2 eV), leaving a dangling bond behind.[12] This reaction obviously results in a decrease of the Si—H absorption and a possible increase of the absorption band at 1730–1790 cm^{-1}, which has been attributed to the H-BC configuration.[13] As H-BC and H-AB are not stable configurations, the H atom, thermally assisted, may come back to passivate again the dangling bond it has left behind. Thus, at this stage, the annealing of the created dangling bonds would be a fast process, and, indeed, we have observed rapid annealing of our samples after 2-min light soaking. If the con-

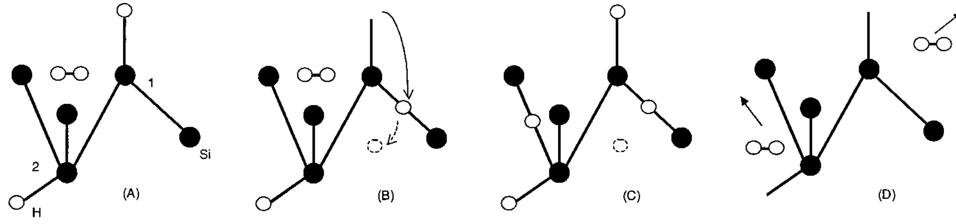
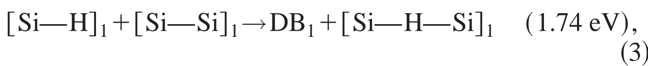


FIG. 6. Simple scheme presenting the different mechanisms occurring during the LS process: (A) the starting environment, the numbers 1 and 2 correspond to the indexes used in the equations describing the DB formation, (B) the recombination of two carriers creates one DB by giving enough energy to the H atom to move in BC or AB position, (C) this results in a breaking of the $H_2{}^i$ that passivates the DB and insert a H in BC position close to a Si—H bond, (D) all the H atoms gather again into two $H_2{}^i$ leaving two DB behind.

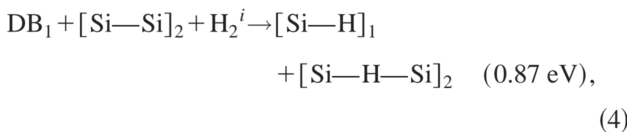
centration of $H_2{}^i$ is as high as predicted,[20] some of the newly created dangling bonds are probably in a close vicinity of a $H_2{}^i$. The newly created dangling bond offers new states for recombination of carriers that could break the equilibrium of this molecule and two hydrogen atoms are freed in the lattice. One, say H1, can passivate the freshly created dangling bond and another one, say H2, can go into a bond-centered configuration for it is this reaction that is the less energy demanding (0.87 eV).[21] We have here a mechanism that favors the increase of the Si—H IR absorption in two ways: first there is some sort of a compensation of the dangling bonds created by the first reaction and, second, the introduction of a H atom in bond-centered position results in an expansion of the lattice, the distance between the Si atoms increasing from 2.4 to 3.2 Å.[12] This expansion may result in a change on the oscillator strength of the Si—H bonds.[22]

If the H atom (H1) passivates a DB that is linked to a Si atom that is already connected to another H atom, either in BC or in AB position, then the Si atom becomes over coordinated. In both cases (H-BC, H-AB) we can then imagine, following the idea of Van de Walle, and also the idea of Safonov *et al.*, that these two H atoms gather again and are freed in the lattice and trapped somewhere under $H_2{}^i$ configuration. If the other H atom (H2), coming from the broken $H_2{}^i$, is in a BC position close to a Si—H bond then the same scenario can take place. At the end of the process two dangling bonds and two $H_2{}^i$ are created. This simple scheme is presented in Fig. 6. Obviously this last part of the mechanism results in a decrease of the number of the Si—H bonds and thus of the Si—H IR absorption. Nevertheless, since the lattice has expanded under the introduction of H-BC, the oscillator strength of the Si—H bond may have increased and the absorption coefficient may still remain higher than in the as-deposited state.

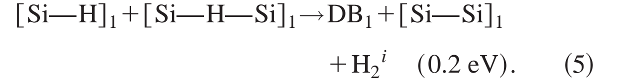
In summary, creation of DB would obey the following reactions:



$$[\mathrm{Si—H}]_1+[\mathrm{Si—Si}]_1\rightarrow \mathrm{DB}_1+[\mathrm{Si—H—Si}]_1 \quad (1.74\ \mathrm{eV}), \tag{3}$$

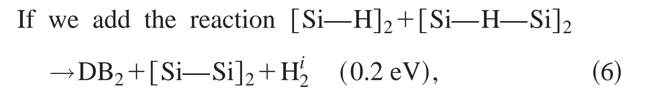


$$\mathrm{DB}_1+[\mathrm{Si—Si}]_2+\mathrm{H_2}^i\rightarrow[\mathrm{Si—H}]_1+[\mathrm{Si—H—Si}]_2 \quad (0.87\ \mathrm{eV}), \tag{4}$$



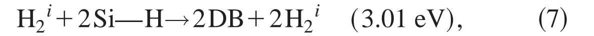
$$[\mathrm{Si—H}]_1+[\mathrm{Si—H—Si}]_1\rightarrow \mathrm{DB}_1+[\mathrm{Si—Si}]_1+\mathrm{H_2}^i \quad (0.2\ \mathrm{eV}). \tag{5}$$

If we add the reaction $[\mathrm{Si—H}]_2+[\mathrm{Si—H—Si}]_2$



$$\rightarrow \mathrm{DB}_2+[\mathrm{Si—Si}]_2+\mathrm{H}_2^i \quad (0.2\ \mathrm{eV}), \tag{6}$$

it means that the global reaction is



$$\mathrm{H_2}^i+2\mathrm{Si—H}\rightarrow 2\mathrm{DB}+2\mathrm{H_2}^i \quad (3.01\ \mathrm{eV}), \tag{7}$$

where $H_2{}^i$ can be considered both as a catalyst on the left-hand side of the reaction and an end product on the right-hand side of the reaction.

From Eq. (7), we obtain a reasonable formation energy of ~1.5 eV per DB. This energy can even be lower if the first H atom goes to an AB position as suggested by Biswas and Li.[23] This movement would cost 1.2 eV according to Ref. 12 and the total formation energy would be of the order of 1.2 eV.

This scenario would be perfect if no passivation of the newly created DB's could occur. Also it does not mean that two DB's are necessarily created in close vicinity. Indeed, the H2 atom may not be in the vicinity of a Si—H bond. In that case, it can either stay in bond-centered position, a configuration which may not be very stable,[12] or diffuse through the lattice migrating from BC to BC position, a diffusion process proposed by Van de Walle *et al.* on the basis of theoretical calculations.[24] While diffusing, this H atom can meet either a Si—H bond, and create a DB according to our simple scheme, or a DB that it will passivate. In the first case two DB are created but in the second case the net number of created DB is zero. Also, one can wonder what happens to the newly created $H_2{}^i$. Indeed, if it is not trapped in a stable configuration it will probably dissociate again releasing two H atoms that could passivate some dangling bonds. In that case the net rate of DB creation is also zero. Then, it is clear that during light soaking many H atoms, depending on the flux of light, are freed in the lattice and that there exists a dynamic equilibrium between creation and annihilation of DB. This equilibrium will tend towards a metastable state if some of the $H_2{}^i$ are trapped during the process. A possible trap for hydrogen under molecular form may be either voids or platelets that could store H_2 molecules.[25] In that case, the metastable DB would be preferably created in close vicinity of voids but all the material would be affected by the pro-

cess. Indeed, the creation/annihilation of DB in the amorphous matrix would result in an expansion of the lattice due to insertion of H atoms in BC or AB position during this process. Also, this dynamic equilibrium, can explain why with, say, 10% of hydrogen present in the material ($\sim 5\times 10^{21}$ at. cm^{-3}), one ends with only $10^{16}-10^{17}$ DB cm^{-3} created after saturation: the creation of DB is not very efficient though the whole process may affect the whole lattice.

We now address the annealing process. According to our light-soaking mechanism the molecular hydrogen produced in reaction (7) is stored in microvoids in *a*-Si:H or platelets located close to the nanocrystallites/*a*-Si:H interface for materials deposited on the edge of crystallization. Depending on the room affordable for the H_2 molecule, it can be stored either under some ''pressure,''[26] that is under some interstitial form, or as a free or less constraint H_2 molecule. It means that the energy of the stored hydrogen is somewhat distributed. Depending on the energy supplied during annealing this hydrogen can be either injected again into the lattice, and make passivates the DB through *diffusion*, or not. Note that Vanecek *et al.* have already speculated that the H atoms moving during annealing could come from microvoids.[27] This process would be rather equivalent to hydrogenation of *c*-Si from a H_2 gas source.[18] The energy distribution of stored hydrogen explains why annealing at 420 K is not very efficient, the provided thermal energy can release only few H atoms. Even annealing at 460 K may not be sufficient if part of the hydrogen is stored under free molecular form. In this case, the thermal energy to break the molecule is too high and the molecule is lost for DB passivation. This behavior was observed on some Ar-diluted samples deposited on the edge of microcrystallinity (see Fig. 3). In such materials it has been shown that hydrogen bonding could be enhanced at the nanocrystallities/*a*-Si:H interface compared to the amorphous matrix.[28] This H-rich interface could be made of platelets.[29] According to Keudell and Abelson, the IR signature of these platelets is an absorption band at 2033 cm^{-1} that we have observed on the Ar-diluted samples presenting some irreversibility of the deep defect density.[6] Irreversibility of the deep defect density upon annealing was also observed on pm-Si:H (see Fig. 4), a material made of nanocrystallities embedded into amorphous matrix. Note that Keudell and Abelson have proposed that platelets are present in pm-Si:H.[29] We then propose that H_2 molecules released during LS are stored in these platelets. Indeed, it was shown that it was the case in *c*-Si (Ref. 26) and in poly-Si.[30] Also Estreicher, Hastings, and Fedders have reported that in *c*-Si the Raman intensity of the interstitial H_2 signal is reduced upon illumination while the amplitude of the platelets-related H_2 signal increases.[18] Moreover, according to our results and to the results of Nickel, Jackson, and Johnson[30] we can reasonably assume that some of these molecules can be lost for DB passivation.

The last point we have to address is how interstitial molecular hydrogen could be incorporated in the material during deposition? According to Robertson, H_2 molecules are formed during removal of hydrogen from the H-rich surface during deposition.[31] Also, recent *in situ* IR measurements have proposed a new mechanism for the construction of the amorphous layer.[32] In this model growth of the *a*-Si:H layer results from direct adsorption of SiH_3 radicals at strained Si—Si bonds. The surface further reconstructs by directly forming surface monohydride and releasing H_2 molecules. These H_2 molecules are mainly emitted toward the plasma in a gas form but one can imagine that part of them are incorporated in the layer under interstitial form.

C. Correlation with other experimental results

We can now have a look at how our model correlates with some established experimental observations.

In this qualitative model, we can see that after light soaking there are more $H_2{}^i$ because they are created during the process. Thus, we expect to observe an expansion of the material since room is needed to store this interstitial hydrogen. Also a lattice expansion of all the material is expected due to the intermediate H-BC configuration. And indeed such an expansion was observed by Gotoh *et al.*[33] This expansion could result in an enlargement of the conduction-band tail, as seen with our MPC technique in all our samples, because of a new ''disorder.'' The question of the range of modification of this ''disorder'' (short range order or intermediate range order) is still a matter of debate,[34] and beyond the scope of this paper.

Here we can come back to the increases of both deep defects and band tail states during light soaking. In our view these increases cannot be independent. Indeed, creation of DB is probably initiated by tail state to tail state recombination. Thus, the number of band tail states certainly plays a role in DB formation. While DB are created an expansion of the lattice results in an increase of the CBT states. This increase in the number of tail states enhances tail-to-tail recombination that in turn favors the creation of DB. In conclusion, creation of deep defect and band tail states are two intricate processes. The description of the evolution of the photocurrent by two stretched exponentials, as we have shown in Fig. 2, is therefore to be considered more as a phenomenological description than coming from a precise mathematical model.

In respect of the whole process described above, we can describe the expected evolution of the number of Si—H bonds or, more precisely, the evolution of the IR absorption band corresponding to Si—H bonds. First, a decrease of this absorption band should be seen when a H atom moves from the Si—H bond to the BC position. Then, the passivation of the newly created DB by a H atom from $H_2{}^i$ would result in some compensation of the breaking of Si—H bonds. This process together with an expansion of the lattice due to incorporation of H-BC atoms, gives rise to a change in the oscillator strength and lead to an increase of the Si-H absorption band. The final creation of a DB by putting two H atoms together leads to a final decrease of the Si-H absorption band whose value should saturate at a higher value than in the as-deposited state because of the lattice expansion. Such an evolution was precisely observed by Sheng, Kong, and Liao.[22]

In this model, though we have not rejected the possibility of H diffusion, note that H diffusion is not needed for the

creation of DB. Consequently, since hydrogen diffusion is not needed to create dangling bonds, it is possible to observe a light-soaking effect even when the illumination is achieved at low temperature (4.2 K).[35]

This model can also account for the better stability observed in materials prepared by hot-wire CVD or materials prepared on the edge of crystallinity with high hydrogen dilution.[36,37] Clearly, hydrogen content is not the key parameter for stability since the HW-CVD material contains only 1% hydrogen or less whereas the second type of material contains more than 15% of hydrogen. As suggested by Vanecek *et al.*[27] and also by Mahan *et al.*,[28] the stability is probably not linked to the hydrogen content but to the peculiar microstructure of materials in which large voids or platelets are surrounded by large zones of rather well ordered and less hydrogenated material. Our model is in perfect agreement with this idea. Indeed, a less number of large voids implies a smaller surface area between voids and amorphous matrix. Thus, for samples having this structure, the flux of H_2 molecules, created during the LS process and to be trapped in voids, would be limited. Hence, creation of metastable DB in the vicinity of these voids or platelets would be lowered compared to the standard *a*-Si:H case where a large number of small voids is present.[38] Concerning the DB created far from these voids, since there is no hydrogen traps they are probably passivated while created by a simple redistribution of H atoms. So in such samples we expect a lower metastability.

In our idea, *a*-Si:H or pm-Si:H could be represented as a hydrogen sponge where the majority of hydrogen released during LS is stored in voids or platelets. If one could empty out the hydrogen from the voids then LS would be more efficient because the voids would be ready to store more hydrogen coming from the LS process. An interesting experiment has been performed by Yoon.[39] A sample presenting a low-temperature hydrogen effusion spectra, with a peak at 350 °C, was annealed at 400 °C. The proportion of defects created by light soaking increased by a factor of 4 compared to the result obtained before exodiffusion. In our view, heating the sample at 400 °C resulted in exodiffusion of hydrogen stored in platelets, and, consequently, this exodiffusion left more room to store the hydrogen created by LS leading to a more efficient process. On the other hand, if one could hydrogenate the material at the deposition temperature to avoid H exodiffusion and structural modifications of the lattice, it should lead to a decrease of the LS influence. Ultimately, a material presenting voids or platelets completely saturated with hydrogen should show an improved stability.

Also, we can address the question of the upper saturation limit of DB creation. The creation of, say, 10^{16}–10^{17} DB/cm^3 in continuous wave (cw) illumination is far below the available number of voids estimated to be equal to 3×10^{19} cm^{-3}.[38] Thus, it is apparent that under "standard" LS process the number of created DB is not limited by the number of available voids. However, it was shown that using a pulsed light it was possible to create up to 3×10^{18} DB/cm^3,[40] much higher than that one obtains with cw illumination but still below the number of available voids. Actually, according to our model, we expect to find an upper limit of the metastable DB of the same order as the number of voids in standard *a*-Si:H that is of the order or slightly higher than 10^{19} cm^{-3}. Experiments should be performed in this way to confirm this prediction.

The fact that DB are preferably created close to voids means that the mean distance between two DB should be of the same order of the mean distance between two voids (30–100 Å). This estimated value is in agreement with the results of Yamasaki and Isoya.[41]

Finally, another very important point is that there is no correlation between Si-H and DB because there is no reason for these two species to be created one close to the other. This fits the electron spin resonance results of Stutzmann[42] as well as the results of Yamasaki and Isoya.[41]

V. CONCLUSION

We have studied the evolution of the DOS of many samples prepared by rf PECVD under various conditions. For all the studied samples we have found that light-soaking results in an increase of the deep defect density and of a broadening of the conduction-band tail. For some of these samples, mainly those prepared on the edge of crystallinity or for the polymorphous materials, we have also observed some anomalous behaviors. In particular, the annealing process was unable to restore the DOS of the as-deposited state. Since none of the existing models of the SW effect could propose satisfactory explanation for this behavior, we have developed a model. This model proposes that, during the LS process, defect formation is mediated by interstitial molecular hydrogen present in the material. It also suggests that voids or platelets play the role of hydrogen traps by capturing hydrogen during LS and releasing it during annealing. With this model we can fully account for our results. For instance, our model predicts a modification of the lattice structure responsible for the broadening of the CBT in agreement with the observed material expansion. Assuming that part of the hydrogen trapped in platelets could not be released during annealing to passivate the DB created during light soaking, we can explain the irreversible modifications of the DOS that we have observed for pm-Si:H or materials deposited on the edge of crystallinity.

We have also shown that many established experimental results found in the literature can be explained by means of our model. Finally, we have suggested a few experimental tests of this model that will be a part of future work.

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[1] D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[2] H. M. Branz, Phys. Rev. B **59**, 5498 (1999).
[3] R. Butté, S. Vignoli, M. Meaudre, R. Meaudre, O. Marty, L. Saviot, and P. Roca I Cabarrocas, J. Non-Cryst. Solids **266–269**, 263 (2000).
[4] U. K. Das, A. R. Middya, J. K. Rath, C. Longeaud, D. L. Williamson, and P. Chaudhuri, J. Non-Cryst. Solids **276**, 46 (2000).
[5] W. B. Jackson and C. C. Tsai, Phys. Rev. B **45**, 6564 (1992).
[6] C. Longeaud, D. Roy, P. Chaudhuri, N. D. Gupta, P. P. Ray, S. Vignoli, R. Meaudre, M. Meaudre, and L. Saviot in *Amorphous and Heterogeneous Silicon-Based Films 2001*, edited by J. B. Joyce, J. D. Cohen, R. W. Collins, J. Hanna, and M. Stutzmann, Mater. Res. Soc. Symp. Proc. No. **664** (Materials Research Society, Pittsburgh, 2001), p. 23.1.
[7] J. P. Kleider and C. Longeaud, in *Hydrogenated Amorphous Silicon*, edited by H. Neber-Aeschbauer (Scitec, Zurich, 1995), p. 597.
[8] J. Kocka, M. Vanececk, and A. Triska, in *Amorphous Silicon and Related Materials*, edited by H. Fritzsche (World Scientific, Singapore, 1988), p. 297.
[9] M. Meaudre and R. Meaudre, J. Phys.: Condens. Matter **13**, 5663 (2001).
[10] C. Longeaud, D. Roy, and Z. Teukam Hangouan, Appl. Phys. Lett. **77**, 3604 (2000).
[11] P. Roca I Cabarrocas, S. Hamma, P. St'ahel, C. Longeaud, J. P. Kleider, R. Meaudre, and M. Meaudre, in *Proceedings of the 14th European Photovoltaic Solar Energy Conference, Barcelona, Spain*, edited by H. A. Ossenbrick, P. Helm, and H. Ehmann (Stephens & Associates, Bedford, 1997), p. 1444.
[12] B. Tuttle and C. G. Van de Walle, Phys. Rev. B **59**, 12 884 (1999).
[13] R. Darwich, P. Roca I Cabarrocas, S. Vallon, R. Ossikovski, and P. Morin, Philos. Mag. B **72**, 363 (1995).
[14] C. G. Van de Walle and B. Tuttle, in Amorphous and Hetrogeneous Silicon Thin Films: Fundamentals to Devices-1999, edited by H. M. Branz, R. W. Collins, H. Okamoto, S. Guha, and R. Schropp, Mater. Res. Soc. Symp. Proc. No. **557** (Materials Research Society, Pittsburgh, 1999), p. 275.
[15] S. Heck and H. M. Branz, in Amorphous and Hetrogeneous Silicon Thin Films: Fundamentals to Devices-1999, edited by H. M. Branz, R. W. Collins, H. Okamoto, S. Guha, and R. Schropp, Mater. Res. Soc. Symp. Proc. No. **557** (Materials Research Society, Pittsburgh, 1999), p. 347.
[16] A. N. Safonov, E. C. Lightowlers, and G. Davies, Phys. Rev. B **56**, R15517 (1997).
[17] J. Chevallier and B. Pajot, in *Interaction of Defect in Semiconductors*, edited by S. Pizzini (Trans Tech, Zurich, in press).
[18] S. K. Estreicher, J. L. Hastings, and P. A. Fedders, Phys. Rev. B **57**, R12663 (1998).
[19] A. H. Mahan and M. Vanecek, in Amorphous Silicon Materials and Solar Cells, edited by B. L. Stafford, AIP Conf. Proc. No. **234** (AIP, New York, 1991), p. 195.
[20] P. A. Fedders, D. J. Leopold, P. H. Chan, R. Borzi, and R. E. Norberg, Phys. Rev. Lett. **85**, 401 (2000).
[21] C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).
[22] S. Sheng, G. Kong, and X. Liao, Solid State Commun. **116**, 519 (2000).
[23] R. Biswas and Y.-P. Li, J. Non-Cryst. Solids **266–269**, 401 (2000).
[24] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 10 791 (1989).
[25] Y. S. Kim and K. J. Chang, Phys. Rev. Lett. **86**, 1773 (2001).
[26] A. W. R. Leitch, V. Alex, and J. Weber, Phys. Rev. Lett. **81**, 421 (1998).
[27] M. Vanecek, Z. Remes, J. Fric, E. Sipek, A. Fejfar, J. Kocka, U. Kroll, A. H. Mahan, and R. S. Crandall, in *Proceedings of the 13th European Photovoltaic Solar Energy Conference, Nice, France*, edited by W. Freiesleben, W. Palz, H. A. Ossenbrick, and P. Helm (Stephens & Associates, Bedford, 1995), p. 242.
[28] A. H. Mahan, J. Yang, S. Guha, and D. L. Williamson, in Amorphous and Hetrogeneous Silicon Thin Films: Fundamentals to Devices-1999, edited by H. M. Branz, R. W. Collins, H. Okamoto, S. Guha, and R. Schropp Mater. Res. Soc. Symp. Proc. No. **557** (Material Research Society, Pittsburgh, 1999), p. 269.
[29] A. Von Keudell and J. R. Abelson, J. Appl. Phys. **84**, 489 (1998).
[30] N. H. Nickel, W. B. Jackson, and N. M. Johnson, Phys. Rev. Lett. **71**, 2733 (1993).
[31] J. Robertson, J. Appl. Phys. **87**, 2608 (2000).
[32] A. Von Keudell and J. R. Abelson, Phys. Rev. B **59**, 5791 (1999).
[33] T. Gotoh, S. Nonomura, M. Nishio, N. Masui, S. Nitta, M. Kondo, and A. Matsuda, J. Non-Cryst. Solids **227–230**, 263 (1998).
[34] S. Gupta, R. S. Katiyar, S. Z. Weiz, and I. Balberg, J. Non-Cryst. Solids **266–269**, 496 (2000).
[35] H. Fritzsche, in Amorphous and Microcrystalline Silicon Technology-1997, edited by S. Wagner, M. Hack, E. A. Schiff, R. Schropp, and I. Shimizu, Mater. Res. Soc. Symp. Proc. No. **467** (Material Research Society, Pittsburgh, 1997), p. 19.
[36] C. R. Wronski, in Amorphous and Microcrystalline Silicon Technology-1997, edited by S. Wagner, M. Hack, E. A. Schiff, R. Schropp, and I. Shimizu, Mater. Res. Soc. Symp. Proc. No. **467** (Material Research Society, Pittsburgh, 1997). p. 7.
[37] X. Xu, J. Yang, and S. Guha, J. Non-Cryst. Solids **198–200**, 60 (1996).
[38] A. H. Mahan, D. L. Williamson, B. P. Nelson, and R. S. Crandall, Phys. Rev. B **40**, 12 024 (1989).
[39] J. H. Yoon, J. Non-Cryst. Solids **266–269**, 455 (2000).
[40] M. Stutzmann, M. C. Rossi, and M. S. Brandt, Phys. Rev. B **50**, 11 592 (1994).
[41] S. Yamasaki and J. Isoya, J. Non-Cryst. Solids **164–166**, 169 (1993).
[42] M. Stutzmann, in *Amorphous and Microcrystalline Silicon Technology-1997*, edited by S. Wagner, M. Hack, E. A. Schiff, R. Schropp, and I. Shimizu, Mater. Res. Soc. Symp. Proc. No. 467 (Material Research Society, Pittsburgh, 1997), p. 37.