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MEDIATION OF LIGHT-INDUCED METASTABLE DEFECT FORMATION IN HYDROGENATED AMORPHOUS SILICON BY INTERSTITIAL HYDROGEN AND VOIDS

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A large set of samples was deposited by radio frequency powered glow discharge under various conditions of temperature, power, gas pressure and dilution of silane. Density of states of each sample was studied in the as-deposited, light-soaked and annealed states by means of the modulated photocurrent and constant photocurrent methods. Upon light-soaking we have systematically found an increase of both the deep defect density and of the conduction band tail states. Moreover, for samples deposited on the edge of crystallinity and for polymorphous materials, irreversible modifications of the density of states were observed after light-soaking followed by annealing. None of the existing models of the metastability accounting for these behaviors we propose a new model in which light-induced creation of dangling bonds is mediated by interstitial hydrogen. During light-soaking the hydrogen atoms generated by the breaking of Si-H bonds gather to form interstitial hydrogen molecules that are trapped into voids or platelets. During annealing, these molecules are broken and H atoms are released in the lattice passivating the metastable dangling bonds. This qualitative model fully explains our experimental results and also many other experimental observations reported in the literature.

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Keywords: Amorphous silicon, Hydrogen, Metastability

1. Introduction

One of the major limitation to obtain high and stable conversion efficiencies in thin films solar cells based on hydrogenated amorphous silicon (a-Si:H) is the light induced degradation of the electronic properties of this material. Researches to understand and eventually to minimize this phenomenon, known as the Staebler and Wronski (SW) effect [1], have been growing steadily during the last twenty years. Many models have been proposed to explain the SW effect and the role of hydrogen incorporated into the lattice is now recognized to be predominant. This paper is not intended to be a review of the existing models. For this purpose a complete book will be necessary. Moreover, such a review can be already found in the literature [2]. Despite this large number of models, it appears that none of them can satisfactorily explain the results of the density of states (DOS) measurements that we have made on a large set of samples.

For the present study, samples have been prepared by rf glow discharge under various conditions of temperature, rf power, gas pressure and dilution of silane. The DOS of these samples has been studied in the as-deposited, light-soaked and annealed states. Two surprising results have been obtained. First, upon light-soaking, we have observed a broadening of the conduction band tail suggesting that the lattice structure is modified by this process. Second, for some samples, after light-soaking, it was impossible to restore by annealing the optoelectronic properties and the DOS measured in the as-deposited state. In particular the deep defect density remained higher than that measured in the as-deposited state, suggesting that some hydrogen, removed from the Si-H bonds during light-soaking and essential to passivate the dangling bonds (DB), had been trapped and lost either during the light-soaking or the annealing process. This unexpected behaviour was mainly observed on polymorphous materials (pm-Si:H) [3] and on samples deposited on the edge of crystallinity [4] and, thus, depends on the peculiar microstructure of the samples. This new phenomenon attracted our attention on the possible nature of the H atoms traps 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 by annealing, and H_2 molecule is a possible candidate. In c-Si and a-Si:H, clusters, voids or platelets offer enough room to store these molecules and can be considered as possible hydrogen traps. It is surprising that voids, despite their large quantity in a-Si:H, have attracted so 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 clusters, voids or platelets contribute to the SW effect and that fully account for our results as well as for the results of many other experiments.

In section 2, we present the different deposition conditions under which samples have been prepared and the different techniques used to study the optoelectronic properties of these samples. In section 3, we present the evolution of the DOS of studied samples that we have observed under successive light soaking and annealing at different temperatures. We will present some detailed analysis and studies that we have achieved on some peculiar types of samples. In section 4, we present some of the recent developments on the role of hydrogen in c-Si as well as in a-Si:H, in particular during the light-soaking and annealing processes. Then we present our model and compare the expected outcomes with recent results of characterizations performed by other research groups on various types of a-Si:H thin films.

2. Samples and experiments

Many types of samples, prepared in different laboratories under various conditions, have been studied. In this paper we concentrate on a set of 37 samples that have been analysed in detail but it is worth mentioning that more than a hundred of samples have been studied. All these 37 samples were deposited in radio frequency (13.56 MHz) powered plasma enhanced chemical vapor deposition (rf-PECVD) systems. The gas introduced in the discharge were either pure silane, or a mixture of silane and helium or argon or hydrogen. The deposition parameters (temperature T_d, dilution ratios, total gas pressure or the rf power) were varied to obtain different series of materials.

All the deposition conditions are summarized in Table 1. In this table we also give some information on the type of the materials (amorphous, polymorphous, close to microcrystalline), and on the hydrogen content. For instance, concerning the Ar diluted series, there is a clear evolution of the material from amorphous to microcrystalline structure with increasing power [4, 6].

Table 1. 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 Dens. (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 Diluted	523	1	65.8	35.8-122.5	[amorphous at low power, edge of crystal at high power]	16-9 (IR)
	523	1.5	26.4	20.4-81.6		9 (IR)
	523	5	26.4	20.4-449		11-5 (IR)
	523	10	26.4	20.4-353		9-13 (IR)
He Diluted	523	45	80	33	amorphous	12-15 (IR)
	473	3	52-184	79	polymorphous	14 (ERDA)
H Diluted	423	2	78.9-289.5	110	polymorphous	15-19 (ERDA)
	423	15	13-52.6	11	polymorphous	---

The experimental procedure was the same for all the samples. They were first annealed under vacuum 1 or 2 hours at the deposition temperature for samples deposited at 423 K or at 460 K for samples deposited at higher T_d, 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, either 2 min or up to full saturation. Accelerated light soaking of the samples was achieved at 80 °C under the water filtered light of a xenon lamp. To ensure a rather uniform absorption trough the sample thickness, 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 (LS) 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. We have observed that, for all the samples deposited at 423 K the annealing at the deposition temperature had to be followed by an annealing at 460 K because the annealing at 420 K was inefficient to fully 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 and AD states were the same or until no change in the DOS could be obtained. The DOS below the Fermi level was estimated afterward by CPM.

In each different state of the samples we have also measured the dark conductivity and its activation energy, the electron mobility lifetime product by steady state dark and photoconductivity and the hole diffusion length L_d by the steady state photocarrier grating technique.

3. Results

3.1. Light soaking results

For all the series of samples, one sample chosen arbitrarily has been light-soaked for 2 min only. The DOS was then measured by MPC. After a short annealing (1 or 2 hours) the sample was then light-soaked to saturation. All the samples exhibited the same behavior: 2 min light soaking resulted in an increase of the deep defect density but had almost no influence on 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. Yet we believe that there exists a sample-dependent time range 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 the deep defect density, larger than the increase measured after only 2 min, and a broadening of the CBT. This behavior was seen on **all** the studied samples, and, consequently, we assume 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.

A question arises from the broadening of the CBT concerning the possible evolution of the optical absorption upon light soaking. Since this broadening occurs mainly for the deepest states of the CBT we believe that it could not be detected by transmission measurements. The CPM measurements being mainly sensitive to the states below the Fermi level, we do not see any experiment that could confirm this broadening of the CBT. Actually, to our knowledge there are only few reports about the evolution of the optical absorption upon LS [9, 10]. The first paper [9] deals with above-gap optical change and the link with the purpose of our paper is not clear at present. The second paper [10] is quite interesting. From precise CPM measurement of the Urbach energy E_u of AD and light-soaked samples, the authors report a slight increase of E_u after LS. Of course, we have not performed our MPC measurements on the same samples, and our CPM measurements were not accurate enough because of interference fringes, but since we observe a systematic broadening of the CBT on all our samples we may conclude that both the conduction and valence band tails are affected by the LS process. If one assumes that the number of created states is of the same order of magnitude for both tails it is not surprising that these states can be more easily detected in the conduction than in the valence band tail since the former is much thinner than the latter.

We have also to underline that an increase of the capture cross section of the probed sates 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, proportional to the capture cross section, is the attempt to escape frequency of the states at the energy E and μ is the extended states mobility of the carriers interacting with the localized states. The plots of the DOS (or the MPC-DOS) are done assuming that the electron mobility is of the order of 10 $cm^2V^{-1}s^{-1}$ and that ν is independent of the energy and equal to 10^{12} s^{-1}, two values which 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. For instance, Meaudre and Meaudre have recently reported an increase of both the DOS and the capture cross section of states close to the Fermi level upon light-soaking (See ref. 11 and references therein).

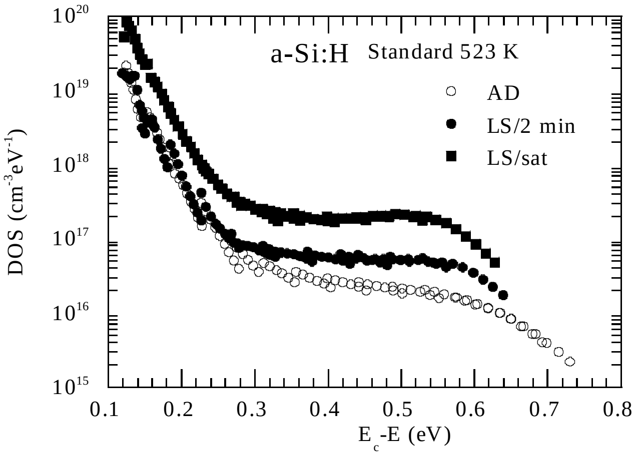

Fig. 1. Evolution of the DOS of a standard sample measured by MPC after 2 min light-soaking (LS/2 min) and after saturation (LS/sat) compared to the as-deposited (AD) DOS.

It is worth mentioning that a broadening of the CBT as seen by the MPC technique, either due to an increase of the DOS or of the capture cross section resulting from light soaking, should result in a decrease of the drift mobility measured by the time of flight (TOF) technique. To our knowledge such a decrease was never reported in the literature. A possible explanation is that TOF experiments are performed on rather thick samples (~ 4 µm or more). Consequently, it is not possible to obtain an uniform broadening of the CBT because of the limited range of light penetration in the depth of the sample. Such a non uniform aging of a a-Si:H film was demonstrated by measurements performed on a 6 µm thick He diluted sample [12]. If samples are light soaked on one side one can assume that LS leaves unchanged the major part of the layer and, thus, the drift mobility may be only little affected. Another possible explanation is that only the shallowest states of the CBT are limiting the drift mobility. These states may be less affected by the LS process than the deepest states of the CBT and thus an evolution of the CBT may be difficult to detect by TOF.

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:

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

We have found this behavior on almost all our samples irrespective of the preparation conditions. As an illustration we present in Fig. 3 the LS kinetics measured on a sample prepared under argon dilution. The values of τ_1, τ_2, β_1 and β_2 are reported on the Fig.s.

Note that the form of Eq. (1) has been chosen only to show that a single stretched exponential distribution cannot 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. One can wonder if the evolutions of these two distributions are independent or not. In the first case we can use two stretch exponential distributions to fit the kinetics, but not in the second case. This point will be further developed later.

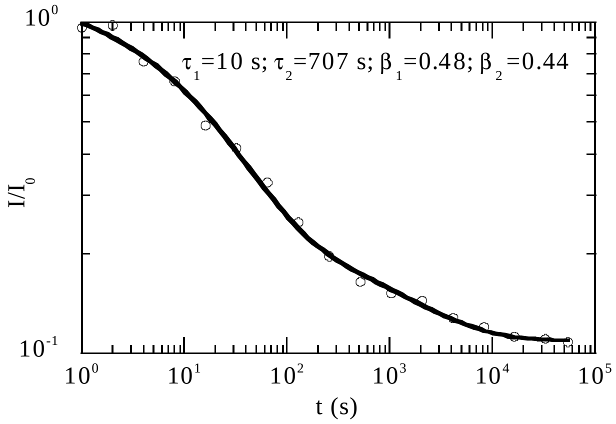

Fig. 2. Evolution of the photocurrent with time measured on the sample of Fig. 1 during light-soaking normalized to the value measured in the AD state.

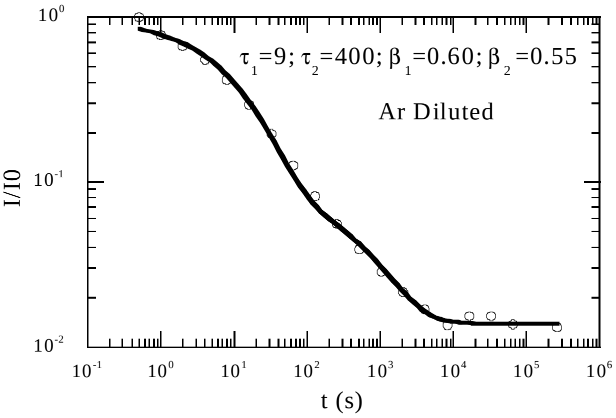

Fig. 3. Evolution with the LS time of the photocurrent measured on a sample prepared with argon dilution. The photocurrent has been normalized to the value measured in the AD state.

3.2. Annealing results

During the annealing process, many different evolutions, mainly depending on the deposition parameters, have been observed.

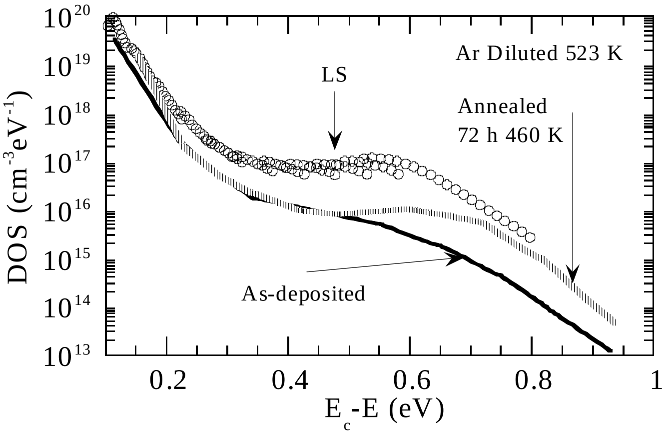

Fig. 4. DOS measured by MPC of an Ar diluted sample. Only the envelops of the DOS are presented for the measurement in AD (full line) and annealed states (dashed line). In the LS state, only the points obtained at the highest frequencies at which the experiment has been done are displayed. Clearly annealing 72 h at 460 K does not restore the deep states to their AD values.

For samples deposited at 523 K, some samples had their DOS totally restored after annealing at 460 K, but for many samples, mostly those prepared under Ar dilution, we have observed that, even after 72 hours annealing, the deep states density was still higher than the deep states density measured in the AD state. This behavior is illustrated in Fig. 4.

However, for deposition temperatures above or equal to 473 K all the samples except two among 23 had their conduction band tail restored as in the AD 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 [13]. The same remark was done by Han *et al.* about the states created in the valence band tail by the LS process [10]. This behaviour indicates that i) for some samples, hydrogen is probably stored in some place during light-soaking from where release of hydrogen and, hence, DB passivation is not possible by thermal annealing even at 460 K, and ii) if we attribute the broadening of the CBT to structural changes as Han *et al.* did for the valence band tail [10], 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.

3.2.1 Annealing of standard material deposited at 423 K

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 broadened. We then annealed these samples at 460 K and the deep defect density was fully restored but it was impossible to restore the CBT to its AD value (See Fig. 5). 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 cycle did not modify the DOS. This behaviour is shown in Fig. 6.

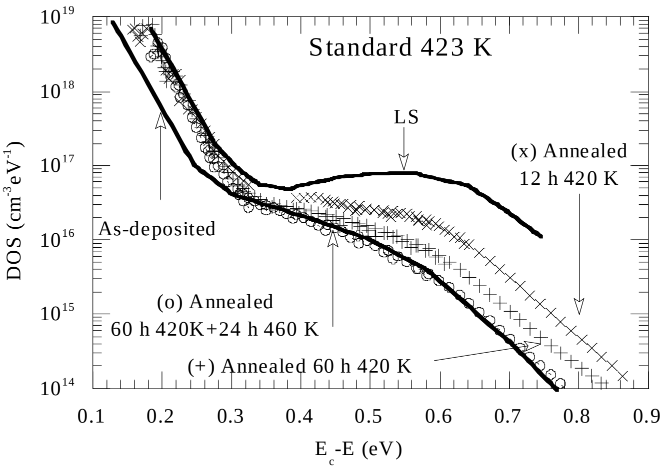

Fig. 5. Evolution with LS and annealing of the DOS measured by MPC of a standard sample deposited at 423 K. After 60 h annealing at 420 K (+) the DOS is not restored to its AD value. Annealing 24 h more at 460 K restores the deep defect density but not the CBT (o).

At this point one can wonder if the irreversibility we have observed for the CBT is due to LS or to annealing at a temperature higher than T_d. To find an answer, we have studied two layers of standard material deposited at 423 K in the same run called (A) and (B) in the following. Both layers presented the same DOS in the AD state, as measured by MPC and CPM, and no evolution of the DOS upon annealing at 420 K. Part (A) of the film was then light-soaked to saturation, annealed 24 hours at 420 K plus 24 hours at 460 K, light-soaked a second time and annealed 30 hours at 460 K and finally light-soaked a third time and annealed 12 hours at 460 K. Part (B) of the film was annealed at 460 K during 24 h, light-soaked to saturation, annealed 24 hours at 460 K, light-soaked a second time to saturation and finally annealed 48 h at 460 K. After each step we have measured the electronic parameters and the DOS by MPC and CPM. The complete investigation of both layers is summarized in Fig. 7.

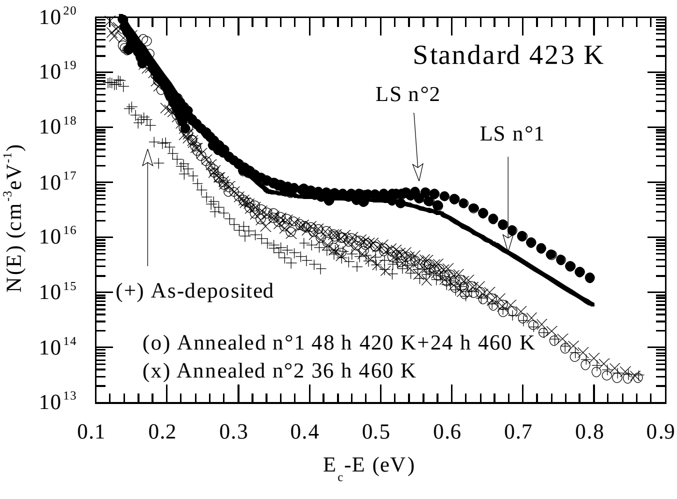

Fig. 6. Evolution of the DOS of a standard sample deposited at 423 K upon successive LS/ annealing cycles.

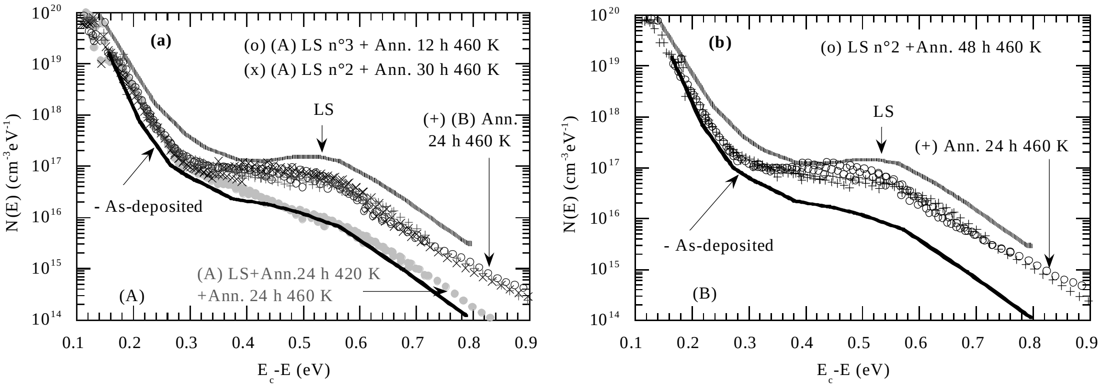

Fig. 7. Evolutions of the MPC-DOS of part (A) (a) and (B) (b) of the same sample after the different procedures we used.

Since all the MPC-DOS measured after each LS were the same only one of them is shown in Fig. 7. We have also observed the same behaviour with the absorption coefficients measured by CPM.

The behaviour of layer (A) was the following (see Fig. 7.a). The first LS increased both the deep defect density and the CBT. Annealing at 420 K decreased but not restored the DOS. After annealing at 460 K the deep defect density measured by MPC was roughly set back to its AD value, though slightly higher, but the CBT remained enlarged in contrast with the annealing results obtained on samples prepared at 523 K. After the second LS/ annealing cycle the deep defect density increased. The third LS/ annealing cycle gives the same MPC-DOS as after the second one.

In Fig. 7.b it can be seen that annealing 24 h the layer (B) at 460 K resulted in an increase of both the deep defect density and the CBT, the MPC-DOS being the same as for sample (A) after the second LS/annealing cycle. Further LS/annealing cycles led to the same DOS as after the first annealing.

The evolution of the CBT of part (A) after the first LS/annealing at 420 K then 460 K process corresponds to what we have observed on all the standard samples prepared at 423 K: the final MPC-DOS presents an enlarged CBT. The experiments performed on part (B) explain this result. Annealing of part (B) at 460 K results in an increase of the MPC-DOS (deep defects and CBT). As far as the CBT is concerned, our measurements clearly indicate that annealing a layer at a higher temperature than the deposition temperature induces some structural modifications that are reflected in the enlargement of the conduction band tail. It seems that the final value of the CBT measured on standard samples deposited at 423 K which have been light-soaked and annealed at 460 K is likely due to the annealing process alone. This means that we have to consider two types of structural modifications: a first one induced by the LS process and a second one resulting from annealing at a temperature above the deposition temperature. Both result in a broadening of the CBT. It has been observed an expansion of the material during light degradation [14]. Hence, a LS structural modification is seen on all the samples whatever the deposition temperature. For samples deposited at high T_d (523 K) microstructure can be restored by annealing at a lower temperature than T_d (460 K). For samples deposited at low T_d (423 K) annealing at the deposition temperature cannot restore the structural modification induced by LS and annealing at a higher temperature than T_d induces irreversible structural modifications. In that sense annealing is not precisely the reverse process of light-soaking.

The sudden increase of the deep defect density of part (A) after the second LS/annealing at 460 K cycle was observed only on this sample. The experiments performed on part (B) explain this result. For the part (B) annealed at 460 K, the increase of the deep defect density above the Fermi level is accompanied by a decrease of the deep defect density below the Fermi level, measured by CPM (see Fig. 8), an increase of L_d from 203 to 237 nm, and an increase of the activation energy from 0.85 eV to 1.05 eV. Our interpretation of this behaviour, based on the defect pool model [15], is that the material was probably very slightly p doped : annealing at 460 K has enhanced and revealed this doping. Once the (B) layer has been annealed, further LS / annealing cycles led to the same DOS both above (see Fig. 7.b) and below the Fermi level as shown by the absorption coefficient of Fig. 8.

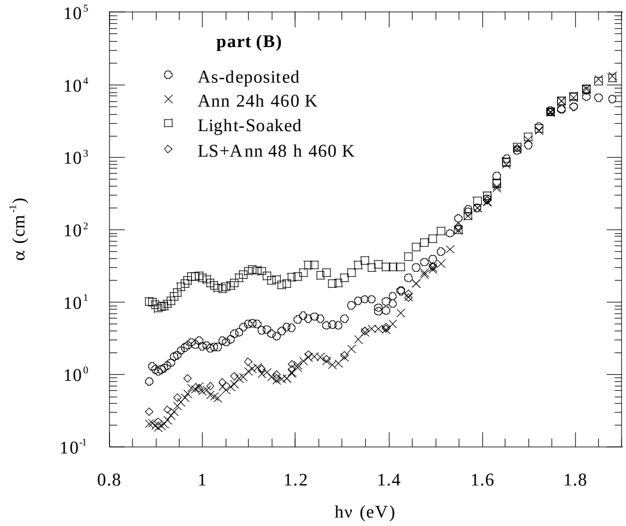

Fig. 8. Evolution of the absorption coefficient measured by CPM of layer (B) after annealing at 460 K, light soaking, and light soaking plus annealing at 460 K.

Our results would suggest that annealing of the sample reveals the dopant according to the evolution of the DOS of part (B) upon annealing at 460 K whereas the LS process passivates the boron atom by H bonding due to the H atoms released during light degradation [16]. Since the following successive LS/annealing cycles do not modify the DOS of part (B) it means that, as already mentioned above, annealing at 460 K is not the exact reverse process of light-soaking. This would explain why many LS/annealing cycles are needed for part (A) to reach the same DOS as part (B). The first light-soaking of part (A) quenches completely the dopant that cannot be completely revealed by the first annealing. A second LS/annealing cycle is needed for that. Annealing at 460 K can be then considered as more efficient to reveal dopant atoms than LS is to passivate them.

As a conclusion, structural modifications are underlined by a broadening of the CBT. For standard samples deposited at 423 K, this broadening after a LS/annealing cycle is mainly due to structural modifications induced by the annealing process performed at a higher temperature than the deposition temperature.

3.2.2 Annealing of polymorphous material deposited at 423 K

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 hours (See Fig. 9).

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 pm-Si:H samples except one among ten. For these samples LS/annealing cycles results in irreversible changes in terms of both passivation by hydrogen and structure of the lattice. In addition, the DOS evolves after each further LS/annealing at 460 K cycle. This behaviour is shown in Fig. 10. For this sample, prepared at 129 Pa, at least three LS/annealing cycles were necessary to obtain a rather reproducible evolution of the DOS measured by MPC upon this process. Finally, neither the CBT nor the deep defect density were restored to their as-deposited values.

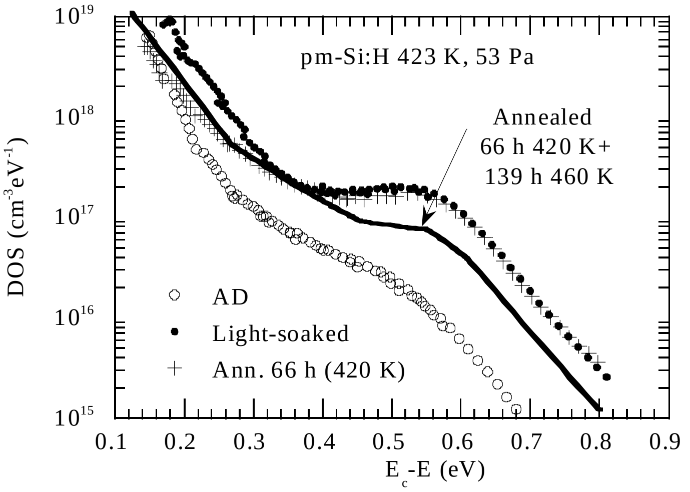

Fig. 9. Evolution with LS and annealing of the DOS measured by MPC of a pm-Si:H sample deposited at 423 K. It can be seen that after annealing at 420 K for 66 h, the annealed DOS (+) is not very different from the LS DOS (●), both being much higher than the AD DOS (o). Annealing at 460 K does not restore the AD DOS either.

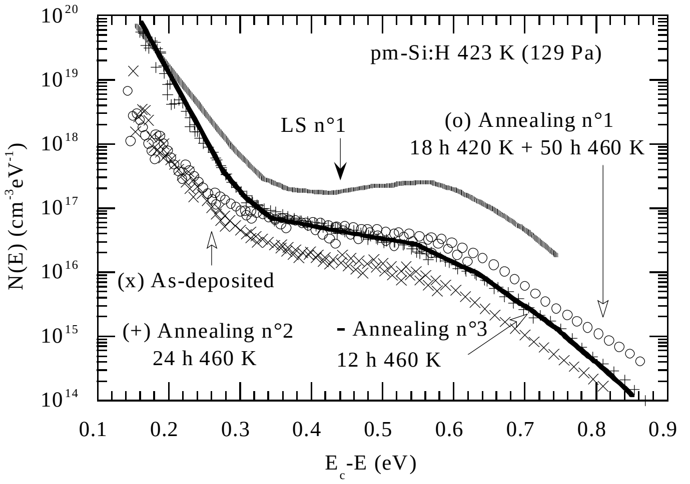

Fig. 10. Evolution of the DOS measured by MPC of a pm-Si:H sample prepared at 129 Pa following successive LS/annealing cycles.

It is not surprising to observe different behaviours 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 [17, 18]. On these samples, it was shown from Fourier Transform Infra Red spectroscopy, that the absorption band around 2000-2100 cm^{-1} could be decomposed into three different bands : one band at 2000 cm^{-1}, one band at 2100 cm^{-1} for some samples, these two bands being the "usual" ones, and an extra band around 2030 cm^{-1} [17, 18]. This extra band has been attributed to a-Si:H groups located at the boundary of nanocrystallites in a platelet-like structure [18]. The evolution of the integral of the latter band with deposition pressure, for a series of samples prepared under the same conditions except the total pressure, is presented in Fig. 11. It can be seen that the band at 2030 cm^{-1} decreases with increasing pressure. It is precisely the material exhibiting the highest contribution of this band that presented the larger "irreversibility" upon the LS/annealing process [19]. Since we have noted a systematic correlation between the presence of this extra band and the irreversibility of transport properties, even on polymorphous samples prepared under helium dilution (not presented here), we then believe that there exists a direct link between the microstructure of the samples and their behaviour upon LS/annealing cycle. This link is explained in the model below.

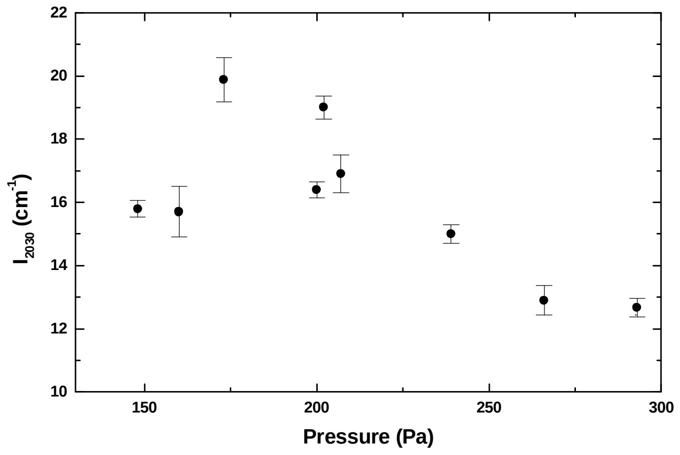

Fig. 11. Evolution of the integral of the absorption band at 2030 cm^{-1} with the deposition pressure for polymorphous samples.

Table 2. Evolution of the CBT and of the deep states upon annealing after light-soaking for 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	--	--	[Restored except two samples among 17]	restored
		edge of crystal				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

As a summary of the different evolutions of the transport properties and DOS that we have observed on the studied samples, we present in Table 2 the evolution of the CBT and of the deep states of the different types of samples upon annealing.

From the above behaviours 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 sample microstructure, whereas LS does not depend so much on these conditions.

4. Discussion

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

4.1. H_2 in a-Si:H and c-Si

Breaking a Si-H bond is probably not the simple abstraction of the H atom as this process requires a large energy of 3.6 eV. A less energy demanding mechanism has been proposed in which the H atom goes first into bond-centered position (H-BC) between two Si atoms leaving a DB behind [20]. The 1.74 eV required to shift the H atom from Si-H to H-BC could be provided by carrier recombination from tail states to tail states. An experimental confirmation of the H-BC creation has been given by Darwich *et al.* from Infra-Red (IR) measurements [21]. They have shown that at the beginning of the LS process new absorption lines, attributed to an increase of the H-BC population, appear in the spectra. According to Darwich *et al.* the growth of the H-BC lines is correlated with a decrease of the Si-H IR absorption lines. They have also noted that after a few hours of light-soaking these new absorption lines disappeared and that the absorption spectrum was the same as in the annealed state. 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. C. G. Van de Walle and B. Tuttle have proposed that another H atom comes to passivate the newly created DB left by the H atom gone in BC position [22]. This would result in an increase of the Si-H IR absorption. The Si atom turns to be over coordinated and, according to C. G. Van de Walle and B. Tuttle [22], 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 an "intermediate precursor", and such an intermediate precursor was put into evidence by Heck and Branz [23].

It is worth to note that, according to Safonov *et al.*, 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 [24]. We have here another mechanism that would result in creation of H_2 molecules.

Finally, it was shown experimentally 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 [25]:

$$\text{Si-H} + \text{H} \rightarrow \text{DB} + H_2 \qquad (0.2\ \text{eV}) \tag{2}$$

All the mechanisms described above 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, during LS in a-Si:H 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.

Since H_2^i can be an end product we may suggest that H_2^i plays an active role during the LS process. According to Chevallier [25], H_2^i in T-site and H_2^*, an equivalent of the $M(Si\text{-}H)_2$ 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^* [26]. 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 [24]. 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 CVD [27], 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 P. A. Fedders *et al* [28]. 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. 26, H_2^i can be easily dissociated in close vicinity of a non hydrogenated vacancy, we propose that the new dangling bond, created by the migration of the previous H atom toward the BC position, can promote 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.

4.2. Model for the Staebler-Wronski effect

We then propose the following mechanism for light soaking:

1. The recombination of carriers from tail states to tail states results in the breaking of Si-H bonds. The energy released is not enough to free H atoms in the lattice, that would requires 3.6 eV, but sufficient to move the H atoms in BC position (1.74 eV) or in anti bonding (AB) position (1.2 eV) leaving dangling bonds behind [20].

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 [21]. During this first step the kinetics of annealing of the created dangling bonds must be high because H-BC and H-AB are not stable configurations. Consequently, the H atoms, thermally assisted, may easily come back to passivate again the dangling bonds they have left behind, and, experimentally, we have indeed observed rapid annealing of our samples after only 2 min light soaking.

2. The reaction in step i/ affecting the whole lattice it would not be surprising to find some of the new dangling bonds close to a H_2^i, assuming that the concentration of H_2^i is as high as predicted [28]. Recombination of carriers at these new dangling bonds could help to break the H_2^i molecule releasing two hydrogen atoms in the lattice. The less energy demanding reaction (0.87 eV) consists in the passivation of the freshly created dangling bond by one H atom (H1) and the insertion of the second one (H2) into a bond centered position [29].

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 during step i/ 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 Å to 3.2 Å [20]. This expansion may result in a change on the oscillator strength of the Si-H bonds [30].

3. If H1 passivates a DB linked to a Si atom which is already connected to another H atom, either in BC or in AB position, then the Si atom becomes over coordinated. If we follow the suggestions of C. G. Van de Walle and of Savonof *et al.* we can assume that, in both cases (H-BC, H-AB), the two H atoms gather again, are freed in the lattice and trapped somewhere under H_2^i configuration. If the H2 atom, coming from the broken H_2^i, is in a BC position close to a Si-H bond then the same mechanism as for the H1 atom can occur. At the end of the process two dangling bonds and two H_2^i are created. This simple scheme is presented in Fig. 12.

This last step should lead to a decrease of the number of the Si-H bonds and thus of the Si-H IR absorption but, since the lattice has expanded under the introduction of the H atoms in BC position, the oscillator strength of the Si-H bonds may have increased and the Si-H IR absorption may still remain higher than in the AD state.

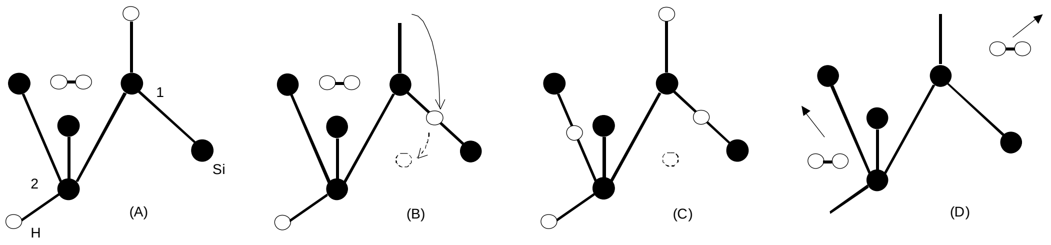

Fig. 12. Simple scheme presenting the different mechanisms occurring during the LS process: (A) the starting environment, the numbers 1 and 2 correspond to the indexes used in the equations describing the DB formation, (B) the recombination of two carriers creates one DB by giving enough energy to the 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.

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

$$[\text{Si-H}]_1 + [\text{Si-Si}]_1 \rightarrow \text{DB}_1 + [\text{Si-H-Si}]_1 \qquad (1.74\ \text{eV}) \qquad (3)$$

$$\text{DB}_1 + [\text{Si-Si}]_2 + \text{H}_2^{\text{i}} \rightarrow [\text{Si-H}]_1 + [\text{Si-H-Si}]_2 \qquad (0.87\ \text{eV}) \qquad (4)$$

$$[\text{Si-H}]_1 + [\text{Si-H-Si}]_1 \rightarrow \text{DB}_1 + [\text{Si-Si}]_1 + \text{H}_2^{\text{i}} \qquad (0.2\ \text{eV}) \qquad (5)$$

If we add the reaction: $[\text{Si-H}]_2 + [\text{Si-H-Si}]_2 \rightarrow \text{DB}_2 + [\text{Si-Si}]_2 + \text{H}_2^{\text{i}}$ (0.2 eV), (6)

it means that the total reaction is:

$$\text{H}_2^{\text{i}} + 2\ \text{Si-H} \rightarrow 2\ \text{DB} + 2\ \text{H}_2^{\text{i}} \qquad (3.01\ \text{eV}), \qquad (7)$$

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 [31], since this movement would only cost 1.2 eV according to Ref. 20. The total formation energy would be of the order of 1.2 eV.

The very simple mechanism described above takes only a few Si-H bonds and H atoms into account, but one has to consider the whole matrix to foresee all the possibilities of its evolution. For instance the H-BC H2 atom may not be close to a Si-H bond. In that case, since the H-BC configuration is not stable [20], this atom may diffuse through the lattice from a BC position to the next one as suggested by C. G. Van de Walle on the basis of theoretical calculations [32]. While wandering, the H2 atom may gather with the H atom of another Si-H bond and form H_2^i or may meet a DB that it will passivate. In the first case, as in our simple scheme, two DB are created, but, in the second case, the net rate of creation of DB is equal to zero. We have also to consider different evolutions for the created H_2^i. Indeed, if it is not trapped in a stable configuration it will probably dissociate and the released H atoms may passivate some dangling bonds. In that case the net rate of DB creation is also zero. As a conclusion, 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, and voids, clusters or platelets are excellent candidates for trapping H_2 molecules [33]. Thus, though the whole lattice may be affected by the light soaking process, the metastable DB would be preferably created in close vicinity of voids. Finally, this dynamic equilibrium and the creation of metastable DB only in the vicinity of voids or clusters, can explain why with, say, 10% of hydrogen present in the material (~$5\text{x}10^{21}$ 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 modify the whole lattice.

We now address the annealing process. According to our assumptions on the LS mechanism, the molecular hydrogen produced in reaction (7) is stored in microvoids in a-Si:H or platelets located close to the nano-crystallites/a-Si:H or clusters/a-Si:H interface for materials deposited on the edge of crystallization. The energy of the stored hydrogen molecule may be somewhat distributed. Indeed, it can be trapped under some interstitial form, that is under some "pressure" [34], or under a less constraint or even free molecule. Thus, annealing could provide enough thermal energy to break this molecule or not. In the first case, during annealing H atoms are injected in the lattice and passivate the metastable DB through diffusion, but in the second case LS results in irreversible changes. It is worth mentioning that some authors have already speculated that, during annealing, the H atoms could be injected from microvoids [35]. It means that the annealing process could be consider as an equivalent of the hydrogenation of c-Si from a H_2 gas source [26]. The energy distribution of stored hydrogen explains why annealing at 420 K is not very efficient since the provided thermal energy can release only few H atoms. Even annealing at 460 K may not be enough 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. The irreversibility of the deep defect density was observed on some Ar diluted samples deposited on the edge of microcrystallinity [6] (See Fig. 4) and in pm-Si:H samples (See Fig. 9). In the first type of materials it has been shown that hydrogen bonding could be enhanced at the nanocrystallites/a-Si:H interface compared to the amorphous matrix [36]. Some authors have also proposed that clustered Si-H groups of columnar shape could be considered as a starting environment for the crystallization [37]. According to Keudell and Abelson, this H rich interface could be made of platelets whose IR signature is an absorption band around 2030 cm^{-1}[38]. They have also proposed that platelets were present in pm-Si:H were the same IR signature has been observed, a proposition also advanced by other authors [18] (see Fig. 11).

To give a complete picture of a LS/annealing cycle, we then propose that H_2 molecules released during LS are mainly stored in these platelets. This assumption is supported by the fact that such a behaviour was observed in c-Si [34] and in poly-Si [39]. Also Estreicher *et al.* 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 [26]. Conclusively, according to our results and to the results of Nickel *et al.* [39] we can reasonably assume that some of these molecules can be lost for DB passivation.

To conclude this section, we would like to give a few hints on the way interstitial molecular hydrogen could be incorporated in the material during deposition. Recent developments on the deposition process can provide some information on this issue. In many models H_2 molecules are formed during removal of hydrogen from the H-rich surface during deposition [40, 41]. For instance, recent in situ Infra Red measurements have proposed a new mechanism for the construction of the amorphous layer : the 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 [41]. Of course, most of these H_2 molecules are released in the plasma but one can imagine that part of them are incorporated in the layer under interstitial form.

4.3. Correlation with other experimental results

To support and illustrate the model described above we would like to show that it fits rather well with many experimental observations.

First of all we would like to stress that this model tacitly assumes that amorphous silicon thin films can be divided in two regions. A first one, for which LS has almost no influence since no hydrogen traps are available, and a second one in the vicinity of voids (or clusters or platelets) relatively rich in hydrogen. According to the model the metastable defect creation would take place mainly in this second region. We can note that some authors are even going further by describing a-Si:H as a two-phase material in which LS sensitive zones are surrounded by a more ordered and poorly hydrogenated matrix [42]. It is also worth mentioning that these authors have observed during the LS process an evolution of the IR absorption around 2025 cm^{-1}, a value not far from the 2030 cm^{-1} observed on samples presenting irreversible modifications upon LS/annealing cycles.

It was recently shown that LS was accompanied by an expansion of the material [14, 43]. This modification of the lattice structure is probably responsible for the CBT broadening that we have observed on all the studied samples from MPC measurements. Our qualitative model accounts for this expansion for two reasons: first, the introduction of H atoms in H-BC position increases the Si-Si bond length and, second, the generated extra H_2^i atoms need room to be stored. The influence of the modification of the lattice structure on the "order" of the material (Short Range Order or Intermediate Range Order) is still a matter of debate [44], and beyond the scope of this paper.

Taking the expansion of the material into account, we can come back to the validity of Eq. (1). In our view the increases of both deep defects and band tail states during light soaking cannot be independent. Indeed, the number of band tail states certainly plays a role in DB formation if one assumes that this formation is initiated by tail state to tail state recombination. While DB are created an expansion of the lattice results in an increase of the CBT states. This increase of the number of tail states enhances tail to tail recombination which 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 and 3, is therefore to be considered more as a phenomenological description than coming from a precise mathematical model.

The LS mechanism described above fits with experimental observations of the evolution of the Si-H bonds IR absorption band [21, 30]. According to our model, we expect a first decrease of this band when H atoms move from Si-H to H-BC positions. Then, the passivation of the newly created DB by H atoms from H_2^i compensates, at least partly, the breaking of Si-H bonds. This process, together with an expansion of the lattice due to incorporation of H-BC atoms that should give rise to a change in the oscillator strength, leads 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 *et al.* [30].

In this model, the creation of metastable DB is not conditioned by a possible diffusion of the H atoms during light-soaking, though this possibility has not been rejected. Therefore, metastable DB may be generated by illumination even at low temperatures (4.2 K) and this behaviour was indeed reported by H. Fritzsche [45].

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 [46, 47]. 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 M. Vanecek *et al.* [35] and also by A. H. Mahan *et al.* [36], 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 poorly hydrogenated material. Our model is in perfect agreement with this idea. Indeed, the creation of metastable DB should depend on the flux of H_2 molecules to be trapped in voids. Since, a small number of large voids implies a smaller area between voids and the amorphous matrix than in the case of a large quantity of voids, a material with a low concentration of large voids should be more stable than standard a-Si:H in which a large number of small voids is present [48]. Concerning the DB generated far from these voids, since there is no hydrogen traps they are probably passivated while created by a simple redistribution of H atoms.

Going further following this 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 J. H. Yoon [49]. 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 four 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. This assumption has been recently confirmed by isochronal annealing performed on pm-Si:H and µC-Si materials [18]. Vignoli *et al.* have shown that successive annealing lead to both an hydrogen exodiffusion and a decrease of the IR absorption band around 2030 cm^{-1}, indicating that hydrogen is released from platelet-like structures upon this 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} [48]. 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 [50], 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}. In this respect, a value of 1.1×10^{19} cm^{-3} light induced DB was recently reported by C. Ohigara and co-workers [51].

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 [52].

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 ESR results of Stutzmann [53] as well as the results of Yamasaki and Isoya [52]

5. Conclusions

Evolutions of the DOS and of the electronic parameters of many samples prepared under various conditions of rf-PECVD have been investigated. It was shown that for all the studied samples LS results in an increase of the deep defect density and a broadening of the conduction band tail. The broadening of the CBT was also evidenced for samples annealed at higher temperature than the deposition temperature. We conclude that structural modifications of the amorphous matrix were responsible for this behaviour. We have also observed that for some samples, either prepared on the edge of micro-crystallinity or polymorphous materials, annealing was unable to restore the deep defect density to its AD value. None of the existing models for the SW effect taking these two effects into account we propose a qualitative model. In this model the creation of dangling bonds is mediated by interstitial hydrogen and voids. The abstraction of H atoms from Si-H bonds is catalysed by H_2^i molecules. These H atoms released during LS are assumed to be trapped as interstitial hydrogen molecules in voids, clusters or platelets. This model fully explains our results. For instance, it predicts structural modification of the lattice in agreement with the observed material expansion and accounting for the broadening of the CBT. Assuming that part of the hydrogen trapped in platelets could not be released during annealing to passivate the metastable DB created during light-soaking, our model explains the irreversible evolution of the DOS upon LS/annealing cycles observed for pm-Si:H or materials deposited on the edge of crystallinity.

This model not only describes our experimental results but is also in good agreement with some recent studies on the SW effect and is comforted by its ability to explain and link together many established experimental results reported in the literature.

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