Metastable defects in hydrogenated amorphous silicon

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Abstract. The electronic structure of hydrogenated amorphous silicon (a-Si:H) is in a state of metastable equilibrium and can change upon application of external stimuli. We study the effect of thermal quenching and light soaking in lithium-doped a-Si:H, on its conductivity and thermopower. We present evidence showing that the metastable state obtained after fast quenching is different than that obtained after light exposure. Experiments on chalcogenides show that they are not affected by thermal quenching although they change upon light soaking. This is in contrast with lithium doped a-Si:H in which both effects are observed. Our experiments suggest that hydrogen present in a-Si:H plays an important role by controlling heterogeneities and potential fluctuations in a-Si:H. Light soaking appears to enhance these potential fluctuations, whereas fast cooling seems to have little effect on them.

Keywords. Amorphous silicon; Staebler Wronski effect; thermal induced metastabilities; thermopower; potential fluctuations; heterogeneities.

1. Introduction

Staebler and Wronski (1977) and Street (1991) discovered that a-Si:H thin films undergo a metastable change upon exposure to visible light (Staebler Wronski effect). They found that the dark conductivity as well as photoconductivity reduce after light soaking for a few hours and this change seems permanent at room temperature. Exposure to infra-red light does not bring back its original state. The sample can, however, be restored by annealing at about 180°C for about 1–2 h. The long relaxation at room temperature and the inability to erase the effect of light soaking by infra red light, leads to the conclusion that movement of atoms, rather than the trapping of charge carriers is responsible. ESR experiments (Dersch et al 1980) show that light soaking creates dangling bonds.

It was believed for quite some time that the only important feature that needs to be considered to explain the effect of light soaking is the creation of dangling bonds (Street 1991), which results from the movement of hydrogen present in a-Si:H. However, fresh evidence shows that other defects are also created. Thus, we now speak of photostructural changes involving movement of hydrogen. Infra-red absorption experiments of Zhao et al (1995) show an increase in the number of Si–H bonds, upon light soaking. Also, the rate of creation of dangling bonds can not be correlated uniquely to the rate at which photoconductivity decreases upon light soaking (Stradins and Fritzsche 1994). Furthermore, the changes observed upon light soaking are too large to be explained by the creation of dangling bonds alone. Fritzsche (1995) has listed various other evidences which show that dangling bonds are not the only defects created, as they alone cannot explain the present data. He suggests that photo-induced structural changes occur upon light soaking, which are, in addition to the creation of dangling bonds.

Inspite of much activity, this Staebler Wronski effect in a-Si:H is, so far, neither understood nor eliminated. In addition, a-Si:H also suffers from thermal metastability (Street et al 1986). Its conductivity for $T < T_E$ depends on the rate at which it is cooled

from $T > T_E$, T_E being called the equilibration temperature. The value of T_E depends on the nature and concentration of doping and is typically around 170°C for phosphorous-doped a-Si:H. For $T > T_E$, the properties of a-Si:H are independent of the cooling rate.

It has been suggested (Kakalios and Street 1987) that the light-induced metastability and thermal-induced metastability might have a common origin. They may be caused by the movement of hydrogen in a relatively rigid silicon matrix. Several microscopic models, involving hydrogen motion, have been proposed for the light-induced metastability (Agarwal 1995). In the thermal-induced metastability, T_E is thought to be analogous to the glass transition temperature T_g, above which hydrogen is relatively more mobile. However, no glass transition is clearly visible as a step (Matsus *et al* 1988; Battezzati *et al* 1991) in differential scanning calorimetry (DSC) experiments on a-Si:H. Further, our measurements on chalcogenide glasses, which show T_g clearly in DSC curves, show no evidence of thermal metastability in these glasses (Agarwal *et al* 1993). Nevertheless, the thermal instability in a-Si:H has been attributed to it being a "Hydrogen Glass" (Street *et al* 1987). Here we present these and other studies on lithium-doped a-Si:H and show that heterogeneities play an important role. We propose that the movement of hydrogen changes the heterogeneities present in a-Si:H, which in turn influence the potential fluctuations. We also present evidence indicating that the light soaking increases the long range potential fluctuations whereas thermal quenching leaves them unchanged.

2. Potential fluctuations in a-Si:H

The long-range potential fluctuations affect the electronic properties of a-Si:H as they modulate the positions of the valence and conduction band edges in space (Fritzsche 1971). These fluctuations may be elastic when they arise from a non-homogeneous distribution of charged dopants making the valence and conduction band move in the same direction with no change in the mobility gap. In addition, density fluctuations caused by the inhomogeneous distribution of hydrogen may give rise to inelastic fluctuations (Reimer *et al* 1980), which give a spatial variation of the gap. Overhof and Beyer (1981, 1983) suggest that a function $Q(T)$, defined as $Q = \ln \sigma + eS/k$ (where σ and S are the conductivity and thermopower respectively), can give information about these potential fluctuations. They have shown that the slope E_Q, of Q vs $1/T$ curve, is a measure of the potential fluctuations present. Thus measurements of $\sigma(T)$ and $S(T)$ in different metastable states can provide useful information about changes in potential fluctuations, which may be too small to be detected by structural measurements.

Figure 1 shows the results of fast quenching (FQ) and light soaking (LS) on a Li-doped a-Si:H film prepared by the glow discharge of SiH_4. Lithium is introduced by thermal diffusion (experimental details are given in Agarwal (1995)). All $\sigma(T)$ curves, measured while heating, meet at a common equilibration temperature $T_E \approx 390\,\mathrm{K}$ and become one for $T > T_E$. For $T < T_E$, σ in FQ state is higher than the SC and LS states. FQ and LS states are reversible and can be transformed into SC state by heating above T_E.

These results are in agreement with the published work of Winer and Street (1989) on Li-doped a-Si:H and are similar to the phosphorous-doped a-Si:H (Agarwal 1995).
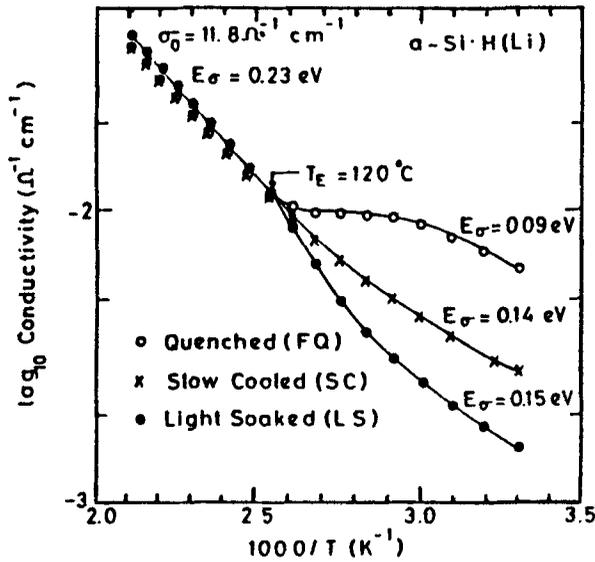
Figure 1. Conductivity of a lithium doped a-Si:H as a function of $10^3/T$ in the slow cooled (SC), fast quenched (FQ) and light soaked (LS) states.
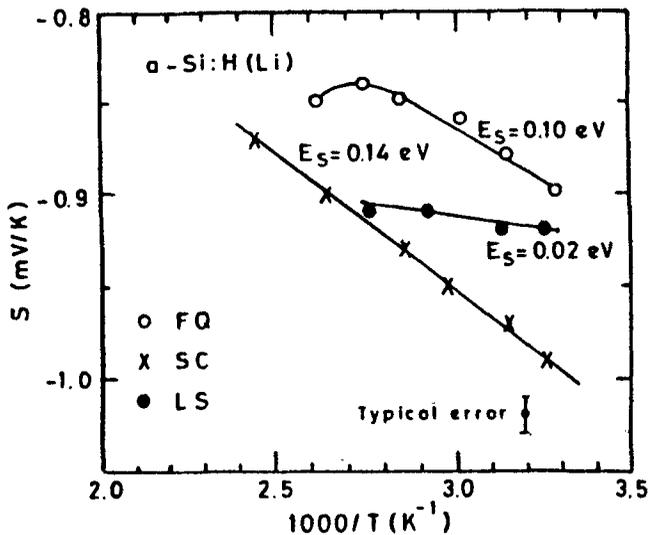

Figure 2. Thermopower $S(T)$ for a lithium doped a-Si:H in the FQ, SC and LS states.

Figure 2 shows the thermopower measurements in the FQ, SC and LS states of the same a-Si:H (Li) sample. Following Overhof and Beyer (1981, 1983), we plot $Q(T)$ in figure 3 which shows some interesting features. We find that the slope $E_Q = 0.0 \pm 0.02$ eV in the slow cooled (SC) state increases to about 0.14 ± 0.02 eV after light soaking (LS). In contrast, E_Q is almost unchanged after fast quenching (FQ). This suggests that light soaking increases potential fluctuations in a-Si:H (Li), whereas thermal quenching leaves them relatively unchanged.
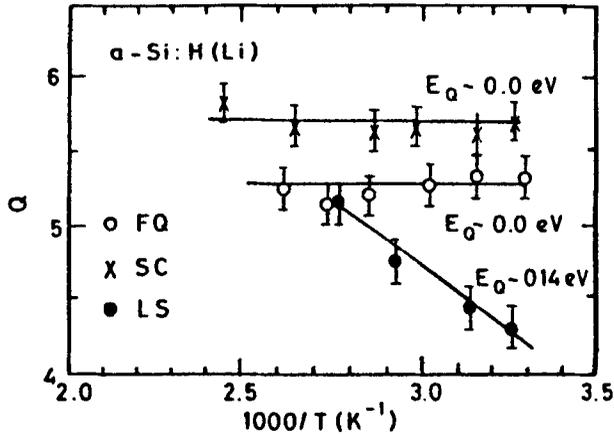
Figure 3. Q as a function of $1/T$ for the sample of figures 1 and 2 in the FQ, SC and LS states.

3. Role of hydrogen

Hydrogen is known to be distributed non uniformly in a-Si:H (Reimer *et al* 1980). In the so called 'Hydrogen Glass Model' (Street *et al* 1987), the thermal-induced metastability is explained by proposing T_E to be similar to the glass transition temperature T_g, above which a glass becomes soft. Here, however, it is only hydrogen which is assumed to become more mobile above $T > T_E$, whereas Si matrix remains rigid. The isothermal relaxation of the quenched state is observed to be a stretched exponential of the form $\approx \exp - (t/\tau)^\beta$. This can be explained by diffusion of hydrogen if the hydrogen diffusion constant $D_H \propto t^{\beta-1}$. The measurements of D_H are consistent with this hypothesis (Street *et al* 1987) and therefore support the idea that hydrogen is responsible for the quenching effects.

To further check the validity of the Hydrogen Glass Model, we looked (Agarwal *et al* 1993) for quenching effects on the conductivity of several chalcogenide glasses in which DSC measurements showed T_g to be about the same as the T_E observed in a-Si:H (Li), and whose activation energies are also similar to that of a-Si:H (Li). Among the glasses chosen were, $Ge_{15}Se_{85}$ ($T_g \approx 400$ K), $Ge_{22}Se_{68}Ag_{10}$ ($T_g \approx 410$ K) and $Ge_{20}Se_{8-x}$ As_x ($0 \leqslant x \leqslant 15$, with 435 K $\leqslant T_g \leqslant 520$ K). However, after an initial irreversible change, no reversible quenching effect on $\sigma(T)$ could be observed. In contrast, light soaking effects in the chalcogenide glasses are well known (Pfeiffer *et al* 1991). Light soaking shifts the optical absorption edge and induces metastable states in several chalcogenides (Pfeiffer *et al* 1991). In figure 4 we show the result of light soaking on the conductivity of a chalcogenide glass $Ge_{16}As_{35}Te_{28}S_{21}$ (Agarwal and Fritzsche 1974). This effect, incidentally, is of the opposite sign than the Staebler Wronski effect in a-Si:H.

4. Discussion

Our observation of a common T_E for the light-soaked (LS) and fast-quenched (FQ) states, seems to indicate that LS and FQ affect a-Si:H (Li) in a similar fashion. Further,
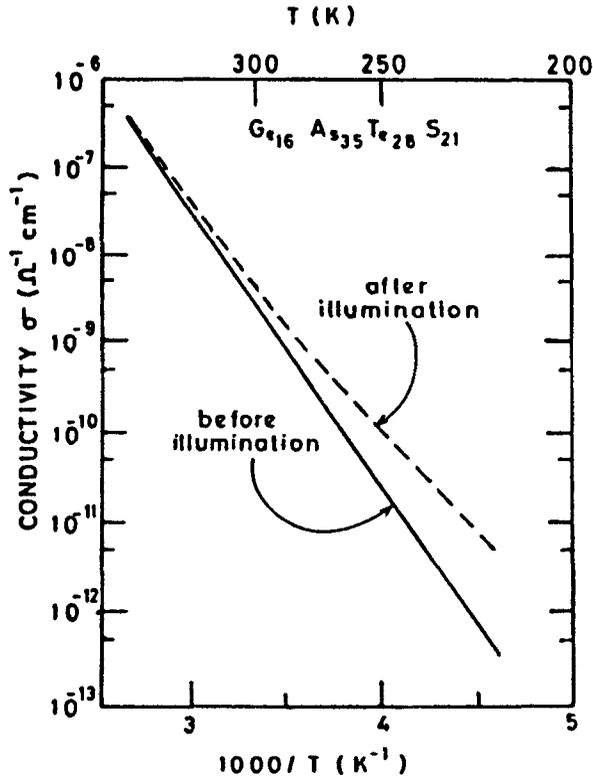
Figure 4. Effect of light soaking on the chalcogenide glass thin film $Ge_{16}As_{35}Te_{28}S_{21}$.

relaxation of LS state is also found to follow a stretched exponential behaviour (Agarwal 1995). This behaviour is similar to that of the FQ state. However, a closer look shows that the temperature dependences of β and τ are quite different (Agarwal 1995) in the two cases. In addition, changes in σ upon FQ and LS are in opposite directions (figure 1). These results, alongwith our observations in §§ 2 and 3, suggest that light soaking and fast quenching affect a-Si:H (Li) differently.

Let us look at these results a bit more closely. We have seen that the quenching experiments in a-Si:H can be explained satisfactorily by the 'Hydrogen Glass Model'. The absence of such effects in chalcogenide glasses can be understood as follows: In a-Si:H, hydrogen moves in a rigid network of a-Si for $T > T_E$ and this can result in different frozen-in states for $T < T_E$, depending upon the rate of cooling. The rigid network of Si atoms makes it possible to go back to the slow cooled state, reversibly. In chalcogenides, however, the whole structure becomes soft for $T > T_g$. This might be the reason that no quenching effects, which are reversible, are observed.

One might argue that no such effects are expected in chalcogenide glasses anyhow, because they contain lone pair orbitals which allow them new bonding configurations without breaking too many bonds. However, they do show light soaking effects (Pfeiffer *et al* 1991). Chalcogenides contain no hydrogen. But they have heterogeneities, which are caused by local variations in composition or density of constituent atoms, due to disorder. As remarked earlier, variations in local density are present in a-Si:H also. Obviously, this means that recombination and trapping kinetics upon exposure to

light may be different in different regions. This might affect the heterogeneities present and, hence, the potential fluctuations upon light soaking.

5. Summary and conclusions

We have presented the effect of fast quenching and light soaking on lithium-doped hydrogenated amorphous silicon as well as some chalcogenide glasses. We find that fast quenching changes the conductivity of a-Si:H (Li) near room temperature reversibly but has no effect on chalcogenide glasses, which is reversible upon annealing. Our investigations show that although hydrogen movement may be responsible for both the thermal as well as light-induced metastabilities in a-Si:H (Li), the two metastabilities change a-Si:H (Li) differently. In particular, we find that in a-Si:H (Li), light soaking increases the long range potential fluctuations, whereas the changes in potential fluctuations caused by quenching are insignificant.

Acknowledgements

References

Agarwal P 1995 *Thermal and light induced metastabilities in phosphorous and lithium doped hydrogenated amorphous silicon*, Ph. D. Thesis, IIT Kanpur

Agarwal P, Agarwal S C, Bhattacharya E, Kumar S and Kumar A 1993 *Indian J. Pure & Appl. Phys.* 31 367

Agarwal S C and Fritzsche H 1974 *Phys. Rev.* **B10** 435

Battezzati L, Demichelis F, Pirri C F, Tagliaferro A and Tresso E 1991 *J. Non-Cryst. Solids* **137/138** 87

Dersch H, Stuke J and Beichler J 1980 *Appl. Phys. Lett.* **38** 1456

Fritzsche H 1971 *J. Non-Cryst. Solids* **6** 49

Fritzsche H 1995 *Solid State Commun.* **94** 953

Kakalios J and Street R A 1987 *AIP Conf. Proc.* **157** 179

Matsus S, Nasu H, Akamatsu C, Hayashi R, Imura T and Osaka Y 1988 *Jap. J. Appl. Phys.* **27** L132

Overhof H and Beyer W 1981 *Philos. Mag.* **B43** 433

Overhof H and Beyer W 1983 *Philos. Mag.* **B47** 377

Pfeiffer G, Paesler M A and Agarwal S C 1991 *J. Non-Cryst. Solids* **130** 111

Reimer R A, Vaughan R W and Knights J C 1980 *Phys. Rev. Lett.* **44** 193

Staebler D L and Wronski C R 1977 *Appl. Phys. Lett.* **31** 292

Stradins P and Fritzsche H 1994 *Philos. Mag.* **B69** 121

Street R A (ed.) 1991 *Hydrogenated amorphous silicon* (Cambridge: University Press) (For a review of properties of a-Si:H see for example, this book)

Street R A, Kåkalios J and Hayes T M 1986 *Phys. Rev.* **B34** 3030

Street R A, Kakalios J, Tsai C C and Hayes T M 1987 *Phys. Rev.* **B35** 1316

Winer K and Street R A 1989 *J. Appl. Phys.* **65** 2272

Zhao Y, Zhang D, Kong G, Pan G and Liao X 1995 *Phys. Rev. Lett.* **74** 558