

Electronic structure of amorphous semiconductors

S C AGARWAL

Department of Physics, Indian Institute of Technology, Kanpur 208 016, India

Abstract. The effect of light soaking and thermal quenching on the electronic structure of hydrogenated amorphous silicon (*a*-Si:H) and chalcogenide glasses was studied. It was found that lithium doped *a*-Si:H shows both light and thermal induced changes in electronic transport properties. In contrast, chalcogenides do not show any effect of thermal quenching, although they exhibit changes upon light soaking. By analysing the conductivity and thermopower data we have concluded that the light soaking increases the potential fluctuations present in lithium doped *a*-Si:H, whereas quenching does not change them. A model qualitatively explaining these effects is presented.

Keywords. Hydrogenated amorphous silicon; transport properties; chalcogenides.

1. Introduction

Amorphous semiconductors are prepared by rapid quenching from the vapour or liquid phase and are, therefore, expected to be in a state of metastable equilibrium. Annealing at higher temperatures can induce transition from one metastable state to another. Similarly, exposure to light (or other particles, e.g. electrons) can also induce metastable changes. These metastable changes in atomic configurations may alter a variety of physical and chemical properties, e.g. density, hardness, elastic constants, chemical solubility and optical and electronic properties (For a review, see, Pfeiffer *et al* 1991). These changes are sometimes reversible upon annealing but sometimes not. Amongst the irreversible changes, one of the most spectacular effect is the giant photo-contraction observed in amorphous germanium based chalcogenide films (Singh *et al* 1979). Upon exposure to light the obliquely deposited *a*-Ge₂₅Se₇₅ films undergo a thickness reduction of up to 12%. This has been attributed to the loss of material from the film upon exposure (Harshvardhan and Hegde 1987). However, here we do not wish to discuss these and other interesting irreversible effects. Instead, we would like to talk about those changes which can be reversed by annealing to a sufficiently high temperature, which we may call the equilibration temperature T_E . We may think of T_E as the temperature above which the time taken to go from one structural configuration to another is shorter than the time scale of the experiment. Thus T_E can be thought to be analogous to the glass transition temperature T_g observed in glasses. In the chalcogenide glasses, the glass transition is usually visible quite clearly as a step in a differential scanning calorimetry (DSC) curve. In contrast, in the DSC curves on tetrahedrally bonded amorphous semiconductors (e.g. *a*-Ge, *a*-Si etc.) the glass transition is not so obvious (Battezzati *et al* 1991). For example, Matsuo *et al* (1988) observe a peak (and not a step) in DSC curve in their fast quenched phosphorous doped hydrogenated amorphous silicon (*a*-Si:H) thin films. In addition, it is not possible to make *a*-Si:H by quenching from the melt. For these reasons, the tetrahedrally bonded amorphous semiconductors are not accepted as conventional glasses. Nevertheless, the instabilities observed in *a*-Si:H have been attributed to the glassy behaviour. Here, we examine whether the light induced and

thermal induced instabilities in *a*-Si:H have a common origin and whether they can be attributed to the glass like behaviour of *a*-Si:H.

2. Metastabilities in *a*-Si:H

2.1 Light induced metastabilities in *a*-Si:H

Let us begin with the reversible changes in *a*-Si:H upon exposure to light, namely the well known Staebler-Wronski effect (SWE) (Staebler and Wronski 1977). The dark conductivity σ of undoped amorphous silicon decreases upon exposure to higher than band gap light (light soaking). The activation energy ΔE (slope of $\ln \sigma$ vs $1/T$) increases. The effect is reversible upon annealing at about 200°C for about an hour. The light soaking effect is observed in doped *a*-Si:H also. Electron spin resonance shows that light soaking creates dangling bonds (Hirabayashi *et al* 1980; Dersch *et al* 1981). In addition, other metastable defects are also created, as observed by space charge limited currents and other experiments (Misra 1984; Zhang *et al* 1994). Also, photo-conductivity decreases and sub-band gap absorption increases as new defects are created. Creation of these defects obeys stretched exponential (Shimakawa *et al* 1991).

Considerable work has been done on SWE because of its obvious implications for the *a*-Si:H solar cells. It was initially suggested that SWE was related to the stress in the *a*-Si:H films (Stutzmann 1985) but later work showed this not to be true (Guha *et al* 1985). Also, the role of impurities such as nitrogen and oxygen has been studied by Tsai *et al* (1984). In spite of much activity, however, the origin of SWE remains far from clear (Shimizu 1993).

Here, I would like to discuss briefly the light induced effects observed in *a*-Si:H multilayers which although appear to be of the sign opposite to SWE, can be understood in terms of SWE. I am referring to the so-called persistent photoconductivity of PPC observed in doping modulated (Kakalios and Fritzsche 1984) as well as quantum well type multilayers (Agarwal and Guha 1985a). These multilayers are the amorphous analogs of the crystalline superlattices. It is found that the dark conductivity of these layers, measured parallel to the layers, increases after a short exposure to light, and remains high for several hours or days, even at room temperature. The attempts to explain this effect in terms of charge separation of photocarriers in the built-in field of the *n* and *p* layers for the doping modulated structure have met with difficulties (For a review, see for example, Agarwal 1990), as listed here: (i) PPC is observed at 300 K which is too high a temperature. In crystalline doping superlattices PPC is observed only at liquid helium temperatures, (ii) PPC continues to rise even after exposure of a few hundred seconds. One can estimate the built-in field strengths from the dopings of the adjacent layers. For the intensity of light used, one would expect PPC to saturate within a few milliseconds as the bands become flat and no further charge separation takes place, (iii) exposure to sub-band gap light does not quench PPC. It can only be annealed out, and (iv) if PPC were to be accounted for by charge separation effects, it would scale with the difference in the Fermi levels of *n* and *p* layers. Experiments do not confirm this.

We found (Agarwal and Guha 1985b) that unlayered compensated *a*-Si:H also show PPC (see figure 1). In addition, PPC is present only in those samples in which electrons are the majority carriers. An elegant explanation is provided by Hamed and

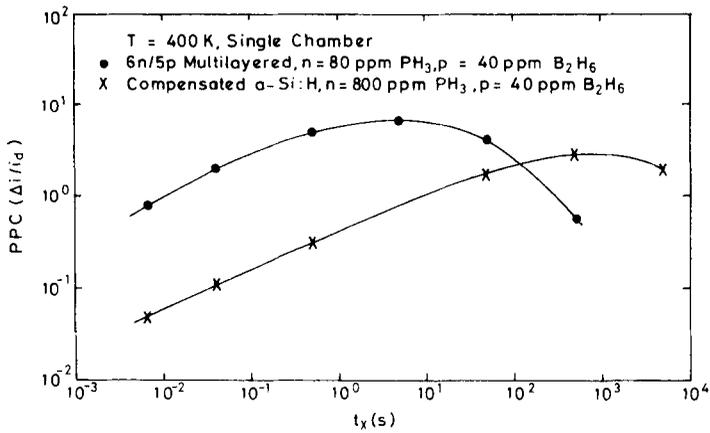


Figure 1. PPC of a doping modulated multilayered *a*-Si:H sample and of a compensated sample as a function of exposure time t_x , measured at 400 K. The 6 *n* layers in the multilayered samples have a gas phase doping of 90 ppm PH_3 in SiH_4 . These are alternated with 5 *p* layers with a doping level of 40 ppm of B_2H_6 . The thickness of each layer is about 275 Å. The doping levels in the compensated sample are $\text{PH}_3/\text{SiH}_4 = 800$ ppm and $\text{B}_2\text{H}_6/\text{SiH}_4 = 40$ ppm. Notice the small PPC for long exposure times for both samples (After Agarwal and Guha 1985).

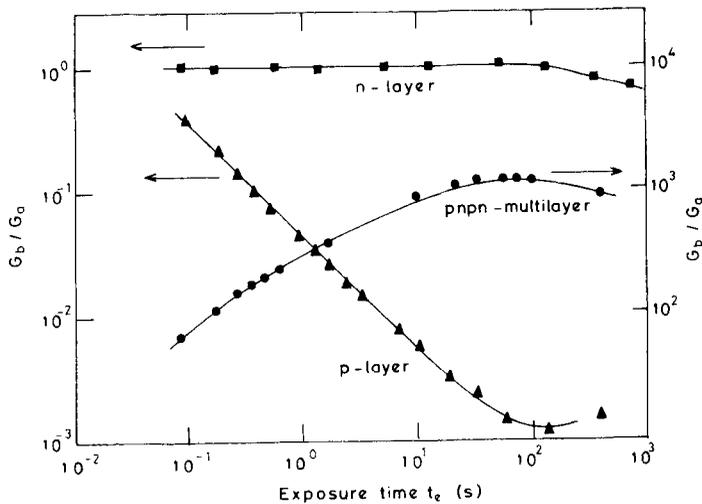


Figure 2. Ratio of the conductance G_b (measured 5 min after exposure) to G_a (conductance in the annealed state) for singly doped *n* and *p*-type and multilayered *a*-Si:H (after Hamed and Fritzsche 1989).

Fritzsche (1989) and Hamed (1991) in terms of the normal SWE. As is clear from figure 2, short light exposures shift E_F in a *p* layer towards the centre but leave *n* layer unchanged, thus resulting in a nett upward shift of E_F . This results in an increased conductivity. For longer exposures, one expects a decrease in PPC as the conductivity of *n* layer starts decreasing (see figure 2). This is indeed observed (cf. figure 1).

Hamed (1991) has shown by computer simulations that this model can explain quantitatively the PPC in layered as well as compensated films. In compensated films, the compositional and structural inhomogeneities associated with boron doping are probably responsible for this effect. Similarly, PPC in heterostructure may be caused by an upward shift of E_F in the insulating layer, upon light exposure (Hamed *et al* 1991).

2.2 Quenching effects in *a*-Si:H

Although first reported by Ast and Brodsky (1979), it caught attention only after the work of Street *et al* (1986). Fast quenching from a temperature higher than the equilibration temperature T_E results in an increased dark conductivity σ in phosphorous and boron doped *a*-Si:H. Figure 3 shows this effect on a lithium doped *a*-Si:H film. The experimental details are given elsewhere (Agarwal P 1995). The slow cooled (SC) and fast quenched (FQ) states are obtained by heating the sample to about 200°C and cooling at a slow rate (SC: 1 K/min) or a fast rate (FQ: 400 K/min) respectively to room temperature. Also shown in the same figure is the effect of light soaking (LS) the sample at room temperature by exposure to heat filtered white light from a tungsten halogen lamp. The data are taken while heating the sample in SC, LS or FQ state. We see that although the effect of LS is to decrease σ , and FQ increase σ ; T_E is the same in the two cases (120°C). Further, the LS and FQ states relax following a stretched exponential of the form

$$Y(t) = \exp[-(t/\tau)^\beta], \quad (1)$$

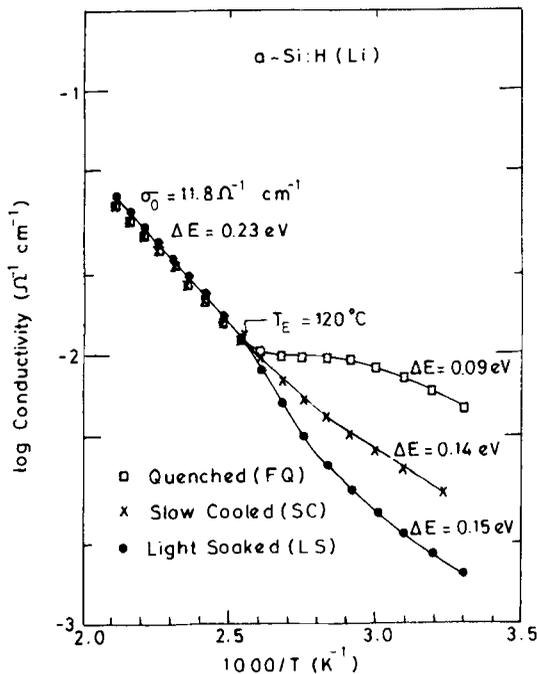


Figure 3. Effect of quenching (FQ) and light soaking (LS) on the conductivity of a lithium doped *a*-Si:H. Also shown is the conductivity in the annealed slow cooled state (SC). Note that all curves meet at a single point $T_E = 120^\circ\text{C}$ and continue as one for $T > T_E$.

where

$$Y(t) = [\sigma(t) - \sigma(\infty)] / [\sigma(0) - \sigma(\infty)].$$

These results are in agreement with those reported in the literature (Winer and Street 1989). Kakalios *et al* (1987) explain the results of fast quenching in their *P* and *B* doped samples on the basis of the so called hydrogen glass model. In this model, hydrogen diffuses in a rigid matrix of silicon atoms more freely for $T > T_E$ than for $T < T_E$. Thus T_E is like the glass transition temperature T_g . Quenching from $T > T_E$ freezes the sample in a metastable state. It relaxes to the SC state by diffusion of hydrogen. It can be easily shown that the decay represented by (1) is expected provided the diffusion constant of hydrogen $D_H \propto t^{\beta-1}$, with β being the same as in (1). Street *et al* (1987) measured D_H using deuterium tracer monitored by SIMS and found that D_H indeed obeys this time dependence. Thus the hydrogen glass model seems to explain the thermal induced metastability.

3. Metastability in chalcogenide glasses

As noted earlier, *a*-Si:H is not accepted as a glass in the traditional sense. In any case, the glass transition is not clearly visible in *a*-Si:H in DSC curves (Matsuo *et al* 1988). This raises questions about the validity of the hydrogen glass model. Since one can easily identify T_g by DSC in chalcogenides, we tried to look for quenching effects in these semiconducting glasses. Two different compositions $\text{Ge}_{15}\text{Se}_{85}$ ($T_g \approx 125^\circ\text{C}$) and $\text{Ge}_{22}\text{Se}_{68}\text{Ag}_{10}$ ($T_g \approx 135^\circ\text{C}$) were chosen in bulk and thin film form. Surprisingly, no

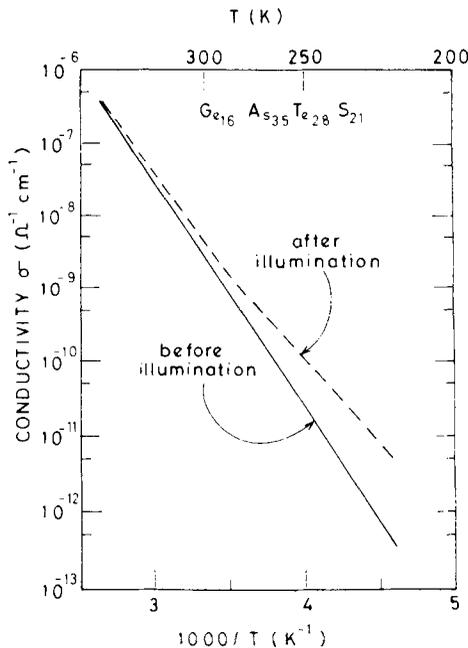


Figure 4. Dark conductivity in a chalcogenide glass before illumination (solid line) and after the sample was cooled from 300 to 77 K under illumination (dashed line). The curves are independent of heating rate and the effect of illumination cannot be erased by exposure to infrared light (After Agarwal and Fritzsche 1974).

quenching effect could be seen in their conductivity, although quenching rates similar to *a*-Si:H were used (Agarwal *et al* 1993).

At first sight, it may appear that no such effects are expected in chalcogenide glasses, anyhow. In chalcogenides E_F is pinned because of negative correlation energy. Chalcogenides are different from the tetrahedrally bonded amorphous semiconductors because they contain lone pair (LP) orbitals and are less prone to metastabilities because LP orbitals allow them new bonding configurations without breaking too many bonds.

However, photodarkening in chalcogenides, such as *a*-As₂S₃ and *a*-As₂Se₃, is well known (Pfeiffer *et al* 1991). This is a change in E_{opt} upon light exposure and has been interpreted as being caused by changes in the intermediate range order. The effect of light soaking on the dark conductivity of a chalcogenide glass is shown in figure 4 (Agarwal and Fritzsche 1974). This reminds one of Staebler-Wronski effect (with opposite sign) since it can only be annealed out and cannot be erased by exposure to sub-band gap light. More recently, Naito and Okuda (1993) and Shimakawa *et al* (1993) have compared the effect of light soaking in amorphous silicon and chalcogenides. They point out the similarities and differences between the effect of light soaking on these two different categories of materials and present models to explain these.

It is therefore, intriguing that although chalcogenide glasses with a clear glass transition in DSC, show photostructural changes upon light soaking, they do not show thermal quenching effects. On the other hand, the quenching effect observed in *a*-Si:H has been attributed to its glass like behaviour, although no clear glass transition is observable in DSC experiment on *a*-Si:H.

4. Comparison of light induced and thermally induced metastabilities in *a*-Si:H

It has been suggested that the motion of hydrogen in a rigid matrix of silicon is responsible for both light soaking and quenching effects in *a*-Si:H. This is supported by the observation that T_E is same for the two cases (figure 3) and that the return to the SC state follows a stretched exponential in both cases. However, a closer look shows that the parameters β and τ have a different temperature dependence for the FQ and LS states (Agarwal 1995). τ is thermally activated in both, but has a higher activation energy in LS than in FQ. Similarly β shows a peak in LS state but is found to increase and saturate at $\beta = 1$, in FQ state, as a function of temperature. This is not expected, if LS and FQ states were relaxing through the same process, as has been proposed (Jackson and Kakalios 1988). Finally, figure 5 shows the results of measurement of thermopower S in the SC, LS and FQ states. For band conduction we can write

$$\sigma = \sigma_0 \exp[-(E_c - E_f)/kT],$$

and

$$S = -(e/k)[(E_c - E_f)/kT + A(T)].$$

Following Overhof and Beyer (1981) we define a function

$$\begin{aligned} Q &= \ln \sigma + |eS/k| \\ &= \ln \sigma_0 + A(T) = Q_0 + E_Q/kT. \end{aligned}$$

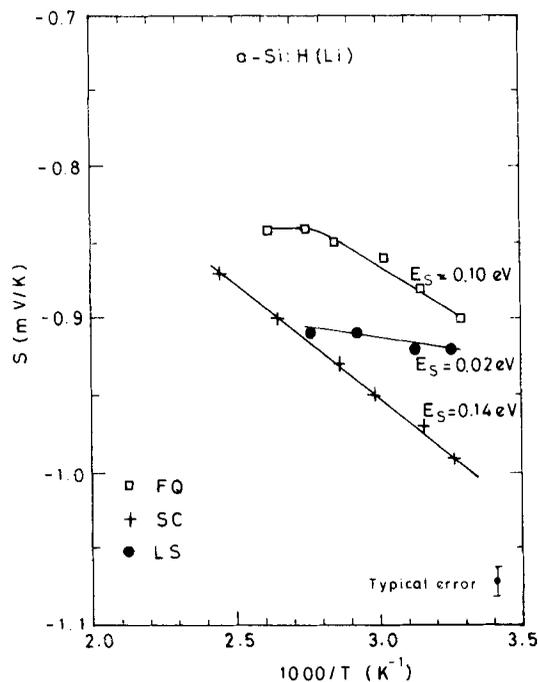


Figure 5. Thermopower S plotted as a function of $1/T$, for the lithium doped a -Si:H sample of figure 3 in the FQ, SC and LS states.

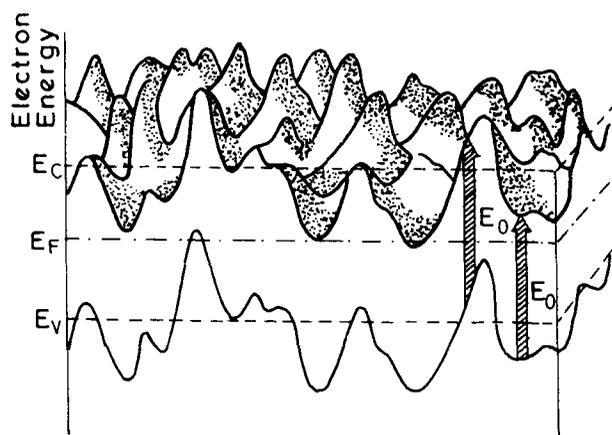


Figure 6. Sketch of the symmetric part of long wavelength potential fluctuations as might be present in a -Si:H, because of inhomogeneities. The antisymmetric part in which the valence and conduction band states are shifted in the opposite directions, is not shown, for clarity (After Fritzsche 1971).

This function Q is unaffected by the statistical shift of E_f , since $E_c E_f$ has been eliminated. Further, E_Q is related to the potential fluctuations in the material. In a -Si:H these may be caused by the heterogeneities present in it. In addition, the donor impurities may also contribute to them (Howard and Street 1991). Figure 6 shows the symmetric part of such fluctuations, as may be present in amorphous silicon

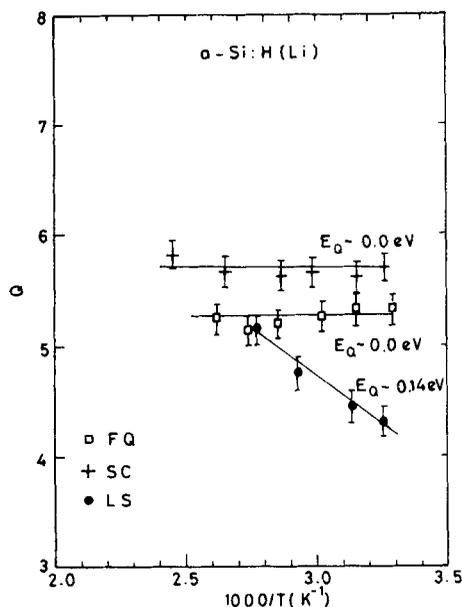


Figure 7. The function Q (defined in the text) plotted as a function of $1/T$ for the a -Si:H(Li) sample in the FQ, SC and LS states.

(Fritzsche 1971). Figure 7 shows the plot of Q vs $1/T$ in the SC, LS and FQ states. The slope E_Q is negligible for the SC state and does not change much upon FQ. However, it increases to ≈ 0.15 eV in the LS state. This shows that LS and FQ affect the lithium doped a -Si:H differently. LS increases the potential fluctuations whereas quenching does not.

5. Summary and conclusions

Metastabilities in amorphous semiconductors have been discussed. The persistent photoconductivity in a -Si:H doping modulated multilayers, observed after a brief light exposure at room temperature has been explained in terms of Staebler-Wronski effect in a -Si:H. This shows that sometimes opposite looking effects might have a common explanation. We have also tried to see whether light soaking (LS) and fast quenching (FQ) have a common origin.

Doped a -Si:H shows both light soaking (LS) and fast quenching (FQ) effects, whereas chalcogenide glasses show only LS and no FQ effect. Since the FQ in a -Si:H seems to be explained satisfactorily by the hydrogen glass model, the absence of this (FQ) effect in chalcogenide glasses comes as a surprise. This is particularly so if we note that in a -Si:H no glass transition is clearly visible in DSC, whereas chalcogenides show this glass transition quite clearly. It appears, therefore that the presence of hydrogen is really necessary to observe this quenching effect. One needs a rigid matrix (Si) in which a mobile species (hydrogen) moves. It is not so in chalcogenides. In chalcogenides, the whole structure may become soft for $T > T_g$ thus making it difficult to see a quenching effect which is also reversible.

Light soaking and fast quenching are shown to affect lithium doped a -Si:H differently. In particular, the analysis of thermopower and conductivity measurements

indicate that LS increases the potential fluctuations in *a*-Si:H(Li) whereas it leaves them unchanged upon quenching. Thus the change in σ upon quenching must be the result of an upward movement of E_f because of movement of hydrogen or lithium in Si matrix. The effect of light soaking is probably related to the nonhomogeneous distribution of charge centres generated during optical exposure (Hauschildt *et al* 1982). This may be the result of structural inhomogeneity present in *a*-Si:H. NMR experiments show a two-phase hydrogen structure in even the best quality *a*-Si:H (Reimer 1981). Photo excited electron and holes tend to drift into the regions where the mobility gap is narrower and more recombinations occur in these regions, creating light induced defects there. This increases the inhomogeneity of the defect centres. This in turn enhances the potential fluctuations. Thermal quenching, on the other hand, will try to make the material more homogeneous by distributing defects more uniformly throughout the film. Since our *a*-Si:H(Li) does not have much potential fluctuations in the SC state, FQ does not change potential fluctuations significantly.

Acknowledgements

I am grateful to Prof. H Fritzsche for introducing me to this exciting field of amorphous semiconductors and for providing many insights and ideas. I would also like to thank my students and colleagues for useful collaborations and discussions. This work is supported in part by the Department of Science and Technology, New Delhi.

References

- Agarwal P 1995 *Thermal and light induced metastabilities in phosphorous and lithium doped hydrogenated amorphous silicon*, Ph D Thesis, Indian Institute of Technology, Kanpur
- Agarwal P, Agarwal S C, Bhattacharya E, Kumar S and Kumar A 1993 *Indian J. Pure Appl. Phys.* **31** 367
- Agarwal S C 1990 *Bull. Mater. Sci.* **14** 257
- Agarwal S C 1995 *Bull. Mater. Sci.* (to appear)
- Agarwal S C and Fritzsche H 1974 *Phys. Rev.* **B10** 4351
- Agarwal S C and Guha S 1985a *Phys. Rev.* **B31** 5547
- Agarwal S C and Guha S 1985b *Phys. Rev.* **B32** 8469
- Ast D G and Brodsky M H 1979 *Proc. 14th Intl. Conf. Phys. of Semicond, AIP Conf. Proc. No. 43* (ed.) B L H Wilson (Bristol and London: Institute of Physics) p. 1159
- 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 1981 *Appl. Phys. Lett.* **38** 456
- Fritzsche H 1971 *J. Non-Cryst. Solids* **6** 49
- Guha S, den Boer W, Agarwal S C and Hack M 1985 *Appl. Phys. Lett.* **47** 947
- Hauschildt D, Fuhs W and Mell H 1982 *Phys. Status Solidi* (b) **111** 171
- Hamed A J 1991 *Phys. Rev.* **B44** 5585
- Hamed A and Fritzsche H 1989 *J. Non-Cryst. Solids* **114** 717
- Hamed A, Fritzsche H, Deng X-M, Kohler S and Gupta R 1991 *J. Non-Cryst. Solids* **137/138** 287
- Harshvardhan K and Hegde M S 1987 *Phys. Rev. Lett.* **58** 567
- Hirabayashi I, Morigaki K and Nitta S 1980 *Jap. J. Appl. Phys.* **19** L357
- Howard J A and Street R A 1991 *Phys. Rev.* **B44** 7935
- Jackson W B and Kakalios J 1988 *Amorphous silicon and related materials* (ed.) H Fritzsche (Singapore: World Scientific) p. 165
- Kakalios J, Street R A and Jackson W B 1987 *Phys. Rev. Lett.* **59** 1037
- Kakalios J and Fritzsche H 1984 *Phys. Rev. Lett.* **53** 1602
- Matsuo S, Nasu H, Akamatsu C, Hayashi R, Imura T and Osaka Y 1988 *Jap. J. Appl. Phys.* **27** L132

- Misra D S 1984 *Determination of the density of localized states in well characterized thin films of hydrogenated amorphous silicon prepared by glow discharge*, Ph D Thesis, Indian Institute of Technology, Kanpur
- Naito H and Okuda M 1993 *J. Non-Cryst. Solids* **164-166** 207
- Overhof H and Beyer W 1981 *Philos. Mag.* **B43** 433
- Pfeiffer G, Paesler M A and Agarwal S C 1991 *J. Non-Cryst. Solids* **130** 111
- Reimer J A 1981 *J. Phys.* **42** C4-715
- Shimakawa K, Inami S and Elliot S R 1991 *J. Non-Cryst. Solids* **137/138** 1017
- Shimakawa K, Kondo A, Hayashi K, Akahori S, Kato T and Elliot S R 1993 *J. Non-Cryst. Solids* **164-166** 387
- Shimizu T 1993 *J. Non-Cryst. Solids* **164-166** 163
- Singh B, Rajagopalan S, Bhat P K, Pandya D K and Chopra K L 1979 *Solid State Commun.* **29** 167
- Staebler D L and Wronski C R 1977 *Appl. Phys. Lett.* **31** 292
- Street R A, Kakalios J and Hayes T M 1986 *Phys. Rev.* **B34** 3030
- Street R A, Tsai C C, Kakalios J and Jackson W B 1987 *Philos. Mag.* **B56** 305
- Stutzmann M 1985 *Appl. Phys. Lett.* **47** 21
- Tsai C C, Stutzmann M and Jackson W B 1984 *AIP Proc.* **20** 242
- Winer K and Street R A 1989 *J. Appl. Phys.* **65** 2272
- Zhang Q, Takashima H, Zhou J-H, Kumeda M and Shimizu T 1994 *Phys. Rev.* **B50** 1551