JOURNAL OF MATERIALS SCIENCE **38** (2003) 51–55

A hydrogen pathway for electronic processes in amorphous silicon

A. SINGH
School of Physics and Materials Engineering, Monash University,
P.O. Box 27, Wellington Road, Clayton VIC 3800, Australia
E-mail: Anirudh.Singh@spme.monash.edu.au

The characteristic difference in the diamagnetic fractions of hydrogen in doped and undoped amorphous hydrogenated silicon (a-Si : H), as obtained through MuSR modelling, is investigated by first reviewing recent calculations of the electronic energies of interstitial hydrogen. This results firstly in the identification of a charge transfer process between dopant atoms and hydrogen interstitials that provides a new mechanism for dopant passivation. It is concluded, however, that the increase in the diamagnetic fraction with temperature in doped a-Si : H can only be explained by the diffusion of hydrogen interstitials to charged dangling bond sites. These two interactions, of interstitial hydrogen and dopants on the one hand, and hydrogen and dangling bond defects on the other, are then used to propose a hydrogen pathway between dopants and dangling bond defects that explains why the process of doping amorphous silicon is always accompanied by the formation of charged dangling bonds.

1. Introduction

It is well known that hydrogen diffuses in amorphous hydrogenated silicon (a-Si : H) [1]. Although several proposals have been made [2, 3], no satisfactory picture has emerged of the specific mechanism or mechanisms for this diffusion.

MuSR experiments can be used to model the nature and behaviour of hydrogen (H) in crystalline silicon (c-Si) [4, 5] and a-Si : H [6, 7] by the muonium atom $\mu^+ e^-$, which is chemically very similar to H. Such experiments can show whether insersitial H exists as the paramagnetic or diamagnetic state in semiconductors.

We have carried out MuSR studies of the diamagnetic states of H in both undoped and doped a-Si : H. The original intention was to compare the fraction (F_d) of hydrogen that exists in diamagnetic state in doped and undoped samples. This fraction shows a curious difference between the two types of samples in its temperature dependence. To arrive at a satisfactory explanation for this effect, it is necessary first to determine the electronic levels of all possible diamagnetic centres in this material. Such a review of the literature yields fresh insights into two hydrogen-related phenomena in a-Si : H—that of dopant de-activation and the long standing puzzle of how hydrogen mediates between dopants and dangling bonds to produce charged defects according to the defect compensation model [8].

This paper begins by presenting a MuSR study of the diamagnetic fraction (F_d) in amorphous silicon. A review of the theoretical determinations the electronic levels of H interstitial levels is then used to construct a composite energy level diagram of H states relative to netural hydrogen (H^0) in free space. This figure immediately reveals the possibility of a dopant–interstitial H interaction not considered before. This new mechanism for dopant de-activation, however, does not account for the temperature dependence of F_d. A detailed consideration of all possibilities shows that the rise in F_d with temperature can only be explained by a process in which diffusing H interstitials interact with charged Si dangling bonds.

These two H diffusion processes are then used to propose a hydrogen pathway between dopants and defects which explains, for the first time, how H might act as a mediator in the production of charged defects during the doping process in a-Si : H.

2. Experimental

The a-Si : H samples for the MuSR experiments were prepared by glow discharge deposition on aluminium foil at substrate temperatures of 230°C. The mole fractions of the precursors were controlled to yield dopant concentrations of $\sim 10^{18}$ cm^{-3}. The MuSR measurements were carried out at the Rutherford Appleton Laboratory, U.K. on the EMU beamline in the transverse field geometry at an applied magnetic field of 20 gauss. Sample temperatures approaching 5 K could be achieved using a liquid helium closed cycle refrigerator. The measurement consisted of essentially determining the forward-backward asymmetry in the counts of positrons liberated when the implanted positive muon underwent beta decay with a mean lifetime of 2.2 μs. The raw data was collected using the in-house data acquisition system MCS, which consists of five processes that control the sample temperature, magnets, the data acquisition (i.e., recording histograms of the

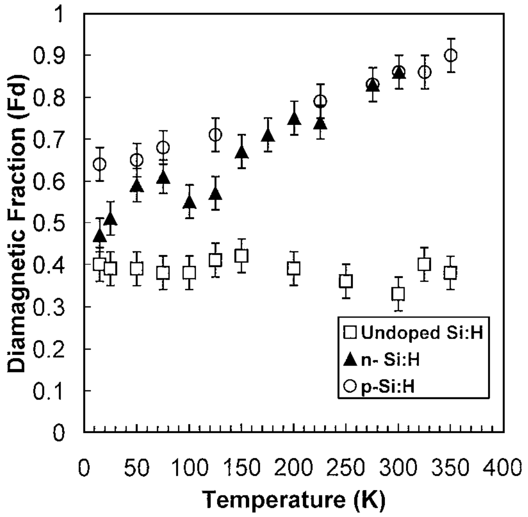

Figure 1 Temperature dependance of the diamagnetic fractions in undoped, p-type and n-type amorphous hydrogenated silicon (undoped Si : H, p-Si : H, n-Si : H).

positron counts from the detectors), and the windows and display features. This raw data was then fitted with theoretical curves generated by the data fitting program UDA.

The diamagnetic fraction for a run was found by comparing the initial asymmetry of the experimental histogram as obtained above with that derived from a silver standard.

3. MuSR results

The diamagnetic fractions (F_d) of undoped a-Si : H and p-type and n-type a-Si : H were determined as a function of the temperature in the 10–350 K range. The results are displayed in Fig. 1. The temperature independence of this fraction in undoped a-Si : H is similar to that for a-Si noted earlier [9]. The doped samples display diamagnetic fractions which are both higher than the undoped material, and which rise linearly with temperature. A straight-forward explanation for this behaviour is not readily available. To interpret this result in terms of known hydrogen centres, a rigorous analysis must first be carried out of all such diamagnetic species.

4. Identification of diamagnetic species in silicon

Fig. 2 shows the positions of all possible paramagnetic and diamagnetic hydrogen centres in silicon that have been identified to date.

The paramagnetic centres are the tetrahedral hydrogen H_T, the bond-centre hydrogen H_{BC}, and the hydrogen-related dangling bond configuration H_{DB} [10, 11]. Tetrahedral hydrogen site is located at the tetrahedral site near the cage centre of the silicon matrix, and has an isotropic hyperfine constant. Bond-centre hydrogen H_{BC} is located at the mid-point of a stretched Si—Si bond, and is characterised by an anisotropic hyperfine constant. The hydrogen-related dangling bond H_{DB} may be viewed as H_{BC} with one of the Si—H bonds broken.

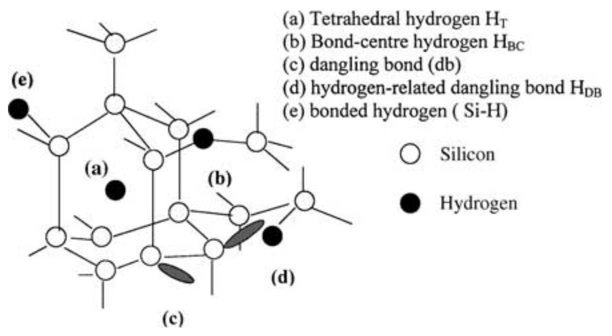

Figure 2 The positions of paramagnetic and bonded hydrogen centres in the silicon matrix.

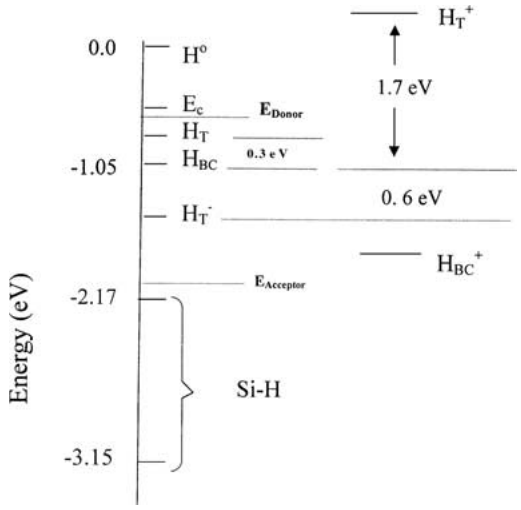

Figure 3 A composite energy level diagram derived from the theoretically determined positions [12, 13] of paramagnetic and diamagnetic hydrogen electronic levels in silicon relative to hydrogen in free space (H^0). There is insufficient information on the exact position of the H_{BC}^+ level.

At the low hydrogen concentrations modelled by MuSR, the diamagnetic fraction (F_d) can only be due to bonded hydrogen i.e., Si—H, and the charged states of the paramagentic centres noted above, i.e., H_{BC}^+, H_{BC}^-, H_T^+, H_T^-. Which of these actually exists will be determined by their stabilities in the host matrix. Theoretical estimates of the electronic levels of all these paramagnetic and diamagnetic centres have been performed over the last decade [12, 13]. Such calculations by Van de Walle [12] show that H_{BC} is 1.05 eV below H^0 in free space, H_T is approximately 0.3 eV higher than H_{BC}, and Si—H lies between 2.17 and 3.15 eV below the free space value, depending on its exact location in the silicon structural matrix. It is also noted that H^+ is stable only as H_{BC}^+, and H^- as the H_T^- species. The former centre is favoured in p-type silicon, while the latter state is preferred in n-type silicon. Experimental evidence for the existence of H_T^- in n-type silicon is provided by the field drift experiments of Tavendale *et al.* [14]. The existence of H^+ in p-type silicon is inferred from the rapid drift of hydrogen in an electric field applied to such hydrogenated material [15]. The position of the level for H_{BC} a few tenths of one electron-volt below E_c in Si has been experimentally established after the E_3' DLTS centre [16–19], and the AA9 EPR centre [20] were both identified as being the same as H_{BC}.

Jones [13] shows that H_T^- is more stable than H_{BC} by 0.6 eV, and H_T^+ is higher in energy than this centre by 1.7 eV. He also notes that H_{BC}^+ is much more stable than H_{BC}. The positions of these charged interstitials and the corresponding paramagnetic levels relative to H in free space are shown in Fig. 3.

The net picture that emerges is that

(i) H_T^+ is an unlikely site in any host
(ii) the stable diamagnetic centres are Si—H and H_{BC}^+ in intrinsic and p-type hosts, and Si—H and H_T^- in n-type Si.

Turning our attention to amorphous silicon in particular, it is first noted that this host is characterised by high densities of dangling bonds and a distribution of Si—Si bondlengths, including a significant component of (extended) weak bonds. The higher dangling bond concentration here as compared, for instance, with crystalline silicon will give rise to more Si—H bonds. One also expects H_{BC} to be more stable here, as its most stable state occurs for an Si—Si separation of 1.38 times the normal bondlength [13].

5. Interpretation of the diamagnetic curves

5.1. Undoped a-Si : H

Why the diamagnetic fraction is constant with temperature here becomes apparent when one first notes the extra stability of H_{BC} in this host, which makes ionisation of this species with temperature rise more difficult. Secondly, one must recall a result noted earlier [21] regarding changes in the relative concentrations of H_T and H_{BC} with temperature in undoped a-Si. It was noted there that H_T appears to convert to H_{BC} with temperature rise. The energy level diagram of Fig. 3 shows why this must be so. It is seen that H_T is higher in energy than H_{BC}. Ionisation of H_T to H_T^+ is energetically forbidden as the latter is 1.4 eV higher in energy. It is possible for H_T to become negatively charged. However this requires the presence of an electron source, which is not available in undoped a-Si : H. The only possible channel by which H_T can lose energy is via conversion to H_{BC}, from which it is evidently separated by an energy barrier. This barrier can be overcome via thermal activation, with the net result that the paramagnetic centres change in nature, leaving the diamagnetic fraction intact.

5.2. Doped a-Si : H

The explanation of the curves for doped silicon is best performed in two stages: (a) the higher F_d native to these materials as compared to undoped silicon and (b) the increase of this fraction with temperature.

The generally higher levels of F_d must be due to the presence of H_{BC}^+ and H_T^- in the p and n-type a-Si : H, respectively, as these have been theoretically shown to be stable in the respective materials [12, 13]. An additional contribution to this diamagnetic fraction comes from the bonded hydrogen found in the conventional model of dopant de-activation [22]. This involves dopant-hydrogen complexes in which the hydrogen is bonded to silicon at the bond-centre position in the case of p-type silicon, or antibonding position in the case of n-type silicon. Both these involve an Si—H bond not found in undoped silicon, and thus lead to an increase in the diamagnetic fraction.

The possible mechanisms for the creation of the centres noted above must be considered in detail to ascertain whether they contribute to (a) or (b) above.

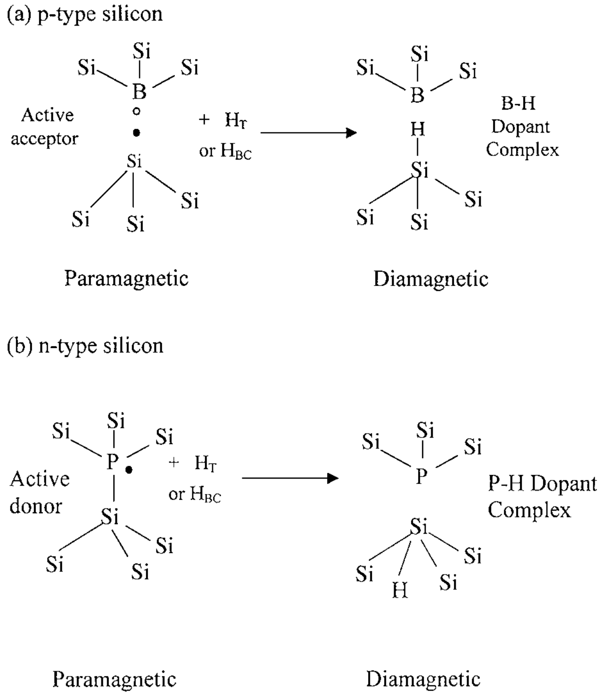

Figure 4 How the conventional model of dopant passivation leads to the generation of diamagnetic centres in silicon. (a) Idealised reaction between paramagnetic hydrogen and an active boron acceptor atom leading to a (de-activated) dopant complex; (b) the corresponding reaction in the case of the phosphorous donor atom.

5.2.1. Conventional dopant passivation

The formation of these dopant complexes are depicted in Fig. 4. These processes do contribute to the conversion of paramagnetic to diamagnetic fraction, and thus to an increase in F_d. However, because of the reactivity of the dopant atoms, these reactions are expected to reach completion during the film growth stage. There have certainly been no reports of any temperature-dependent behaviour in of these species in as-deposited a-Si : H films. Thus they must contribute to the temperature-independent component of F_d.

5.2.2. Dopant-interstitial electron transfer

As we have seen, the existence of the charged H_T^- and H_{BC}^+ interstitials in doped silicon has been firmly established, both experimentally and theoretically. As a high diamagnetic fraction implies a smaller paramagnetic fraction, the present study shows that the creation of charged interstitials happens at the expense of the neutral counterparts. As the dopants are the only sources of charge in doped amorphous silicon, there must be a mechanism through which dopants react with interstitials to give rise to charged dopant-interstitial pairs. To understand how such pairs can form, recall that in n type silicon, the dopant atoms (say phosphorous) provide a level 0.045 eV below E_c. These are occupied at 0 K, but ionise rapidly by room temperature through thermal activation of the electrons to the conduction band according to the equation

$$P + \Delta E \rightarrow P^+ + e^- \text{ (to conduction band)}$$

If the silicon is hydrogenated, however, then a level due to H_T is present a few tenths of one eV below the donor levels, and the electron may be donated instead to this level, creating the H_T^- centre as shown below:

$$H_T + e^- \text{ (from P)} \rightarrow H_T^-$$

The net process is the transfer of an electron from the dopant to the interstitial

$$P + H_T \rightarrow P^+ + H_T^- \qquad (1)$$

giving rise to a charged dopant-interstitial pair.

This reaction does not require thermal activation. However, whether it proceeds will depend on the electron correlation energy for the H_T^- centre. Johnson *et al.* [15] show that monatomic hydrogen in silicon has a large negative correlation energy (ca. −0.36 eV). We thus expect the above reaction to proceed spontaneously in n-type silicon.

It is interesting to note that through this reaction, H_T has effectively de-activated the dopant (phosphorous) atom, as it is no longer capable of generating a charge carrier. The process is thus a new dopant de-activation mechanism in hydrogenated amorphous silicon, reported here for the first time. It competes directly with deactivation via the conventional complex formation.

In the case of p-type silicon with, e.g., boron as the dopant, acceptor levels will exist just above E_v. These will be empty at 0 K. In the absence of interstitial hydrogen, the dopant atoms will quickly ionise to produce negatively charged dopant ions throughthermal activation, as follows:

$$B + \Delta E \rightarrow B^- + h^+$$

where B is the boron atom, ΔE is the energy difference between E_v and the acceptor level, and H^+ is the hole created in the valence band through the activation process.

However, in a-Si : H the H_{BC} level, which is positioned well above the acceptor levels, will be able to donate electrons to the dopant atoms (filling up the acceptor levels) without the need for thermal activation viz:

$$H_{BC} + B \rightarrow B^- + H_{BC}^+$$

Thus, in p-type materials, H_{BC} will ionise spontaneously by donating an electron to the acceptor atom (and thereby de-activating it).

Why electrons are not donated to the H_{BC} level in the n-type material, and why there is no transition between the H_T and acceptor levels in p-type silicon becomes clear when one notes that these alternative electronic transitions will require a net input of energy (i.e., the reactions between the respective dopant and interstitial centres will be endo-thermic).

It is thus evident that the charged diamagnetic centres H_T^- and H_{BC}^+ should form spontaneously in n- and p-type materials, respectively. However, as these ionisations will take place at the lowest temperatures, they will, once again, only contribute to the temperature-independent components of the diamagnetic fractions of the doped materials.

6. Temperature-dependent diamagnetic fraction in doped a-Si : H

The above mechanisms for increase in F_d in doped silicon over the levels present in undoped material can only explain the temperature-independent component. To explain the temperature dependence, a different mechanism must be invoked. This is obtained by first considering the nature of hydrogen diffusion in a-Si : H. Street and co-workers [23] show that

(i) In undoped a-Si : H, hydrogen does not begin to diffuse until temperatures as high as 470 K
(ii) doping increases the diffusion rate, which is some ten times higher in p-type than in n-type a-Si : H
(iii) doping produces charged dangling bond defect D^+, D^- (i.e., Si_3^+, Si_3^-).

Thus, following the completion of film growth, one expects significant concentrations of D^+ to exist in p type, and D^- in n type material. The rise in the diamagnetic fraction with temperature may then be explained by reactions between the charged defects and the hydrogen interstitials which diffuse to the site of these defects. In the case of phosphorous dopant, for example, the process may be represented:

$$H_T + Si_3^- \rightarrow H_T^- + Si_3^0 \qquad \Delta E = -0.8 \text{ ev} \qquad (2)$$

Assuming the D^- level is 0.1 eV below D^0 level [24], this process is exothermic, with a net enthalpy change of −0.8 eV, and will thus proceed.

As a paramagnetic centre is converted to a diamagnetic one, this leads to an increase in F_d. The size of this change will depend on the diffusion rate of the interstitials, which increases as the temperature rises. We thus have a temperature-dependent diamagnetic fraction.

A similar interstitial-defect reaction is possible in the case of p-type material. Here however, the diffusing interstitial is H_{BC}, which becomes positively charged after reacting with D^-. Possible sequence of structural changes resulting from these interstitial-defect reactions are shown in Fig. 5.

7. A hydrogen pathway for defect compensation

Two hydrogen-related processes have been considered above. In the first, an interstitial hydrogen reacted with a dopant, and in the second the interstitial reacted with a dangling bond defect. These two processes enable the identification of a possible mechanism via which hydrogen mediates the charge transfer in the defect compensation model proposed by Street [8]. Taking Equation 1 and the reverse of Equation 2, we have:

$$P_3^0 + H_T \rightarrow P_4^+ + H_T^- \qquad \Delta E = -0.85 \text{ EV}$$

$$Si_3^0 + H_T^- \rightarrow H_T + Si_3^- \qquad \Delta E = +0.80 \text{ EV}$$

The net process, in which a neutral dopant and neutral dangling bond is converted to a charged dopant-defect

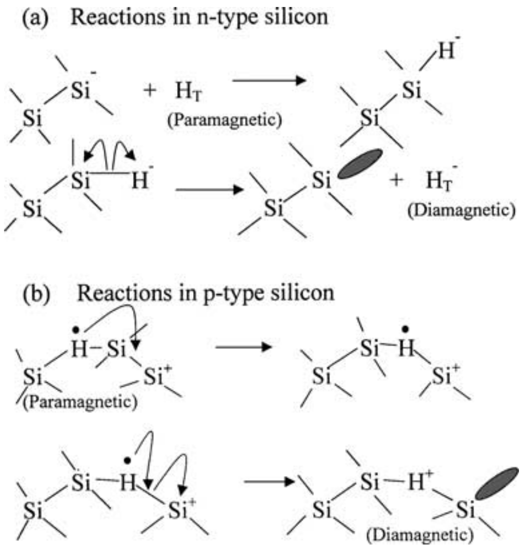

Figure 5 Reactions between diffusing paramagnetic hydrogen interstitials and dangling bond defects resulting in diamagnetic centres. The reactions shown are between (a) negatively charged dangling bond D^- and H_T and (b) positively charged dangling bond D^+ and H_{BC}.

pair, is just exothermic. This becomes even more likely when one considers the defect pool model for a-Si : H [25]. A similar mechanism may be proposed for the creation of D^+ defects in p-type material. Here however, the diffusing interstitial is H_{BC}.

This proposed mechanism for a hydrogen-mediated creation of charged defects clearly requires more elaboration and discussion. But it is clear that this is a promising beginning towards elucidating the role hydrogen plays in the defect compensation model proposed by Street.

8. Summary and conclusion

The difference between the diamagnetic fractions of undoped and doped a-Si : H can only be explained after a detailed analysis of the possible diamagnetic hydrogen centres in these hosts. These are found to be the bonded hydrogen state Si—H and the interstitial H_{BC}^+ in undoped and p-type amorphous silicon, and Si—H and H_T^- in n-type material. Dopant-hydrogen complexes that may form according to the conventional model of dopant de-activation are also noted to be diamagnetic.

This analysis leads to the discovery of a new dopant de-activation mechanism in which the de-activation proceeds via the production of charged dopant-interstitial pairs. It is noted, however, that the creation of these charged states will not contribute to the rise in the diamagnetic fraction with temperature. It is concluded that the rise of F_d with temperature in the doped samples can only be explained by a process in which interstitial hydrogen diffuses to charged silicon dangling bond defects where charge exchange takes place.

The two processes, in which interstitial hydrogen reacts with dopants on the one hand and with dangling bonds on the other, are then used to propose a possible mechanism by which hydrogen might mediate in the generation of charged defects as explained by the defect compensation model [8].

Acknowledgements

The experimental work for this study was undertaken while the author was employed by the University of Leicester, U.K. under EPSRC Grant numbers GR/F18015 and GR/H67638. The MuSR measurements were carried out at the Rutherford Appleton Laboratory, Didcot, U.K. with the help and guidance of S. F. J. Cox, Chris Scott and Steve Cottrell. The author is also grateful to John Pilbrow of Monash University, Australia, for providing the support that made this work possible.

References

1. W. BEYER, *Phys. Stat Solidi* (a) **159** (1997) 53 and references therein.
2. R. A. STREET, *Physica* B **170** (1991) 69.
3. H. M. BRANZ, *J. Non-Cryst Solids* **266–269** (2000) 391.
4. J. H. BREWER, K. M. CROWE, F. N. GYGAX, R. F. JOHNSON and B. D. PATTERSON, *Phys Rev Lett.* **31** (1973) 143.
5. S. F. J. COX and M. C. R. SYMONS, *Chem Phys Lett.* **126** (1986) 516.
6. A. SINGH and E. A. DAVIS, in 22nd International Conference on the Physics of Semiconductors (World Scientific, London, 1995) Vol. 3, p. 2697.
7. A. SINGH, *J. Mater. Sci.* **31** (1996) 1991.
8. R. A. STREET, *Phys Rev Lett.* **49** (1982) 1187.
9. E. A. DAVIS, A. SINGH, S. F. J. COX, S. R. KREITZMAN, T. L. ESTLE, B. HITTI, R. L. LICHTI, D. LAMP, R. DUVARNEY, D. W. COOKE D, M. PACIOTTI and A. C. WRIGHT, *J. Non-Cryst Solids* **137/138** (1991) 17.
10. B. D. PATTERSON, *Rev. Mod. Phys.* **60** (1988) 89.
11. K. MORIGAKI, H. HIKITA, M. YAMAGUCHI and Y. FUJITA, *J. Non-Cryst. Solids* **227–230** (1998) 338.
12. C. G. VAN DE WALLE, *ibid.* **227–230** (1998) 111.
13. R. JONES, *Physica* B **170** (1991) 181.
14. S. J. TAVENDALE, S. J. PEARTON and A. A. WILLIAMS, *Appl. Phys. Lett.* **56** (1990) 949.
15. N. M. JOHNSON, C. HERRING and C. G. VAN DE WALLE, *Phys. Rev Lett.* **73** (1994) 130.
16. L. C. KIMERLING, P. BLOOD and W. M. GIBSON, *Inst, Phys. Conf.* **46** (1979) 273.
17. K. IRMSCHER, H. KLOSE and K. MAASS, *J. Phys.* C **17** (1984) 6317.
18. B. HOLM, K. BONDE and B. BECH NIELSEN, *Phys. Rev. Lett.* **66** (1991) 2360.
19. N. M. JOHNSON and C. HERRING, *Mater. Sci. Forum* **143–147** (1994) 867.
20. YU. V. GORELKINSKII and N. N. NEVINNYI, *Physica* B **170** (1991) 155.
21. A. SINGH, *J. Mater Sci.* **31** (1996) 1991.
22. N. M. JOHNSON, *J. Non-Cryst. Solids* **137/138** (1991) 11.
23. R. A. STREET, C. C. TSAI, KAKALIOS and W. B. JACKSON, *Phil. Mag.* B **56** (1987) 305.
24. K. WINER, *Ann. Rev. Mater. Sci.* **21** (1991) 1.
25. *Idem.*, *J. Non-Cryst Solids* **137/138** (1991) 157.

Received 2 January 2002
and accepted 26 April 2002