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## Structural disorder and optical gap fluctuations in amorphous silicon

A P Sokolov†, A P Shebanin‡, O A Golikova§ and M M Mezdrogina§

† Institute of Automation and Electrometry, Universitetsky Prospekt 1, Novosibirsk 630090, USSR

‡ Institute of Geology and Geophysics, Universitetsky Prospekt 3, Novosibirsk 630090, USSR

§ A F Ioffe Physical Technical Institute, Politechnicheskaya 26, Leningrad 194021, USSR

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**Abstract.** Optical absorption and Raman spectra in a number of a-Si, a-Si:H and a-(Si:H):B samples have been investigated. It is shown that the optical gap changes are weakly correlated with the changes in  $\tau_0$  peak width in Raman spectra but are well correlated with the changes in the  $\tau_A$  peak intensity. The correlation between the amplitude of optical gap fluctuations, determined from the optical absorption spectra, and the  $\tau_A$  peak intensity has been observed. These results suggest that the optical gap and the amplitude of its fluctuations in amorphous silicon and its alloys depend not only on bond-angle dispersion but also substantially on the degree of structural disorder on a scale of about 4–6 Å or greater.

### 1. Introduction

Studies of amorphous silicon and its alloys indicate that variations in the material preparation technique or post-preparation treatments lead to considerable changes in the network structural order. The latter allow substantial changes in the electronic properties and vibrational spectra of the samples; the optical gap  $E_G$  varies up to 0.3–0.5 eV, the width of the Urbach tail varies up to 2–3 times [1, 2] and the width of the  $\tau_0$  peak  $\Delta$  in the Raman spectra changes considerably [3–5]. The most important point is to explain variations in electronic properties on the basis of structural aspects. It was shown that the value of  $\Delta$  is related to the bond-angle dispersion [3, 4] and the analysis of the correlation between  $E_G$  and  $\Delta$  changes allows one to conclude that short-range structural order plays an important role [3–5].

Variations in preparation conditions lead also to substantial changes of the low-frequency  $\tau_A$  peak intensity  $I_{\tau_A}$  in the Raman spectra of amorphous silicon. However, the variations in low-frequency Raman spectra and their correlations with changes in optical properties have not been investigated except the correlation between  $I_{\tau_A}$  and  $E_G$  for a-Si and a-Si:H films recently observed [6]. From the analysis of the results a conclusion was drawn that the optical properties of amorphous silicon depend strongly on the degree of structural order on a scale of about 5 Å or greater [6].

In the present paper, optical absorption and Raman spectra have been investigated for a wide number of a-Si, a-Si:H and a-(Si:H):B samples. The variations in  $E_G$ ,  $\Delta$  and  $I_{\tau_A}$  have been studied. The analysis of the results obtained shows that  $E_G$  correlates

weakly with  $\Delta$ , but the increase in TA peak intensity is well correlated with a decrease in optical gap and with an increase in its fluctuations amplitude. The latter has been determined from the analysis of optical absorption spectra by the method suggested in [7]. These correlations confirm the conclusion of [6] that the degree of structural order on a scale of about 4–6 Å or greater in amorphous silicon has an important effect on its electronic properties. Some suggestions concerning the structure and optical properties of so-called ‘ideal a-Si’ have been made from the analysis of the results obtained.

## 2. Experimental results

The unhydrogenated a-Si films were prepared by RF sputtering at  $T_s = 20^\circ\text{C}$ , the a-Si:H films were prepared by triode glow discharge (25% SiH<sub>4</sub> + 75% He) at  $T_s = 280\text{--}320^\circ\text{C}$ . Some of the samples were annealed at  $T_A = 200\text{--}500^\circ\text{C}$ . The a-(Si:H):B films were prepared by triode glow discharge. Some were doped by the addition of B<sub>2</sub>H<sub>6</sub> to the gas mixture (the B<sub>2</sub>H<sub>6</sub>-to-SiH<sub>4</sub> gas ratio was 4.5%) at  $T_s = 240\text{--}320^\circ\text{C}$ ; another doping method used was ion implantation [8]. The H concentration in the hydrogenated films was 2–8%. The results of investigations on a-Si:H samples prepared with a silane–argon mixture and HF decomposition with a high (10–16%) H concentration and published in [9] were also analysed.

The optical transmittance and reflectance spectra were measured using a Shimadzu spectrophotometer. The optical absorption coefficient was obtained by numerical inversion of the equations for transmittance and reflectance. Right-angled Raman spectra were recorded using 514 nm excitation and a U-1000 double-monochromator system. The spectral slit widths were 4 cm<sup>-1</sup>. The polarization of the excitation light was parallel to the scattering plane. All measurements were made at room temperature.

The spectral dependence of interband optical absorption in amorphous semiconductors is usually analysed using a quadratic approximation

$$(\alpha h\omega)^{1/2} = \beta(h\omega - E_g^2) \quad (1)$$

but the best approximation of the spectral dependence of  $\alpha$  for amorphous silicon is cubic [1, 10]:

$$(\alpha h\omega)^{1/3} = \gamma(h\omega - E_g^3). \quad (2)$$

So, the spectral dependence of  $\alpha$  was analysed in both the quadratic and the cubic approximations (figure 1). The slopes  $\beta$  and  $\gamma$  and the values of the optical gap  $E_g^2$  and  $E_g^3$  were obtained by a least-squares fit of these approximations (figure 1). The range of data points from about 200 up to about 500 eV<sup>1/2</sup> cm<sup>-1/2</sup> was taken into account for the quadratic approximation (1) and from about 30 up to about 80 eV<sup>1/3</sup> cm<sup>1/3</sup> was taken into account for the cubic approximation (2). In the first case,  $E_g^2$  varies from 1.32 to 1.76 eV and the slope  $\beta \approx 700 \pm 30 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$  for all samples under investigation. This is in agreement with the results in [2]. However, in the second case,  $E_g^3$  varies from 0.95 to 1.6 eV and the slope  $\gamma$  varies from 58 to 80 cm<sup>-1/3</sup> eV<sup>-2/3</sup> (figure 1). A difference between  $\gamma$  for a-Si and a-Si:H samples was observed earlier in [10].

Figure 2 shows Raman spectra for the same samples and demonstrates the changes in TO peak width and TA peak intensity. Figure 3 represents the TO peak full width  $\Delta$  vs the TA peak intensity normalized to the TO peak intensity, i.e.  $I_{TA}/I_{TO}$  for different samples. It can be seen that a simple correlation between them is absent; for a-Si:H and

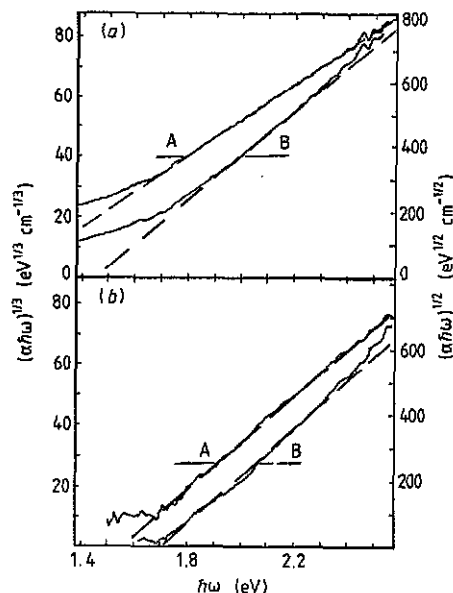


Figure 1. Optical absorption spectra in the cubic (curve A) and quadratic (curve B) approximations for (a) a-Si and (b) a-Si:H samples.

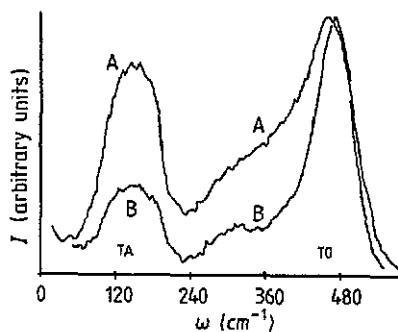


Figure 2. Raman spectra for the same a-Si (curve A) and a-Si:H (curve B) samples. The TA and TO peaks are marked.

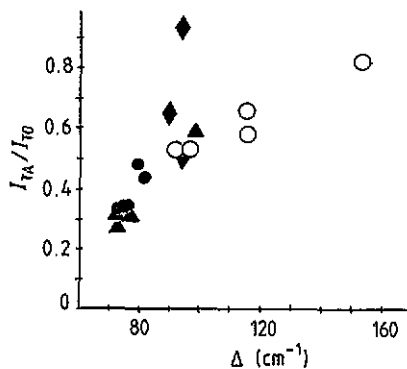


Figure 3.  $I_{TA}/I_{TO}$  against  $\Delta$  for a-Si (○), a-Si:H (●), a-Si:H:B doped from the gas phase (◆) and by ion implantation (▲).

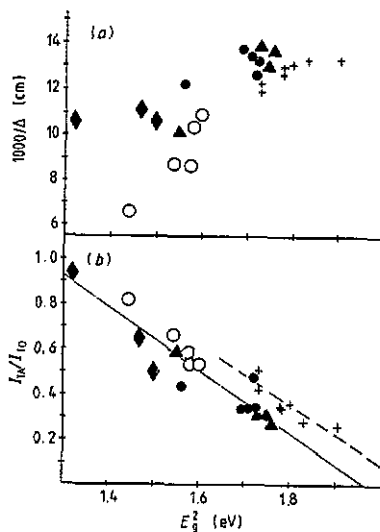


Figure 4. (a)  $\Delta^{-1}$  against  $E_g^2$  for a-Si (○), a-Si:H (●) and a-Si:H:B doped from the gas phase (◆) and by ion implantation (▲). The data of [9] for a-Si:H films with a high concentration of H (+) are also shown. (b)  $I_{TA}/I_{TO}$  against  $E_g^2$  for the same samples. Linear approximations are shown.

a-(Si:H):B samples the changes in  $\Delta$  are much lower than those in  $I_{TA}$ . A similar result has been found earlier for a-Si:H [11] and for a-(Si:H):B [12].

### 3. Correlations between Raman and optical spectra changes

The nature of anomalous spectral dependence of interband optical absorption in amorphous silicon has been unclear up to now. In [7] a simple model was proposed to describe the cubic dependence of  $\alpha$  (equation (2)). Let us suppose that the spectral dependence (1)  $\alpha = (\beta^2/h\omega)(h\omega - E_G)^2$ , which is characteristic for the majority of amorphous semiconductors, is valid in every local part of the a-Si sample, but  $E_G$  fluctuates spatially owing to structural disorder. In this case the optical absorption coefficient may be written as

$$\alpha = \frac{\beta^2}{h\omega} \int_0^{h\omega} (h\omega - E_G)^2 P(E_G) dE_G \quad (3)$$

where  $P(E_G)$  is the  $E_G$  distribution function. If  $P(E_G)$  is nearly constant in some energy region from  $E_{Gmax}$  to  $E_{Gmin}$ , i.e.  $P(E_G) \approx (E_{Gmax} - E_{Gmin})^{-1} = 1/\Delta E_G$ , the spectral dependence (2) will be obtained:

$$\alpha = (\beta^2/3h\omega \Delta E_G)(h\omega - E_{Gmin})^3. \quad (4)$$

Here  $E_g^3$  is a minimal value of  $E_G$  and the slope  $\gamma$  is given by

$$\gamma = (\beta^2/3 \Delta E_G)^{1/3}. \quad (5)$$

For quantitative comparison of equation (5) with the experimental results the value of  $E_{Gmax}$  is needed, but Novikov *et al* [7] took into account the fact that  $E_g^2$  is some average value of  $E_G$  and supposed that  $\Delta E_G \sim (E_g^2 - E_g^3)$ . The above results show that the change in  $E_g^2$  from 1.32 to 1.76 eV is accompanied by a decrease in  $E_g^2 - E_g^3$  from 0.37 to 0.16 eV and by the increase in  $\gamma$  from 58 to 80  $\text{cm}^{-1/3} \text{eV}^{-2/3}$ . So, the change in structural order is accompanied by variations in the optical gap, as well as by a change in the amplitude of its fluctuation  $\Delta E_G$ .

To separate the role of structural order in modifying optical properties we compared their changes with the changes in the Raman spectra (figure 4). The majority of workers analysed the correlation between  $E_G$  and  $\Delta$ . The latter is a sensitive measure of structural order on a short-range scale (first and second coordination spheres) and is proportional to the bond-angle dispersion  $\Delta\theta$  [4, 13]. A correlation between  $E_g^2$  and  $\Delta^{-1}$  has been observed for a-Si, but not for a-Si:H [4, 9]. It has been supposed [4] that the variations in  $E_g^2$  for a-Si:H films may be decomposed into two terms:

$$\Delta E_g^2 = (\Delta E_g^2)_{\text{alloy}} + (\Delta E_g^2)_{\text{order}} \quad (6)$$

where the first term is due to alloying effects for a fixed short-range structural order and the second term is only due to this structural order. So,  $E_g^2$  in a-Si:H have been explained by alloying effect of H and the first term has been estimated  $(\Delta E_g^2)_{\text{alloy}} = 2.3 \times 10^{-2} \text{ eV}$  for 1% of H [4].

The plot of  $\Delta^{-1}$  against  $E_g^2$  for different samples under investigation shows (figure 4(a)) that the relation between changes of  $E_g^2$  and  $\Delta^{-1}$  in a-Si differs from that in a-Si:H and a-(Si:H):B. In the latter case the changes in  $E_g^2$  are accompanied by weak changes in the TO peak width. On the contrary, the correlation between  $E_g^2$  and  $I_{TA}/I_{TO}$  is nearly

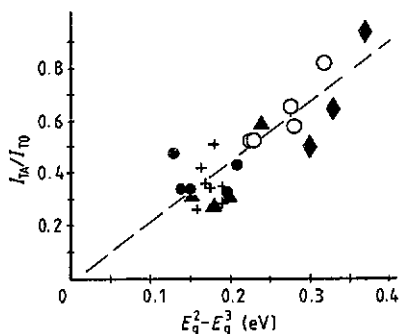


Figure 5.  $I_{TA}/I_{TO}$  against  $E_g^2 - E_g^3$  for the same samples as used for figure 4. The linear approximation is shown.

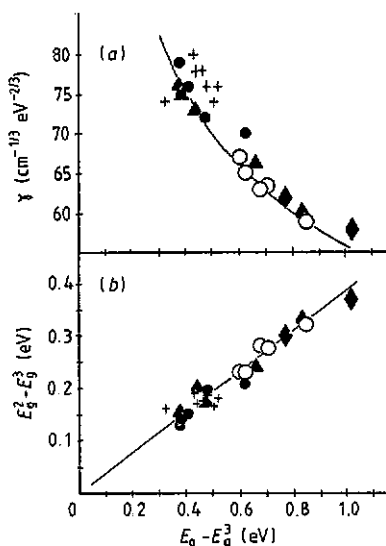


Figure 6. (a)  $\gamma$  against  $E_o - E_g^3$  for the same (figure 4) samples and calculated (equation (5)) curve. (b)  $E_g^2 - E_g^3$  against  $E_o - E_g^3$  for the same (figure 4) samples.

the same for all samples under investigation (figure 4(b)), but there is a shift in the case of a-Si:H samples with a high H concentration, which can be related to the difference of  $E_g^2$  on 0.1 eV. However, for samples of all series,  $E_g^2 - E_g^3$  correlates with  $I_{TA}/I_{TO}$  (figure 5).

#### 4. The TA mode intensity

In contrast with the TO mode, the description of the TA mode in vibrational spectra of amorphous Si and Ge is under discussion at present. However, it is shown that the correlation effects beyond second neighbours must be taken into account in this spectral range [14, 15]. To describe the inelastic neutron scattering data Buchenau *et al* [15] have proposed a model of bond-bending vibrations, where the movement of eight atoms is considered. This group of atoms has a size of about 4–6 Å. So, the TA mode is related to the vibrations of structural fragments with the scale of about 4–6 Å or greater. Probably, these are collective vibrations of Si tetrahedra.

The intensity of Raman scattering in disordered solids is known to be proportional to the density  $g(\omega)$  of vibrational states multiplied by the light-vibration coupling constant  $C(\omega)$  [16]. So, the variations in low-frequency TA peak intensity may be related to the variations in  $g(\omega)$  or  $C(\omega)$ . Changes in both  $g(\omega)$  and  $C(\omega)$  in the low-frequency range have been observed from analysis of inelastic neutron and Raman scattering spectra [17], but changes in the density of states must be weaker, since in this frequency range  $g(\omega)$  in the amorphous state is less than twice that in the crystalline state [14]. On the other hand,  $C(\omega) = 0$  for crystalline Si in the low-frequency range, but  $C(\omega)$  in amorphous solids depends on localization of the vibrational excitations and, according to [18, 19], is proportional to squared amplitude of elastic and elasto-optical constant

fluctuations:  $C(\omega) \sim \langle \delta p^2 \rangle$ . It is necessary to note that an approximation of acoustic weakly perturbed vibrations has been used for the description of the low-frequency Raman spectra in the model [18, 19]. Substantial deviation of  $g(\omega)$  in the frequency range of the TA mode from Debye behaviour enables us to conclude that this approximation is not valid. However, it can be generally concluded that the TA peak intensity in Raman spectra is determined by structural order on a scale of about 4–6 Å or greater (beyond second neighbours). Probably, it is related to the amplitude of the dihedral angle fluctuations or to disorder in the arrangement of Si tetrahedra.

## 5. Discussion

Consideration of  $\Delta$  and  $I_{TA}/I_{TO}$  shows (figure 3) that atoms of hydrogen and boron introduced into a-Si give a weak effect on the short-range structural order (Si tetrahedra) but have an influence on structural order on a medium-range scale (arrangement of the Si tetrahedra). This conclusion is supported by the results of diffraction measurements [20], which show that introduction of H into a-Si modifies the radial distribution function mainly on a scale of about 4–6 Å, where more pronounced peaks are observed. Recently it has been observed [12] that  $I_{TA}/I_{TO}$  in a-(Si:H):B increases rapidly with increase in B concentration up to 3–5%, but further increase in the concentration really has no influence on  $I_{TA}/I_{TO}$ . This concentration dependence supports our conclusion that the introduction of B atoms changes the structural order of amorphous silicon on a medium-range scale (in its microvolume, which includes some tens of atoms).

The analysis of figure 4(a) shows that a simple relation between the short-range structural order and the optical gap for a-Si alloys is absent. On the other hand it is difficult to expect that such a large variation in the optical gap as about 0.3–0.4 eV may be associated with the alloying effect only of a small (about 4–5%) concentration of boron atoms.

However, figure 4(b) shows that  $E_g^2$  correlates with  $I_{TA}/I_{TO}$  for all types of sample. What does this correlation mean? According to [1, 2], the optical gap of an amorphous semiconductor may be written in the following way:

$$E_G = E_o(0) + D(\langle u^2 \rangle_T + \langle u^2 \rangle_X) \quad (7)$$

where  $E_o(0)$  is the optical gap without structural disorder at  $T = 0$  K,  $D$  is the deformation potential,  $\langle u^2 \rangle$  is an averaged squared displacement of atoms due to thermal vibrations ( $\langle u^2 \rangle_T$ ) or structural disorder ( $\langle u^2 \rangle_X$ ). Consequently, both  $E_g^2$  and  $I_{TA}/I_{TO}$  are connected with the amplitude of fluctuations of constants in disordered solids. In the general case the term  $(\Delta E_g^2)_{\text{order}}$  must consider structural order not only on a short-range scale but also on a medium-range scale (about 4–6 Å or greater) and the observed correlation (figure 4(b)) enables us to suppose that the influence of medium-range structural order on  $E_g^2$  is strong.

A linear approximation of the observed correlation shows that  $E_g^2 \approx 1.97 \pm 0.1$  eV at  $I_{TA} = 0$  (figure 4(b)), but this value is equal to about 2.07 eV for samples with a high concentration of hydrogen (data from [9]) (figure 4(b)). The values obtained must correspond to the optical gap  $E_o$  without any structural disorder:  $\langle u^2 \rangle_X = 0$  (equation (7)). If one takes into account the thermal variation in  $E_g^2$  ( $dE_{og}/dT \approx 4 \times 10^{-4}$  eV K<sup>-1</sup> [1]), the value of  $E_o(0)$  can be estimated from equation (7):  $E_o(0) \approx 2.09$  and  $E_o(0) \approx 2.19$  in the first and second cases, respectively. They coincide with the expected optical gap in 'ideal a-Si',  $E_o \approx 2.0$ –2.2 eV, which was estimated earlier from the correlations of

the Urbach slope and  $E_g^2$  [1, 2]. So, for  $I_{TA} \rightarrow 0$ ,  $E_g^2$  tends to be equal to the value of the optical gap of the 'ideal a-Si', which has no Urbach tails. The variation in  $E_o$  in different series of samples may be associated with the alloying effect of H (the term  $(\Delta E_g^2)_{\text{alloy}}$  in equation (6)). If one takes into account the fact that the concentration of H in the samples investigated in [9] was 7–10% higher than the concentration in other investigated samples (see section 2), the alloying term may be estimated:  $(\Delta E_g^2)_{\text{alloy}} = (1-1.5) \times 10^{-2}$  eV for every 1% H. This value is considerably lower than the value obtained earlier [4]. The difference obtained is explained by another estimation of the term  $(\Delta E_g^2)_{\text{order}}$ ; only the effect of bond-angle fluctuations have been taken into account in [4] but, if the total effect of structural order were taken into account, the value of  $(\Delta E_g^2)_{\text{order}}$  would be higher and, consequently, the alloying term in equation (6) would be lower.

However, for all types of sample,  $I_{TA}/I_{TO}$  correlates well with  $E_g^2 - E_g^3$  (figure 5). A linear approximation shows that  $E_g^2 - E_g^3 \rightarrow 0$  at  $I_{TA} \rightarrow 0$ . The above results enable one to suppose that structural distortions on a medium-range scale (about 4–6 Å or greater) lead to spatial fluctuations of the optical gap and decrease its average value  $E_g^2$ .

Quantitative comparison of the experimental and estimated (equation 5) values of  $\gamma$  may be obtained if it is suggested that  $E_{G_{\text{max}}} = E_o(300 \text{ K})$ . Figure 6(a) shows good agreement for all types of sample. Moreover, very good correlation is observed for estimations of the amplitude of the optical gap fluctuations obtained by different methods (figure 6(b)): from the analysis only of the optical absorption spectra  $E_g^2 - E_g^3$  and from comparison of the optical absorption and Raman spectra changes  $E_o - E_g^3$ . These results support the fact that the analysis of the optical absorption spectra proposed in [7] may be used to estimate the amplitude of the optical gap fluctuations. This analysis enables one to determine the width of the electronic band tail, which lies between the band states and the Urbach tail. The width of the tail between the valence band and the Urbach tail in a-Si:H is found to be approximately 0.15 eV [21], which is close to the  $E_g^2 - E_g^3$  value obtained for a-Si:H samples (figure 6).

So, the analysis of observed correlations (figures 4–6) allows one to suppose that very high spatial fluctuations, caused by strains and deformations of the structure on a medium-range scale (about 4–6 Å or greater), exist in amorphous silicon. The amplitude of these structural fluctuations depends on the evaporation conditions and thermal treatment of the samples and may be varied by the introduction of doping atoms. In the case of a-Si the amplitude of the fluctuations correlates with the bond-angle dispersion width (figure 3). Probably, it is explained by the rigid four-coordinated structural network. On the other hand, introduction of doping atoms may considerably transform the medium-range structural order although it affects the bond-angle fluctuations weakly. These structural fluctuations modulate the electronic structure and lead to some spatial fluctuations of the gap. The latter form an electronic band tail and decrease the average value of the optical gap. The width of the tail as well as the decrease in the optical gap depend on the amplitude of these structural fluctuations.

From this point of view, 'ideal a-Si' has no fluctuations on a scale of about 5–10 Å. Probably, this corresponds to 'ideal' packing of Si tetrahedra or to formation of the correct six-member rings. In this case the intensity of the  $TA$  peak in Raman spectra and the amplitude of the optical gap fluctuations tend to zero and the optical gap tends to be equal to the value of  $E_o$ .

## 6. Conclusion

Analysis of Raman spectra in a wide set of the samples of amorphous Si and its alloys shows that rather strong changes in structural order on a medium-range scale (about



4–6 Å or greater) and weak changes in short-range structural order occur in a-Si:H and a-(Si:H):B. The optical gap observed for these samples does not correlate with the TO peak width in Raman spectra but does correlate well with the  $T_A$  peak intensity. Analysis of the optical absorption spectra allows one to estimate the amplitude of spatial fluctuations of the optical gap  $\Delta E_G$ . It is observed that the optical gap fluctuations correlate well with the changes in the  $T_A$  peak intensity:  $\Delta E_G \rightarrow 0$  and  $E_G$  tend to be equal to the value of the optical gap of the 'ideal a-Si' at  $I_{TA} \rightarrow 0$ . From the analysis of the above results it can be concluded that not only do the optical properties of amorphous silicon and its alloys depend on the bond-angle fluctuations. Structural order on a medium-range scale (about 4–6 Å or greater) also has a significant influence on the properties of the materials.

### Acknowledgments

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