

Nanostructural disorder in hydrogenated amorphous silicon

F. SAVA

National Institute R&D for Materials Physics, Atomistilor str. 105 bis, P. O. Box MG.7, 077125
Bucharest-Magurele, Romania

The structure of amorphous silicon and amorphous hydrogenated silicon has been investigated starting from a large model of amorphous silicon (2052 atoms). The modifications induced in a-Si model by when hydrogen is introduced have been revealed. The diffusion of hydrogen leads to a nanostructuring effect in the continuous random network of amorphous silicon. The effect of hydrogen on the distributed distortion defects in silicon network has been modelled. The most strained bonds have been broken and hydrogen was attached to the dangling bonds on silicon. A free energy relaxation process was carried out in the frame of a Monte - Carlo – Metropolis procedure. There was demonstrated that, by nanostructuring, the total free energy of the model decreases. The variation of the bond stretching and bond bending energy as a function of the number of broken bonds indicated a dominant contribution of the bond bending term. The modelling shows, undoubtedly, the disappearance of many structural defects that probably are related to the deep electronic states in the gap of amorphous silicon.

(Received: August 1, 2007; accepted September 7, 2007)

Keywords: Amorphous silicon; Nanostructure; a-Si:H, Structural modelling; Defects

1. Introduction

Amorphous silicon is a robust material that has been engineered for many years in order to be applied in various devices: photovoltaic cells, thin-films transistors, imaging, colour sensors, radiation detectors, displays, etc...[1, 2, 3]. There are still a lot of problems to be clarified from the fundamental point of view [4,5,6]. The structure is not completely understood. The aging and the transition from amorphous to crystalline state, especially for amorphous hydrogenated silicon is still a subject of debate. Recently, the nanostructural properties of amorphous silicon raised a large interest, due to the very attractive results got on nano and micro-crystalline silicon [7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. New applications emerged and papers that simulate the silicon based devices or investigates the performance of solar cells have been published[17, 18, 19, 20]. Studies related to the light induced phenomena, luminescence properties of silicon [21], light induced degradation , improvement of the efficiency of the solar cells, and various properties of amorphous silicon have been published [22, 23, 24, 25, 26, 27]. New preparation methods, as e.g. deposition in expanding thermal plasmas were applied to disordered silicon [28].

Recently silicon clusters in silicon monoxide films have been observed and investigated [28].

We carried out a modelling study on a large cluster of silicon in order to understand the amorphous state of silicon and hydrogenated silicon as well as the structuring of silicon when more and more hydrogen is added. The nano-structuring that are strongly related to the development of the defect in the silicon network is one of the purposes of the paper.

2. Experimental

The starting structural model used in the modelling study is a physically build model from plastic units simulating the tetrahedral silicon atoms. The model has 2052 atoms (Fig. 1) [29]. The big cluster of silicon atoms has been relaxed in the frame of valence field theory after the procedure of Keating [30] with the force constants given by Martin [31], using a Monte Carlo-Metropolis method of relaxation. The pair distribution function reproduces quite well the radial distribution function of the amorphous silicon. This is a strong argument that the model is a realistic one and can serve for the investigation of various properties of amorphous silicon starting from the structural configurations and geometrical coordinates of the atoms. The model is used in this paper for evidencing the configuration of defects and the nanostructuring of silicon when more and more hydrogen are introduced into the semiconductor network.

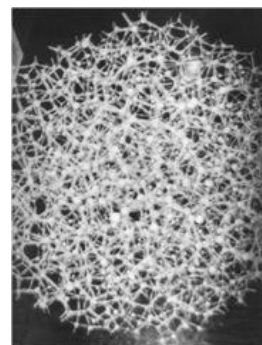


Fig. 1. Structural model for amorphous silicon (2052 atoms).

In order to get a model for the nanostructured silicon we simulated the diffusion of the molecular hydrogen. In our view the silicon cluster situated in an environment containing hydrogen allows the diffusion of H_2 molecules due to large voids characteristic for the tetrahedral structures. The diffusion rate is low at normal pressure and temperature, while is strongly enhanced at high temperatures and pressures. The hydrogen molecule enters into the silicon network and migrates along the regions with distorted bonds. In the places where the silicon-silicon bond is very distorted, the electrical field created by the deviation from sp^3 bond breaks the H_2 molecule. By a reciprocal interaction the Si-Si bond is also broken and both hydrogen attach to the «dangling bonds» thus created. Step by step more and more bonds are broken in the silicon network. During this process, due to more local freedom, in the neighbourhood of every hydrogenated bond a local relaxation of the network takes place, the bonding distances and bond angles approach the ideal tetrahedral values for silicon. As a consequence, the quasi-continuous amorphous network of silicon is transformed in a new configuration characterized by an assembly of small nano-amorphous domains, separated by hydrogenated interfaces.

The procedure for simulation of the nano-structuring consists in the sequential breaking of the most distorted Si-Si bonds at a time. Thus atoms with three covalent bonds appear, the fourth one being satisfied by hydrogen. The whole model is energetically relaxed using Keating type interaction potentials and a Monte-Carlo Metropolis computer procedure. The free energy used in relaxation is calculated as the sum of bond stretching and bond bending energy for every atom. The process was stopped when the number of bonds with significant distortion are eliminated from the model. In our model 677 Si-Si distorted bond have been broken and the 1354 dangling bonds were neutralized by hydrogen atoms. Thus the models was strongly fragmented in amorphites and a specific «worm-like» structure was obtained.

3. Results and discussion

Fig. 2 shows the plot of the evolution of the average bonding distance per model, when Si-Si bonds are broken and the energy relaxation is carried out. It is observed that by increasing the number of Si-Si broken bonds, the remaining ones are relaxed towards the ideal value (2.35 Å, null distortion), while the second order distance tends to the ideal (tetrahedral) value of 3.8374 Å.

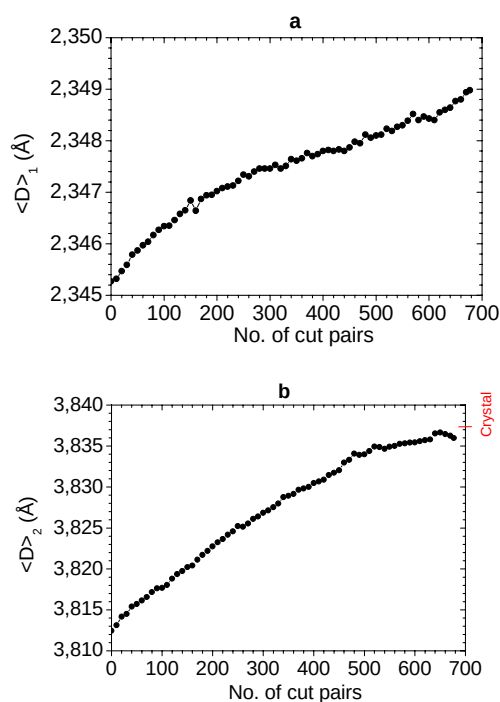


Fig. 2. The evolution of the first order distance (bonding distance) (a) and second order distance (the distance between the second order neighbours) (b) with the advancement of nanostructuring of the amorphous silicon.

The relaxation of the structure towards the ideal parameters can be explained by the gradually disappearance of the mechanical strains in the network.

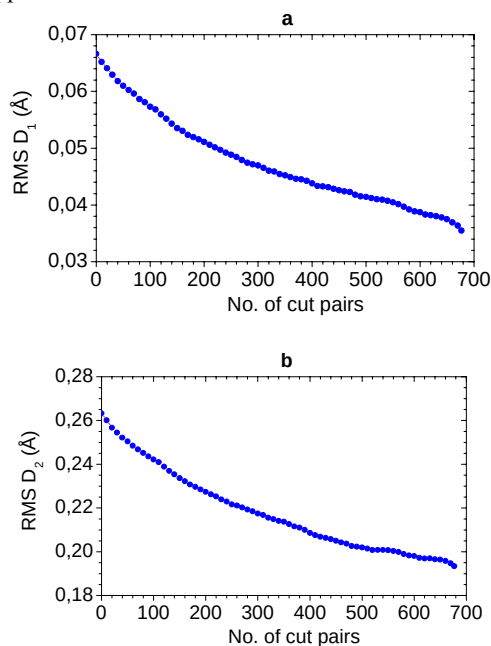


Fig. 3. The evolution of the width of the bonding length distribution (a) and of the width of the second order length (characteristic to the tetrahedral configuration of silicon) (b), as a consequence of breaking of a fraction of silicon bonds.

Fig. 4 a, b shows the evolution of the model with respect to the bonding angle: the average bonding angle and the width of the distribution of the bond angles. One remarks that, as opposite to the other parameters, the mean value of the bond angle tends to a value higher than that of the ideal tetrahedral value (109.46668°). This means that, as a general effect, a deviation from the tetrahedral configuration takes place and this is in agreement with a possible bond dehybridization due to the new hydrogen bond formation.

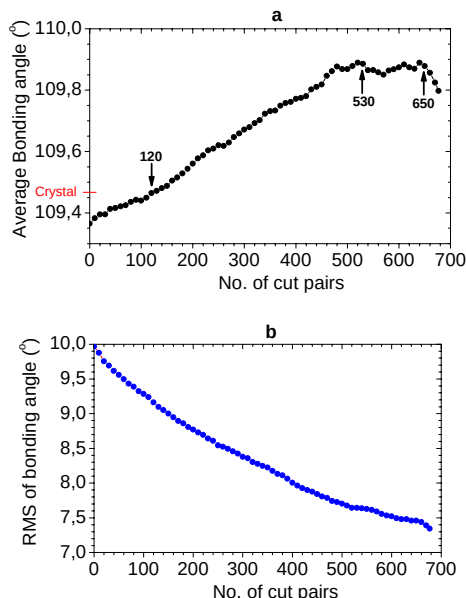


Fig. 4. The evolution of the average angle between the tetrahedral bonds (a) and of the width of the bonding angle distribution (b) in the nanostructured silicon model.

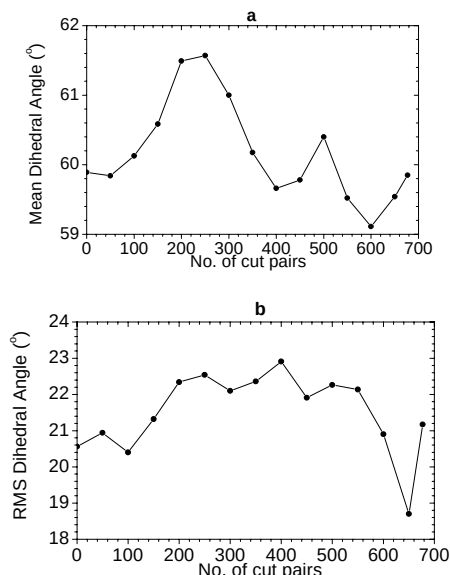


Fig. 5. The evolution of the dihedral angle (a) and of the width of the dihedral angle distribution (b) in the silicon model subjected to nanostructuration.

Fig. 5 shows the evolution of the dihedral angle and dihedral angle distribution during nanostructuration of silicon. It is observed that the average dihedral angle exhibits the tendency to deviate slightly (with 1.5°) from the angle characteristic to staggered (trans) bond, while the breadth of the distribution remains nearly constant, but, nevertheless, very large: $21 - 22^\circ$. This means that the characteristic configuration with staggered bonds is preserved in the model during nanostructuration.

4. Discussion

The nanostructuration of amorphous silicon can be easily obtained by hydrogenation. The modelling results shows that amorphous nano-silicon can be obtained. Although the nano-domains are not crystalline, they are more ordered than the amorphous silicon as a whole. The size of the cluster subjected to nanostructuration is ~ 30 Å. This value is in agreement with the result of a study performed by Szekeres et al. [28] who observed in the electron microscope silicon cluster having the diameter around 30-40 Å. According to the TEM (HRTEM) images of the SiO_x films annealed at 1000°C for 30 minutes the size of the crystallites is below 40 Å. In most of the cases the silicon nano-crystallites have an irregular shape. From the analysis of the HRTEM images the authors of [28] found the average size of the nanocrystallites to be 30 Å. Due to this small size, the interfaces between the silicon nanocrystallites and amorphous oxide are not well-defined crystal planes producing defect centers.

Fig. 6 shows a computer image of the model of amorphous silicon, as well as the model of nano-amorphous silicon. It can be easily observed the „worm-like” structure in the nanostructured model (b), while the amorphous model (a) is more compact.

The worm-like structuring is supposed to be related to the diminishing of the density of deep electronic states in the forbidden gap of the semiconductor (silicon). The phenomenon of gap cleaning, determined by hydrogen atoms, was discovered in 1975 by W. Spear and LeComber [32,33]. From those times the magical effect of hydrogen has been used in the development of a new amorphous material: a-Si:H, able to be doped, and, therefore, to be used in the photovoltaic cells and other applications.

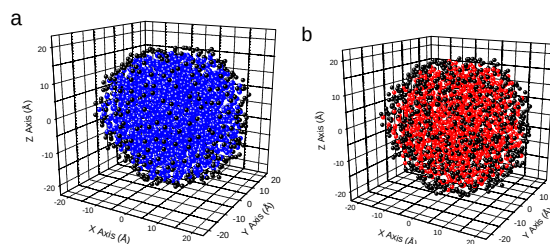


Fig. 6. a. The model for amorphous silicon (1575 atoms with 4 bonds (blue); 477 surface atoms having 3 or 2 bonds) b. The model for the nanostructured silicon. (1100 atoms linked to hydrogen (red); 952 remaining atoms (black) are not transformed by nanostructuration; 475 atoms have not dangling bonds).

This leads us to the conclusion that the nano-silicon is a new material intermediary between ideal amorphous and ideal crystalline ones. It is suggested that this new material could exhibit properties at variance with both amorphous and nano-crystalline ones, including luminescence properties similar to those in nano-crystalline silicon. Properties approaching those of porous silicon are also expected.

5. Conclusions

We have developed a nanostructural model for amorphous silicon. The model has been characterized by the atomic-scale parameters. It is suggested that in such a structure new and interesting properties related to quantum behaviour of the small silicon clusters could appear.

Acknowledgment

The author acknowledges the help of the Prof. Dr. M. Popescu. The research was carried out in the frame of the contract 41N/ 2006, Project: PN06-410102.

References

- [1] D. Carlson, C. R. Wronski, *Apl. Phys. Lett.* **28**, 671 (1976).
- [2] P. G. LeComber, W. E. Spear, A. Gaith, *Electronics Letters*, **15**, 179 (1979).
- [3] *Technology and Applications of Amorphous Silicon*, Ed. R. A. Street, Springer, Heidelberg, 2000.
- [4] D. Weaire, *J. Optoelectron. Adv. Mater.* **8**(6), 2011 (2006).
- [5] E. V. Emelianova, M. Brinza, V. I. Arkhipov, G. J. Adriaenssens, *J. Optoelectron. Adv. Mater.* **7**(2), 951 (2005).
- [6] W. Fuhs, *J. Optoelectron. Adv. Mater.* **7**(4), 1889 (2005).
- [7] M. L. Ciurea, V. Iancu, I. Stavarache, *J. Optoelectron. Adv. Mater.* **8**(6), 2156 (2006).
- [8] M. L. Ciurea, *J. Optoelectron. Adv. Mater.* **8**(1), 13 (2006).
- [9] F. Finger, R. Carius, T. Dylla, S. Klein, S. Okur, M. Güneş, *J. Optoelectron. Adv. Mater.* **7**(1), 83 (2005).
- [10] D. Dimova-Malinovska, *J. Optoelectron. Adv. Mater.* **7**(1), 99 (2005).
- [11] R. Carius, T. Merdzhanova, S. Klein, F. Finger, *J. Optoelectron. Adv. Mater.* **7**(1), 121 (2005).
- [12] S. Okur, O. Goktaş, M. Güneş, F. Finger, R. Carius, *J. Optoelectron. Adv. Mater.* **7**(1), 73 (2005).
- [13] E. Bunte, K. H. Jun, H. Stiebig, *J. Optoelectron. Adv. Mater.* **7**(4), 1899 (2005).
- [14] Brüggemann, *J. Optoelectron. Adv. Mater.* **7**(1), 495 (2005).
- [15] S. Reynolds, V. Smirnov, F. Finger, C. Main, R. Carius, *J. Optoelectron. Adv. Mater.* **7**(1), 91 (2005).
- [16] M. Güneş, O. Göktaş, S. Okur, N. Işık, R. Carius, J. Klomfass, F. Finger, *J. Optoelectron. Adv. Mater.* **7**(1), 161 (2005).
- [17] I. A. Rusu, G. Popa, S. O. Saied, J. L. Sullivan, *J. Optoelectron. Adv. Mater.* **8**(5), 1935 (2006).
- [18] W. Fuhs, L. Korte, M. Schmidt, *J. Optoelectron. Adv. Mater.* **8**(6), 1989 (2006).
- [19] H. Brüggeman, M. Rösch, *J. Optoelectron. Adv. Mater.* **7**(1), 65 (2005).
- [20] M. Sendova-Vassileva, F. Finger, S. Klein, A. Lambert, *J. Optoelectron. Adv. Mater.* **7**(1), 481 (2005).
- [21] T. Aoki, T. Shimizu, D. Saito, K. Ikeda, *J. Optoelectron. Adv. Mater.* **7**(1), 137 (2005).
- [22] T. Merdzhanova, R. Carius, S. Klein, F. Finger, D. Dimova-Malinovska, *J. Optoelectron. Adv. Mater.* **7**(1), 485 (2005).
- [23] M. E. Donertaş, M. Güneş, *J. Optoelectron. Adv. Mater.* **7**(1), 503 (2005).
- [24] T. A. Abtew, D. A. Drabold, *J. Optoelectron. Adv. Mater.* **8**(6), 1979 (2006).
- [25] I. Balberg, Y. Dover, *J. Optoelectron. Adv. Mater.* **8**(6), 1996 (2006).
- [26] K. Lips, C. Boehme, T. Ehara, *J. Optoelectron. Adv. Mater.* **7**(1), 13 (2005).
- [27] M. Brinza, G. J. Adriaenssens, *J. Optoelectron. Adv. Mater.* **7**(1), 73 (2005).
- [28] A. Szekeres, T. Nikolova, A. Paneva, A. Cziraki, Gy. Kovacs, I. Lisovskyy, D. Mazunov, I. Indutnyy, P. Shepeliavyy, *J. Optoelectron. Adv. Mater.* **7**(3), 1383 (2005).
- [29] M. Popescu, *J. Non-Cryst. Solids*, **75**, 477 (1985).
- [30] P. N. Keating, *Phys. Rev.* **145**, 637 (1966).
- [31] R. Martin, *Phys. Rev.* **1**, 4005 (1970).
- [32] W. E. Spear, P. G. LeComber, *Solid State Comm.* **17**, 1193 (1975).
- [33] W. E. Spear, P. G. LeComber, *Philos. Mag.* **33**, 935 (1976).

*Corresponding author: fsava@infim.ro