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SELF-ORGANIZATION AND SIZE EFFECTS IN AMORPHOUS SILICON

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Abstract. *Self-organization and size effects in amorphous silicon have been investigated by modelling of the structure at nanoscale. The size effect related to the disorder in silicon is treated by the free energy balance in nanometric clusters using valence force field theory.The computed structural and energetical parameters of three continuous random network (CRN) models of amorphous silicon with 2052, 156 and 155 atoms are compared with the experimental values.In order to show the importance of the interfaces between different a-Si clusters, two networks of 200 and 205 atoms were modelled separately and then linked using an amorphous and a crystalline interface.Also the voids in the a-Si clusters are investigated.*

Keywords: size effects, amorphous silicon, nanometric clusters

I. Introduction

Extended research is dedicated for creating highly structured nanomaterials. One key issue is to form discrete organized nanoparticle aggregates, as opposed to extended homogeneous arrays [1, 2]. These discrete aggregates allow getting three-dimensional structures with diverse magnetic, electronic, and optical properties. Moreover, these assemblies could be placed on the surfaces to create devices and sensors in the 2-40 nm range. A “mortar” with recognition element-functionalized polymers is used to assemble complementary nanoparticle “bricks” [3]. Other alternative is to trigger the formation of specific aggregates or atomic configurations in rather homogeneous matrices using the energy controlled self-assembling processes. The formation of discrete regular atomic scale particles of controlled size and shape and spatial arrangement is an important step on the way to controlled nanoparticle assembly.

Amorphous, glassy and, in general, disordered materials are governed by laws not completely understood till now. The metastable configuration of the atoms gives to material the possibility to choose one among various pathways to change its free energy when, by providing some energy, the system is

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pushed to modify the quasi-equilibrium states in one of the multiple states of higher/lower energy. Small steps that ensure the adiabatic phase-change accomplish this task. During energy action a self-organized state can be reached. The self-organization phenomenon ensures the reversibility of the atomic state during energy exchange with the surrounding medium.

Self-assembly can be defined as “the process of self-organization of one or more entities as the total energy of the system is minimized to result in a more stable state”. This process of self-assembly inherently implies:

a) some mechanism where movement of entities takes place using diffusion, electrical fields, etc.;

b) the concept of ‘recognition’ between different elements, that results in self-assembly;

c) where the ‘recognition’ leads to the binding of the elements dictated by forces (electrical, covalent, ionic, hydrogen bonding, van der Waals, etc.) such that the resulting physical placement of the entities pushes the system in the state of lowest energy.

Self-assembly processes could have a variety of applications. They are important in any case where micro- or nano-scale objects of one type need to be placed or assembled at specific sites on another substrate. Applications could include i) detection and diagnostic ii) fabrication of novel electronic/optoelectronic systems, and iii) new material synthesis.

There was a high interest in recent years to develop concepts and approaches for self-assembled systems for electronic and optical applications. Material self-assembly has been demonstrated in a variety of semiconductors (GaAs, InSb, SiGe) using Stranski-Kastranov strain-dependent growth of lattice mismatch epitaxial films [4-7]. There is a continuous interest in assembling semiconductor transistors [8] carbon nanotubes [9,10] and quantum wires [11,12] which can be used as active devices for memory and logic applications.

The self-organization in amorphous materials seems to be of potential interest for three-dimensional integration of nanoscale devices.

The applications of hydrogenated amorphous silicon (a-Si:H) are: thin film transistors (TFTs) [13], organic light emitting diodes [14], active-matrix liquid-crystal displays (AMLCDs) [15], radiation imaging [16], solar cells[17], waveguides [18] and optical fibers [19]. Also, different a-Si nanostructures like nanotubes [20] and nanowires [21] can been built.

Due to its highly potential for applications, a lot of works were devoted to understand the structure of amorphous silicon and hydrogenated amorphous silicon. Three simulation techniques are highly used: first principle molecular dynamics (DFT) [22], Monte-Carlo [23, 24]and Reverse Monte-Carlo (RMC) [25]. Cooper et al. [22] showed by first principle molecular dynamics that 3.96 is the average first coordination for a-Si.Gibson et al. [26] revealed that in an unannealed a-Si film, more that 50% is topologically crystalline. Smets et al. [27] showed that there is a threshold in a-Si(H). Above 14% H, there are microscopic voids, while below 14% H, there are divacancies decorated with silicon. Recently has been shown that amorphous silicon [28] exhibits a glass transition at around 1000 K. The interface between a-Si and c-Si is very important [29].

In this chapter we demonstrate by simulation procedures applied to structural models, the possibility to have self-organization processes in tetrahedrally bonded amorphous semiconductors with special emphasis to amorphous silicon. The recent experimental data support the self-organization in amorphous hydrogenated silicon.

2. Modelling of self-organization in amorphous silicon

One of the materials developed in applications was amorphous hydrogenated (halogenated) silicon. The question [30] whether a structural state exists in hydrogenated amorphous silicon (a-Si:H) between the amorphous state of short-range order and the microcrystalline state of long-range order has stimulated a renewed interest. This state of intermediate order might be disordered enough to spoil the crystalline selection rules for optical transitions, hence providing for the strong optical absorption desired in photovoltaic devices (e.g. solar cells). It may be yet ordered enough to inhibit any structural changes and photoinduced defects that decrease the photocarrier lifetimes. Such a decrease ultimately leads to reduced efficiencies of these photovoltaic devices during long light exposure. The decrease or elimination of this degradation, which is called the Staebler-Wronsky degradation (SWD) after its discoverers [31] is one of the major goals in the research of a-Si:H and related materials.

The understanding of device stability is increasingly focused on the nature of heterogeneity within the amorphous silicon material [32]. Detailed studies have been carried out and rewarding results were obtained. An intermediately ordered phase of silicon has been suggested to be implicated in both amorphous and microcrystalline a:Si:H [33]. Tsu et al. [34] have recently shown that in a-Si:H special chain-like objects (CLO) at the nanometer scale are produced. These CLO’s are quasi-one-dimensional, having 2-3 nm widths and lengths of ~30 nm or more. Significantly, they show a high degree of order along their length, implying very low levels of bond angle distortion. It is remarkable that the high quality a-Si:H material used in the production of solar cells having superior photoelectronic performance, especially in regard to the Staebler-Wronski degradation effect, has elevated levels of CLO's. This enhanced performance seems to be a result of the intermediate order of the CLO's that are essentially strain-free. With this sort of heterogeneity, an a-Si:H film can reach an overall more relaxed state than it could if it were composed of a homogeneous amorphous matrix. This sort of heterogeneity comprised of the continuous random network (CRN) and the quasi-linear CLO components, should offer few interfacial defects, compared to (say) the CRN and the rather rigid three-dimensional microcrystalline structure.

The disordered, amorphous state of silicon and germanium was firstly thought in terms of the continuous random network (CRN) models for the atomic arrangement. The first CRN model was developed by Polk [35] for amorphous germanium. Later, Steinhardt et al. [36] and Popescu [37] succeeded to find more realistic models by using a Monte Carlo procedure for free energy minimization in the models. The Keating approximation for the covalent bond [38] and the force constants deduced by Martin [39] were used in the calculations. An excellent agreement of the structural data (radial distribution function, density) deduced from the CRN model with those experimentally found for germanium proved the general validity of the model. Moreover, the calculated free energy of the CRN model is in fairly good agreement with the crystallization energy of germanium as known from the literature [40].

In order to investigate the structure of amorphous silicon and to see how the structural details influence the energetical factors of the models, we developed several random network models with various numbers of atoms.

The models were relaxed with the stretching bond force constant α and bending bond force constant β in the frame of the Keating approximation for the covalent bond [38] with the values given by Martin [39]. In Table 1 are put together the structural and energetical data for the first relaxed CRN model of silicon with 155 atoms (Fig. 1 a), for the biggest relaxed model of a-Si with 2052 simulated atoms (Fig. 1 b), and for the CRN model with only even-fold rings (mostly 6 and 8-fold rings) (156 atoms) (Fig. 1 c). The modelling data are compared with the experimental data on amorphous silicon. There are shown the rms deviations of the first and second order distance due only to structure, as calculated in [41].

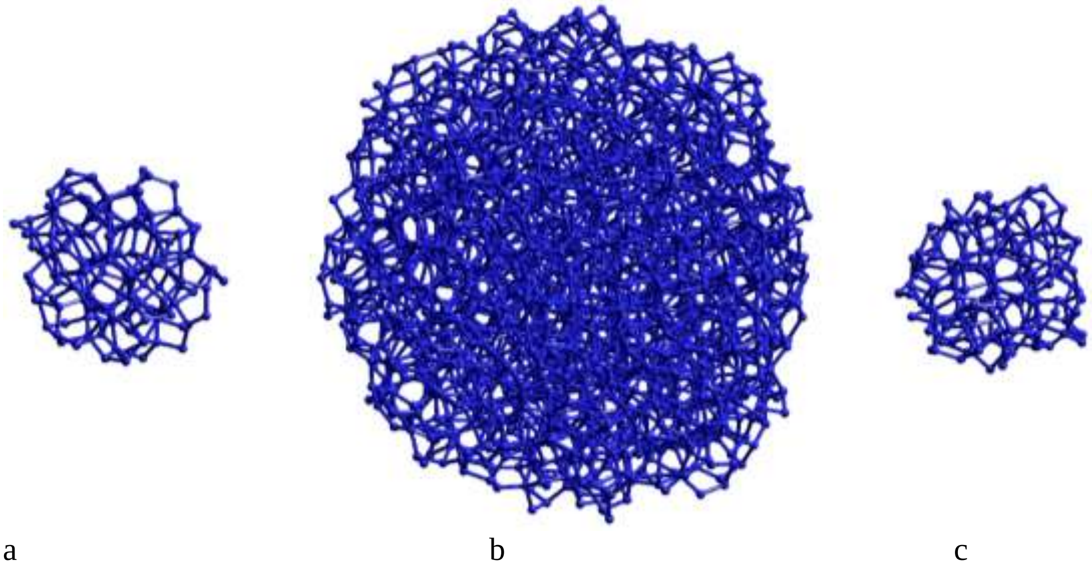


Fig. 1. Continuous random network models for amorphous silicon with a) 155 atoms, b) 2052 atoms, c) 155 atoms.

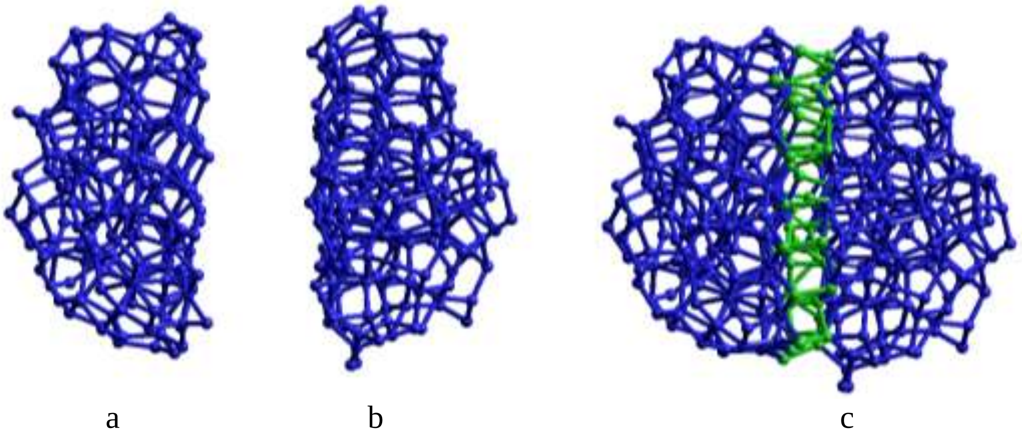
The highest free energy is characteristic to the model with even-fold rings of atoms: CRN(156). The largest CRN model (with 2052 atoms and a diameter of ~4 nm) shows the largest free energy, if compared to the other CRN models with a mixture of even and odd rings of atoms. The bond angle distortion (BAD) becomes larger when the percent of five-fold rings decreases. The calculation has shown that dihedral angles are not uniformly distributed. The CRN(155) and CRN(156) models favour a more uniform dihedral angle distribution while the CRN(2052) model shows a dihedral distribution with a significant but large maximum around the dihedral angles of 60^o and 180^o this values accounting for a preferred staggered configuration of the atoms. This aspect seems to be not related to the percent of the 5-fold rings in the models with odd and even rings of atoms.

Table 1. Structural and energetical data for CRN models of amorphous silicon.

a-Si models	**CRN(155)**	**CRN(2052)**	**CRN(156)**	**a-Si (experimental)**
5-fold/6-fold rings	0.600	0.480	0	-
7-fold/6-fold rings	0.840	1.090	0	-
rms deviation of bonding distance (Å)	0.036	0.067	0.095	0.089 [44] 0.100 (crystal) [41] 0.118 (crystal) [41]
rms deviation of second order distance (Å)	0.198	0.259	0.304	0.249 [44] 0.141 (crystal) [41] 0.226 (crystal) [41]
rms tetrahedral angle distortion	6.684^{o}	9.977^{o}	13.601^{o}	9.6^{o} [44], 10^{o} [34]
mean bond stretching energy per bond (meV)	10.32	36.54	53.13	-
mean bond bending energy per bond (meV)	21.18	47.54	88.87	-
total mean free energy per bond (meV)	31.50	84.08	142.00	-

CRNs are ideal networks and can be rarely produced. In fact they must include an enough large amount of free energy due to growing misfit in the compact arrangement of atoms when the volume of CRN increases. This misfit appears e.g. when the crystalline like arrangement of the tetrahedral units in germanium and silicon is substituted by dodecahedral-pentagonal configurations (amorphons or modified Voronoipolyhedra) [42], which are incompatible with the long-range order characteristic to crystal. With this idea in mind we tried [43] to see what happens if a model of amorphous silicon of minimum free energy is split in two amorphous domains, which, subsequently, were relaxed separately.

Fig. 2 c shows the model of amorphous silicon with 405 atoms (diameter ~2.5 nm) where the cutting line between the two domains (amorphites),M1 (Fig. 2 a) and M2 (Fig. 2 b), is clearly seen.



a b c

Fig. 2. Continuous random network models for amorphous silicon with a) 200 atoms, b) 205 atoms, c)405 atoms composed by linking of(a) and (b) clusters (the separation between two amorphous domains areclearly seen).

Table 2 shows the free energy data after computer relaxation of the model as a whole (M) and for the two separated and relaxed domains (M1 and M2).

Table 2. The free energy and structural characteristics of the CRN(405) relaxed model of amorphous silicon before and after separation in two domains.

Models (atoms)	mean bond stretching energy per bond (meV)	mean bond bending energy per bond (meV)	total mean free energy per bond (meV)	Bond angle distortion (^{o})	rms bond distortion (Å)	rms 2-nd order distance (Å)
M (405)	39.74	46.01	85.75	10.178	0.072	0.273
M1 (200)	22.88	39.60	62.48	9.086	0.053	0.237
M2 (205)	23.28	37.25	60.53	8.821	0.053	0.232
M1 + M2	23.08	38.43	61.51	8.954	0.053	0.2345

As can be seen from the Table 2 the splitting of the CRN (405) model for amorphous silicon allows for a significant diminishing of the total free energy of the model.

Earlier in a letter to Nature [45] was evidenced the importance of the energy balance in the core and at the surface of a CRN cluster of amorphous germanium. Later, it was shown [46] that for the surface atoms it is necessary to introduce a d-orbital contribution to sp^3 hybridization of germanium bonds. The character of the bonds is changed by the distortions. Individual bonds are described by orthonormalized s-p-d hybrids pointing in the right directions and having the right strength, so as to eliminate strain; energy is stored mainly by promoting some of the electrons into d-orbitals [51]. This type of approach is popular with the crystal chemists, though mostly only bond angle distribution, but not bond lengths are accounted for. Consequently, a new energy term must be introduced, or an approximation based on softening of the Keating force constants must be considered. In the case of amorphous silicon or germanium the bond distortions are accompanied by a slight modification of the electrical charge on atoms. The more bent atoms exhibit higher electrical charge. Guttman [47] has shown that bond stretching and bond bending on silicon atoms in a-Si lead to a mean electrical charge of ~0.2 e.u. per atom. The charge transfer from atom to atom in the amorphous network characterized by bonding deformations implies the diminishing of the bending forces because the ionic interactions increase on the account of the covalent ones. Softening of the Keating force constants determines the reduction of free interface energy in spite of the larger distortions of the bonds appeared on the interface between amorphites.

Therefore, we are lead to the idea that the true, realistic model of tetrahedrally bonded amorphous semiconductors must suppose a meander-like structure, where CRN domains of limited size create an entanglement of fine inter-domains boundaries which are extended over all the volume of the material. This new picture for amorphous semiconductors can open the way toward understanding the specific phenomena observed experimentally as e.g. centres of defects different from dangling bonds, hydrogen diffusion, aging, etc. In fact, symmetry breaking in continuous random networks seems to be a natural concept, usually encountered in many phenomena from the nuclear physics to astrophysics.

If the symmetry is broken and several domains are formed, is it possible to get a state of lower free energy, as a consequence of self-organization? The separation of the models in several domains gives rise to boundaries, which must be compared, to the experimentally observed CLO's [34].

During self-organization with the formation of inter-domain boundaries hydrogen diffuses at the surface of the amorphous domains. The surface is stabilized with low distortion bonds and crystalline-like organization. The formation of a fractal surface that minimizes the free energy of the surface is probably the characteristic feature in this case.

The energy introduced in the self-organized system can shift the equilibrium of the atom network. The amorphous domains can be "re-amorphized" and a new melted/solidified phase with different characteristics can be reached. High-energy irradiation raises the metastability minimum of the amorphous phase, while low energy irradiation can trigger modifications according to which the system descends to a lower metastability minimum. Thus, a fine-tuning by switching to various configurations in a reversible manner can be obtained.

The simulations performed for a-Si point out the natural tendency of the a-Si material to divide in small domains separated by boundaries. The boundary atoms take a structural configuration with low distortion bonds, and crystalline-like (diamond and/or wurtzite) arrangement. A tentative simulation of crystalline-like arrangement at the boundary between two CRN domains was carried out on a CRN model with 499 atoms, Mixt499 (Fig.3).

We introduced two silicon layers (2 × 47 atoms), one layer connected to the amorphite M1 and the other to the amorphite M2 of the CRN (405) model (44 links). Thereafter, the two amorphites were merged by the intermediary of the dangling bonds at the surface of every extended amorphite. A new CRN model with 499 atoms has been thus obtained (Fig. 3). This model was relaxed. In the second stage we changed topologically the two layers in order to obtain a crystalline-like configuration (6-fold, chair-like rings), thus simulating the crystallization of a thin region situated in-between the amorphites (Fig. 4 and model Cryst(499) in Table 3). A new relaxation was performed.

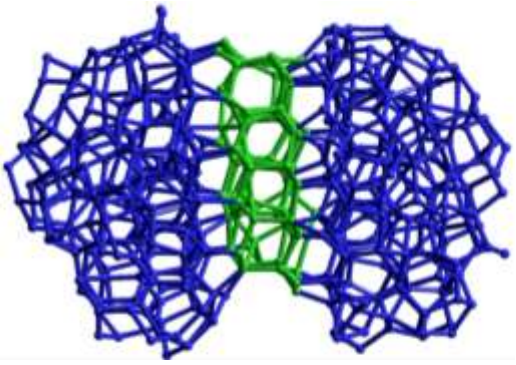


Fig. 3. The model of amorphous silicon with 499 (405 + 94) atoms having an additional double layer between two amorphites.

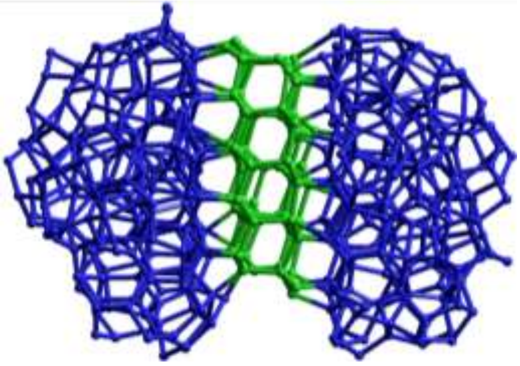


Fig. 4. Model of amorphous silicon with 499 (405 + 94) atoms with crystallized inter-domain boundaries.

In the next stages the crystallized region with a thickness of ~0.5 nm and the diameter of ~2.5 nm was decoupled step by step from the bodies of the amorphites by cutting a percent of the links with amorphites, starting with the most distorted bonds (models: Decoupl. 1-5, Table 3). After relaxation, the structural and energetical parameters were calculated for every step of simulation both for the diamond-like crystalline configuration and for the rest of the amorphites. The results are shown in Table 3.

Table 3. The structural and energetical parameters for the CRN(499) model for amorphous silicon with crystallization at the interface of the amorphous domains (BAD = bond angle distortion).

Model	decoup bonds (%)	rms(r_1) (Å)	rms(r_2) (Å)	*BAD (^{o})*		Stretching energy (eV)	Bonding energy (eV)	Total energy (eV)
				Crystallite	*Amorphite*			
Mixt 499	0	0.070	0.265	10.735	9.748	34.871	114.844	149.715
Cryst 499	0	0.068	0.256	6.020	9.715	33.567	101.094	134.661
Decoupl 1	21	0.065	0.255	5.144	9.523	28.886	90.989	119.875
Decoupl 2	38	0.065	0.252	4.457	9.397	26.720	85.078	111.798
Decoupl 3	54	0.062	0.249	4.043	9.340	25.409	81.795	107.204
Decoupl 4	69	0.060	0.246	3.261	9.233	22.426	77.214	99.640
Decoupl 5	75	0.055	0.246	2.629	9.111	19.224	73.525	92.749

It is remarkable that bond angle distortion (BAD) in the crystallized layer diminishes step by step when the coupling with the amorphites becomes poorer. This means that the thin crystallite becomes freer of constraints and takes a more and more correct structure. Finally for 75 % reduction of the bonding constraints with the amorphites, the BAD reaches the value of 2.629^o. This corresponds to 11 bonds between crystallite and amorphites from a total of 44 bonds acting in the initial topological configuration. The low value of the BAD is to be compared with the experimental value deduced for CLO's observed in TEM and characterized by Raman scattering: BAD ~ 0^o. The agreement is fairly good.

As resulted from our simulation experiments the main aspect of the formation of a crystallite with low distortion of the bonds is the decoupling of the most part of its bonds with the amorphous network. This is undoubtedly triggered by the presence of the hydrogen, which diffuses and satisfies the dangling bonds appeared during formation of the crystalline thin film. Only in amorphous hydrogenated silicon with enough high concentration of hydrogen it is possible to have such diffusion process with the satisfaction of the dangling bonds and separation of the crystalline configurations in-between the amorphous domains of the material.

3. Interstitial sphericalvoids in simulated amorphous networks of silicon.

We have developed several models of amorphous clusters of silicon. Two different clusters with 200 and 205 atoms were relaxed and for the final structureswith minimum free energy the interstitial spherical voids distribution were calculated. Hereafter, the two models were merged and the new structure was relaxed and, finally, the interstitial sphericalvoids distribution was recalculated (for comparation, the voids between the two clusters are not taken into account). The distribution of void's size proved to be significantly different (Fig. 5 a, b).

We have modelled also the special structure of the merged clusters when in between of the two clusters (200 + 205 atoms) is put an amorphous layer (94 silicon atoms) and, respectively, a crystalline layer (94 silicon atoms). The new void distribution only in two models with 200 and 205 atoms after relaxation is represented in Figure 5 c, d. All the distribution from Fig. 5a-d contains interstitial spherical voids which may overlap up to 99.9%.

The small differences in the distribution of void structure in all the studied cases are evidenced in the calculated cumulated distribution of voids (Fig. 6). The largest variation of the void distribution is specific for the merged of clusters with a crystalline interface.

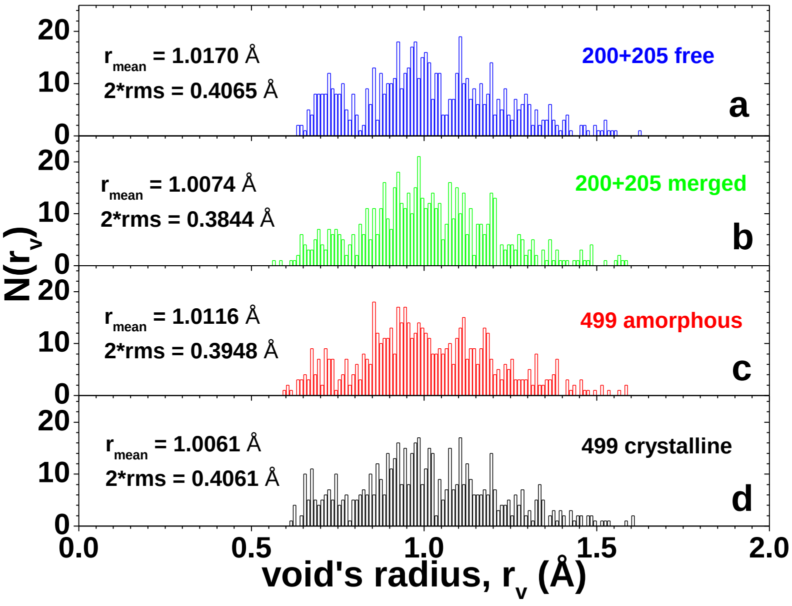


Fig. 5. Histograms of the void radius (r_v) in simulated clusters with 200 and 205 silicon atoms then they are: a) free clusters, b) merged clusters, c) merged clusters with a crystalline interface (94 silicon atoms in amorphous double layer), d) merged clusters with an crystalline interface (94 silicon atoms incrystalline double layer)

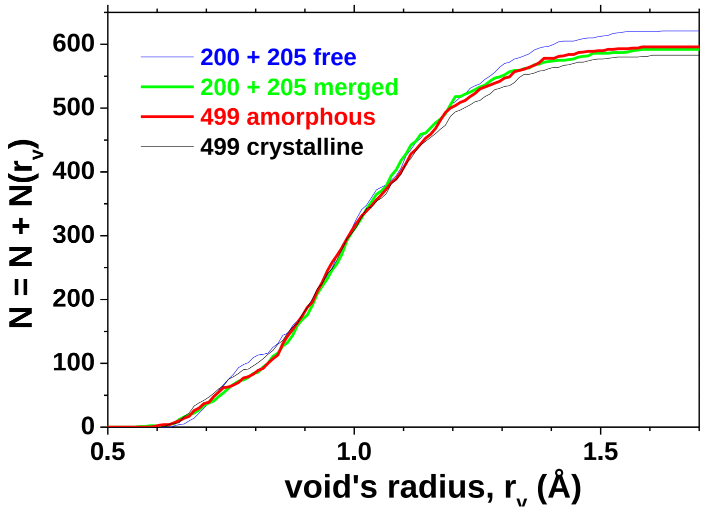


Fig. 6. The cumulative distributions of void's radiusin simulated clusters with 200 and 205 silicon atoms then they are free clusters and merged clusters, after computer relaxation in all the cases.

The normalized interstitial voids radius (r_V) distributionsin crystalline (Fig. 7 a) and amorphous (Fig. 7 b) silicon with 455 atomsare presented in Fig. 8. Thedisordered lattice is obtained from corresponding crystalline lattice by introduction of topological defects (Wooten-Winer-Weaire defects [48]).All the distribution from Fig. 8 contains interstitial spherical voids which may overlap up to 1 %.

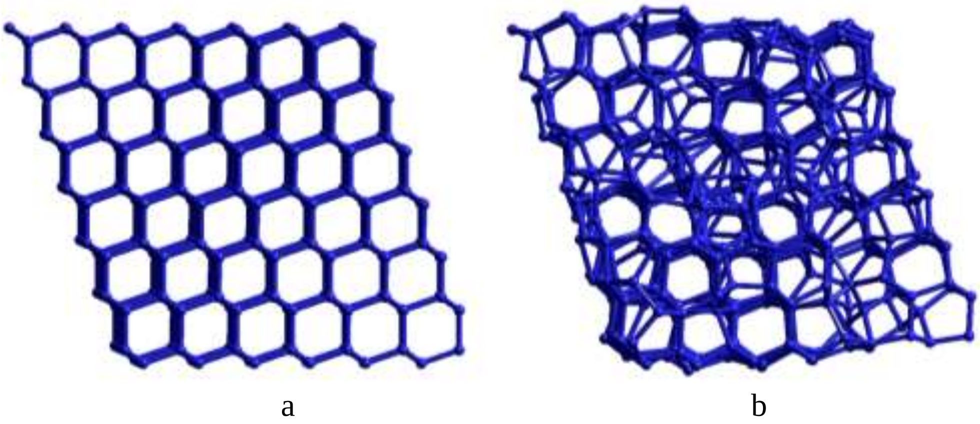

a b

Fig. 7. Model of 455 silicon atoms in: a) crystalline state, b) amorphous state (56 deformons in crystalline silicon domain).

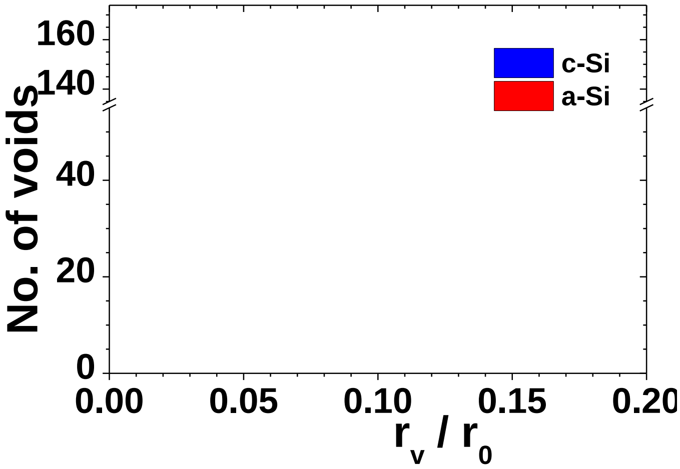


Fig.8. The normalized voids' radius (r_v/r_0) distribution in crystalline and amorphous silicon with 455 atoms (r_0 is the covalent radius of silicon and carbon: r_0(Si) = 0.117 nm and r_0(C) = 0.071 nm).

The interstitial voids in the silicon lattices are important for understanding the origin of first diffraction peak in the structure factor of amorphous silicon (Fig. 9b).Fig. 9b shows the structure factor of the amorphous silicon model after relaxation. Elliott [49] has demonstrated in rather seminal papers that the so-called FSDP in glasses depends on the distribution, size and ordering of voids. Popescu and Sava [50] suggested that the voids distribution into an amorphous material is essential in the amplification or vanishing of the first diffraction peak (FDP).

We have simulated the filling of the interstitial voids in amorphous silicon, by introduction in the centre of the voids of ions with atomic number identical to that of silicon, without covalent bonds between silicon and ions. The diffraction pattern of the model shows the decrease of the first diffraction peak (FDP) as a measure of filling the voids (Fig. 9b).

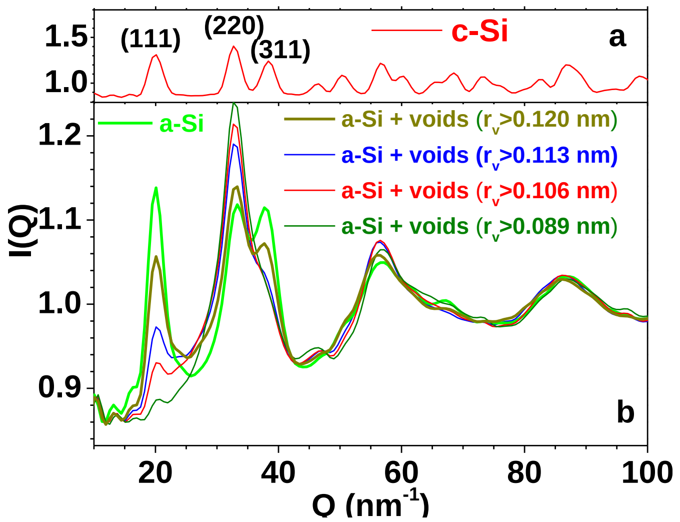


Fig.9. a) The structure factor of the crystalline silicon model (455 atoms). b) Diffraction pattern of the amorphous silicon model (455 atoms) with gradually occupied voids with ions non-bonded in the lattice.

4. Discussion

Amorphous hydrogenated silicon of improved quality for photovoltaic devices can be prepared by hydrogen dilution of the processing gas. This increase in quality, as measured, for example, by a decrease of the Staebler-Wronski degradation, is accompanied by an increase in the concentration of chain-like objects, CLO's in TEM micrographs. The formation and the particular features of CLO's can be explained on the basis of self-organization in CRN networks of amorphous silicon by splitting the rather uniform structure in homogeneous and less constrained domains linked through low distortion crystallite-like configurations [34]. It seems that hydrogen (H) or fluorine (F) are playing in amorphous silicon the role of glass modifiers as Na or Ca atoms are playing in a-SiO_2 when silicate glasses are formed, i.e. conferring to structurally deficient, but interconnected network, a polymeric character.

As opposite to microcrystalline and nanocrystalline silicon, which are composed from crystalline domains surrounded by amorphous boundary layers, the device quality silicon can be viewed as composed from amorphous nanodomains surrounded by crystalline boundaries. The crystalline arrangement can be diamond-like or a mixture of diamond-like and wurtzite-like configurations due to constraints at boundaries, which allow for eclipsed orientation of the bonds. The high quality amorphous silicon is in fact a new-type of self-organized structure characterized by meander-like crystalline configurations that defines the rather homogeneous amorphous domains. This type of silicon will be called nano-amorphous silicon because it is a reverse structure of nanocrystalline silicon, a well-known material.

The importance of d–orbital bonding both in amorphous tetrahedrally semiconductors and in chalcogenide glasses is remarkable.

In amorphous silicon (germanium models) the contribution of d-orbital bonds has an essential effect in relieving the stresses in the region between the amorphous domains. Thus, the boundaries become thin low-dimensional unstressed and undistorted regions protruding deeper into the material, as observed in TEM pictures. It was shown earlier [51] that the distortion of the local tetrahedral symmetry of atomic bonds in a semiconductor like silicon always leads to such a change in the bond character as to eliminate elastic stresses. This can be achieved for metastable silicon phases by adding small d contribution to the usual sp^3 orbitals. On the basis of a tight binding calculation of the valence band density of states we have demonstrated that the atomic spd orbitals ensuing from this approach yield the correct valence band density of states in CRN (155) and CRN (2052) models.

The stability of the nanostructured amorphous material depends on the way of impeding grain boundary motion. The driving force for such motion is simply the reduction of the total area of grain boundary. This is because the boundaries exhibit a larger free energy, as shown in the CRN models. If the specific energy of the boundary can be made zero or negative, then the driving force for the grain growth vanishes. The domain structure is stable. John Weissmüller [52] advanced this idea in a quantitative form. The basically mechanism is, in its view, the segregation of a minor constituent solute. If, in our case, the hydrogen is the minor constituent solute in amorphous silicon, when the CRN grain grows, less segregated hydrogen is needed because the area of the boundary per unit volume decreases and, thus, the excess hydrogen returns in the grain. The returning of hydrogen in the amorphite enhances the free energy of the amorphite, so that the total free energy change is positive. If this occurs, then the driving force for the amorphite growth vanishes. We are dealing with a grain structure stabilized by segregation. If the hydrogen dilution rate in silane increases, at the temperature of 300 ^{o}C takes place a motion of the boundary by hydrogen diffusion in the inner part of the amorphite. Consequently, the inter-domain region becomes labile and suffers an ordering process, by forming CLO's configurations, i.e. two-dimensional crystalline zones. These crystalline-like configurations stabilize the structure with small-size amorphous domains, well ordered as ideal amorphous phase. The molecular hydrogen seems to be the most important constituent solute for the migration in the amorphites, because other fragments obtained during silane decomposition are heavier and their diffusion is greatly impeded. As concerning the diffusion process, we must observe that high electronegative hydrogen or/and fluorine are able to break up the rather perfect covalent network of silicon. Halogens can be regarded as network modifiers. The adding of an electropositive modifier depolymerizes the structure of amorphous silicon (just as in the case of silicate glasses), with more destructive effect, more concentration of hydrogen is added. The depolymerization of the silicon network seems to be just the factor, which control the separation of the crystalline configurations at the boundaries.

5. Conclusions

The Monte-Carlo simulations of atomic scale structure of amorphous silicon have shown that self-organization in non-crystalline networks is a natural process occurring during network formation and is essentially a splitting of the continuous random network in nanometric homogeneous domains separated by meander-like boundaries characterized by strong ordering of the silicon atoms so that rms deviation of the bond bending angle takes a minimum value. These crystalline boundaries can be identified as special CLO's in TEM pictures of device quality amorphous hydrogenated silicon.

The self-organization of the non-crystalline networks can be viewed as a new phenomenon in network glasses, which can be exploited for producing materials with self-controlled properties, useful in three-dimensional optoelectronic devices.

The size effect in amorphous silicon is clearly demonstrated on the basis of simulation of small clusters. The interface between the amorphous clusters and the role played by that interface (either amorphous or crystalline) is crucial for fine tuning of the properties of this material important for developing new devices for applications inphotovoltaics and sensorics.

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