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Atomic topology and optical properties of amorphous porous silicon, ap-Si

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Abstract

Porous silicon has been studied extensively due to the interesting luminous properties that it displays. However, amorphous porous silicon, ap-Si, is an elusive material difficult to produce and study. Since ap-Si can be visualized as highly defective a-Si we have applied our new thermal process, based on an ab initio molecular dynamics method that uses the Harris functional, to generate samples of ap-Si with 50% porosity starting with a cubic periodic supercell of 216 atoms, from which a porous cell was carved out. The randomizing process was done using a 7.5 fs time step and after the various structures were obtained, their optical gaps were determined. We find that the gaps increase monotonically with the randomness of the structure from 0.004 to 0.580 eV.

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1. Introduction

Porous silicon has been studied extensively, both experimentally and theoretically, due to the interesting luminous properties that it displays [1]. On the other hand, amorphous porous silicon, ap-Si, is a very difficult material to deal with and so far the number of experiments is quite limited and the simulation of its atomic topology and electronic and optical properties is nonexistent. Nevertheless, there are important differences between these two materials that make their study interesting. To mention one, porous crystalline silicon shows a large blue shift of the photoluminescence upon reducing the size of the structures by photo-etch, evidencing quantum confinement effects, whereas no shift has been observed when carrying out the same experiment with ap-Si [2], although the photoluminescence intensity of ap-Si is quite comparable with that of crystalline silicon of the same thickness [3]. Due to the difficulty in the production of ap-Si the literature on the subject is scarce.

In order to simulate the electronic and optical properties of ap-Si it is necessary to find a representative atomic structure. This material can be visualized as a defective amorphous sample and therefore some of the methods we have developed [4] to deal with amorphous semiconductors can be applied.

Amorphous silicon, a-Si, has been thoroughly studied for the last three decades, both experimentally and theoretically, and the scientific and technological relevance of a-Si, pure and hydrogenated, is well known and need not be emphasized here. The study of a-Si, and of a-Ge, have evolved in parallel; early work on their atomic structures started more than four decades ago. Experimentally, this work began with the electrolytic approach of Szekely [5] in 1951 and the pioneering efforts of Richter and Breitling [6] in 1958. Theoretically, the first atomic models of both a-Si and a-Ge appeared in the literature over thirty years ago. Grigorovici and Manaila [7] and Coleman and Thomas [8] in 1968 suggested structures based on arrangements of closely packed simplified Voronoi polyhedra that have the shape of truncated tetrahedra both eclipsed and staggered 60° about their common bond, leading to rings of five atoms and to boat-like rings of six atoms, as in the carbon and silicon amorphous clusters that we have recently studied [9].

Simulationally, the pioneering ab initio Car–Parrinello molecular dynamics approach (CPMD) has permeated all efforts during the last 15 years [10], to the

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point that their thermal processes have been used frequently, almost without questioning. These have generic shortcomings: radial distribution functions (RDFs) that reproduce, at best, the first two peaks of the experimental results; an excess of defects, both dangling and floating bonds, and the non-existence of electronic and/or optical gaps, just to mention the most relevant. Nevertheless, a-Si has been the preferred material to test any new computational development for amorphous samples. For example, Stich et al. [11] and Lee and Chang [12] have applied the CPMD method to a-Si and variants of the Car–Parrinello method have been used by Drabold et al. [13] and by Fedders et al. to study this material [14]. For an up to date account of the situation see Ref. [4].

Since ap-Si is an amorphous sample of silicon with a large percentage of porosity, we used our thermal process to amorphize a 50% porous crystalline supercell with originally 216 atoms to generate a porous random network to use as a basis for calculations of the electronic and optical properties of this material. Two points are in order: first, it is clear that the ap-Si material comes in a variety of porosities that have to be simulated and studied; second, the orientation of the pores and the effect of hydrogenation have to be taken into account to better describe the real material. At present, we are working along these lines, but in what follows we present our results for this particular sample of porous amorphous silicon.

2. Method

We use FASTSTRUCTURE [15], a DFT code based on the Harris functional [16], and optimization techniques based on a fast force generator to allow simulated annealing/molecular dynamics studies with quantum force calculations [17]. We use the LDA parameterization due to Vosko et al. [18] (VWN). The core is taken as full which means that an all electron calculation is carried out, and for the amorphizing a minimal basis set of atomic orbitals was chosen with a cutoff radius of 5 Å, a compromise between cost and accuracy. For the optimization process a cutoff radius of 3 Å was utilized. In order to better simulate the dynamical processes that occur in the amorphization a time step of 7.5 fs was used. The forces are calculated using rigorous formal derivatives of the expression for the energy in the Harris functional, as discussed by Lin and Harris [19]. The evaluation of the 3-center integrals that contribute to the matrix elements in the one-particle Schrödinger equation is the time-limiting feature of FASTSTRUCTURE and each is performed using the weight-function method of Delley [20].

We construct a periodic crystalline supercell with 216 atoms (a crystalline density of 2.33 g/cm^3) and carve a random pore until 50% porosity is obtained. While maintaining the crystalline arrangement of the supercell we carry out a Tauc-like study of the optical absorption to obtain the optical gap [21]. Next we relax this crystalline arrangement to optimize the geometry and once again we calculate the optical absorption curves and the gap. We then amorphize the relaxed crystalline structure by slowly heating it from 300 to 1680 K, well above the glass transition temperature and just below the melting point, in 100 steps of 7.5 fs, and immediately cooling it down to 0 K in 122 steps of 7.5 fs followed by annealing cycles at 300 K (below microcrystallization) with intermediate quenching processes and determine its optical gap. Finally we relax the amorphous structure and determine its gap once more.

3. Results and discussion

After the random pore is carved in the crystalline supercell a large number of dangling bonds are generated and one expects the number of states within the gap of the originally 216 atom crystalline supercell to be large also, Fig. 1(a). Once the electronic energy levels are calculated using FASTSTRUCTURE, the optical absorption curves are obtained according to the method described in Ref. [21] from which the optical gap is extrapolated using an approach similar to the one devised by Tauc, and very common among experimentalists. Clearly, the porous crystalline sample obtained in this process has a large number of dangling bonds and one would expect to find no gap. In fact practically no gap is found: 0.004 eV, Fig. 1(b).

Fig. 2 depicts the atomic topology of the relaxed crystalline sample and its corresponding optical gap. The relaxation process (geometry optimization) relieves the stresses left by the carving of the pore in the crystalline supercell and reduces the number of dangling bonds, Fig. 2(a), diminishing the number of electronic states within the gap; this leads to a larger value of the optical gap: 0.474 eV, Fig. 2(b).

The results of the amorphization of the relaxed crystalline sample using the thermal process described above are presented in Fig. 3(a) and its corresponding optical absorption curve in Fig. 3(b). Surprisingly enough, the value of the gap obtained, 0.575 eV, is close to the one for the relaxed crystalline supercell, which indicates that the relaxation process carried out for the crystalline carved sample leads more to an amorphous sample than to the original crystal-like structure.

Finally Fig. 4 shows the results for the relaxed amorphous porous sample. The atomic topology is depicted in Fig. 4(a) and the optical properties are given in Fig. 4(b). It is clear that the optical absorption curves show a much diminished number of electronic states

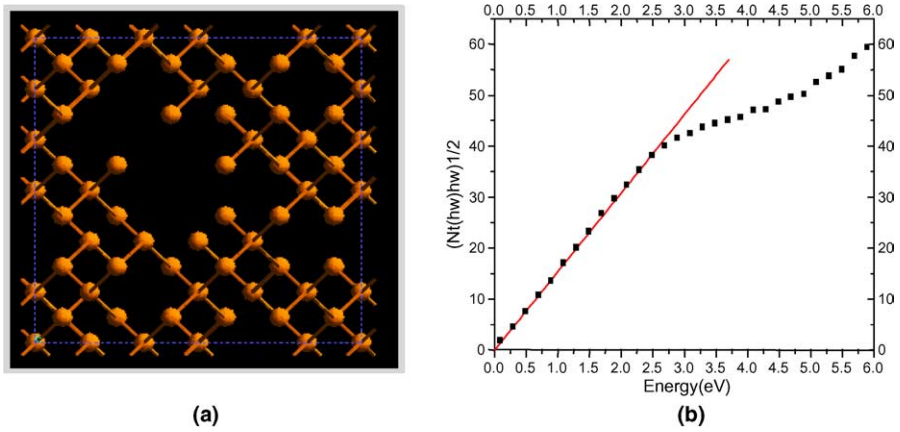

Fig. 1. Periodic 216 atom crystalline supercell carved with a 50% random pore. (a) The random pore can be observed and the inner silicon atoms are left with a large number of dangling bonds. (b) A Tauc-like approach to calculate the optical gap [21] once the optical absorption curves are obtained; there is practically no gap: 0.004 eV.

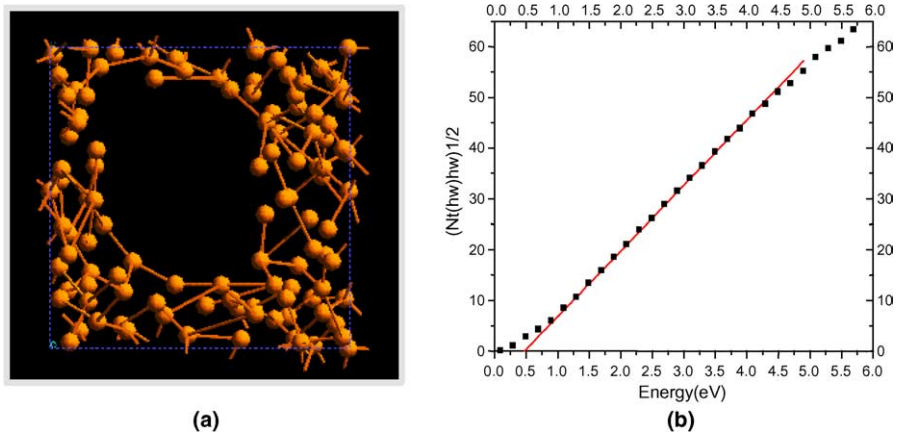

Fig. 2. Relaxed crystalline supercell with 50% porosity. (a) The inner silicon atoms adjust themselves to minimize the number of dangling bonds. (b) The Tauc-like approach gives a gap of 0.474 eV.

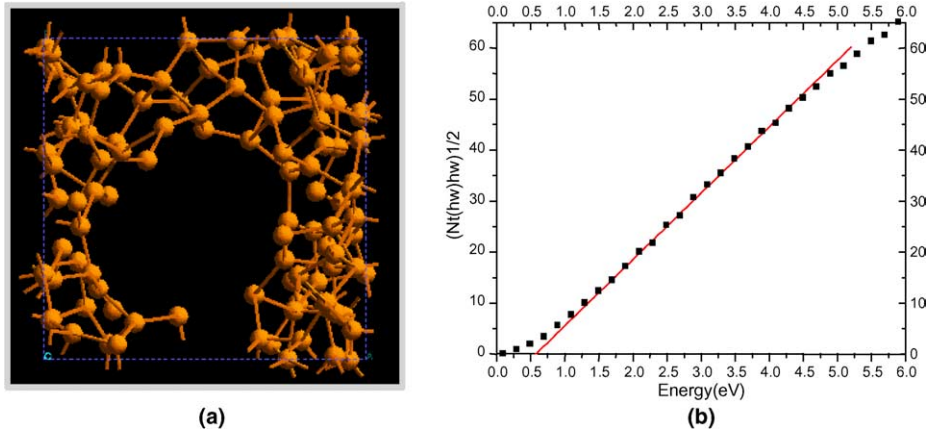

Fig. 3. Amorphous supercell with 50% porosity. (a) The atomic structure has an RDF similar to a-Si [22]. (b) The Tauc-like approach gives a gap of 0.575 eV.

within the gap, and an optical gap practically identical to that obtained for the amorphous supercell.

The table shows the manner in which the optical gap changes for the four samples. The radial distribution

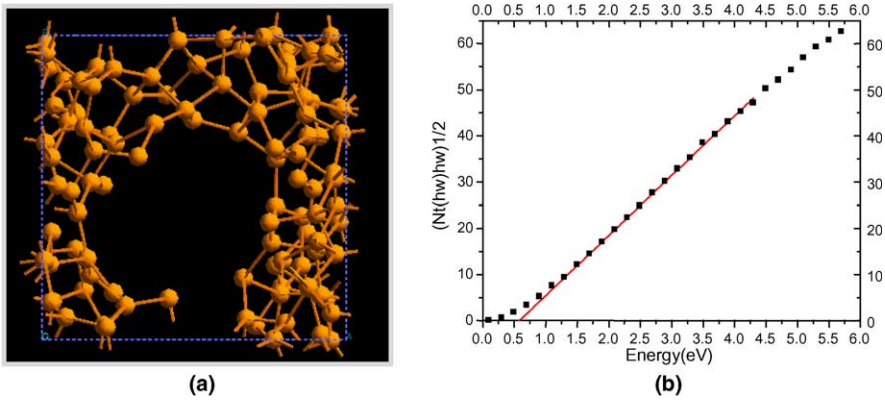

Fig. 4. Relaxed amorphous supercell with 50% porosity. (a) The rearrangement of the inner silicon atoms is minimal. (b) The Tauc-like approach gives a gap of 0.580 eV.

functions, reported elsewhere [22], indicate that the crystalline supercell is the most stressed since the distance between silicons is 2.35 Å, and as soon as it is relaxed it takes the value of 2.55 Å.

Sample	Optical gap (eV)	RDF first peak (Å)
Porous crystalline	0.004	2.35
Porous crystalline relaxed	0.474	2.55
Amorphous porous	0.575	2.55
Amorphous porous relaxed	0.580	2.55

4. Conclusions

Samples of ap-Si have been created using the thermal processes developed previously to generate random semiconducting structures of group IV elements and their alloys. The random porosity considered in this case is 50% and starting with the crystalline carved supercell the gap increases as we first relax it, then amorphize it and finally relax the amorphous sample, Figs. 1(b)–4(b). The atomic structure undergoes severe changes as this evolution occurs, as can be seen in Figs. 1(a)–4(a), and in going from sample 1(a) to sample 2(a) one can see the rearrangement of the pore surface silicons, optimizing the geometry of the cell. The position of the first peak of the corresponding RDFs changes swiftly from the corresponding crystalline value, 2.35–2.55 Å for all the relaxed and amorphous structures. This expansion was observed experimentally several years ago [23] and shows that our procedure is on the correct track to simulate ap-Si. Work is under way to study samples with varying porosities and the nature and dependence of the photoluminescence spectrum.

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References

[1] See for instance the review paper by A.G. Cullis, L.T. Canham, P.D.J. Calcott, J. Appl. Phys. 82 (1997) 909.
[2] R.B. Wehrspohn, J.-N. Chazalviel, F. Ozanam, I. Solomon, Eur. Phys. J. B 8 (1999) 179.
[3] R.B Wehrspohn, J.-N. Chazalviel, F. Ozanam, I. Solomon, Thin Solid Films 297 (1997) 5.
[4] A.A. Valladares, F. Alvarez, Z. Liu, J. Sticht, J. Harris, Eur. Phys. J. B 22 (2001) 443;
F. Alvarez, C.C. Díaz, A.A. Valladares, R.M. Valladares, Phys. Rev. B 65 (2002) 113108;
F. Alvarez, A.A. Valladares, J. Non-Cryst. Solids 299–302 (2002) 259.
[5] G. Szekely, J. Electrochem. Soc. 98 (1951) 318.
[6] H. Richter, G. Breitling, Z. Naturforsch. 13a (1958) 988, and work cited therein.
[7] R. Grigorovici, R. Manaila, Thin Solid Films 1 (1968) 343.
[8] M.V. Coleman, D.J.D. Thomas, Phys. Stat. Solidi 25 (1968) 241.
[9] A.A. Valladares, A. Valladares, R.M. Valladares, M.A. McNelis, J. Non-Cryst. Solids 231 (1998) 209;
R.M. Valladares, C.C. Díaz, M. Arroyo, M.A. McNelis, A.A. Valladares, Phys. Rev. B 62 (2000) 2220.
[10] R. Car, M. Parrinello, Phys. Rev. Lett. 60 (1988) 204.
[11] I. Stich, R. Car, M. Parrinello, Phys. Rev. B 44 (1991) 11092.
[12] I. Lee, K.J. Chang, Phys. Rev. B 50 (1994) 18083.
[13] D.A. Drabold, P.A. Fedders, O.F. Sankey, J.D. Dow, Phys. Rev. B 42 (1990) 5135.
[14] P.A. Fedders, D.A. Drabold, S. Klemm, Phys. Rev. 45 (1992) 4048.
[15] FASTSTRUCTURE_SIMANN, User Guide, Release 4.0.0, San Diego, Molecular Simulations, Inc., September 1996.
[16] J. Harris, Phys. Rev. B 31 (1985) 1770.
[17] X.-P. Li, J. Andzelm, J. Harris, A.M. Chaka, in: Ziegler (Ed.), American Chemical Society, Anaheim Symposium, 1996 (Chapter 26).
[18] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.

[19] Z. Lin, J. Harris, J. Phys.: Condens. Matter 5 (1992) 1055.
[20] B. Delley, J. Chem. Phys. 92 (1990) 508.
[21] F. Alvarez, A.A. Valladares, Appl. Phys. Lett. 80 (2002) 58.
[22] E.R.L. Loustau, R.M. Valladares, A.A. Valladares, in press.
[23] K. Barla, R. Herino, G. Bomchil, J.C. Pfister, A. Freund, J. Cryst. Growth 68 (1984) 727;
I.M. Young, M.I.J. Beale, J.D. Benjamin, Appl. Phys. Lett. 46 (1985) 1133.