Optical gaps of *ab initio* generated random networks for *a*-SiN$_x$ alloys

Fernando Alvarez and Ariel A. Valladares[a)]

Instituto de Investigaciones en Materiales, UNAM, Apartado Postal 70-360, México D.F. 04510, Mexico

We report optical gaps for *ab initio* generated random networks of silicon–nitrogen alloys, *a*-SiN$_x$, for thirteen values of x from 0 to $x = 1.29$, a nearly stoichiometric composition. The random networks were constructed by amorphizing 64-atom periodically-continued diamond-like cells containing silicon and nitrogen, with a new thermal process and a Harris-functional based molecular dynamics code in the local density approximation. The electron energy levels were then calculated and the optical gaps obtained using a Tauc-like procedure that is not sensitive to gap states and band tails. Our results agree with experiment. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1430271]

The properties of *a*-SiN$_x$ alloys have attracted a great deal of attention since they have electrical, optical, and mechanical features useful in a variety of industrial applications and their strong covalent bonding also makes them appealing for basic science. Experimentally[1] it has been found that their optical gaps depend strongly on the nitrogen content x for $0 \leq x \leq 1.33$ so they can be tuned to fit specific needs in solar cells. Their total and partial radial distribution functions (RDFs) are scarce and theoretically no *ab initio* work had been performed until recently[2] where RDFs have been generated for 12 amorphous samples. Although some theoretical work has been done on their electronic structure, optical gaps, and RDFs, no first principles electronic and optical studies have been reported on amorphous cells with gap states. Therefore, any *ab initio* approach that adequately generates, describes and predicts atomic, electronic, and optical features of *a*-SiN$_x$ is relevant due to its wider applicability to other covalent amorphous materials.

Precise *ab initio* calculation of optical gaps in crystalline semiconductors is a difficult problem. The density functional theory always underestimates them since it is a ground state theory and the transition of electrons to the conduction band cannot be adequately described. Nevertheless recent attempts[3] are promising. However, tackling random networks with these techniques is not yet possible since the large number of atoms and the lack of special symmetries in the amorphous cells makes them practically untractable. Moreover, in crystalline solids HOMOs (highest occupied molecular orbitals) and LUMOs (lowest unoccupied molecular orbitals) are identifiable and a "gap," equal to the difference LUMO-HOMO, may be defined. In amorphous materials HOMOs and LUMOs are usually associated to states *within* the gap and consequently their difference bears little resemblance to any meaningful value of a gap. Therefore it is important to generate, from first principles, realistic amorphous structures and to devise alternative methods to determine their optical gaps.

The experimental and theoretical activity prior to 1990 is well documented in an article by Robertson where pertinent references can be found.[4] Experimentally, there were electronic structure studies of *a*-SiN$_x$ in the range $0 \leq x < 2$ performed by Kärcher *et al.*[5] using x-ray photoelectron spectroscopy where the valence band was thoroughly analyzed and the Si–N bonding studied. Also, some of the work on RDFs and optical gaps is reported in Ref. 1. It is now clear that the optical gap of *a*-SiN$_x$ increases, slowly at first, as x increases and close to the stoichiometric compound, $x = 4/3 = 1.33$, the gap acquires its largest values.[1] Some theoretical efforts are based on the semiempirical tight binding approach[4] where optical gaps are calculated. Xanthakis *et al.*[6] do not consider gap states and they use a parameterized Kittler–Falicov method that draws upon parameters obtained by Robertson before 1990. Bethe lattice calculations have been done by Martín-Moreno *et al.*[7] and by San-Fabián *et al.*[8] also using semiempirical parameters. Ordejón and Ynduráin[9] do nonparameterized calculations of *a*-SiN$_x$ where the equilibrium positions of Si and N atoms in clusters are ported to the alloy network constructed *ad hoc* and obtain a wealth of information, including optical gaps; however, tetrahedral coordination of silicon and threefold planar coordination of nitrogen is assumed throughout. A general characteristic of all calculations/simulations done is that gap states, when considered, are introduced either by hand, progressively replacing Si by N, or by the algorithms that generate the random networks.

Recently a new approach to the *ab initio* generation of atomic random networks has been devised and the radial features obtained closely resemble the experimentally determined partial and total RDFs.[2,10] Since it is clear from previous work that quenching from a melt generates undesirable structures[11] a different path was taken. Crystalline diamond structures with 64 atoms each [$(64-y)$ silicons, y substitutional nitrogens, and $x = y/(64-y)$] were amorphized by linearly heating them from room temperature to just below the corresponding melting point for each x, and then cooling them to 0 K.[2,10] This was done using a Harris-functional based, molecular dynamics code, *FastStructure_SimAnn*,[12] within the local density approximation.[13]

To determine the temperature for each sample we linearly interpolated between the values for pure silicon and for the stoichiometric concentration. Since the time step was

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[a)]Electronic mail: valladar@servidor.unam.mx

TABLE I. Contents, melting temperatures, densities, and gaps for a-SiN$_x$.

| Sample	x	Melting temp. (K)	Density (g/cm^3)	Average gap (eV)
Si$_{64}$N$_0$	0.000	1680	2.329	1.09
Si$_{59}$N$_5$	0.085	1747	2.435	1.11
Si$_{54}$N$_{10}$	0.185	1814	2.512	1.05
Si$_{49}$N$_{15}$	0.306	1881	2.600	1.19
Si$_{44}$N$_{20}$	0.455	1948	2.694	1.69
Si$_{39}$N$_{25}$	0.641	2015	2.803	2.49
Si$_{34}$N$_{30}$	0.882	2082	2.931	3.41
Si$_{33}$N$_{31}$	0.939	2095	2.957	3.73
Si$_{32}$N$_{32}$	1.000	2108	2.988	4.10
Si$_{31}$N$_{33}$	1.065	2122	3.017	4.31
Si$_{30}$N$_{34}$	1.133	2136	3.048	4.28
Si$_{29}$N$_{35}$	1.207	2149	3.081	4.69
Si$_{28}$N$_{36}$	1.286	2162	3.115	4.95

FIG. 1. Optical absorption curves for a set of *minimal* (min), *standard* (std), and *enhanced* (enh) orbitals in pure silicon and a-SiN$_{1.29}$; r_c is the cutoff radius used for the wave functions.

kept constant for all runs, 6 fs, and the temperatures increased with x (Table I) the heating/cooling rate varied from 2.30×10^{15} K/s for pure silicon, to 3.11×10^{15} K/s for $x = 1.29$. The atoms were allowed to move within each cell with volume determined by the corresponding density and content (Table I). The densities were taken from the experimental results of Guraya *et al.*[1] We then subjected each cell to annealing cycles with intermediate quenching processes and, at the end, they were energy optimized to assure that the final structures had a local energy minimum. An all electron calculation was carried out, and a *minimal* basis set of atomic orbitals, with cutoff radii of 5 Å for the amorphization, 3 Å for the optimization and for the electron energy level calculations was used.

Two randomizing runs for each x value were performed and from $x = 0.882$ on (a-Si$_{34}$N$_{30}$) the number of substitutional nitrogens was increased one at a time to be able to map the widening of the gap for these concentrations. Once the 26 atomic structures were created the corresponding optical gaps were determined by a method close to the Tauc approach[14] and averaged by corresponding pairs. To calculate the optical gaps we first obtained the electronic structure of the amorphous cells at the Γ point of the Brillouin zone, a common procedure in the field, in order to find the energy levels in the valence and conduction bands and proceeded to obtain α, the optical absorption coefficient.

One characteristic feature of optical absorption in amorphous semiconductors is that certain selection rules, which apply to optically induced transitions in crystalline materials, are relaxed. For interband absorption the following assumptions are commonly made:[15]

(a) The matrix elements for the electronic transitions are constant over the range of photon energies of interest and are given by $D = \pi(a/\Omega)^{1/2}$, where a is the average lattice spacing and Ω is the volume of the specimen.[15]

(b) The k-conservation selection rule is relaxed. Under these conditions, the optical absorption coefficient α for interband transitions is given by

$$\alpha = \frac{8\pi^4 e^2 \hbar^2 a}{n_0 cm^2 \omega} \int N_V(E) N_C(E + \hbar\omega) dE,$$

where the integration is over all pairs of states in the valence and conduction bands separated by an energy $\hbar\omega$;[15] n_0 is the refractive index.
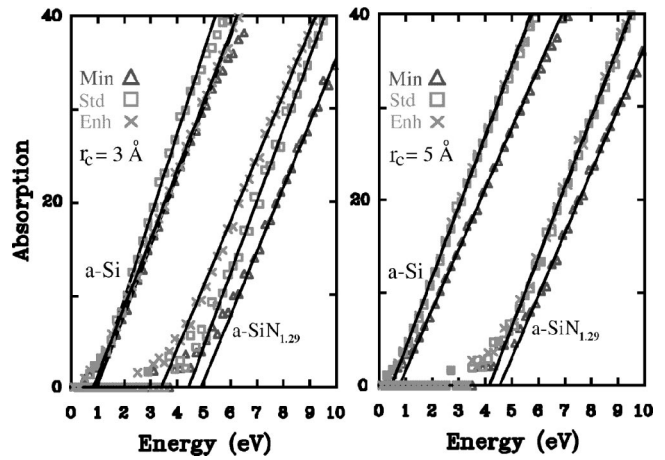
For amorphous tetravalent semiconductors this leads to the well known relationship $\sqrt{\alpha(\omega)\hbar\omega} = \text{const} \ (\hbar\omega - E_0)$ obtained by Tauc[14] under the assumption of parabolic bands, formula that has been used extensively by experimentalists to obtain the optical gap E_0 by plotting $\sqrt{\alpha(\omega)\hbar\omega}$ vs $(\hbar\omega - E_0)$. Since α is proportional to the fraction of energy lost by the wave on passing through the material this implies that it is proportional to the number of electronic transitions from the valence to the conduction band, $N_t(\hbar\omega)$. So plotting $\sqrt{N_t(\hbar\omega)\hbar\omega}$ instead of $\sqrt{\alpha(\omega)\hbar\omega}$ should give the same type of behavior as experimentally observed although with a different slope; however, the intersection with the horizontal $\hbar\omega$ axis, the optical gap E_0, remains unaltered. This is precisely what we do: we look at the intersection of the linear fit to the $\sqrt{N_t(\hbar\omega)\hbar\omega}$ data to find the optical gap.

Both the cutoff radius[16] and the completeness of the orbital set[17] play a role in simulations. To test this we calculated the energy levels using the three orbital sets of *FastStructre_SimAnn: minimal* (*sp*-valence), *standard* (double-numeric basis set), and *enhanced* (double-numeric-with-polarization basis set), for two cutoff radii: 3 and 5 Å. The results are shown in Fig. 1 for pure silicon and for the highest content sample $x = 1.29$. The combination that best describes the experimental results is the *minimal* set with 3 Å; compare to values of ≈ 2.6 Å used by Sankey *et al.*[16]
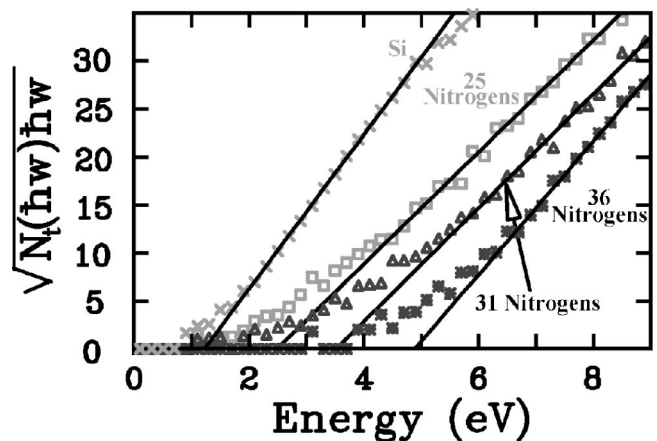

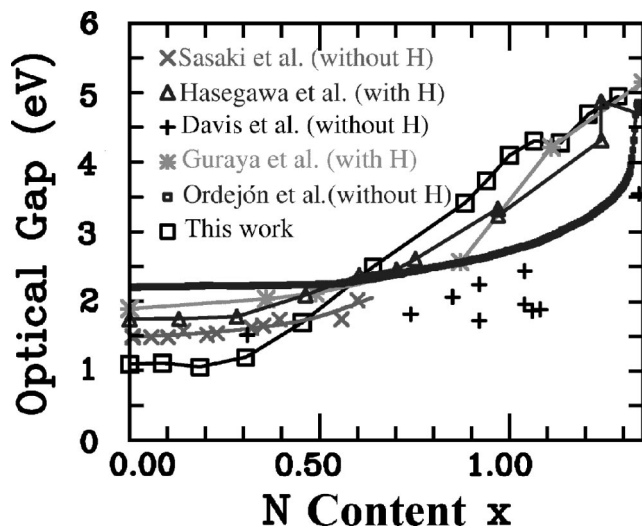FIG. 2. Some typical theoretical Tauc-like curves. The number of nitrogens is indicated.

FIG. 3. Comparison of our results with experimental and theoretical (Ordejón *et al.*) optical gaps for a-SiN_x, with and without hydrogen. Lines are drawn as guides to the eye.

Figure 2 shows some representative curves of this type from which our gap values, Fig. 3, were obtained. Figure 2 shows that the gap states and band tails do not mask the calculated gaps. The behavior of the Tauc *slope* as a function of x, found experimentally by Hasegawa *et al.*,[1] is also reproduced here since the slope diminishes first and increases afterwards. Figure 3 contains experimental results both for hydrogenated and nonhydrogenated samples[1] and the theoretical results of Ref. 9. The behavior of our optical gaps clearly changes for $x \approx 1.1$, the percolation threshold of Si–Si bonds.[18]

In conclusion, we have devised an approach based on *ab initio* methods to calculate realistic optical gaps of amorphous materials. The optical gaps are obtained by a Tauc-like procedure applied to all electronic transitions between the valence and conduction band states. For a-SiN_x, with $0 \leq x \leq 1.29$, this technique leads to gap values in agreement with experiment.

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