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Author
Joannopoulos, J.D.

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ELECTRONIC STRUCTURE OF CRYSTALLINE POLYTYPES AND AMORPHOUS Si

J. D. Joannopoulos and Marvin L. Cohen

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Electronic Structure of Crystalline Polytypes and Amorphous Si[*]

J. D. Joannopoulos and Marvin L. Cohen

Department of Physics, University of California

and

Inorganic Materials Research Division, Lawrence Berkeley Laboratory

Berkeley, California 94720

ABSTRACT

We have calculated the density of states and the imaginary part of the energy dependent dielectric constant for four polytypes of Si using pseudopotential and tight binding models. Comparisons are made with the experimental results for amorphous Si.

We have calculated the optical properties and density of states of certain polytypes of Ge[1] and Si using the Empirical Pseudopotential Method[2] and the recent tight binding model developed by Weaire and Thorpe[3]. The structures we chose were Ge and Si in the diamond, "wurtzite", Si III[4] and Ge III[4] structures. Where diamond is face-centered cubic with 2 atoms per primitive cell (FC-2), wurtzite is hexagonal 2H with 4 atoms (2H-4), Si III is body-centered cubic with 8 atoms (PC-8) and Ge III is simple tetragonal with 12 atoms per primitive cell (ST-12). The Si III and Ge III structures are complicated, dense, metastable crystalline phases which are recovered from

high pressure experiments and persist at normal pressures. When Ge occurs in the Si III structure it is called Ge IV.[5] Because of this rather unfortunate terminology we shall use the notation described above in parentheses for these various structures. In this paper we shall describe very briefly a few of our results on the Si polytypes with a more detailed presentation to be published elsewhere.[6]

SiFC-2, Si2H-4[7], SiBC-8 and SiST-12 provide us with a series of structures that become more and more locally disordered. What we imply by local or short-range disorder is that we have a crystal (long range order) and yet the atoms in the primitive cell of our crystal are in a "disordered" tetrahedral arrangement. The FC-2, 2H-4 and BC-8 structures are all similar in that they have sixfold rings of bonds and one type of atomic environment. The ST-12 structure, however, is very novel in that it has five-fold rings of bonds and two types of atomic environments. The physical properties of this structure would then provide us with a good test for considering a random network model as a model for the amorphous state.

The trend in the density of states as one goes from SiFC-2 to Si2H-4 to SiBC-8 is to acquire a large amount of structure. Although this produces a smoothing out effect for the conduction band the two broad low energy humps still retain their identity. This is in marked contrast to the SiST-12 case where one finds a complete mixing of these two peaks (Fig. 1) which also seems to be the case for the amorphous phase.[8] Furthermore Si2H-4 and SiBC-8 exhibit a gradual sloping of the valence band edge which is in direct contrast to SiST-12 and amorphous Si where one finds a very

sharp valence band edge (Fig. 1). A very interesting feature of the SiST-12 structure is that the gap is approximately 1.6 eV or twice as large as the SiFC-2 gap. This is probably due to the presence of   a large number of five-fold rings which would omit antibonding s-like states from the top of the conduction band. This was suggested by Weaire[3] but the extent to which it might happen was shown when we calculated the density of states for an ideal ST-12 structure using the Weaire model.[3] We found approximately a 200% increase in the gap obtained from a calculation on FC-2 using the Weaire model and an ad hoc 2.0 eV broadening of the delta function peak at the top of the valence band. If we include the variation of bond lengths and angles for the real ST-12 structure, as in the EPM case, we would get variations in the hamiltonian matrix elements and the gap would get smaller.

These results however are not inconsistent with the fact that the amorphous phase has a gap comparable to the FC-2 phase. Since the bulk density of amorphous Si[8] is similar to that of SiFC-2 we must require a fewer number of five-fold rings per atom than SiST-12 and one would expect a smaller increase in the gap. However, it is conceivable that variations in bond length and angle could reduce the gap back to its original size. Thus the presence of five-fold rings does not necessarily imply an increase in the gap.

The optical properties of SiFC-2, Si2H-4 and SiBC-8[6] are all similar in that the ϵ_2 spectrum consists of two or three strong peaks in the vicinity of 4.0 eV. In contrast the ϵ_2 spectrum for SiST-12 consists of a large hump centered around 3.5 eV (Fig. 1). This type of spectrum is very

novel for a crystal. The overall qualitative agreement between the ϵ_2 for SiST-12 and amorphous Si is quite encouraging and shows that long range disorder and k non-conservation is not a requisite for the quantitative and qualitative features of the amorphous ϵ_2.[9] We also find that the hump for SiST-12 can be associated with transitions along the Σ and Δ directions as in SiFC-2 which is in contrast to an enhancement of the Λ peak as suggested by Stuke.[10]

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Figure Caption

Fig. 1. Top: the density of states for SiST-12 obtained from our pseudo-potential calculation and the amorphous density of states obtained by Pierce et al. (Ref. 8) with units in states per eV-atom. The amorphous curve was normalized with respect to Herman's calculation of the density of states for SiFC-2 (Ref. 11).

Bottom: the imaginary part of the dielectric function ϵ_2 obtained by averaging over parallel and perpendicular components for SiST-12 from an EPM calculation (solid line) and the ϵ_2 obtained by Pierce et al. (Ref. 8) for amorphous Si (dashed line).
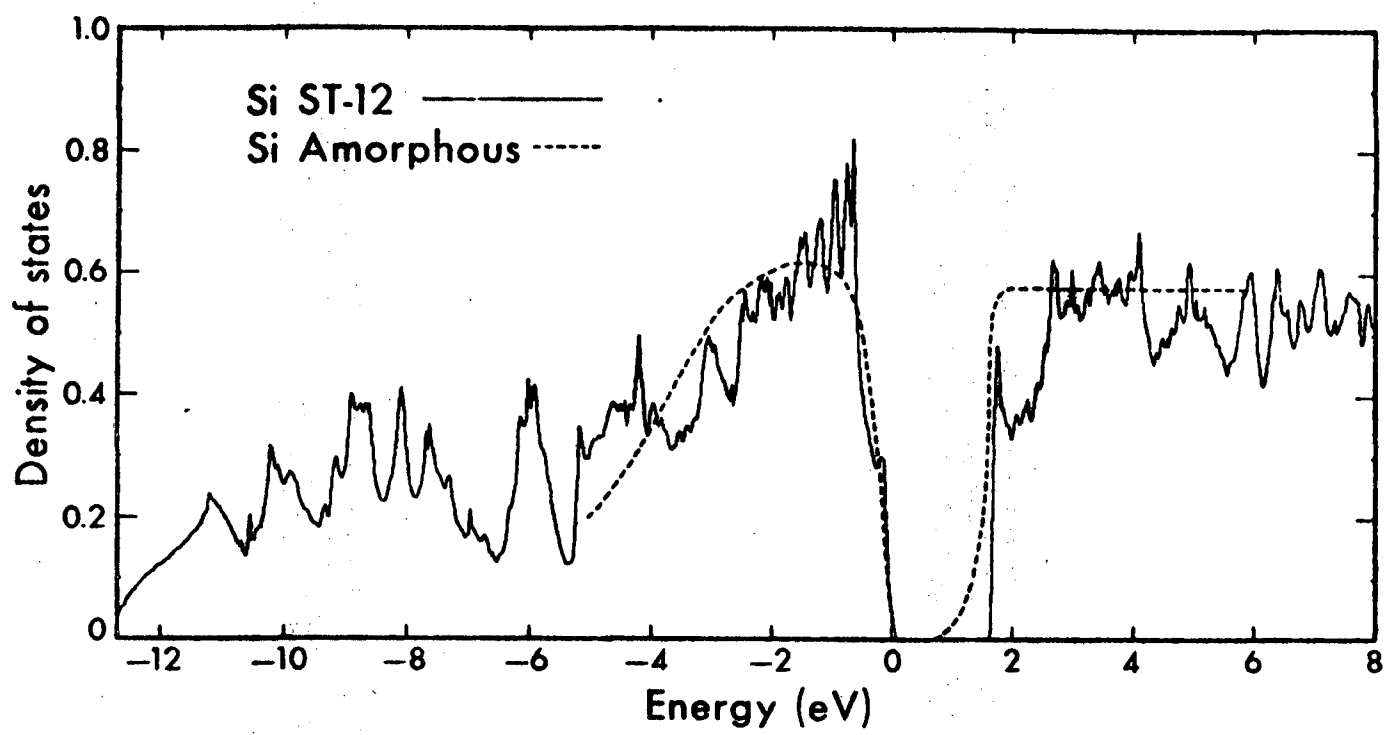
Fig. 1