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Electronic Density of States of Amorphous III-V Semiconductors

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Abstract

A short-range disorder model is used to predict the prominent features of the density of states of amorphous III-V semiconductors. Confirmation of this model would establish the existence of III-III and V-V bonds in these materials.

Up to now there has been a considerable amount of experimental[1-5] and theoretical[6-14] research on the optical properties and density of states spectra of amorphous group IV elements (i.e. Ge and Si). A natural extension of this work would be similar studies of III-V compounds such as GaAs. The optical spectra of the amorphous III-V's[15] are similar to those of amorphous group IV elements as one might expect and can be understood[14] in the same way as the optical properties of amorphous Ge and Si. However, the density of states of amorphous III-V compounds is as yet unknown. Ultraviolet and x-ray photoemission spectra could be used to obtain the density of states spectra for these semiconductors and our calculations indicate that a great deal of information about the chemical bonding and electronic structure

of these materials could be obtained from studies of this type. For example, it may be possible to establish the existence of Ga-Ga and As-As bonds in amorphous GaAs using photoemission spectra.

In this work we use a short-range disorder (SRD) model to predict the density of states of amorphous III-V compounds. The SRD approach has been used successfully[11-14] to interpret the structure in both the density of states and reflectivity in amorphous Ge and Si (using calculated spectra for complex crystalline polytypes of these materials). The only theoretical predictions for amorphous III-V's until now have been due to Kramer et al.[16] who use a long-range disorder model in the sense of a complex band structure (CBS) calculation. The CBS method, however, leaves the filled valence band density of states almost completely unaltered in the amorphous case. This is invalid in the case of amorphous Ge and Si and we believe it is also invalid in the case of amorphous III-V compounds.

Using GaAs as a prototype of the III-V's we will analyze the charge distribution for the electronic states associated with specific bands or parts of bands which are responsible for the prominent features of the density of states spectra. We can then use the SRD model to predict the changes in the density of states arising from changes in the charge distribution or bonding configurations.

In Fig. 1 the theoretical density of states for crystalline GaAs is given. This spectrum was calculated using the empirical pseudopotential method[17] (EPM) and we show only the filled valence band. The crystalline structure of GaAs dictates that every Ga atom be surrounded by four As

atoms and vice versa. Thus there is only one type of bond in the crystalline case, i.e. a GaAs bond which we shall call an unlike bond.

Now some information about the average distribution of the electrons in each band can be obtained from charge density calculations[18] and this is shown schematically at the bottom of Fig. 1. In the lowest energy band the electrons see the stronger As potential and are concentrated around the As atoms. They are essentially the As s-like states and are detached in energy from the rest of the valence band. The electrons in the next band at higher energies are now more concentrated around the Ga atoms and in the bond. Finally the electrons in the two bands at the top of the valence band are essentially concentrated in the bond with a slight shift toward the As ions.

From the structural point of view, an important and distinct feature of the amorphous III-V structure is the possibility of having like nearest neighbors, or like bonds, in addition to the normal unlike bonds. This would be a necessary consequence if the amorphous GaAs structure could have any odd-numbered rings of bonds. The presence of odd-numbered rings of bonds has been shown[10,13] to be an essential property of the amorphous Ge and Si structure in explaining the shape of the amorphous density of states near the bottom of the valence band.

Added prominence to the feasibility of having like bonds in an amorphous III-V structure has been given by Shevchik and Paul[19] who calculated radial distribution functions (RDF's) for amorphous Ge and some amorphous III-IV compounds. Their results indicate that the RDF's of the amorphous III-V compounds are very similar to the RDF of

amorphous Ge and in particular the RDF of amorphous GaAs is almost identical to that of amorphous Ge. Although an RDF is not a sufficient condition for a particular structure it is at least a necessary condition and this is very suggestive of the structure. Furthermore, Shevchik and Paul found that the contribution of about 10% of like bonds (being a reasonable estimate using the Polk[20] model which also gives the same RDF as amorphous Ge) to the heat of crystallization of amorphous Ge, using Pauling's[21] energy bond model, was very small and thus not sufficient to prohibit their formation.

We also believe that a large number (~ 10%) of like bonds in the amorphous III-V structures is plausible and this must also have direct consequences on the amorphous density of states. Using the fact that we can have a significant number of like bonds in addition to unlike bonds in the amorphous structure and using calculations for the distributions of electrons in the bands we are led to predict an amorphous GaAs density of states that would have the shape shown in Fig. 2a. Superimposed on our suggested amorphous GaAs curve is a plot of the density of states of crystalline GaAs as obtained from an EPM calculation. We notice that every peak should be broadened and this is quite different from the amorphous density of states of Ge (shown in Fig. 2b). The experimentally measured amorphous density of states for Ge obtained by Ley et al.[5], using x-ray photoemission spectroscopy, shows essentially no broadening at all but rather a filling up of the valley between the first two bands (caused by odd-numbered rings of bonds[10,13]) and a steepening of the band edge (caused by deviations in

the bond angles[13]).

In contrast to Ge, the broadening in the density of states of amorphous GaAs is produced by the increase in the overlap integrals between like neighbor atoms and the different types of bonding states that one can now have. Let us examine the amorphous GaAs density of states more carefully.

Concentrating first on the lower energy band, we can estimate the broadening of this band using a simple model. Since the states in this band are localized s-like states centered at As atoms only, we assume that the width of the s-like band is determined in all cases by an overlap integral I between nearest neighbor As atoms. The assumption that only nearest neighbors are important is not too bad for our purposes since from the RDF's[19] we know that the number of second nearest neighbors in amorphous GaAs is essentially the same as that of crystalline GaAs. The width would then be given by the following approximate formula:

$$W = 2Ic \qquad (1)$$

where c is the coordination number of nearest <u>like</u> neighbors. We now take I to be of the form:

$$I = I_0 e^{-KR} \qquad (2)$$

where I_0 and K are parameters and R is the nearest neighbor distance between like atoms. The parameters I_0 and K can now be obtained by fitting W to the theoretical[22] s-band width of the As-metal structure and to the theoretical s-band width of GaAs once the Ga atoms have been removed. With these

estimates for I_0 and K, we now use (1) with $c = 1$ and (2) with R equal to twice the covalent radius[21] of an As atom to estimate the increase in width that will be observed in amorphous GaAs. This gives

$$\Delta W \sim 1\text{eV}$$

so that the lower band in amorphous GaAs should be at least 1 eV wider at half maximum than the width for crystalline GaAs.

We expect that the next peak at higher energy in the amorphous GaAs density of states should be less broadened than the lower peak. Since part of the electrons in this band are spread out in the bond with some charge density localized on the Ga atoms, the difference in overlap between Ga-Ga atoms and As-As atoms in this band with those of Ga-As in this band will be small. Furthermore, this difference in the overlap integral will be smaller than the difference in overlap between As s-like states in zincblende and in like bond configurations.

Finally, we only expect a simple broadening of the bonding states at the top of the valence band. Actually this broadening should be larger than in the middle peak since we have a higher density of electrons which are more localized in the bonds. In fact it may be possible to discern one peak and two shoulders here arising from the three types of bonding states that are possible, with As-As bonding states at lower energy and Ga-Ga bonding states at higher energy than the Ga-As bonding states.

We hope this work will entice experimental investigations. Confirmation of our model will be definite evidence of the presence of a

significant number of like bonds in the amorphous structure. A detailed study of the amorphous density of states may even yield an estimate of the number of like bonds present and the particular clustering configurations that they favor.

Preliminary results on amorphous InP by Ley[23] seem to confirm some of these expectations but a more careful study of sample preparation is under way.

In order to explore these ideas further, we are now studying the density of states of amorphous III-V's using complex crystalline models similar to those used in our calculations on amorphous Ge and Si. We hope to determine the influences of different types of structures on the properties of the density of states.

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Figure Captions

Figure 1 A plot of the density of states (top) for GaAs using an EPM calculation and the typical average distribution of electrons (bottom) corresponding to the three ranges in energy shown.

Figure 2 (a) A sketch of the density of states for amorphous GaAs (solid line) predicted in this paper and a plot of the density of states for GaAs (dashed line) in the zincblende structure. (b) A sketch of the density of states for amorphous Ge (solid line) obtained by experiment (ref. 5) and a plot of the density of states for Ge in the diamond structure.

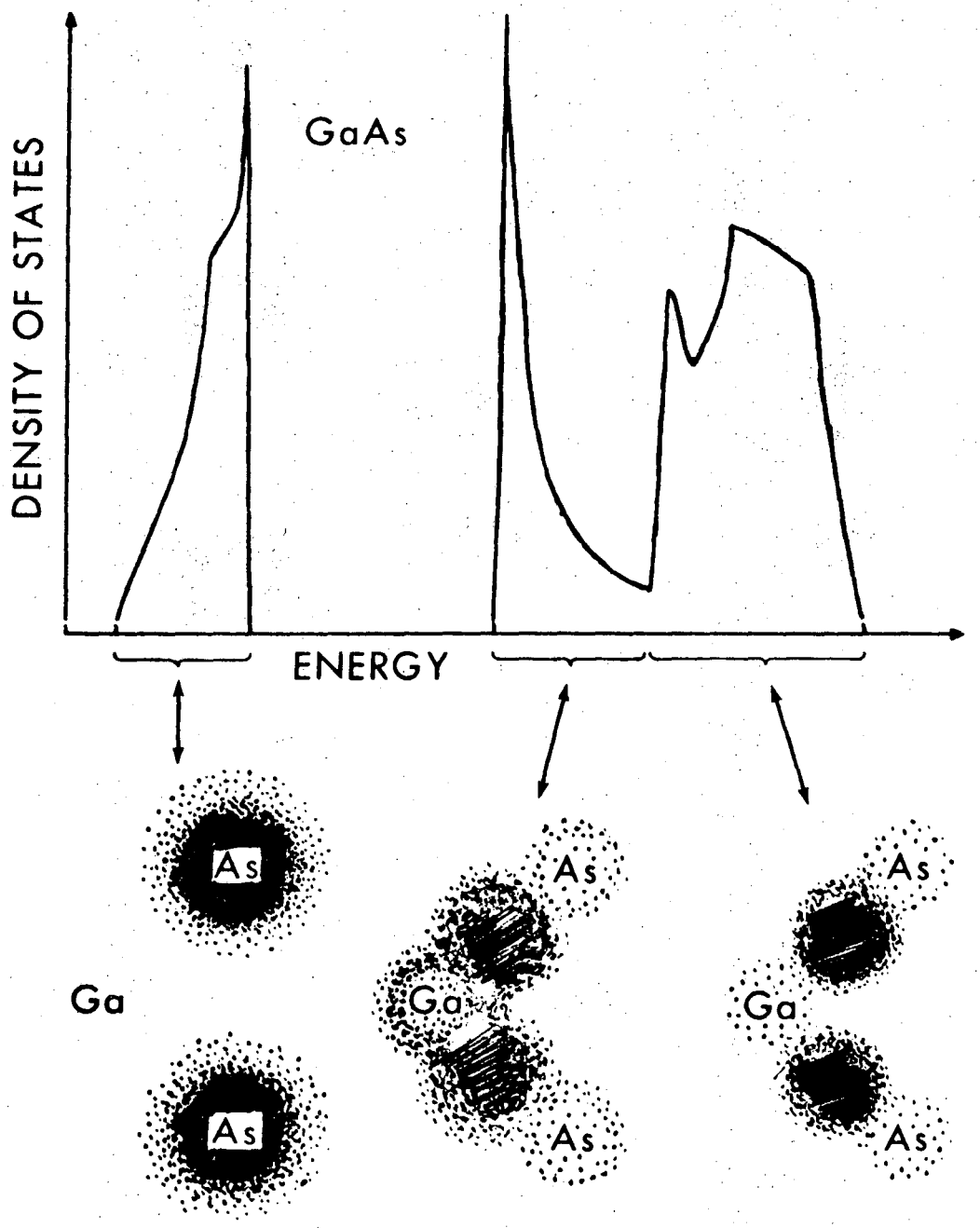

Fig. 1

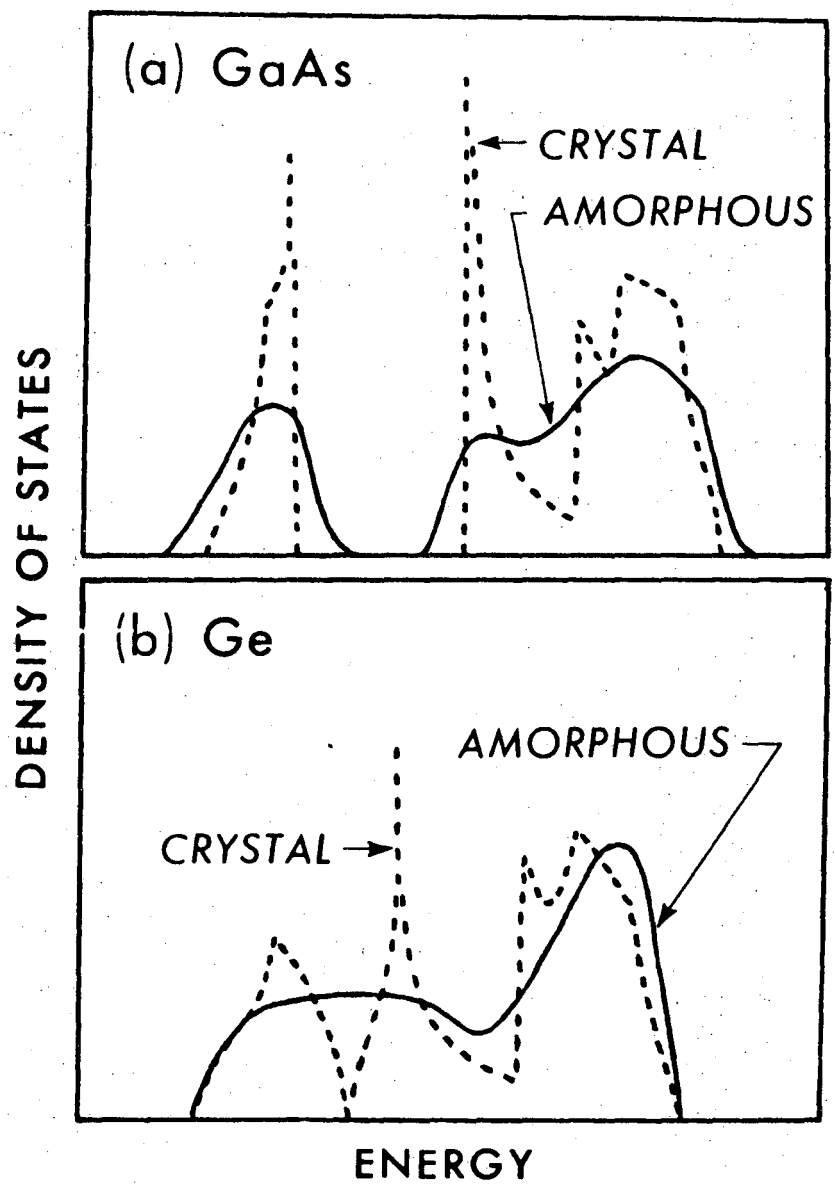
(a) GaAs
CRYSTAL
AMORPHOUS
(b) Ge
AMORPHOUS
CRYSTAL
DENSITY OF STATES
ENERGY

Fig. 2

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