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Optical dielectric function of intrinsic amorphous silicon

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The imaginary part of the optical dielectric function $\epsilon_2(\omega)$ has been calculated using a continuous-random-tetrahedral network as the structural model for the atomic positions. Here the electronic energies and wave functions are determined by first-principles calculations with the method of linear combinations of atomic orbitals (LCAO), and the momentum matrix elements are evaluated directly from the LCAO wave functions. The calculated dielectric function is in good overall agreement with experiment. At energies within 1 eV above the threshold, the ϵ_2 curve shows some structures that are due to interband transitions between the localized states near the band gap.

I. INTRODUCTION

Much progress has been made in the past few years toward a quantitative understanding of the electronic structure of intrinsic amorphous silicon (a-Si).[1-3] The use of the continuous-random-tetrahedral networks (CRTN) as structural models for the atomic positions has been successful in accounting for the observed radial distribution function (RDF).[4-8] Of special interest are the CRTN that are constructed to have a periodic boundary condition.[6-8] For these networks the electronic energies can be calculated by essentially the same general methods as those developed for crystalline solids. The main difference is that the periodic CRTN have much more atoms in a unit cell than do ordinary crystals, hence the computational work becomes more difficult. Nevertheless, first-principles calculations of the electronic structure of a-Si based on the structural model of Henderson[7] with 61 atoms per unit cell (H-61) and the model of Guttman[8] with 54 atoms per unit cell (G-54) have been performed by means of the method of linear combinations of atomic orbitals (LCAO). The G-54 network gives a valence band (VB) structure which is in good agreement with experiment, and a band gap of 0.67 eV.[2] This value, although somewhat smaller than the experimental value of 1.1–1.8 eV,[9] should be regarded as satisfactory, considering the fact that the reported experimental values themselves vary appreciably and that the atomic positions of a-Si are modeled by a periodic CRTN with only 54 atoms in a unit cell. On the other hand, no band gap is found for the H-61 network,[1] presumably because the distortion from perfect tetrahedral coordination (deviation of the atomic positions from those in a Si crystal) is too high.

The calculated RDF for the static G-54 network is shown in Fig. 1(a). In order to make comparison with the experimental data of Moss and Graczyk[10] which are not corrected for broadening effects, we apply a Gaussian broadening ($\sigma = 0.083$ Å) to Fig. 1(a) and the result is displayed in Fig. 1(b) along with the experimental data. The agreement is seen to be good. While the G-54 CRTN undoubtedly is an oversimplified representation of the a-Si structure, it does provide quite satisfactory RDF as well as electronic energy spectrum. Furthermore it is sufficiently simple so that one can obtain the electronic wave functions from a first-principles calculation. This then leads to the possibility of using these wave functions to theoretically determine certain properties of a-Si related to the electronic states. Comparison with experiment gives an assessment of the ultimate predictive capability of this kind of theoretical approach.

In this paper we present a calculation of the dielectric function (imaginary part) based on the G-54 structural model, and compare the results with experimental measurements. In the theoretical dielectric functions are found special features which are traced to the localized behaviors of some electronic states.

II. DIELECTRIC FUNCTION

Calculation of the electronic wave functions has been described in our earlier papers.[1,2] For the αth atom located at the lattice point designated by $\vec{\rho}_\alpha$ in a unit cell of the G-54 network, we form the usual LCAO Bloch sum as

$$b_{j\alpha}(\vec{k},\vec{r}) = \sum_{\nu} e^{i\vec{k}\cdot\vec{R}_\nu}\phi_j(\vec{r}-\vec{\rho}_\alpha-\vec{R}_\nu)\,, \tag{1}$$

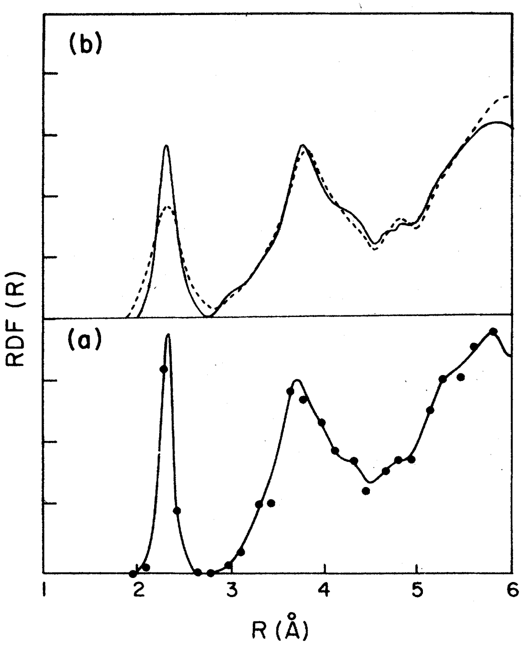

FIG. 1. (a) Calculated RDF for the static G-54 structural model. (b) The solid curve is a Gaussian-broadened version of curve (a) and the dashed curve is the experimental RDF, Ref. 10.

where $\vec{R}_\nu$ denotes the translational vector for the νth unit cell, and ϕ_j is an atomiclike orbital of Si with j covering $1s, 2s, 2p, 3s, 3p$. We then orthogonalize each $3s, 3p$ Bloch sum to all the $1s, 2s, 2p$ core Bloch sums, i.e.,

$$b'_{i\alpha}(\vec{k},\vec{r})=b_{i\alpha}(\vec{k},\vec{r})+\sum_{l\gamma} a_{i\alpha,l\gamma}b_{l\gamma}(\vec{k},\vec{r}), \qquad (2)$$

where the prime in b'_i signifies orthogonalization and

$$\begin{aligned} &\alpha,\gamma=1,2,3,\ldots,54,\\ &i=3s, 3px, 3py, 3pz,\\ &l=1s, 2s, 2px, 2py, 2pz. \end{aligned} \qquad (3)$$

The one-electron wave functions of a-Si are expanded by $b'_{i\alpha}$. The $3s$ and $3p$ orbitals span the complete occupied VB and the unoccupied conduction band (CB) as

$$\psi_q^{\mathrm{VB}}(\vec{k},\vec{r})=\sum_{i\alpha} V^q_{i\alpha}b'_{i\alpha}(\vec{k},\vec{r}), \qquad (4)$$

$$\psi_m^{\mathrm{CB}}(\vec{k},\vec{r})=\sum_{i\alpha} C^m_{i\alpha}b'_{i\alpha}(\vec{k},\vec{r}). \qquad (5)$$

With 54 atoms per cell, there are 108 subbands in the VB and 108 subbands in the CB, the subband indices being q and m, respectively. The imaginary part of the dielectric function is

$$\epsilon_2(\omega)=\frac{e^2}{3\pi m^2\omega^2}\sum_{qm}\int\delta[E_m(\vec{k})-E_q(\vec{k})-\hbar\omega] \times|\langle q\vec{k}|\vec{p}|m\vec{k}\rangle|^2 d\vec{k}. \qquad (6)$$

We evaluate the momentum matrix elements for each q-m pair from the wave functions in Eqs. (4) and (5) for eight primary $\vec{k}$ points in the Brillouin zone (BZ). Because of the relatively large unit cell, the quasi-BZ is very small and there are 216 bands for each k point. Calculation based on the weighted average of eight $\vec{k}$ points in the BZ is adequate. A comparison of the calculated ϵ_2 using an energy window of 0.2 eV with the experimental data[11] is shown in Fig. 2. Good agreement is seen for the peak position as well as the general shape. It is interesting to note that although the joint density of states (JDOS) has its maximum at about 10 eV,[1] the frequency dependence of matrix elements shifts the peak energy of ϵ_2 to 3.9 eV. The same kind of downward shift in peak energy has been found in crystalline Si,[12] and two polymorph forms of Si.[13]

III. NEAR-THRESHOLD BEHAVIOR

Upon reducing the energy window to 0.1 eV, we find some structure in the ϵ_2 curve at energies within 1 eV above the threshold which is displayed in Fig. 3. To understand it, we compute the energy dependence of the square of the momentum matrix elements (M^2) and of JDOS/ω^2. They are also oscillatory near the onset as is evident from Fig. 3. Particularly all three local maxima of M^2 coincide in energy with the corresponding ones of ϵ_2.

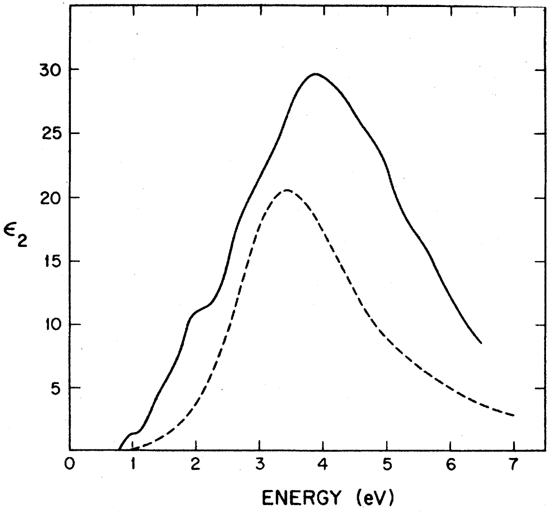

FIG. 2. Comparison of the calculated imaginary part of dielectric function ϵ_2 (solid curve) with experimental results (dashed curve) of Ref. 11.

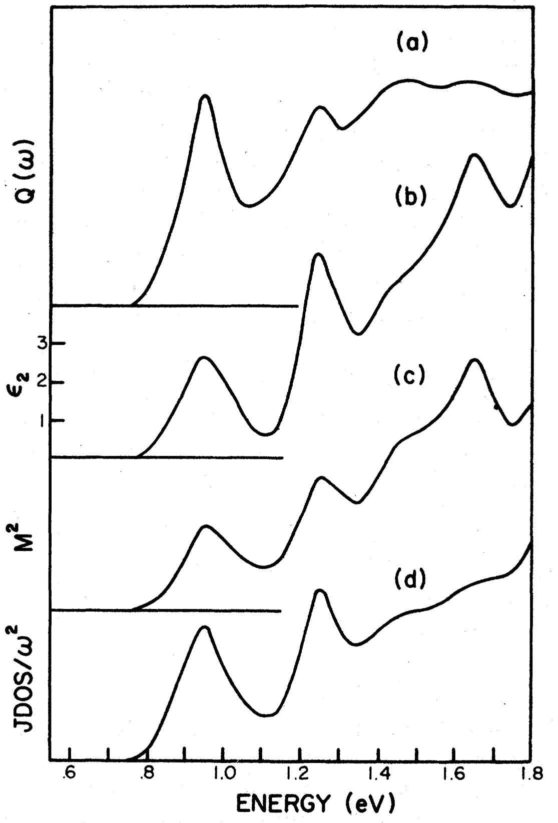

FIG. 3. Variations of (a) $Q(\omega)$, (b) ϵ_2, (c) M^2, and (d) JDOS/ω^2 with energy from onset to 1.8 eV.

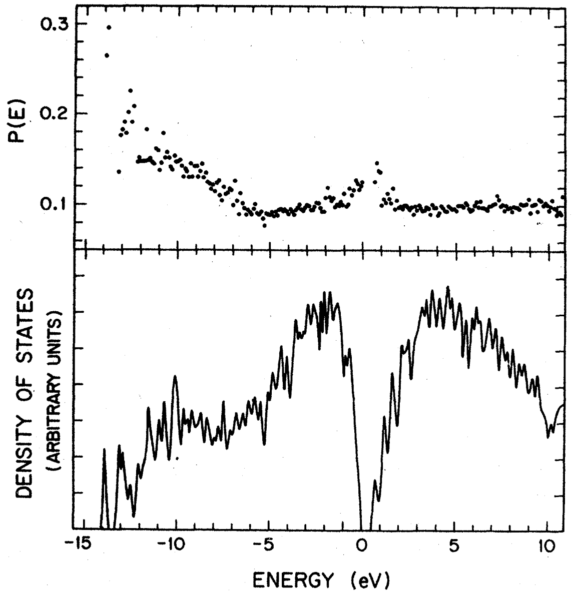

FIG. 4. The valence-band and conduction-band DOS of a-Si (lower curve) with the corresponding localization parameter $P(E)$ in the upper half of the graph.

Since a large momentum matrix element is often associated with localized states, we examine the degree of localization for the electronic states of a-Si. To this end we apply the criterion of Mulliken[14] to assign, for each $|q\vec{k}\rangle$, the fraction of electron charge attributed to each atom α which is designated as $f(\alpha,q\vec{k})$. Since the sum of $f(\alpha,q\vec{k})$ over α is unity, the average value (over α) of f equals $\frac{1}{54}$ and is also the f value for a state with equal distribution at all atoms, i.e., a completely delocalized state. Departure from this perfectly even distribution is therefore taken as a quantitative measure of localization. Accordingly we define the localization parameter of a state as

$$P(q\vec{k})=\left(\sum_{\alpha=1}^{54}[f(\alpha,q\vec{k})-\bar{f}\,]^2\right)^{1/2} \tag{7}$$

which ranges from zero for a completely delocalized state to unity for a state localized at one site. The mean value of $P(q\vec{k})$ for those states having energy between E and $E+\Delta E$ is denoted by $P(E)$ and is exhibited in Fig. 4 in juxtaposition with the density of states (DOS). The most striking feature is the steep rise in P for the levels at the bottom of VB. Also conspicuous is the peak just above the onset of CB. In each case there is a corresponding peak in the DOS curve at the same energy. The states immediately below the band gap also show appreciable localization. In fact it is the localized states on two sides of the band gap that are responsible for the oscillatory variation of M^2 near the threshold. For illustration we define the joint localization of the initial-final pairs associated with a transition frequency ω as

$$Q(\omega)=\sum_{qm}\int P(q\vec{k})P(m\vec{k})\delta[E_m(\vec{k})-E_q(\vec{k})-\hbar\omega]\,d\vec{k}\,. \tag{8}$$

The dependence of $Q(\omega)$ on $\hbar\omega$, which is included in Fig. 3, is indeed very similar to the curve for M^2.

For comparison we have performed a similar study for the polymorph form of Si which has a simple tetragonal crystalline structure with 12 atoms per unit cell (ST-12). No local maxima are found in the M^2 curve (versus ω), and $P(E)$ remains constant to within 5% over the entire VB and CB. Thus the localization is due to positional disorder of the atomic sites which results in fluctuation of the electron density from one atom to another. Upon examing the G-54 network, we find a group of five adjacent atoms with largest bond length contraction. The very bottom states of VB consist primarily of bonding s-type orbitals at these five atoms (f about 0.12) with little admixture from their neighbors ($f\sim 0.04$). Right above these states is a group which is localized in another aggregate of atoms with smaller bond contraction; the variation of f is also less abrupt. The states near the top of VB are predominantly p like, and show preferential population at some of the atoms in those two aggregates and at their neighboring atoms. Typically half of the charge cloud is shared by about 10 atoms. Localization in more or less the same domain is also found for the low CB states with about 40% s character. The states at the top of CB show virtually no localization.

The presence of localized states near the band gap of an amorphous system has been predicted previously by using the approaches of formal theories.[15] In the present work we are dealing with a much more concrete system. Thus it is possible to understand the origin of the localized states specifically from the detailed nature of structural disorder. To understand the localization of the bottom VB states, we note that since a slight bond-length contraction results in a lowering of the potential (of the one-electron Hamiltonian) in that vicinity, the lowest states in the VB are expected to localize in the region of maximum bond-length contraction. For an explanation for the localization of the top VB states, let us consider two Si CRTN clusters, called A and B, with cluster A having somewhat smaller bond lengths than B. It follows that the lower VB edge of A extends below that of B and the upper VB edge of A above that of B. If we merge these two clusters, the states originally associated with cluster A in the middle part of VB will mix with the corresponding ones of cluster B producing extended wave functions. Those states near the upper edge of the VB in A, however, have no counterparts in B of the same energies. Consequently they have less mixing with the cluster-B states and the resulting wave functions have higher amplitude in the domain of small bond lengths. The same analysis applies also to the states at the bottom of the CB of cluster A. For an aggregate of five or six bond-contracted atoms in a nonplanar ring form, a simple superposition of s-type orbitals can provide a completely bonding function, but one cannot have bonding simultaneously between all adjacent pairs using only p orbitals because of their directional character. Thus the p-like states near the top of the VB in general have less tendency to localize than the s-like states at the bottom.

In this paper the term localization is used in a broad sense of an uneven distribution of electron density over the 54 atoms, and does not necessarily imply strong concentration of the wave function in a small region. The values of the localization parameter for the near-gap states are expected to depend on the detailed structural distortion of the CRTN in a complicated way. Since the G-54 network is only a first attempt for a realistic modeling, the near-threshold oscillation of ϵ_2 as shown in Fig. 3 should not be taken in a quantitative sense. In fact the G-54 network probably has somewhat too large distortion. Upon reducing the distortion, the oscillatory pattern may well change or even decrease significantly. The extent to which these oscillations are present in an intrinsic a-Si solid would have to be determined by calculations based on more refined structural models. Nevertheless, our present work indicates that local maxima near the threshold of the ϵ_2 curve for intrinsic a-Si may arise as a result of a certain degree of structural distortion.

IV. CONCLUSIONS

The use of CRTN as structural models for a-Si has made it possible to calculate from first principles the electronic energies and wave functions of these amorphous systems. From these wave functions we compute the dielectric function $\epsilon_2(\omega)$. Based on the G-54 CRTN, the calculated dielectric function is in good overall agreement with experiment. Near the threshold we find several local maxima in the ϵ_2 curve which are due to transitions from the localized states in the upper edge of VB to those in the bottom of CB. The pattern of these local maxima is expected to depend quite sensitively on the detailed structural disorder and therefore may vary significantly upon improving the CRTN model. On the other hand, the localized states near the band gap do not play an important role in ϵ_2 above $\hbar\omega = 2$ eV, thus the shape of ϵ_2 above 2 eV would not be so sensitive to the detailed structural disorder.

In the case of intrinsic a-Si (void-free) as considered in this paper, the fluctuation of the electron distribution over the disordered lattice results in electronic wave functions of different degree of localization which may produce enhancement of ϵ_2 at some frequencies near the threshold. Such enhancement is of special interest in the development of a-Si solar cell. For intrinsic a-Si, as we have seen, the states near the band gap do not have very high degree of localization. By introducing point defects such as impurity atoms, it may be possible to produce highly localized states near the gap, thereby increasing the absorption in the visible region. One possible way of accomplishing this is by hydrogenation. At the present time, no CRTN for hydrogenated a-Si has been reported; however, when a suitable CRTN model becomes available, a theoretical analysis similar to the one in this paper should be very useful for studying the electronic and optical properties of the hydrogenated samples.

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