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Temperature dependence of the optical response: Application to bulk GaAs using first-principles molecular dynamics simulations

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We present an approach that takes into account lattice dynamical effects in calculating the optical response of semiconductors by averaging over several perturbed configurations of a supercell extracted from molecular dynamic simulations. The validity of this approach is confirmed by comparing our results for the dielectric function of bulk GaAs in the range of 0–700 K with our and other highly accurate ellipsometry measurements. The results of our approach resolve the serious discrepancy in energy and line shape between the latest optical models, all of which neglect lattice dynamics, and experiment.

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I. INTRODUCTION

Optical techniques yield a wealth of information about the fundamental properties of materials. They are widely used in leading-edge research and semiconductor technology and applied as noninvasive tools to monitor and characterize materials growth and reactions at surfaces and interfaces.[1] The optical properties of semiconductors are known to be strongly influenced by lattice dynamics at finite temperature, and even at 0 K they are affected by the zero-point motion.[2] Lattice dynamics are expected to be even more important for surfaces[3,4] and clusters. In spite of the importance of relating the optical properties to dynamical processes on the atomic scale, none of the optical response calculations published to date takes explicitly into account the effects of lattice dynamical processes.

The accurate first-principles description of the optical response was challenging for decades. An important step toward first-principles quantum mechanical calculations of the linear bulk and surface optical properties of semiconductors was taken in 1998, when excitonic effects with local field corrections were incorporated into the theory.[5–7] Subsequently, more efficient models based on time dependent density-functional theory were developed.[8,9] Recent calculations[10] on the optical response of the prototype cubic semiconductors that include *GW* corrections and excitonic effects demonstrate a common problem of these models, namely, a systematic shift of the calculated peaks to higher energy as compared to room temperature measurements. Moreover, in all these calculations, an unphysically large Lorentzian broadening was needed to bring the calculated peak widths into satisfactory agreement with experiment (see, e.g., Ref. 6). The obvious limitation of these and other models is that they neglect lattice dynamics, as they were all based on an ideal crystallographic lattice.

In this paper, we describe a general approach that explicitly incorporates lattice dynamical effects into first-principles calculations of the optical response of semiconductors. We combine calculations with measurements of the dielectric function of the prototype semiconductor GaAs and demonstrate very good agreement between the energy shifts and line shapes of the critical points over a wide range of temperature.

In this paper, the experimental procedures are described in Sec. II, and details of the molecular dynamic simulations and the electronic structure and optical response calculations are reported in Sec. III. In Sec. IV, the experimentally observed temperature dependencies of the dielectric functions are presented, compared with the theoretical results, and discussed. The conclusions of this work are summarized in Sec. V.

II. EXPERIMENTAL METHOD

Measurements of the dielectric function of GaAs in the temperature range from 22 to 750 K have been reported by Lautenschlager *et al.*[11] We extend the dielectric function measurements to 1070 K. Our classical spectroscopic ellipsometer in a rotating polarizer-sample-analyzer configuration[12] is attached to a horizontal metal organic vapor phase epitaxy reactor.[13] After chemically cleaning and etching the epiready GaAs (001) wafers, they were heated under group V stabilization using arsine (AsH_3). The remaining oxide desorbed in the hydrogen atmosphere of the reactor (10 kPa). Details of the *in-situ* monitoring of the oxide desorption can be found in Ref. 14. A homoepitaxial buffer of more than 100 nm was grown at 923 K to overgrow any remaining nonidealities of the substrates.[15] The dielectric function was measured over a range of temperature settings of the heating system, which was calibrated by means of an eutectic sample. The sample was heated to a maximum of 1070 K to avoid the increasing desorption of As that occurs at higher temperatures. The critical points of the dielectric functions were determined from the second derivative in the parabolic band approximation.[16,17]

III. THEORETICAL METHOD

The physical mechanisms responsible for the temperature dependencies of the optical properties of semiconductors are traditionally separated into lattice dynamics in the harmonic approximation (i.e., phonons) and anharmonic effects including thermal expansion.[2] Lattice vibrations modulate the overlap of the electronic wave functions between neighboring atoms, thereby influencing the widths of the energy bands, the energies of interband transitions, and the optical response.

The dielectric function of bulk GaAs can be calculated by averaging over a sufficient number of representative configurations of a supercell perturbed by lattice vibrations, following the ergodic hypothesis. We based our calculations on a supercell containing eight atoms (four Ga and four As). Because the time scale of optical transitions is much shorter than that of lattice vibrations, we calculated the dielectric functions of several representative configurations of the supercell adiabatically.

The representative configurations were extracted from first-principles molecular dynamic (MD) simulations based on density-functional theory (DFT) using the plane-wave self-consistent-field mode (plane wave) of the software package QUANTUM-ESPRESSO.[18] A plane-wave basis set with an energy cutoff of 15 Ry was used, and the Brillouin zone was sampled at eight $\boldsymbol{k}$-vectors. The equilibrium volume of the ideal supercell was determined by minimizing the total energy in the zinc-blende structure, resulting in a cell dimension of 10.22 a.u. To establish the average temperature in the MD simulation, the atoms of the supercell were randomly displaced and then allowed to move under the action of the atomic forces. We found that 10 000 steps, each of 20 a.u. of time ($1\text{ a.u.}=2.42\times 10^{-17}$ s), were sufficient to equilibrate the system, and we extracted the representative configurations over the following 5000 steps.

Traditionally, in a MD calculation, the temperature of any configuration is obtained from the kinetic energies of the atoms. However, the effect of using a small supercell, as in the present calculation, is to displace the phonon modes toward the Brillouin zone boundary. As a result, fewer phonon modes are excited in the supercell than in the real crystal, so the MD calculation of the kinetic energies of the atoms overestimates the temperature of the configuration. Instead, we extracted the temperature of each configuration from $\langle u^2\rangle$, the mean square displacement per atom of the configuration.

In the harmonic approximation, we determined the relationship between $\langle u^2\rangle$ and temperature (T) from the phonon density of states of bulk GaAs calculated by Giannozzi *et al.*,[19]

$$\langle u^2\rangle = \frac{\hbar^2}{M}\int \frac{D(E)[n(E,T)+0.5]dE}{E}, \qquad (1)$$

where $\hbar$ is Dirac's constant, M is the mass of one primitive unit cell, which contains one Ga and one As atom, E is the phonon energy, and $D(E)$ is the phonon density of states normalized to one primitive unit cell. The occupation of the phonon modes is given by the Bose-Einstein distribution function $n(E,T)=\{\exp[E/(k_BT)]-1\}^{-1}$, where k_B is Boltzmann's constant and the extra term 0.5 accounts for the zero-point motion of the lattice.

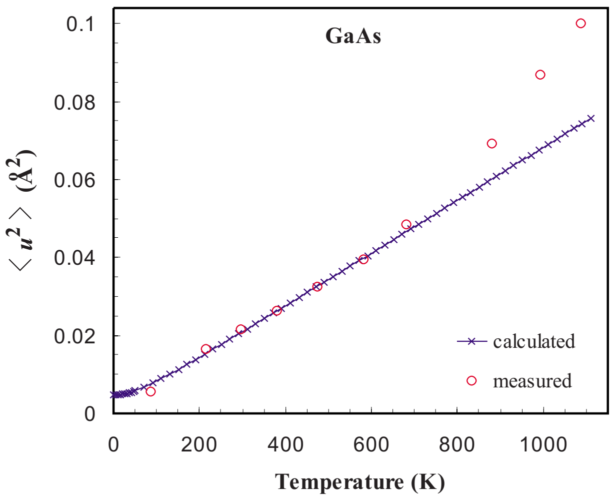

FIG. 1. (Color online) The calculated mean square displacement $\langle u^2\rangle$ of GaAs in the harmonic approximation in the temperature range from 0 to 1100 K, compared with experimental measurements in the range from 85 to 1100 K (Refs. 20 and 21).

In Fig. 1, $\langle u^2\rangle$ for GaAs calculated from Eq. (1) in the range from 0 to 1100 K is compared with the results of x-ray diffraction measurements in the range from 85 to 1100 K (Ref. 20) (original data from Ref. 21). The calculated $\langle u^2\rangle$ at 0 K is due to the zero-point motion of the lattice. To our knowledge, no experimental data have been reported in the range from 0 to 85 K, where zero-point motion makes an important contribution to $\langle u^2\rangle$. In the range from 85 to 600 K, the calculated $\langle u^2\rangle$ is in very good agreement with the experimental data. At higher temperatures, the experimental $\langle u^2\rangle$ is strongly enhanced by anharmonic effects. Hence, for GaAs, Eq. (1) is a good approximation only in the temperature range from 0 to about 600 K, where $\langle u^2\rangle$ is dominated by harmonic effects (phonons), and anharmonic effects can be neglected. To extract the temperature of each configuration from $\langle u^2\rangle$, the calculated curve in Fig. 1 was used in the range from 0 to 600 K, while the experimental curve was used above 600 K. Since the temperature fluctuates significantly during the MD simulation, we selected only configurations within ±1 K of the average temperature below 600 K and within ±10 K above 600 K.

The software package WIEN2K[22] was used to calculate the electronic structure and the optical properties of each selected configuration self-consistently on the basis of DFT by the full-potential linear-augmented-plane-wave method. Exchange and correlation were treated in the generalized-gradient approximation (GGA).[23] The dielectric function of each selected configuration was calculated in the independent-particle random-phase approximation as implemented in the WIEN2K linear optics package.[24] The dielectric function of cubic GaAs is isotropic, so the dielectric tensor contains only equal diagonal elements ε^{ii} $(i=x,y,z)$, and the imaginary part of the dielectric function was calculated by evaluating the expression,

$$\varepsilon_2^{ii}(\omega) = \frac{\hbar^2 e^2}{\pi m^2 \omega^2} \sum_{vc} \int_{\mathbf{k}} d\mathbf{k} p_{vc}^i(\mathbf{k}) p_{cv}^i(\mathbf{k}) \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega], \tag{2}$$

where v and c label valence and conduction states of energy $E_v(\mathbf{k})$ and $E_c(\mathbf{k})$, respectively, $p_{cv}^i = \langle c, \mathbf{k} | p^i | v, \mathbf{k} \rangle$ is the matrix element of the momentum operator $\mathbf{p}$, ω is the angular frequency of the photons, and m and e are the electron mass and charge, respectively. The integral over the wave vector $\mathbf{k}$ is evaluated over the first Brillouin zone. In evaluating Eq. (2), no Lorentzian broadening was applied.

It is known that DFT underestimates the energies of the conduction states and hence the energy gaps in semiconductors, and that, to a good approximation, the energies of the conduction states can be corrected by applying a $\boldsymbol{k}$-independent energy shift called the *scissor shift*.[25] In the present calculations, the energy gaps of the configurations were corrected by applying a scissor shift of 0.80 eV.

A large number of $\boldsymbol{k}$-vectors are needed to adequately sample the Brillouin zone because the cubic symmetry of the ideal GaAs configuration is broken when the atoms are perturbed by lattice vibrations. 864 irreducible $\boldsymbol{k}$-vectors were used in the self-consistent cycles, and 23 300 irreducible $\boldsymbol{k}$-vectors were used to calculate the optical matrix elements. To allow for thermal expansion, the experimentally observed temperature dependence of the lattice constant of bulk GaAs (Ref. 26) was taken into account.

The electronic energy bands of the configurations of GaAs in the vicinity of the energy gap, and hence the calculated dielectric functions, are dominated by the {111}, {200}, and {220} Fourier components of the lattice potential. Because the periodic boundary conditions applied in our electronic structure calculations replicate the supercell throughout the lattice, some of the configurations that are generated by our MD simulations cause sizable displacements of one or more low-index lattice planes. This effect modifies the corresponding Fourier components of the lattice potential, resulting in spurious band shifts that may reduce or eliminate the energy gap. It also modifies the geometrical structure factor of the configuration relative to that of the ideal lattice. Because the atomic displacements increase with increasing temperature, these unrepresentative configurations are increasingly prevalent at higher temperature, limiting our calculation of the dielectric function of GaAs to a maximum temperature of about 700 K. By using larger supercells, this upper temperature limit can be increased.

At the end of the MD simulation, the temperature and the geometrical structure factor of each configuration were calculated from the atomic coordinates. We calculated the dielectric functions of only those selected configurations in the required temperature range whose geometrical structure factors for the low-index planes {111}, {200}, and {220} were minimally perturbed relative to those of the ideal lattice. Following the standard scheme in first-principles calculations of the electronic and optical properties of complex materials (see, for example, Ref. 27), the dielectric functions of the selected configurations were averaged to yield the dielectric function of bulk GaAs. We found that to achieve adequate convergence, it suffices to average the calculated dielectric functions over no more than eight configurations distributed throughout the equilibrated part of the MD simulation. This was verified by comparing the results with tight-binding calculations in which up to 100 configurations were used. Also, we demonstrated that an eight-atom supercell is sufficiently large to model the dielectric function by showing that the dielectric functions of an eight-atom supercell and a 64-atom supercell calculated using the tight-binding method are very similar. As the calculation of the dielectric function of a single configuration is by far the most time-consuming step, this approach greatly enhanced the practicality of our method of calculation.

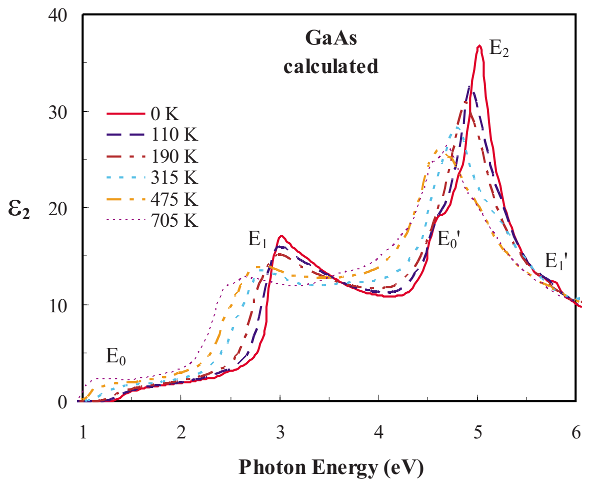

FIG. 2. (Color online) Calculated imaginary part of the dielectric function of GaAs in the temperature range from 0 to 700 K.

IV. RESULTS AND DISCUSSION

Our calculated plots of the imaginary part of the dielectric function $\varepsilon_2(E)$ in the range from 0 to 700 K are shown in Fig. 2. Below 200 K, several interband transition peaks are clearly resolved. They include the direct gap transition onset E_0 close to 1.4 eV, peak E_1 at approximately 3.0 eV, the strongest peak E_2 around 5.0 eV with shoulder E_0' close to 4.6 eV, and the weak peak E_1' at 5.8 eV. As no Lorentzian broadening was applied in our dielectric function calculations, the widths of the peaks are entirely due to shifts in the electronic energy bands that are induced by lattice vibrations. At 0 K, all of the peaks are significantly broadened as compared with the corresponding peaks calculated for the ideal GaAs lattice, reduced in amplitude by about 25%, and shifted to lower energy by about 50 meV by zero-point motion. With increasing temperature, they are progressively broadened and shifted to lower energy. At room temperature and above, the shoulder E_0' and peak E_1' are smeared out, while peaks E_1 and E_2 remain strong and are shifted to lower energy by 0.2 and 0.3 eV, respectively, as compared with the corresponding peaks of the ideal lattice. We found that bulk thermal expansion has only a minor effect on the calculated critical point energies of GaAs, producing a linear shift to lower energy of 3.6 meV/100 K.

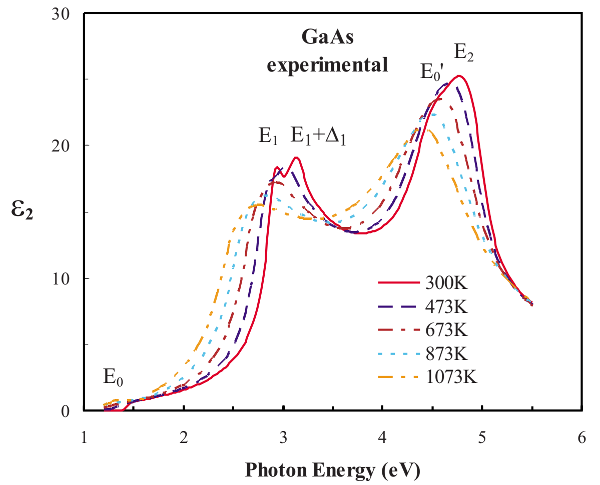

FIG. 3. (Color online) Measured imaginary part of the dielectric function of GaAs in the temperature range from 300 to 1070 K.

Our $\varepsilon_2(E)$ measurements in the range of 300–1070 K are shown in Fig. 3, and measurements in the range of 22–750 K have been reported by Lautenschlager *et al.*[11] With increasing temperature, the principal optical peaks broaden, decrease in amplitude, and shift to lower energy. The calculated energy dependencies of peaks E_1 and E_2 are compared with experiments in Fig. 4. The very good agreement in energy shifts and line shape between the calculated dielectric function of GaAs and experiment over a wide range of temperature confirms the validity of our approach. Moreover, the calculated energy shifts account for the discrepancies in the energies of the main peaks E_1 and E_2 between experiments and recent optical calculations.[10]

To make the present computationally intensive calculations more tractable, we did not include spin-orbit interaction except for a calculation based on a perturbed lattice at 0 K (not shown) and we did not take into account excitonic effects. The inclusion of spin-orbit effects in GaAs results in the splitting of peak E_1 into E_1 and $E_1+\Delta_1$, which is consistent with experimental observations below 300 K (see Fig. 3 and Ref. 11). Excitonic effects are known to enhance peak E_1 and to suppress peak E_2 in GaAs,[6] but they are not expected to influence the relative energies of these peaks.[27] The neglect of excitonic effects results in a discrepancy in the relative strengths of peaks E_1 and E_2 between our calculation and experiment.

V. CONCLUSIONS

We have presented a general approach that meets the long-standing need to take into account lattice dynamical effects in first-principles calculations of the optical response of semiconductors. First, we based our calculations of the dielectric function of bulk GaAs on an eight-atom supercell perturbed by lattice vibrations extracted from MD simulations. Second, to achieve adequate convergence of the dielectric function, we found that it is sufficient to average over only about eight representative configurations of the supercell. Finally, we selected the representative configurations by examining both the temperature and the geometrical structure factor of each configuration at the end of the MD simulation. As the calculation of the dielectric function of each single configuration is by far the most time-consuming step, this approach greatly contributes to the practicality of our method of calculation.

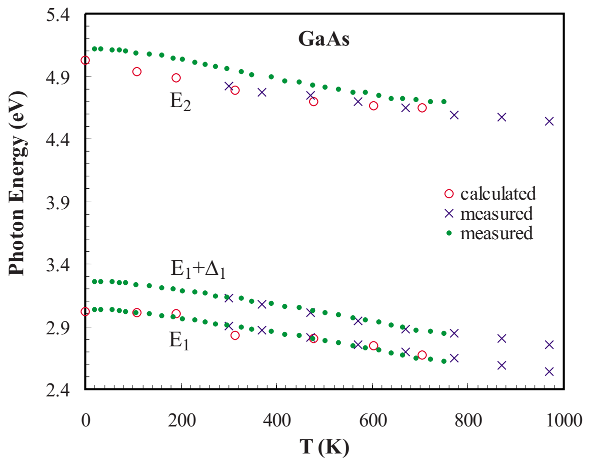

FIG. 4. (Color online) Temperature dependence of the main critical point energies of the imaginary part of the dielectric function of GaAs. The results of our calculations are represented by circles. Our experimental data are represented by crosses, and those of Ref. 11 are represented by dots.

We conclude that lattice dynamics is responsible for the major energy shifts and broadening observed experimentally, while thermal expansion accounts for only minor shifts in the spectra. The neglect of dynamical effects in previous calculations based on the ideal lattice explains why they failed to account for the observed temperature dependence of the optical response. In particular, the systematic shift to higher energy of the calculated spectra in recent calculations that include *GW* corrections and excitonic effects, relative to the experimental spectra at room temperature, is consistent with the energy shift predicted by our temperature dependent calculations. Our approach opens the way to comprehensive first-principles calculations of the optical response of semiconductors at finite temperature, including both excitonic and spin-orbit effects.

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