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Real-space Green's-function approach to study the effects of disorder on the frequency spectrum of Si/Ge alloys

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It is demonstrated that the real-space Green's-function method provides a reliable and efficient framework to treat disorder in alloys. The method has been used to calculate the frequency spectrum of $Si_{0.5}Ge_{0.5}$. The results obtained by this method not only reproduce the three-mode behavior which cannot be obtained by mean-field approximations such as the coherent potential approximation but also correctly predicts the intensities of the peaks associated with the three modes which cannot be easily obtained by the supercell approach.

In recent years, the success of growing atomically controlled semiconducting heterostructures has prompted a concerted effort to study epitaxially grown systems such as GaAs/AlAs and Si/Ge for their potential technological applications.[1] In theoretical investigations of these systems, in particular, superlattices (SL's) with alloy components and graded interfaces, it is important to properly account for the effects of disorder and the internal strain field due to the misfit of the lattice constants of the components. In order to understand the dynamics of these composite systems, it is essential to understand first the role of disorder in simple semiconducting alloys. This has prompted several studies of the semiconducting alloys.[2-4]

The analysis of the dynamics of alloys requires two ingredients: (i) a reliable knowledge of the interatomic force constants, and (ii) a procedure to correctly handle the disorder. For the former, in addition to the availability of semiempirical potentials,[5] methods based on the local-density approximation (LDA) have been developed for both Si/Ge (Ref. 4) and GaAs/AlAs (Ref. 3) systems with a few hundred atoms. For the treatment of disorder, the most commonly used theoretical techniques are still methods based on the mean-field approximation such as the coherent-potential approximation (CPA). In the coherent-potential approximation,[6] the disordered medium is replaced by an effective medium which reflects the average of the disorder.[7] Hence the detailed structure of the density of states is usually smeared out. Recently, Gironcoli and Baroni[8] demonstrated that, for $Si_{0.5}Ge_{0.5}$, the CPA failed to reproduce a three-mode behavior in the vibrational density of states (DOS), while the supercell (SC) calculation using an *ab initio* force constant yielded the peaks in the DOS associated with Si-Si, Ge-Ge, and Si-Ge vibrations which were in good agreement with the observed Raman spectrum.[9] However, there is an intrinsic limitation to this approach imposed by the size of the cell. The implementation of the supercell calculation to random alloys involves the generation of the random configuration of atomic species according to their concentration in a large cell, which is then periodically repeated.[3,8] The DOS corresponding to that particular configuration is obtained by a straightforward diagonalization of the dynamical matrix. The average DOS (ADOS) of the alloy is obtained by averaging over several random configurations. If the number of atoms N in the cell is not sufficiently large, the deviation from the given atomic concentrations, being of the order of $1/\sqrt{N}$, can introduce a bias in the intensities of the peaks associated with the impurity configurations. In addition, the imposed periodicity will further enhance the bias. On the other hand, if N is too large, the computing time for the diagonalization of the ADOS can be excessive. This is an intrinsic bottleneck of this approach. In fact, the size effect showed up in the supercell calculation of Gironcoli and Baroni.[8] The ratio of the intensities of the peaks associated with Ge-Ge, Si-Ge, and Si-Si in the DOS of $Si_{0.5}Ge_{0.5}$ must of the order of 1:2:1. However, the result of Gironcoli and Baroni (see Fig. 1) gave the ratio as 1:1:0.5, an indication that the supercell containing 512 atoms used by Gironcoli and Baroni is not sufficient to provide details of the DOS. The computation undertaken by Gironcoli and Baroni is already very demanding. It is just not practical to extend the calculation to larger and larger cells.

In this paper, we use an approach based on the real-space Green's function (RSGF) (Refs. 10–13) to treat the effects of disorder in the dynamics of $Si_{0.5}Ge_{0.5}$. The method involves calculating the local Green's function (LGF), which leads directly to the determination of the local DOS (LDOS). Therefore, the method is tailor-made for the calculation of the ADOS of disordered systems. In this method, a convergence procedure is used that provides a reliable and efficient scheme to calculate the LGF of an infinite system.[12,13] This procedure allows one to determine the LGF as accurately as one desires or one can afford without introducing any truncation or boundary effects. This is a key feature which distinguishes our method from the recursion method.[14] A detailed comparison of the recursion method and our method has been reported in Ref. 13. The outstanding feature of our method is that, at a given stage of its development, it in-

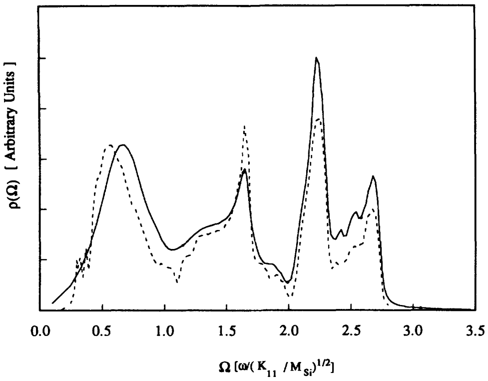

FIG. 1. Average DOS of $Si_{0.5}Ge_{0.5}$ obtained by the present method (full lines) is compared with the results obtained by the supercell method of Ref. 10 (dashed lines). In our calculation, DOS is averaged over 32 random configurations that correspond to different possibilities of the five atoms in region 1, while the surrounding is generated randomly.

cludes all the information concerning all the degrees of freedom within that step. Thus, if the convergence of a system property is reached according to a preset criterion, the result will faithfully represent the system property. The treatment of disorder is exact in our approach for a given random configuration within the prescribed tolerance limit.

For a random alloy where the interatomic force constants are of finite range, the dynamical matrix can be represented in the real-space representation as a block-tridiagonal matrix.[15] For example, one may start with any locality consisting of a certain number of atoms in the system. One may label this locality as region 1 and designate the matrix describing the region as h_1. One may next label the region which is composed of atoms interacting directly with the atoms in region 1 as region 2. The matrix describing this region is designated as h_2, with v_{12} as the matrix describing the interaction between regions 1 and 2. Region 3 is then defined as the region composed of atoms which interact directly with the atoms in region 2 and which are not already included in region 1. The matrix of region 3 is designated as h_3, with v_{23} the matrix of interaction between regions 2 and 3. This partitioning process can proceed until the entire system is included. In this way, the matrix of the system, H, is expressed as a semi-infinite block-tridiagonal matrix with the first diagonal block given by h_1. It should be noted that the dimensions of the diagonal block matrices h_i's are in general different. In fact, the dimension of h_i is usually an increasing function of i.

The solution to the Green's function of a general block-tridiagonal matrix was obtained by one of us (S.Y.W.) and his co-workers previously.[16] The salient feature of the method is that the burden of calculating the Green's function of a very large system is shifted to the computation of the LGF's corresponding to the diagonal blocks, h_i's, and a series of matrix multiplications. The dimension of h_i is usually very small compared to the system matrix H. This approach then provides a powerful means to calculate the Green's function of a very large or an infinite system.

Let us denote by G_{11} the LGF corresponding to region 1. Because of the semi-infinite nature of the system matrix, as described above, it can be shown that[16]

$$G_{11}(z)=\Delta_1^+(z)=\{z-h_1-v_{12}\Delta_2^+v_{21}\}^{-1}\ , \tag{1}$$

where the forward (backward) Green's function Δ_1^+ (Δ_1^-) is given by

$$\Delta_i^{\pm}(z)=\{z-h_i-v_{i,i\pm1}\Delta_{i\pm1}^{\pm}v_{i\pm1,i}\}^{-1}\ . \tag{2}$$

The calculation of $\Delta_1^+(z)$ can be accomplished by a limiting process such that[12]

$$\Delta_1^+(z)=\lim_{m\to\infty}\Delta_1^{+(m)}\ , \tag{3}$$

where

$$\Delta_1^{+(m)}(z)=\{z-h_1-v_{12}[z-h_2-\dots v_{m-1,m}[z-h_m]^{-1}v_{m,m-1}\dots]^{-1}v_{21}\}^{-1}\ . \tag{4}$$

From Eq. (4), it can be seen that $\Delta_1^{+(m)}(z)$ is simply the forward Green's function of region 1 when the system matrix H is truncated at the mth step. Equation (3) then states that Δ_1^+ can be calculated as the limit to the sequence $\{\Delta_1^{+(m)}(z)\}$. It turned out that there exists a recursive relation which links the computation of $\Delta_1^{+(m)}$ to that of $\Delta_1^{+(m-1)}$. This relation can be written as[13]

$$\Delta_1^{+(m)}=\Delta_1^{+(m-1)}+R_m\ , \tag{5}$$

where

$$R_m=A_{m-1}\Delta_m^-A_{m-1}^T\ , \tag{6}$$

with

$$A_{m-1}=A_{m-2}\Delta_{m-1}^-v_{m-1,m}\quad (m>2) \tag{7}$$

and

$$A_1=\Delta_1^-v_{12}\ . \tag{8}$$

From Eq. (2) and the semi-infinite nature of the system matrix as described previously, one obtains

$$\Delta_1^-(z)=\{z-h_1\}^{-1}\ . \tag{9}$$

The terms in the sequence $\{\Delta_1^{+(m)}\}$ can now be computed efficiently and without redundancy. Initially, the backward Green's function Δ_1^- is calculated using Eq. (9). It is then substituted into Eq. (8) to determine A_1. The subsequent Δ_m^-'s and A_{m-1}'s are calculated using Eqs. (2)

and (7), respectively. The successive terms of $\{\Delta_1^{+m}\}$ are finally obtained using Eqs. (5) and (6).

The local vibrational DOS in region 1 is related to the LGF by

$$\rho_1(\omega^2) = -\frac{1}{3n_1\pi} \operatorname*{Im}_{\varepsilon\to 0} \operatorname{Tr} G_{11}(\omega^2 + i\varepsilon) \;, \tag{10}$$

where n_1 is the number of atoms in region 1. Therefore, only the trace of Δ_1^+ is relevant for the calculation of the local DOS [see Eq. (1)]. The convergence procedure for the calculation of the LDOS is then set up as follows. For a given ε at a certain ω^2, the terms in the sequence $\{\Delta_1^{+(m)}\}$ are calculated as outlined above. The sequence is considered as having reached its limit when all the corresponding diagonal elements of $\Delta_1^{+(m)}$ and $\Delta_1^{+(m-1)}$ are within a given tolerance. The criterion of convergence is given by

$$\frac{(R_m)_{\text{diag. element}}}{(\Delta_1^{+(m-1)})_{\text{diag. element}}} < L_c \quad \text{for all diagonal elements} \;, \tag{11}$$

where L_c is a preset tolerance with R_m given by Eq. (6). The converged value of the trace of the local Green's function is then used to determine $\rho_1(\omega^2)$ from Eq. (10). It should be noted that this convergence procedure will yield a result as accurate as the convergence criterion without any boundary effect associated with an arbitrary truncation of the system at the outset. To ensure the reliability of our calculation, the entire process should be repeated for a series of decreasing ε until no additional feature appears in the LDOS.

The analysis of dynamics of Si/Ge alloys is done with the method outlined above using the semiempirical force constants of Wilke, Masek, and Velicky.[5] Although *ab initio* force constants have been developed for Si/Ge systems,[4] we intentionally chose the semiempirical force constants. The rationale behind this choice is the following. If the mass disorder is the dominant factor in a Si/Ge system, the simpler force-constant model can yield reasonable DOS results. On the other hand, if the lattice mismatch is an important factor, the calculation based on the semiempirical force constants would not be able to give correct DOS results. In the case of $\mathrm{Si_{0.5}Ge_{0.5}}$, the masses of Si and Ge differ by a factor of 2.6 but the lattice mismatch of Si and Ge is also appreciable. So, in principle, questions can be raised as to whether semiempirical force-constant models can be used at all.

In the calculation of ADOS of $\mathrm{Si_{0.5}Ge_{0.5}}$ using Eq. (10), two different schemes were used. In the first scheme (I), a five-atom cluster is included in region 1. The atomic species at the sites in the remaining part of the system are generated randomly according to their atomic concentrations in the alloy. The average DOS was obtained by averaging over 32 configurations, each corresponding to one of the possible configurations of the five-atom cluster plus the randomly generated surrounding. In the second scheme (II), only one atom (either Si or Ge) is placed in region 1. The atomic species at the remaining sites of the system are generated randomly. The average DOS was obtained by averaging over several random configurations.

In Fig. 1, the ADOS of $\mathrm{Si_{0.5}Ge_{0.5}}$ of the present calculation using the first scheme is compared with that obtained by Gironcoli and Baroni[8] using the SC approach. Except for the intensities associated with the three peaks (Ge-Ge, Si-Ge, and Si-Si), the agreement between these two curves is excellent, especially since the interatomic force constants used in the present calculation were obtained by fitting the experimental data. In the fitting procedure, Wilke, Masek, and Velicky[5] used the Born model and assumed the same force constants (α,β) for all Si-Si, Si-Ge, and Ge-Ge bonds. The excellent agreement in the general features of the two curves, in particular the locations of the peaks, indicates that the mass difference is still the dominant factor contributing to the effect of disorder for Si/Ge systems even though the lattice mismatch in this case is substantial. One of the striking features of the present calculation is that the ratio of the intensities of the three modes (Ge-Ge, Si-Ge,and Si-Si) is correctly given by 1:2:1, as it should be for a binary alloy with 50% of one component and 50% of the other. This ratio, however, is not predicted by the supercell calculation. Furthermore, in the SC calculation one finds some anomalous structures in the low-frequency regime which is not found in our ADOS calculation. The size effect in the supercell calculation may be responsible for these anomalous structures in the low-frequency regime.

In scheme I of our calculation, where there are five atoms in region 1, the convergence criterion requires that all 15 diagonal elements of the LGF G_{11} satisfy Eq. (11). If, on the other hand, only one atom is placed in region 1 as in scheme II, it is expected that fewer steps in the calculation of the terms in the sequence $\{\Delta_1^{+(m)}\}$ are needed for the LGF to converge. The tradeoff, however, is that more configurations might have to be included in the averaging process to recover the detailed features of the DOS. In Fig. 2, a series of three curves are shown. They all correspond to the situation where only one atom (ei-

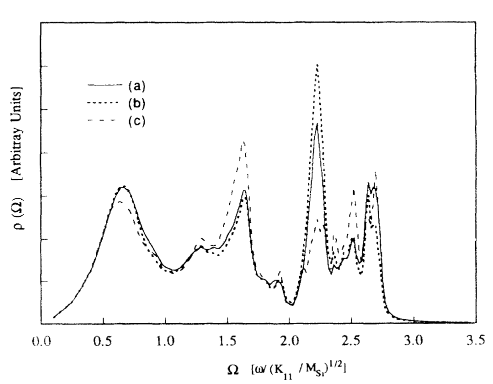

FIG. 2. Curves *a*, *b*, and *c* show the ADOS corresponding to 16, 12, and 4 random configurations. In these sets of calculations only one atom (either Si or Ge) is placed in region 1, and the rest of the surrounding is generated randomly according to atomic concentrations. In the above plots, *n* random configurations with a Si atom in region 1, and *n* random configurations with a Ge atom in region 1 have been considered with *n* equal to 8, 6, and 2, respectively.

ther Si or Ge appearing with equal probability) is in region 1. They differ in the number of random configurations that are included in the averaging process. In the cases presented, there are 2, 6, and 8 configurations associated with a Si atom in region 1, and an equal number of configurations associated with a Ge atom in region 1. The series of curves then represent the ADOS corresponding to averaging over 4, 12, and 16 random configurations. From Fig. 2, it can be seen that the ADOS begins to settle when 12 configurations are included, and the ADOS corresponding to 16 configurations is almost similar to the ADOS shown in Fig. 1. This observation is very satisfying because scheme II of our calculation is not a cluster-dependent calculation. These results therefore establish that the method of the real-space Green's function is a reliable and efficient technique for the study of disordered systems. For all curves shown in Figs. 1 and 2, the preset tolerance is $L_c=0.05$ and $\varepsilon=0.1$ in the reduced unit of K_{11}/M_{Si} with K_{11} being the diagonal element of the force-constant matrix.

In this paper, we have shown that the real-space Green's-function approach correctly predicts every feature of the frequency spectrum of $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$. This demonstrates that the RSGF is a reliable tool to study disordered systems. The reliability stems from the fact that the local environment is systematically surveyed until the system property (e.g., DOS) is converged within the preset tolerance criterion. The effect of the local environment is faithfully reflected as the calculation of the successive terms in the sequence $\{\Delta_1^{+(m)}\}$ is carried out. The convergence process is dictated solely by the nature of the system. In fact, the size of the system actually used in the computation of the local Green's function is no more than what is required by the convergence of the LGF. Hence there is an intrinsic optimization of the computational time. This natural selection of the size needed for the calculation of the LGF also eliminates any undesirable effects associated with ad hoc assumptions about the size of the system or other truncation schemes that are usually employed in the calculation of the LGF.[8,17] Furthermore, in our scheme for calculation of the LGF, matrix inversions and multiplications involve only matrices of dimensions very small compared to the dimension of that part of the system which is needed to reach the convergence. This feature further improves the efficiency of the method in terms of both the computing time and memory space. Finally, the result of our calculation suggests that semiempirical force constants give very good results for the DOS of Si/Ge alloys. This result may prove to be of crucial importance in the dynamics of more complex systems such as superlattices with alloy components where it can considerably simplify the calculation.

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