Mechanical and Electronic Properties of Strained Layer Superlattices Studied by Density Functional TB and Path Probability Methods

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ABSTRACT

The atomic and electronic structures of semiconductor heterostructures including steps, misfit dislocations and interface disorder are studied by using the density-functional tight-binding (TB) method. Atomic structures of misfit dislocations both edge type 1/2 <110> (001) and 60°dislocations in the semiconductor heterostructures, like Si-Ge superlattices and GaAs/Si systems are studied by using order of N [O(N)] calculational method. The path probability method (PPM) in the statistical physics is used to study the influence of the interface disorder on the electronic properties of the semiconductor heterostructures. The fracture behavior of semiconductor heterostructures under applied stress is also investigated and debonding mechanism between the two different semiconductor layers is discussed. It is shown that the junction relaxation influences quite significantly on the electronic and mechanical properties of semiconductor heterostructures.

keywords: density-functional TB method, superlattice, orbital peeling method, semiconductor heterostructure, path probability method (PPM).

1. INTRODUCTION

The semiconductor heterostructures, quantum wells and quantum dots are now of crucial importance for the modern device technologies and material applications [1-4]. Nanoscale materials like fullerene, carbon nanotubes and carbon related materials also provide us a wide variety of applications, since their discovery, due to their unique molecular structure, electronic and mechanical properties [5-7]. Accordingly, the needs to work with large lattice mismatched systems becomes increasingly important. However, little is known about the atomistic mechanism of strained layer epitaxial growth, e.g., thin film growth on semiconductor substrate by molecular beam epitaxy (MBE) [1]. In most lattice mismatched heteroepitaxial systems, the initial growth mode consists of the formation of a two-dimensional (2D) pseudomorphic layers. During the growth of thicker layers, the increasing misfit strain gives rise to the formation of coherent, dislocation-free three dimensional (3D) islands or the formation of misfit dislocations. In addition, it leads to intermixing near the interface [8]. Recently, the strain driven intermixing has been reported for Ge/Si(001) systems [1,3-4]. Atomic species disorder at the interface is also an important ingredient in discussing the properties of the semiconductor heterostructures. It is noted that the semiconductor heterostructures are never in equilibrium, and therefore the junction profile can be changed by thermal means or by elastic stresses [9-11].

The compositional intermixing in the semiconductor heterostructures is undesirable for many devices based on the heterostructures where a smooth and abrupt interface is needed for the device performance. On the other hand, because the interface intermixing alters the electronic and optical properties sensitively, it may be used to tune the optoelectronic quantum-well device parameters [9]. Interface intermixing may be enhanced by impurities or point defects. For instance, Ga vacancies are known to mediate diffusion on the group III zincblende sublattices, and GaAs grown by MBE at low substrate temperatures is a unique material containing a huge number of intrinsic point defects, As antisites and Ga vacancies.

In the present study, the atomic diffusion in the semiconductor interface is investigated via the vacancy mechanism of diffusion using the non-equilibrium irreversible statistical mechanical approach, the path probability method (PPM) [11]. The effective pair interaction energies between the constituent atoms are derived using the zeros-poles method [12] taking into account the misfit strains at the interface. The so-called zero-poles orbital peeling method is used within the framework of TB theory and direct configurational averaging method. The interface mixing influences quite significantly the electronic and mechanical properties of the semiconductor heterostructures. We will show that even for the very early stage of the junction relaxation, the interface electronic properties are strongly influenced by the interface disorder. The PPM is applied to study the interface disorder due to interdiffusion at the tetrahedrally coordinated semiconductor heterostructures [9-11].

2. CALCULATIONAL METHOD AND RESULTS

2.1 Density Functional TB Method

Our method of energetics for obtaining the semiconductor heterostructures is based on the linear

combination of atomic orbitals (LCAO) scheme of Seifert, Eschrig and Bieger [13-15], and we follow exactly their procedure. In this approximation, the Kohn-Sham orbitals, ψ_i, of the system containing N atoms are expanded in terms of Slater-type functions and spherical harmonics:

$$\phi_\nu(\mathbf{r}) = \sum_{n,\alpha,l_\nu,m_\nu} \alpha_{n\alpha} r^{l_\nu+n} \exp(-\alpha r) Y_{l_\nu m_\nu}(\frac{\mathbf{r}}{r}) \,. \tag{1}$$

Using the Slater-type orbitals, we perform a self-consistent solution of the modified all-electron single-atom Kohn-Sham equations:

$$[T + V^{psat}(r)]\phi_\nu(\mathbf{r}) = \varepsilon_\nu^{psat}\phi_\nu(\mathbf{r}) \,, \tag{2}$$

$$V^{psat}(r) = V_{nucleus}(r) + V_{Hartree}[n(r)] + V_{xc}^{LDA}[n(r)] + (\frac{r}{r_0})^N \tag{3}$$

and determine the single-atom electron wave functions and potentials. The additional term $(r/r_0)^N$ appearing in V(r) in the above eqn. (3) forces the wave functions to avoid areas far from the nucleus, thus resulting in an electron density that is compressed in comparison to the free atom.

Then, the Kohn-Sham equations of the condensed matter systems are solved within a non-self-consistent treatment

$$\hat{H}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}); \; \hat{H} = \hat{T} + V_{eff}(\mathbf{r}) \quad , \tag{4}$$

where $V_{eff}(\mathbf{r})$ denotes the effective one-electron potential.

It is now well established that the total energy of the system within the TB approach can be written with the usual tight-binding equation as a sum over the 'band-structure' energy and a short-range repulsive two-particle potential [14-16]:

$$E_{tot}(\{\mathbf{R}_k\}) = \sum_i n_i \varepsilon_i(\{\mathbf{R}_k\}) + \sum_k \sum_{<l} V_{rep}(|\mathbf{R}_l - \mathbf{R}_k|) + \frac{1}{2}\sum_{\alpha,\beta}\gamma_{\alpha,\beta}\Delta q_\alpha \Delta q_\beta \tag{5}$$

where n_i denotes the occupation number of Kohn-Sham orbital i. The short-range repulsive energies $V_{rep}(R)$ are determined as the difference of the cohesive energy resulting from self-consistent total-energy calculations on molecular and crystalline reference systems and the related band-structure energy, E_{BS}, for different values of interatomic distances R:

$$V_{rep}(R) = E_{LDA}^{SCF}(R) - E_{BS}(R) \quad . \tag{6}$$

The third term of eq.(5) is added for treating long-range Coulomb interactions. From eqn. (5) one can now derive the interatomic forces as

$$F_{ij} = -\frac{\partial E_{tot}}{\partial R_{ij}}, \quad i = 1,2,\ldots N; \quad j = 1,2,3 \tag{7}$$

acting on the nuclei.

Then, it is possible to apply the O(N) density matrix method of non-orthogonal basis [17], and we will determine the stable atomic configurations of the semiconductor heterostructures.

2.2 Orbital Peeling Method

Before going into the details of the PPM, we firstly estimate the effective pair interaction energies between the constituent atoms in the system. The effective pair interaction energies are very important quantities in discussing the thermodynamic stability of the alloy systems. For instance, it is known that crystalline $Si_{1-x}Ge_x$ mixture is a random alloy at room temperature, and this mixture phase separates into Si-rich and Ge-rich phase below the critical temperature $170<T_c<240$K [18]. It is important (but difficult) to predict qualitatively whether the tendency for phase separation is increased or decreased in the strained superlattice or in the strained overlayers. Recently, it has been pointed out that the amorphous network of a Si-Ge mixture, under thermodynamic equilibrium, does not phase separate. In the present study, we investigate the segregation behavior in the semiconductor heterostructure by calculating the ordering energy ε [$=\varepsilon_{AA}+\varepsilon_{BB}-2\varepsilon_{AB}$] between the constituent atoms A and B, using the tight-binding (TB) electronic theory and orbital peeling method.

The change in the band structure energies ΔF due to introduction of the local perturbation (point defect, or solute atom) is calculated from the following formula [12]

$$\begin{aligned}\Delta F &= \int^{E_F}(E - E_F)\Delta\rho(E)dE \\ &= -\sum_{il} Z_{il} + \sum_{il} P_{il} - (N_P - N_Z)E_F + \sum_{il} Z_{il}^0 - \sum_{il} P_{il}^0 + (N_P^0 - N_Z^0)E_F^0 \,,\end{aligned} \tag{8}$$

where Z_{il} (Z^0_{il}) and P_{il} (P^0_{il}) are the zeros and poles of the Green's function $\overline{G}_i$ (or $\overline{G}_i^0$) corresponding to a recursion starting from coordination sphere i+l as if the previous coordination spheres were absent. N_z (or N^0_z) and N_p (or N^0_p) are the total numbers of zeros and poles of the lattice including the local perturbation (or without it). We perform the calculations of ΔF for a single solute as well as for a pair of the solutes and derive the pair interaction energies between them. The ordering energies of Si_xGe_{1-x} mixture are calculated to be 19meV, and 35meV for the unrelaxed and relaxed atomic configurations, respectively. The order of magnitude of these ε values may be compared with the enthalpy of formation $\Delta H(a\text{-}Si_{1-x}Ge_x)=-14$meV/atom

(x=0.5) for the amorphous a-SiGe alloy at 100K calculated by Tzoumanelas and Kelires [18].

In the present study, we investigate the electronic density of states and the related physical properties of the semiconductor heterostructures using the $sp^3d^5s^*$ model [19,20] for the atomic configurations determined by the molecular dynamics method. The TB parameters of $sp^3d^5s^*$ model for elemental semiconductors are given in Table 1.

	C	Si	Ge
a(Å)	3.5668	5.43	5.6563
E_s	-1.0458	-2.0196	-3.2967
E_p	7.0850	4.5448	4.6560
E_d	27.9267	14.1836	13.0143
E_{s*}	38.2661	19.6748	19.1725
ssσ	-4.3882	-1.9413	-1.5003
s*s*σ	-2.6737	-3.3081	-3.6029
s*sσ	-2.3899	-1.6933	-1.9206
spσ	5.4951	2.7836	2.7986
s*pσ	5.1709	2.8428	2.8177
sdσ	-2.7655	-2.7998	-2.8028
s*dσ	-2.3034	-0.7003	-0.6209
ppσ	7.5480	4.1068	4.2541
ppπ	-2.6363	-1.5934	-1.6510
pdσ	-2.1621	-2.1073	-2.2138
pdπ	3.9281	1.9977	1.9001
ddσ	-4.1813	-1.2327	-1.2172
ddπ	4.97779	2.5145	2.5054
ddσ	-3.9884	-2.4734	-2.138
Δ/3	0.0	0.0195	0.1325

Table 1: Empirical TB parameters for group-IV semiconductors of $sp^3d^5s^*$ model. The lattice constant a are given in unit of Å at room temperature; all other parameters are given in units of eV with the energy zero at the valence band maximum.

2.3 Path Probability Method

In general, the deposited films on the substrate allowing interlayer mixing have lower surface energy than the corresponding ones without interlayer mixing. In the present study, we use the path probability method (PPM) to study the interlayer mixing of the semiconductor heterostructures.

In the PPM procedure, the path probability function (PPF) is given in terms of the path variables, and then we maximize the PPF to derive the most probable path relations, to obtain the differential equations to describe how the system changes in time. The PPF P is made of three factors: $P = P_1$, P_2 P_3. P_1 is for the jump probabilities including the common activation energy contribution, P_2 is for the activation energy contribution, and it depends on the initial energy level, and does not depend on the final energy. P_3 is for the number of way, and needs careful counting near the interface.

Summarizing the PPM calculations of the junction relaxation of semiconductor heterostructures, we have found the following characteristic features:
(i) At the initial stage of relaxation of a sharp profile, overshooting of the profile occurs.
(ii) Near a sharp junction profile, the atom flux changes sign during relaxation.
(iii) Near the junction, the chemical potential gradient becomes zero at a different time t* from that of the atom flux. There is a time period in which atoms do not flow downhill along the chemical potential gradient.
(iv) The local chemical potential gradient in non-equilibrium state depends not only on the density gradient but also on atomic pair correlation.
(v) While the overshooting is occurring, the free energy of the entire system monotonically decreases.
(vi) The overshooting can be understood by a kinetic reasoning as due to the repulsion of atoms.

For the relaxation process, we can suggest that the lar ge and measurable interlayer mixing occurs at the Ge/Si(001) heterojunction at the initial stage of the relaxation. For heterojunctions like GaAs/AlAs(001) we allow cationic intermixing, which very likely takes place during the growth process. For treating the interdiffusion in the (001) direction of zincblende structure, we simply take one of the sublattices.

In addition, we have also found that the interface disorder influences quite significantly the electronic and mechanical properties of the semiconductor heterostrucutres. Even for the very early stage of the junction relaxation, i.e., after ~100 time steps, the electronic states of the heterojunction are influenced quite significantly by the interface disorder compared with those of the sharp interface. We have found that when one of atoms in the core of the misfit dislocations (both 1/2 <001> (001) edge type and 60˚ shuffle set dislocation) in GaAs/ZnSe(001) system is changed by interface mixing, the dislocation induced gap state is drastically altered, it even leads to the disappearance of the gap states [2]. This indicates that the appearance of electronic bound states of the misfit dislocations must be calculated on the basis of the precise atomic geometries in the core region of the misfit dislocations.

2.4 Lattice Green's Function Method

The fracture behavior of semiconductor heterostructures under applied stress is investigated with the use of the lattice Green's function method [21-23]. For simplicity, we firstly consider the two-dimensional (2D) model system, i.e., 2D square lattice with tetragonal distortion which is deposited on the 2D square lattice substrate, rather than treating the cumbersome diamond cubic or zincblende crystals. The essence of the lattice Green's function method for the fracture problem is summarized as follows.

We introduce a crack in the lattice, where the atomic

bonding between the atom pair facing one another across the cleavage plane is annihilated. Then the force constant matrix **Φ*** of the cracked lattice is obtained from that of the perfect crystal by introducing the force terms on the cleavage surface that annihilate the bonds there. Thus **Φ*** can be written formally as

$$\Phi^* = \Phi - \delta\,\Phi, \tag{9}$$

$$\delta\Phi = [\Phi]_{\text{crack faces}}\,. \tag{10}$$

The solution of the crack problem is obtained by the Dyson equation [21-23]

$$\mathbf{G}^* = \mathbf{G} + \mathbf{G}\delta\,\Phi\mathbf{G}^*\,, \tag{11}$$

together with the "master equation" $\boldsymbol{u}=\mathbf{G}^*\boldsymbol{F}$ for the Green's function, where $\boldsymbol{u}$ and $\boldsymbol{F}$ represent the displacement and external force vectors, respectively.

For simplicity, the external forces are taken to be the atomic pair forces acting on the two atoms near the center of the crack, in addition to the so-called "thermal misfit stress" arising from the difference in the thermal lattice expansion coefficients in the heterostructures. In the present study, the effects of misfit strains in the film layers on the crack properties are investigated by modifying the non-linear cohesive force law at the crack tip region. We calculate the crack stability diagram for the interface crack as well as for the "vertical crack" located perpendicular to the interface plane. It has been found that the critical stress for the crack opening and lattice trapping of the interface crack are decreased compared to these in the bulk crystal. The dislocation emission criterion for the interface crack is also significantly different from those of the bulk crystal.

3. CONCLUSIONS

We have studied the atomistic and mechanical properties of nanoscale semiconductor heterostructures, using the O(N) TBMD and path probability methods. This method is very efficient and reliable scheme to study properties of large scale systems. In the present study, we have considered semiconductor (001) heterostructures with ideal interfaces as well as those with interface disorder. For heterojunctions like GaAs/AlAs and ZnSe/GaAs, we allow cationic intermixing, which very likely takes place during the growth process. For treating the interdiffusion in the (001) direction of zincblende structure, we use a vacancy mechanism of diffusion and simply takes one of the sublattices. We have found that the interface disorder influences quite significantly the electronic properties of the semiconductor heterostructures. We have also found that the properties of defects like dislocations and cracks in nanoscale materials depend sensitively on the size of the crystallites and differ significantly from those of the bulk materials.

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