A new Embedded Atom Method potential for atomic-scale modeling of metal-silicon systems

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Summary

A new formulation of EAM potential is developed for the description of interatomic interactions in metal-silicon systems. The potential is based on reformulation of the Embedded Atom Method (EAM) potential for metals and Stillinger – Weber (SW) potential for silicon in a compatible functional form. The potential is parameterized for Au-Si system and tested by comparing the predicted energies and structural properties of representative Si-Au structures to the results of LDA calculations. First molecular dynamics simulations performed with the new potential for a Au monolayer island on the 2×1 reconstructed Si (001) surface showed formation of a silicide region at room temperature as observed experimentally and in earlier Modified EAM (MEAM) simulations. The preliminary results obtained with the new computationally-efficient EAM potential show considerable promise for investigation of metal – semiconductor interfacial phenomenon.

Introduction

The miniaturization of the micro-electronic devices and interconnects down to the nanometer scale has called upon considerable interest in the understanding of the metal – silicon interfacial phenomenon at the atomic scale. Molecular dynamics and Monte Carlo atomistic simulation techniques have a potential for providing detailed information on the structure and properties of the interfaces. The progress in this direction, however, is hampered by the lack of reliable and computationally efficient interatomic potentials for metal-silicon systems. For metals, the Embedded Atom Method (EAM) [1] is currently the method of choice in classical atomistic simulations, whereas the majority of atomistic simulations for silicon are performed with either Stillinger – Weber (SW) [2] or Tersoff (TF) [3] potentials. The Modified Embedded Atom Method (MEAM) by Baskes [4] includes parameterization for both metals and silicon and, thus, provides an opportunity to study metal-silicon systems. However, the angular screening function used as a cutoff mechanism in MEAM makes this potential to be computationally expensive. Moreover, the binding energies for surface adatoms on the 2×1 reconstructed (100) Si surface predicted with the

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MEAM potential were found to be significantly larger than those predicted with electronic structure calculations [5]. A comprehensive comparative study of the 2×1 reconstructed Si (001) surface performed with a particular emphasis on diffusion paths and activation energies [6] pointed to the overall better performance of SW potential [7] as compared to TF [8] and MEAM potentials [5]. The reformulation of the SW potential into the framework of the MEAM potential by Thijsse [9] provides a possible direction towards the development of a united metal-silicon potential retaining the properties of SW silicon, but the angular screening leaves the MEAM potential computationally expensive. In this work, an alternative computationally efficient potential based on reformulation of EAM and SW potentials in a compatible functional form is presented. Simulation results for several representative Si-Au structures are related to LDA calculations and earlier MEAM simulations.

The EAM potential with explicit angular dependence

In the most straightforward formulation, the combined energy for the SW and the EAM potentials can be written as

$$E_i = \sum_{j\neq i}\frac{1}{2}\phi(r_{ij}) + F(\rho_i) + \sum_{k>j}\sum_{j>i}\lambda\exp\left[\frac{\gamma}{r_{ij}-r_c}+\frac{\gamma}{r_{ik}-r_c}\right](\cos\theta_{jik}+1/3)^2 \qquad (1)$$

were $\varphi(r_{ij})$ is the pair potential term, $F(\rho_i)$ is the embedding function, r_{ij} is the distance between atoms i and j, ρ_i is the total electron density at atom i due to all other atoms in the system, and the third term is the three-body angular term in the SW potential with θ_{jik} corresponding to the angle between vectors $\vec{r}_{ij}$ and $\vec{r}_{ik}$ originating from atom i. The electron density ρ_i is calculated as a linear summation of partial electron density contributions from all neighboring atoms j. The linear summation can be converted into summation of a product of partial electron densities from atoms j and k, which in turn can be separated [9] into pair terms ($j = k$) and unique triplets ($k > j$, $j > i$):

$$\rho_i = \sum_{j\neq i} f_j(r_{ij}) = \left(\left[\sum_{j\neq i} f_j(r_{ij})\right]^2\right)^{1/2} = \left(\sum_{k\neq i}\sum_{j\neq i} f_j(r_{ij}) f_k(r_{ik})\right)^{1/2} =$$

$$= \left\{\sum_{j\neq i}[f_j(r_{ij})]^2 + 2\sum_{k>j}\sum_{j>i} f_j(r_{ij}) f_k(r_{ik})\right\}^{1/2} \qquad (2)$$

This formulation of the EAM has a three-body term in the expression for the total electron density function, which allows us to reformulate the combined EAM-

SW potential given by Eq. (1) into conventional EAM form with an angular dependent electron density for Si atoms, as defined by the following equations:

$$E_i = \sum_{j \neq i} \frac{1}{2} \phi(r_{ij}) + F(\rho_i) \tag{3}$$

$$\rho_i = \left\{ (1-h) \sum_{j \neq i} \left[f_{ij}(r_{ij}) \right]^2 + 2 \sum_{k>j} \sum_{j>i} f_{ij}(r_{ij}) f_{ik}(r_{ik}) (\cos\theta + 1/3)^C \right\}^{1/2} \tag{4}$$

where the partial electron density contributions are defined by the type of bond rather than the type of the neighboring atom only, hence in Eq. (4) we have $f_{ij}(r_{ij})$ instead of $f_j(r_{ij})$. Two parameters, h and c, are added to ensure that the potential described by Eqs. (3) and (4) reduces to the conventional EAM for pure metal and SW for pure silicon. For metals, $h = c = 0$ excludes the angular dependence and thus reduces to the original EAM potential. For silicon, $h = 1$ and $c = 2$ are used to reduce the electron density function into the three body function of SW potential. To ensure that the potential reduces to the original SW form, functions $f_{ij}(r_{ij})$ and $F(\rho_i)$ are defined for Si atoms as

$$f_{ij}(r_{ij}) = f_e \exp\left(\frac{\gamma \sigma_{ij}}{r_{ij} - r_c} \right); \qquad F(\rho_i) = \frac{\lambda \varepsilon}{2(f_e)^2} \rho_i^2 \tag{5}$$

where parameters γ, σ_{ij} and r_c are taken from the original SW potential and the parameter f_e is chosen based on the characteristics of metal-Si interaction. For the Si-metal interaction, the presence of a silicon atom contributes to the electron density of a neighboring metal atom through the first (radial) term of Eq. (4), whereas the presence of a metal atom contributes to the electron density of a neighboring Si atom through the second (angular) term of Eq. (4). While the parameters for Si-Si and metal-metal interaction are defined by the original EAM and SW potentials, the functional form and parameterization of electron density and pair functions for metal–Si interaction can be adjusted to reproduce the thermodynamic and structural properties of corresponding silicides and/or properties of metal-Si interfaces.

Application to Au–Si system

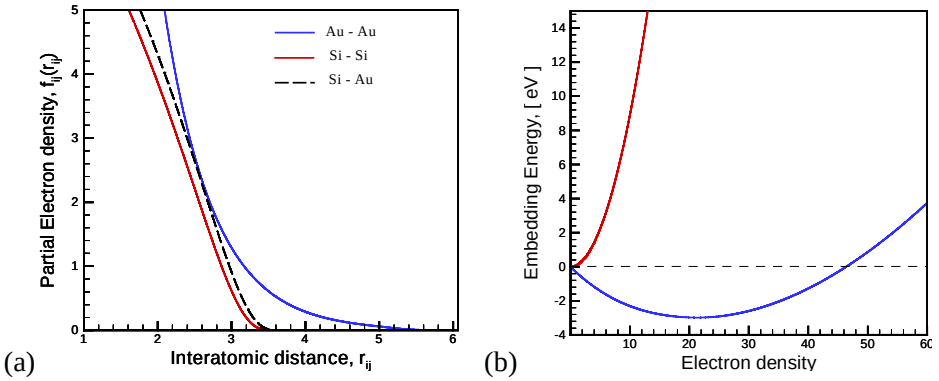
In this section we present the results of the first test of the potential for Au-Si system. The formulation of EAM by Johnson [10] is used for Au. Au-Si interaction is described with the same functional form for the pair potential and the partial electron density as for the SW silicon. In the absence of reliable experimental thermodynamic data for Au-Si system, the parameters of the parts of the potential describing Au-Si interaction are chosen based on the results of calculations performed within the local density approximation (LDA) for several representative Au-Si structures [11]. The following set of parameters

(σ^{AuSi} = 2.13805 Å, ε^{AuSi} =1.5 eV, r_c^{AuSi} = 3.8437 Å, $f_e^{SiSi} = f_e^{AuSi}$ = 16.0, and γ = 1.2) provides a good match between the LDA and angular-dependent EAM results for the cohesive energy and lattice constant of the Au/Si alloy in the $L1_2$ structure, the Au vacancy formation energy in the B1 (NaCl) structure, and the energy of substitutional Au atom in the crystalline Si matrix. There is also a good agreement between the values of the Au-Si bond length in the $AuSi_4$ cluster. The value of the total energy predicted for $AuSi_4$ with EAM potential, however, is almost half of that obtained in LDA calculations. The results of the calculations performed with LDA, MEAM [11], and angular-dependent EAM are shown in Table 1. The plots for the partial electron density functions for Si – Si, Au – Au and the Si – Au interactions and the embedding functions for Au and Si are shown in Figure 1.

	LDA [11]	EAM	MEAM [11]
Energy of Au vacancy in B1 structure [eV]	5.672	6.088	5.672
Energy of substitutional Au atom in c-Si [eV]	6.944	8.445	7.087
Lattice constant of $L1_2$ structure [Å]	4.025	4.0844	4.150
Cohesive energy of $L1_2$ structure [eV/atom]	4.533	4.473	4.939
Total energy of $AuSi_4$ cluster [eV]	16.5	8.4445	17.45
Au-Si bond length in $AuSi_4$ cluster [Å]	2.25	2.3489	2.01

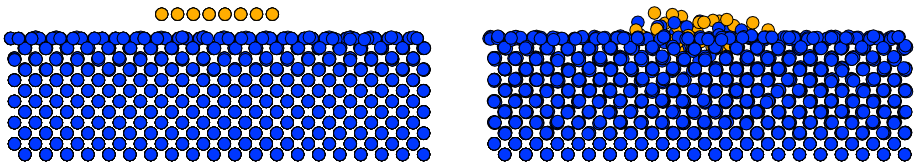
Table 1. Properties of Au/Si systems predicted in LDA [11], MEAM [11], and angular-dependent EAM calculations. The energies of Au vacancy and substitutional impurity are defined as the energy needed to remove an Au atom to infinity.

As an additional test of the potential, we perform molecular dynamics simulations of the evolution of a two-dimensional island of 32 Au atoms on the 2×1 reconstructed Si(001) surface. The Si substrate consists of 12 monolayers with 200 atoms each. The initial configuration of the Au/Si system is shown in Figure 2(a). Fast intermixing between the Au and the Si atoms is observed at a temperature of 350 K, as clearly visible in the snapshot showing a side view of the system at 100 ps after the start of the simulation in Figure 2(b). The observation of intermixing agrees with the results of Low–Energy Ion Scattering (LEIS) experiments [12] and recent MEAM calculations [11] which indicate the formation of silicides at the Au-Si interface even at a very low Au coverage (0.11 ML). Thus it can be concluded that the simple and computationally efficient EAM potential with an explicit angular dependence provides a reasonable description of Au-Si system with the accuracy that is comparable to that of the more complex and computationally expensive MEAM potential.



(a) (b)

Figure 1. Plots of the partial electron density functions $f_{ij}(r_{ij})$ and embedding functions $F(\rho_i)$ used in simulations of Au-Si system described within the framework of angular-dependent EAM potential. The partial electron density functions are shown in (a) for Si-Si (red line), Au-Au (blue line), and Au-Si (dashed line) interactions. The embedding functions are shown in (b) for Au (blue line) and Si (red line). The antibonding embedding energy for Si is a mere fitting aimed to reproduce the original SW potential and should not be considered as a bond order function.



(a) (b)

Figure 2. Initial (a) and final (b) configurations in a molecular dynamics simulation of an evolution of a two-dimensional island of 32 Au atoms on the 2×1 reconstructed Si(001) surface upon annealing at 350 K for 100 ps. The side view of the system in (b) shows the intermixing of Au and Si atoms.

Conclusions

A combined EAM – SW potential is suggested in this paper for the description of interatomic interactions in metal-silicon systems. The potential is based on reformulation of the EAM potential in a form that includes an explicit angular dependence for the electron density functions for Si-Si and Si-metal interactions and reduces to conventional SW potential for pure silicon. The potential is computationally more efficient as compared to MEAM and allows for an easy extension to different material systems for which SW and EAM potentials have been parameterized. First tests simulations indicate that the

angular-dependent EAM potential is capable of providing a good description of energies and structural characteristics of Au-Si system predicted in LDA calculations. The intermixing of Au and Si atoms at low Au coverages on Si (001) surface agrees with experimental observation of the silicide formation at room temperature. The preliminary results obtained with the new potential show considerable promise for investigation of metal nanostructures on silicon surfaces and other interfacial phenomena. Significant further work is needed, however, to optimize the functional form and parameters of electron density contributions in metal-Si interactions.

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