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Tight-binding-based empirical potentials: molecular dynamics of wafer bonding

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Abstract

Molecular dynamics simulations using tight-binding methods or based on an empirical potential derived from the tight-binding approximation have been employed to describe atomic interactions at interface created by the macroscopic wafer bonding process. The bond order potentials including π-bonds are used to predict the interaction of diamond wafer surfaces: strong covalent bonding is possible for flat and clean C(0 0 1)-2 × 1 surfaces under ultrahigh vacuum (UHV) conditions and at room temperature, C(1 1 1)-2 × 1 surfaces will bond very weakly and debond already at moderate temperatures. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Wafer bonding, i.e. the creation of interfaces by joining two wafer surfaces, has become an attractive method for many practical applications to microelectronics, micromechanics or optoelectronics [1]. For biomedical applications it is desirable to bond together diamond layers with no intermediate bonding layer present. Silicon–silicon bonding is possible without an intermediate bonding layer if performed under ultrahigh vacuum (UHV) conditions. Covalent bonding of silicon can thus be accomplished even at room temperature as also predicted by molecular dynamics simulations [2,3]. Subsequently, UHV bonding of GaAs/GaAs and InP/GaAs has also been shown to work successfully [4,5].

However, the atomic processes determine the behavior of extended defects at a microscopic level, thus influencing the macroscopic properties of bonded materials. While, in principle, it is now possible to predict material properties by using quantum-theoretical ab initio calculations with a minimum of free parameters, the only method to simulate atomic processes with macroscopic relevance is the molecular dynamics (MD) method using suitably fitted many-body empirical potentials. Investigating perfect or distorted surfaces (steps, reconstruction, adsorbates, facets, mistilt, twist rotation) of different semiconductor materials enables one to study the elementary processes and the resulting defects at the interfaces as well as to characterize the ability of the potentials itself.

The MD simulations have successfully been used to describe UHV bonding experiments for Si(1 0 0) [3], and hydrogen-passivated hydrophobic bonding process [6], and to analyze the defect structure at bonded interfaces [7–9]. For instance, starting with two perfect and parallel-oriented Si

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blocks with perfectly aligned 2×1 reconstructed (1 0 0) surfaces yields perfectly bonded structures. Fast heat transfer, 90° starting configuration, or including steps or small rotational misorientations result in configurations no longer perfectly coordinated. After bonding over steps partial dislocations are left or special structural units occur, called the 42m dreidel. The screw dislocations forming the network of the (0 0 1) low-angle twist grain boundary can dissociate intrinsically into two 30° partials along the {1 1 1} glide planes, and the nodes at the intersections are formed by symmetrical characteristic groups of atoms. Little has been reported on the bonding of amorphous silica (a-SiO_2) surfaces [10,11], which may be the basis to describing hydrophilic wafer bonding. In addition, the transferability of the simulations to other materials systems is not well suited up to now. On the other hand, conventional transmission (TEM) and high-resolution electron microscopy (HREM) structure imaging has been applied to investigate the resulting interfaces and the defect structures at an atomic level [12], which in combination with calculated IR spectra provides a good experimental evidence of the results.

As in the case of silicon wafer bonding, MD simulations are applied to understand the atomic processes at the interfaces of bonded diamond structures. Special attention will be drawn to the question of whether the energy locally released during the bonding process may lead to the transformation of thermodynamically metastable diamond to thermodynamically stable graphite. Such a graphitization process prevents the use of bonded diamond layers in devices because of the poor mechanical properties of graphite layers.

2. Method

The modeling of the interaction of diamond surfaces by molecular dynamics simulations is far more difficult than for silicon as the π-bonding character at the surfaces has to be considered. Calculations based on a full quantum mechanical description are far too time-consuming for macroscopically relevant systems. Simple models based, for instance, on the Stillinger–Weber potential or the Tersoff potential (which were used successfully for silicon [3–9]) are inappropriate to describe the properties of different carbon structures. In particular, a model that will predict reliably how diamond surfaces interact must at least describe diamond, graphite and the diamond surfaces correctly.

Therefore, it is of importance to find physically motivated semi-empirical potentials starting mostly with the moments of the electron density and using tight-binding representations [13]. A second moment approximation of the tight-binding model can be used to establish a general form at the level of the Tersoff potential with at least only four free fit parameters [14,15]. A further enhancement is possible based on the bond order potential (BOP4) [16,17], which is given up to the further-level continued fraction of the Greens function. Its ability is demonstrated in the following (see also [18,19]); the details will be published elsewhere. Fig. 1 describes schematically the relation between the bond order terms used in the Tersoff potential and the steps in the derivation of the analytical form of the bond order potentials. We use an orthogonal tight-binding model in the parametrization of Xu et al. [20] to describe the interatomic interactions. The molecular dynamics simulations are performed using the implementation of Horsfield et at. [17]. Within this model, the exact tight-binding bond orders are approximated by analytical expressions for the σ- and the π-bond, hence allowing molecular dynamics simulations at a speed comparable to that achieved by other empirical methods. Since the bond orders predicted by this model are in good agreement with the exact bond orders, the simulations of free surfaces and interacting surfaces agree well with the tight-binding results as shown in the results below. The model is able to describe carbon in the graphitic and diamond phases reasonably well. The bond lengths and energies of the C(0 0 1)-2×1 and the C(1 1 1)-2×1 reconstruction are in good agreement with the experimental results and quantum mechanical calculations.

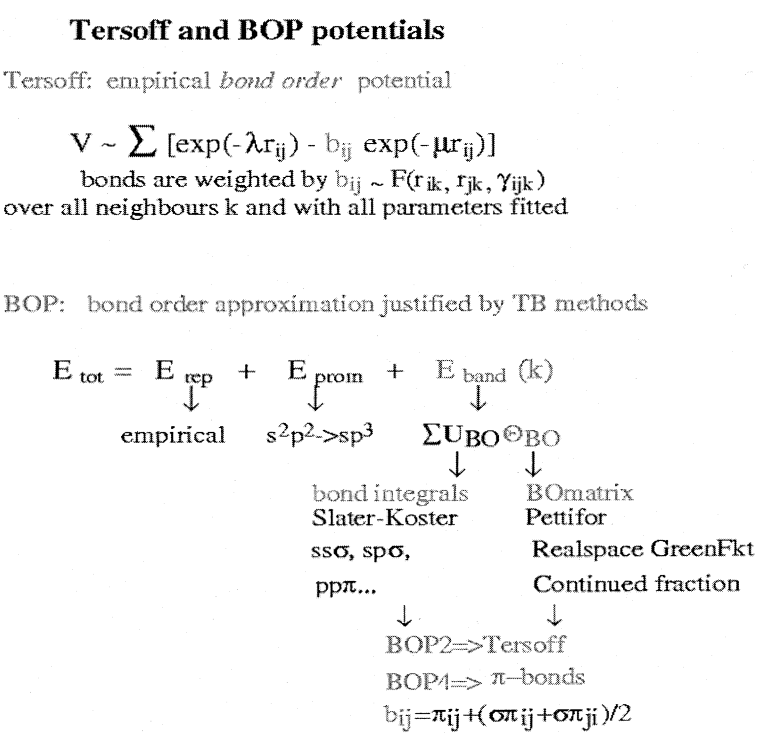

Fig. 1. Bond order terms used in the Tersoff potential versus the derivation of the analytical form of the bond order potentials.

3. Results

The simulations show that covalent bonds can form between C(0 0 1)-2 × 1 surfaces already at room temperature. Fig. 2(a) shows the result of the simulation for a small cell using a tight-binding MD. The tight-binding level of the simulation is necessary to describe π-bonds correctly. Both direct tight-binding and the semi-empirical MD using a BOP4 potential, which, however, enables one to use far more atoms in the calculation, show the same bonding behavior, i.e. structures and energies. The dimerized structure of the surfaces are still present but the bonds change from the "double bond" character to a "single bond" one, with an interface of fourfold coordinated atoms forming. Due to the broken π-bond of the dimer, the dimer bond length increase from 1.4 to 1.67 Å, the bond length between the dimers of the two surfaces is 1.55 Å and the interface energy is 6.57 J/m^2. For a 90° twist rotation or monoatomic steps, covalent bonding is possible, too, leading to the dreidel structure as in silicon [7] and an energy of 6.72 J/m^2.

Using a similar starting configuration for C(1 1 1)-2 × 1 surfaces, the simulations show that the surfaces repel each other rather than form a covalently bonded interface because the environment of the surface atoms is far more graphite-like than that of the C(0 0 1)-2 × 1 surfaces, preventing spontaneous bonding. However, covalent bonding can be achieved if one starts with a distance between the surfaces of about 1.8 Å, which might be realized via weak external forces or van der Waals forces. In this case, small structural changes (i.e. bond lengths and bond angles) within the surfaces allow the bonding between them, as shown in Fig. 2(b), here applying the BOP4 potential. There is almost no energy gain from such an interface compared to two isolated surfaces. Simulations at room temperature show that the surfaces stick together indicating that there is an energy barrier to separate them again. At a simulation temperature of approximately 500 K the surfaces debond.

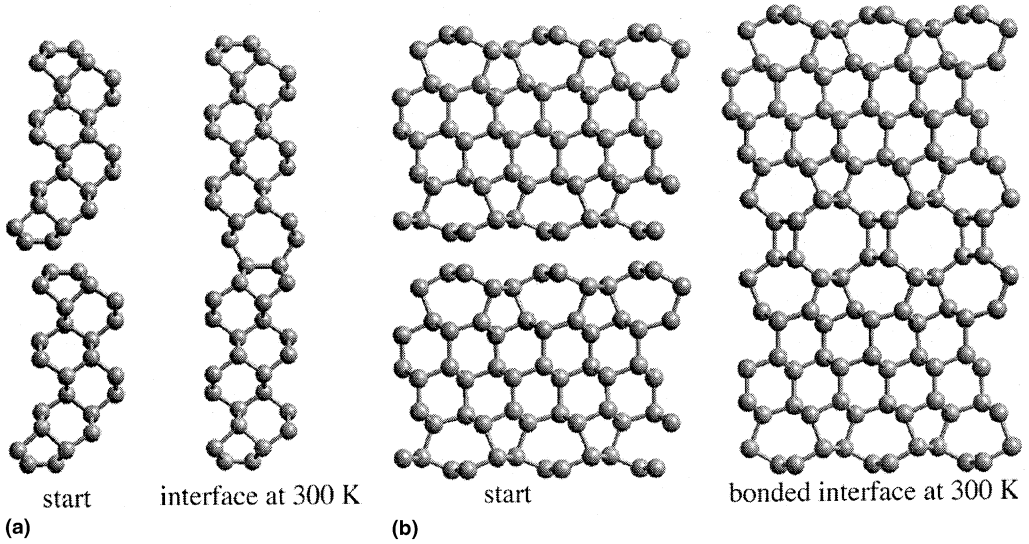

Fig. 2. MD simulations of bonding diamond surfaces: (a) C(0 0 1)-2 × 1 with tight-binding MD, (b) C(1 1 1)-2 × 1 and using a BOP4 potential.

For room temperature bonding, the simulations predict no graphitization. While the interface consisting of C(1 1 1) surfaces debonds already at moderate temperatures, the interfaces generated of C(0 0 1) surfaces are predicted to be very stable. Graphitization along the (1 1 1) planes occurred at approximately 2000 K. It turned out to be impossible to create a perfect bulk material by heating up the interface and breaking the dimer bonds. This is demonstrated in Fig. 3, showing typical examples of incomplete bonding at C(1 1 1) surfaces. Because of the weak bonding of the C(1 1 1) surfaces, debonding occurs at steps as shown both for the mono- and the diatomic step structures in Figs. 3(a) and (b), respectively. Fast heat transfer results in metastable configurations fivefold bonded as in Fig. 3(c). The metastable configurations may be generated due to restriction of the next neighbor interaction of the short-range BOP potential. To overcome this deficiency the interlayer

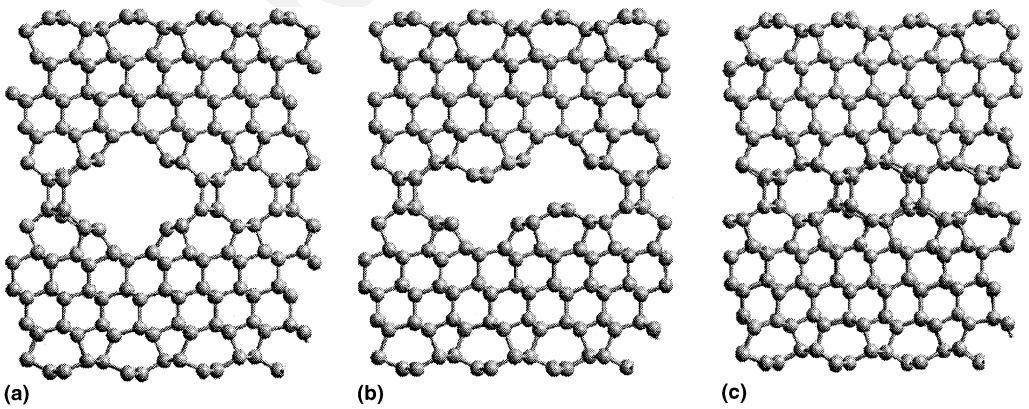

Fig. 3. MD simulations of metastable structures at bonded C(1 1 1)-2 × 1 surfaces: (a) interacting monoatomic steps, (b) debonding at diatomic steps, and (c) fivefold bonds as result of fast heat transfer.

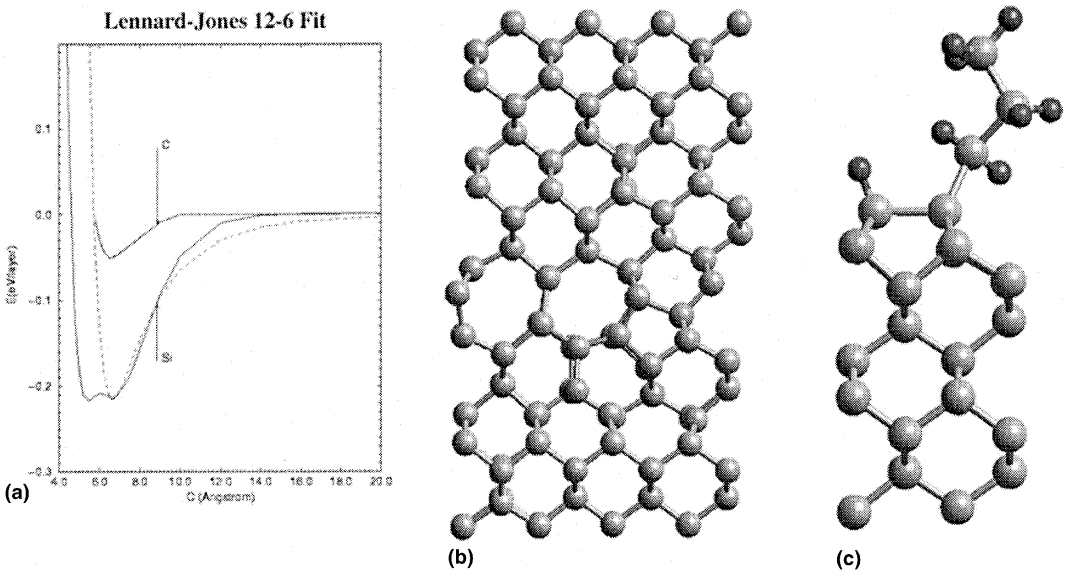

Fig. 4. (a) The interaction minimum energy for graphite C and "graphitic" Si as function of the lattice parameter c (continuous curves, DFT database with optimized lattice constants $a_C = 0.244$ nm and $a_{Si} = 0.386$ nm) and for best Lennard–Jones fit (dashed curves), (b) C(0 0 1)-2 × 1 bonding over steps, and (c) C_3H_7 radical attached to a C(0 0 1)-2 × 1:H surface (one H is desorbed and not shown).

forces must be included into the empirical potential by combining smoothly a suitably parametrized short-range potential with a long-range potential at a common cutoff. Fig. 4(a) shows the fit of a Lennard–Jones potential to a LDA data basis varying the c/a ratio of the lattice constants up to the minimum which characterizes the physical absorption [21].

The effect of surface steps is of great interest because it is important to know whether surfaces steps will prevent the formation of a continuous interface, or whether bonding over steps is possible as in the case of silicon. For simulations including surface steps, much bigger models are necessary, which can be described solely using the BOP4 potential. To investigate the effect of surface steps, we prepared a model in which both of the interacting surfaces had a monoatomic height step. At room temperature, the upper terraces interact as in the case of perfect surfaces. The lower terraces are too far apart so that no bonds form between them. The simulation shows, however, that bonding over steps is possible at elevated temperature without melting the bulk material or transformation to graphite (Fig. 4(b)).

Inspired by most recent experiments [22] we have also investigated how passivated surfaces can be bonded via reactive organic molecules. In the experiments, complex long-chained organic molecules with reactive end-groups are used. Our tight-binding simulations predict that hydrocarbon radicals can be attached to a hydrogen-passivated C(0 0 1)-2 × 1 surface, see Fig. 4(c). Wafer bonding will then be possible if a similar reaction occurs on a second surface.

4. Conclusion

The simulations show that covalent bonding of diamond surfaces should be possible provided the surfaces are sufficiently flat. Polycrystalline wafers, C(1 1 1) wafers or silicon covered with a diamond-like carbon layer, where a more graphite-like environment of the surface atoms is expected, are probably far more difficult to bond covalently than are C(0 0 1) or silicon surfaces. Bonding over steps will be possible only at elevated temperatures. Hydrogen-passivated surfaces are likely to bond via reactive organic molecules. Thus, simulations

based on potentials derived from the bond order expansion are used to enhance the physical reliability of the method and to predict the bonding behavior of a wide variety of semiconductors.

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