

Molecular dynamics studies of interacting hydrogenated Si(001) surfaces

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The interaction of hydrogenated Si(001) surfaces is studied by means of molecular dynamics using an empirical potential. Above a certain critical external force covalent bonds may be formed between the surfaces even at room temperature, leaving a hydrogenated interface. The critical force is related to the assumptions of the molecular dynamics, thus scaling with the potential, heat transfer, boundary conditions, and the weak long-range interaction omitted. Below this critical force, the hydrogen-hydrogen interactions prevent covalent bonding. © 1997 American Institute of Physics. [S0003-6951(97)01542-8]

Silicon wafer bonding has become a technology that is increasingly used for the fabrication of silicon-on-insulator substrates, power devices and silicon-based sensors and actuators.^{1,2} Most of the applications are realized on hydrophobic or hydrophilic bonding under atmospheric conditions followed by an annealing step to reach high bonding energies. For various applications it would be desirable to perform wafer bonding at room temperature with a bonding energy close to that of the bulk material. Recently, covalent bonding was shown to be possible even at room temperature under ultra-high vacuum (UHV) conditions.³ However, it might be desirable to reach the bulk bonding strength also for passivated surfaces in order to make this technique easier and more relevant for industrial applications.

Classical molecular dynamics (MD) simulations with sufficiently large systems and using suitable empirical potentials have been shown to give insight into the physics of the bonding process for silicon surfaces under UHV conditions.⁴ In addition, possible interface structures were predicted to result from the bonding process, from which the corresponding HREM contrast were simulated^{5,6} to interpret the experimental observations.

Chung *et al.*⁷ have demonstrated that they are able to bond various cleaned semiconducting materials under UHV conditions, applying external forces. In the present paper MD simulations demonstrate that it should be possible to bond hydrogen-passivated silicon surfaces under similar conditions.

We use the parametrization of the Tersoff potential, proposed by Murty and Atwater,⁸ for modeling silicon-hydrogen interactions. The potential expresses the total energy V of the system as the sum of pairwise interactions V_{ij} :

$$V = \frac{1}{2} \sum_{ij} V_{ij}, \quad (1)$$

$$V_{ij} = f_c(r_{ij}) (A e^{-\lambda r_{ij}} - b_{ij} B e^{-\mu r_{ij}}), \quad (2)$$

where r_{ij} is the distance between atoms i and j , $f_c(r_{ij})$ is a cutoff function which determines the range of interaction, and b_{ij} is an empirical bond order term which depends on the neighbors of the bond. The parameters depend on the atomic species i and j as well as on their next neighbors.

This potential reduces itself to the Tersoff (II) potential⁹ in the absence of hydrogen, and to the potential used by Brenner¹⁰ for hydrocarbons in the absence of silicon. This empirical potential correctly describes the properties of hydrogenated Si(001). The possible surface reconstructions, ranging from (1×1) to (3×1) patterns depending on the hydrogen coverage, and their energies are in good agreement with the experimental data.^{11,12} The potential yields good results also for small molecules like SiH₄ and Si₂H₆, and hydrogen defects in silicon. It was used to study the diffusion and bonding of SiH₃ molecules on the Si(001) surface.¹³

Since covalent bonding of the surfaces was of interest, van der Waals forces were neglected, which allow hydrophobic bonding of passivated surfaces having bond energies of about 10 mJ/m² at room temperature.^{14,15} Our calculations are restricted to the Si(001)-3×1 surface, but the qualitative behavior is not expected to change at higher or lower hydrogen coverage.

All calculations were performed for a constant number of atoms and a constant volume at a fixed temperature of 300 K (NVT-Ensemble). The model (336 Si atoms and 64 H atoms) consists of two Si(001)-3×1 surfaces (see Fig. 1), which corresponds to a hydrogen coverage of 4/3 monolayers. Periodic boundary conditions are applied to the direc-

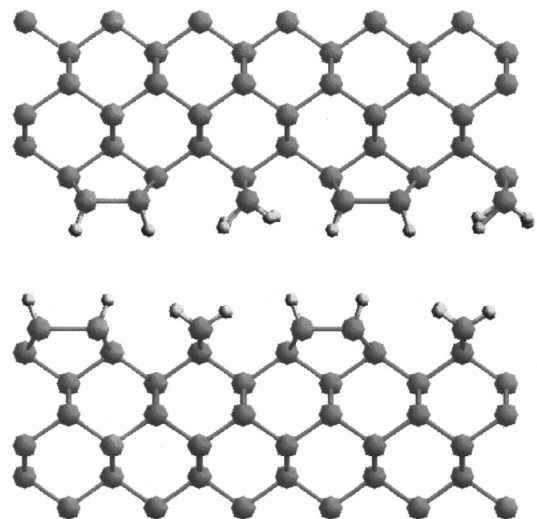


FIG. 1. Snapshot of an initial configuration of (100)-silicon wafer bonding with a 4/3 monolayer hydrogen coverage.

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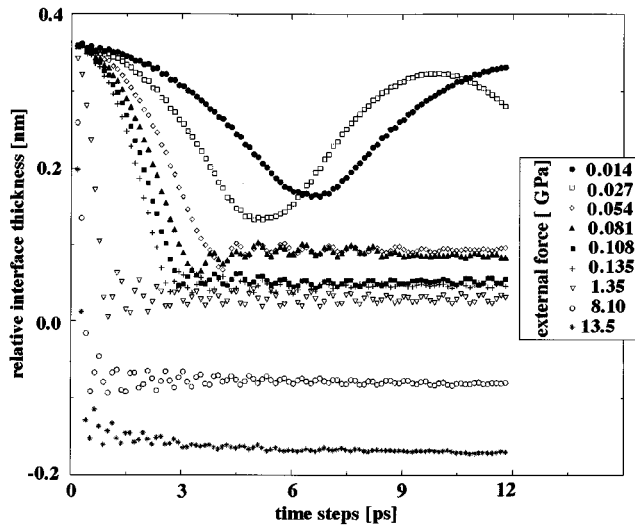


FIG. 2. Equilibrium distances of hydrogenated Si surfaces as a function of the MD simulation time for different external forces applied.

tions parallel to the surfaces, whereas all atoms can move freely in the third direction. Starting with a separation below the cutoff range of the hydrogen–hydrogen interactions, the distance of the surfaces increases due to the strong repulsive forces of the hydrogen atoms. Since we have neglected van der Waals interactions, there is no equilibrium distance where the surfaces stick together.

To model the behavior if external forces are applied, we start from a surface distance larger than the cut-off range. External forces in the direction perpendicular to the interface are added to the interatomic forces of the two outermost atomic layers of each slab. A time step of 1.2×10^{-16} s is used to account for the fast dynamics of the hydrogen atoms.

Figure 2 shows the distance of the surfaces versus the simulation time for different applied external forces. The distance is defined as follows: It is the difference of the average z coordinates of the uppermost and the lowest atomic layers of the whole model, subtracting the thickness of a perfect Si crystal with the same number of atomic layers. This allows one to measure the distance of the surfaces also for bond breaking and rearrangements at the interface. At a weak external force of about 10^{-12} N/atom, the surfaces approach each other, and start to interact by repelling each other, which leads to an oscillatory behavior. Because of our model extension, this force per atom corresponds to an outer normal stress (or pressure) of about 13.5 MPa. Thus, in the following, ‘‘force per atom’’ and ‘‘outer stress’’ are synonymously used, with all data given in Pa.

For increasing external forces, as seen for a stress of 27 MPa in Fig. 2, the time average distance of the surfaces decreases. For an external force of 54 MPa, the surfaces are so close together that the silicon atoms of one surface may interact with the hydrogen atoms of the opposite surface, causing a weak attraction of the surfaces. With the external forces ranging between 54 and 81 MPa, the distance of surfaces varies only slightly. There are different patterns of ordering of the hydrogen atoms between the silicon surfaces. However, we have not investigated this effect in detail since this ordering is expected to depend also on van der Waals forces between the hydrogen atoms. In order to check

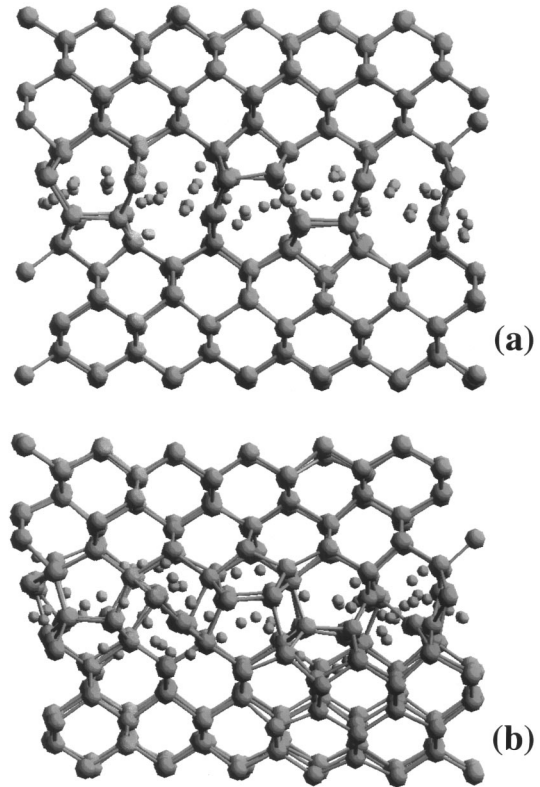


FIG. 3. Typical MD snapshots of bonded, hydrogenated Si surfaces after applying different external stresses, (a) 108 MPa, (b) 13.5 GPa.

whether such a configuration actually shows some adhesion between the surfaces, or whether the observed distance between the surfaces is only due to a dynamic equilibrium of the external force and a repulsion between the surfaces, the external force was switched off and the calculation was continued for further 10^5 time steps. As a result, we obtained a small relaxation, but no separation of the surfaces. Figure 3 demonstrates this effect, showing qualitatively equivalent snapshots of the surface relaxation without debonding, for stresses of 108 MPa [Fig. 3(a)] and 13.5 GPa [Fig. 3(b)], i.e., near the critical force and the maximum value applied, respectively.

Further increasing the external forces causes an increasing number of silicon-silicon interactions between the surfaces, and a further decrease of the distance. As a consequence, hydrogen atoms desorb from the surface, being able to diffuse into the crystals or, more likely, along the interface [Fig. 3(b)]. The interface itself consists of two distorted layers of silicon atoms. Some of the free bonds are saturated with hydrogen, and the previous surface reconstruction is still observable. The thickness of the system is now smaller than that of an equivalent perfect Si crystal of the same number of atomic layers. However, besides the deformations directly at the interface and some hydrogen interstitials, there are no additional defects created in the bulk material, since the applied forces are always smaller than the theoretical shear stress of about 40 GPa, and the critical force is much smaller than the Peierls stress of about 4 GPa.

To investigate whether the disordered interface result from the hydrogen which is still present, we performed simulations for clean surfaces using the same potential. It turned

out that a molecular dynamics run using this potential will not lead to a perfect crystal. For the range of external forces tested in our simulations, this result is independent of the fact whether external forces are applied, or not. In previous calculations using a modified Stillinger–Weber potential,⁴ the results strongly depended on the way in which the temperature of the system and the energy gain at the interface were treated.

In our simulations, the critical force necessary to attain the adhesion of the surfaces is somewhere between 50 and 80 MPa. However, for various reasons, the force which is indeed experimentally necessary, possibly differs from the value reported here: First, one has to consider that we are dealing with empirical potentials, and, second, the boundary conditions as well as the restricted size of the model may not capture all the experimental conditions. Thus the resulting critical force depends on the assumptions of the molecular dynamics modeling as, e.g., heat transfer, elastic coupling, and neglecting weak long-range interactions.

Our molecular dynamics simulations indicate that covalent bonding of hydrogenated Si(001) surfaces may occur if external forces are applied. The forces have to exceed a certain critical value, which is necessary to impose silicon–hydrogen interactions across the opposite surfaces. Below this critical force, only hydrogen–hydrogen interactions of the opposite sides may occur, thus preventing covalent bonding. The value of this critical force as well as the resulting interface structure might be refined by the use of boundary conditions, which can describe thermal and elastic effects.

However, it was our aim to show that, in principle, covalent bonding of the surfaces is possible, even if the latter are saturated with hydrogen, provided sufficiently large external forces are applied. The magnitude of the forces for which we predict covalent bonding is in a range which can experimentally be obtained. Corresponding experiments are in progress.

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