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Enhanced semi-empirical potentials in molecular dynamics simulations of wafer bonding

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Abstract

Molecular dynamics simulations using suitably fitted empirical potentials have been employed to describe atomic interactions at interfaces created by the macroscopic wafer bonding process. Investigating perfect or distorted surfaces (steps, reconstruction, adsorbates, facets, mistilt, twist rotation) of different semiconductor materials as well as of silica enables one to study the elementary processes and the resulting defects at the interfaces as well as to characterize the ability of the potentials used. Preliminary simulations on the basis of empirical potentials developed by the bond order tight-binding approximation, yield enhanced interface structures and energetic relaxations as well as transferability to new materials systems. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Empirical molecular dynamics; Wafer bonding; Bonded interfaces; Tight-binding potentials; Bond order approximation; Dislocation interaction

1. Introduction

According to the importance of wafer bonding for semiconductor electronics and micromechanics applications (see the reviews [1,2]) there is an increasing interest to describe the atomic forces at the interfaces. The atomic processes determine the behaviour 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 miminum of free parameters, e.g., density functional (DFT) based approximations, the only method to simulate atomic processes with macroscopic relevance is the molecular dynamics (MD) method using suitably fitted many-body empirical potentials. Such simulations enable a large number of particles (10^4–10^9) and sufficient relaxation times (10–1000 ps) to be considered. However, the electronic structure and the nature of the covalent bonds can only be described indirectly. Therefore, it is of importance to find physically motivated semiempirical potentials starting mostly with the moments of the electron density and using tight-binding representations [3]. 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 [4]. A further enhancement is possible based on the bond order potential (BOP4) [5], which is an approximation up to the fourth-level continued fraction of the Greens function. Its ability is demonstrated in the following for Diamond wafer bonding, the details will be published elsewhere.

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The MD simulations have successfully been used to describe ultra-high-vacuum bonding experiments for Si(100) [6], hydrogen passivated hydrophobic bonding processes [7], and to analyze the defect structure at bonded interfaces [8–10]. However, little has been reported on the bonding of amorphous silica (a-SiO_2) surfaces [11,12], which may be the basis or a first step to describe 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 [13], which in combination with calculated IR-spectra provides a good experimental evidence of the results.

2. Method

The method of molecular dynamics (MD) solves Newton's equations of motion for a molecular system, which results in trajectories for all particles considered in the system. Thus, MD provides a tool suitable for simulating time-dependent processes at an atomic level as, e.g., the growth of crystals, the reordering of interfaces, the interaction between adatoms and surfaces as well as the relaxation of core structures of lattice defects. The calculations are performed with the fifth-order predictor–corrector algorithm of Gear using a constant volume (NVE ensemble) or a constant pressure (NpT ensemble) and time steps of the order of 0.25 fs to ensure the proper calculation of surface modes. NVE is preferred for free surfaces and simulations to calculate the diffusion constants, whereas NpT enables the relaxation of the cell dimensions and the application of an outer pressure, which is important for glass generation and the simulation of wafer interfaces, respectively. For controlling the system temperature, either all particle velocities are slightly rescaled at each time step, or solely the outer layers of the structure model, still applying periodic boundary conditions parallel to the interfaces. In the latter case, the energy dissipation and thus the dynamic bonding behaviour are controlled by the transfer rates of the kinetic energy at the borders of the model describing an energy flux into a macroscopic substrate. In addition, for straight defects created at the interfaces the system is coupled elastically to the bulk wafers.

As mentioned above, the interatomic forces in covalent solids can completely be described only if the influence of the local environment according to the quantum electronic structure is also included. Simple pair potentials and potentials of the valence force field or related types as, e.g., the Keating (K) potential, are restricted in their validity to solely small deviations from the equilibrium. However, empirical potentials have been developed, which allows one to simulate the non-local many-body interaction sufficiently well. The potential most often used for semiconductors is the Stillinger–Weber (SW) potential, consisting of two- and three-body interactions, with a smooth cut-off behind the nearest neighbour distance, and which is fitted to the cohesive energy, the lattice constant, and the melting point. It supports a symmetric quasi-five-fold coordinated reconstruction at interfaces and fails for large distortions in the surrounding of defects. Nevertheless, it allows the next neighbour interaction to be included by rescaling, which is a presupposition to the simulation of the dynamical behaviour without preordered surfaces and prescribed topology. Thus, e.g., the interaction of two silicon surfaces can be studied by correctly revealing the 2×1 reconstruction of a clean Si(100) surface. The potential used for silica is the modified Born–Mayer–Huggins (BMH) ionic pair interaction combined with a weak three-body term. The BMH interaction combines a repulsion and a Coulomb term, which is screened to avoid the long-range Ewald sums, the three-body term is similar to SW. In addition, a Rahman–Stillinger–Lemberg (RSL) term was used for the water interactions.

The potential of Tersoff (here are at least three parametrizations TI, TII, TIII) consists of a third-order cluster structure and has the shape of a bond order, which is a complete other functionality. It predicts the asymmetric reconstruction with fourfold coordinated atoms at interfaces with defects. Therefore, it was applied to investigate the cores of 60° partial dislocations in Si and other defects left after bonding two wafers. Because of the short range of the Tersoff potential it was supposed that the bond topology is given by the usual process starting with separated Si blocks of a suitable surface structure and orientation (surface reconstruction, steps and adsorbates) and applying long-range potentials. For hydrogenated Si-wafer bonding, the Tersoff potential, proposed by Murty and Atwater, was used to model the silicon–hydrogen interaction. The potential is equivalent to TII without hydrogen, and to the potentials used by Brenner for hydrocarbons without silicon. Thus hydrogenated Si(001) surfaces are well described including reconstructions of the (1×1) and (3×1) types.

Most of the existing potentials available are of the SW or T types, compared to each other [14] they offer advantages and disadvantages in range of validity, physical meaning, fitting and accuracy as well as applicability. Such restrictions exist for other potential types, too, even if the embedded atom approximation (EAM) is used or special environment dependencies are constructed to enhance the elastic properties near defects, as, e.g., in [15]. In addition, all potentials are not well applicable for long range interactions. The dif-

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ficulty of developing suitable empirical potentials is threefold: one has to guess a functional form, motivated by physical intuition, fitted to ab initio and experimental data bases as well as reflecting nonfitted properties. Tight binding approximations allow to develop physically motivated potentials. The repulsive energy is assumed to be an embedded pair interaction and the promotion energy reflects the energy difference of valence s and p electrons. The most important part is the expansion of the bond energy into hopping matrix elements, which directly are given by the two centre integrals of Slater and Koster, and bond order terms. The bond order terms can be approximated by Lanczos recursion algorithm [16], where the level of the continued fraction determines the functional form and the applicability.

3. Results

The molecular dynamics simulation starting with two perfect and parallel-oriented Si blocks with perfectly aligned 2 × 1 reconstructed (100) surfaces and applying a slow heat transfer approach yields perfectly bonded structures [6]. However, a fast heat transfer, a starting configuration, with the dimer rows in orthogonal domain orientation, or including steps or small rotational misorientations, result in configurations no longer perfectly coordinated. The energy flux at surfaces is the driving force for the bonding process over atomic steps, too. The upper terraces behave like perfect surfaces, i.e., a weak attraction owing to the next neighbour interaction initiates the dimers to rearrange and to create new bonds. The energy the bonds have gained dissipates, increasing the kinetic and elastic energies of the bulk. The resulting avalanche effect implies the bonding of the lower terraces, too. However, after bonding over double layer steps, a disturbed interface and defects are left which may finally relax to 60° partial dislocations or shuffle-set dislocations accompanied by a row of vacancies. Monolayer steps rotate the dimerization direction in the neighbouring domains and give rise to a stacking fault of either intrinsic or extrinsic type, depending on the dimer orientation in the adjacent terraces. Thus the interfaces between, or outside, the single-layer steps are characterized by a 90° twist-rotation. The effect of a small twist angle as a rotational misorientation without other defects at the surface, results in a mosaic-like interface structure. After sufficient relaxation under slow heat transfer conditions almost all atoms have a bulk-like environment separated by misfit dislocations, which may have a high rate of kinks. The influence of adsorbates has been investigated, e.g., for hydrogenated surfaces assuming two Si(001)–3 × 1 blocks [7], corresponding to a hydrogen coverage of 4/3 monolayers, and NVE at 300 K. A time step of 0.12 fs is used to account for the fast dynamics of the hydrogen atoms. External forces in the direction perpendicular to the interface are added to the interatomic forces of the two outermost atomic layers of each slab. The main result of the corresponding MD simulations consists in the finding of an energy barrier characterized by a critical pressure of about 80MPa to overcome the repulsion forces and to create covalent bonds across the hydrogenated interfaces.

Using the Tersoff or BOP-like potentials and metastable or well-prepared starting configurations yields further structure relaxation and energy minimization [8–10]. Fig. 1 shows some of the resulting minimum structural units and defect core reconstructions, which can be confirmed by DFT calculations if the units are small enough. The 90° twist boundary and using the SW potential showed a metastable fivefold coordinated interface with a symmetric structure normal to the interface characterized by a Pmm(m) layer group. The relaxation of the same configuration through the Tersoff potential is (2 × 2) reconstructed and can be imaged to consist of structural units with a $\bar{4}2m$ (D_{2d}) point group symmetry, thus called the $\bar{4}2m$ dreidl (cf Fig. 1a). The dreidl fits two rotated half crystals of minimal structural disorder and fourfold coordination described by a P($\bar{4}$)m2 layer symmetry. The interface energy is reduced by approximately 20%. Similarly, the two sets of a/2[110] screw dislocations (S) in the network, which accommodates a small rotational twist, relax into a configuration breaking symmetry: it has twice the period of the array distance corresponding to the twist angle and shows two different types of intersections (T1 and T2 in Fig. 1a, right hand side). They are formed by symmetrical characteristic groups of atoms having the same point group symmetry 222 (D_2) as the core structures of individual screws. Most of the atoms forming T1 remain fourfold with large bond-angle and bond-length distortions, but there are two atoms in the unit with a fivefold surrounding. The T2-nodes are formed by more complicated atomic groups, however, showing solely a fourfold coordination. MD simulations as well as TEM and HREM investigations showed that the screw dislocations forming the network of the (001) low-angle twist grain boundary can dissociate intrinsically into two 30° partials along the {111} glide planes (cf Fig. 1b), i.e., emitting the partials (P1,P2) into the bulk. A 3-step relaxation using SW, K and T potentials were necessary to reach the minimum-energy structure. Comparing the perfect screw (S) with the dissociated configuration shows that there are bonds parallel to the dislocation line (cf the ⟨111⟩ projections). Comparing the experimental HREM image (cf Fig 1c) with simulated ones allows one to directly analyse the core configurations of the partials in (110)-projection.

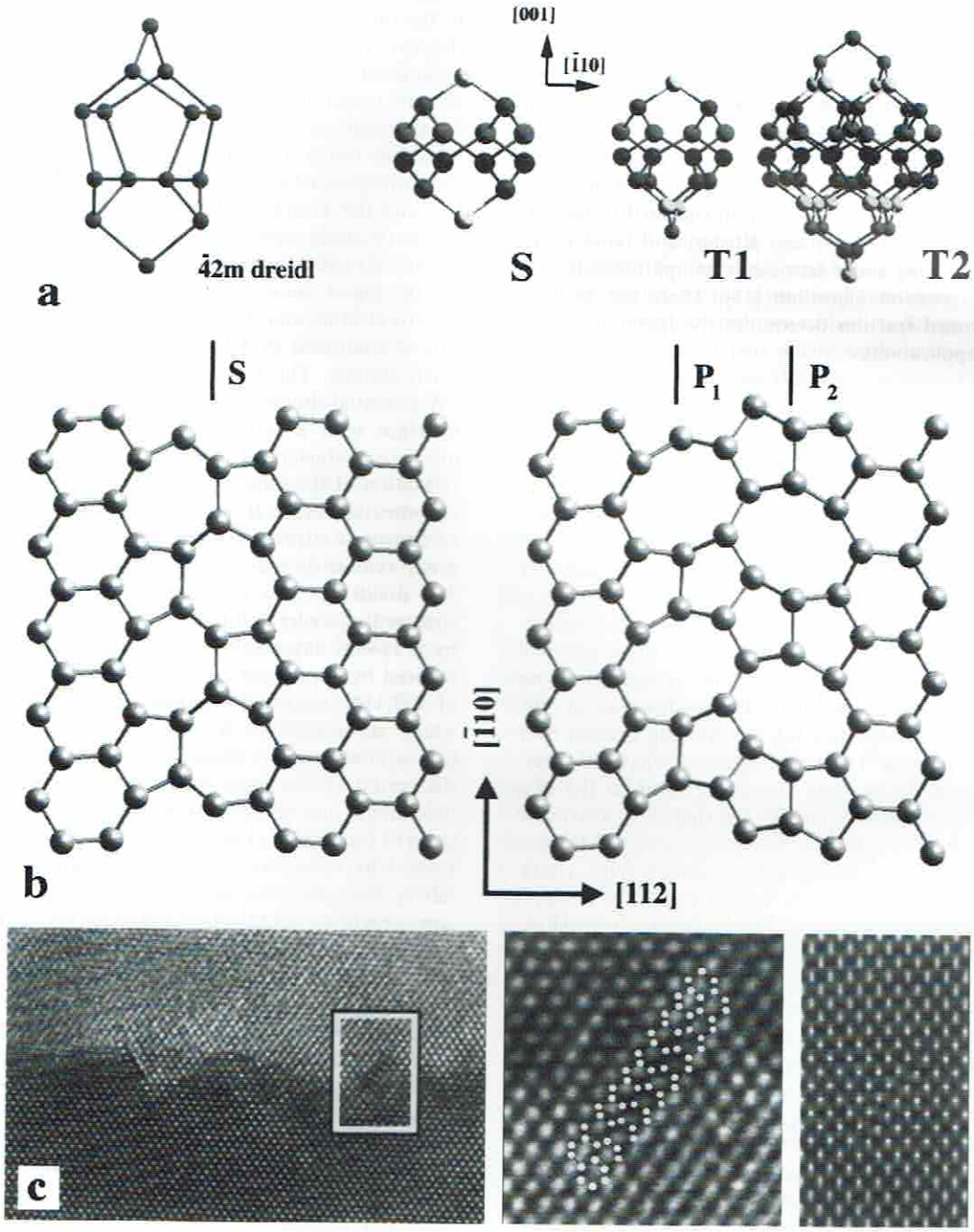

Fig. 1. Defect core reconstructions: (a) 4̄2m dreidl as the structural unit of a 90° twist boundary and the core structures of the two stable nodes (T1,T2) for fully TII-relaxed screw (S) networks; (b) (111) projections of the perfect 1/2[110] screw dislocation (S) and the dissociated 30° partials (P1, P2) after 3-step MD relaxation with SW, K, and TII potentials; (c) [110] cross-sectional HREM image of a wafer-bonded twist boundary, enlarged stacking fault ribbon bounded by two 30° partials, and image simulation from the MD relaxed model with (P1, P2).

Fig. 2 demonstrates the MD simulation of the silica amorphization, hydroxylation and bonding. The generation of amorphous silica models starts from crystalline silica structures. Free surfaces were generated from annealed glass models using further relaxation at a constant volume by extending the simulation box normal to the surface, with reflecting walls at the top and bottom of the cell, and applying periodic boundary conditions otherwise. After relaxation, the reconstructed surfaces were bombarded with H_2O groups (Fig. 2a). These relaxed silica glasses have a highly reactive surface. Water molecules settling on the surface have at least three different kinds of bonding sites. They correlate to sites with dangling bond, with reduced oxygen bridges (Q_3-sites), or where silanols are created by cracking Si—O bonds in the surface. Two adjoining hydroxylated surfaces, each covered with 1–2 monolayers of water are brought into contact to simulate the wafer bonding between silica and/or hydrophilic Si. Fig. 2b presents a snapshot of the interface at 0.8 T_g after 250 ps. Longer and shorter silica strands loosen from the surface and migrate into the gap. This bridging effect occurred at temperatures higher than the glass transition (T_g) or during long-time simulations. The many open spaces indicate that smaller portions of the surface have broken from this layer and most probably migrated into the gap. Pits formed in one area of the surface through the action of temperature and pressure, help to form bridging covalent bonds in other sections of the wafer. There are three different regimes, which can be related to experimental observations: the short-time behaviour at low temperatures and pressures leads to hydrogen-bonded surfaces with a low bonding energy. The bonding energy can be increased either by increasing the temperature and/or the pressure, or by tempering at lower temperatures for sufficiently long times. Increasing the temperature and/or pressure enables to dissolve the silanol and water groups and to lower the diffusion barriers. Thus the interface gap can be closed by forming direct silica-silica bonds. The long-time behaviour shows a reactive rearrangement of the surface, which locally leads to strong silica bonds even at low temperatures.

Finally, in Fig. 3 the BOP4 potential is used to simulate the bonding process of diamond. Two different surfaces are used, viz. (001) and (111) with an

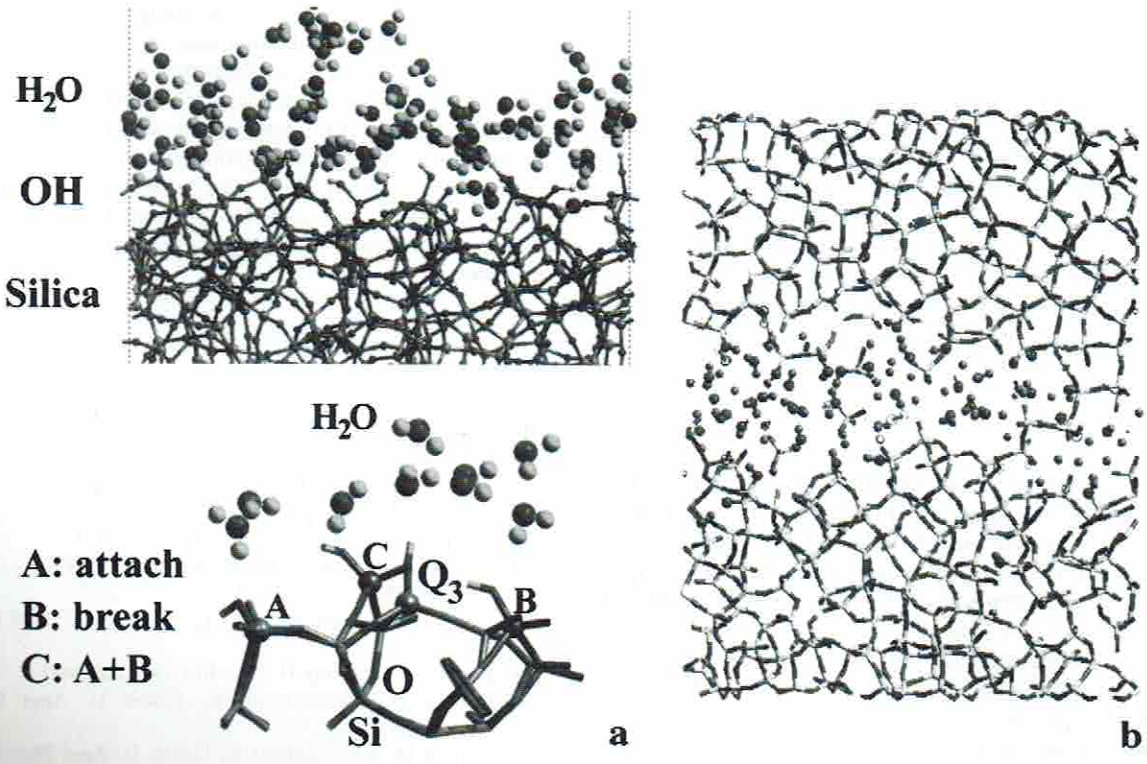

Fig. 2. Snapshots of MD simulated hydrophilic wafer bonding: (a) water deposition and silanol reaction sites; (b) covalent silica bond formation at $p = 5$ GPa, $T = 0.8\ T_g$, $t = 250$ ps.

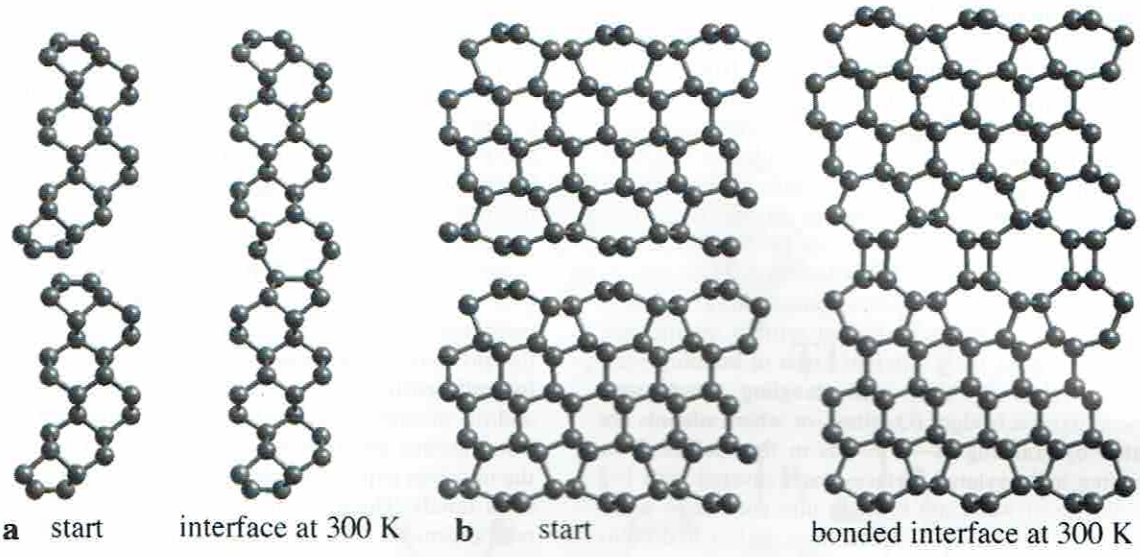

Fig. 3. MD simulations of bonding diamond surfaces: (a) C (001)–2 × 1 with tight-binding MD; (b) C (111)–2 × 1 and using a BOP4 potential.

equivalent reconstruction in Fig. 3a and b, respectively. Both the tight-binding MD in Fig. 3a and the semi-empirical MD using a BOP4 potential in Fig. 3b, which enables one to use far more atoms in the calculation and which demonstrates the quality of the fit, show the same bonding behaviour. The tight-binding level is necessary to describe correctly the π-bonds. The dimers remain, the π-bonds are broken during the bonding process, there is no graphitization at temperatures not too high. The fourfold coordination is the resulting stable minimum structure. On the (111) surface, therefore, the outermost dimers must be rearranged from threefold coordinations to a fourfold one.

4. Summary

Molecular dynamics simulations based on empirical potentials are used to investigate the elementary steps of bonding two Si(001) wafers. The system is coupled elastically to the bulk wafers, and the energy dissipation is controlled by the transfer rates of the kinetic energy at the borders of the model. Calculated bonding energies and forces strongly depend on the surface termination, native oxides, adsorbates, and the process control. Twisted starting configurations, steps or rotational misorientations result in special interface configurations mostly no longer perfectly coordinated. Bonding energy and forces are determined not only by the surface structure but also by surface adsorbates as shown by MD of hydrogen on hydrophobic Si and by water–silanol reactions on silica surfaces describing the hydrophilic termination. The simulations lead to a better understanding of the physical processes at the interfaces and support the experimental investigations, especially the electron microscope structure analysis. Simulations based on potentials derived from the bond order expansion are used to enhance the physical reliability of the investigations and to predict the bonding behaviour of a wide variety of semiconductor surfaces.

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