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Semiconductor-surface restoration by valence-mending adsorbates: Application to Si(100):S and Si(100):Se

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A set of criteria is proposed for choosing adsorbates that can lead to restoration of the ideal bulk-terminated geometry on semiconductor surfaces. Two systems, Si(100):S and Si(100):Se, which are likely to fulfill the surface-restoration criteria are investigated in detail through first-principles calculations. These restored surfaces are energetically stable against structural changes such as embedding the adsorbates in subsurface sites.

It has long been recognized that surfaces of semiconductors have a structure different from that of the bulk. The reconstruction of the surface strives to minimize the high energy of broken covalent bonds, which would exist on an ideal bulk-terminated plane. Recently, the restoration of semiconductor surfaces to their original bulk-terminated geometry has been achieved by carefully chosen adsorbates: the surface layer consists entirely of adsorbate atoms, at positions very close to those of a bulk-terminated plane.[1-4] The restored geometries are structurally very simple, yet they represent real solid surfaces. Thus, they are ideally suited for detailed experimental and theoretical studies that critically test our understanding of the physics of semiconductor surfaces (see, e.g., Ref. 3).

The idea of surface restoration by adsorbates was nascent in studies of more than a quarter of a century ago, but several of the suggested restorations proved impossible to realize [e.g., the restoration of Si(111) by group-III elements, see Ref. 5]. In view of this situation, it is desirable to develop a set of empirical criteria for evaluating surface-adsorbate combinations that can lead to semiconductor surface restoration. [In developing the criteria it is convenient to use, without loss of generality, the Si(111) surface as "proving ground."] The aim here is to give a semiquantitative formulation of notions that have led to successes in surface restoration and can hopefully serve as guides for further studies. The proposed criteria point to two possible candidates for restoration of the Si(100) surface, namely S and Se. The structural and electronic properties of the Si(100):S and Si(100):Se systems were analyzed in detail through first-principles quantum-mechanical calculations. A related system, Ge(100):S, has recently been observed experimentally[4] and studied theoretically.[6]

The most important aspect of surface restoration is a valence difference between the substrate and the adsorbate such that, when adsorbate atoms replace the bulk-terminated plane, all broken covalent bonds are eliminated [we shall refer to such atoms as valence-mending adsorbates (VMA's)]. In the case of Si (valence 4), a bulk terminated (111) plane consists of threefold bonded atoms with one broken covalent bond, containing a single unpaired electron on each surface atom. This situation can be mended by replacing the surface Si atoms by adsorbates of valence either 3, which would eliminate unpaired electrons, or 5, which would create a pair of nonbonding electrons. The latter is sensible only if the extra pair of electrons can be accommodated in a state of energy lower than the lowest antibonding (conduction) state of the semiconductor, otherwise the restored geometry would be unstable. These observations form the first criterion for surface restoration: with respect to a given substrate, VMA's must be either of a lower valence, such that the occupancy of broken bonds is eliminated, or of a higher valence, such that broken bonds are reduced to fully occupied nonbonding states.

The first criterion does not guarantee that the resulting structure is stable. For instance, using this criterion alone, it would seem that both group-III and group-V adsorbates can restore the Si(111) surface to its ideal geometry. However, only group-V adsorbates have this effect,[1-3] whereas group-III adsorbates form complicated reconstructions.[7-9] In order to determine whether a given VMA can lead to a structurally stable restored surface, we shall examine the structure of bulk phases of the adsorbate. This is motivated by the following observation: The bulk phase of those group-V elements which lead to restoration of Si(111) (e.g., P or As) is a layered structure in which every atom has three close neighbors bonded through *sp* hybrids,[10] similar to the ideal Si(111) surface. In contrast, the bulk phase of group-III elements which do not restore the Si(111) bulk-terminated geometry (e.g., Al, Ga, or In), is a close-packed metallic structure with the number of neighbors varying from twelve (Al) to four (In) (Ref. 10) and significant contribution of *d* electrons to metallic bonding. Thus, the second criterion is the requirement that the adsorbate must exist in a bulk phase with the same local bonding geometry as in the restored surface.

An additional criterion is necessary to discriminate between elements of different atomic size due to the possibility of adsorbate-induced surface stress.[11] In particular, VMA's of higher valence than the substrate may require large volume per atom to accommodate nonbonding electrons. One way to predict whether a given VMA is likely to induce large surface stress, is to compare the covalent radii of adsorbate and substrate atoms: When the covalent radii are similar (to within few percent), the prospects for stability increase, since the substrate-adsorbate

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bonds in the restored surface will have a bond-length compatible with both constituents, which tends to reduce the stress. Another aspect that can contribute to stress is the difference between the bond angles of the adsorbate in its bulk phase and in the restored surface geometry. A large difference between these angles can be detrimental to the stability of the restored surface.

A final criterion concerns chemical reactivity, which may adversely affect surface restoration. It is possible that a particular VMA candidate reacts strongly with substrate atoms, forming volatile molecules, for example. In this case, the net result might be a continuous etching of the surface, rather than the formation of a stable adsorbed layer. Alternatively, it may be difficult to deposit a desired VMA to a surface, if its molecular compounds do not decompose on the surface under normal adsorption conditions. One way to quantify this criterion is in terms of changes in bond energy: The formation of the restored surface, starting with the clean reconstructed surface and a molecular compound of the adsorbate, should be an exothermic process but the energy released should not be large on the scale of surface bond energies, otherwise undesired reactions such as etching may follow.

The surface restoration criteria can prove useful in cases of technological importance such as the Si(100) surface, which is used widely as a substrate in electronic devices. In reconstructed form the surface atoms on Si(100) lean toward one another in pairs and form dimer bonds, resulting in a (2×1) periodicity. In the ideal bulk-terminated geometry each surface atom is twofold bonded to subsurface atoms and has two broken bonds.

According to the first criterion, natural VMA choices for Si(100) would be elements with valence 2 or 6. Using the second criterion, we conclude that the best choices are group-VI elements (O, S, Se, Te) because they tend to form structures with twofold coordination and sp^3 bonding hybrids, precisely as required for the restoration of Si(100). According to the third criterion, two of the choices among group-VI elements, namely S and Se, seem particularly promising: the average bond length in their bulk phases is close to that of bulk Si (it differs by -12% for S and -0.4% for Se, see Ref. 10). The fourth choice Te can be dismissed according to the third criterion since its average bulk bond length differs from that of Si by $+22\%$.[10] Finally, O can be dismissed on several grounds: In solid O the atoms are not bonded through single covalent bonds[10] (the second criterion is not satisfied), the Si—O bond length is much shorter than Si—Si bonds (by -32% in the tetrahedrally bonded SiO_2, so the third criterion is not satisfied) and the Si—O bond is energetically much stronger than Si—Si bonds,[12] making the formation of a stable O overlayer on Si(100) unlikely (the fourth criterion is also violated). Using bond-energy values from Ref. 12, we estimate that the restoration of Si(100) by S and Se would be exothermic, with bond-energy gains of 1.5 and 0.4 eV per surface atom, respectively, whereas restoration by O would lead to a bond-energy gain of 4.2–5.3 eV (depending on the reference molecular form of O), which is large on the scale of Si surface bond energies (typically ~ 2 eV). For this reason, studies of O adsorption on Si(100) are usually concerned with the stable surface and subsurface positions where O atoms can be incorporated, rather than with the formation of a surface O layer (see, for example, Ref. 13). In Table I a summary of the structural properties of bulk S and Se is provided, which illustrates their overall similarity to the ideal Si(100) geometry.

A detailed investigation of S and Se terminated Si(100) was undertaken in the context of density-functional theory (DFT) and the local-density approximation (LDA), using norm-conserving pseudopotentials and a large plane-wave basis (including plane waves of kinetic energy up to 10 Ry). The calculations were performed in a slab configuration consisting of eight Si layers. Full atomic relaxation was included by minimization of the calculated Hellmann-Feynman forces. The main features of the relaxed geometries, which indeed resemble closely the ideal Si(100) surface, are given in Table I. The electronic valence charge distributions resulting from these atomic geometries are shown in Fig. 1(a) and 1(b) for Si(100):S and Si(100):Se, respectively. These figures contain Si—group VI—Si surface chains as well as Si chains two layers deeper from the surface. Well-defined covalent bonds between the adsorbates and the substrate are visible along the surface chains. These bonds have a charge distribution similar to covalent bonds found in the bulk of III-V semiconductors.[14] This similarity arises from the valence difference between Si and group-VI atoms which is exactly the same as that between the two constituents of a III-V semiconductor.

We consider next the surface electronic states of Si(100):S and Si(100):Se. Since group-VI atoms were chosen (i.e., VMA's of higher valence than the substrate), we expect fully occupied surface states. Figure 2 displays

TABLE I. Structural parameters of bulk phases of S and Se (from Ref. 10) and of the ideal and restored Si(100) surfaces (bond lengths are in Å, bond angles in degrees).

	Bond length	Bond angle	Basic unit
Rhombic S	2.05	107.9	Puckered S_8 molecules
Rhombohedral S	2.06	102.2	Puckered S_6 molecules
Hexagonal Se	2.32	105.0	Spiral Se chains
Monoclinic Se	2.34	105.5	Puckered Se_8 molecules
Ideal Si(100)	2.35	109.4	
Restored Si(100):S	2.24	118.4	
Restored Si(100):Se	2.34	110.2	

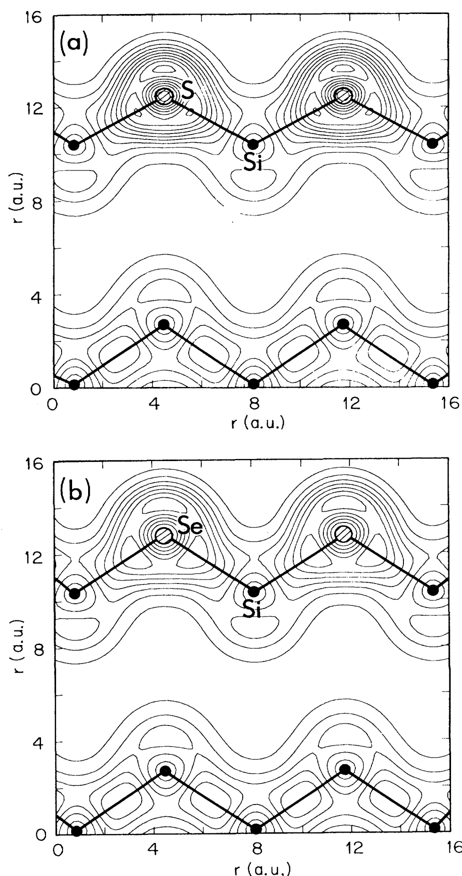

FIG. 1. Electronic charge distribution of (a) the Si(100):S and (b) the Si(100):Se surfaces on a plane containing the surface Si—group VI—Si chains.

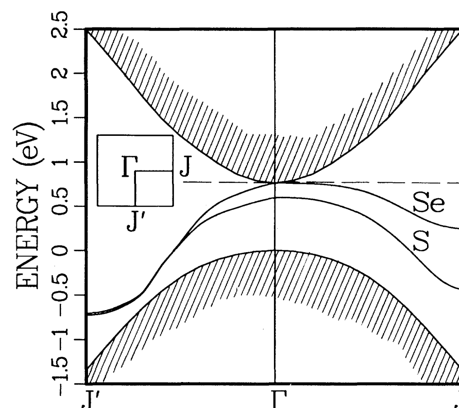

FIG. 2. Energy of the highest occupied surface states along high-symmetry directions of the SBZ (shown in inset) for Si(100):S and Si(100):Se. The shaded area is a projection of bulk conduction bands from a bulk-Si calculation (see text). The dashed line is the Fermi level for Si(100):Se [the Fermi level for Si(100):S lies 0.08 eV lower]. The S and Se surface states are given with respect to the valence band maximum of the slab.

the energy of the highest occupied surface state for the S- and Se-covered surfaces along high-symmetry directions of the surface Brillouin zone (SBZ). The projected bulk bands in Fig. 2 were obtained from a bulk-Si calculation using the same computational parameters (unit cell, plane-wave basis, and BZ sampling) as the slab calculation (a 12 layer slab was used for the band energies). This was necessary to insure that the bulk bands have the proper symmetry and to correct for quantum-size effects on the band gap (in the slab calculation the symmetry along the ΓJ and $\Gamma J'$ directions is broken and the band gap is widened). The energy of the highest occupied surface states lies within the band gap of the substrate. These states have p character and are centered at the group-VI atoms. A similar state in the Ge(100):S system lies lower in energy, near the top of the valence band of Ge.[6] This is probably a consequence of the different relative energy of S valence states with respect to the Si and Ge substrates.

It is likely that electron self-energy effects, which are treated only approximately in DFT and LDA, will give somewhat different energy for the surface states shown in Fig. 2. By analogy to previous studies,[15] we expect that self-energy corrections will lower the energy of these fully occupied surface states, thereby increasing the band gap for the restored surfaces [the DFT and LDA values for the band gaps are 0.16 eV for Si(100):S and 0.0 eV for Si(100):Se].

Finally, we investigate the energetics of structural changes of the restored geometries which will provide a measure of their stability. The different structures considered (shown in Fig. 3) consist of embedding and mixing the adsorbates with substrate atoms at various concentra-

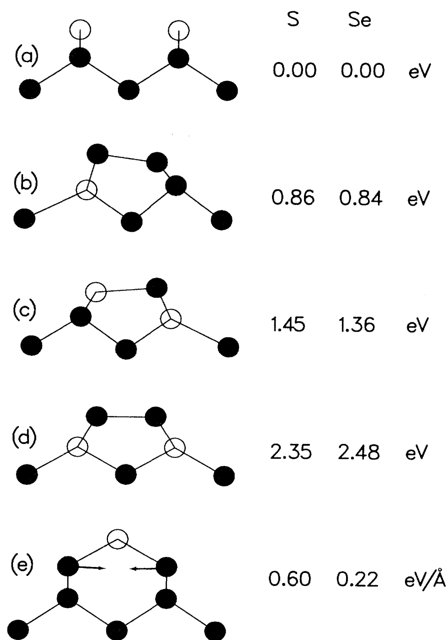

FIG. 3. Relative energies [per (1×1) surface unit cell] of different structures: (a) Restored surface; (b) embedded half monolayer of group-VI atoms; (c) full monolayer of group-VI atoms partially embedded; (d) full monolayer entirely embedded; (e) forces on Si atoms, after removing alternate group-VI atoms along the Si—group VI—Si chains.

tions and depths. Figure 3(a) is the restored geometry, which defines the zero of energy in each case. This geometry is stable against tilting of the group-VI surface atoms in the direction perpendicular to the Si—group VI—Si chains, either in phase or π out of phase.[16] Figure 3(b) corresponds to embedding *half* a monolayer of group-VI atoms under Si atoms. In this configuration the six valence electrons of each adsorbate atom are accommodated by its four bonds to Si atoms and by the two dangling bonds on the surface Si atoms. The energy of this geometry is substantially higher than the restored Si(100):VI surface [see Fig. 3(b)]. Partial mixing of a *full* monolayer of adsorbate atoms with surface Si atoms, as shown in Fig. 3(c), also results in an energy increase. Last, an entire monolayer of group-VI atoms embedded under a layer of Si dimers, as shown in Fig. 3(d), has even higher energy.

The restored surfaces are stable against all of the alternative structures considered above, which span a range of environments for the group-VI atoms. This, however, does not cover the possibility of etching, i.e., the formation of volatile molecules consisting of Si and group-VI atoms. First-principles calculations for this case are not feasible at present, due to the many possible pathways in phase space. Thus, the overall stability of the two restored surfaces can only be assessed by qualitative arguments. First, we note that the S—Si bond energy is larger than that of Si—Si,[12] suggesting that formation of volatile Si_nS_m molecules may indeed be a dominant factor, inhibiting the formation of Si(100):S. This is consistent with experimental observations concerning deposition of CdS on Si,[17] and the temperature dependence of S adsorption on Si(100).[18] This problem is expected to be less severe for Se, although, depending on deposition conditions, it may still be present (see Ref. 19). Second, the Si—group VI—Si angles on the restored surfaces are, in general, larger than the average angle in the bulk phases of S or Se (see Table I). This could give rise to considerable compressive stress along the Si—group VI—Si chains, especially in the case of S. The relative importance of this effect can be estimated by calculating the forces on the two Si atoms bonded to a surface group-VI atom, after removing alternate group-VI atoms along a chain, as shown in Fig. 3(e). The calculated forces, given in Fig. 3(e), indicate the presence of a compressive stress along the Si—group VI—Si chains which is larger in the Si(100):S system than in the Si(100):Se system by a factor of 3. This stress can be relieved by creation of vacancies along the surface chains (the number of vacancies along a chain that would result in optimal Si—group VI—Si bond angle while preserving the optimal Si—group VI bond length, is 3.3% for Se and 10% for S). To summarize, both chemical reactivity and induced stress would tend to inhibit formation of Si(100):S, whereas restoration of Si(100) by Se seems more likely.

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