Surface defects and core excitons at the (2×1) asymmetric-dimer (100) surface of Si

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Predictions are given for the chemical trends in (i) deep energy levels associated with 28 sp^3-bonded substitutional defects, and (ii) energies of Hjalmarson-Frenkel core excitons at the (100) surface of Si, reconstructed according to Chadi's (2×1) asymmetric-dimer model. The predictions suggest that P at this surface should produce a deep level, and that the Hjalmarson-Frenkel surface core exciton should have a binding energy that is strongly site dependent.

In this paper we report a semiquantitative theory of defects at the Si(100)-(2×1) surface with its outer layer reconstructed according to Chadi's asymmetric-dimer model.[1] Our approach is to solve for the band-gap eigenvalues E of the secular equation,

$$\det[1 - G_s(E)V] = 0 ,$$

where $G_s(E)$ is the surface Green's function and V is the defect potential of Hjalmarson *et al.*[2,3] Thus we follow the theory of bulk deep levels,[2] while evaluating G_s using the theory of Allen,[4] evanescent-wave techniques,[5] and the empirical tight-binding basis of Vogl *et al.*[3] A similar method has been applied extensively and successfully to defects at III-V(110) surfaces by Allen *et al.*,[6] and has provided a unified explanation of observed Schottky barrier heights.[7] Details of the method and calculational procedures are available elsewhere.[8]
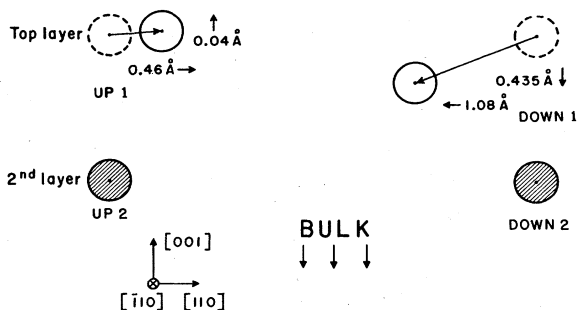
The results of the calculation are predictions of deep

FIG. 1. Illustration of the geometrical structure of Chadi's asymmetric-dimer model for the Si(100)-(2×1) surface in the approximation that only the first plane of atoms undergoes relaxation. The surface is at the top of the figure. The circles denote rows of atoms in the (001) surface, viewed along the (110) direction (referred to the usual face-centered-cubic bulk directions). The rows of atoms in the top layer are displaced from their unreconstructed positions (dashed circles) to the open-circle positions. The displacements of the surface atoms employed for the present work are denoted by arrows. The second-layer rows of atoms are denoted by shaded circles. The plane of the up-1 and down-1 atoms in the plane of the paper lies below the corresponding up-2 and down-2 plane by a perpendicular distance $\sqrt{2}a_L/4$. The up-1 to up-2 distance is $\sqrt{3}a_L/4$, where a_L is the lattice constant.

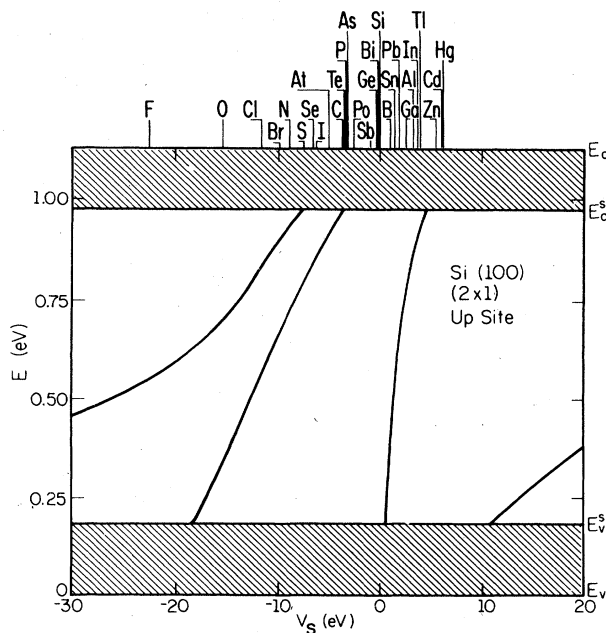
FIG. 2. Predicted deep energy levels for substitutional defects at the up site of the Si(100)-(2×1) surface, reconstructed according to Chadi's asymmetric-dimer model, versus defect potential V_s. The relevant defects appear at the top of the figure at their values of V_s. The shaded area denotes the calculated surface-state bands (which are known experimentally to lie $\simeq 0.5$ eV lower than the calculation predicts[11]). The qualitative features of the calculation and chemical trends of the theory are important and meaningful results.
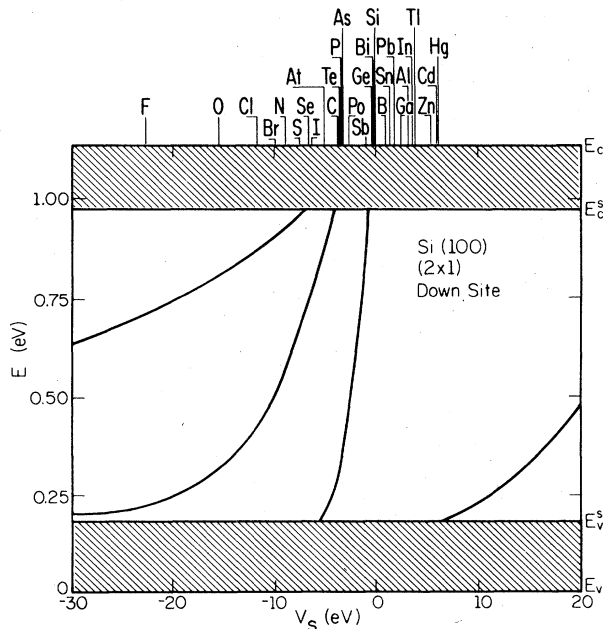
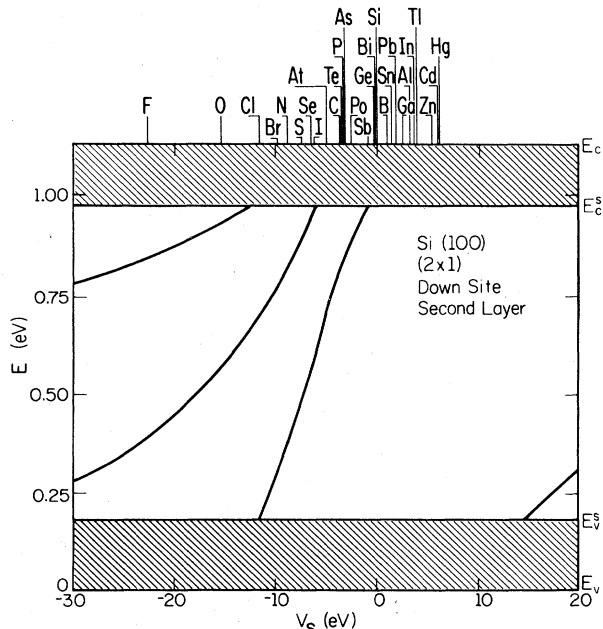FIG. 3. Deep levels at the down site of the Si(100)-(2×1) surface.

FIG. 5. Deep levels for defects at the down site of the second layer from the Si(100)-(2×1) surface.

trap energies E versus defect potential V. V is actually a diagonal matrix in the local sp^3s^* basis, centered on the defect site $V = (V_s, V_p, V_p, V_p, 0)$; in order to present results as a function of a single parameter V_s, we use the rule $V_p = 0.5 V_s$.[9] Figure 1 shows the asymmetric-dimer model reconstruction; Figs. 2—5 show the predicted defect levels for atoms at the "up" and "down" sites of the first and second layers of the asymmetric-dimer reconstructed surface (see Fig. 1).

A major result is that the "deep" defect levels for atoms at the "up" and "down" sites and in the second and first layers[10] are different. This is shown explicitly in Figs. 6 and 7 for the P substitutional impurity and Si vacancy (which corresponds to $V_s \to \infty$), respectively. (Consider only the qualitative aspects of the predictions; do not take the precise energy levels literally; the expected uncertainty is $\simeq \pm 0.5$ eV.[11,12])
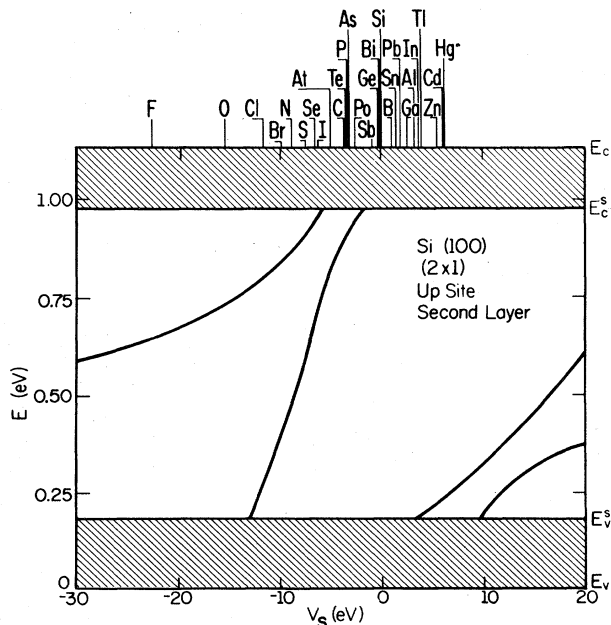

FIG. 4. Deep levels for defects at the up site of the second layer from the Si(100)-(2×1) surface.
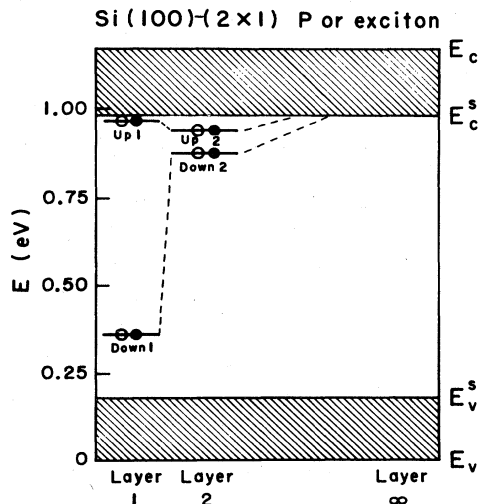

FIG. 6. The predicted energy levels within the surface band gap for substitutional P or a Hjalmarson-Frenkel core exciton (Ref. 13), as a function of layer number (∞ means bulk). The first- and second-layer deep levels all coalesce into a deep resonant level in the bulk. Closed (open) circles denote electronic (hole) occupation of the neutral defect levels. Sites are denoted, e.g., down 2 meaning the second-layer site beneath the down-1 site.
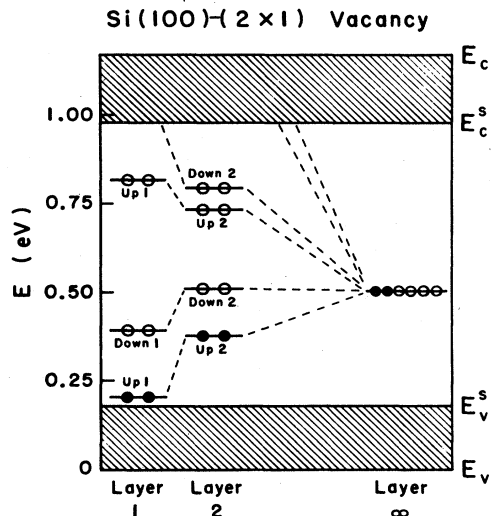
FIG. 7. The vacancy levels predicted to lie in the gap for the Si(100)-(2×1) surface as a function of layer number (∞ means bulk). Electronic (hole) occupation is denoted by closed (open) circles. The first- and second-layer levels all coalesce into the bulk T_2 vacancy deep level (Ref. 2), which, when neutral, contains two electrons and four holes.

Almost all impurities will produce at least one deep level in the gap for one of the four sites near the surface. In particular, the bulk shallow dopants P [Fig. 6 (Ref. 13)] and As, when near or at the surface, are predicted to yield deep levels in the gap. Hence, the Si(100)-(2×1) asymmetric-dimer surface of heavily doped Si should have many extrinsic surface states, with the number being roughly proportional to the surface concentration of dopants.

At the surface, P produces levels near both the middle and the top of the fundamental band gap of Si—a striking prediction that may have direct bearing on the Si $2p$ "core-exciton anomaly"—that the observed binding energy of the Si $2p$ core exciton appears to be considerably larger than predicted by shallow-impurity theory.[14] Insofar as a $2p$ core hole has a charge distribution similar to a proton, the core electron sees the effective nuclear charge Z of Si increased by unity to $Z+1$; that is, it sees a phosphorus defect potential.[13] Thus the energy level of the surface core exciton should approximately equal the energy of a P surface impurity, and the theory predicts that there should be core excitons at the Si(100) surface

with apparent binding energies relative to the conduction-band edge, ranging from $\simeq 0.2$ eV on the up site of the first layer to more than half the band gap ($\simeq 0.8$ eV) on the down site. The important point is not the absolute values of the predicted binding energies (which have significant theoretical uncertainties[12]) but that the variation of binding energy from site to site can be large.

It is possible that this dramatic site dependence of the Si surface core-exciton binding energy has been observed, although not recognized as such. Several authors have reported widely different Si $2p$ core-exciton binding energies,[14] from 0.1 to 0.9 eV, with some speculation that the proximity of the core exciton to the surface affects the binding energy. This variation is comparable with what we predict, 0.2—0.8 eV. Perhaps these diverse experimental results can be understood as due to experiments sensitive to core excitons at different sites.

This site-dependence occurs in part because electronic charge transfers from the down layers to the up layers at the surface. Thus the up site is a pseudo-anion site and the down site is a pseudo-cation at this surface. Chemically, the down site becomes more sp^2-bonded and the up site becomes more p backbonded.[15] The down cation site exhibits the larger exciton binding energy, as expected: In III-V semiconductors cation core excitons generally have larger binding energies than anion excitons. This is because the conduction-band states are cationlike, whereas the valence-band states are anionlike. This trend of the cation-site levels lying below the corresponding anion-site levels holds for the surface vacancies as well as for P or the core exciton.

The present results illuminate the richness of the spectra of surface impurities. At the present, however, there are few data for the energy levels of known surface impurities; we hope that the present work will stimulate more experiments in this direction and provide a guide for elucidating the chemical trends in data.

ACKNOWLEDGMENTS

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us to display the calculated results as a function of the single parameter V_s, and therefore to comprehend the global chemical trends in defect levels more easily. For a prescription for determining more accurately the energy levels of a specific defect from the curves of Figs. 2—5, without making the approximation $V_p \simeq 0.5 V_s$, see also H. P. Hjalmarson, Ph.D. thesis, University of Illinois, 1979; H. P. Hjalmarson, R. E. Allen, H. Büttner, and J. D. Dow, J. Vac. Sci. Technol. **17**, 993 (1980).

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