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# Reversal in the order of impurity binding energies with atomic energies

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Whereas atomistic models predict that binding energies of donor levels in semiconductors increase with the ionization potential of the free impurity atoms, we find that a special enhancement of the screening in the solid predicts, for chalcogen impurities in silicon, a reversal in this order.

Attempts to systematize the observed binding energies of deep defect levels in semiconductors according to the properties of the isolated impurity atoms has been a central theme in semiconductor physics.[1–4] The underlying concept, used in defect theories as diverse as effective-mass,[1] tight-binding,[2,3] and chemical scaling[4] approaches, has been that the binding energies $E_b^I$ of different impurities $I$ in the same host crystal are ordered according to the ionization potentials $IP_I$ of the isolated impurity atoms, if one considers the same crystal site location and charged state for all impurities. While these approaches consider a rather idealized situation where all impurities in a class (e.g., a column in the periodic table) are assumed to take the same location in a given crystal (e.g., unrelaxed substitutional site), they have nevertheless been very successful in organizing an otherwise chaotic data base of defect levels in terms of simple elemental scales.[3] In this paper we explore the microscopic nature of such scaling arguments and establish the limits of their validity.

Various theoretical approaches have displayed the atomistic scaling hypothesis in different forms. They all predict a monotonic[2–4] or near-monotonic[1] variation of $E_b$ with the defect-induced potential perturbation $\Delta V$. In turn, $\Delta V$ directly reflects in these theories the difference between the impurity ($I$) and host ($H$) *atomic* ionization potentials. For example, $\Delta V \propto IP_I - IP_H$ in tight-binding models,[2–3] $\Delta V \propto V_I^{\rm ps} - V_H^{\rm ps}$ in central-cell-corrected effective-mass models[1] (where $V_I^{\rm ps}$ is the bare pseudopotential of the free ion, whose depth is proportional[5] to $IP_I$, and $\Delta V \propto |\chi_I - \chi_H|^2$ in chemical scaling models[4] (where $\chi_i$ is the atomic electronegativity, proportional[5] to $IP_I$). The underlying premise in these approaches is that the balance that exists in an isolated atom between the bare potential $V^{\rm ps}$ and the screening potential $V^{\rm scr}$ is inherently similar (or maintains a causal scaling relation) to that prevailing for an impurity atom bonded to a solid. Modern computational techniques for deep defects in solids[6,7] offer an opportunity to explore these relationships in detail, in that they are now able to solve for the electronic response $\Delta V^{\rm scr} = V_I^{\rm scr} - V_H^{\rm scr}$ to a specified external perturbation $\Delta V^{\rm ps} = V_I^{\rm ps} - V_H^{\rm ps}$ in a *self-consistent* and precise manner, rather than postulate the screening potential.[1–3] In this paper we identify a defect system—substitutional column VI impurities, O, S, and Se in silicon—where the self-consistent screening in the solid reverses the order of the effective potentials $\Delta V^{\rm eff} \equiv \Delta V^{\rm ps} + \Delta V^{\rm scr}$ to $\Delta V_{\rm O}^{\rm eff} > \Delta V_{\rm S}^{\rm eff} \cong \Delta V_{\rm Se}^{\rm eff}$ relative to the atomically controlled order of the bare pseudopotentials $\Delta V_{\rm O}^{\rm ps} < \Delta V_{\rm S}^{\rm ps} \leq \Delta V_{\rm Se}^{\rm ps}$ (or ionization potentials $IP_{\rm O} > IP_{\rm S} \geq IP_{\rm Se}$). This leads to the interesting situation where the atom with the largest ionization potential (O) has the lowest binding energy as an impurity. This series-reversal phenomena is shown to arise mainly from a solid-state effect: the overscreening of $\Delta V^{\rm ps}$ in a polarizable solid by a sufficiently electronegative element. The analysis of the effect provides considerable insight into the phenomenological scaling hypothesis. It further shows that the construction of the screened impurity perturbation from atomic quantities, used extensively in effective-mass and tight-binding models, is not generally valid.

The computational tool that we utilize is the quasi-band crystal-field Green's function method, described in detail elsewhere.[7] It characterizes the impurity and host atoms by the first-principles nonlocal (i.e., dependent on the angular momentum $L$) atomic pseudopotentials[8] $V_L^{\rm ps}$, and describes the screening potential $V^{\rm scr}[\rho(\vec{r})]$ in the local density formalism as arising from the interelectronic Coulomb ($C$) and exchange-correlation (XC) potentials $V^{\rm scr} = V_C[\rho] + V_{\rm XC}[\rho]$ set up by the self-consistent electronic charge density $\rho(\vec{r})$. The host crystal is represented by a realistic self-consistent pseudopotential band structure. A number of computational advances[7] permit us to avoid muffin-tin or finite cluster approximations, as well as early truncations in spectral sums.

Figure 1(a) displays the $r$-multiplied pseudopotential perturbation $r\Delta V_L^{ps}(r)$ for the $s$ wave of Si:O, Si:S, and Si:Se. As expected from atomic considerations,[5] the O atom with its deepest atomic $s$-orbital energy [$IP = 28.5$ eV (Ref. 9)] has the most attractive $\Delta V^{ps}$, whereas Se with its shallowest atomic $s$ energy [$IP = 20.15$ eV (Ref. 9 )] has the least attractive $\Delta V^{ps}$ [S is close to Se since its $IP$ is 20.20 eV (Ref. 9)]. The upper panel in Fig. 1(a) shows for these impurities the spherical part ($l = 0$) of the self-consistent screening perturbation. It measures the change in screening potential due to the displacement of electronic density in response to $\Delta V^{ps}$. Both $r\Delta V^{ps}$ and $r\Delta V^{scr}$ attain their asymptotic limits of $-2\Delta Z$ and $2\Delta Z$, respectively, where $\Delta Z = 2$ is the difference in valence between the column VI impurity and Si. The screening, which in a linear-response approach for fixed $\Delta Z$ depends weakly on the impurity,[1] is seen to vary considerably from O to S and Se. The most electronegative element in the series (O) is seen to be capable of best attracting electronic charge to it, resulting in the most repulsive screening potential. However, relative to the free atoms the propensity for attracting charge to the impurity is considerably different in the solid. This can be appreciated from Fig. 2. It displays the impurity-induced radial charge

$$Q_{\mathrm{solid}}(R) = \int_0^R [\rho_{\mathrm{Si}:I}(\vec{r}) - \rho_{\mathrm{Si}}(\vec{r})] d\vec{r}$$

in a sphere of radius $R$ around the impurity, as well as the analogous quantity for the free atoms

$$Q_{\mathrm{atoms}}(R) = \int_0^R [n_I(\vec{r}) - n_H(\vec{r})] d\vec{r} \ ,$$

where $n_I(\vec{r})$ are the free-atom pseudocharge densities. The charge densities of the impurity-containing solid ($\rho_{\mathrm{Si}:I}$) and pure host crystal ($\rho_{\mathrm{Si}}$) are calculated independently in a self-consistent fashion. The difference between $Q_{\mathrm{solid}}(R)$ and $Q_{\mathrm{atoms}}(R)$ is denoted in Fig. 2 as a shaded area, and represents the excess charge around the impurity in the solid. Whereas the excess charge in *atomic* O and S (relative to Si) is seen to already exceed at $r \lesssim 3$ a.u., its asymptotic value $\Delta Z = 2$, when placed in the solid, O attracts significantly more charge then S, relative to their atomic states. It is this screening enhancement which produces the most repulsive $\Delta V^{scr}$ in Si:O.

Figure 1(b) displays the spherical part of the $s$-wave effective potentials [sum of $\Delta V^{ps}$ and $\Delta V^{scr}$ in Fig. 1(a)] for the three impurities. It is seen to delineate the space around the impurity into two regions with different properties. In the inner central cell (region I; $r \lesssim 0.25d$), $\Delta V^{eff}$ is dominated by $\Delta V^{ps}$ and hence maintains the atomic order $\Delta V_{\mathrm{O}}^{eff} < \Delta V_{\mathrm{S}}^{eff} \lesssim \Delta V_{\mathrm{Se}}^{eff}$. In the outer central cell (region II; $r \gtrsim 0.3d$), $\Delta V^{scr}$ dominates $\Delta V^{eff}$ and the order is reversed to $\Delta V_{\mathrm{O}}^{eff} > \Delta V_{\mathrm{Se}}^{eff} \gtrsim \Delta V_{\mathrm{S}}^{eff}$. Clearly, localized

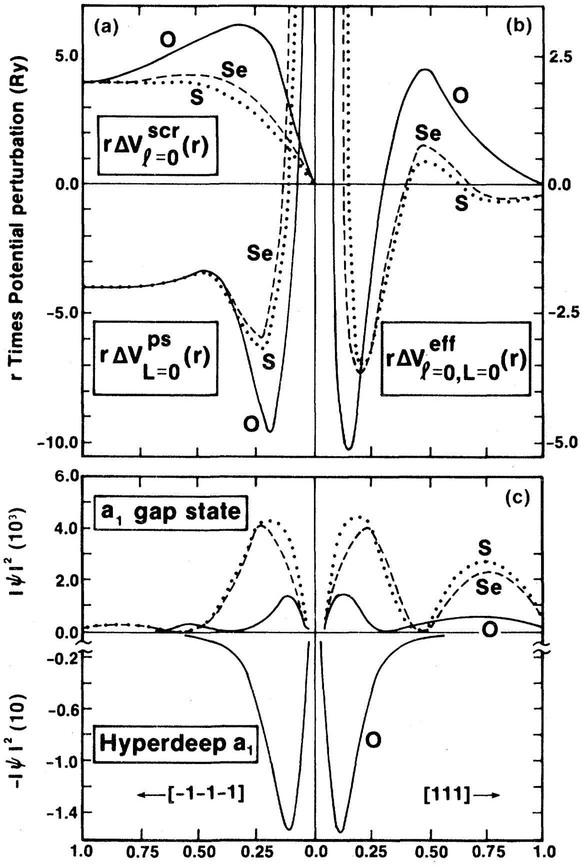

FIG. 1. (a) Screening ($r\Delta V^{scr}$) and pseudopotential ($r\Delta V^{ps}$) perturbations, (b) effective potential perturbation ($r\Delta V^{eff}$), and (c) orbital densities of the gap and the hyperdeep $a_1$ defect levels, for substitutional chalcogen impurities in silicon. Distance is measured in units $d$ of the nearest-neighbor separation (4.44 a.u.).

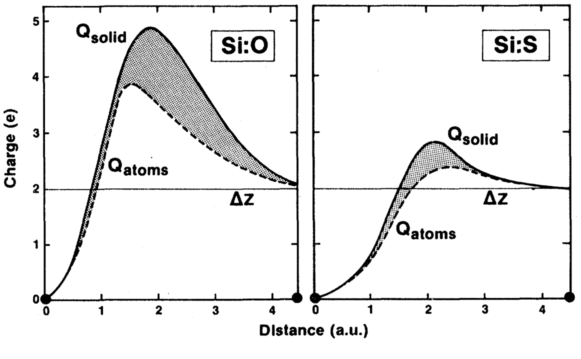

FIG. 2. Charge relative to Si enclosed in a sphere of radius $R$ for O and S. $Q_{\mathrm{solid}}$ and $Q_{\mathrm{atoms}}$ denote results for impurities in solids and in free space, respectively. The shaded area denotes the excess charge in the solid.

impurity states whose wave functions sample predominantly region I are likely to have a reversed order of binding energies relative to impurities with extended wave functions which are affected predominantly by the potential in region II. As we will shortly see, the orthogonality principle for states of the same angular symmetry (e.g., $a_1$) can produce in the solid orbitals that occupy essentially these different parts of space.

The variation with atomic ionization energies in the spatial extent of defect wave functions can be appreciated qualitatively from a simple molecular-orbital model.[2] The *s* orbital of an impurity atom (with orbital energy $-IP_I^s$) combines with the $a_1$ (*s*-like) states of the host crystal to form a bonding, hyperdeep, and nodeless $a_1$ state, as well as an antibonding $a_1$ gap level with an orthogonality node.[10] As the atomic-orbital energy becomes more negative relative to the characteristic $a_1$ energy of the host, the hyperdeep level will be localized more on the impurity site and be tightly bound (appearing eventually *below* the valence band of the host, like a core state), whereas the antibonding gap level will become more extended as it is expelled from the domain of the hyperdeep level by the orthogonality condition. (Similarly, the *p* orbital of the impurity combines with the $t_2$ states of the host to produce a similar $t_2$ bonding-antibonding pair. However, the higher centrifugal barrier associated with the $l > 0$ $t_2$ states prevents even the bonding orbital from being very localized.) Hence, if $IP_I - IP_H$ is sufficiently large, the space around the impurity is delineated into an "impurity sphere" (with a radius characteristic of the atomic impurity orbital, and occupied by the hyperdeep orbital), and an "impurity doughnut" (occupied by the antibonding gap state). These simple considerations are borne out by detailed calculations.

Figure 1(c) shows for chalcogen impurities in Si the square of both the hyperdeep and the gap $a_1$ wave functions along the $\pm[111]$ crystal directions. The wave functions of the hyperdeep states are found to be nearly identical to those of the atomic *ns* state; the same order of orbital energies is found. These wave functions are localized almost entirely in region I: 95–100% of the charge is enclosed in $r \leq d/2$. On the other hand, the antibonding $a_1$ gap states have most of their amplitude in region II and beyond: for O, S, and Se, respectively, only 0.7%, 5.6%, and 6.1% of the charge is enclosed at $r \leq d/2$, and 8.8%, 29%, and 27% at $r \leq d$ (indicating that the energy of this level may not be calculated accurately by small cluster models[11] whose radius is $1-2d$). The fact that the impurity sphere and impurity doughnut states occupy nearly mutually exclusive parts of space suggests that they will respond to the different ordering of the effective potentials in regions I and II. Figure 3 shows the energies of the antibonding $a_1$ (doubly occupied) and $t_2$ (empty) levels of chalcogen impurities in Si. The $a_1$ gap level of O has the smallest one-electron binding energy [relative to the conduction-band (CB) minimum]: $E_{CB} - 0.06$ eV; it extends into the CB as a resonance. The one-electron binding energies of Se and S are $E_{CB} - 0.26$ eV and $E_{CB} - 0.29$ eV, respectively.[12] Hence the most electronegative (or highest *IP*) element in the series has the smallest binding energy! The empty $t_2$ levels appear similarly as a CB resonance for O and as shallow gap levels (extending as resonances into the CB) for S and Se. We note that, while the $a_1$ level reversal is predominantly a solid-state effect (cf. Fig. 2), it is already signaled by the properties of the atoms: the atomically screened $L = 0$ pseudopotential of O crosses that of Se (Refs. 5 and 8) (at $r = 0.9$ a.u.). On the other hand, no crossing exists for the $L = 1, 2$ pseudopotentials.

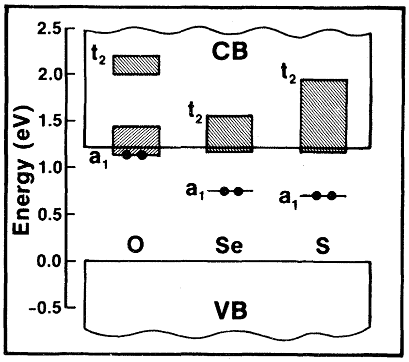

FIG. 3. Energies of the $a_1$ and $t_2$ gap levels and resonances (shaded) for substitutional chalcogen impurities in silicon.

The discovery of a reversal of donor binding energies in a series of substitutional impurities with decreasing electronegativities has an interesting experimental implication. If the most electronegative impurity in the series (e.g., O) is observed experimentally to be deeper than the less electronegative impurities (e.g., S, Se), this implies the former to be relaxed. This is indeed the case for chalcogens in silicon.[12] In general, one would expect the level-reversal effect to occur if $IP_I - IP_H$ is large enough, producing a delineation of space between the bonding and antibonding orbitals (but not too large, since then the antibonding counterpart of the hyperdeep level may not be in the gap), and if $\chi_I - \chi_H$ is sufficiently large (resulting in a significant overscreening). Both criteria point to a high heat of impurity solution. While chalcogen impurities in Si ($\Delta Z = 2$) evidently satisfy these conditions (e.g., $IP_O - IP_{Si} = 15$ eV; $\chi_O - \chi_{Si} = 2.4$ on Sanderson's scale), it is yet unknown how common this phenomena is for impurities left of column VI in the periodic table (e.g., O on the As site in GaAs has $\Delta Z = 1$ and $IP_O - IP_{As} = 11.5$ eV, $\chi_O - \chi_{As} = 1.3$ and may not show a reversal).

## ACKNOWLEDGMENT

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[10] Since the antibonding state is a donor level and hence derived from the conduction band, it cannot originate solely from the valence-band $a_1$ states, as suggested by the defect molecule model (Refs. 2 and 3). This state is properly viewed as a conduction-band state pulled down into the gap by the attractive $\Delta V^{\mathrm{eff}}(\vec{r})$.

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[12] To get ionization energies, the one-electron binding energies need to be corrected by a transition state procedure. The correction is small for the extended gap states. The procedure yields $E_{\mathrm{CB}}-0.32$ eV and $E_{\mathrm{CB}}-0.29$ eV for the $a_1$ gap levels of S and Se, respectively. This agrees closely with the most recent experimental determination of the $D^0 \rightarrow D^+$ ionization energies, i.e., $E_{\mathrm{CB}}-0.32$ and $E_{\mathrm{CB}}-0.30$ eV for S and Se which are believed to be substitutional in silicon [H. G. Grimmeiss, E. Janzen, and B. Skasstam, J. Appl. Phys. 51, 3740, 4212 (1980)]. No equivalent data are available for O, which is presumed to be relaxed into an interstitial site. In this case, $\Delta V^{\mathrm{ps}}$ needs to be replaced by the far more attractive potential. The relaxed O, which does not concern us here, will hence have a significantly larger binding energy then substitutional O.