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SUBSTITUTIONAL 3d IMPURITIES IN SILICON: A SELF-REGULATING SYSTEM

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A precise self-consistent calculation of the electronic structure of neutral substitutional 3d impurities in silicon within the local density formalism reveals striking chemical regularities. The remarkable compression of the energy level ladder corresponding to different charged states in a narrow energy gap is shown to result from a special charge self-regulating mechanism, much like homeostasis in biology. In contrast to free transition atoms, a s→d population cross-over can occur in this system.

The properties of transition atom (TA) impurities in semiconductors have been the subject of extensive research over the past 25 years[1-3]. In this Communication we present the first ab-initio self-consistent study of the electronic structure of TA impurities in an infinite semiconducting host crystal. This is made possible by very recent advances[4] in the self-consistent Green's function formulation of hyperlocalized impurity states with interacting d orbitals. We have calculated the electronic properties of all substitutional 3d impurities, from Ti through Zn, in silicon. We use the quasi band crystal-field method described in detail elsewhere[4]. It reflects to a very good approximation (~0.1 eV in energies and 2-3% in charge densities) the predictions of the physical input—first principles nonlocal pseudopotentials[5], unrelaxed lattice geometry and a Fermi-Dirac level occupation scheme—rather than computational approximations. The calculation reveals a number of striking chemical regularities, identifies a self-regulating behavior which enables the system to sustain many charged energy levels in a narrow energy range, and predicts a s → d population inverssion in the ground state.

Chemical Trends: Fig. 1 shows the variations in the defect-induced e and t_2 energy levels in silicon along the 3d impurity series. Gap level occupation numbers are indicated for the neutral defects. For resonances, we plot only their peak energies. The 10-fold degenerate atomic 3d level splits in the crystal into a four-fold degenerate e-type and a six-fold degenerate t_2-type crystal field resonances (CFR). This pair appears for Si:Zn near the bottom of the valence band (VB) as atomiclike, highly localized (% localization in the central cell q = 90%), d-like (98% d) states. As one progresses to lighter impurities, these VB resonances delocalize and hybridize with the host p-states and their energy as well as (crystal-field) splitting increases. The highly localized e^{CFR} level first penetrates the band gap for Si:Mn ("e threshold"), whereas the t_2^{CFR} level, repelled by the large density of host t_2 states at $\sim E_{VB}-1$ eV, is pinned inside the VB and never makes it to the gap. The antibonding counterpart of t_2^{CFR} is the dangling bond hybrid (DBH) level t_2^{DBH}. It is a hybrid between the four neighbouring Si dangling bonds with a smaller admixure of impurity atomic orbitals. It starts in Si:Zn just above the VB maximum as a delocalized (q = 22%), predominantly p-like (77% p, 22% d) acceptor state. As one moves to lighter impurities, the energy of t_2^{DBH} increases smoothly, and the state disappears for the first time into the conduction band for Si:Co ("t_2 threshold"). The level is then pinned inside the conduction band by the repulsion (avoided crossing) from the large density of t_2 host states at $\sim E_{VB}+3.8$ eV.

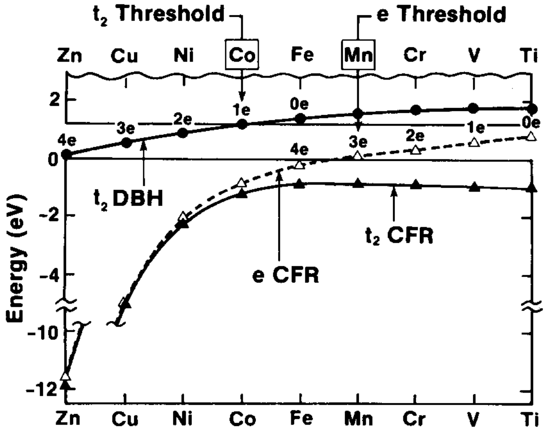

Fig. 1: Defect-induced energy levels for neutral substitional Si:TA.

There are four notable features in the results of Fig. 1. First, for a given impurity, the system sustains

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either a t_2 or an e gap level, but not both (Si:Fe is a marginal case), in contrast with early assumptions[1,6]. Second, a large part of the impurity charge appears in resonances (e.g., t_2^{CFR}) and is therefore directly available for screening, in contrast with the interstitial case where all of the impurity valence electrons occupy gap states[3b]. Third, the gap levels are not pinned inside the band gap[7]; their energy continues to rise monotonically as Z decreases. The limiting separation between the bonding and antibonding t_2 levels is not determined by the optical band gap (1.2 eV) but rather by the homopolar gap (4.8 eV), which separates regions of highest t_2 density of states in the valence and the conduction bands, respectively. Fourth, Mn forms a demarcation point in the 3d series, delineating the lighter impurities (with an impurity-like gap state e^{CFR}) from the heavier impurities (with a host-like gap state t_2^{DBH}). These chemical trends are consistent with the recent DLTS results of Kimerling et al. for the levels assigned by these authors to isolated TA impurities.[2] They observed the Mn demarcation point, the monotonic increase in the electron trap energies in going from Si:Zn to Si:Mn, and the abrupt disappearance of the (t_2^{DBH}) electron traps for elements lighter than Mn.

Stability of Charged States: Whereas the first few ionization potentials of a sp-electron atom usually span a large energy range[8], when such an atom forms a shallow impurity state in a semiconductor (e.g., Si:P), it can sustain a number of ionized states in a very narrow energy range inside the band gap, often ~0.1 eV. Both phenomena are understandable. Characterized by a weak central cell potential, the low effective mass and the large dielectric constant of the host crystal combine to produce a small effective Rydberg R* and very extended orbits ($q \approx 1\%$) for the impurity level. Even if the intra atomic Coulomb energy per electron U is not small, the energy E_{gap} of this extended orbit varies only slowly with its occupation number N (proportional to the formal net charge Q_{net}). On the other hand, for free atoms, the localized nature of the bound orbitals and the correspondingly large free atom Coulomb energies U^o lead to a rapid variation in the orbital energy with the amount of electronic charge Q(N) on the atom, $E(N) = E_o + UQ(N)$. E.g., for Mn, the d^5 through d^2 ionization energies (α-ϵ) are[8] 33.7, 51.2, 72.4, and 95 eV, respectively, leading to $U_d^0 \doteq 20$ eV/e. Surprisingly, however, when a TA exists as an impurity in a semiconductor, it can sustain, in a narrow (band gap) energy range, a large number of different ionization states[1,2] although the charge in the gap level is localized almost entirely on the impurity atom (e.g. q = 82% for the gap level in Si:Mn). The present calculation explains this remarkable spectral compression in terms of a self regulating behavior of the screening potential. The observation of this unusual "electronic elasticity" of the central cell supports the prediction of Haldane and Anderson.[6]

Using the self-consistent electronic charge density $\rho_D(r)$ of the defect-containing system and the charge density $\rho_V(r)$ of the crystal with a vacancy, we calculate an effective impurity charge $Q = \int_0^R (\rho_D - \rho_V)dr$, where R = 4.44 a.u. is the radius of the central cell. We further partition Q into a contribution $Q_{gap}(N)$ from the N electrons occupying the impurity-induced gap levels, and a contribution $Q_{VB}(N)$ from the (perturbed) valence band charge. Separate self-consistent calculations are done for each N, corresponding to different formal charged states (e.g., $Q_{net} = 3-N$ for Si:Mn). Before describing the results, consider the prediction of simple models. In a simple electrostatic point-ion model, the displaced VB charge is given by $Q_{VB} = Z(1 - 1/\epsilon_o)$ and hence does not depend on N but only on the magnitude of the positive core charge Z and the static dielectric constant ϵ_o. Further, in this limit, $Q_{gap} = N/\epsilon_o$, since each impurity electron is viewed as a screened point charge. Likewise, a simple rigid band argument, or a non self-consistent calculation assume that Q_{VB} does not depend on N. Our calculation reveals a very different situation. Figure 2a shows for Si:Mn the variation with N of the two contributions $Q_{gap}(N)$ and $Q_{VB}(N)$ to Q as calculated self consistently. We see that whereas the contribution $Q_{gap}(N)$ of the gap state e^{CFR} increases with N nearly linearly (as expected), the contribution $Q_{VB}(N)$ of the VB state decreases, leading to $Q(N) = Q_{gap}(N)+Q_{VB}(N)$ that varies with N considerably more slowly than Q_{net}. Consequently, despite the fact that, like in the free TA, all of the impurity valence electrons are enclosed in the central cell (e.g., for Mn^0, Q = 7e), the energy ϵ_{gap} of the gap level (Fig. 2b) increases only very slowly with N, in sharp contrast to the free atom.[8] The slope U_d = 0.2-0.3 eV is two orders of magnitude smaller than the bare atomic value[9] U_d^0. The redistribution in chemical

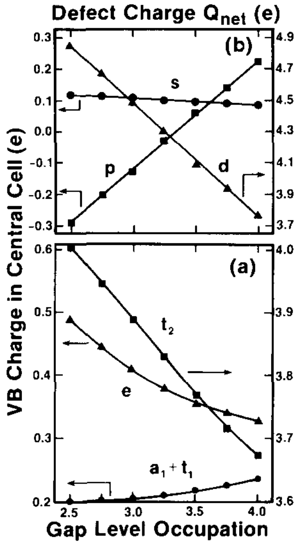

Fig. 2: (a) The contributions of the gap level $Q_{gap}(N)$ and the valence band $Q_{VB}(N)$ to the central cell charge Q, as a function of the gap level occupation N. (b) Variation in central cell charge Q and gap level energy E_{gap} with N.

bonding responsible for this effect is illustrated in Fig. 3a which analyzes $Q_{VB}(N)$ in terms of the various wave function representations. It is seen that whereas the a_1 and t_1 valence states remain largely unresponsive to the change in the gap-level occupation, the e and t_2 VB charges tend to reduce their amplitudes in the central cell as N increases. An angular momentum analysis of the VB wave functions reveals (Fig. 3b) that the reduction in $Q_{VB}(N)$ results from a strong reduction of its (localized) d charge, accompanied by a smaller increase in the (delocalized) p charge. Hence, much like a pool below a waterfall or the self-regulating control mechanisms known in biology (homoestasis), the Si:TA system responds to adding charge to the gap levels by inducing its VB states to leak out of the central cell. This is accomplished by undoing the p-d hybridization (Fig. 3b). It leads to a weak Q(N) variation and the consequent pinning of many charged states in the gap. We suspect a similar self-regulating behavior to occur in other systems whenever localized partially occupied states coexist with an itinerant manifold with which it can exchange charge (e.g., surface states valence fluctuation).

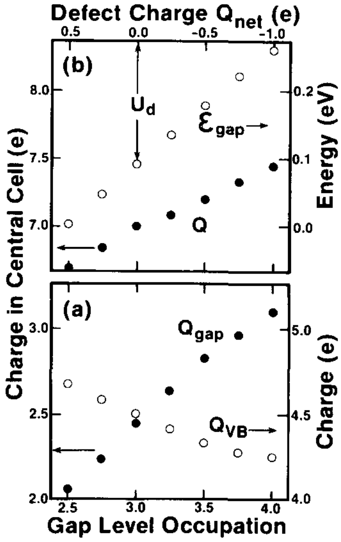

Fig. 3: Analysis of the valence band contributions function representations, and (b) orbital contributions. $Q_{VB}(N)$ in Si:Mn in terms of: (a) wave

Effective Electronic Configuration: Whereas the large atomic U_d^0 values of TA lead to the well-known preference for occupying the 4s shell before the 3d shell is completed, small U_d values in the solid may lead to a population inversion in the ground state. We calculate the effective orbital configuration ΔQ_ℓ of neutral substitutional TA in silicon by performing an angular momentum decomposition of occupied wave functions, yielding $Q = \sum_\ell \Delta Q_\ell$. This defines an "isolated" effective impurity atom with orbital occupation numbers ΔQ_ℓ ; when placed at a silicon vacancy, it produces the overall charge distribution of the self-consistently described Si:TA system. For large host interatomic spacing, ΔQ_ℓ reduces to the free TA orbital configuration $d^m s^n$. Fig. 4 shows that whenever the 3d shell can accomodate more than its electrons (i.e., TA lighter than Ni), the s electrons are promoted into it, leading to a d^{n+m} configuration. Remarkably, TA impurities in Si tend to develop a noble-atom-like configuration by filling the d shell without resorting to an ionic charge transfer from the host. In Cu, and Zn, most of the s charge is promoted into the p states. Our results are in sharp contrast to the Ludwig-Woodbury model[1] that hypothesized an opposite, $(d^n s^2 \to d^{n-2} s^1 p^3)$ promotion to explain their EPR results.

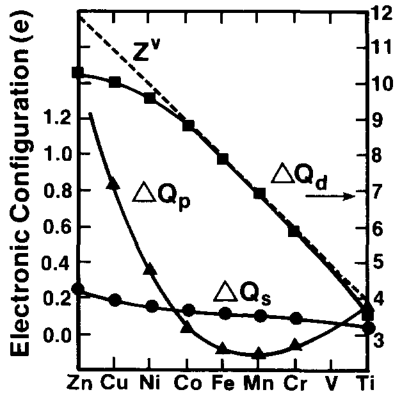

Fig. 4: The effective electronic configuration ΔQ_ℓ of TA impurities in Si. Z^v denotes the total number of atomic valence electrons.

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[9] The correction to U_d due to the long-range Coulomb interactions set by the charge outside R = 7.4 a.u. estimated perturbationally to be smaller than 0.1–0.2 eV, indicating that R^* is small. Further, Fig. 2b illustrates the correction needed to transform the one-electron energies of Fig. 1 to ionization energies. Using the transition state method, the $e^3 \rightarrow e^2$ ionization energy is calculated as the one-electron eigenvalue of $e^{2.5}$. The correction is seen to be small (0.1 eV).