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ELECTRONIC STRUCTURE OF SUBSTITUTIONAL 3d TRANSITION ATOM IMPURITIES IN SILICON

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We report the results of a self-consistent calculation within the local density approximation for all the substitutional 3d transition atom (TA) impurities in an extended silicon host crystal using the quasi band Green's function method. Chemical trends in the gap state energies and 3d-like resonances are discussed as well as trends in the effective electronic configuration of TA impurities. An explanation for the remarkable property that many different charged states of TA impurities exist in the narrow band gap, despite the fact that the corresponding ionized states of the free TA span a range of ~ 60 eV, is proposed.

APPROACH

We have used the quasi band crystal field (QBCF) self-consistent Green's function method$^{(1),(2)}$, which is particularly well suited for impurities with highly localized wave function components. This method employs a dual representation in the defect wave functions $\{\psi_i\}$. The first representation is in terms of an impurity-centered local orbital basis $\{g_a(\bar{r})\}$

$$\psi_i(\bar{r}) = \sum_a C_{ia}\, g_a(\bar{r}) \ , \qquad (1)$$

while the second representation is in terms of quasi band Bloch functions $^{(1)}$ (of band index n and wave vector $\bar{k}$):

$$\psi_i(\bar{r}) = \sum_n^M \sum_k A_i(n,\bar{k})\ \Phi_{nk}^{QB}(\bar{r}) \ . \qquad (2)$$

The expansion coefficients $A_i(n,\bar{k})$ are in a simple way related to the C_{ia} in Eq.(1). This leads to the standard Koster-Slater type Green's function theory for impurities represented by the potential perturbation ΔV, e.g.,

$$\sum_a\{\delta_{a'a} - \sum_{b'} G^0(E)_{a'b} <g_b|\Delta V|g_a>\}C_{ia}=0, \qquad (3)$$

but with a *rapidly converging* band summation in the Green's function:

$$G^0(E)_{ab} = \sum_n^M \sum_k \frac{<g_a|\Phi_{nk}^{QB}><\Phi_{nk}^{QB}|g_b>}{E-E_{nk}^{QB}} \ . \qquad (4)$$

If quasi bands are not used for TA impurities, $M \sim 10^4$, whereas if quasi bands are used, $M \simeq 20$.

By choosing the basis functions g_a as products of radial functions and Kubic harmonics, the expansion in Eq(1) leads to a particularly convenient way for expressing physical quantities like wave functions, change in charge-density, perturbation potential etc., and simple inclusion of pseudo-potential non-locality, which is important for treating TA impurities.

The present calculation is performed in the local density approximation with exchange parameter $\alpha = 1.0$ and using first-principles non-local pseudopotentials for the impurity atoms. The electronic occupation of energy levels is in increasing order of one-electron energies without leaving holes behind (the aufbau principle).

RESULTS

Chemical trends: The calculated defect energy levels are shown in Figure 1. The notation 4e,

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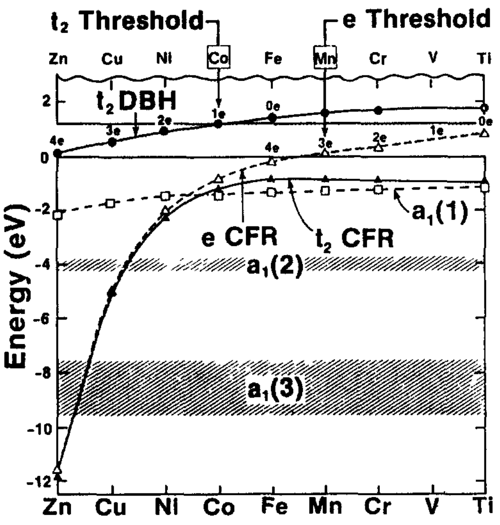

FIGURE 1.

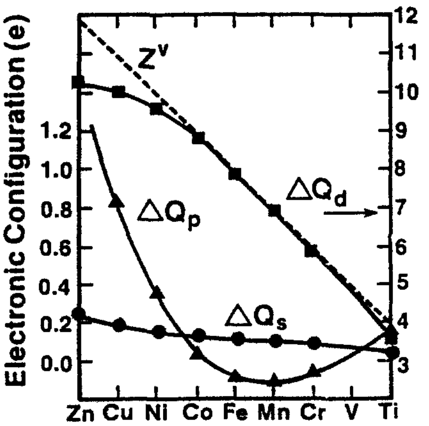

FIGURE 2.

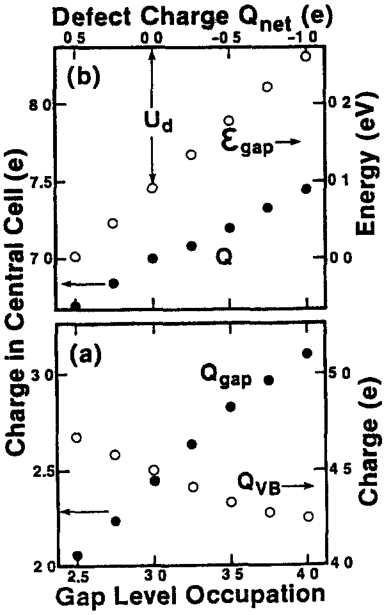

FIGURE 3.

3e etc. indicates the gap level occupation for the neutral state of the impurity.

The major localized defect level of highest energy is the t_2 dangling bond hybrid (DBH), appearing for Si:Zn just above the valence band maximum and disappearing into the conduction bands for Si:Co. The $\ell=1$ component of the t_2-DBH wave functions is qualitatively characteristic of a host-like dangling bond (vacancy) wave function. However, a significant amount of impurity-like d-character (~20% for Si·Zn and increasing almost monotonically to 45% for Si:Ti) is hybridized into the DBH state via the $\ell=2$ component (hence the name dangling bond hybrid).

Moving in Figure 1 to more negative energies, one observes two groups of defect levels, denoted as the e and t_2 crystal field resonances (CFR). The t_2-CFR is systematically below the e-CFR level. Both the e and t_2 CFRs are very much atomic-like in the inner central cell region. Considering their orbital momentum content, the e-CFR is essentially a 100% d-state, whereas the t_2-CFR is 80-100% d-like. Both CFRs start out at the Si:Zn end as being very localized but delocalize monotonically as one progresses to the Si.Ti end of the series.

Effective electronic configuration: To study the distribution of charge among the various ℓ-components of the wave functions, it is instructive to define an effective impurity atom for the defect system. To this end, let Q_ℓ denote the total charge contained in the ℓ:th angular momentum component of all occupied wave functions. We then define an effective electronic configuration ΔQ_ℓ as

$$\Delta Q_\ell = Q_\ell\,(\text{impurity}) - Q_\ell(\text{vacancy}). \qquad (5)$$

Figure 2 shows the variation of ΔQ_ℓ across the 3d series for the various Si:TA systems. The total number of impurity valence electrons Z^V is shown for comparison (dashed line). The interesting result of this figure is that whenever the 3d shell can accomodate the s-electrons (i.e. to the left of Ni d^8 in the periodic table), the latter are promoted into it. Hence, whereas Fe, Mn, Cr and Ti have 6,5,4 and 2 valence d-electrons in the free atom, respectively, they have about 8,7,6 and 4 d-electrons when placed substitutionally in silicon. This is in marked contradiction to the Ludwig-Woodbury model, which hypothesizes that for substitutional 3d elements, the d-electrons will be promoted into the sp shell to form a tetrahedral hybrid (e.g., $d^n s^2 \rightarrow d^{n-2} s^1 p^3$). For the completely filled 3d elements Zn and Cu, however, we find that the d-electrons are being promoted into a p-state, yielding the effective configuration $s^{0.24} p^{1.56} d^{10}$ for Zn and $s^{0.19} p^{0.84} d^{9.92}$ for Cu.

It should also be noted that the components Q_ℓ of the effective impurity atom is calculated within a sphere whose radius is equal to the Si-Si bond length (4.44 a.u.). Since $Q=\sum Q_\ell \approx Z^V$, it follows that the change in charge-density is essentially confined to this central-cell (CC) region.

Stability of charged states: TA impurities in silicon exhibit the remarkable property that many different charged states (e.g., Mn^{+2}, Mn^{+1}, Mn^0, Mn^{-1}, Mn^{-2}) exist in the narrow (1.2 eV) band gap region, whereas the corresponding ionized states of the free TA span a range of ~60 eV, despite the fact that the impurity charge is concentrated to the CC region. Our calculation explains this remarkable behaviour in terms of two related effects: (i) As the occupation N of the impurity gap level is changed, the effective electronic charge $Q(N)=\sum Q_\ell(N)$ in the CC region varies considerably slower. This is illustrated in Figure 3 for Si:Mn. Figure 3a shows the contributions from the valence bands, $Q_{vb}(N)$, and from the gap level, $Q_{gap}(N)$, versus the gap level occupation number N (N=3 for $Si{:}Mn^0$). It is clear that even if $Q_{gap}(N)$ increases almost linearly with N, $Q_{vb}(N)$ decreases with N to give a relatively slow increase in the effective charge $Q(N)=Q_{vb}(N)+Q_{gap}(N)$ (Figure 3b). (ii) Assume that by changing the charge of the impurity by ΔQ electrons, the defect gap level changes by $\Delta\varepsilon$ eV according to

$$\Delta\varepsilon_n = U_n \cdot \Delta Q\ , \qquad (6)$$

where U_n is the intraatomic Coulomb repulsion energy. For free space TA, $U_{3d} \approx 20$ eV/e. In the impurity case, Si:Mn, however, $U_n \approx 0.4$ eV/e (c.f. Figure 3b). Thus, the interaction with the solid reduces U_n by essentially a factor of 10^2.

The small U_n values for the Si:TA systems explain the effective impurity atom configuration discussed earlier (c.f. Figure 2). Whereas the large atomic U_{3d} values lead to the well-known preference for occupying the 4s shell before the 3d shell is completed, small U_n values in the solid may hence lead to population inversion in the ground state.

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