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Theory of substitutional and interstitial 3d impurities in silicon

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The chemical regularities in the electronic structure of substitutional and interstitial 3d impuri-ties in silicon are studied through a self-consistent local-density-functional Green s-function cal-culation.

Despite 25 years of basic and applied research on the properties of transition atom (TA) impurities in
semiconductors, they have been subjected only re-
cently to theoretical studies.

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In this Communica-

tion we report the first theoretical study of the elec-tronic properties of all tetrahedral substitutional (S)
and interstitial (I) 3d impurities in an infinite host
semiconductor. We use the recently developed'
first-principles quasiband crystal-field Green's-function method within the local density formulation of interelectronic interactions. The calculation is ful-ly self-consistent, uses ab initio nonlocal pseudopo-
tentials, '

avoids any spherical approximations to the
potential or finite cluster models, and assumes an un-
relaxed lattice. It reflects to within an excellent ap-

proximation (-0.1 eV in energies and 2—3'/o in
charge densities) the predictions of the physical in-put, not computational approximations. We describe the chemical trends and the unifying physical princi-
ples underlying the diversity of phenomena in this
system.
Figure 1 displays the variations in the impurity-

induced gap energy levels for Sand Iimpurities in
silicon. The overall trends in these energies agree with previous cluster calculations.

'
The results
show four notable features. First, the e level is below the t2 level for S impurities, whereas the order is reversed for Iimpurities (as predicted by the point-ion model and cluster calculations'). Second, the e-t2 crystal-field splitting for Simpurities is 1.5—3 times larger than for Iimpurities, reflecting the
stronger and more anisotropic crystal-field potential

at the Ssite. The splitting for Iimpurities is about 5 times larger than that calculated in the spherical po-

tential (muffin-tin) cluster approximation. ' Third,
the model predicts a number of simple chemical trends in the system's electrical activity with the site location of the impurity. For example, whereas an isolated Cu impurity is predicted to be electrically

inactive in an Isite (with filled r6e~ shells), it is predicted (and found) to be electrically active as a triple acceptor t e when displaced into an Ssite.

The model also predicts the light Iimpurities (V, Cr,
Mn) are capable of both

i71nsiti5on

site. rebjected

S-7Tj ET BT /Xii0 8.43 Tf 339.95 520.4 Td48(We)Tunica-

p

i

silicon

light

impurities

Tmmun8Tj ET BT(Ni 8.21 Tf463.944 456.12 Td Vn)

tims i7(Mn))cted

larger times
W812 Tf 111.38 312. TfidTj ET BT /Xi0 8.2 8.66 Tf 164.25 111.45 Td V, impurities

an

with

a calculation the number

the BT /T ng-4Xi0BT

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(b)

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Distance (a.u.

)

FIG. 3. Decomposition of the radial impurity charge

Q

into the gap contribution Qs,

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and the valence-band contri-

bution AQva for (a) I and

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configuration of the impurity atom in the solid, one
has to subtract the impurity-independent background
contribution of the host states penetrating the central
cell from QID. We subtract the i-decomposed host
charge QIH(A) for /impurities, and the i-decomposed
vacancy charge'-Q~r(R) for Simpurities. This de-fines effective orbital configurations QID —QIH and
Qto —Qty of "isolated" I and Simpurity atoms, respectively, renormalized by their self-consistent in-teractions with the crystal. We find that (Fig. 5)
whenever the d shell can accommodate more than its
eiectrons (TA lighter than Cu) the s electrons are pro-

moted into the d sheii, leading to an =d"+ conftgura tion. In contrast to free atoms, the energy cost of this process is likely to be small due to the substantial
reduction of Uq in the solid. Our results confirm the
classical hypothesis of %oodbury and Ludwig, '

sug-

gesting an s d promotion for Iimpurities, but con-

tradict their assumption of a reversed d sp promo-tion for Simpurities.
Our predicted s-d population inversion further sug-gests a simple explanation to the diffusion puzzle". ~hereas Ni is known to be an extremely fast I diffuser in Si (diffusion constant D —10~ cm'/s, typical of liquids), the lighter TA, like Ti, are ex-

tremely immobile in silicon (D -10 ' —10 '0
cm'/s). We suggest that this is so because Ni has an effective noble-atom-like closed-shell configuration =d'0 in silicon and is therefore both small and chem-ically passive. On the other hand, Ti and V exist in silicon as open-shell species with large perturbation radii and hence have a far greater propensity for both steric and chemical interactions with the host.

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