PHYSICAL REVIEW B VOLUME 27, NUMBER 8 15 APRIL 1983 Electronic structure of

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TABLE I. Summary of data pertaining to

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calculations.

According to the recent work of Brotherton
et al.,

there are three categories of sulfur level in
silicon, termed S I, S II, and S III. Measuring ener-
gies with respect to the minimum of the conduction band E„the S I levels occur in a pair at E,—0.18 eV (A level) and E,—0.38 eV (8 level). These S I levels appear in high concentration

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I

C
IO

D
C
0
0.0

Si:0

)::'.:::)to'
SM

CB a1

Si:S

::::tCB2

== a,

Si:Se

D
C

Io -So-
@

4l
C
I

tVB
2

V/FA a1

- 10.0—

—a, (3s) —

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TABLE II. Summary of calculated gap levels of a & symmetry for substitutional Si:0, Si:S, and Si:Se. The numbers represent distance from the conduction-band edge. All values are in eV. We show the results of the present work both as orbital energies and as removal energies (transition-state values) that can be compared with experiment. For comparison, the observed values for the C center are given. The values from Ref. 36 are interpolated graphically. Workers 0 S Se

Fletcher (Ref. 35)
Hjalmarson et al. (Ref. 36)
Pantelides and Sah (Ref. 37)
Pantelides (Ref. 38)
Bernholc et al. (Ref. 39)
Present Work
Orbital energies
Removal energies
Expt. [C 54.65 Td (Present)Tj ET BT323.19 9.63 Td96ET B (54 BT /XiXi4s 8.52 Tf 213.27 561.48 Td (as)T (54ET BT 5(a4 8.17 Tf 129.01 776

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TABLE IV. Energies, orbital density localization parameters q and

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TABLE V. Population analysis of the occupied states for the 0, S, and Se in Si. See defini-
tions in text and in Ref. 22.

Impurity

0

Angular

momentum

l=o
1=1
l =2
1=3
l =4
Qa

Qi'

2.4260
0
0
0.0934
0.0132
2.533

Qt

0
0
0.2575
0
0.0800
0.368

t)
Qi

0
0
0
0.3883
0.0689
0.457

Q

2

0
7.5024
0.8198
0.1399
0.1777
8.640

2.4260
7.5024
1.1073
0.6216
0.3494

Q'"=12.00

l =0
1 =1
1=2
1=3
1=4

Q

lX

2.8498
0
0
0.1562
0.0170
3.0230

0
0
0.4362
0
0.1002
0.5364

0
0
0
0.5248
0.0857
0.6110

0
6.1644
1.0646
0.1809
0.1895
7.5994

2.8498
6.1644
1.5008
0.8619
0.3924
Q

'"=l l.77

Se l=o
l=l
l =2
1=3
l =4

Q

Cl

2.8128
0
0
0.1526
0.0165
2.9819

0
0
0.4695
0
0.1809
0.5714

0
0
0
0.5431
0.0877
0.6008

0
6.0450
1.1468
0.1897
0.1809
7.4624

2.8128
6.0450
1.6163
0.8854
0.3870

Q"'= 11.75

only its valence sp orbitals. Indeed, the chemistry of S compounds suggests the decisive role of d hy-bridization (e.g.,

the near linearity of the HzS mole-
cule, impossible within the sp-bonding picture, as opposed to the 105' bond angle in H20). We note that the pronounced non-sp character of the central cell charge for Si:S and Si:Se cannot be faithfully re-vealed by tight-binding models '

(which restrict
the basis set to sp orbitals only; hence only off-center d character is allowed), or by local pseudopotential models3 (which force the d part of the wave func-tions to sample the same potential that the sp piece "feels"; hence d states are artificially pushed to higher energies}. Table V also shows that the e and ti character of the system is relatively small and fairly constant along the series, consistent with the fact that there are no strongly localized defect-induced e and t~ resonances in the system (the shal-low e level is extended and effective-mass-like; cf. Sec. V). Finally, if one subtracts from the Q~ values of Table V the corresponding values for the Si va-
cancy,

'

one finds that the effective configuration of substitutional oxygen in silicon is closer to s'p5 (sp bonding) than to its free-atom configuration s p" (p
bonding).

IV. REVERSAL OF ORDER OF DEFECT LEVELS WITH ATOMIC IONIZATION ENERGIES

In this section we discuss the calculated chemical

trends in the binding energies of the a & gap levels, in light of intuitive chemical models advanced on the basis of the data of Table I. The basic phenomena is that the order of the a ~ binding energy that we find (E,—0.06, E,—0.29, and E,—0.26 eV for Si:0, Si:S, and Si:Se, respectively; cf. Table II}shows a re-versal in order relative to the atomic energy differ-ences for the s orbitals (hE, =15, 6.7, and 6.7 eV for 0, S, and Se, respectively; cf. Table I). This reversal
persists when very accurate pseudopotentials are
used (the trans-density-functional pseudopotentials of Ref. 20, which, among others, is norm conserv-ing), when careful basis-set convergence studies are conducted, and when the asymptotic sum rule

[lim, EV(r) =2(Zo —Zs;) =4] is strictly en-
forced. (The reversal may not occur if there is in-
sufficient variational flexibility outside the central cell, where most of the amplitude of the gap wave function is concentrated.)
The underlying concept, used in defect theories as

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hV "(r)=V '(impurity) —V"'(host) (2)

associated with it. The screening is calculated as a
sum of the interelectronic Coulomb term V„[p(r)]
and the exchange-correlation term V„,[p(r)], both

diverse as effective-mass, tight-binding, '

and

chemical scaling approaches, has been that the
binding energies Eb of different impurities I in the
same host crystal are ordered according to the ioni-

the

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5.0

IK

c
0

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2.5-

20

CB
tg-

2.

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turbed host states) and not by an overcomplete set
(e.g., a combination of pure host and impurity-atom
orbitals). The binding energies of these levels hence
reflect the degree of attractiveness of the screened
donor potential in that part of space where the de-
fect wave function is concentrated: A strongly at-tractive donor potential [e.g., Si:S in Fig. 4(b)] leads
to a deeper gap level, whereas a weaker donor poten-
tial [Si:0,Fig. 4(b)] leads to a shallower donor ener-
gy. The atomic energies of the impurity need not
dictate the binding energies in the solid: They mere-
ly reflect one component of the donor potential (the
pseudopotential}. Tj ET BT /Xi11 8.58l8 Tf 236.16 Td (54 Tf 10ere-aTj -aTicj ET BT /Xi11 8.89 Tf 275.7048.89 Tf 272.88 559980ere-aT

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the conduction band near point X. For this to be
correct, the expansion coefficient in the general
equation (4) should yield ~A; (k)

~ =1 for this

k

point, i.e.

, k=(2sr/a)(0, 0,0.8). We find (Fig. 9)
that the bottom of the conduction band indeed con-

tributes approximately 25% to the impurity gap wave function of

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Kravitz [L. C. Kravitz, Ph.D. thesis, Harvard Univer-
siy, 1965 (unpublished)], who found a marked decrease

in the resonance signal for photon energies)0.59 eV.

The identification with S II (D level) is thus very plau-
sible.

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