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Electronic structure. of copper, silver, and gold impurities in silicon

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The electronic structure of Cu, Ag, and Au impurities in silicon is studied self-consistently using the quasiband crystal-field Green s-function method. We find that a substitutional model results in

a two-level (acceptor and donor), three-charge-state (A+, A, and 3) system, which suggests that these defects are amphoteric. Our results show that these substitutional impurities form e-type and t2-type crystal-field resonances (CFR) near the center of the valence band and a dangling-bond hy-brid {DBH) t2 level in the gap. The e

" and t2" states are fully occupied and represent the per-
turbed and hybridized impurity atomic orbitals (not simply a "d' " configuration). They are mag-
netically and electrically inactive but are predicted to be optically active in the uv, producing both impurity-bound core excitons as

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the diffusion occurs via a

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and they include the standard

T temperature correction.
The overall picture is that Si:Cu has

a triple acceptor (in-
dicating that it takes a substitutional or near-
substitutional site), but Si:Ag and Si:Au have a single ac-ceptor and a single donor each.
In the work of Braun and Grimmeiss, threshold ener-
gies were measured for the Au acceptor, both through
electron emission from the conduction band (at E,

—0.555 eV) and through hole emission from the
valence band (at E, +0.61 eV). The sum of these energies (1.166 eV) was close to the Si band gap at the temperature at which the experiment was done, suggesting that the gap
level relaxes in

a similar way when the carrier is either in
the conduction or the valence band. For the Au donor,
the corresponding results were E,

—(0.75

—0.83) eV for
electron emission and E, +0.345 for hole emission, which similarly implies

a small net relaxation difference. Photo-
luminescence experiments show a sharp emission line
and

a peak at 0.78 eV (i.e.

, at -E,+0.37 eV), which is at-
tributed to the donor final state. This is close to the value

of -E„+0.345 eV obtained under equilibrium thermal
emission.

Using the best-established values for the single-acceptor
and single-donor energies of Si:Au, one would obtain an
effective Mott-Hubbard Coulomb repulsion energy of U=E(OI+)

—E(OI

—)=0.28 eV, if it were assumed that
both transitions resulted from the same center (i.e.

, the
impurity was "amphoteric"). For Si:Ag, one obtains
U=0. 32 eV. This point is, however, the subject of an
ongoing controversy. We discuss this point next.

D. Is Si:Au amphoteric?

Whereas twenty years ago it seemed to have been universally accepted that gold forms

a substitutional im-

purity in silicon, and that this center is responsible both for the acceptor level at E(0/

—)=E„+0.63 eV and the
donor level E(OI+

)=E„+0.35 eV (amphoteric center),
recent conflicting measurements on emission and capture
cross sections have raised some doubts on this identifica-

tion. A recent compilation" of cross sections

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scatter in temperature dependence of the emission rates
and the corresponding scatter in the X„values for Si:Au
(1 &X„&48).
Fewer experimental values are available for the donor
degeneracy factor Xz. Lang eI; al."

found Xq ——5.7,
whereas Brotherton and Lowther" ' '

suggested from their
data that X& ——3.6. This is similar to Xz ——3.7, which they
deduced for the Pt center, suggesting to them a similar
transition in both cases, one related primarily to an im-
purity s-like level rather than a lattice-vacancy-like level.
However, a recent very careful study showed Xz——20,

close to the value Xz ——16 obtained earlier by Bruckner. ' Accepting this recent value X&——20+2, obtained by two
independent methods with two different devices on the
same Si wafer, one concludes that Lowther's conclusion of
the similar origin of the donor transitions in Si:Au and
Si:Pt and his contention that acceptor and donor transi-
tions in Si:Au commence from two different levels (with large and small relaxation changes, respectively) are both
unsupported by recent data.
The way in which degeneracy factors can be used to
delineate different electronic structure models for these

centers has been illustrated by Ralph. He considered
two possible energy-level models for Si:Au: the one-
electron level, leading to acceptor and donor action, could be either ligandlike (i.e., p-type orbitals) or impuritylike
(i.e., d-type orbitals). In the first case, the neutral and
negatively charged centers Au and Au would have p
and p" configurations, respectively; whereas, in the latter
case, the configurations would be d and d, respectively.
These differing possibilities would then lead to different
predictions of electronic degeneracies. Ralph then ob-
tained the many-electron multiplet terms appropriate for
either case and delineated the ground-state from the
excited-state configurations on the basis of an assumption
of strong Coulomb and spin-orbit interactions. Hence, he
obtained (acceptor) electronic degeneracy factors ranging from —,

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to 4 for the p-orbital model and a degeneracy fac-
tor of 4 for the d-orbital model. Although the results
were not conclusive and omitted the vibrational entropy
factor, he favored the latter results on the assumption that
the electrically active levels in Si:Au were presumably
similar to those in 3d-doped Si, where the overriding role
of the d component had been established. This question
of the orbital origin of the electrically active gap levels
remained unsolved.

F. Electron paramagnetic resonance

Another factor contributing to the lack of a microscop-ic model for group-IB impurities in Si is the failure to ob-
serve any EPR that could be associated with an isolated
impurity. Recently, Hohne observed the EPR of gold-
related centers in Si. In addition to the signal of Cu-Au
clusters, he also observed another center with a highly an-isotropic g factor, suggestive of a very low C~l, symmetry. He concluded that since a Jahn-Teller (JT) distortion can-
not lower the symmetry below C2„, the even lower C&I,
symmetry he observed had to be related to complex for-
mation with a nearby defect, such as carbon, sulfur, or a
3d atom. Two other centers [denoted as Au(1) and

Au(2)] were initially thought to be related to substitution-al gold; however, Kleinhenz and co-workers
showed that the Au(1) spectrum was identical to that of the Fe-Au complex observed by them earlier.

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The
failure

Bruckne 315.346ET BT /Xor SiAu(2)]

t3

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ously observed)

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upper valence band (VB3)

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transition-atom d orbitals, one might take the point of
view that these orbitals are chemically inert (corelike) and
that group-IB impurities in Si behave essentially as mono-
valent s' species. The view of group-IB elements as
monovalent

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Property CU Ag Au

(

Ip)expt
(

Ip)expt

(IP)SR
(IP)SR
sR(LD)
ed (LD)

&rd)Lo
&s (HF)
NR(HF)
&r.)HF

Oxidation states
0

r»(A)
Electronegativity

7.73
20.29
9.25
15.73
5.67
8.36
2.76
0.97
7.75
20.14
2.97
0.92

2,(1)
1.35
1.9

7.58
21.49
9.17
16.86
5.72
10.70
2.93
1.37
7.06
19.21
3.30
1.31

1.60
& 1.9

9.22
20.50
11.20
15.64
7.41
10.03
2.70
1.57
6.98
17.98
3.39
1.

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IV. METHOD

We have used the self-consistent quasiband crystal-field

(QBCF) Green's-function method of I.indefelt and
Zunger to solve for both substitutional Ag and Au and
interstitial Au impurities in silicon within the local-
density approximation. This complements results ob-
tained earlier for the substitutional Cu impurity. We
have constructed semirelativistic pseudopotentials (i.e., a
single-component wave function with a relativistic poten-
tial, not including spin-orbit interactions) using the same procedure previously employed to introduce other core ef-
fects into the pseudopotential (e.g.,

self-interaction-

corrected pseudopotentials). Our procedure is analo-
gous to that proposed by Kleinman (producing indeed
very similar results), but does not achieve "norm conser-
vation" through manipulation of the potential; instead,
this is achieved through the Zunger-Cohen original pro-
cedure. We use an exchange coefficient of n,= 1, as be-
fore. The resulting (pseudopotential) atomic orbital en-
ergies and ionization energies are given in Table I. The QBCF method has been previously tested for the unre-laxed Si vacancy and applied to numerous other prob-
lems, including substitutional and interstitial 3d im-
purities in Si, the core exciton

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and substitutional 3d

impurities in GaP, ' '

and chalcogen impurities in sil-
icon. ' We will not repeat the details of the method
here; the interested reader is referred to these previous
publications on this subject. We note that in calculating
the levels of the charged states 3+ or 3 we extend the
integration of the change in charge density up to a dis-
tance R, that assures the electrostatically correct charge
of I/eo and —I/ec for A+ and A, respectively (where
eo is the dielectric constant). The same cutoff R, is used
for the neutral state. A small, effective-mass correction
for the long-range electrostatic potential (omitted from
the Green's-function calculation) is then outside R, ap-
plied to the calculated eigenvalues.

tronic charge q; enclosed within a sphere of nearest-
neighbor radius (4.44 a.u. in Si) around the impurity, for each of the impurity-induced states i, into its angular momentum l components. The results are normalized to
one electron. We now proceed with the identification of
these calculated impurity-induced states.

0.06—

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I

t

Si:Ag

CFR

~ 0.04-

0.02—

A. Crystal-field resonances

The occupied tz" and e

" levels appear as reso-
nances around the center of the valence band, and show a
nonmonotonic ordering (Ag is the deepest) and an octa-
hedral level arrangement (e " above t2"). The total
electronic charge enclosed in these levels within a

nearest-neighbor sphere (q; in Table II) shows the ec"
state to be over 90% localized and the t2" state to be 70—80% localized. The degree of localization of both
levels decreases somewhat with atomic number Z, paral-
leling the increased size of the nd atomic orbitals (cf.
(rd)LD——0.97, 1.37, and 1.57 a.u., respectively, for Cu,
Ag,

and

Table).The these

n p Au inreso- relatihe of

the t2" lo

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Si

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levels for

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unr(laxe7,)Tj ET BT /Xi9 8.73 Tf 240.892522 Td (substitutional)Tj ET BT /Xi9 9.26 Tf 54.562490.56 Td (Cu,)Tj ET BT /Xi9 9.26 Tf 22.11 240 Td (Ag,)Tj ET BT /Xi9 8.73 T

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anelin-bo(nd)Tj ET BT /Xi9 9.32 Tf1811.561699.44 Td (ybrid2")Tj ET BT /Xi9 9.77 Tf2618.891698.78 Td (DBHs),

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r(enzation)Tj ET BT /Xi9 9.4 Tf 789.33813.44 Td ET BT /Xi9 12.47 TfTd (thes0)Tj ET BT /Xi9 8867 T /Xi9 12.47 TfTd (theu10.78944 p44 694p44 694p44 69

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Au'-

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l

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3.0 4.0

Distance (a.u.)

tion (Table II) shows the e

" level to be pure d-like,
whereas the t2" level is strongly d-like, with some ad-
mixture of p character from the tails of the ligand sp or-
bitals. Figure 4 depicts the radial charge density of the
e
" wave function (for Ag we sum the densities of the
two resonances) and for Si:Ag and Si:Au (results for Si:Cu
were presented previously), showing some delocalization
with increasing atomic

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These

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TABLE III. Population analysis of the ground state of substitutional Si:Cu (Refs. 73 and 86), Si:Ag, and Si:Au. For cornpar-ison, the results for the silicon vacancy (Ref. 86) are also given.

Qi'

1.709
0.000
0.000
0.141
0.016

0.000
0.000
4.293
0.000
0.086

Si.Cu
0.000
0.000
0.000
0.453
0.070

Q

2

0.000
2.978
6.909
0.156
0.189

1.709
2.978
11.202
0.750
0.361

1.824
0.000
0.000
0.138
0.017

ge

0.000
0.000
4.202
0.000
0.081

Qi'

Si.Cu
0.000
0.000
0.000
0.406
0.066

Q

2

0.000
2.783
6.657
0.144
0.186

Qs

1.824

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e

" and

t 2" valence-band levels become slightly more
deeply bound, with more localized wave functions. This enhanced localization around the impurity contributes an additional 0.05e and 0.20e, from
fro

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o t9 o'"(gfg)'", Ag s "p

'

(dfg)'", and Au
0.30 0.65(gg)

9.54

VI. INTERSTITIAL GOLD IN SILICON

We have calculated self-consistently the

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0.12

0.10—

C$

0.08- I

U

0.06— ~~

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(b) (c)

1.2—

0.8—

0.4—

0.0—

-2—

C
LLI 4

Substitu-

Vacancy + Interstitial ~ tional

/

a'„a', (0/+),'

(3

/

(0/),.'t-

/

~t {O/-) (0/+) i

/'

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'

(+/2+) //
I

e (+/2+) a,
{2+/3+)

t4

t'

t2 ~" (

/2-)-

T

(O/+)

e

-8—

- 10—

- 12—

and Au. The N =2, 3,4 system can show an
N=2~N=3 transition [first acceptor, AE '
the vacancy or first donor, hE (+/0) in Si:Au]

(0/
as well

) in-

as an N =3~N =4 transition [double acceptor
b,E '

(—/2 —) in the vacancy, first acceptor hE '

be

information

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Si:Au].
normal,
the acceptor

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Si:Au

b,

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(+/0)
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gap
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S. D. Brotherton and J. Bicknell, J. Appl. Phys. 49, 667 (1978).
S. Braun and H. G. Grimmeiss, J. Appl. Phys. 45, 2658
(1974).
~K. D. Glinchuk and N. M. Litovchenko, Fiz. Tverd. Tela 6,
3701 (1964) [Sov. Phys.

—Solid State 6, 2963 (1965)].
~D. V. Lang, H. G. Grimmeiss, E. Meijer, and M. Jaros, Phys.
Rev.

B 22, 3917 (1980).
"'(a) C. T. Sah, L. Forbes, L. I. Rosier, A. F. Tasch, and A. B. Tole, Appl. Phys. Lett. 15, 145 {1969);(b) L. D. Yau and C. T. Sah, ibid. 21, 157 (1972).
O. Engstrom and H. G. Grimmeiss, J. Appl. Phys. 46, 831 (1975).
W. Fahrner and A. Goetzberger, Appl. Phys. Lett. 21, 329 (1972).
~K. D. Glinchuk, A. D. Denisova, and N. M. Litovchenko, Fiz. Tverd. Tela 7, 3669 (1966) [Sov. Phys.

—Solid State 7,
2963 (1966)].
45J. Mazzaschi, J. C. Brabant, Mme. B. Brousseau, J. Barrau, M. Brousseau, F. Voillot, and P. Bacuvier, Solid State Com-mun. 39, 1091 (1981).
L. A. Ledebo and Zhan-Guo Wang, Appl. Phys. Lett. 42, 680 (1983).
~7R. M. Feenstra and S. T. Pantelides, Phys. Rev.

B (to be pub-
lished).

~8K. Nagasawa and M. Schulz, Appl. Phys. 8, 35 (1975). ~

(a) J. E. Lowther, J. Phys.

C 13, 3665, 3681 (1980); (b) S. D.
Brotherton and J. E. Lowther, Phys. Rev. Lett. 44, 606 (1980).
50R. Kassing, L. Cohausz, P. van Staa, W. Mackert, and H. J. Hoffman, Appl. Phys.

A 34, 41 (1984).
5~8. Bruckner, Phys. Status Solidi

A 4, 685 (1975).
H. I. Ralph, J. Appl. Phys. 49, 672 (1978).
53M. Hohne, Phys. Status Solidi

B 99, 651 (1980); 109, 525
(1982); 119,K117 (1983).
54V. S. Postnikov, V. I. Kirillov, Yu. A. Kasputin, N. N. Pri-bylov, Yu. I. Kozlov, and V. V. Misneev, Fiz. Tekh. Polupro-vodn. 14, 2265 (1980) [Sov. Phys.—Semicond. 14, 1342 (1980)].
G. D. Watkins, in Lattice Defects in Semiconductors 1974 (IOP, London, 1975), p. 1.
G. W. Ludwig and H. H. Woodbury, Phys. Rev. 126, 466 (1962).
57(a) J. C. M. Henning and E. C. J. Hgelmeers, Phys. Rev.

B 27,
4002 (1983};(b) R. F. Milligan, F. G. Anderson, and G. D. Watkins, ibid. 29, 2819 (1984).
58D. Thebault, J. Barrau, M. Bousseau, Do Xuan Thanh, J. C. Brabant, F. Voillot, and M. Ribault, Solid State Commun. 45, 645 (1983).
5~G. W. Ludwig and H. H. Woodbury, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 223.
U. Kaufmann and J. Schneider, Adv. Electron. Electron