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Electronic states of simple-transition-metal impurities in silicon*

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The $X\alpha$ scattered-wave cluster method has been used to investigate the electronic properties associated with simple substitutional transition-metal impurities in silicon. The impurities studied were chosen from the $3d$ row of the periodic table and include chromium, cobalt, nickel, copper, and zinc. In all cases the defect behavior (donor or acceptor) has been correctly determined, and the calculated position of the corresponding defect level in the gap has been found to be in good agreement with the measured values in all cases except that of cobalt. Trends in the electronic behavior of $3d$ transition metal defects are discussed and correlated with the local bonding properties of the host-defect system.

I. INTRODUCTION

Defects that produce energy levels deep in the bandgap of a semiconductor have long been difficult to investigate from a theoretical point of view, although such defects are often of fundamental importance in understanding the semiconductor's electronic properties. A particularly important class of such defects, and one which has received scant theoretical attention, is composed of the transition-metal impurities in group-IV and -III-V semiconductors. Such impurities give rise to a remarkable sequence of levels deep in the band gap of the host material,[1,2] often corresponding to several different charge states of the impurity. Despite the richness of the observed effects, however, theoretical modeling of such impurities has not been particularly successful. It shall be the purpose of this paper to report on the results of recent calculations of the electronic properties associated with selected neutral, substitutional transition-metal impurities in silicon. These calculations are to be viewed as a first step toward a systematic study of such defects, the purpose of which is to try to understand the basic physical and chemical mechanisms involved.

The basic problem in the theoretical description of these and other defects which produce levels deep in the bandgap of the host material is that the associated perturbing potential and wave functions are usually quite localized in real space, whereas most standard theoretical approaches such as effective-mass theory[3,4] are rooted in the extended formalism of $\vec{k}$ space. Such a representation is not really well suited to the study of localized properties. Recent improvements of the standard theory using generalized pseudopotential techniques[5] have widened the range of applicability somewhat, but even with these improvements the formalism is not well suited to the study of transition-metal defects.

An alternative approach to the study of localized defects is the defect-molecule or cluster method proposed by Coulson and Kearsley.[6] In this approach one utilizes the localized nature of the defect properties of interest and, to a first approximation, replaces the host solid by a molecular cluster consisting of only those host atoms in the vicinity of the defect. The localized electronic properties associated with the defect are then determined by a direct comparison of results obtained from an "ideal" cluster (without the defect) and a defect cluster containing the appropriate defect. Such an approach has already been successfully applied to the study of lattice vacancies in group-IV[7,8] and -IV-VI[9,10] semiconductors, as well as simple impurities in silicon,[11,12] and is expected to work equally well in the present case of transition-metal impurities in silicon.

The results to be described in this paper have been derived from the investigation of an 18-atom cluster consisting of five silicon atoms (a central site plus its four nearest neighbors), plus 12 hydrogenlike atoms added at the sites of the 12 next-nearest neighbors in order to saturate the "dangling bonds" at the cluster surface.[13] The corresponding defect clusters have been formed by replacing the central silicon atom by an appropriate neutral transition-metal atom. The transition-metal impurities employed in this study include chromium, cobalt, nickel, copper, and zinc. These impurities span the range of the $3d$ transition metals that are known to produce levels deep in the gap of silicon.[1,2] The cluster model described here is essentially identical to that employed by Cartling *et al.*[11,12] in their study of the effects of selected simple impurities in silicon, except for the fact that interstitial spheres have not been employed to try to account for non-muffin-tin corrections to the cluster potential. Such spheres were shown to have minimal effect on the final results[11] and have been neglected for con-

venience.

The electronic properties of the clusters have been calculated using the self-consistent $X\alpha$ scattered-wave method originally formulated by Johnson and co-workers.[14-16] Basically, one assumes a muffin-tin approximation to the cluster potential and uses multiple-scattering theory, coupled with the local $X\alpha$ approximation for exchange,[16] to solve for the self-consistent cluster energy levels and associated wave functions. The calculational formalism is by now well documented in the literature and the reader is referred elsewhere[14,15] for details. The values of the exchange parameters (i.e., the α's) for silicon and the various transition-metal impurities have been taken from the tabulated values of Schwarz.[17] The value $\alpha = 0.727$ appropriate to silicon has also been used for each of the 12 hydrogen saturators (as these are meant to simulate missing silicon sites) as well as in the intersphere and extramolecular regions. The radii of the muffin-tin spheres have been taken to be the same for all atoms in the cluster and have been assigned the value of 2.22 a.u., which is half of the nearest-neighbor Si-Si distance in bulk silicon.

The valence-energy-level spectra appropriate to the clusters to be discussed in this paper are shown schematically in Figs. 1 and 2. In all cases the clusters exhibit tetrahedral symmetry and the energy levels are therefore labeled according to the irreducible representations of the tetrahedral point group T_d.

FIG. 1. Calculated energy level spectra for the clusters representing (a) "ideal" silicon and silicon with the substitutional transition metal impurities (b) chromium and (d) cobalt. (c) The energy level spectrum appropriate to a silicon vacancy, where X denotes the vacancy. Also indicated are the (occupied) valence and (unoccupied) conduction bands obtained from the cluster model.

FIG. 2. Calculated energy level spectra appropriate to substitutional (a) nickel, (b) copper, (c) and zinc transition metal impurities in silicon clusters.

II. RESULTS

First consider the "ideal" Si_5H_{12} cluster [Fig. 1(a)]. If one fills states according to the Pauli principle, one finds that those states below and including the $1T_1$ level at -0.676 Ry are fully occupied, while the levels above and including the $3A_1$ level at -0.598 Ry are unoccupied. The gap between the occupied and unoccupied states is 0.078 Ry,[18] or about 1.05 eV, which is surprisingly good agreement with the accepted experimental value of 1.15 eV for bulk silicon[19] at 0 °K. The lowest-lying occupied levels are primarily s-like in character, while those lying nearer the top of the occupied band are more p-like, in agreement with the x-ray emission data[20] on bulk silicon. Cartling[12] has already discussed the adequacy of the Si_5H_{12} cluster as a representation of bulk silicon and so this topic will not be mentioned further here, other than to point out that this simple 18 atom cluster does a surprisingly good job of re-

producing all of the essential features of bulk silicon that are thought to be important in the determination of localized excitations.

Now consider what happens when the central silicon atom in the Si_5H_{12} cluster is replaced by a chromium impurity. The corresponding energy levels of this $CrSi_4H_{12}$ cluster are shown in Fig. 1(b). The spectrum looks similar to that of Si_5H_{12} except that the A_1 levels are shifted upward in energy, and a new state, labeled $0E$ in Fig. 1(b), appears in the previously empty gap region between the occupied and unoccupied levels. The upward shift of the A_1 levels has already been discussed by Cartling[12] and has to do with the fact that these states now receive contributions from the $4s$ states of chromium rather than $3s$ levels of silicon.

The origin of the extra E state in the $CrSi_4H_{12}$ spectrum can be attributed to the extra d-levels introduced into the cluster by the substitution of chromium for silicon. In the presence of the tetrahedral symmetry of the impurity environment the tenfold-degenerate $3d$ levels of atomic chromium are split into fourfold-degenerate E and sixfold-degenerate T_2 orbitals. The $0E$ level at $-.63$ Ry of Fig. 1(b) is primarily composed of this crystal-field-split E level from the chromium impurity, although there is also a fair amount of mixing (30%) of the silicon antibonding orbitals of E symmetry from the unoccupied conduction states. The T_2 level that originates from the Cr $3d$ levels, on the other hand, does not primarily retain its atomic character, but instead interacts strongly with the silicon T_2-bonding orbitals. Both of the bonding T_2 orbitals of Fig. 1(b) (at -0.733 and -0.698 Ry, respectively) have about 35% of their contribution from the chromium $3d$ electrons.

It is useful, at this point, to think of the creation of a substitutional impurity as a two-step process. One first removes a silicon atom from the lattice, creating a silicon vacancy, and then one places the appropriate impurity at the vacant lattice site. The electronic properties associated with the creation of a silicon vacancy have been discussed elsewhere[21] and the results will only be summarized here. The energy level spectrum corresponding to a vacancy in the present model is shown in Fig. 1(c) (labeled XSi_4H_{12}, where X denotes the vacancy). The major effect of the creation of the vacancy is the breaking of bonds between the central site and its neighbors. This is reflected in the spectrum of Fig. 1(c) by the raising of the $2T_2$ bonding level of the ideal spectrum [Fig. 1(a)] out of the occupied states into the energy gap. The $2T_2$ level in the gap of the XSi_4H_{12} spectrum is then an acceptor level associated with the broken bonds at the vacancy site.

In the case of a chromium impurity, this $2T_2$ level is found to move back into the occupied valence band, corresponding to the formation of bonds between the chromium atom at the silicon vacancy site and the neighboring silicon atoms. The new bonding orbitals now, however, have s–d contributions from the chromium atom rather than s-p character, as was the case when silicon occupied the central site. Similar behavior was calculated by Cartling[12] for the case of a substitutional iron impurity in silicon.

Neutral chromium has six valence electrons. The interpretation of the present calculation is that four of these electrons become involved in the formation of tetrahedal bonds with the neighboring silicon atoms, repairing the broken bonds introduced by the creation of the silicon vacancy, while the remaining two electrons go into what are primarily nonbonding atomic d-like impurity levels deep in the silicon band gap. Such a chromium impurity acts like a donor and the position of the donor level in the present calculation is given by $E_v + 0.051$ Ry $= E_v + 0.69$ eV,[22] where E_v denotes the valence band edge.

Now suppose that the impurity is cobalt rather than chromium. The appropriate energy level structure is shown in Fig. 1(d) (labeled $CoSi_4H_{12}$). In addition to the already discussed upward shift of the A_1 levels, Fig. 1(d) differs from 1(a) in the fact that one finds additional E and T_2 levels [labeled $0E$ and $0T_2$, respectively, in Fig. 1(d)] within the Si_5H_{12} valence states, while the level corresponding to the $2T_2$ level of Fig. 1(a) is shifted out of the occupied valence states into the gap.

The new $0E$ and $0T_2$ states are primarily atomic-like cobalt $3d$ levels, although there is some mixing of silicon orbitals of the same symmetry in each case. The $0E$ level at -0.742 Ry has about 85% of its contribution from the cobalt $3d$ states, while the $0T_2$ levels at -0.760 Ry has approximately 77% cobalt d character. The $2T_2$ level at -0.589 Ry in Fig. 1(d) is quite analogous to the just discussed $2T_2$ acceptor level in the vacancy cluster spectrum [Fig. 1(c)].

In contrast to the situation involving the chromium impurity, the cobalt d levels do not interact strongly with the neighboring silicon atoms but instead retain their atomiclike character for the most part. The defect levels associated with the substitutional cobalt impurity seem to be associated with the broken bonds at the impurity site, and not with the d states of the impurity atom itself. Of course the cobalt impurity also perturbs and shifts the position of the acceptor level in the gap.

The results for neutral nickel, copper, and zinc impurities in silicon follow the same qualitative trend as does cobalt. The corresponding energy

TABLE I. Comparison of the calculated values of the energies of selected transition-metal impurity levels to measured values (taken from Ref. 1). All energies are in eV. Also listed in parentheses is the type of impurity, with (*D*) representing donors and (*A*) acceptors.

Impurity	Measured energy (type)	Calculated energy (type)
Chromium	$E_v +0.74$ (*D*)	$E_v +0.70$ (*D*)
Cobalt	$E_v +0.62$ (*A*) $E_v +0.52$ (*A*) $E_v +0.35$ (*D*)	$E_v +1.03$ (*A*)
Nickel	$E_v +0.82$ (*A*) $E_v +0.23$ (*A*)	$E_v +0.83$ (*A*)
Copper	$E_v +0.52$ (*A*) $E_v +0.37$ (*A*) $E_v +0.24$ (*A*)	$E_v +0.57$ (*A*)
Zinc	$E_v +0.60$ (*A*) $E_v +0.31$ (*A*)	$E_v +0.26$ (*A*)

level spectra are shown in Figs. 2(a)–2(c), respectively. In each case one finds extra $0E$ and $0T_2$ levels to be introduced into the occupied valence states, while the $2T_2$ level of Fig. 1(a) is pushed out of the occupied valence states into the gap region between the occupied and unoccupied levels.

As one goes along the row of the periodic table from cobalt to nickel to copper to zinc, one finds that the new $0E$ and $0T_2$ levels move down in energy through the silicon valence states. In the cases of Co, Ni, and Cu, these levels remain within the silicon valence band, but retain much of their atomic *d*-like character. Such states can be interpreted as *d*-like resonances in the valence band. In the case of a zinc impurity the $0E$ and $0T_2$ levels become well separated in energy from the bottom of the silicon valence levels and have the unmistakable character of core states, being essentially 100% $3d$-like.

As was the case for a cobalt impurity in silicon, the $2T_2$ level in the gap of Figs. 2(a)–2(c) is associated with broken bonds between the central atom and its silicon neighbors. As one goes along the sequence cobalt to nickel to copper to zinc, one finds that this acceptor level approaches closer to the occupied valence states, indicating that the impurity potential becomes more attractive (or less repulsive) with increasing Z. The calculated energies of this acceptor level[22] are shown in Table I for the various cases considered, and varies from $E_v + 1.03$ eV in the case of $CoSi_4H_{12}$ to $E_v + 0.26$ eV in the case of $ZnSi_4H_{12}$. The $2T_2$ level has about 17% *d* character for $CoSi_4H_{12}$, 9% for $NiSi_4H_{12}$, 4% for $CuCi_4H_{12}$, and no *d*-character for $ZnSi_4H_{12}$.

III. DISCUSSION AND CONCLUSIONS

Two types of behavior emerge from this study of substitutional transition metal defects in silicon, with chromium and iron exhibiting quite different properties than cobalt, nickel, copper, and zinc. To understand this behavior it is useful to consider the relative energies of the $3d$ and $4s$ levels in the free $3d$ transition metal atoms. Herman-Skillman-type calculations[23] of the free atoms have been done in this investigation for all of the transition-metal atoms considered here and one finds that, as one goes along the row of the periodic table, the atomic $3d$ level starts out above the $4s$ level in energy, but lowers in energy with respect to the $4s$ level as Z increases, passing through somewhere around Mn. In chromium, the atomic $3d$ level lies about 0.9 eV above the $4s$ level, while in iron the order is reversed, with the $3d$ level now being about 2 eV below the $4s$ level.[24] As one continues along the row this ordering ($4s$ above $3d$) remains, but the separation between the two levels continues to increase, going from 3.3 eV for cobalt to 4.8 eV for Zn.

One reason why chromium and iron form bonds with the neighboring silicon atoms, while cobalt, nickel, copper and zinc do not, seems to be that the atomic $4s$ and $3d$ levels are close enough in energy in the former case so that tetrahedral *s-d* hybrids can be formed without a terrible expenditure of energy. This energy can then be regained by the extra stability obtained from the bonding configuration. The atomic $4s$ and $3d$ levels of cobalt, nickel, copper, and zinc, on the other hand, are too far separated for the formation of *sd* hybrid orbitals to be energetically feasible, and so such orbitals are not formed and bonding with the silicon neighbors does not occur.

At this point it would be desirable to compare the theoretical results of this study to the available experimental data. However, comparison is difficult because of uncertainties in the identification of defect level structure with specific impurities. In most cases, levels have been assigned to various transition-metal defects, but it has often not been possible to ascertain such things as the charge state of the defect or its position in the lattice (whether it is interstitial or substitutional, or perhaps in some sort of deformed substitutional site or in a complex). Without such information, comparison between theory and experiment is difficult. In Table I are listed measured values of the defect levels associated with the transition metal defects considered in this paper. The values quoted in this table are taken from the book by Milnes (Ref. 1) and cover the experimental situation up until about 1972 or so.

By comparing the results of the present study to the experimental values listed in Table I, one sees that the extremely simple model used in this paper correctly predicts whether or not the transition metal impurity will act as a donor or acceptor, and even seems to give reasonable good quantitative agreement with the position of the defect levels with respect to the valence band edge in all cases except cobalt. Of course, this assumes that the experimental values are appropriate for substitutional impurities. Nickel, copper, and zinc are thought to be substitutional,[1] while the situation for chromium and cobalt is unclear. Agreement between theory and experiment in the present case indicates that chromium may also be substitutional. Cobalt does not seem to fit into this simple scheme and may involve more complicated defect configurations than considered here.

It should also be pointed out that the present study does not include such effects as lattice relaxation and/or distortion in the presence of the impurities. In fact, in most cases considered here, the impurity levels are only partially occupied, leading to the possibility of a Jahn-Teller-type of distortion to lower the symmetry and split this degeneracy. Such distortions may lead to shifts in the energies of the calculated defect levels, but there is no *a priori* way to predict these effects in the present model without redoing the calculations in a self-consistent fashion for the new cluster configuration. Such calculations have not yet been done but are under consideration for future investigations.

It should be noted that more than one experimental value is listed for many of the impurities in Table I. These could correspond to different charge states of the impurity. For impurities donating more than one electron to defect levels in the gap, for example, one would observe more than one ionization potential. Such effects can be studied in the present model by removing an electron from the defect levels, effectively ionizing the impurity, and redoing the calculation to obtain the new position of the direct level. Such calculations are in progress and the results will be reported at a later time.

Before closing, a comment about the simple model used in this calculation is in order. There are two major sources of error in this study: the finite size of the cluster, and the use of a muffin-tin approximation to the cluster-potential. The effect of the rest of the solid seems to have been handled in a satisfactory fashion by the use of the hydrogenlike atoms to saturate the dangling bonds of the silicon atoms surrounding the defect site. It is by now well established that the nearest neighbor coordination is the most important factor affecting the electronic properties of tetrahedrally bound semiconductors, and the present model includes this explicitly. As for the muffin-tin approximation, non-muffin-tin corrections can be included in an approximate fashion by the use of overlapping muffin-tin spheres.[16] Preliminary calculations indicate that such a procedure changes the actual values of the energies of the defect levels with respect to the band edges somewhat, but does not alter any of the conclusions reached in this paper. A more detailed study is being carried out and will be published at a later date.

To summarize, a simple 18 atom cluster has been used to study the electronic properties associated with various transition metal defects in silicon. The model has correctly identified the trends in behavior of the defects and has provided an explanation of this behavior in terms of the local bonding properties of the solid. The calculated energy levels associated with the defect are in surprisingly good agreement with experiment, considering the problem of identifying the experimental defect levels with specific defect configurations. The effect of different charge states of these impurities is under investigation using this same model. Altogether, a great deal of information and understanding has been obtained, and the cluster technique has been shown to be a rather powerful technique for the study of these strongly localized effects.

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[1]A. G. Milnes, *Deep Impurities in Semiconductors* (Wiley, New York, 1973).
[2]S. M. Sze and J. C. Irvin, Solid State Electron. 11, 599 (1968).
[3]W. Kohn and J. M. Luttinger, Phys. Rev. 98, 915 (1955).
[4]S. T. Pantelides and C. T. Sah, Phys. Rev. B 10, 621 (1974).
[5]S. T. Pantelides and C. T. Sah, Phys. Rev. B 10, 638 (1974).
[6]C. A. Coulson and M. J. Kearsley, Proc. R. Soc. A 241, 433 (1957).
[7]F. P. Larkins, J. Phys. C 4, 3065, 3077 (1971).
[8]R. P. Messmer and G. D. Watkins, Phys. Rev. Lett. 25, 656 (1970); Phys. Rev. B 7, 2568 (1973).
[9]L. A. Hemstreet, Phys. Rev. B 11, 2260 (1975).
[10]L. A. Hemstreet, Phys. Rev. B 12, 1212 (1975).
[11]B. G. Cartling, B. Roos, and U. Wahlgren, Chem. Phys. Lett. 21, 380 (1973).
[12](a) B. G. Cartling, J. Phys. C 8, 3171 (1975); (b) 8,

3183 (1975).
[13]E. B. Moore, Jr. and C. M. Carlson, Solid State Commun. 4, 47 (1966).
[14]K. H. Johnson, J. Chem. Phys. 45, 3089 (1966).
[15]K. H. Johnson, in *Advances in Quantum Chemistry*, edited by P. O. Löwdin (Academic, New York, 1973), Vol. 7, p. 143.
[16]J. C. Slater, *The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974).
[17]K. Schwarz, Phys. Rev. B 5, 2466 (1972).
[18]This value represents the difference in energies between the unrelaxed $3A_1$ and $1T_2$ levels of Fig. 1(a). The transition state procedure outlined in Refs. 15 and 16 has not been applied.
[19]G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. 111, 1245 (1958); Phys. Chem. Solids 8, 388 (1959).
[20]G. Wiech, Z. Phys. 207, 428 (1967).
[21]L. A. Hemstreet (unpublished).
[22]The calculated value represents the energy difference between the appropriate unrelaxed impurity level and the unrelaxed valence-band edge.
[23]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).
[24]This value has not been calculated here but has been crudely estimated from Fig. 3 of Ref. 12b.