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Metastable impurities in semiconductors: Si:Mg and Si:Be

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Using 30-year-old ideas on Fermi-energy- (ϵ_F) induced stability enhancements in impure semiconductors, it follows that if two impurity sites with different electrical levels exist, one can expect to find, inside the band gap, a critical Fermi energy ϵ_F^b such that one site is stable for $\epsilon_F > \epsilon_F^b$ and the other for $\epsilon_F < \epsilon_F^b$. This bifurcation of the site-preference energies leads to general metastabilities, as demonstrated here for Si:Mg and Si:Be, using self-consistent local-density total-energy calculations.

Many of the characterization techniques of impure solids aim at establishing the impurity's "site preference."[1-5] The propensity of a given impurity atom to select a specific geometric site when diffused at equilibrium into a solid has generally been perceived to be an innate property of the impurity and host atoms.[1-5] Such tendencies have therefore been discussed in terms of classical constructs of metallurgy and structural chemistry, including factors such as size and electronegativity mismatch (e.g., the Hume-Rothery rules[1]), crystal-field stabilization energies,[2] orbital radii,[3] work functions, and electron densities (e.g., the Miedema rules[4]), and general chemical bonding models.[5] While these classification schemes were generally successful both at the limits of zero-gap materials (i.e., in metallurgy[1,3,4]) and for wide-band-gap materials (e.g., in ionic crystals and coordination compounds[2]), application of such site-preference rules to semiconductors has led to perplexing situations: For example, among divalent impurities, both Be (Ref. 6) and Zn (Ref. 7) appear to "select" in Si the substitutional site, whereas Mg, having similar atomic size, electronegativity, etc., was observed only at the tetrahedral interstitial site;[8] in Ge, all divalent impurities take up the substitutional site.[9] Diffused-in $3d$ impurities[10] take up interstitial sites in Si, but substitutional sites in III-V and II-VI compounds.

More than 30 years ago it was realized[11(a)-11(c)] that the introduction by the impurity of ionizeable electrical levels inside the semiconductor band gap can affect the system's stability [hence, also solubility[12(a)]], depending on the position of the Fermi energy ϵ_F relative to the electrical levels. This is so because these electrical levels depend on the impurity site. These ideas were used some time ago to understand site-dependent solubility,[12(a)] diffusion,[12(a)] and migration enhancement[12(b)] in semiconductors, and more recently were reintroduced by several groups in the context of modern calculations on metastability and diffusion enhancement.[13] As was first pointed out by Longini and Greene,[11(b)] these Fermi-level dependences lead to particularly interesting behavior in the case of amphoteric impurities. They show that the site preference of amphoteric impurities is strongly dependent on the Fermi level and that in general these impurities will prefer minority-type sites. In this paper we focus on the interesting possibilities of bistability, metastability, and bifurcation of the stable site. We discuss in detail how a Fermi-energy shift can change the stable site of an impurity. Using Be and Mg in Si as examples, we show how these ideas can lead to the existence of a bifurcation in the site preference as a function of ϵ_F, and how this can lead to metastability, whereby the site characterized experimentally after the sample is quenched to low temperatures is *not* the stable one. Temperature-dependent changes in the Fermi energy are shown to lead to metastable impurities in normal processing.

By way of a general example, consider an impurity or defect A which can adopt one of two lattice configurations α or β in a host crystal, such that on site α the charge states A_α^0, A_α^+ can exist, and on site β the charge states A_β^0 and A_β^- are possible. Such is the case, for example, for[14] ZnSe:Li, where the Zn-substitutional position β leads to an acceptor with ionization energy $\Delta E_\beta(0/-)$, whereas the interstitial position α supports a donor with energy $\Delta E_\alpha(0/+)$ (Fig. 1). $E[A_\beta^0]$ and $E[A_\alpha^0]$ denote the total energies of the impurity and host system when the impurities are neutral; as such, they do not contribute carriers to the "Fermi sea," hence these energies do not depend on ϵ_F. In their charged states, however, electrons are exchanged

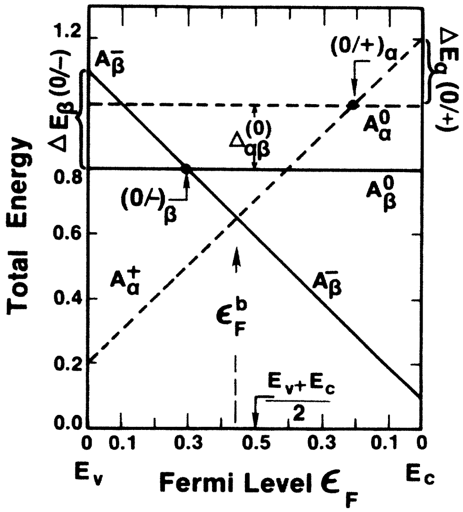

FIG. 1. Schematic total energy diagram for an impurity with two sites: β, a single acceptor, and α, a single donor.

between the impurity and the Fermi sea so that the total energies are

$$E[A_\alpha^+,\varepsilon_F]=E[A_\alpha^0]+\Delta E_\alpha(0/+)+\varepsilon_F-E_c\ ,$$
$$E[A_\beta^-,\varepsilon_F]=E[A_\beta^0]+\Delta E_\beta(0/-)-\varepsilon_F+E_v\ . \qquad (1)$$

Figure 1 shows a graphical representation of these equations; as ε_F is raised from the valence-band maximum (E_v) towards the conduction-band minimum (E_c), $E[A_\alpha^+,\varepsilon_F]$ rises and $E[A_\beta^-,\varepsilon_F]$ decreases (both linearly), reflecting the change in total energies[11,12] as the electron or hole is removed from the impurity to ε_F. Observe that a bifurcation point ε_F^b can exist, at which $E[A_\alpha^+,\varepsilon_F^b]=E[A_\beta^-,\varepsilon_F^b]$. From Eq. (1), one obtains

$$\varepsilon_F^b[A_\alpha^+/A_\beta^-]=\tfrac{1}{2}(E_v+E_c)+\tfrac{1}{2}\{E[A_\beta^0]-E[A_\alpha^0]\}$$
$$+\tfrac{1}{2}\{\Delta E_\beta(0/-)-\Delta E_\alpha(0/+)\}\ . \qquad (2)$$

If $\varepsilon_F<\varepsilon_F^b$ then A_α^+ is the lowest-energy thermodynamic ground state, whereas if $\varepsilon_F>\varepsilon_F^b$ then A_β^- is the ground state; in this case, A_α^0 and A_β^0 are never the ground state for any value of ε_F. Expressions similar to Eq. (2) can be constructed by analogy for any other charge states, e.g., for the system $\{A_\alpha^{2+},A_\alpha^+,A_\alpha^0,A_\beta^0,A_\beta^-$, and $A_\beta^{2-}\}$ pertinent to Be and Mg in Si (see Fig. 3 below) we have

$$\varepsilon_F^b[A_\alpha^{2+}/A_\beta^{2-}]=\tfrac{1}{2}(E_v+E_c)+\tfrac{1}{4}\Delta_{\alpha\beta}^{(0)}+\tfrac{1}{4}\delta_{\alpha\beta}^{(0,-,0,+)}$$
$$+\tfrac{1}{4}\delta_{\alpha\beta}^{(-,2-,+,2+)}\ , \qquad (3)$$

where

$$\delta_{\alpha\beta}^{(-,2-,+,2+)}=\Delta E_\beta(-/2-)-\Delta E_\alpha(+/2+)\ ,$$
$$\delta_{\alpha\beta}^{(0,-,0,+)}=\Delta E_\beta(0/-)-\Delta E_\alpha(0/+)\ ,$$

and the stability difference of the neutral impurities is $\Delta_{\alpha\beta}^{(0)}=E[A_\beta^0]-E[A_\alpha^0]$.

If ε_F^b is inside the band gap, the system is bistable; the choice between the two sites is then decided by the value of ε_F at the experimental conditions at which the impurity is introduced into the system (usually high-temperature diffusion).[6-10] If after the sample is quenched to a low-temperature,[6-9(b)] atomic mobilities are small and activation barriers to structural changes are large, the high-temperature configuration may persist. This *bistability* can then lead to a *metastability*: At the high introduction temperature, the semiconductor is intrinsic, hence $\varepsilon_F\cong\frac{1}{2}(E_v+E_c)$. In the example of Fig. 1, A_β is then quenched in as the majority site. If at lower temperatures there are more β impurities than α, these cannot all be A_β^- (this will violate charge neutrality). Therefore, A_β^0 and A_β^- must have a distribution such that ε_F is pinned at $E_v+\Delta E_\beta(0/-)$. However, at this ε_F, Fig. 1 shows that the α site is more stable, hence, metastability. We have not described in detail the processing conditions for which this metastability will occur. This obviously depends on the rate at which the equilibrium between the two sites is established compared to the quenching rate. What we *can* say, however, is that *if*, for such a system, electrically active impurities are observed, i.e., there is an excess of impurities on one of the sites, they *must* be metastable.

For what systems is a bifurcation point likely to exist in the band gap? First, sites α and β must support charges of opposite signs.[15] This condition can be satisfied in principle by many common impurities and defects, e.g., if an *sp*-electron impurity (I) with valence $Z_{\rm I}$ can exist both interstitially and substitutionally on a host (H) site with valence $Z_{\rm H}$, such that $Z_{\rm H}-Z_{\rm I}<0$. Examples that are possible *a priori* include ZnSe:Li, GaAs:Cu,Zn, Si:Li,Au,Mg,B, or the combination of a cation vacancy (multiple acceptor, type β) and an anion antisite defect (multiple donor, type α). Second, the corresponding electrical levels must be in the band gap. This excludes impurity atoms with large ionization potentials (whose donor states are in the valence band) or with small electron affinities (whose acceptor states are in the conduction band). Third, the stability difference $\Delta_{\alpha\beta}^{(0)}$ of the neutral impurities must be sufficiently small [Eqs. (2) and (3)]. This restrictive condition is likely to exclude cases where one site is exceptionally stable because of chemical reasons (e.g., isocoric substitutional impurities such as GaAs:Zn, Si:Al, or Si:S which effectively heal the vacancy dangling bonds), or when one site is exceptionally unstable, either because of steric size effects (large impurity in a small volume site), or because of chemical effects (e.g., substitutional Li in Si, healing only $\frac{1}{4}$ of the dangling bonds). This condition is likely to be satisfied, however, when the impurity at both α and β is equally inert (e.g., substitutional and interstitial nonbonding impurities in Si such as He, Be, or 3*d* impurities[10]), or when the impurity has an equal number of bonding electrons on both sites α and β, e.g., substitutional and interstitial impurities with $Z_{\rm H}-Z_{\rm I}=Z_{\rm I}$ (i.e., Si:Be, Mg and ZnSe:Li). We choose the low-solubility divalent impurities[6-8] in Si as an illustrative example, most likely to satisfy the bifurcation conditions.

Mg was observed[8] to have in Si both a single *donor* $\Delta E_{\rm TI}\times(0/+)=E_c-0.11$ eV and a double *donor* $\Delta E_{\rm TI}\times(+/2+)=E_c-0.26$ eV [hence, its inferred[8] tetrahedral interstitial (TI) site]. Electron paramagnetic resonance (EPR) experiments and optical absorption studies[8] confirm the TI site. In contrast, Si:Be, Si:Zn, Ge:Be, and Ge:Zn have substitutional (S) geometries: Si:Be has an *acceptor* level[6] $\Delta E_{\rm S}(0/-)=E_v+0.145$ eV; its double acceptor (observed[9] in Ge) was not seen in Si, but Zn was observed[7] to have in Si both *acceptor* levels, i.e., $\Delta E_{\rm S}(0/-)=E_v+0.32$ eV, and $\Delta E_{\rm S}(-/2-)=E_v+0.66$ eV. Figure 2 shows the calculated relative total energies $E[M]=(E[{\rm Si}_nM_m]-nE[{\rm Si}])/m$ of various sites for the neutral $M=$ Be, Mg impurities in Si. We use the self-consistent nonlocal pseudopotential total-energy method,[16] with Wigner's correlation, nonlocal, analytically continued pseudopotentials,[17] a number of special **k** points equivalent to ten points in the primitive diamond unit cell, a plane-wave basis with cut-off values of 10 Ry (15 Ry for tests), and a supercell geometry consisting of eight (16 for tests) atoms. The convergence errors in the total energies, due to both supercell size and basis-set cutoff, are found to be below 0.2 eV. Nearest-neighbor lattice relaxations around the impurity have been calculated by energy minimization assisted by quantum-mechanical forces.[16] We also show the energy for bulk metallic solid, the antifluoride silicides M_2Si, as well as the energies of the free M atoms. We find that (i) these impurities are less stable than the metal plus

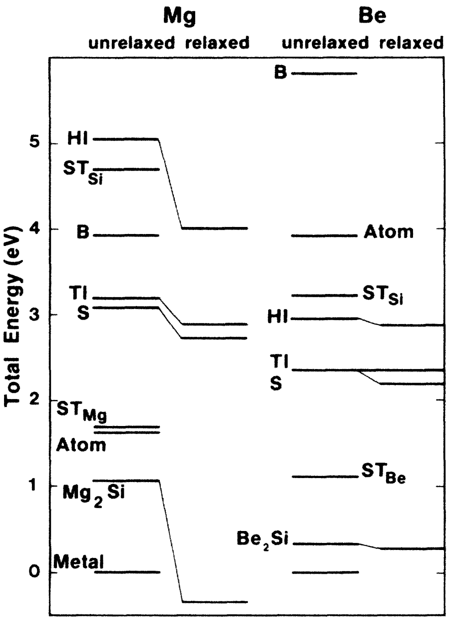

FIG. 2. Calculated total energies $E[M]$ for neutral impurities in Si. S, TI, and HI refers to substitutional, tetrahedral interstitial, and hexagonal interstitial, respectively. ST_{Si} is a substitutional impurity next to a Si tetrahedral interstitial, B is a bond-centered impurity (with the two neighboring Si allowed to relax along the ⟨111⟩ direction to their mirror image position), and ST_M refers to a substitutional M next to a tetrahedral interstitial M. Also shown are the ground-state impurity atomic energy (Atom) and the energy of the bulk silicide M_2Si. The free metal is chosen as the zero of energy.

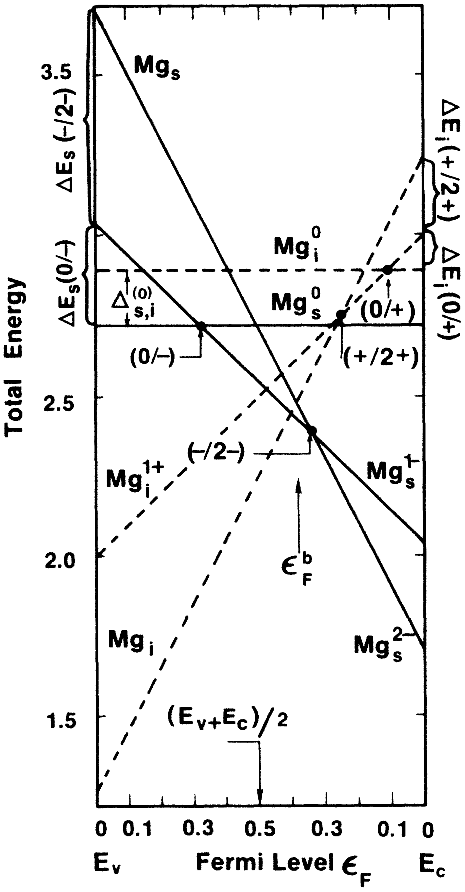

FIG. 3. Total energy diagram for the various charge states of substitutional (S) and tetrahedral interstitial (i) Si:Mg, using the band gap as the unit of energy.

silicon; Mg impurities are also less stable than the free impurity atom plus silicon, whereas the converse is true for Be impurities (except site B), (ii) when a S and a TI impurity are placed next to one another, the stability is enhanced considerably relative to the isolated pairs (by 1.25 eV and 1.4 eV for Be and Mg, respectively), clarifying the reason why these impurities tend to aggregate (unless special measures are taken[8]), (iii) Mg induces much larger lattice relaxations than does the smaller Be impurity, (iv) Mg silicide (Mg_2Si) is *more stable* (after relaxation to its equilibrium lattice constant) than the Mg metal plus Si, whereas the Be silicide is *less stable* than Be metal plus Si, clarifying the observation[18] that bulk Mg_2Si exists, but no Be silicide exists and, (v) the configurations α and β most likely to satisfy the bifurcation conditions [Eq. (3)] are S and TI: Their stability difference is as small as $\Delta^{(0)}_{S,TI} \cong -0.1$ eV (of the order of the uncertainty in the calculation). Since calculated supercell local density energy levels and band gaps are prone to systematic errors[13] (but not total energies), we use instead the observed electrical levels and band gap, and approximate the unknown Mg acceptor levels by those of Zn. (The two elements have similar p-orbital energies and the observed acceptor level[9(b)] for substitutional Zn and Mg in Ge are within 10%. Furthermore, small differences relative to Mg are inconsequential to our argument below, as can be seen from Fig. 3.) Using the calculated $\Delta^{(0)}_{S,TI}$ (Fig. 2) we show in Fig. 3 the total energy diagram for Si:Mg. We find for Si:Mg the bifurcation energy $\varepsilon_F^b[\mathrm{Mg}_{TI}^{2+}/\mathrm{Mg}_S^{2-}]$ to be *above midgap,* whereas a similar calculation for Be places it *below midgap.* The difference arises from the fact that Be has more tightly bound electrons (i.e., it is closer to a rare-gas atom) than Mg, hence larger ionization energies, and the crossover points $\Delta E_{TI}(0/+)$ and $\Delta E_{TI}(+/2+)$ shift down in the gap. Using the data of Figs. 2 and 3, we have solved numerically the equations of mass action[14] for all charge states of S and TI Si:Mg, as well as the electron (n) and hole (p) concentrations (at a fixed impurity concentration of[18(b)] 10^{15} cm^{-3}). We find the relative equilibrium concentration profiles shown in Fig. 4, verifying the dominance of TI over S at high temperatures (where the sample is seen to be intrinsic), and a crossover temperature of 600 K, where electrical compensation[14] should occur. Our result then indicates that when these impurities are introduced in a high-temperature intrinsic sample[6,8] [$\varepsilon_F \cong (E_v+E_c)/2$] the stable sites are interstitial Mg and substitutional Be. Our foregoing discussion hence suggests that the observation at low temperature by absorption and EPR experiments[6,8] of precisely these site symmetries corresponds therefore to *metastable sites.*

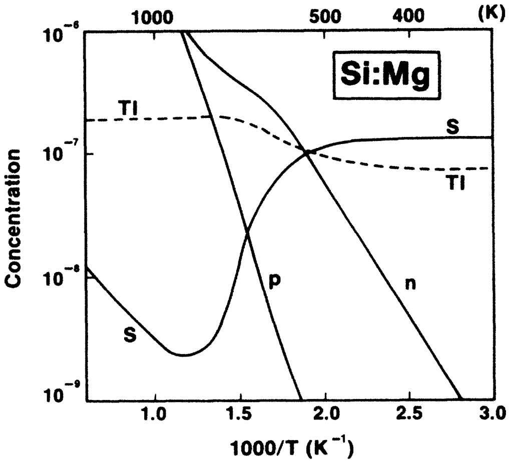

FIG. 4. Relative equilibrium concentration profiles for S and TI sites of Si:Mg. The temperature variation of the band gap and entropy effects other than variational entropy have been neglected.

Indeed, some hints in this direction are already provided by the experimental data,[6,8] showing the disappearance of the characteristic EPR signals after long storage and various light-induced metastabilities.

The conditions leading to bifurcation and metastability are likely to exist in other systems as well: data on[14] ZnSe:Li, 3*d* impurities[10] in Si, and[19] Si:Au suggest the possibility of a similar situation. For example, using the calculated[20] $E_{\mathrm{S}}(0/-)$ and $E_{\mathrm{TI}}(0/+)$, $E_{\mathrm{TI}}(+/2+)$ for Si:Cr we find a substitutional-interstitial bifurcation point to exist in the Si band gap for $0.2 > \Delta^{(0)}_{\mathrm{S,TI}} > -0.9$ eV. Only the (metastable) TI site will be observed in quenched-in samples if $\Delta^{(0)}_{\mathrm{S,TI}} > -0.4$ eV. Similarly, for[19] Si:Au, ε^{b}_{F} is in the gap if $0.6 \geq \Delta^{(0)}_{\mathrm{S,TI}} > -1.6$ eV. This general mechanism for bifurcation and metastability suggests that if one can experimentally control ε_F *at the impurity introduction stage* (e.g., by varying the temperature and dopant concentration) to be at a given side of ε^{b}_{F}, a desired impurity site can be engineered or by slow cooling of the sample (e.g., substitutional Si:Mg in highly *n*-type Si).

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