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**Invited**

# Defects in Semiconductors

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Simple physical concepts are presented for understanding the electronic structure of impurities in semiconductors. We first consider them undistorted in the Td interstitial or substitutional site. Lattice distortions are then treated as Jahn-Teller in origin and therefore predictable in terms of the electronic configuration of the defect. It is proposed that the metastability of DX and EL2 in GaAs and its alloys may be understood within this framework.

## 1. INTRODUCTION

In the perfect semiconductor crystal, there is a completely filled valence band, an empty conduction band, and a forbidden gap in between, where no electronic states can exist. Introducing a defect into the crystal destroys the perfect periodicity of the lattice and in so doing can introduce electronic states into the gap, often profoundly changing the electrical and optical properties of the material.

There are an infinite variety of defects, ranging progressively from those of atomic dimensions, to complexes, aggregates, voids, dislocations, grain boundaries, interfaces, surfaces, etc. All are important. Still, in a talk such as this, I must limit myself. What I will attempt to do therefore here is only to give a brief overview of what we think we may have learned about the physics of the simplest of the defects - the point defects. If we understand these, we have clearly made an important first step towards understanding the more complex ones which can be considered in a sense as simply arrays constructed from point defect "building blocks".

## 2. CONCEPTS

In Fig. 1, we illustrate the characteristic hydrogenic energy levels of an isolated neutral atom vs. its nuclear charge Z in relation to the valence band and conduction band edges of a typical semiconductor. If we could cut out an atomic size spherical cavity in the semiconductor (without significantly perturbing it) and insert an impurity atom, we see in this simple illustration that there are a large number of possible atoms (possible Z's) which would like to bind an electron within the forbidden gap.

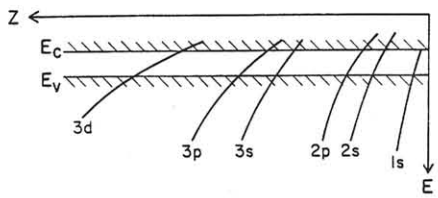


Fig. 1. Neutral atom energy levels vs. Z, shown relative to the band edges of a typical semiconductor.

To improve on this simple picture, we next consider the effect of overlap and interaction between the electronic states of the impurity and the semiconductor host. To do this, we first consider <u>interstitial</u> impurities, for which the model of Fig. 1 is most directly applicable since the cavity is created in a low electron density region of the host and perturbs it the least. Next we consider <u>substitutional</u> impurities. Here it is instructive to treat first the lattice <u>vacancy</u>, which is the "cavity" into which the impurity is inserted. It, in turn, provides the host electronic states with which the impurity must interact.

## 3. INTERSTITIAL IMPURITIES

In Fig. 2, we illustrate the additional effect of the interaction of the isolated

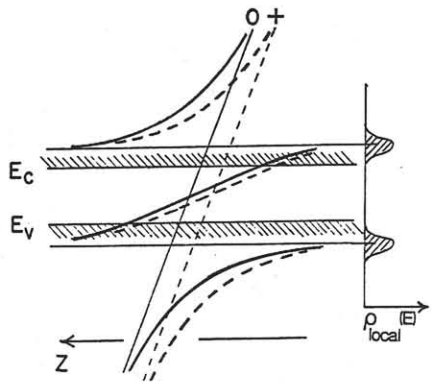


Fig. 2. Simple model for the interaction between the electronic levels of an interstitial atom and the near band edge host states. Shown are the results for a neutral and positively charged atom.

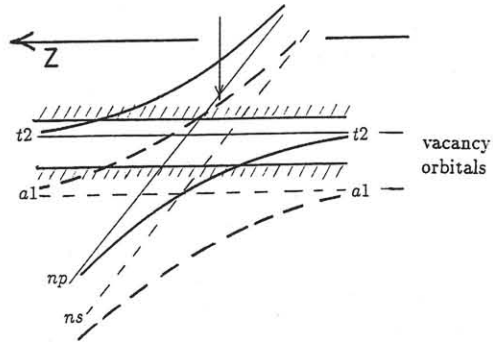


Fig. 3. The level structure for a substitutional impurity viewed as the result of interaction between its s and p valence orbitals and the a1 and t2 orbitals of the vacancy into which it is inserted. The arrow indicates Z for the missing host atom.

atom states with the host. We show schematically a density of states which have localized character around the cavity and with which the interstitial atom will interact forming bonding and antibonding "molecular" orbitals. Quantum mechanically, interacting levels cannot cross, the net result being therefore to squeeze more states into the gap. We show also in the figure the effect of changing the charge state of a given atom by drawing a corresponding set of curves for singly positive charged atoms. The large difference in ionization energies for the isolated atom are also greatly compressed in the semiconductor by this effect.

The net result therefore is that interaction with the near band edge states serves to confine states in the gap, both vs. Z, and vs. charge state for a given impurity. The result of the first is that most interstitial impurities should produce levels in the gap and that of the second is that several charge states may be stable for each impurity (greatly reduced Hubbard correlation energy U).[1]

## 4. SUBSTITUTIONAL IMPURITIES

Unlike the case for the interstitial, cutting out a cavity for a substitutional impurity is not a small perturbation to the host. Instead, we are in effect creating a lattice vacancy by removing a host atom and rupturing the strong chemical bonds to its four neighbors. The atomic orbitals of the impurity atom will overlap and interact strongly therefore with the symmetric s-like (a1 symmetry) and p-like (t2 symmetry) vacancy molecular orbitals that can be formed from the dangling bonds of the four neighbors that protrude into the cavity.

This is illustrated in Fig. 3 where we illustrate schematically the strong interaction and level repulsion between the atomic s and p orbitals of an inserted atom and the vacancy a1 and t2 orbitals respectively. [In the figure, the a1 and t2 vacancy orbitals have been located energetically as expected for an elemental semiconductor such as silicon.[2] The arguments that follow are the same however for a partially ionic semiconductor such as GaAs, with a1 and t2 vacancy orbitals in or near the gap still being produced on either sublattice. The only difference is that on the Ga sublattice, the vacancy levels tend to be shifted downwards somewhat because they arise from dangling orbitals on the As neighbors, while the As vacancy levels which arise from Ga orbitals are shifted correspondingly slightly upward.]

An immediate observation here is that the presence of the t2 vacancy orbital in the gap now serves to repel p-like levels from the gap. In fact, states of t2 symmetry only exist now in the gap when the corresponding isolated atomic p-level resides well outside of the gap region and then it approaches that of the vacancy. Still, it approaches the vacancy t2 level only slowly vs. Z, meaning that such states can indeed exist in the gap for a wide range of Z but that when they do, they are essentially vacancy-like in character.

The s-states are freer to enter the gap but again the strong repulsion with the a1 vacancy level serves to make it cross through the gap at a greatly reduced rate vs. Z.

And so the result is somewhat the same as that for the interstitial impurity in that a1 and t2 levels tend to be formed in the gap over a wide range of Z. Similarly, because of the greatly reduced level position shift in the gap vs. Z, the U of the defect levels is also greatly reduced from the free atom values, and several charge states can exist. But the physics is very much different. This is conveniently illustrated by considering a silicon atom as an impurity in silicon. In

the substitutional site, interaction with the vacancy orbitals serves to clear the gap and the vacancy is "healed" (Fig. 3). In the interstitial site, it is optimumly placed energetically to produce a level in the middle of the gap since its atomic energy is close to that of the gap (Fig. 2).

## 5. LATTICE RELAXATIONS

The preceding discussion has assumed that the inserted atom stays on-center when placed in either the interstitial or substitutional site and the neighbors retain their symmetrical Td arrangements around it. There is a fundamental theorem, however, which says that if there is orbital degeneracy associated with the defect, one can expect a symmetry lowering distortion. This is the Jahn-Teller effect.[3] Since t2 (p) levels are three-fold degenerate, we can therefore expect distortions when a t2 level is partially occupied in the gap.

Fig. 4 illustrates some of the important consequences of such a distortion. Shown is a hypothetical deep donor D which undergoes a distortion (mode Q) when it traps an electron into a degenerate orbital in the $D^o$ state. Shown are three adiabatic total energy surfaces, one for the undistorted $D^+$ state, a second displaced upward by the bandgap $E_g$ to represent $D^+$ plus a free electron and hole, and a third when the defect traps an electron, $D^o + h^+$, and distorts. As illustrated in the figure, the electrical level position is defined in terms of the relaxed total energy of each surface. The Jahn-Teller distortion therefore directly alters the position of the level in the gap. Secondly, the intersecting energy curves supply a "multiphonon" mechanism for electron ($\sigma_e$) and hole ($\sigma_p$) capture processes, otherwise difficult for a deep level. Thirdly, carrier capture means entry into a high vibrational state of the resulting charge state and this energy may be utilized for "recombination-enhanced" migration, defect formation, etc.

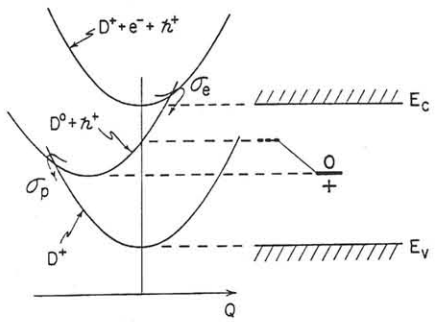


Fig. 4. Configurational coordinate model for a defect with large relaxational change vs. charge state.

Consider, for example, the self-interstitial in silicon. In the $Si^{++}$ charge state, the atomic configuration is $3s^2$, leading to $a1^2$ in the semiconductor which is non-degenerate and we can expect it therefore to reside undistorted in the symmetric Td interstitial site. In the $Si^+$ (or $Si^o$) states, however, one (or two) electrons are added, giving the configuration $3s^2 3p^1$ (or $3s^2 3p^2$), and the corresponding partially occupied $t2^1$ (or $t2^2$) orbitals now predict a distortion. Physically we can think of this as atomic rearrangement so that the p-orbitals on the atom can enter into the bonding. This is indeed precisely the result found from recent state-of-the-art total energy quantum mechanical calculations.[4-6] The calculated energy gains from the distortions are in fact so large as to predict negative-U properties and athermal recombination-enhanced migration, explaining perhaps many of the unusual properties inferred experimentally for the defect.[7]

Several other examples will be cited. We will also suggest that the metastability of the much studied DX and EL-2 centers in GaAs and its alloys may be understood in terms of such Jahn-Teller effects.

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