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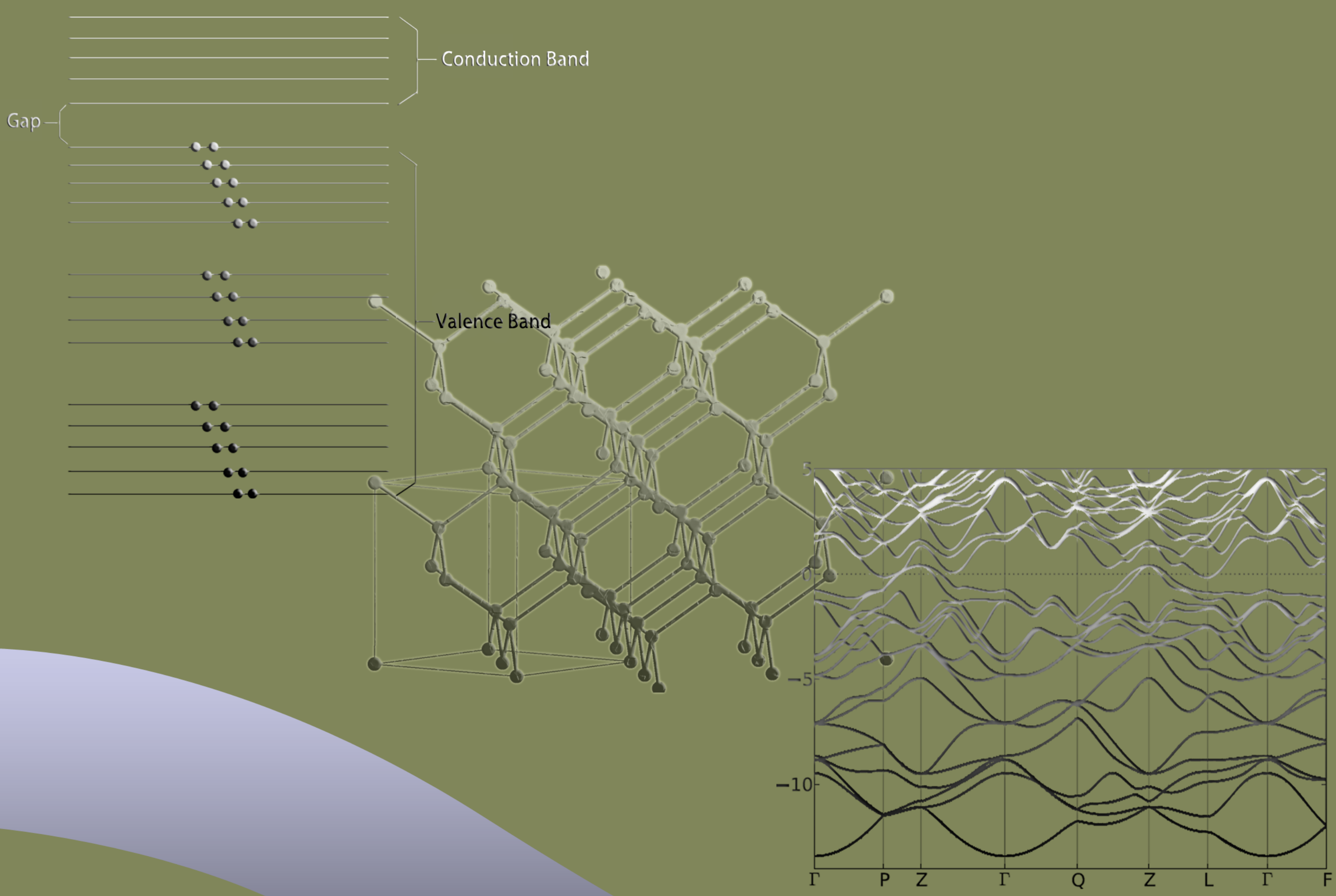
Energy diagram for defects



Introduction

The defects in crystal structure can never be avoided in any cases, and some of the defects do the main the job when implanted into devices. Typical examples include n-type and p-type doped semiconductors, which can be seen everywhere in modern daily life. As a matter of fact, it is the charge state of defects that matters from the perspective of application. For the typical n-type or p-type semiconductors, it is easy to get that they are negatively or positively charged, respectively. However in general cases, how do we describe such charges states from the viewpoint of physics, i.e. what does the energy level diagram look like? Or how do we describe specific defect is negatively or positively charged using energy diagram? Here basics concerning the energy diagram of defects is given. Also the negative-U and positive-U property of defects are also introduced as basic preparation for further reading about defects in crystals.

1. Acceptor and Donor Level

If recalling the description for extrinsic semiconductor, a new energy level is introduced into the bandgap accounting for the conductivity. In Fig. 1., the labeled 'donor energy level' refers to the energy level introduced by n-type doping, from which electrons can easily jump to conduction band to act as charge carrier. As for 'acceptor energy level' introduced by p-type doping, it makes electrons easily be excited from conduction band to stay on the new extra energy level.

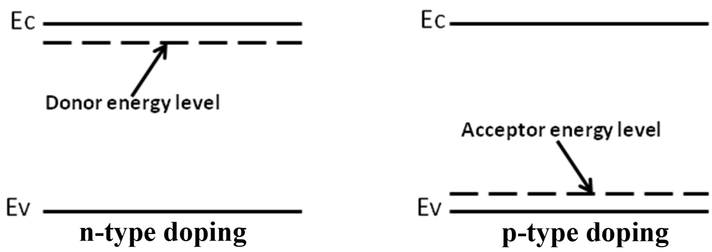


Figure 1. Energy level introduced by dopants within extrinsic semiconductor.

Here if carefully thinking about the depiction method above, the newly introduced energy level is actually the Fermi level of corresponding extrinsic semiconductor. In another word, it is the position change of Fermi level by doping that influence the charge state of n-type or p-type doped defects (the doping, is obviously a kind of defects). Generally, if we are talking about other sorts of defects, similar idea can also apply for specific cases. So here the definition of acceptor level and donor level is introduced. It should be noticed that there is great difference between the definition of acceptor level (or donor level) here with 'acceptor energy level' (or 'donor energy level') above.
As can be seen in Fig. 2., the *acceptor level* and *donor level* is defined as a specific position of energy level. More specifically for intrinsic semiconductor, the defined acceptor or donor level is fixed. It

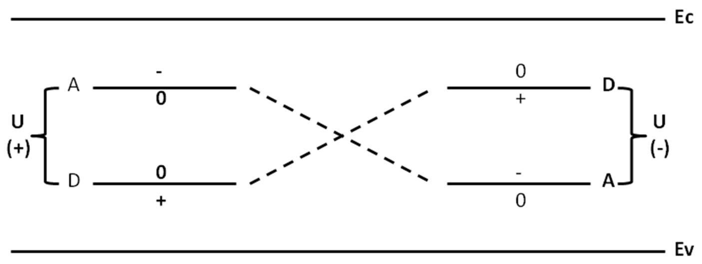


Figure 2. Acceptor level and donor level for the discussion of defects charge states. 'A' here represents *acceptor level*, and 'D' represents *donor level*. The left side refers to positive-U [U(+)] property and the right side refers to negative-U [U(-)] property.

is the new position (the 'new' here refers to extrinsic semiconductor, or in other cases, it refers to the influence of specific defects on Fermi level) of Fermi level relative to the defined acceptor or donor level that determines properties of corresponding defects. When Fermi level (E_f) is above *acceptor level* (in another word, it is closer to bottom of conduction band), according to Fermi-Dirac distribution, there is great chance for electrons to distribute at the bottom of conduction band. If electrons jump to the bottom of conduction band, then it will make the defects negative. To better understand the negative charge state in this case, it is helpful to recall the case of n-type doping in which the defects (the n-type dopant) is obviously negative and also the Fermi level is close to the bottom of conduction band (see Fig. 1., also it is obvious that the Fermi level in this case is above defined *acceptor level*). When Fermi level is below the *donor level* (in another word, it is closer to top of valence band), electrons can easily jump from valence band to the newly formed Fermi level to form holes within valence band. Equally, we can say that the holes on new Fermi level 'jump' to valence top. Hence we can say in this case the defects are positively charged, if, again, the p-type doping defects can be recalled for better understanding.
As for the case when the new position of Fermi level is between the *acceptor level* and *donor level*, the corresponding defect is then neutral.

2. The understanding of charge state based on electron itself

In section-1, the definition of *acceptor level* and *donor level* is given, and the charge state of defects can be determined by looking at the position of the new position of Fermi level. In this part, further understanding for the charge state of defects will be given, and we will focus more on electron itself. When we measure the *d*onor level from the bottom of conduction band, we actually go through the neutrally charged state to positively charged state. In other words, we can imagine bringing the Fermi level all the way down from the bottom of conduction band to *d*onor level, during which it crosses the whole region corresponding to neutrally charged state and terminates at the boundary between neutrally and positively charged states. Furthermore, the charge state changing from neutral

to positive means electron should be kicked out from the originally neutral defects. So we can say energy needed to bring Fermi level down from the bottom of conduction band to $d$onor level equals that for kicking electron out from neutrally charged defect.
As for the $a$cceptor level, again measured from the bottom of conduction band, it means the energy needed to bring Fermi level down to the $a$cceptor level. This part of energy then equals the energy for kicking electron out from originally negatively charged defect to make the defect neutral in charge. If the original charge state of defect is neutral, the existing electrons within the defect is somehow closed packing. As for negatively charged defects, there should exist external electrons, which does not belong to the closed packing of electrons, within the defects. So there should exist Coulomb repulsion between the closed packing of electrons and external electrons, which then makes the energy needed to kick the external electrons out of the defects much smaller than that for kicking electron out from neutral defects. This is why the $a$cceptor level is usually above the $d$onor level in energy diagram, and the energy difference between the $a$cceptor level and $d$onor level is called 'U'.

Moreover, if we notice the definition of ionization energy of atom, which gives the energy needed to kick electron out from neutral atom, the $d$onor level here then can be likened to ionization energy. Also the electron affinity refers to the energy needed to peel electron out of the negatively charged atoms (actually should be called anion), which then can be likened to $a$cceptor level here.

3. Positive-U and Negative-U

In section-2, the definition of 'U' is given, and also it is pointed out that the $a$cceptor level is usually above $d$onor level, which means the U value is usually positive. This is just the commonly defined *Positive-U* property of specific defects. However, the position of $a$cceptor level and $d$onor level can be changed from case to case. And the changing is related to the interaction (hybridization) between impurities band with original band states or the dielectric shielding of the Coulomb interactions (for details, refer to the article Negative-U Properties for Defects in Solids by George D. Watkins). Even in some cases, the $a$cceptor level can be lower than $d$onor level, and this case is called *Negative-U* property of defects.