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Su-Huai Wei, Jie Ma, and Tim A. Gessert
National Renewable Energy Laboratory

Ken K. Chin
New Jersey Institute of Technology

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CARRIER DENSITY AND COMPENSATION IN SEMICONDUCTORS WITH MULTI DOPANTS AND MULTI TRANSITION ENERGY LEVELS: THE CASE OF Cu IMPURITY IN CdTe

Su-Huai Wei¹, Jie Ma¹, T.A. Gessert¹, and Ken K. Chin²

¹National Renewable Energy Laboratory, Golden, CO 80401.

²Department of Physics and Apollo CdTe Solar Energy Research Center, New Jersey Institute of Technology, Newark, NJ 07102

ABSTRACT

Doping is one of the most important issues in semiconductor physics. The charge carrier generated by doping can profoundly change the properties of semiconductors and their performance in optoelectronic device applications, such as solar cells. Using detailed balance theory and first-principles calculated defect formation energies and transition energy levels, we derive general formulae to calculate carrier density for semiconductors with multi dopants and multi transition energy levels. As an example, we studied CdTe doped with Cu, in which V_{Cd} , Cu_{Cd} , and Cu_i are the dominant defects/impurities. We show that in this system, when Cu concentration increases, the doping properties of the system can change from a poor p-type, to a poorer p-type, to a better p-type, and then to a poor p-type again, in good agreement with experimental observation of CdTe-based solar cells.

INTRODUCTION

The CdTe solar cell is one of the most promising thin-film photovoltaic technologies. However, it has a relatively low efficiency (16.5%) [1] compared with its theoretical limit, ~29%. [2] One of the main reasons is because of the low doping level or hole concentration of CdTe. Therefore, to improve the CdTe cell solar conversion efficiency, it is necessary to understand and control its doping properties. Traditionally, a dopant is distinguished as a donor or an acceptor, a single donor (acceptor) or a double donor (acceptor), and a shallow or a deep dopant. These classifications of dopants are well defined when a single dopant is concerned, as shown in most of the text books [3]; however, when a system contains multi dopants and each dopant has multi transition energy levels, then the situations are more complicated.

For example, Sb substitution on the Te site, Sb_{Te} is a single acceptor when it stays alone, but it can behave as a donor when it coexists with other shallower acceptors, such as Cd vacancy V_{Cd} , because in this case electrons at the higher Sb_{Te} level can donate to the lower V_{Cd} level. Moreover, a dopant can usually donate (accept) one or two or even more electrons, thus the dopant can have several charge states and the population of the dopants in each of the charge states depends on the transition energy level, temperature, the coexistence of other

defects, and ultimately the resulting Fermi energy of the electrons. A comprehensive understanding of how to treat these complicated situations has not been presented in the common text books [3], which usually describe, for simplicity, only a single donor or acceptor.

In this work, we will first derive some general formulae to show how to calculate charge carrier concentrations as a function of temperature and dopant concentrations when a system contains multi dopants with multi transition energy levels [4,5]. In our approach, all the dopants are treated equal, i.e., we do not pre-classify the dopants. The charge states of the dopants are obtained self-consistently.

To be more concrete, we will use the doping of Cu in CdTe as an example to describe how the formulae are derived and how dopants interact with each other. The concept can be easily extended to other semiconductor systems. We choose CdTe:Cu as an example because CdTe is one of the most important thin-film solar cell materials and it generally contains Cd vacancies as the most important intrinsic defect, which is a double acceptor, and Cu as an important impurity for improving the efficiency. Cu substitution on the Cd site, Cu_{Cd} , is usually a single acceptor and Cu interstitial, Cu_i , is usually a single donor.

Experimentally, the observed effect of Cu on p-type doping in CdTe is very interesting [6]. After the CdTe polycrystalline thin film is deposited using a method such as close space sublimation (CSS), and a $CdCl_2$ process is performed, the film is coated with ZnTe:Cu, followed by annealing at a certain temperature for back contact. The concentration of Cu in the sample is controlled by the annealing temperature. We noticed that a very low level of Cu inclusion may further reduce the already low conductivity (due to the low p-doping level) of the intrinsic CdTe thin film. Increasing the level of Cu involvement to a certain level, a reversal from deterioration to improvement of conductivity occurs, which leads to an optimized CdTe thin film confirmed by the high efficiency of the solar cell. Further incorporation of Cu into CdTe, however, will turn it from a p-type to an insulating type or even an n-type. Such a complicated and puzzling effect on the property and quality of the CdTe thin film—changing from a poor p-type to a poorer p-type, then to a better and optimized p-type, and then to an insulating type, when Cu incorporation in CdTe increases—has not been fully understood or explained.

THEORETICAL DESCRIPTION

The concentrations of holes (positive charge) and electrons (negative charge) in the system are given by

$$\begin{aligned} p_0 &= N_v e^{(E_v - E_f)/k_B T} \\ n_0 &= N_c e^{-(E_c - E_f)/k_B T} \end{aligned} \quad (1)$$

where E_f is Fermi energy, E_v and E_c are valence band maximum (VBM) and conduction band minimum (CBM), respectively. It is usually convenient to set $E_v = 0$ and $E_c = E_g$, where E_g is the band gap. N_v and N_c are the effective density of states of the valence bands and conduction bands, respectively. After doping, the dopants in the system are partially ionized at a finite temperature. Suppose the concentrations of negative and positive charge induced by dopant ionizations are N_A^- and N_D^+ . The charge neutrality condition is rewritten as

$$p_0 + N_D^+ = n_0 + N_A^- \quad (2)$$

Solving this equation self-consistently, we can get the Fermi energy and hole/electron concentration at equilibrium as a function of temperature and dopant concentrations.

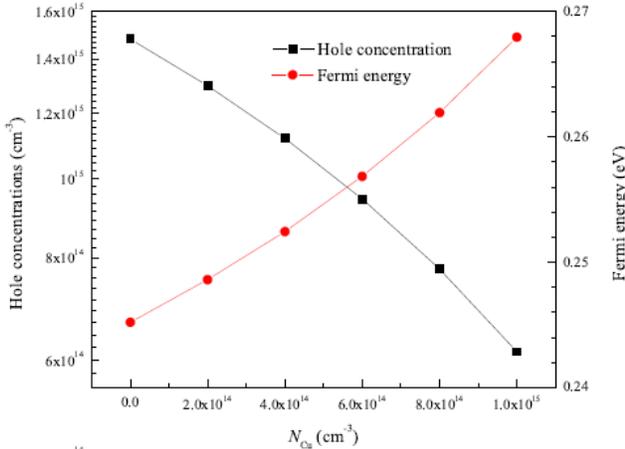


Figure 1 The hole concentration (black square) and Fermi energy (red dot) versus N_{Cu} . At very low Cu concentration, all Cu go to vacancy sites. The hole concentrations decrease as Cu density increases. In this calculation, initial Cd vacancy concentration is $N_{V_{Cd}} = 10^{15} \text{ cm}^{-3}$, $\mu_{Cd} = -0.2 \text{ eV}$ and $T = 300 \text{ K}$. The result here does not depend on the chemical potential of Cd.

For a system with a dopant α that has multiple charge states, the number of the dopant α in charge state q is given by

$$n_\alpha(q) \propto g_q e^{-\Delta H_f(\alpha, q)/k_B T} \quad (3)$$

So after we know the formation energy of dopant α at charge state q (e.g., using first-principles method [7]) and

its degeneracy factor g_q , we can calculate the population $n_\alpha(q)$ when the total number of defect α is known. For a single defect level that can hold one spin-up and one spin-down electron, such as those derived from CBM, the number of possible electron configurations is given by 1, 2, and 1, when this defect level has no electron, one electron, or two electrons.

For a doubly degenerate level that can hold up to two spin-up and two spin-down electrons, such as those derived from VBM of zinc-blende semiconductors with light hole and heavy hole states, the number of possible electron configurations is given by 1, 4, 6, 4, 1, when this defect level has 0, 1, 2, 3, or 4 electrons. In general, $g_q = \sum_i \exp(-E_i/k_B T)$ with the summation over all the possible configurations, where E_i is the energy of the i th configuration relative to the lowest energy $E_1 = 0$. For simplicity we assume the energies are all the same, i.e., $E_i = 0$ for all configurations, which is true for most cases. However, for some cases such as neutral V_{Cd} , the assumption does not hold exactly. Even in this case, our test calculations show that the reduction of the degeneracy factor does not affect our results below. A similar degeneracy factor can be derived for other situations.

For a defect with multi transition energy levels, such as V_{Cd} , the number of defects in charge state q is given by

$$n_\alpha(q) = N_\alpha \frac{g_q e^{-\Delta H_f(\alpha, q)/k_B T}}{\sum_q g_q e^{-\Delta H_f(\alpha, q)/k_B T}} \quad (4)$$

where N_α is the total concentration of defect α and the summation is over all the possible charge states.

For a dopant atom that can form multi defects, such as Cu in CdTe, which can form either Cu_{Cd} or Cu_i , the number of dopants in charge state q of i th type of defect is given by

$$n_\alpha(q, i) = N_\alpha \frac{g_{q,i} e^{-\Delta H_f(\alpha, q, i)/k_B T}}{\sum_{q,i} g_{q,i} e^{-\Delta H_f(\alpha, q, i)/k_B T}} \quad (5)$$

The meaning of every term in the above equation is obvious.

RESULTS AND DISCUSSIONS

Because there are Cd vacancies in the system and the formation energy of Cu occupying Cd vacancies is strongly negative, Cu occupies those vacancies spontaneously until no Cd vacancies exist. The transition energy level of Cu_{Cd} is higher than that of V_{Cd} , so as the concentration of Cu increases, the concentration of the hole decreases (see Fig. 1). This explains why initially the system turns from a poor p-type to a poorer p-type when the Cu is introduced at a very low concentration.

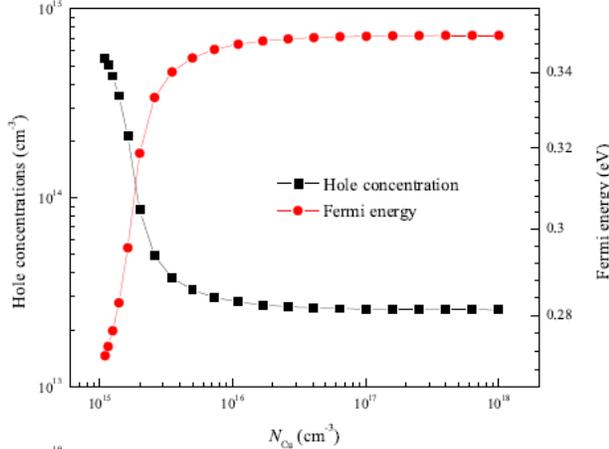


Figure 2 The hole concentration (black square) and Fermi energy (red dot) versus N_{Cu} . In this calculation, $\mu_{Cd} = -0.2$ eV and $T = 300$ K. The hole concentration decreases monotonically and eventually the Fermi energy is pinned.

Next, we add more Cu into the system. Under the Cd-rich growth ($\mu_{Cd} \sim 0$) condition, the formation energy of $Cu_i(+)$ in a p-type sample is smaller than that of Cu_{Cd} , so Cu prefers to go to the interstitial sites that compensate the p-type dopants. Therefore, the hole concentration will keep decreasing as Cu concentration increases (see Fig. 2). However, under Cd-poor conditions ($\mu_{Cd} \sim \mu_{CdTe}$), the formation energy of Cu_i is larger than that of Cu_{Cd} and Cu prefers to be at the substitutional site as an acceptor. Therefore, the hole concentration increases (see Fig. 3). It is clear from the above analysis that the behavior of Cu doping depends sensitively on the chemical potential of Cd. With a low μ_{Cd} , one may observe a turning from poor p-type to better p-type, which eventually saturates. However, the turning from a better p-type to an insulating type is not observed under these equilibrium doping conditions.

In realistic experiments, incorporation of Cu is usually done at a high temperature such as 600 K and the sample is then quenched to room temperature (300 K) for measuring the carrier density. In this case, the populations of dopants should be calculated at doping temperature and the hole concentration should be calculated at the measuring temperature. Because the formation energy of ionized defects also depends on the Fermi energy, we have to do self-consistent calculations twice: first, self-consistently calculating the populations of Cu_{Cd} and Cu_i at doping temperature and then, assuming the impurity has difficulty changing its sites preference at low temperature, keeping the impurity populations fixed and calculating the hole concentration at measuring temperature self-consistently. We have performed the calculations with $\mu_{Cd} = -0.6$ eV. The results are shown in Fig. 4. It shows a clear peak of hole concentration, which is in agreement with the experiments—changing from a poor p-type to a better p-type and then to a poor p-type again. Similar results are obtained for $\mu_{Cd} = -0.2$ eV (see Fig. 5).

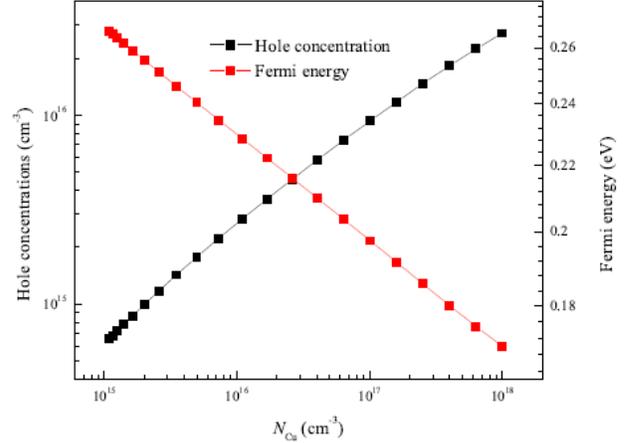


Figure 3 The hole concentration (black square) and Fermi energy (red dot) versus N_{Cu} . In this calculation, $\mu_{Cd} = -0.6$ eV and $T = 300$ K. The hole concentration increases monotonically.

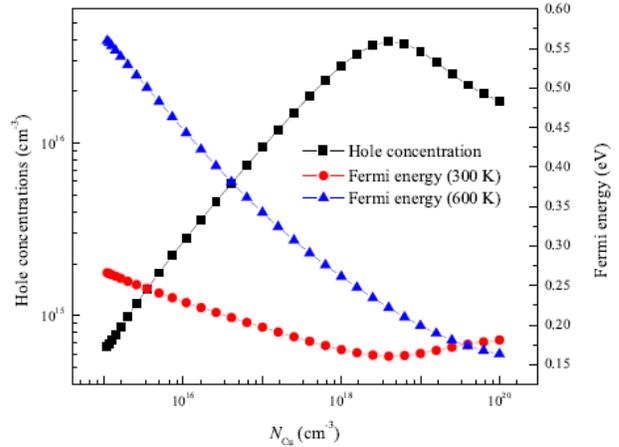


Figure 4 The hole concentration (black square) and Fermi energies at growing temperature (blue triangle) and measuring temperature (red dot) versus N_{Cu} . In the calculation, the populations of Cu_{Cd} and Cu_i are calculated self-consistently at 600 K and the hole concentration is calculated self-consistently at 300 K with $\mu_{Cd} = -0.6$ eV. A clear peak of hole concentration has been built up.

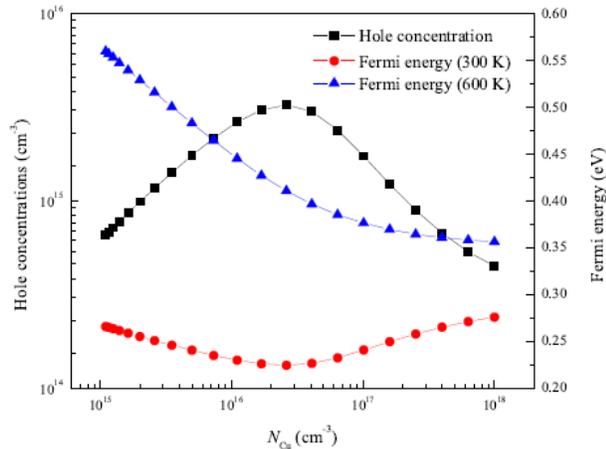


Figure 5 The hole concentration (black square) and Fermi energies at growing temperature (blue triangle) and measuring temperature (red dot) versus N_{Cu} . In the calculation, the populations of Cu_{Cd} and Cu_i are calculated self-consistently at 600 K and the hole concentration is calculated self-consistently at 300 K with $\mu_{Cd} = -0.2$ eV. A clear peak of hole concentration has been built up.

CONCLUSIONS

In conclusion, in this work general formulae are described to derive carrier concentration as a function of Fermi energy and dopant concentration in a multi dopant and multi transition energy level system. By analyzing the competition between the dominant defects V_{Cd} , Cu_{Cd} , and Cu_i using the concept described in this work, we have successfully explained why the properties of the CdTe thin film show such puzzling changes—changing from a poor p-type, to a poorer p-type, to a better p-type, and to a poor p-type again when the Cu doping level is gradually increased. The model proposed here is general and can be applied to any other multi dopant and multi transition energy level system.

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