Search for the Major Chlorine-Related Defects in CdTe:Cl

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Dmitry Krasikov[1], Andrey Knizhnik[1], Boris Potapkin[1], Timothy Sommerer[2]
[1] Kintech Lab Ltd., 1, Kurchatov Sq., Moscow 123182, Russia
[2] GE Global Research, Niskayuna, NY 12309 U.S.A.

ABSTRACT

Understanding the effect of chlorine-related defects on the CdTe electric properties is important both for obtaining high resistivity CdTe-based detectors and for high efficiency CdTe-based thin-film solar cells. The actual mechanism of the effect of Cl on electric properties of CdTe is not clear and different sometimes contradictory hypotheses appear. For example $Cl_{Te}V_{Cd}$ shallow acceptor complex defect was proposed both as a reason of increased carrier concentration in CdTe thin film and also as a reason of high resistivity of CdTe:Cl thin films. In the present work we are trying to clarify the effect of Cl on CdTe electric properties and to find the reason of high resistivity of CdTe:Cl crystals using first principles calculations and defect chemistry modeling. For the first time we are trying to develop a model capable to describe experimental data on both high temperature and room temperature conductivity of CdTe:Cl.

INTRODUCTION

To better understand the effect of chlorine on the defect structure of CdTe it can be useful to analyze the known data on CdTe:Cl single crystals aimed for usage as radiation detectors. It has been experimentally established that the room temperature resistivity of Cl-doped CdTe single crystals increases with Cl concentration, reaching values up to 10^9-10^{10} Ω·cm [1,2,3,4]. As follows from experimental and theoretical works [5,6,7], high resistivity (HR) in CdTe cannot be obtained without deep defect levels in the band gap of CdTe.

The known Cl-related defects in CdTe are shallow donors Cl_{Te} (chlorine on tellurium site) and Cl_i and shallow acceptor A-center [8]. Cl-related DX-centers that could provide a deep charge transition levels in the band gap are unable to be formed in CdTe crystals [9]. So, no deep Cl-related defect that can explain high resistivity of CdTe:Cl was proposed yet. As a consequence, from time to time appear the efforts to model electric properties of CdTe:Cl with shallow defects only. For example in work [8] the defect chemistry model for Cl-doped CdTe crystal was proposed that includes only shallow Cl-related defects. Authors of work [10] tried to show using defect chemistry modeling that shallow defects rather than deep defects can be responsible for CdTe:Cl high resistivity at room temperature.

In the present paper we investigate the reasons of low resistivity in a system with shallow levels only, using first principles calculations and defect chemistry modeling we show that among two deep defects, Cl_i and Cl_{Te}-$Cl_{Cd,}$ the latter is more probably the reason of high resistivity in CdTe:Cl.

CALCULATION DETAILS

Optimization of the atomic structures of defects in different charge states, calculations of the formation energies and analysis of the atomistic mechanisms of the defects formation were performed using the projector augmented wave method with Perdew–Burke–Ernzerhof (PBE)

functional as implemented in VASP code [11]. Calculations of the ionization levels of defects were performed using Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [12]. In all calculations 64 atoms supercell with a 2×2×2 Γ-centered mesh of k-points was used, VBM value was corrected by aligning the core potential of atoms far away from the defect.

Following the approach in works [8,18,13] we developed a defect chemistry model with V_{Cd}, Cd_i (V_{Te} has the same effect as Cd_i) and Cl-related defects in which the concentrations of defects are equilibrated and frozen at HT, and the material properties are then calculated at RT. Concentration of defects are supposed to be frozen at RT because at low temperature the equilibration of defects can be hampered by the high energy barriers for the processes that underlie the defect diffusion, mutual interaction, and defect escape. Interstitial defects with low diffusion barriers can be mobile at RT, but vacancies usually have higher diffusion barriers and are frozen at RT. For example the barrier height for V_{Cd} diffusion was calculated as 1.07 eV, while only 0.4 eV for Cd_i diffusion [14]. The substitution defects like Cl_{Te} and defect complexes are even less mobile than the vacancies because of the more complex diffusion mechanism in which the defect transitions are less probable. Diffusivity of Cl_i defect is unknown so the barrier for Cl_i diffusion was calculated in the present work using climbing-image nudged elastic band method implemented in VASP. The characteristic times of the defect recharging are much shorter than those of the defect diffusion, so the defect charges and carrier concentrations can be equilibrated at RT.

FIRST PRINCIPLES STUDY OF Cl-RELATED DEFECTS

The most probable site for interstitial chlorine in (0), (-1) and (-2) charge states is the site with the surrounding of four Cd tetrahedron (Figure 1 left). In the (+1) and (+2) charge states the most stable site is the site in Cd-Te bond (Figure 1 right). Cl_i defect was found to be amphoteric with (+1/-1) charge transition level at about 0.83 eV above VBM, therefore it will have charge (+1) at Fermi level values from 0 to 0.83 eV. Any diffusion pathway of Cl_i^{+1} defect contains two types of steps. Step 1 with breaking Cl-Cd bond and rotation around Te atom has energy barrier about 1.25 eV and step 2 with breaking Cl-Te bond and rotation around Cd atom with energy barrier about 0.55 eV (see Figure 1 right). Therefore step with barrier 1.25 eV is included in any diffusion pathway and Cl_i^{+1} can be treated as frozen-in at room temperature.
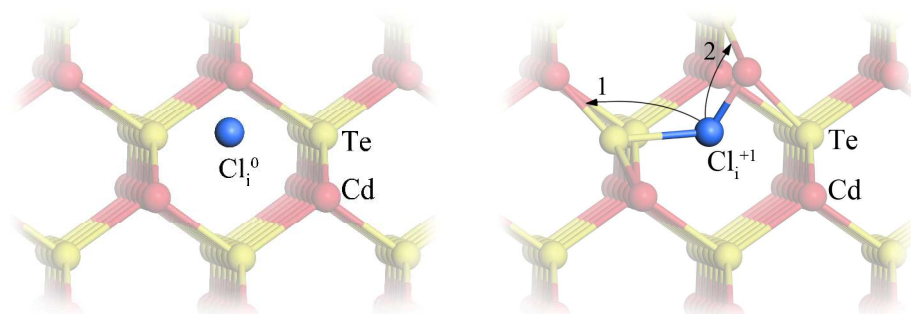

Figure 1. Left: atomic structure of Cl_i defect in (0), (-1) and (-2) charge states. Right: atomic structure of Cl_i defect in (+1) and (+2) charge states and elementary steps of diffusion pathway corresponding to the rotation around Te atom (step 1) and Cd atom (step 2).

Cl_{Te} was found to be a single shallow donor defect with ionization energy near CBM. $Cl_{Te}Cl_{Cd}$ defect complex was found to be a negative-U double acceptor with ionization level $\varepsilon_{0/-2} \approx 0.9$ eV above VBM. Atomic structures of this defect in neutral and (-2) charge state are presented on Figure 2.
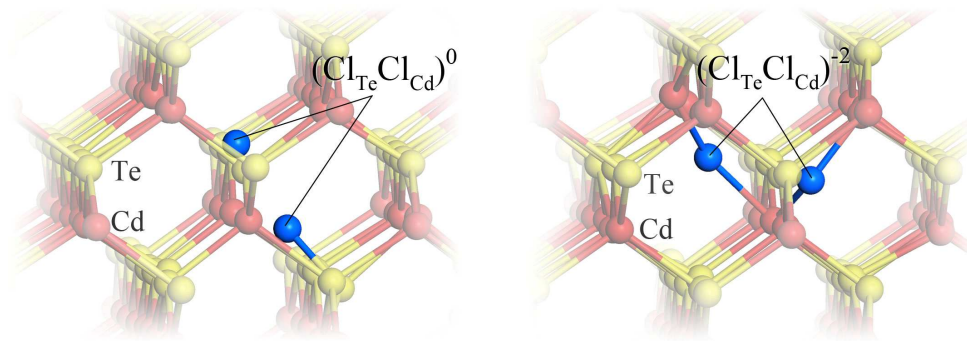
Figure 2. Atomic structure of Cl$_{Te}$Cl$_{Cd}$ defect in two charge states.

The overall formation mechanism of Cl$_{Te}$Cl$_{Cd}$ complex is exothermic:

$$Cl_{Te}^{+1}+V_{Cd}^{-2}+Cl_i^{+1} \rightarrow Cl_{Te}Cl_{Cd} \qquad \Delta E \approx -1.6 \text{ eV}$$

$$\left(Cl_{Te}V_{Cd}\right)^{-1}+Cl_i^{+1} \rightarrow Cl_{Te}Cl_{Cd} \qquad \Delta E \approx -0.4 \text{ eV}$$

though the formation of two defects (Cl$_{Te}$V$_{Cd}$)$^-$ + Cl$_{Te}^+$ is more favorable that the formation of single Cl$_{Te}$Cl$_{Cd}$ defect.

We also calculated the ionization levels of V$_{Cd}$: ε$_{0/-1}$=0.2 eV, ε$_{-1/-2}$=0.5 eV; our results are in a very good agreement with recent result by Biswas and Du [10].

ANALYSIS OF THE RESISTIVITY IN CASE OF SHALLOW LEVELS ONLY

Shallow defects are the defects with ionization level shallow enough to not to change the ionization level after cooling down to RT. It has been claimed in work [10] that shallow defects are responsible for HR in CdTe:Cl. However, only one possible equilibrium compensation type (donor-acceptor) was considered in work [10], while 3 other compensation types (acceptor-hole, electron-hole, donor-electron) that in principle cannot give HR after cooling, were neglected (see Ref. [15] for details).

At high donor concentration if the acceptor formation energy is low enough, donor-acceptor self-compensation can indeed take place. The concentrations of the donors and acceptors are very close in this case, however the excess charged defect density that equal to the majority carrier concentration is formed (Figure 3 left) and will remain after cooling from high temperature (HT) to RT due to the defect concentration freezing-in and will produce the excess carrier density preventing the system from attaining HR at RT.

For attaining HR the excess charged defect density should not exceed maximum values of hole/electron density for given resistivity, p_{max}^{RT} and n_{max}^{RT}. So the boundary values of HT Fermi level are

$$\varepsilon_{min}^{HT} = kT \ln \frac{-p_{max}^{RT} + \sqrt{\left(p_{max}^{RT}\right)^2 + 4N_cN_v e^{-\frac{E_g}{kT^{HT}}}}}{2N_c e^{-\frac{E_g}{kT^{HT}}}},$$

$$\varepsilon_{max}^{HT} = kT \ln \frac{n_{max}^{RT} + \sqrt{\left(n_{max}^{RT}\right)^2 + 4N_cN_v e^{-\frac{E_g}{kT^{HT}}}}}{2N_c e^{-\frac{E_g}{kT^{HT}}}}, \qquad (1)$$

where N_c and N_v – density of states in conduction and valence band, respectively, E_g – CdTe

band gap.

We supposed the lower boundary of resistivity in HR material as 10^8 Ω·cm. Figure 3 right shows the dependence of the width of Fermi level range at HT, $\varepsilon_{max}^{HT} - \varepsilon_{min}^{HT}$, on the annealing temperature (temperature at which the defect concentrations are equilibrated). This width is about 0.3 eV when the annealing temperature coincides with RT and falls rapidly with the temperature increase. This result means that achieving HR in the system with shallow levels only is practically impossible. So, donor-acceptor self-compensation is not a sufficient condition for HR, therefore, an additional phenomenon such as deep defects recharging should be involved to provide HR at RT.
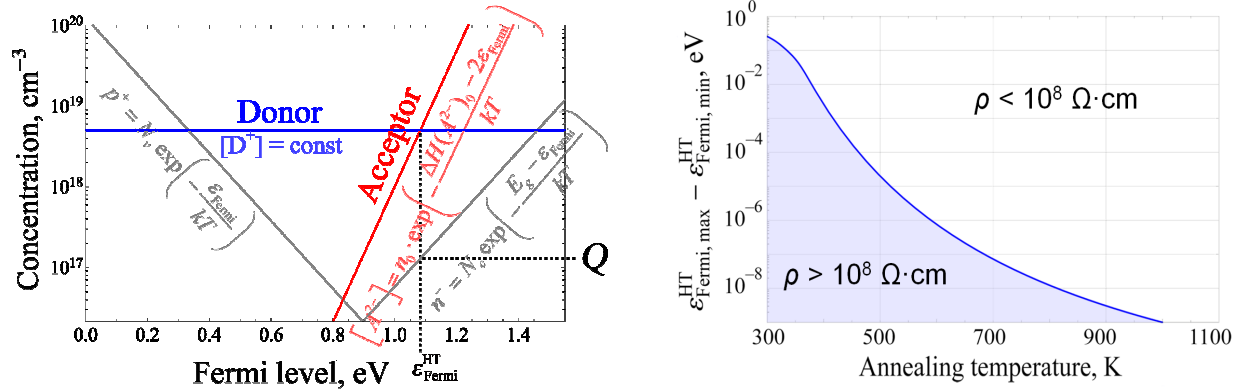

Figure 3. Left: formation of the excess donor density Q in a system with fixed concentration of shallow donor and adjustable shallow acceptor concentration. Right: dependence of the width of HR Fermi level range $\varepsilon_{max}^{HT} - \varepsilon_{min}^{HT}$ on the annealing temperature. The resistivity is calculated at RT. HR is attained in shaded region.

Possible effect of non-shallow V_{Cd} ionization levels on the resistivity of CdTe was analyzed. The equilibration of defect concentrations was assumed to be at 1373 K (typical CdTe single crystal preparation temperature), the resistivity was calculated at RT, where the ionization degree of V_{Cd} will change. It was established that in case of deep acceptor levels, the excess charged acceptor density can be reduced significantly upon cooling, which allows to obtain HR at RT at specific positions of a deep ionization level of acceptor. According to our results, HR values reported in the literature can be obtained if the ionization level of V_{Cd} is at least 0.6 eV or higher (see work [15] for details). No HR can be obtained with ionization level below 0.5 eV. Therefore we conclude that the presence of non-shallow V_{Cd} defect is not sufficient to explain the experimentally observed resistivity of CdTe:Cl after cooling from HT.

We can also conclude that while the existence of $Cl_{Te}V_{Cd}$ shallow acceptor complex was confirmed experimentally [16, 17], it does not manifest itself in the experimental data on CdTe:Cl conductivity probably due to low concentration. Therefore, $Cl_{Te}V_{Cd}$ complex is not the major acceptor in CdTe:Cl single crystals.

SIMULATION OF RESISTIVITY USING MODEL WITH DEEP DEFECTS

Defect chemistry models that describe Hall data of pure CdTe and conductivity of CdTe:Cl at HT were described in literature previously [18,19,8]. In the work [8] the model with V_{Cd}, Cd_i, Cl_{Te} defects and $Cl_{Te}V_{Cd}$ defect complex was used to describe the increased conductivity of CdTe:Cl samples at 600-700°C. However these defects, being too shallow, cannot be used to simulate HR observed in Cl-doped single crystals.

To analyze the possible effect of $Cl_{Te}Cl_{Cd}$ complex we included Cl_{Te}, and $Cl_{Te}Cl_{Cd}$ defect complex in the model. Ionization levels of V_{Cd} ($\varepsilon_{-1/-2}$=0.2 eV, $\varepsilon_{-1/-2}$=0.5 eV) were fixed. Parameters of the model (defect formation energies and $Cl_{Te}Cl_{Cd}$ ionization level) were fitted to reproduce different sets of experimental data. The fitted value of $Cl_{Te}Cl_{Cd}$ ionization level (0.85 eV above VBM) was found to be very close to the value from our first-principles calculations.

The obtained set of the parameters is probably not the best and should be treated as preliminary. Yet the obtained model is capable, with the same set of parameters of defects, to reproduce qualitatively the experimental data on Hall data of pure CdTe at HT and conductivity of CdTe:Cl at HT (Figure 4 left), as well as the increase of resistivity with increase of Cl content and the formation of HR CdTe:Cl at room temperature (Figure 4 right). High resistivity values are achieved when RT Fermi level is pinned at the ionization level of the chlorine double acceptor complex. The step at the resistivity values (10^5-10^6 $\Omega\cdot$cm) on Figure 4 right is due to the pinning of RT Fermi level at the cadmium vacancy second ionization level.
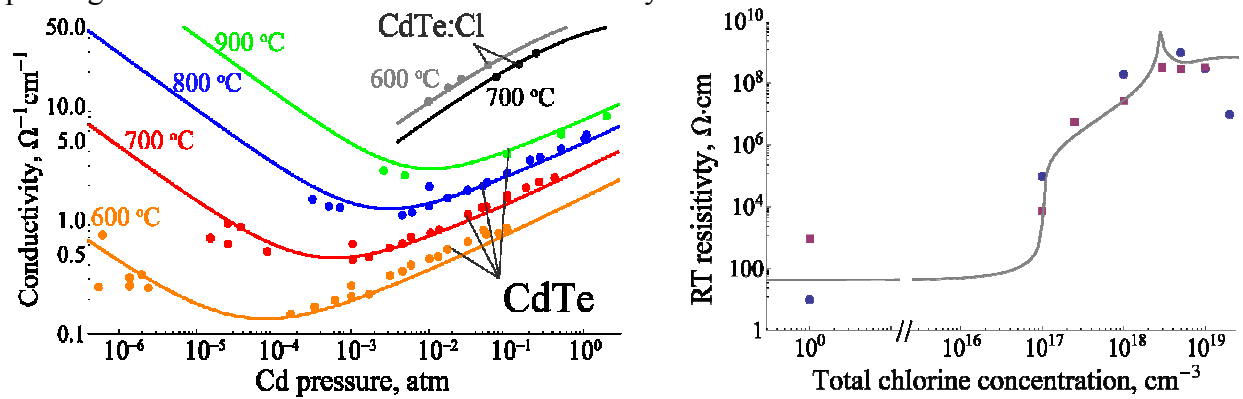

Figure 4. Left: experiment (dots) and simulation of Hall data of intrinsic CdTe [19] and CdTe:Cl with $5\cdot10^{18}$ cm^{-3} of chlorine [8]. Right: experimental (dots, from Refs [9,10]) and simulated RT resistivity of CdTe:Cl with different chlorine content.

Next, the possible effect of Cl_i amphoteric defect on CdTe electric properties was analyzed. By varying the Cl_i formation energy we established that if Cl_i would be the major Cl-related defect (Cl_i formation energy is low), then high resistivity can be attained due to its recharging. However in this case the concentration of Cl_i^{-1} at HT increases considerably leading to a stronger compensation of Cl_{Te}^{+1} defect and hence, lower conductivity. Good fit of the experimental conductivity dependence on Cd partial pressure of CdTe:Cl cannot be obtained in this case. If the Cl_i formation energy is high enough so that the HT conductivity of Cl-doped sample can be reproduced (but the concentration of Cl_i defect is still higher that the excess acceptor defect density $[V_{Cd}] - [Cl_{Te}]$ at HT), then HR is not achieved due to transition into *n*-type.

So, we found that introducing both types of deep Cl-related defects (Cl_i and $Cl_{Te}Cl_{Cd}$) can lead to a good fit of RT resistivity dependence on Cl density. However, simultaneous fitting of the HT conductivity data from work [8] is possible only with $Cl_{Te}Cl_{Cd}$ defect complex since the concentration of this complex is somewhat reduced at high Cd pressures that leads to a weaker compensation of Cl_{Te} donor and, consequently, higher conductivity.

CONCLUSIONS

It is shown that shallow defects V_{Cd}, Cd_i, $Cl_{Te}V_{Cd}$, Cl_{Te} cannot explain the experimentally observed high resistivity of CdTe:Cl. Deep acceptor complex $Cl_{Te}Cl_{Cd}$ is proposed as a reason of this high resistivity. Defect chemistry model is built that is capable to reproduce the experimental

data on CdTe and CdTe:Cl conductivity at HT and the dependence of resistivity on Cl content in CdTe:Cl at RT.

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