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Modeling of Diffusion Motion of in Nanoparticles in a CdTe Crystal during Laser-Induced Doping

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In order to solve the problem of the ohmic contact between the crystal surface and the metal electrode in the manufacturing process of the X/γ-ray detector, this paper uses a laser to probe the doping process of In/CdTe crystals in different media. In this experiment, the Traveling Heater Method (THM) is used to obtain CdTe(111) crystals that meet the requirements ($\rho > 10^9 \Omega \cdot \text{cm}$). In and Au materials are respectively coated on the surface of the crystal sample by the vacuum thermal evaporation method to obtain the crystal sample meeting the requirements. The high-resistance p-type CdTe crystal of a relatively thick In film is irradiated with nanosecond laser pulses, the In film is used as an n-type doping source and as an electrode after laser irradiation.

Keywords: CdTe, laser induced doping, X/γ-ray detectors.

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Introduction

Cadmium telluride is an important group II-VI semiconductor material, and it has a direct transition band structure, the lattice constant is 0.6481 nm, the band gap is 1.5 eV, the electron mobility at room temperature is $1050 \text{ cm}^2/(\text{V}\cdot\text{s})$, the hole mobility at room temperature is $80 \text{ cm}^2/(\text{V}\cdot\text{s})$, the effective mass is 0.096. CdTe ($Z_{\text{Cd}} = 48$, $Z_{\text{Te}} = 52$) can be doped with various impurities to produce n-type or p-type semiconductor materials [1-3]. When the Cd position is replaced by In, an n-type semiconductor is formed. When Cu, Ag, Cl are used to replace the Cd position, a p-type semiconductor is formed [3]. The p-type CdTe crystal used in this experiment is doped with Cl element, and the resistivity is ($> 10^9 \Omega \cdot \text{cm}$). CdTe has a very high light absorption coefficient ($> 5 \times 10^5/\text{cm}$). A CdTe film with a thickness of only 2 μm has an optical absorption coefficient of more than 90% under standard conditions AM 1.5, and the highest theoretical conversion efficiency reaches 28 % [4]. Second, High-resistivity cadmium telluride (CdTe) semiconductor is a basic material for fabrication of high energy radiation

direct-conversion detectors operating at room temperature and covering a wide energy range from a few keV to many MeV [1, 2].

The purpose of this article is to study the effect of the defect structure of In-doped CdTe on the properties of semiconductor near-surface regions. The basic idea of the present research is to utilize indium both as a dopant source and anode electrode for p-type CdTe crystals using nanosecond laser irradiation. Laser processing of CdTe has been successfully used to modify the structure and properties of surface nano-layers and change different characteristics of the semiconductor. Of particular interest is application the laser assisted doping technique to suppress the dopant self-compensation mechanism, and reach introducing and efficient electrical activation of In atoms in CdTe [5-10]. We have continued development and optimization the methods of chemical surface processing of CdTe crystals, laser induced doping technique for creation of a built-in p-n junction by nanosecond laser irradiation of the CdTe crystals pre-coated with a relatively thick In film which serves both as an n-type dopant source and electrical contact (electrode) after the doping and deposition of the second electrode [7-

10]. The formation of a surface nano-layer highly-doped with In in semi-insulating detector-grade p-like CdTe crystals and creation of In/CdTe/Au diodes with a shallow and sharp p-n junction has been studied and mechanism of laser-induced doping is analyzed.

I. Theory

The electrical properties of CdTe single crystals strongly depend on defect formation processes, which are usually treated by the theory of quasi-chemical defect reactions (QCDR) [11], where the concentration of each defect is given by reaction constant, defect formation energy and deviation from stoichiometry. In addition, the concentration of foreign defects depends on the chemical potential of doped element. At high temperatures during crystal growth or annealing under definite component over pressure the chemical diffusion is fast and the equilibrium between point defect creation processes is quickly established. Then the quick freezing of some equilibrium defect structure results in electron redistribution only, which allows to determine a correlation between room temperature electrical properties and initial defect

spectrum. The principal task to be solved is a decision about dominant point defects in CdTe, which control the defect statistics. There was a wide discussion whether Te vacancies (V_{Te}) or Cd interstitials (Cd_i) dominate as donor defects near Cd saturation conditions [12, 13]. This question cannot be resolved by electrical measurements because both temperature and pressure dependencies of the concentration of the defects are formally identical.

The different models of defect structure on Te-rich side were proposed assuming Cd vacancy (V_{Cd}), Te anticite (Te_{Cd}) or Te interstitial (Te_i) [14]. The experimental results of electrical measurements in Te-rich CdTe are not consistent at all [12, 13]. Thus, there is still controversy concerning formation and ionization energies of the defects in different references [12, 13]. In our model, we used the formation and ionization energies of the defects obtained from ab initio calculation [13], which fit our experimental result well. It follows that Cd_i dominates near Cd saturation conditions and Te_{Cd} and V_{Cd} dominate near Te saturation conditions.

Using QCDR formalism, the equilibrium concentrations of neutral native defects may be written by following equations:

$$[Cd_i^X] = n_0(P_{Cd}/K)exp[-(E_{Cd_i} + U_{Cd_i}^{vib})/K_bT + S_{Cd_i}^{vib}], \quad (1)$$

$$[V_{Cd}^X] = n_0(K/P_{Cd})exp[-(E_{V_{Cd}} + U_{V_{Cd}}^{vib})/K_bT + S_{V_{Cd}}^{vib}], \quad (2)$$

$$[Te_{Cd}^X] = n_0(K^2/P_{Cd}^2)exp[-(E_{Te_{Cd}} + U_{Te_{Cd}}^{vib})/K_bT + S_{Te_{Cd}}^{vib}], \quad (3)$$

where E is the relevant defect formation energy, P_{Cd} is at overpressure fixed Cd, the energy U^{vib} and the entropy S^{vib} denote contributions to the vibrational free energy, n_0 is the Cd or Te atom density, the constant K is given by:

$$K = (K_bT)^{\frac{5}{2}} \left(\frac{m_{Cd}}{2Ph^2} \right)^{\frac{3}{2}}, \quad (4)$$

K_b is the Boltzmann constant and T is the temperature

in Kelvin; h is the Planck's constant and m_{Cd} is the mass of Cd-atom, the label X is used for neutral defects. In behaves amphoterically in CdTe and creates donor (In_{Cd}) and acceptor (In_{Te}) defects by incorporation in the Cd and Te sublattices, respectively. Due to the self-compensation mechanism [15], the family of relevant point defects is significantly extended by the complexes between native and foreign ones:

$$[In_{Cd}^X] = [V_{Cd}^X]exp[(\mu_{In} - E_{In_{Cd}} - U_{In_{Cd}}^{vib})/K_bT + S_{In_{Cd}}^{vib}], \quad (5)$$

$$[In_{Te}^X] = [V_{Te}^X]exp[(\mu_{In} - E_{In_{Te}} - U_{In_{Te}}^{vib})/K_bT + S_{In_{Te}}^{vib}], \quad (6)$$

$$[In_i^X] = n_0exp[(\mu_{In} - E_{In_i} - U_{In_i}^{vib})/K_bT + S_{In_i}^{vib}], \quad (7)$$

$$[In_{Cd}V_{Cd}^X] = (12[In_{Cd}^X]^2[V_{Cd}^X]/n_0)exp[-(E_{In_{Cd}V_{Cd}} + U_{In_{Cd}V_{Cd}}^{vib})/K_bT + S_{In_{Cd}V_{Cd}}^{vib}], \quad (8)$$

$$[2In_{Cd}V_{Cd}^X] = (66[In_{Cd}^X]^2[V_{Cd}^X]/n_0)exp[-(E_{2In_{Cd}V_{Cd}} + U_{2In_{Cd}V_{Cd}}^{vib})/K_bT + S_{2In_{Cd}V_{Cd}}^{vib}], \quad (9)$$

$$[In_{Cd}In_{Te}^X] = (4[In_{Cd}^X][In_{Te}^X]/n_0)exp[-(E_{In_{Cd}In_{Te}} + U_{In_{Cd}In_{Te}}^{vib})/K_bT + S_{In_{Cd}In_{Te}}^{vib}], \quad (10)$$

where the chemical potential μ_{In} of In is defined by the In doping density.

The concentration of multiply ionized defects are calculated for acceptors and donors by the relations:

$$[X^{Z-}] = [X^X](g_{X^{Z-}}/g_{X^X})exp[(Z\mu_F - E_a^1 - \dots - E_a^Z)/K_bT], \quad (11)$$

$$[X^{z+}] = [X^x](g_{xz^+}/g_{xx})\exp[(E_d^1 + \dots + E_d^z - Z\mu_F)/K_bT], \quad (12)$$

where E_a and E_d are the acceptor and donor one-electron ionization energies and μ_F is the Fermi energy; g_{xz^+} (g_{xx}) is the degeneracy of the defect and z denotes the ionization degree.

The experimentally determined temperature dependence of energy gap is given by [16]:

$$E_g = 1.622 - 3.5 \cdot 10^{-4}T - 1.1 \cdot 10^{-7}T^2. \quad (13)$$

At high temperatures, the complicated structure of the conduction band including both G_{IC} and L_{IC} valley in the Brillouin zone must be taken into account. The experimental data of the Hall mobility of electrons μ_H exhibit substantially stronger decrease above 600 °C in comparison with its theoretical prediction [17]. This effect is explained within the model of multivalley conduction, where the parabolic L_{IC} -valley with effective mass $m_L = 0.35 m_0$ is assumed and the G_{IC} - L_{IC} valley separation ΔE (eV) = $0.29 \cdot 10^{-4}T(K)$ is obtained from the fit of the high-temperature μ_H [18].

The equilibrium defect structure of doped material was determined by Fermi energy μ_F , cadmium chemical potential μ_{Cd} and In chemical potential μ_{In} . For the numerical solution, the quasi-chemical set of expressions (1) ~ (12) must be complemented by the electric neutrality equation and the In balance equation, which ensure that the total charge is zero and the total In density is constant. The formation and vibration energies of native defects were calculated ab initio [13]. It was found that the calculated formation energies agree well with our experimental values for undoped samples. Except for the donor In_{Cd} and the acceptor In_{Te} [15], the electric character of other In related defects is yet not known reliably.

In order to fabricate the In/CdTe/Au diode structure, the industrial high-resistance p-type CdTe crystal single crystal plate obtained by the mobile heating method has a size of $5 \times 5 \times 0.5$ mm³ and a resistivity of (2 - 4) $10^9 \Omega \cdot \text{cm}$ at room temperature. The surface of the crystal is mechanically treated (cutting, grinding, polishing), then chemically treated (washing, etching, rinsing) and the sample is dried. The metal electrodes (In and Au) are

deposited by thermal evaporation in a vacuum.

II. Result and Discussion

When a powerful laser is irradiated on a crystalline material, part of it will be reflected from the surface of the material, part of it will pass through the surface of the material, part of it will be scattered, and most of it will be absorbed by the surface of the material. The surface of the crystal absorbs laser energy through various mechanisms, which can be roughly divided into five categories: inverse in-induced radiation, photoionization, multiphoton absorption, impurity absorption and hole absorption. Among them, the two types of reverse radiation and photoionization play a leading role. After the material absorbs the laser energy, the particles in it will receive the excess energy. These particles will receive the excess energy transfer energy due to collision with each other, and the macroscopic temperature of the material will increase significantly. When the intensity of the applied laser light is high enough and the energy density of the laser light exceeds the destruction threshold of the material, the surface of the material and the ejected material will form material vapor and continue to absorb energy. From a few picoseconds (Ps) to a few nanoseconds (ns), the vapor temperature of the material further increases, the degree of ionization also increases, and high temperature and high pressure plasma is generated. The plasma continues to absorb the subsequent laser energy, forcing its energy to quickly concentrate in the focal area, so that the high-temperature and high-pressure plasma expands outwards adiabatically at supersonic speed to form a high-pressure wave front. As the vapor temperature decreases, the expansion rate of the plasma will decrease, and finally, the high-pressure wavefront will separate from it, forming a shock wave.

A diagram of the matrix deformation of In atoms implanted with different laser shock energies. Figure 1(a) shows the deformation of In atom matrix implanted with 60 mJ/cm² laser energy. In atoms are implanted inside the matrix, but the depth of the implantation of the matrix is

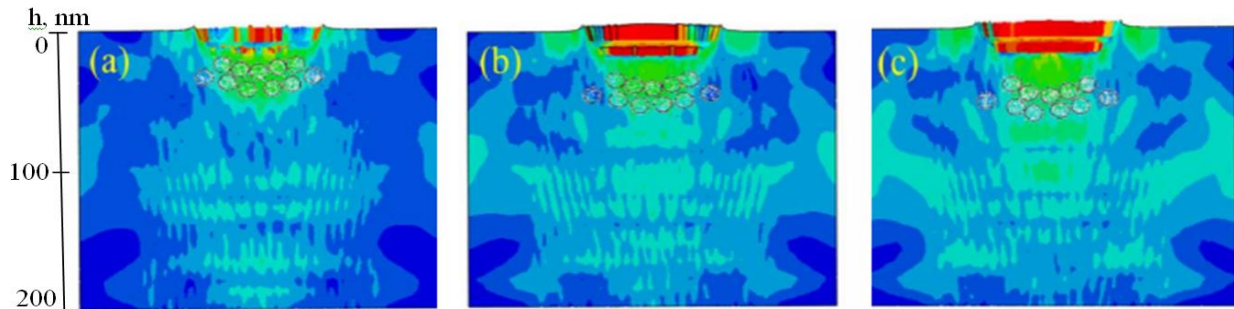


Fig. 1. Simulated doping conditions under different laser energy densities (the balls represent In atoms, the green area represents the shock wave, the red area represents the plasma generated by the laser action and the blue area represents CdTe crystal block; Laser energy density: (a) 60 mJ/cm², (b) 110 mJ/cm², (c) 170 mJ/cm²).

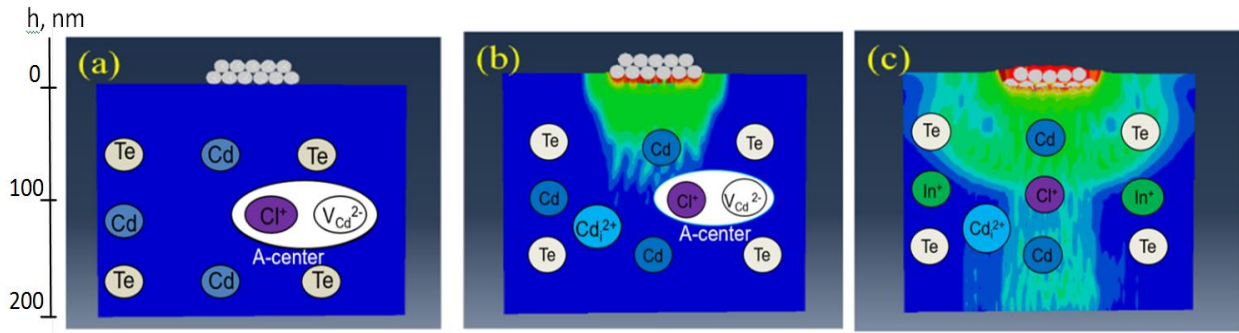


Fig. 2. (a) - Simulated image before laser irradiation (the balls represent In atoms in the In nanolayer, The green area represents the shock wave and entire blue area represents CdTe crystal block); (b) - Simulated diffusion diagram of In nanoparticles under laser irradiation; (c) - Simulated diffusion diagram of In nanoparticles after laser irradiation.

shallow, and the degree of dispersion of In particles is also small. Figure 1(b) shows the deformation of In atom matrix implanted with 110 mJ/cm^2 laser energy. The depth of In atoms implanted into the matrix increases. Figure 1(c) shows the deformation of In particle matrix implanted with 170 mJ/cm^2 laser energy. It reaches the deepest, and the plastic deformation of the matrix is the largest, and the degree of dispersion is also greater.

The semi-insulating Cl compensates the atomic structure of the CdTe crystal surface layer (a), and the transition of its point defect structure after (b) and after laser-induced doping (c) is shown in Figure 2. High-resistance CdTe:Cl semiconductors contain a large number of intrinsic and impurity point defects, especially cadmium vacancies (V_{Cd}) and chlorine as substitute impurities for interstitial (Cl_i) or tellurium sites (Cl_{Te}). These defects are usually aggregate compound defects ($V_{Cd}-Cl_{Te}$), ($V_{Cd}-2Cl_{Te}$) or ($V_{Cd}-Cl_i$) [16, 19]. In the detector-grade CdTe:Cl or CdTe:In semiconductors, a typical composite acceptor defects called A centers ($[In_{Cd}^+ \cdot V_{Cd}^{2-}]^-$, ($V_{Cd}-Cl_{Te}$), ($V_{Cd}-In_{Cd}$)) and neutral defect complexes $[2In_{Cd}^+ \cdot V_{Cd}^{2-}]$ and $[In_{Cd}^+ (In_{Cd}^+ \cdot V_{Cd}^{2-})^-]$. This defect determines the p-type conductivity of the material (Figure 2a).

As mentioned above, in the case of laser-induced modification of the CdTe structure and properties, in the case of irradiation of the CdTe crystals pre-coated with a relatively thick (much thicker than the radiation absorption depth) In film, was the action of laser-induced shock wave that could be considered as a stream of phonons which were being scattered by existing point and extended defects of the CdTe structure. This action stimulated the dissociation of defect complexes, the ultra-fast diffusion of In impurities (pressure diffusion), the desorption and segregation of interstitial atoms [19]. In the case of direct irradiation of CdTe, the effect of nanosecond laser pulses causes annealing of the semiconductor surface area. Due to the dissociation of the ($V_{Cd}-X$) complex, a large number of V_{Cd} and Cd_i (X are defects) are formed, and Cd atoms are promoted from Desorption in the CdTe lattice (Figure 2b) [19]. However, some simple point defects formed complexes (especially A center ($V_{Cd}-Cl_{Te}$)). In the case of nanosecond laser irradiation of In/CdTe structure, the laser-induced stress and shock

wave involved In atoms penetrate into the area near the metal-semiconductor interface [17, 20]. Because the laser excites the pressure diffusion and migration process of In atoms in the V_{Cd} , and then "freezes" very quickly, the solid phase high In concentration doping of the CdTe nanolayer occurs. A large number of electroactive point defects (donors) In_{Cd} , Cd_i and Cl_{Cd} are formed without the formation of compensatory acceptor complexes ($V_{Cd}-X$), especially in the A center such as ($V_{Cd}-Cl_{Te}$) and ($V_{Cd}-In_{Cd}$) (Figure 2c) [18-20].

Conclusions

The use of laser radiation for doping CdTe crystals in argon proves that In/CdTe/Au diodes fabricated in energy density: 170 mJ/cm^2 have very high rectifying properties. In particular, the structure has a very high forward current at a relatively low leakage current. This is a simple and feasible version of the theory of crystal doping technology and the formation of diode structures. The advantages of laser doping of CdTe crystals have been confirmed. Laser doping by irradiating the In/CdTe structure with nanosecond laser pulses is a solid-phase process without heating a large number of CdTe crystals, which avoids damage to the crystal. Under the action of a laser, the phenomenon of self-compensation of dopants is overcome, and a high concentration of In is introduced into a thin surface layer of CdTe. Consequently, in the region of the CdTe surface, shallow and sharp p-n junctions can be obtained. The superiority of laser-induced doping with a relatively thick In dopant film is confirmed. One of the key features of laser technology for doping a p-type CdTe crystal layer with a very high concentration of n-type impurities is the use of a relatively thick In dopant film. Provides laser-induced doping without heating the region of the deep In film and CdTe crystal, avoiding thermally induced changes and deterioration of the structure and characteristics of the semiconductor. The developed technique of laser-induced doping and formation of a p-n junction in CdTe crystals has been successfully used for the fabrication of X/ γ -ray detectors which have been employed in the instruments for environment monitoring and security [21].

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Моделювання дифузійного руху наночастинок In у кристалі CdTe при лазерно-індукованому легуванні

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Для вирішення проблеми омичного контакту між поверхнею кристалу та металевим електродом у процесі виготовлення детекторів рентгенівського та гамма випромінювання в цій роботі представлено використання лазер для процесу легування In/CdTe у різних середовищах. В якості експериментальних зразків використовувались високоомні ($\rho > 10^9 \Omega \cdot \text{см}$) кристали CdTe(111), які отриманні методом протяжного нагрівача (ТНМ). Контактні матеріали In та Au наносились на відповідну поверхню кристалу методом вакуумного термічного випаровування, в результаті отримували зразки, що відповідають заданим параметрам. Високоомні кристал р-типу CdTe із відносно товстою плівкою In опромінювались наносекундними лазерними імпульсами, In-плівка слугувала як джерело легуючої домішки n-типу та як електрод після лазерного опромінення.

Ключові слова: CdTe, лазерно-індуковане легування, детектори X/γ-випромінювання.