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ARTICLE

High Dose Ion Beam Irradiation Effects on the Electrical and Optical Properties of CdZnTe:In Crystals

Xu Lingyan[1,2], Liu Zhe[1,2], Liang Lu[1,2]

[1] State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China; [2] Key Laboratory of Radiation Detection Materials and Devices, Ministry of Industry and Information Technology, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

Abstract: Effects of ion beam irradiation defects on electrical and optical properties of CdZnTe (CZT) crystals were studied. CZT crystals grown by the modified vertical Bridgman method were irradiated by Ar heavy ions with fluences ranging from 10^{14} cm^{-2} to 10^{15} cm^{-2}. Results show that IR transmittance spectra vary from the high-straight type (before radiation) to the ascending type (after radiation), and light absorption by radiation induced free charge carriers occurs significantly in the mid-infrared light range. Current-voltage (*I-V*) characteristic curve of the irradiated CZT crystals becomes extremely asymmetrical and current increases sharply with the increase of negative voltage due to single-surface irradiation in the near-surface area. Hall measurements show that the net carrier concentration largely increases from ~10^6 cm^{-3} (before radiation) to ~10^{16} cm^{-3} (after radiation), and the conduction type remains unchanged, since donor levels are considered to be the dominant among all the radiation-induced crystal defects.

Key words: semiconductors; radiation effects; electrical properties; optical properties

Hard X-ray and γ-ray detectors produced by high-resistivity CdZnTe (CZT) crystals can operate at room temperature with high detection efficiency in a wide energy range. Thus, CZT crystals have been considered as the most promising materials for room temperature radiation detectors[1-3]. During the practical working processes in various application fields, e.g., border security, anti-terrorism, space physics, medical imaging, industrial inspection, nuclear safety monitoring, detectors often need to experience extreme radiation environment. When operating under high-energy and high-flux radiation environment for long periods, various types (neutron, ion, X-ray, etc.) of radiation sources inevitably interact with crystal lattice of the detector materials, resulting in radiation defects, which can markedly alter the material properties and detection performances[4-6]. The maximum tolerated cumulative dose (radiation hardness) in the crystals, mainly determined by the radiation source type and the detector materials, will result in severe deterioration of the spectroscopic behavior or even overall breakdown of the detection system. Moreover, the existential state of radiation damage is unstable after radiation and can change under several external factors, leading to the uncertainty of the device performances. Therefore, radiation damage becomes the most serious problem for radiation detectors in the actual application environment. Krylyuk et al discovered a large number of Frenkel defects produced after high-dose irradiation, since the incident energy is high enough to displace the host atoms in CdTe crystals. The generation of Cd vacancies followed by creating complexes with donors, results in a dramatic decrease in the isolated donor concentration[7]. Cavallini et al monitored the evolution of radiation induced trap defects with the increase of radiation dose, and tried to correlate the balance between deep and shallow donors and acceptors with the electrical compensation process, which determines the resulting material resistivity. They also compared the radiation results obtained for CdTe and CdZnTe detectors in order to clarify the origins of identified defect levels[8-10]. Cola et al observed the change of space charge due to one-carrier trapping on deep levels in strong optical irradiated Ohmic and Schottky Cd(Zn)Te detectors, which can

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Corresponding author: Xu Lingyan, Ph. D., Associate Professor, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi’an 710072, P. R. China, Tel: 0086-29-88495414, E-mail: xulingyan@nwpu.edu.cn

result in a general decrease of the electric field on the irradiated side[11]. These researches have reported various types of radiation effects in CdTe and CdZnTe detectors. Among them, heavy ion irradiation, with characteristics of high deposition energy, large interaction depth, big damage section, and high defect concentration, has attracted more and more attention in recent years[12-15]. In this study, we are concerned with the irradiation effects in CZT crystals using Ar heavy ions as the radiation source. Based on the general estimation of radiation induced defective states through the energy transfer theory, we are able to explore the reasons for the variation of photoelectric properties in the ion irradiated CZT crystals. A detailed understanding of the radiation effects of radiation detectors helps to control and to improve the effective utilization in the practical applications.

1 Experiment

A set of In-doped $Cd_{0.9}Zn_{0.1}Te$ single crystals with dimension of 5 mm×5 mm×1 mm were cut from an ingot grown by the modified vertical Bridgman (MVB) method in Imdetek Ltd. Their positions are close to each other, within 10 mm along the axial direction of the same as-grown ingot, to ensure similar crystal properties. The energy bandgap of CZT crystal samples is about 1.6 eV. All the samples were n-type conduction with high resistivity of ~10^{10} Ω·cm. They were carefully polished and etched to obtain nice surfaces. These CZT crystals were irradiated by Ar (6.17 MeV/u) heavy ions in vacuum, with fluences ranging from 10^{14} cm^{-2} to 10^{15} cm^{-2} at the Institute of Modern Physics (IMP) of the Chinese Academy of Sciences (CAS). We made comparisons for electrical properties, optical properties and carrier transport properties of CZT crystals before and after ion radiation. Infrared (IR) transmission microscope imaging system was used to obtain the size distribution and concentration of Te inclusions with diameter >1 μm. IR transmittance spectra with wavenumber in the range of 500~4000 cm^{-1} were measured by a Fourier transform infrared (FTIR) spectrophotometer (Nicolet Nexus 670). Agilent 4155C setup was employed for the current-voltage (*I*-*V*) characteristic curves, to assess Ohmic contact and to determine the material resistivity. Parameters related to carrier transport properties were observed by the Van de Pauw method based on Hall effect.

2 Results and Discussion

CZT crystals can be scanned in three-dimension by IR transmission microscopy, with sample holder integrated to a motorized *X*-*Y*-*Z* translation stage. The typical IR images in CZT crystals before and after radiation were selected and analyzed, as shown in Fig.1. It is observed that a large number of Te inclusions with diameter in the range of 2~6 μm are uniformly distributed in CZT crystals before radiation. Surface density of Te inclusions is calculated to be ~7.75×10^4 cm^{-2}. Te inclusions are the most common bulk defects in CdTe and CdZnTe crystals, which will severely influence material properties and uniformity[16,17]. After radiation, Te inclusions

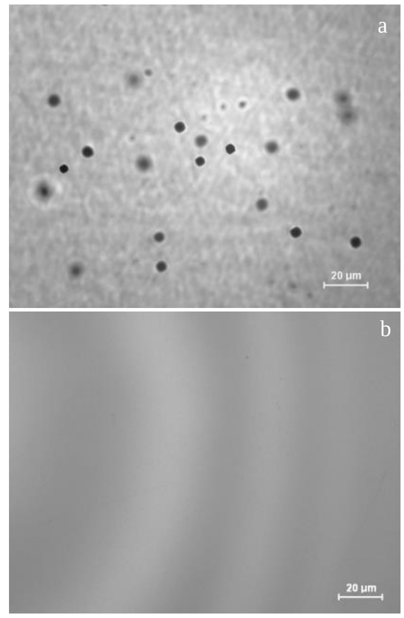

Fig.1 Typical IR images in CZT crystals before (a) and after (b) radiation

almost completely disappear throughout the entire crystals, which can be explained by thermal effect accompanied by ion irradiation in vacuum. Temperature gradient is formed in the bulk, and thermal effect is similar to temperature-gradient annealing. Bensalah et al also discovered the elimination of Te inclusions during the bombardment with argon ions[18]. According to the temperature gradient zone melting mechanism, Te inclusions can be effectively reduced or even eliminated in CdZnTe and CdMnTe crystals through thermo-migration[19-23]. Lee et al reported the relation between migration velocity and effective diffusion coefficient by considering interface kinetics, thermal conductivity and Soret effect[24].

Fig. 2 shows the IR transmittance spectra of CZT crystals before and after radiation. The former is basically straight in the whole wavenumber range, and the transmittance value is

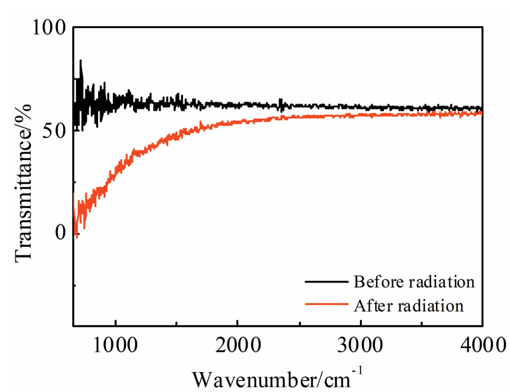

Fig.2 IR transmittance spectra of CZT crystals before and after radiation

~61%. There are four types of IR transmittance spectra, i. e., descending type, ascending type, low-straight type and high-straight type, representing four types of wafer qualities[25]. And as-grown CZT crystals belong to the high-straight type, corresponding to high comprehensive performance with low dislocation density and high resistivity. IR transmittance spectrum of the irradiated CZT crystals will increase with the increase of wavenumber, and the transmittance value tends to be stable (58%) after 2000 cm^{-1}. CZT crystals after radiation belong to the ascending type. IR transmittance spectra have commonly been used to characterize CZT crystal quality[26]. And the comparison of the IR transmittance spectra before and after radiation demonstrates the deterioration of crystal quality caused by ion irradiation. Moreover, the absorption of the incident light in the irradiated CZT crystals focuses on the mid-infrared range (5~20 μm), which is mainly caused by the transition of free charge carriers in the band structure. It can be concluded that irradiation effects produce a large number of free carriers in the near-surface area, since effective depth of interaction between high-energy ions and CZT crystals is about 50 μm in the injection direction below the surface.

I-V characteristic curves of CZT crystals before and after radiation were measured under different bias voltages, as shown in Fig.3. Bulk resistivity of as-grown CZT crystals was calculated to be ~1.40×10^{10} Ω·cm at room temperature by fitting *I-V* curve in the low-voltage (-0.01~0.01 V) region. Since contact and surface properties have little effect on *I-V* curves under low voltage [27,28], in this case, leakage current is dominated by bulk properties, and the slope corresponds to the effective bulk resistivity. As shown in Fig. 3a, there is a general increase in the current with the increase of applied bias, indicating good linearity and symmetry in the whole voltage range (-100~100 V). *I-V* curve before radiation reveals uniform composition and good quality of as-grown CZT crystals, which is consistent with observations from IR transmittance spectra before radiation. As voltage increases, *I-V* curve after radiation becomes extremely asymmetrical. There is still good linearity under positive voltage, and current increases sharply with the increase of negative voltage due to single-surface irradiation. The influence of the interfacial layer between contact electrode and semiconductor surface on the current transport process gradually becomes evident with increasing the voltage[28-30]. And interaction between high-energy ion irradiation and CZT crystals mainly occurs in the near-surface area. Thus, the rapid increase of current in the high-voltage range of the *I-V* curve can be ascribed to high-concentration free carriers induced by irradiation effects,

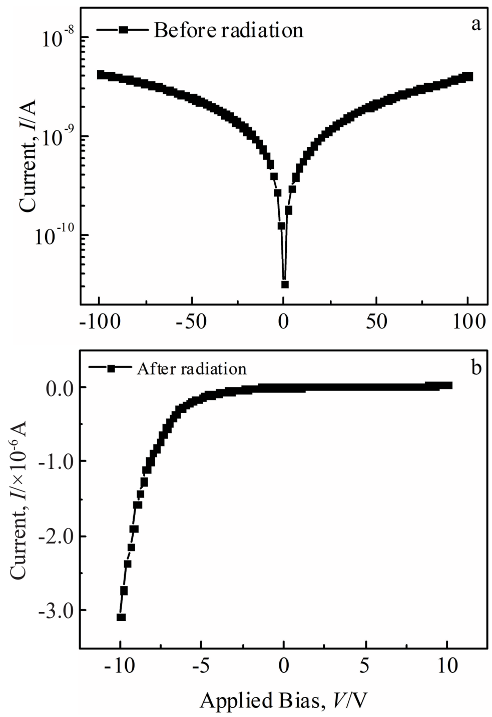

Fig.3 *I-V* characteristic curves of CZT crystals before (a) and after (b) radiation

which is also revealed by observations from IR transmittance spectra of the irradiated CZT crystals.

Table 1 shows Hall measurement results of CZT crystals before and after radiation. The concentration of net free charge carriers in CZT crystals is highly increased from ~10^6 cm^{-3} (before radiation) to ~10^{16} cm^{-3} (after irradiation), which is consistent with observations from IR transmittance spectra of CZT crystals after radiation. The concentration of Cd vacancies (acceptors) increases by thermal effect, according to the thermodynamic equilibrium model. Moreover, a large number of irradiation induced defects are generated due to the interaction between high-energy ions and CZT crystals in the near-surface area. Conductivity is mainly determined by the compensation between donor and acceptor defects, and deep-level defects are responsible for stabilizing the compensation conditions against the variation of shallow-level defects[31-33]. Thus, the compensation between thermal effect generated defects and irradiation induced defects will contribute to the

Table 1 Hall measurement results of CZT crystals before and after radiation

Parameter	Before radiation			After radiation		
Temperature/K	295.55	295.42	295.28	296.24	296.17	296.07
Magnetic field/T	0.2	0.5	0.8	0.2	0.5	0.8
Net density/cm^{-3}	9.51×10^6	7.99×10^6	7.54×10^6	7.27×10^{16}	7.24×10^{16}	7.23×10^{16}
Hall mobility /$cm^2\cdot V^{-1}\cdot S^{-1}$	212	252	267	844	848	849
Conduction type (n/p)	n	n	n	n	n	n

net carrier density and the conduction type. As-grown CZT crystals possess n-type conduction, and Hall measurements also reveal n-type conduction in the irradiated crystals. So we speculated that donor levels are the dominant among all the irradiation induced defects.

3 Conclusions

1) Irradiation effects in CdZnTe crystals were investigated using Ar heavy ions with fluences ranging from 10^{14} cm^{-2} to 10^{15} cm^{-2}. We made comparisons for electrical properties, and optical properties of CZT crystals before and after ion irradiation.

2) IR transmission microscope imaging measurements show that Te inclusions almost completely disappear after radiation due to thermal effect. IR transmittance spectra vary from the high-straight type (before radiation) to the ascending type (after radiation), revealing the deterioration of crystal quality. A large number of radiation induced charge carriers lead to the absorption of mid-infrared light.

3) *I-V* characteristic curve of as-grown CZT crystals shows good linearity and symmetry, and that of the irradiated CZT crystals becomes extremely asymmetrical due to single-surface irradiation.

4) Hall measurement results demonstrate the considerable increase of the concentration of net free charge carriers in CZT crystals from ~10^6 cm^{-3} (before radiation) to ~10^{16} cm^{-3} (after irradiation). The conduction type remains unchanged in the irradiated crystals, and donor levels are considered to be the dominant among the irradiation induced defects.

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高剂量离子辐照效应对CdZnTe:In晶体光电性能的影响

徐凌燕[1,2]，刘　哲[1,2]，梁　璐[1,2]

(1. 西北工业大学 材料学院 凝固技术国家重点实验室，陕西 西安 710072)

(2. 西北工业大学 材料学院 辐射探测材料与器件工信部重点实验室，陕西 西安 710072)

摘　要：研究了离子辐照效应对CdZnTe（CZT）晶体光电性能的影响。采用Ar离子对改进的垂直布里奇曼法生长的CZT晶体进行辐照，剂量范围为10^{14}~10^{15} cm^{-2}。红外透过光谱测试结果表明，辐照前晶体样品的高直型光谱转变为辐照后的上升性光谱。辐照诱导产生的高浓度自由载流子引起的光吸收在红外透过光谱的中红外范围内占主导地位。由于离子辐照发生在单侧照射面的近表面区域，辐照后晶体样品的*I-V*特性曲线变得极不对称。在负偏压的条件下，电流随着电压的增大而急剧增大。霍尔效应测试结果表明，辐照前晶体样品的净载流子浓度约为10^6 cm^{-3}，而辐照后的净载流子浓度大幅增加，约为10^{16} cm^{-3}。CZT晶体的导电类型在离子辐照前后并没有发生变化，施主缺陷能级在辐照诱导缺陷中占主导地位。

关键词：化合物半导体；辐照效应；电学性能；光学性能

作者简介：徐凌燕，女，1987年生，博士，副教授，西北工业大学材料学院，陕西 西安 710072，电话：029-88495414，E-mail：xulingyan@nwpu.edu.cn