

室温辐射探测器用 CdMgTe 单晶质量提升策略

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摘 要: 碲镁镉(CdMgTe)晶体是一种理想的室温辐射探测新材料。为了提升晶体质量和探测器性能, 采用 Se 气氛对 CdMgTe 晶体进行退火改性。退火后, Se 以化学吸附的形式部分取代了 Te, 晶体中 Mg 和 Se 元素含量增加, 禁带宽度最多增加了 0.042 eV。随着退火时间的延长, Te 夹杂相密度不变, 红外透过率和显微硬度先减小后增大, 电阻率逐渐降低。最佳退火条件为 Se 气氛下 773 K 退火 120 h, 此时晶体质量最好, 红外透过率达 63.6%。由该晶体制备的室温辐射平面探测器性能最佳, 电子迁移率达 344.47 cm²/(V·s), 对能量为 5.48 MeV 的 ²⁴¹Am α 粒子的能量分辨率和载流子迁移率寿命积($\mu\tau$)_e 分别为 17.2% 和 1.32×10⁻⁴ cm²/V。

关键词: 室温辐射探测器; 碲镁镉晶体; 硒气氛退火; 电阻率

中图分类号: TN304.2 文献标志码: A 文章编号: 0454-5648(2025)07-1981-12

网络出版时间: 2025-05-26



1 Introduction

Cadmium magnesium telluride (CdMgTe), as a group II-VI CdTe-based compound semiconductor, can be used in room-temperature radiation detection^[1]. It is regarded as an ideal material for such detectors. However, CdMgTe crystals grown by melt methods, including the vertical Bridgman and zone melting techniques, often exhibit major defects like vacancies, dislocations, twins, and inclusions^[2], severely impacting the crystal quality and detector performance. It is thus necessary to enhance the quality of as-grown CdMgTe crystals via annealing treatment. CdTe-based crystals are typically annealed using some elements like Cd, Te, or In,^[3-5] alloys such as Cd/Zn^[6-7], powders like CdTe or CdMnTe^[8-9], and H₂ atmosphere^[10]. Recent studies show that selenium (Se) can significantly reduce harmful defects like subboundary networks and Te inclusions in CdTe-based crystals, enhancing the crystal quality through its favorable segregation coefficient and intense solid-solution hardening

effect^[11-13]. Roy *et al.*^[14] reported that the Frisch-grid radiation detector made of Cd_{0.9}Zn_{0.1}Te_{0.98}Se_{0.02} crystal had a resolution of 0.87%–1.50% and ($\mu\tau$)_e reached 6.6×10⁻³ cm²/V for γ ray with an energy of 662 keV, which was expected to be a new generation of room-temperature radiation detection materials. Kim *et al.*^[15] also found that adding Se to CdZnTe could improve the hole lifetime and energy resolution of the detector.

The existing research on effect of Se on CdTe-based crystals mainly focus on the crystal growth and deep-level defects of as-grown crystals^[16-21]. It is supposed that Se have the similar effect on CdTe-based semiconductor materials as Te due to Se and Te in the same family of the periodic table.^[22] In this paper, Se was introduced into CdMgTe crystals via vapor phase diffusion as an advanced annealing strategy to enhance the both crystal quality and detector performance. In addition, the effect of annealing time on the crystal defects, microhardness, optical and electrical properties, and detector performance was also investigated.

收稿日期: 2024-11-28。 修订日期: 2024-12-27。

基金项目: 西北工业大学凝固技术全国重点实验室开放课题 (SKLSP202318); 长安大学大学生创新训练计划项目 (202410710098)。

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Received date: 2024-11-28. Revised date: 2024-12-27.

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2 Experiment

The annealing source was a high-purity Se (7N), and the slices with the dimensions of 5 mm×5 mm×2 mm were selected from an In-doped (concentration of 1×10^{-5}) CdMgTe ingot grown by a modified vertical Bridgman method under Cd excess condition [2]. Fig. 1 shows a schematic diagram of the crystal growth, annealing, detector preparation, and performance testing for CdMgTe. Prior to annealing, the slices were mechanically polished with an MgO suspension and then treated with a 2% Br₂-MeOH solution to eliminate scratches and any damaged layers. The slices and the source were positioned at opposite ends of a quartz annealing device,

with quartz crucibles evacuated to a pressure of 10^{-5} Pa. Compared to Te, Se has a lower melting point and a higher vapor pressure. To minimize the volatilization of elements in CdMgTe, a lower annealing temperature was selected to maintain the stoichiometric ratio of the as-grown crystals within acceptable limits. According to some previous studies of CdTe-based crystals annealed in Te atmosphere [23–24], an annealing temperature of 773 K was chosen for both the slices and the source. Effect of annealing time on CdMgTe crystal properties was investigated at different holding time (*i.e.*, 30, 60, 120 h, and 240 h). CdMgTe planar room-temperature radiation detectors were fabricated *via* evaporating Au electrodes onto the both sides of the annealed crystals.

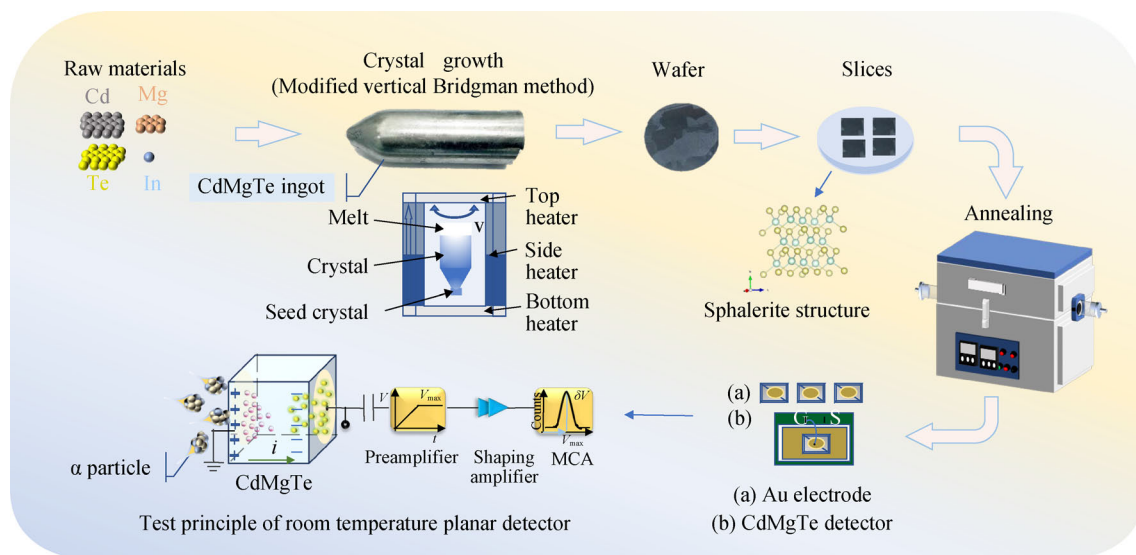


Fig. 1 Schematic diagram of crystal growth, annealing, detector preparation and performance testing for CdMgTe

The band gap was determined by a model UV-3150 near-infrared spectrometer (NIR, Shimadzu Scientific Instrument Inc., Japan) in a wavelength range of 600–1200 nm. The surface oxidation and impurities in CdMgTe crystals before and after annealing were analyzed by a model EscaLab 250Xi X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific Co., USA). Te inclusions were determined by a model MicronViewer 7290A infrared transmission microscope (IRTM, Electrophysics Co., USA) with a 1 μ m resolution and a model S4800 field emission scanning electron microscope (FESEM, Hitachi Co., Ltd., Japan). The microhardness was assessed by a Vickers indentation tester. The infrared (IR) transmittance of the crystals

before and after annealing was determined by a model Nicolet Nexus 670 IR spectrometer (Thermo Scientific Co., USA). was used to evaluate the crystal quality of CdMgTe before and after annealing was evaluated by a model LabRAM Raman spectrometer (Horiba Scientific Co., Japan) equipped with a 532 nm laser. The current-voltage (I – V) characteristics of CdMgTe crystals before and after annealing were measured by a model 4155C semiconductor parameter analyzer (Agilent Co., USA). The carrier mobility in CdMgTe roomtemperature radiation detectors was determined by a time-of-flight (TOF) technology. The energy spectrum of CdMgTe detectors was acquired by an ORTEC measurement system with uncollimated ²⁴¹Am α particles with an

energy of 5.48 MeV as an irradiation source.

3 Results and discussion

3.1 Effect of Se atmosphere annealing on crystal composition and band gap

For CdMgTe as a direct band gap semiconductor, the NIR spectrum provides a non-destructive method for band gap measurement. Fig. 2(a) shows the NIR spectra of CdMgTe crystals both before and after annealing in Se

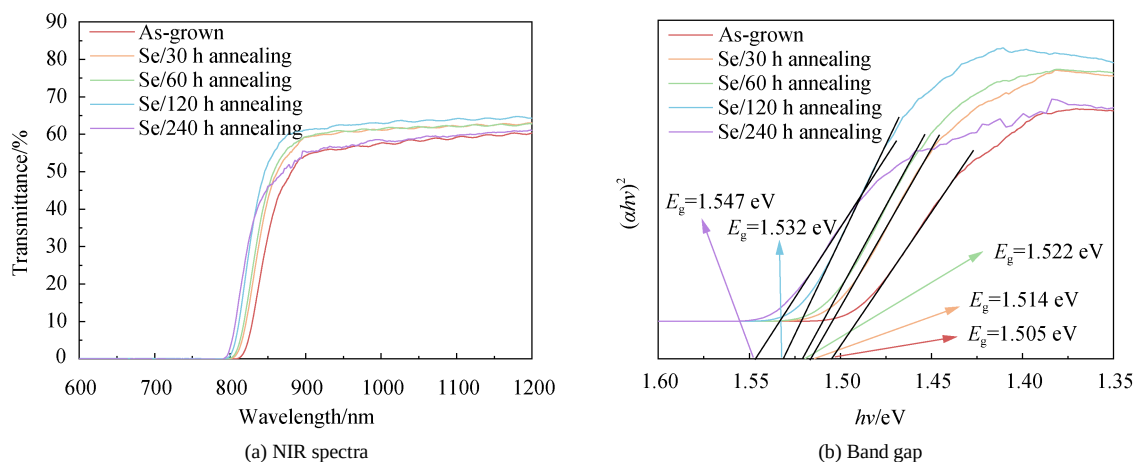


Fig. 2 NIR spectra and band gap of CdMgTe crystals before and after annealing in Se atmosphere

where α represents the absorption coefficient, A is the proportional constant, $h\nu$ is the photon energy, E_g is the band gap and γ is the index that characterizes the transition of electrons from the valence band to the conduction band. For direct bandgap semiconductors, γ equals 1/2. The band gap of CdMgTe crystals before and after Se atmosphere annealing, as determined by extrapolation fitting, is shown in Fig. 2(b). CdMgTe is a ternary alloy, in which Mg atoms partially replace Cd atoms within the binary CdTe crystal lattice, or it can be considered a single solid solution composed of MgTe and CdTe. The band gap of the as-grown crystal is 1.505 eV, whereas the band gap of the annealed CdMgTe crystals increases with holding time sequentially to 1.514 eV (30 h), 1.522 eV (60 h), 1.532 eV (120 h), and 1.547 eV (240 h). The surface composition of the crystals before and after annealing in Se atmosphere is analyzed using EDS, and Table 1 shows the results. The actual concentrations of Mg can be expressed as x_1 ($x_1 = [\text{Mg}] / ([\text{Mg}] + [\text{Cd}])$), and the actual concentration of Se can be expressed as x_2 ($x_2 = (\text{Se}) / ((\text{Te}) + (\text{Se}))$). The concentrations of Mg and Se increase, while those of Cd and Te decrease as the

annealing time increases. As is well known, the band gap of semiconductor crystals, such as CdMgTe, can be determined via analyzing the absorption edge in NIR spectra. Note that the transmittance exhibits a linear relationship with wavelength in the range of 800–850 nm. Consequently, the band gap of CdMgTe crystals is determined by^[1]

$$\alpha = \frac{A(h\nu - E_g)^\gamma}{h\nu} \quad (1)$$

annealing time increases. This indicates that the equilibrium vapor pressure between CdMgTe crystals and Se annealing source is not achieved at 773 K, which is similar to that of low resistivity CdMgTe crystals annealed in Te atmosphere.^[4] Consequently, the volatilization of Cd from the slice results in a relative increase in Mg content. Furthermore, the combined content of Mg and Cd as well as that of Te and Se remain approximately 50%, indicating that Mg replaces Cd, and Se replaces Te. In the case of $\text{CdTe}_{1-x}\text{Se}_x$ crystals, the band gap is decreased by 4 meV when x is less than or equal to 0.1 (corresponding to a Se concentration of 10%). The band gap is at its minimum when x reaches 0.4, and it then increases with further increasing x ^[25–26]. However, each percentage of Mg atoms can increase the band gap by 17 meV, leading to a continuous increase in the band gap following Se atmosphere annealing.

Fig. 3(a–f) show the XPS spectra of CdMgTe crystals before and after Se atmosphere annealing for 120 h. In the as-grown crystals, the peaks for Cd 3d_{3/2} and Cd 3d_{5/2} are at 410.6 eV and 413.9 eV, respectively, Mg 1s at 1303.3 eV, TeO 3d_{3/2} and TeO 3d_{5/2} at 585.2 eV and 574.8 eV,

respectively, Te (element) at 582.4 eV and 571.7 eV, Te^{2-} (CdMgTe) at 581.7 eV and 571.2 eV, Mg—OH/Mg—O at 530.1 eV, and Cd—O at 529.0 eV. After annealing in Se atmosphere, the core energy levels of Cd 3d, Mg 1s, Te 3d, and O 1s remain unchanged. The Se 3d core spectrum

can be resolved into Se 3d_{3/2} and 3d_{5/2} peaks, which are located at 54.22 eV and 52.65 eV, respectively.^[27] The results indicate that Se interacts with CdMgTe matrix *via* diffusion and chemisorption, forming chemical bonds that effectively result in the partial substitution of Se for Te.

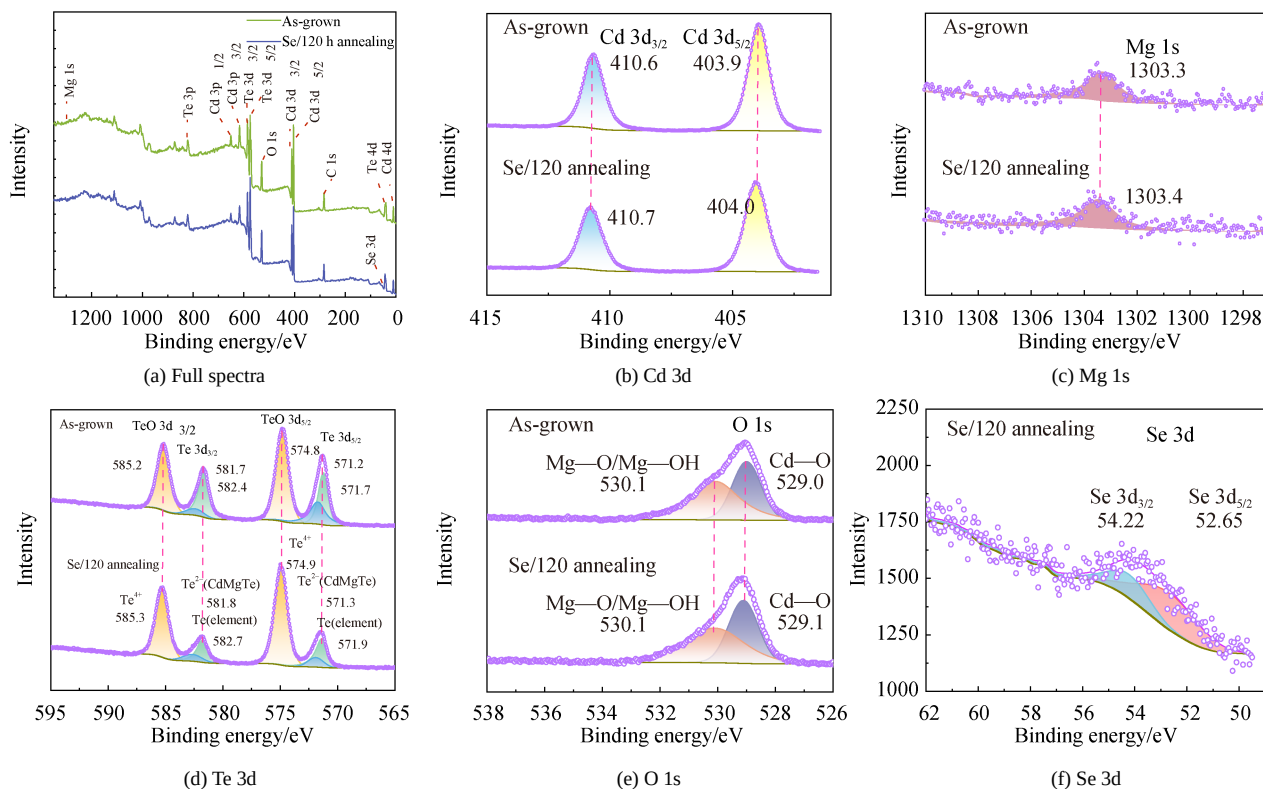


Fig. 3 XPS spectra of CdMgTe crystals before and after Se atmosphere annealing for 120 h

Table 1 Contents of elements Cd, Mg, Te and Se in CdMgTe crystals before and after annealing in Se atmosphere

Annealing time/h	x/%				$x(\text{Mg})/[x(\text{Mg})+x(\text{Cd})]$	$x(\text{Se})/[x(\text{Te})+x(\text{Se})]$
	Mg	Cd	Te	Se		
As-grown	2.80	47.5	49.76	0	5.56	0
Se/30 h	4.01	46.85	49.03	0.19	7.89	0.38
Se/60 h	4.09	46.77	49.08	0.21	8.05	0.43
Se/120 h	4.12	46.62	48.70	0.58	8.12	1.17
Se/240 h	4.46	46.01	48.30	1.24	8.83	2.50

x is mole fraction.

3.2 Effect of Se atmosphere annealing on Te inclusions

Te inclusion, acting as charge trapping centers, poses one of the major challenges in crystal growth, particularly for thick detectors that require long drift paths. The IRTM images of CdMgTe crystals before and after annealing in Se atmosphere reveal that increasing the annealing time does not significantly alter the density of Te inclusions. Fig. 4(a) and Fig. 4(b) show the IRTM images of CdMgTe crystals before and after Se

atmosphere annealing for 240 h. Clearly, the densities of Te inclusions for both the as-grown and 240 h annealed crystals are similar at $2.32 \times 10^4 \text{ cm}^{-2}$ and $2.29 \times 10^4 \text{ cm}^{-2}$, respectively. Fig. 4(c–h) show the SEM and EDS images of CdMgTe crystals before and after 240 h annealing. Since Te inclusions are not coherent with CdMgTe matrix, they may detach during the polishing process. They appear as bright areas in the SEM images (see Fig. 4(c) and Fig. 4(d)). The morphology of Te inclusions remains unchanged before and after annealing, being predominantly

hexagonal or nearly spherical without significant thermal migration phenomena, such as migration and merging of Te inclusions^[28]. This indicates that the temperature gradient at 773 K is insufficient to induce a significant

thermal migration of Te inclusions. The results of EDS surface scanning tests confirm that the inclusions consist of Te, and Se is uniformly distributed throughout CdMgTe crystal after annealing.

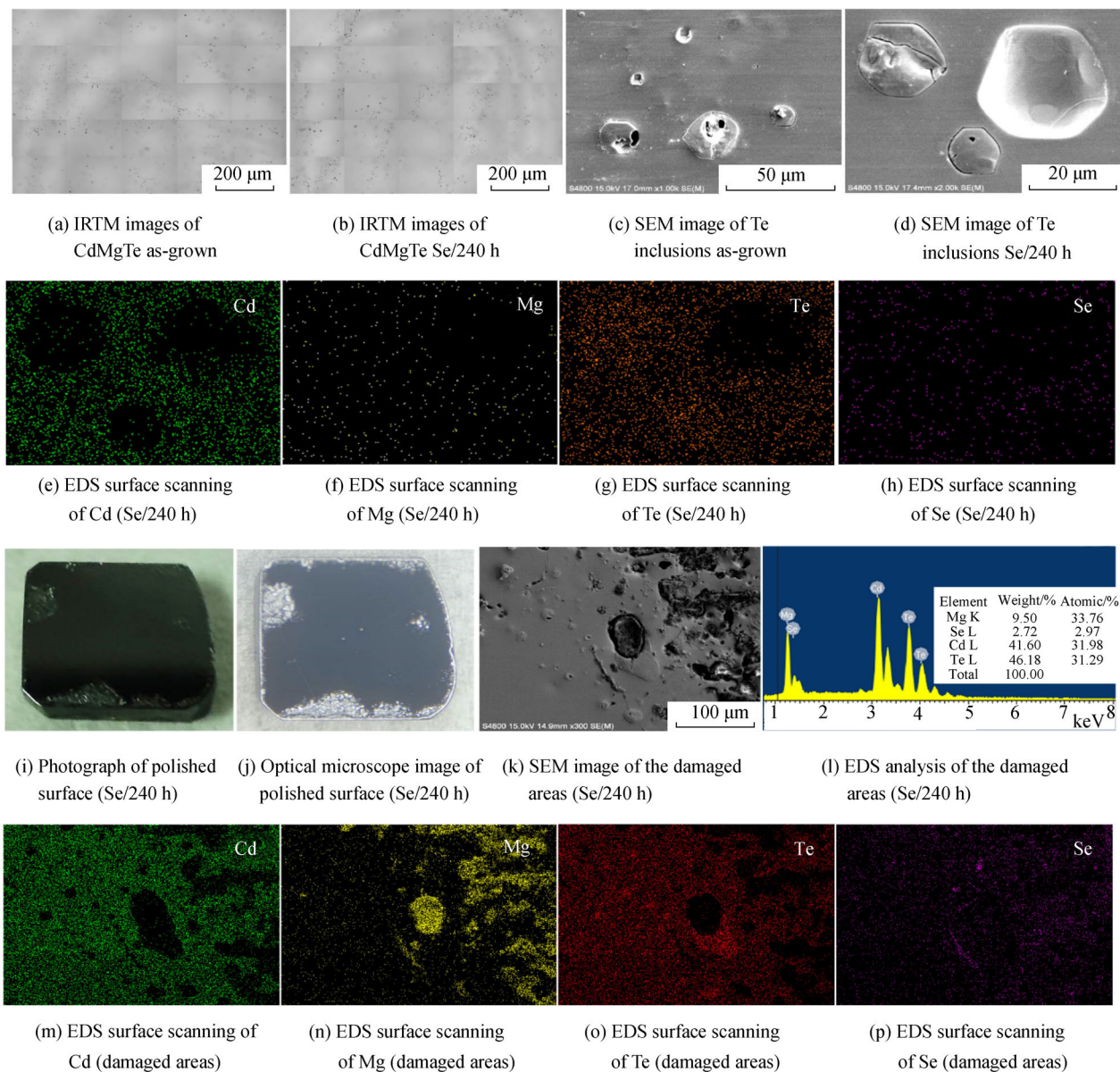


Fig. 4 CdMgTe crystals before and after annealing in Se atmosphere: IRTM images、SEM images and EDS surface scan analysis

Annealing in Se atmosphere can cause damage on the slice surface. The extent of damage is independent of the annealing time, and is predominantly concentrated at the edges and corners of the slices. Fig. 4(i) to Fig. 4(j) show the photograph and optical image of the CdMgTe slice after 240 h annealing. Clearly, the surface of the slice in the damaged areas is severely corroded, characterized by numerous voids and increased roughness. The EDS spectra reveal a significant increase

in the concentration of Mg in these areas, accompanied by a substantial decrease in the concentrations of Cd and Te (see Fig. 4(i-o)). Zaki *et al.* also reported the similar phenomenon during annealing of $\text{Cu}_2\text{ZnSnSe}_4$ films in Sn+Se atmosphere.^[29] This is due to the volatility of elements Sn and Se, leading to rough surfaces and void formation. Note that the surface areas at the edges and corners of the CdMgTe slice that are in contact with Se atmosphere are larger than those at other positions, thus

facilitating a greater Se diffusion. According to the XPS spectra (see Fig. 3), Te is partially replaced by Se. Se in the annealing atmosphere continues to diffuse and displace Te at the edges and corners because Se is volatile easily. As a result, there is a significant reduction in Te content. Also, annealing in Se atmosphere leads to some volatilizations of Cd, with surface roughness and voids being more likely to occur at the edges and corners of the slice.

3.3 Effect of Se atmosphere annealing on microhardness

CdTe-based compound semiconductor crystals are soft and fragile, prone to mechanical damage or even

fracture during wafer fabrication, slicing, and polishing. Annealing can alter the mechanical properties of CdTe-based crystals, including microhardness. Fig. 5 shows the microhardness of CdMgTe crystals before and after annealing. Clearly, the indentation size grows and the hardness value decreases as the applied load (P) increases, which is consistent with the indentation size effect.^[30] Some cracks emerge in the as-grown crystal under an external load of 300 g. As annealing time increases, the number of cracks initially increases and then decreases, with two cracks remaining on the crystal surface after 240 h annealing. This indicates that the microhardness of annealed crystal is lower than that of

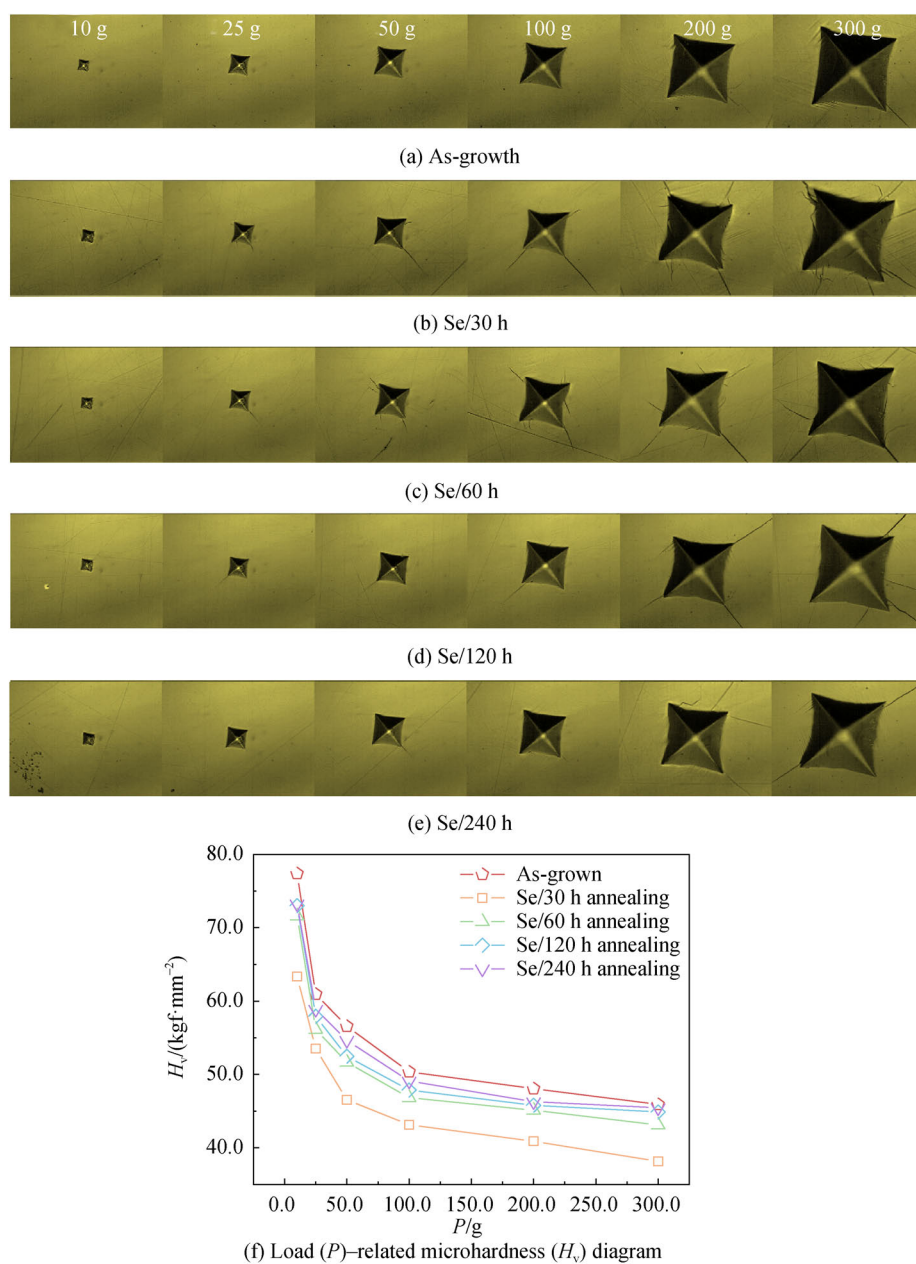


Fig. 5 Microhardness of CdMgTe crystals before and after annealing in Se atmosphere

the as-grown crystal. Under 50 g load, the microhardness of the as-grown crystal is 56.57, while the maximum microhardness of the annealed crystals is 54.66 (after 240 h annealing). Annealing in Se atmosphere results in Cd volatilization and Se diffusion into the lattice. Compared with CdTe and MgTe, CdSe has the smallest bond length, so Se has the optimum solution strengthening effect. The microhardness of CdMgTe crystals before and after annealing can be explained by the hardness formula for tetrahedral coordination semiconductor materials:^[31]

$$H_v \sim \frac{V_2^3}{d^5(V_2^2 + V_3^2)^{3/2}} \sim d^{-5 \sim -11} \quad (2)$$

where V_2 is the covalent energy, V_3 is the ionic energy, and d is the bond length. It is evident that the hardness value is inversely proportional to bond length. The bond length for the relevant compounds is as follows, *i.e.*, MgTe (2.830 Å), ZnTe (2.643 Å), MnTe (2.557 Å), CdTe (2.809 Å), and CdSe (2.631 Å)^[32–33]. Therefore, the microhardness of the annealed CdMgTe crystals decreases. However, the introduction of Se increases the relative concentration of CdSe, leading to an increase in the microhardness. The solution strengthening effect of Se is more pronounced than that of Mg, causing the microhardness to initially decrease and then increase.

3.4 Effect of Se atmosphere annealing on crystal quality

Fig. 6(a) shows the IR transmittance spectra of CdMgTe crystals before and after annealing in Se atmosphere. The IR transmittance of the as-grown crystal is 51.2%, while that of the annealed crystals is 53.1% (after 30 h annealing), 56.7% (after 60 h annealing), 63.6% (after 120 h annealing), and 59.3% (after 240 h

annealing), respectively. The IR transmittance of the crystal after 120 h annealing approaches the theoretical value of 65%, thus satisfying a criterion for high-quality crystals. The high resistance of the as-grown crystals results in a low carrier concentration, with lattice absorption being predominant. More defects in the crystal result in a lower IR transmittance. Despite potential stoichiometric ratio deviations and surface roughness after annealing, the overall crystal quality improves, leading to an increased IR transmittance. Fig. 6(b) shows the Raman spectra of the CdMgTe crystal before and after 120 h annealing in Se atmosphere. In the as-grown crystal, the peaks for $A_1(\text{Te})$, $\text{TO}(\text{CdTe})$, and $\text{LO}(\text{CdTe})$ appear at 126.8, 140.6 cm^{-1} and 162.4 cm^{-1} , respectively. No significant shift in these three peaks occur after annealing. The peak intensity of $A_1(\text{Te})$ is basically unchanged, indicating that Te inclusions are not eliminated during annealing. However, an increase in the peak intensity of $\text{TO}(\text{CdTe})$ and a decrease in that of $\text{LO}(\text{CdTe})$ indicate that the lattice integrity in the annealed crystal is compromised. This can be attributed to the volatilization of Cd and the substitution of Se for Te, resulting in the lattice distortion.

3.5 Effect of Se atmosphere annealing on resistivity

Fig. 7 shows the I - V curves of CdMgTe crystals before and after annealing in Se atmosphere. The leakage current of the as-grown crystal at 100 V is 0.55 nA, with a calculated resistivity of $7.07 \times 10^{10} \Omega \cdot \text{cm}$. The high resistivity of the as-grown crystals is attributed to the excess doping of Cd and In, which effectively compensates for Cd vacancies and reduces the concentration of free carriers. The leakage current after

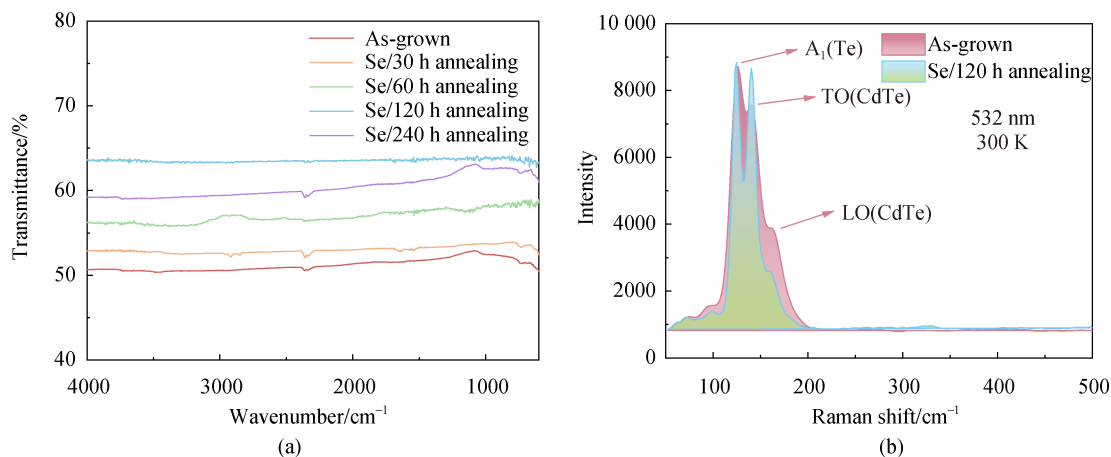


Fig. 6 Crystal quality of CdMgTe crystals before and after annealing

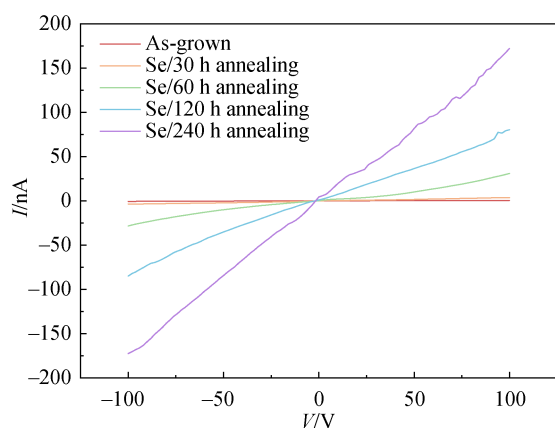
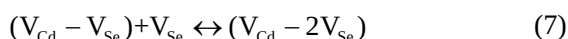
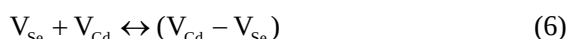


Fig. 7 I - V curves of CdMgTe crystals before and after annealing in Se atmosphere

different annealing time increases progressively to 3.83 nA (after 30 h annealing), 31.05 nA (after 60 h annealing), 80.37 nA (after 120 h annealing) and 172.36 nA (after 240 h annealing), respectively. Consequently, the resistivity values after different annealing time are $1.12 \times 10^{10} \Omega \cdot \text{cm}$ (after 30 h annealing), $1.52 \times 10^9 \Omega \cdot \text{cm}$ (after 60 h annealing), $5.42 \times 10^8 \Omega \cdot \text{cm}$ (after 120 h annealing), and $2.29 \times 10^8 \Omega \cdot \text{cm}$ (after 240 h annealing). During the annealing process, several defects occur according to the following reactions



During annealing, element Cd volatilizes due to its high vapor pressure, leading to the formation of acceptor defect V_{Cd} (see Eq. (3)), while Se partially replaces Te to form Se_{Te} (see Eq. (4)). The volatility of Se causes a partial decomposition of Se_{Te} into Te vacancy (V_{Te}), Se interstitial atom (Se_i), and Se vacancy (V_{Se}) (see Eq. (5)).^[29] Mycielski *et al.*^[26] found that in CdTe crystal containing Se, the once-ionized V_{Se} could lie above the valence band. V_{Cd} can react with In to form an acceptor complex ($\text{V}_{\text{Cd}}\text{-In}$) and with V_{Se} to form an acceptor hole trap ($\text{V}_{\text{Cd}}\text{-V}_{\text{Se}}$) (see Eq. (6)) and neutral complexes ($\text{V}_{\text{Cd}}\text{-}2\text{V}_{\text{Se}}$) (see Eq. (7)) located 50 meV above the valence band. However, the previous literature does not provide specific positions for the defect levels associated

with V_{Se} . The decrease in resistivity after annealing may be attributed to increased concentrations of acceptor V_{Cd} and ($\text{V}_{\text{Cd}}\text{-V}_{\text{Se}}$), thus leading to an increased carrier (hole) concentration and, consequently, a decrease in resistivity. After annealing in Se atmosphere, the crystal resistivity differs from that of IR transmittance. The infrared light absorption can be enhanced due to the increased carrier concentration. Thus, the increased IR transmittance after Se atmosphere annealing for 120 h indicates a significant reduction in crystal defects. However, the reduced defects do not include Te inclusions. Consequently, the weakened absorption of infrared light and improved crystal quality are likely due to the solid-solution strengthening effect of Se.

3.6 Effect of Se atmosphere annealing on detector performance

Roomtemperature radiation detectors with an Au/CdMgTe/Au planar structure are obtained by preparing 3 mm diameter Au electrodes on both sides of CdMgTe crystals (see Fig. 1(b)). ^{241}Am α particle source with an energy of 5.48 MeV is used for detector energy spectrum testing. The formation time is 1 μs and the collection time is 3 min. Fig. 8 shows the results of TOF signals of CdMgTe detectors at different bias voltages. The increased time of detectors fabricated from as-grown crystals is in the order of 10^{-5} s to 10^{-6} s, whereas for those made from annealed crystals, it is in the order of 10^{-7} s. The electron mobility μ_e of the crystal before and after annealing in Se atmosphere for 120 h is calculated to be $40.56 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $344.47 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Also, the μ_e values before and after different annealing durations are $25.16 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $78.16 \text{ cm}^2/(\text{V}\cdot\text{s})$ (before and after 30 h annealing), $54.72 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $172.53 \text{ cm}^2/(\text{V}\cdot\text{s})$ (before and after 60 h annealing), $39.72 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $284.75 \text{ cm}^2/(\text{V}\cdot\text{s})$ (before and after 240 h annealing), respectively. The electron mobility of the detector firstly increases and then decreases as the annealing time increases. The maximum electron mobility can be obtained in detectors prepared from crystals annealed for 120 h. Although the μ_e of the crystals after annealing in selenium atmosphere for 120 h increases by approximately 8.5 times, the resistivity decreases by two orders of magnitude. One possible explanation is that the introduction of Se freezes (or captures) point defects, preventing carrier migration

or forming deep levels, thereby altering the deep level structure and optimizing carrier transport in the detector. Rejhon *et al.* [34] reported that the electrical properties of CdZnTeSe could be affected by two deep-level defects at near the middle band gap, facilitating charge transport in the detector. They also compared the deep level defects of CdZnTe and CdZnTeSe crystals, and found that Se could shift the energy level guide band [35]. If the shifted energy level was close to the Fermi level, it could affect the carrier capture and recombination. This shift could

not be simply attributed to the narrowing of the band gap. The existing literature shows that there is no comprehensive study on the deep level defects of quaternary CdTe-based compounds containing Se. Furthermore, the locations of selenium-related deep level defects, such as V_{Se} and $(V_{Cd}-V_{Se})$, remain uncertain. [36] In this study, the increase in μ_e may be attributed to increased V_{Se} and $(V_{Cd}-V_{Se})$ defect levels, a shift of these levels towards the Fermi level, or a combination of both, ultimately optimizing the carrier transport in the detector.

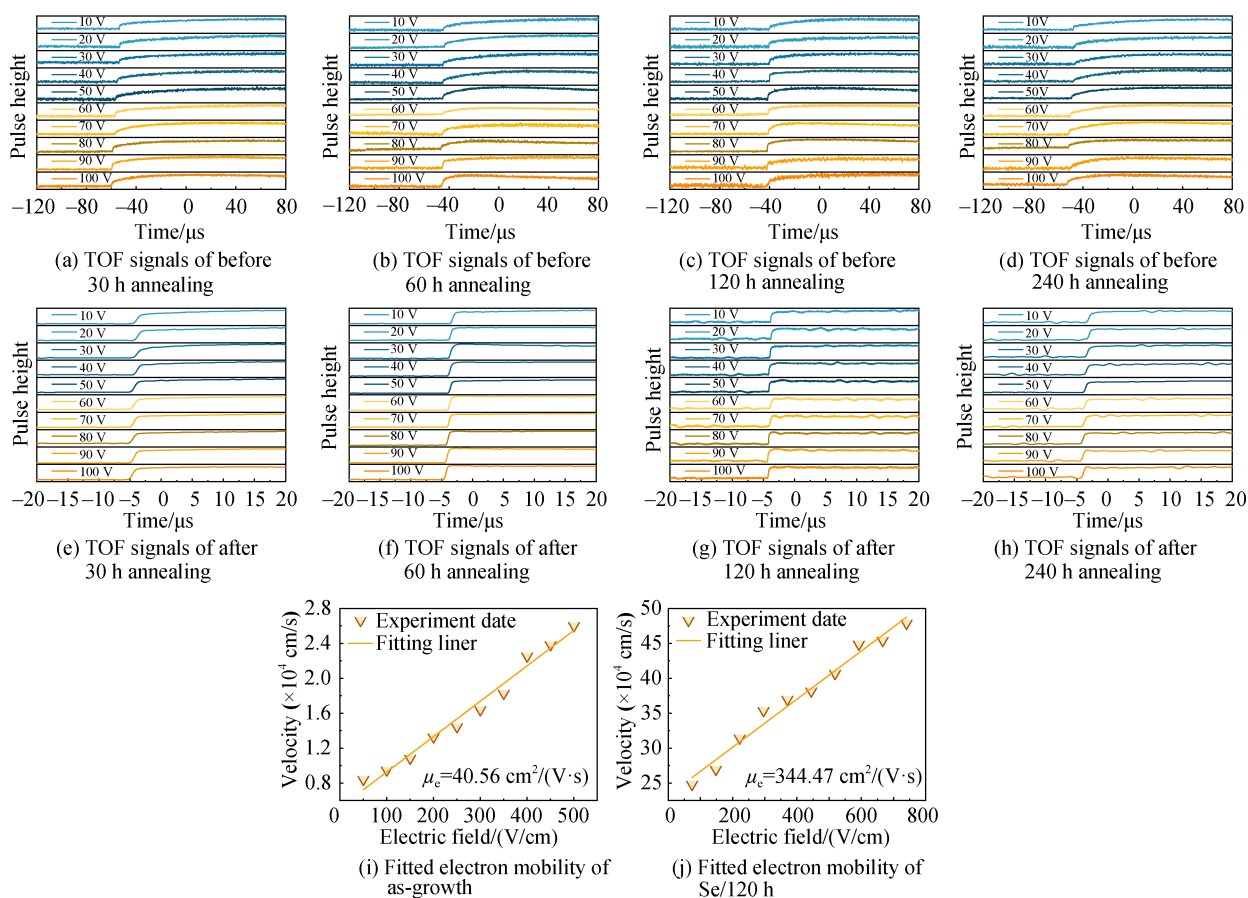


Fig. 8 TOF signals of CdMgTe detectors at different bias voltages and fitted electron mobility of CdMgTe detectors

Fig. 9 shows the energy spectra collection efficiency of the CdMgTe planar detectors. For the detector fabricated from as-grown CdMgTe crystals, no distinct characteristic peaks appear due to the poor quality of the crystals. In contrast, detectors fabricated from annealed crystals exhibit distinct characteristic peaks. The energy resolutions of the detectors under a 100 V bias after different annealing time are 63.6% (after 30 h annealing), 24.3% (after 60 h annealing), 21.7% (after 120 h annealing) and 27.3% (after 240 h annealing), respectively. Also, based on the relationship between collection efficiency

and the channel number at various voltages, the $(\mu\tau)_e$ values for the detectors after different annealing time are calculated to be $7.64 \times 10^{-5} \text{ cm}^2/\text{V}$ (after 30 h annealing), $1.05 \times 10^{-4} \text{ cm}^2/\text{V}$ (after 60 h annealing), $1.32 \times 10^{-4} \text{ cm}^2/\text{V}$ (after 120 h annealing) and $1.19 \times 10^{-4} \text{ cm}^2/\text{V}$ (after 240 h annealing), respectively.

Furthermore, an increase in annealing time corresponds to a higher voltage tolerance in the detectors. The detector fabricated from crystals annealed for 120 h in Se atmosphere demonstrates the optimal performance. Note that the energy resolution of the detector fabricated

from crystals annealed for 120 h, tested at 400 V, is 17.2%, representing the optimum experimental value. When the annealing time increases to 240 h, the energy resolution and $(\mu\tau)_e$ value both decrease. Kim *et al.* [37] reported that Se could reduce the concentration of deep-level hole traps, thereby enhancing the detector performance *via* increasing $(\mu\tau)_h$. However, this work does not measure the detector signal primarily due to the low $(\mu\tau)_h$ value. The $(\mu\tau)_h$ of CdTe-based crystals is approximately 100 times lower than the $(\mu\tau)_e$. [37]

In conclusion, the performance of CdMgTe planar detector can be improved *via* introducing Se through annealing. This provides an idea for the annealing of CdTe-based crystals. In addition, Se can also reduce the concentration of Te inclusions during crystal growth. [38] Introducing Se into CdMgTe crystals may facilitate the growth of a quaternary compound, *i.e.*, CdMgTeSe, which can offer the superior crystal quality and detector performance, thereby expanding the range of materials available for roomtemperature radiation detection.

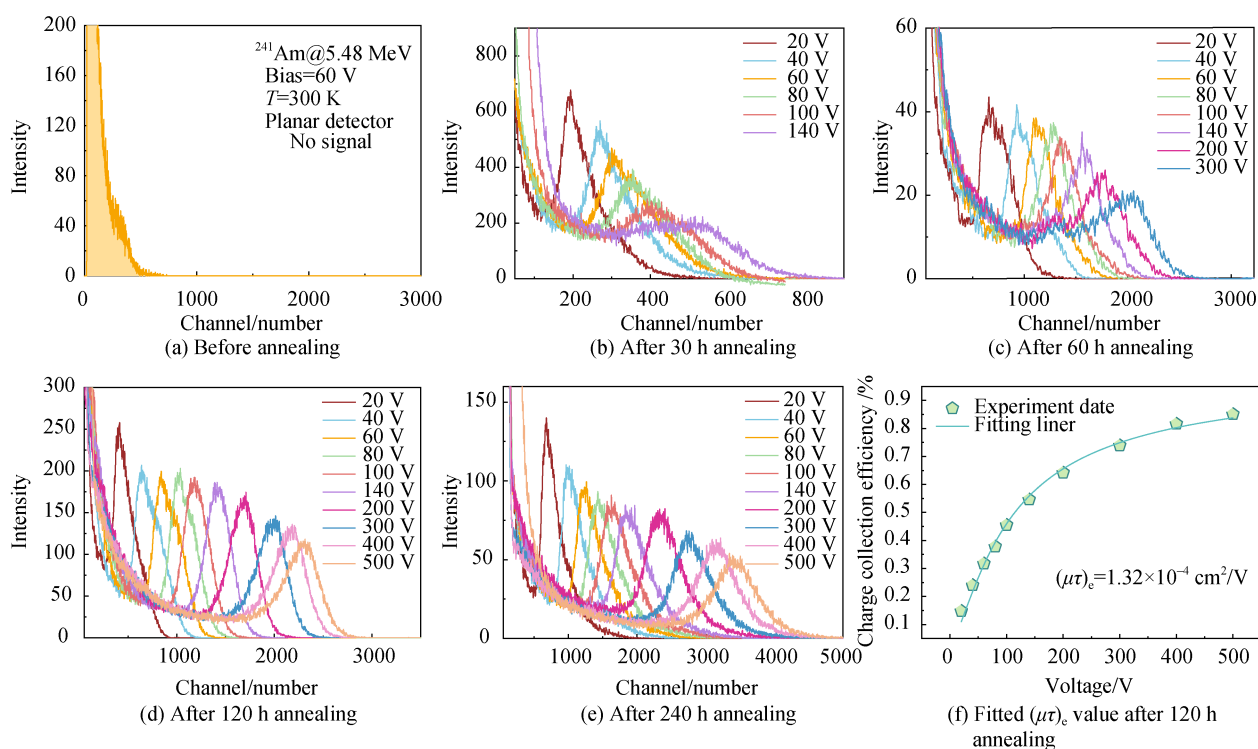


Fig. 9 Energy spectra and collection efficiency of CdMgTe planar detectors

4 Conclusions

An advanced annealing strategy was adopted for enhancing the quality of CdMgTe single crystals in room-temperature radiation detectors. The effect of annealing time in Se atmosphere on the crystal properties and detector performance was investigated.

1) Annealing in Se atmosphere did not prevent the volatilization of Cd in CdMgTe crystals or reduce Te inclusions. Se partially replaced Te through reactions with the CdMgTe matrix *via* diffusion and chemisorption. After annealing, the edges of the slices were corroded, and the decrease in Cd content along with an increase in Mg content resulted in an expanded band gap.

2) The microhardness and the IR transmittance of the crystals firstly decreased and then increased, and the resistivity gradually decreased as the annealing time increased, thus improving the crystal quality. The performance of detectors fabricated from annealed crystals was significantly improved.

3) CdMgTe crystals in Se atmosphere could be obtained under the optimal annealing conditions (*i.e.*, at 773 K for 120 h). The optimal performance of detector was an electron mobility μ_e of 344.47 $\text{cm}^2/(\text{V}\cdot\text{s})$, an energy resolution of 17.2%, and a $(\mu\tau)_e$ product of $1.32 \times 10^{-4} \text{ cm}^2/\text{V}$ for ^{241}Am α particles with an energy of 5.48 MeV. Annealing in Se atmosphere could offer an advanced approach to enhance the quality of CdTe-based crystals.

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Strategy for Enhancing the Quality of CdMgTe Single Crystals for Room-Temperature Radiation Detectors

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Extended Abstract

Introduction Cadmium magnesium telluride (CdMgTe), as a group II-VI CdTe-based compound semiconductor, can be used in room-temperature radiation detection. However, CdMgTe crystals grown by melt methods often exhibit major defects like vacancies, dislocations, twins, and inclusions, severely impacting the crystal quality and detector performance. Some studies show that selenium (Se) can significantly reduce harmful defects like sub-boundary networks and Te inclusions in CdTe-based crystals, enhancing the crystal quality through its favorable segregation coefficient and intense solid-solution hardening effect. Therefore, in this paper, Se was introduced into CdMgTe crystals *via* vapor phase diffusion as an advanced annealing strategy to enhance the both crystal quality and detector performance. In addition, the effect of annealing time on the crystal defects, microhardness, optical and electrical properties, and detector performance was also investigated.

Methods The annealing source was a high-purity Se (7N), and the slices with the dimensions of 5 mm×5 mm×2 mm were selected from an In-doped CdMgTe ingot grown by a modified vertical Bridgman method under Cd excess condition. Prior to annealing, the slices were mechanically polished with an MgO suspension and then treated with a 2% Br₂-MeOH solution to eliminate scratches and any damaged layers. The slices and the source were positioned at opposite ends of a quartz annealing device, with quartz crucibles evacuated to a pressure of 10⁻⁵ Pa. The annealing temperature of both slice and source was selected at 773 K. Effect of annealing time on CdMgTe crystal properties was investigated at different holding time (*i.e.*, 30, 60, 120 h, and 240 h). CdMgTe planar room-temperature radiation detectors were fabricated *via* evaporating Au electrodes onto the both sides of the annealed crystals.

CdMgTe crystals before and after annealing in Se atmosphere were characterized by near-infrared spectrometry (NIR), X-ray photoelectron spectroscopy (XPS), infrared transmission microscopy (IRTM), field emission scanning electron microscopy (FESEM), infrared (IR) spectrometry, Raman spectrometry, and current-voltage (*I*-*V*) measurement. Room-temperature radiation detectors were prepared by evaporation of Au electrodes on both sides of CdMgTe crystals. The carrier mobility was determined by a time-of-flight (TOF) technology. The energy spectrum of the detectors was acquired by an ORTEC measurement system with uncollimated ²⁴¹Am α particles with an energy of 5.48 MeV as an irradiation source.

Results and discussion The band gap of the as-grown crystal is 1.505 eV, and annealing in Se atmosphere does not prevent the volatilization of Cd in CdMgTe crystals or reduce Te inclusions. After annealing, the maximum increase of the band gap is 0.042 eV. Se interacts with CdMgTe matrix *via* diffusion and chemisorption, forming chemical bonds that effectively result in the partial substitution of Se for Te. The solution strengthening effect of Se is more pronounced than that of Mg as the annealing time increases, causing that the microhardness initially decreases and then increases, which is lower than that of the as-grown crystal. The IR transmittance of the crystal after 120 h annealing is 63.6%, which approaches the theoretical value of 65%, thus satisfying a criterion for high-quality crystals. The peak intensity of A₁(Te) is basically unchanged based on the Raman spectra. However, an increase in the peak intensity of TO(CdTe) and a decrease in that of LO(CdTe) indicate that the lattice integrity in the annealed crystal is compromised.

CdMgTe crystal obtained under optimal annealing conditions is fabricated into an Au/CdMgTe/Au planar structure for the room-temperature radiation detector. TOF measurements show a remarkable increase in electron mobility (μ_e), up to 344.47 cm²/(V·s). ²⁴¹Am α particle source with an energy of 5.48 MeV is used for detector energy spectrum testing. The optimal CdMgTe detector exhibits the performance with an energy resolution of 17.2% and a carrier mobility lifetime product $(\mu\tau)_e$ of 1.32×10⁻⁴ cm²/V. Annealing in a Se atmosphere can thus offer an effective approach to enhance the quality of CdTe-based crystals.

Conclusions An advanced annealing strategy was adopted for enhancing the quality of CdMgTe single crystals for room-temperature radiation detectors. After annealing, a decrease in Cd content along with an increase in Mg content resulted in an expanded band gap. The microhardness and the IR transmittance of the crystals firstly decreased and then increased, and the resistivity gradually decreased as the annealing time increased, thus improving the crystal quality. The optimum condition of Se atmosphere annealing was at 773 K for 120 h. The optimal performance of the detector was an electron mobility (μ_e) of 344.47 cm²/(V·s), an energy resolution of 17.2%, and a $(\mu\tau)_e$ product of 1.32×10⁻⁴ cm²/V for ²⁴¹Am α particles with an energy of 5.48 MeV.

Keywords room-temperature radiation detector; cadmium magnesium telluride crystals; selenium atmosphere annealing; resistivity