

Laser-induced thermomigration of Te precipitates in CdZnTe crystals

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ABSTRACT

The thermomigration of tellurium precipitates in a cadmium zinc telluride (CdZnTe) crystal was observed using an infrared (IR) CO₂ laser beam. Te precipitates present in CdZnTe have been shown to thermally migrate along a temperature gradient. Selective energy deposition from an IR laser beam in Te precipitates was investigated as a potentially advantageous approach to speed the annealing of Te precipitates in CdZnTe. Initial results indicate Te precipitates do thermally migrate under IR laser heating.

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1. Introduction

Cadmium zinc telluride (CdZnTe) has been shown to be the most promising material for room-temperature X-ray and gamma-ray spectroscopy grade detectors [1]. However, the yield of relatively large high-quality crystals is challenged due to growth limitations. Retrograde solubility of tellurium (Te) in CdTe causes the formation of Te precipitates within melt-grown crystals. Te precipitates deteriorate device performance in CdZnTe spectrometers and are known to act as charge-carrier traps [2].

CdZnTe crystal growth with the traveling heater method, a form of solution growth, can reduce precipitate formation, thereby producing higher quality spectroscopic grade material. However, the traveling heater method is slow (2–5 mm/day [3]) and requires extremely stable growth environments in which temperature variations must be less than $\pm 0.1^\circ\text{C}$ [4]. High capital investments for extremely stable furnaces coupled with low throughput are not conducive to commercial application.

Bulk thermal annealing has been the most popular method to improve CdZnTe crystal quality. Previous work has shown that an externally applied thermal gradient caused thermal migration of Te precipitates in the direction of the thermal gradient. Migration velocities up to $\sim 50 \mu\text{m}/\text{h}$ have been achieved with an applied

temperature gradient of $\sim 70^\circ\text{C}/\text{cm}$ [5]. Annealing temperatures slightly above 440°C exhibited the best migration results since Te precipitates were shown to melt near 440°C .

Laser annealing studies [6–10] have also been performed, but with little success. In these previous cases, visible or near-infrared (IR) lasers were used, and no laser annealing was done under Cd overpressure. CdZnTe is transparent to IR light, but not to visible light. Thus, the above-mentioned studies heated the entire CdZnTe sample. The lack of Cd overpressure allowed out-diffusion of constituent elements, thus resulting in worse device performance.

2. Theory

The presumed mechanism for migration is that CdZnTe is dissolved within the molten Te precipitate, preferentially at the hotter edge. Further, the previously dissolved CdZnTe recrystallizes preferentially at the cooler edge, thereby reforming the crystal lattice. The overall result is an indirect movement of the Te precipitate towards the hotter region.

Selective heat deposition was hypothesized to mitigate out-diffusion of Cd and Zn as reported in [11] by allowing for lower process temperatures. The present investigation utilized a photon wavelength that readily transmits through CdZnTe but is sufficiently absorbed by Te precipitates. It is hypothesized that the Te precipitates irradiated by the laser preferentially absorb the

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energy on the laser impinging side, which imposes a temperature gradient across the precipitate.

A coherent CO₂ laser was used, providing a 1.8 mm Ø laser beam with a power output up to 63 W. The CdZnTe crystal has a bandgap energy ranging from 1.4 to 1.6 eV, and is transparent to the IR CO₂ laser emission with a wavelength of 10.6 μm (and corresponding photon energy of 0.1169 eV). Pure Te, with a bandgap energy of 0.33 eV, might be expected to be virtually transparent to the CO₂ laser as the photons are not energetic enough to raise electrons across the bandgap. However, strong interband absorption caused by holes creates an absorption peak near 11 μm [12]. At 190 °C, the absorption coefficient is ~100 cm⁻¹ at 10.6 μm and increases with temperature. This fact supports observed experimental results which clearly indicate that transmission of IR light at 10.6 μm is strongly correlated to Te precipitate density [13].

Numerical simulations modeling the laser energy uniformly absorbed at the surface of the Te precipitate were performed. A finite difference code was written to compute the temperature distribution as a function of the radial position and time. Symmetry boundary conditions were applied at the center of the precipitate and adiabatic conditions halfway in between neighboring precipitates (~300 μm) were assumed.

The computed temperature distribution strongly depends on the size of the precipitate and the size and the power of the laser beam. The results clearly indicate that laser pulses lead to significant local heating. The irradiation of a typical 40 μm diameter precipitate with the bare (unexpanded) laser over 2 ms results in a temperature difference between a Te precipitate and the crystal material (CdZnTe) of approximately 80 °C (as shown in Fig. 1). If the pulse is lengthened, or continued, the surrounding material temperature rises, which can result in melting the

crystal. It was observed that a 5 × 5 × 10 mm³ crystal oriented sideways to the 50 W beam indeed melted through after 5 min of continuous exposure. Furthermore, the numerical simulations suggest that time constants on the order of 5 ms are needed to sufficiently cool the sample after the laser pulse to prevent melting (see Fig. 1).

Intermittent laser power was therefore chosen for the operation, thereby allowing for local cooling in order to prevent the crystal from melting during the process. By choosing relatively short pulses (<20 ms) the crystal bulk temperature is essentially maintained by the external thermal environment (furnace) and can be independently controlled. About 60 Hz was chosen as the pulse frequency, thereby allowing for sufficient time (~15 ms) to locally cool down the crystal.

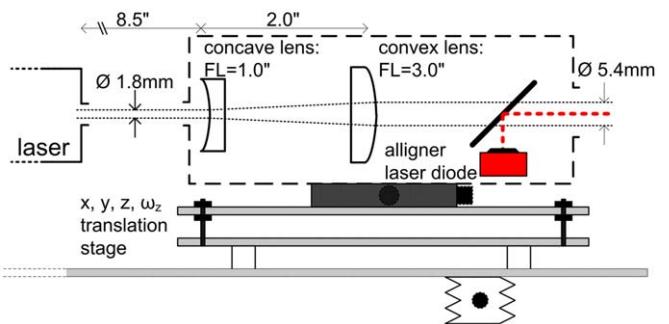


Fig. 2. Laser conditioner arrangement showing the beam expander and the superimposing alignment laser. The laser was aligned to impinge on the CdZnTe sample inside a furnace tube.

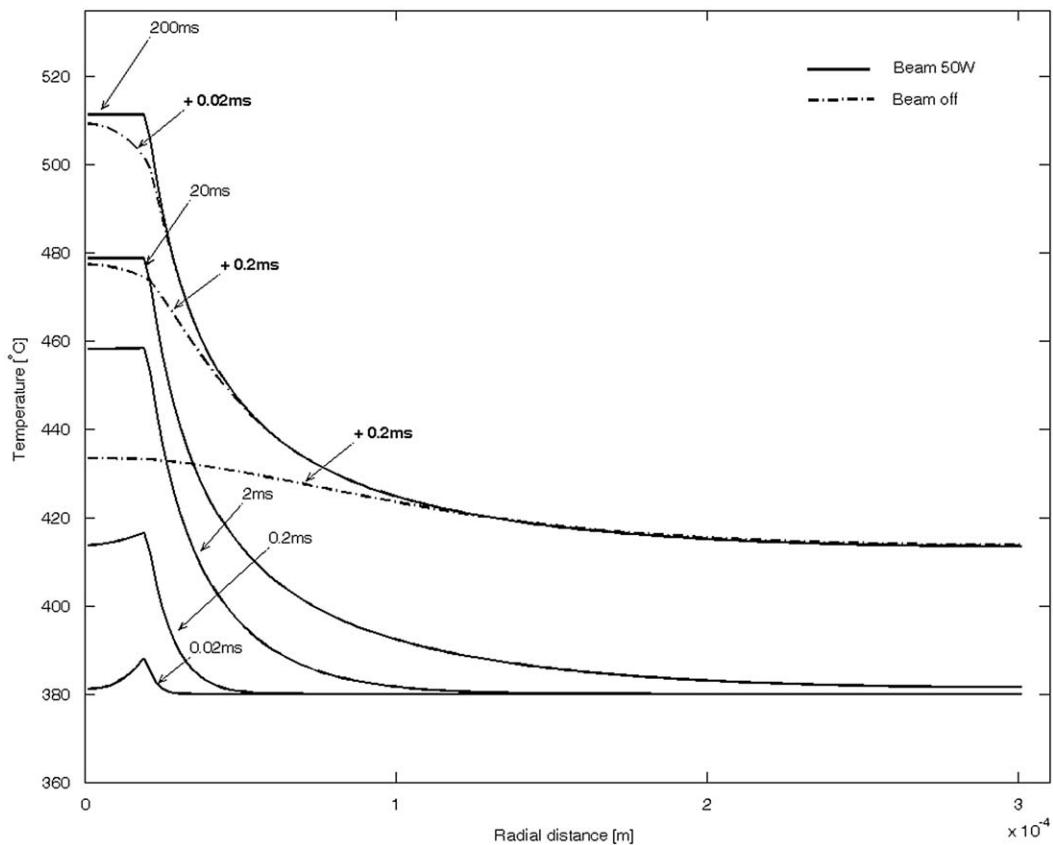


Fig. 1. Numerical simulation of radial temperature profile in the vicinity of a 40 μm precipitate.

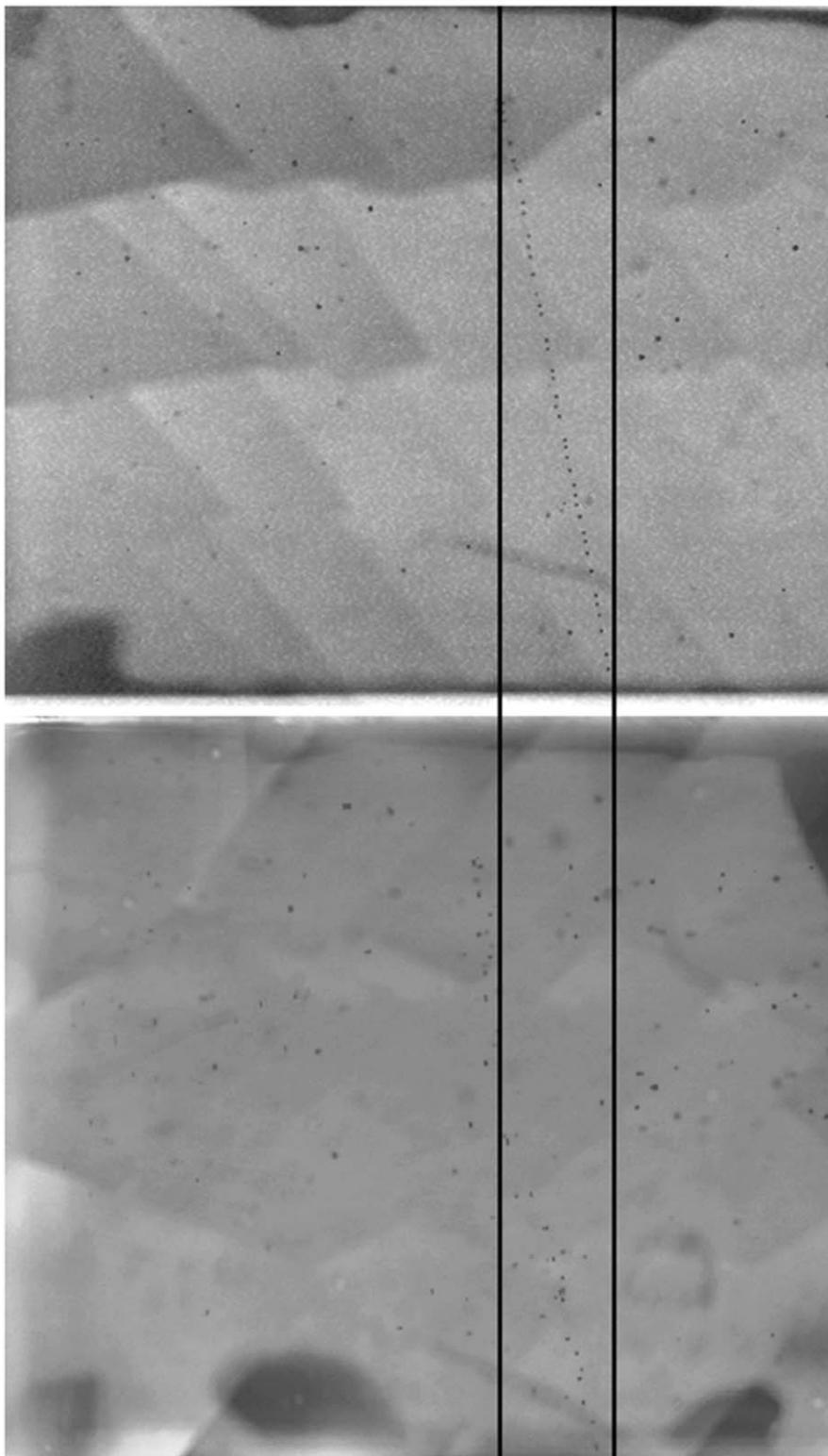


Fig. 3. IR microscope photographs of the investigated CdZnTe crystal before (upper) and after (lower) pulsed laser irradiation. Irradiation was performed on the left side of the device for a period of 100 h. The distance between the two vertical lines is 1 mm.

3. Experimental procedure

The coherent LC-50 D600 CO₂ laser with a wavelength of 10.6 μm, a beam size of 1.8 ± 0.2 mm in diameter and a maximum power of 63 W was aligned to a laser conditioner arrangement as

shown in Fig. 2. The laser conditioner module consisted of two rail-mounted lenses, a visible diode pointer laser and a combiner lens. The laser beam first passed through a collimator lens (0.6 in diameter, (−)1.0 in focal length) to expand the beam. The second collimator lens (0.75 in diameter, (+)3.0 in focal length) was

mounted at a nominal distance of 2.0 in from the first lens in order to achieve a $3\times$ magnification, leading to a $\approx 5.4\text{ mm} \varnothing$ beam.

A $\approx 6 \times 6 \times 10\text{ mm}$ CdZnTe crystal was placed in a single-temperature zone furnace to maintain a controllable thermal environment. The furnace temperature was adjusted to keep the CdZnTe crystal at approximately 300°C . The laser beam was aimed at the front side (square surface) of the CdZnTe crystal. The laser power was set to 50 W and laser pulses of 2.5 ms at 60 Hz were chosen. The crystal was irradiated for 100 h under the described conditions. IR photographs before and after irradiation were recorded. A Nikon Eclipse E400 microscope with a 900-nm light filter (D900/100) connected to a Dage-MTI DC200 microscope camera was used to collect the photographic images before irradiation. The images after irradiation were taken with a higher sensitivity camera (PX-CM-2+). The individual photographs were assembled using commercially available image treatment software. To allow for clear IR photographic images, the two opposing CdZnTe sample sides perpendicular to the microscope lenses were re-polished with first 1200 grit paper, second 4000 grit paper, and finished with a $3\text{ }\mu\text{m}$ alumina powder slurry.

4. Result and discussion

The IR photographs were focused in the center part of the crystal, as shown in Fig. 3. A series of precipitates were originally clustered in a line before irradiation. The centrally located Te precipitates have clearly moved after laser annealing. The precipitates were measured to have moved at a rate of approximately $\sim 3\text{ }\mu\text{m}/\text{h}$ at most. The migration rate is highest at the center of the crystal where the laser beam was focused, whereas precipitates near the sample edges did not noticeably move, indicating that the precipitate migration is due to the laser heating and not heat transfer from other sources (such as the furnace).

As shown in Fig. 4, the CdZnTe crystal surface sustained damage during the laser annealing procedure. The point at which the laser penetrated the crystal became covered with a porous coating of oxide. X-ray fluorescence analysis indicated that the yellow coating was zinc oxide (ZnO). It is assumed that the built up zinc oxide may have absorbed the CO_2 laser energy. It could also be hypothesized that the free charge-carrier absorption became large which lead to increased near-surface heating and zinc oxidation. Thus, it appears feasible that the precipitate movement rate might be greatly increased if the build up of ZnO could be avoided. Furthermore, the sidewalls of the crystal became “cloudy” which may be attributed to Cd and/or Zn out-diffusion, as described in [13].

The non-uniform character of the migration displacement may also indicate the lack of a pronounced thermal gradient that is supposed to direct the precipitate movement. Compared to the

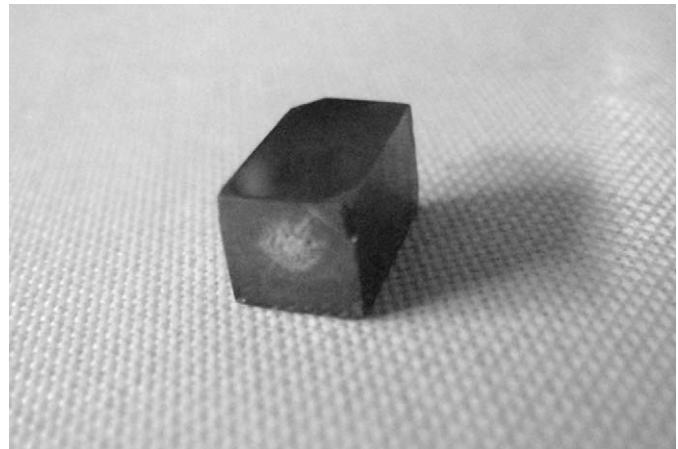


Fig. 4. The CdZnTe crystal sample ($5 \times 5 \times 10\text{ mm}^3$) after 100 h of laser annealing. The marked area, a surface oxide, marks the laser impinging point.

reported migration rate of $\sim 50\text{ }\mu\text{m}/\text{h}$ in [2], the laser-induced migration, as of now, is one order of magnitude slower.

Future work will be dedicated towards optimizing key parameters, such as intermittent laser duty cycle and furnace temperature. Minimizing crystal deterioration and increasing the migration velocity remain the main objectives. Alternatively, Cd and/or Zn overpressures may need to be applied in order reduce Cd/Zn out-diffusion.

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