

Influence of laser irradiation and laser-induced In doping on the photoluminescence of CdTe crystals

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Received 28 January 2003, in final form 4 April 2003

Published 6 May 2003

Online at stacks.iop.org/SST/18/560

Abstract

By investigating the photoluminescence (PL), we have studied laser-induced doping and defect formation in high-resistivity Cl-compensated *p*-like CdTe crystals coated with and without a thin In dopant film. A detailed analysis of the PL spectra has been performed to discuss the laser-stimulated modification of the defect structure in CdTe crystals subjected to irradiation with nanosecond KrF excimer laser pulses with the energy density above the melting threshold. In particular, laser irradiation increased V_{Cd} as a result of the dissociation of (Cd-X) complexes and laser desorption of Cd atoms. Laser-stimulated diffusion of In atoms at Cd vacancies provided doping of CdTe crystals. Fast freezing of a large number of the point defects In_{Cd} impeded the formation of compensating acceptors ($V_{\text{Cd}}\text{-In}_{\text{Cd}}$). This allows us to suppress the self-compensation mechanism, and to introduce and activate the In impurity into a thin surface layer of the crystals without damaging of the structure and properties of the underlying region.

1. Introduction

Cadmium telluride (CdTe) is an important material for optoelectronic device application, in particular for nuclear radiation detection and imaging [1–6]. However, the relative low dopability in the semiconductor is one of the main problems in device fabrication using CdTe [1, 2, 7–9]. It is known that the indium impurity is one of the favourable and most extensively studied *n*-type dopants in CdTe because In_{Cd} has a very shallow transition energy level and relatively low defect formation energy [2, 7, 8]. However, the doping process of CdTe with this impurity is accompanied by the spontaneous formation of compensating opposite-charged native defects or complexes of the dopant. This limits further change of the Fermi energy (i.e. the Fermi level is pinned), thus limiting the charge carrier concentration to a value considerably less than the impurity concentration [7–10]. Thus, one of the most important problems here is the search for an introduction method, which can suppress the

dopant self-compensation phenomenon. For efficient device application of CdTe, the procedure should be processed in such a manner to assure sharp In impurity profiles and thus a low *p*–*n* junction depth, and the applied procedure should not alter the point defect structure and electrical properties of the bulk of crystals [7, 8]. For these purposes, it is convenient to use pulsed laser processing [3–6]. Very fast, non-equilibrium and non-stationary processes such as laser-induced defect formation, heating, melting and following fast cooling of a thin surface layer of the semiconductor under irradiation can provide the conditions for heavy doping of CdTe with impurity concentrations which cannot be achieved by traditionally used equilibrium methods. In particular, this causes a laser-stimulated increase in the impurity diffusion rate as well as freezing of a large number of non-equilibrium point defects [6, 11]. Furthermore, laser implantation of impurities is a promising procedure for doping because the irradiation of semiconductors with high-absorbed laser pulses of nanosecond duration allows us to avoid heating the bulk of

crystals and modifies only a thin surface layer [3–6, 11, 12]. On the other hand, laser irradiation can result in the creation and multiplication of intrinsic point defects, the formation of defect complexes, the generation of dislocations and the disruption of the crystalline structure. These laser-stimulated processes cause degradation of the electrophysical and photoelectric characteristics of the semiconductor [11–15]. Therefore, the study of the laser-induced defect formation in CdTe is of fundamental importance to develop laser procedures for doping of the semiconductor. Photoluminescence (PL) is a highly sensitive technique for the study of semiconductors and gives important information about the evaluation of the quality and composition of the material by probing the electron and hole energy states. In this paper, we present the results of the PL spectra investigation of CdTe crystals subjected to laser irradiation or doping with In impurity by using nanosecond KrF excimer laser pulses. The features of the PL spectra are analysed and the mechanisms of laser implantation of In impurity in CdTe are discussed.

2. Experimental techniques

The (111) oriented *p*-like single-crystal CdTe wafers, obtained from ACRORAD, were the subjects for PL investigations. The resistivity of Cl-compensated CdTe crystals was of the order of $10^9 \Omega \text{ cm}$. The dimensions of the samples were $5 \times 5 \text{ mm}^2$ and the thickness was 0.5 mm. The pulsed radiation source was a KrF excimer laser (248 nm) emitting single pulses of 20 ns duration with the energy density varying in a wide range. The surface processing technique, using a KrF excimer laser, was described in detail in [3–5]. The whole surface area (Te-face) of a sample was uniformly subjected to laser action in a high-pressure argon environment at 300 K. Irradiation was carried out in two different ways. In the first case, the CdTe crystals were subjected to the action of laser pulses directly from the surface. In the second case, the samples were irradiated from the side coated with a thin ($\sim 30 \text{ nm}$) indium dopant film, which had been evaporated on the etched CdTe surface by vacuum deposition without heating the crystal.

Irradiation of the samples with an energy density higher than the melting threshold of CdTe [12] resulted in melting of a thin surface layer followed by crystallization, providing In doping of the surface region of CdTe crystals pre-coated with the dopant film. It was found that the best electrical parameters of In-doped CdTe crystals could be obtained at irradiation with KrF excimer laser pulses with an energy density of 90 mJ cm^{-2} [4]. Therefore, in order to investigate the effect of laser-induced doping and defect formation in CdTe crystals the PL measurements were performed for an initial crystal before irradiation and doping, and for both types of sample: crystals with and without depositing an In film. All samples were irradiated with laser pulse energy density of 90 mJ cm^{-2} at similar annealing conditions [4]. The PL spectra were studied at 20 K using a He–Ne laser as an excitation source and a similar slit-width for all samples.

3. Results and discussion

3.1. Peculiarities of the PL spectra of CdTe crystals

Figure 1 shows PL spectra of the initial CdTe crystal (curve 1), the sample without depositing an In film after laser treatment

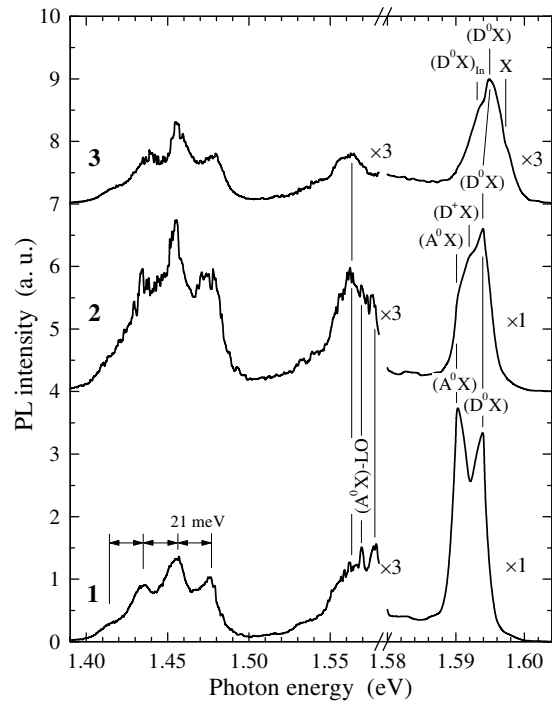


Figure 1. Photoluminescence spectra (at 20 K) of CdTe crystals before laser treatment (curve 1), after irradiation by KrF excimer laser pulses (curve 2) and after laser-induced doping with In impurity (curve 3).

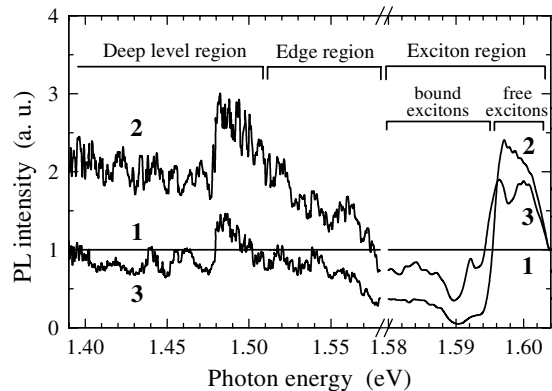


Figure 2. Comparative spectra transformed from the spectra in figure 1, showing relative changes in the photoluminescence intensity of CdTe crystals after irradiation by KrF excimer laser pulses (curve 2) and after laser-induced doping with In impurity (curve 3) with respect to CdTe crystals before laser treatment (curve 1).

(curve 2) and the sample irradiated from the side coated with an In dopant film (curve 3). For the initial samples, a typical PL spectrum of Cl-compensated CdTe is observed (curve 1). For the convenience of the discussion, the PL spectra of all investigated CdTe samples can be divided into three regions: (1) the exciton emission region (1.580–1.604 eV); (2) the edge emission region (1.510–1.580 eV); (3) the deep level emission region (1.390–1.510 eV) (figures 1 and 2). Figure 2 demonstrates the comparative PL spectra of the samples. These spectra were transformed from the PL spectra in figure 1 by normalization of curves 1–3 with respect to the initial spectrum (curve 1).

3.1.1. Analysis of the exciton emission region. The exciton PL is most sensitive to imperfection introduced into the crystal lattice under irradiation and doping. In the exciton emission region of the PL spectrum of the initial CdTe crystal, two close lines are observed (figure 1, curve 1). It is generally accepted that these lines are due to the recombination of excitons bound to shallow impurity or defect centres such as neutral acceptors (a line around 1.590 eV) and neutral donors (a line around 1.594 eV) [2, 6, 9, 10, 13–20]. A prominent line at 1.590 eV designated as (A^0X) is attributed to the decay of an exciton bound to a neutral acceptor originating either from the cadmium vacancy (V_{Cd}) or from a complex including V_{Cd} , where one of the four nearest Te neighbours is replaced by Cl as ($V_{Cd}-Cl_{Te}$) [2, 6, 16], or in the form ($V_{Cd}-2Cl_{Te}$) [17]. The LO-phonon replica of (A^0X), denoted as (A^0X)-LO, is also observed at the energy of about one LO-phonon energy (21 meV) below the prominent line (figure 1, curve 1). A line at 1.594 eV designated as (D^0X) is associated with the recombination of an exciton bound to a neutral donor, probably Cl impurity [2, 6, 16–18]. The PL spectrum of samples before irradiation and doping is dominated by the acceptor bound exciton line, indicating *p*-type conductivity.

Laser irradiation of both types of crystals, i.e. with and without a deposited In film, resulted in the transformation of their PL spectra. Analysing the exciton PL region, we can examine the bound exciton and free exciton ranges. As seen from the normalized PL spectra (figure 2, curves 2 and 3), the emission intensity of CdTe crystals after irradiation decreases in the bound exciton range and increases in the free exciton range. There is only one band in the exciton region of the PL spectra of irradiated and doped samples (figure 1, curves 2 and 3). An asymmetric profile and a large half-width of this band is evidence of a complex nature of the exciton emission due to superposition of several elementary bands which are not separated at 20 K. However, it can be seen from figure 1 (curve 2) that the exciton band consists of at least three lines with maxima at 1.590, 1.592 and 1.594 eV. The dominant component in the exciton band of the PL spectrum of the laser-only irradiated crystal becomes the (D^0X) line, while a peak of the (A^0X) line decreases and very weakly appears. Between these two peaks, another feature at 1.592 eV comes into view, and this is associated with recombination of an exciton bound to an ionized donor (D^+X) [2, 16, 19]. Probably, the appearance of the (D^+X) line in (111) oriented crystals is due to Te_{Cd} antistructural defects exhibiting donor properties [19] because of the enrichment of the surface layer with Te that has been usually observed in CdTe under irradiation by various lasers [6, 11–14].

Changes in the intensities of the (A^0X) and (D^0X) lines after laser irradiation (figure 1, curve 2) are due to the following processes. Naturally, Cl-compensated CdTe crystals have contained a great concentration of Cl-related defects. In this case, chlorine acts as a hydrogenic shallow donor substituting Te atom [2]. However Cl donors are mostly compensated by V_{Cd} with forming ($V_{Cd}-Cl_{Te}$) acceptor defects which are responsible for the self-compensation effect in CdTe [2, 6, 16, 17]. The recombination of an exciton bound to the ($V_{Cd}-Cl_{Te}$) shallow neutral acceptor causes the (A^0X) in the exciton emission region (figure 1, curve 1). Laser irradiation

leads to the dissociation of ($V_{Cd}-Cl_{Te}$) complexes to simple defects as the result of heating, thermal deformation and melting of the surface region of a crystal. Probably, very fast cooling of the melted layer hinders the formation of defect complexes and results in freezing of a large number of simple Cl-related defects. Because the concentration of complex defects ($V_{Cd}-Cl_{Te}$) decreases, the main contribution to the exciton PL of the irradiated crystals comes from the recombination of an exciton bound to a Cl donor and, understandably, the peak of (D^0X) becomes dominant (figure 1, curve 2).

Laser irradiation of the CdTe crystal coated with an In film reduces the intensity of the exciton PL band and shifts its maximum toward the higher energies by 1 meV in comparison with the spectrum of laser-only irradiated samples (figure 1, curves 2 and 3). We can discern three features at 1.593, 1.595 and 1.597 eV in the exciton emission region (figure 1, curve 3). The peak (A^0X) associated with the complex defect ($V_{Cd}-Cl_{Te}$) disappears completely by laser-induced doping. The 1.593 eV exciton emission designated as (D^0X)_{in} is commonly observed in CdTe and has been attributed to exciton trapping at a shallow hydrogenic impurity donor, such as In [2, 10].

We do not observe any deep bound exciton line around 1.585 eV ordinarily attributed to the so-called C-centre, which would be characteristic of high-resistivity CdTe crystals doped with In during growth [2, 9, 10]. This line has been associated with defect complex ($V_{Cd}-In_{Cd}$) acting as an acceptor, which is responsible for self-compensation through balance between the shallow indium donor and this complex acceptor [1, 2, 7–10]. The absence of a 1.585 eV line connected with compensating defects and the emergence of the feature at 1.593 eV indicate that only shallow ($E_D = 14$ meV) donors are introduced [2, 8, 10]. The prominent peak at 1.595 eV (figure 1, curve 3) is interpreted as the decay of an exciton bound to a shallow neutral donor. Probably this peak is due to shifting the exciton transition line denoted as (D^0X) in the spectra of both the initial and laser-only irradiated samples at 1.594 eV (figure 1, curves 1 and 2). The shift of the excitonic transition line by 1 meV towards the higher energies is due essentially to the influence of the local potential fluctuations induced by plastic deformation [2, 20] as a result of fast laser-induced thermal expansion of the crystal. This involves an increase in the bandgap energy probably due to the diffusion, facilitated by the presence of laser-created dislocations, of In impurity, which would substitute for Cd atoms [20].

The observed shift of the bound exciton band maximum corresponds to a change in the PL emission from a shallow-acceptor-bound exciton to a shallow-donor-bound exciton, indicating that the crystal surface layer changes from *p*-type to *n*-type [2, 10]. For the In film-coated samples, a broadening of the (D^0X) band is observed (figure 1, curve 3). This results from the increasing interaction between donors when the excitonic Bohr radius becomes comparable to the mean donor separation. This fact indicates that the CdTe crystals become highly doped [2, 10]. A decrease in the PL intensity in the bound exciton region of the samples after laser processing and doping can be attributed to an increase in the dislocation density and probably as a result of traffic through competing centres and the lower generation rate of excitons [2, 13–15, 20].

Irradiation of CdTe crystals results in an increase in the PL intensity in the region 1.596–1.604 eV, corresponding to an excitation with the participation of free excitons [2]. Both spectra (figure 1, curves 2 and 3) show a weak free exciton emission that is clearly seen in the comparative spectra in figure 2 (curves 2 and 3). The new feature (X) at 1.597 eV (figure 1, curve 3) is attributed to the free exciton transitions [15, 19, 20]. It should be noted that laser treatment of both types of sample, i.e., with and without depositing an In film, results in a decrease in the PL signal in the bound exciton region, while the integral PL intensity in the free exciton emission region increases (figure 2, curves 2 and 3). This indicates that, in spite of some total increase in a number of the laser-induced defects in the treated samples, the crystalline quality is not affected by laser irradiation. Furthermore, an appearance of the feature (X) in the free exciton region of the PL spectrum of the samples irradiated from the In film-coated side (figure 1, curve 3) is evidence of a low defect concentration and an improvement of structural perfection of the CdTe crystals after laser-induced doping.

3.1.2. Analysis of the edge emission region. The edge emission region of the PL spectra of CdTe crystals is actually composed of shallow donor–acceptor pair (DAP) transitions, the recombination of a free charge carrier from the conduction (valence) band with a carrier bound on an acceptor (donor), and LO-phonon replicas of the exciton lines, and it involves shallow alkaline impurities [2, 10, 13–15, 20] and Cl-related defects [2, 17]. In this region of the PL spectrum of the initial CdTe crystals, the asymmetric broad band with a maximum at 1.578 eV is observed and the weak feature at 1.563 eV is discerned (figure 1, curve 1). The peak at 1.569 eV corresponds to the LO-phonon replica of the (A^0X) line. Laser irradiation of both types of sample results in the redistribution of the peak intensity in the broad band. The peak 1.563 eV becomes dominant and others weakly appear (figure 1, curve 2) or disappear (figure 1, curve 3). The integral intensity of the edge emission band increases in the case of crystals without an In film, and decreases for the samples coated with the dopant film (figure 2, curves 2 and 3). The 1.563 eV peak can be attributed to the shallow neutral DAP recombination. The origin of the peak has not been clearly identified; probably it involves the shallow alkaline acceptor impurities Li_{Cd} or Na_{Cd} [2, 10, 13, 15, 20].

3.1.3. Analysis of the deep level emission region. The broad emission band between 1.4–1.5 eV has been known as a defect band, and has been typical of the deep-level PL spectra of Cl-compensated CdTe crystals [2, 4, 6, 9, 10, 13–18, 21]. The PL spectrum in the deep level region of the initial CdTe crystal has a fine structure, that appears as a row of equidistant peaks at 1.477, 1.456, 1.435 and 1.414 eV (figure 1, curve 1) whose energy separation is equal to the CdTe LO phonon energy of 21 meV. The emission at 1.477 eV can be identified as the zero-phonon line of the DAP recombination, where the electron of a shallow donor Cl_{Te} recombines with a hole trapped at the so-called A-centre ($V_{Cd}-Cl_{Te}$) [6, 17, 18]. However, the properties of the 1.477 eV band (its non-elementary nature, the low thermal quenching energy, the weak electron–phonon coupling, etc) [2] are explained by the

complexity of the defects, which possess several spatial forms. In particular, the band around 1.477 eV has been associated with the recombination of a free hole with an electron trapped on a deep donor (h, D^0) probably in the form $Cl_{Te}-Cl_{Te}$ [21], a combination of both a free electron–neutral acceptor (e, A^0) and DAP transitions [17], and the recombination of excitons bound on the donor defects as antistructural defects Te_{Cd} and interstitial atoms Te_i [15]. This band has also been attributed to the recombination on acceptor complex defects involving Cd vacancies and residual impurity atoms of I group metal [14] or In atoms in the form ($V_{Cd}-In_{Cd}$) [20]. The appearance of the line around 1.477 eV was observed in CdTe crystals after laser [13, 14] and mechanical [15, 20] treatments. It was shown [12–14] that the intensity of this line increased with the increase of the density of dislocations introduced under treatments of crystals. This was explained by the recombination of electrons and holes at extended defects.

The most intensive emission band in the deep level region of CdTe crystals is the broad feature centred at 1.456 eV (figure 1, curve 1). The band around 1.456 eV has been commonly observed in the broad impurity region of the CdTe PL spectra and attributed to the direct-donor valence recombination, (e, A^0) and DAP transitions [2, 9, 10, 17, 18, 20, 21]. Probably this band is due to several recombination mechanisms connected with different structure defects. The centre responsible for the emission around 1.456 eV has proven difficult to conclusively identify, but it is generally accepted that it involves a deep acceptor associated with complexes such as ($V_{Cd}-Cl_{Te}$) [2, 17, 18], ($V_{Cd}-2Cl_{Te}$) [2], ($V_{Cd}-In_{Cd}$) [2, 9, 10, 20] and ($V_{Cd}-Al_{Cd}$) [2] or Cu_{Cd} [21].

Direct laser irradiation of the CdTe crystal surface increases the PL intensity in the deep level region (figure 1, curve 2). This is due to the laser-stimulated creation and multiplication of structure defects as a result of fast (~ 20 ns) heating, melting and following solidification and cooling of the surface layer [11–14]. In the case of irradiation of the In-film coated samples, the profile of the PL spectrum in the deep level region is not appreciably changed (figure 1, curve 3). Probably in this case the In film prevents the intense disturbance of the crystalline structure of CdTe crystals. A small shift of the maxima of the deep-level emission bands towards the higher energies is observed (figure 1, curve 3). Considering that the main contribution to the PL deep level region comes from the DAP recombination, this shift ($h\nu \approx 2$ meV) can be caused by the Coulomb term. This is usually observed in DAP transitions of doped CdTe crystals [2, 9, 17, 21] and the shift can be described by the expression

$$h\nu = E_g - (E_A - E_D) + e^2/\varepsilon R + J(R), \quad (1)$$

where E_g is the bandgap, E_D and E_A are the donor and acceptor energy levels respectively, ε is the dielectric constant of the semiconductor, R is the mean distance between DAP components, and $J(R)$ is the exchange component which rapidly decreases with increasing R . The high-energy shift of the DAP emission is evidence of an increase in the Coulomb interaction energy due to a decrease in the mean distance between DAP components. This results from an increase in the donor concentration N_D

$$h\nu = e^2 N_D^{1/3} / \varepsilon. \quad (2)$$

This justifies the presumption that laser irradiation of the In-film coated samples provides In doping and activation of the impurity in the CdTe crystals.

As seen from the normalized PL spectra of CdTe crystals after irradiation, the greatest increase in the PL intensity in the deep level region takes place in the range 1.48–1.50 eV (figure 2, curve 2). An increase in the emission in this region is also observed for samples irradiated from the side coated with a dopant film (figure 2, curve 3). The appearance and increase of the band around 1.48 eV has been generally observed in CdTe crystals after laser [13, 14] or mechanical treatments [15, 20] when dislocation density increases. The emission around 1.48 eV has been associated with carrier recombination at extended defects of the dislocation loop type. From an increase in the emission intensity of the band around 1.48 eV (figure 2, curves 2 and 3), the proposition is induced that KrF excimer nanosecond laser irradiation results in the generation of dislocations in the surface region of CdTe crystals, particularly in the case of samples without depositing an In film. As a result, the intensity of the bound exciton PL decreases (figure 2, curves 2 and 3). Dislocations in CdTe act as sinks for acceptor-type defects [13–15], and this fact can be an additional reason for the decrease of the (A^0X) lines in the exciton region of the spectra of the laser-only irradiated samples (figures 1 and 2, curves 2).

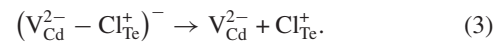
3.2. Analysis of laser implantation process of indium in CdTe crystals

Thus, laser irradiation of CdTe crystals with KrF excimer laser pulse resulted in the transformation of the PL spectra of both types of sample: crystals with and without depositing an In film. This was due to modification of the defect structure of the semiconductor including the formation of simple defects, dissociation of complexes and generation of dislocations. It was presumed that laser irradiation of the samples coated with a dopant film resulted in heavy doping and activation of the In impurity without damaging the crystalline structure of the surface layer. This was confirmed by the domination of the (D^0X) line and its high-energy shift, the emergence of the feature $(D^0X)_{in}$ in the bound exciton region and the high-energy shift of the peak positions of the DAP recombination zero phonon line and its LO replicas in the deep level region (figure 1, curve 3). The decrease in the PL intensity in the edge region indicated that the compensation effect in In-doped CdTe crystals did not occur. An increase in PL intensity in the free exciton range (figure 2, curve 3) and the appearance of the feature (X) in this range (figure 1, curve 3) were evidence of an increase in the structural perfection of the crystals. The additional evidence of the good crystalline quality of the doped CdTe crystals meant that phonon satellites in the PL deep level region were resolved [2].

The energy density of a nanosecond KrF excimer laser pulse, at which melting of a thin (of the order of the depth of laser radiation absorption) surface layer of CdTe crystals starts, has been estimated and determined experimentally as $\sim 50 \text{ mJ cm}^{-2}$ [12]. It has been shown that the best electrical parameters of In-doped CdTe crystals can be provided at the KrF laser pulse energy density of $\sim 90 \text{ mJ cm}^{-2}$ [4]. This value was used in the discussed PL experiments and it coincided

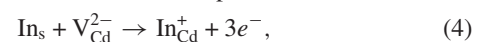
with the melting threshold of CdTe calculated taking into consideration the optical parameters of 30 nm indium film deposited on the CdTe surface.

Laser irradiation of CdTe crystals with high energy density resulted in fast melting and partial evaporation of a thin surface layer as well as intermixing and solubility of indium in a CdTe melt in the case of the samples coated with an In dopant film. The laser annealing of CdTe crystals involved several mechanisms of transformation of the defect structure and it can be interpreted as follows. Fast laser heating of the CdTe crystal surface region to a temperature above the melting point resulted in the dissociation of impurity atoms from complexes. Both $(V_{Cd}-Cl_{Te})$ and $(V_{Cd}-2Cl_{Te})$ complexes in Cl-compensated CdTe crystals were dissociated into Cd vacancies and Cl hydrogenic donors, and then V_{Cd} were partly filled by the nearest accidental impurities atoms or by In dopant atoms. Fast cooling of the molten surface region of the crystal to room temperature hindered the formation of defect complexes such as $(V_{Cd}-X)$, particularly $(V_{Cd}-Cl_{Te})$ and $(V_{Cd}-In_{Cd})$ in the case of In doping. Considering that $(V_{Cd}-Cl_{Te})$ is the major defect complex in Cl-compensated CdTe, the annealing behaviour of laser-only irradiated crystals can be briefly described by the following defect reaction:



As seen from equation (3), V_{Cd} increased after laser irradiation. An additional mechanism for increasing the concentration of cadmium vacancies can be laser-induced desorption of Cd atoms. It was established that irradiation of CdTe crystals with nanosecond laser pulses resulted in the removal of mainly Cd atoms and formed V_{Cd} in a thin surface layer [6, 13, 14]. Cd vacancies diffused into the bulk of the sample. In the laser-recrystallized surface region of CdTe crystals the oversaturated V_{Cd} solid solution was condensed, resulting in the formation of dislocation loops and complex defects [13, 14]. This was the reason for a decrease in the PL quantum yield in the bound exciton region and an increase in the PL band around 1.48 eV (figure 2, curves 2 and 3). In the case of irradiation of the In-film coated samples, laser-created Cd vacancies were partly filled out with In dopant atoms, in particular in the surface region of CdTe crystals. The intensity of the 1.48 eV band, connected with dislocations (figures 1 and 2, curves 3), increased less than that in the PL spectrum of laser-only irradiated crystals (figures 1 and 2, curves 2).

The mechanism of doping of CdTe with In impurity has been generally associated with the incorporation of In atoms at Cd vacancies [1, 2, 6–11]. In addition to process (3), another defect reaction took place, which provided In doping under irradiation of the In-film coated samples



where In_s is the indium dissolved in the surface layer of the crystal. Doping of semiconductors is provided by the following processes: segregation, diffusion and solubility of an impurity. These processes have been studied by many investigators with respect to In incorporation into CdTe, and different effective values of the coefficients of segregation k_{in} , diffusion D_{in} and solubility S_{in} have been obtained [2, 8]. Nevertheless, these parameters can be described by expressions in the following form

$$K_{in} = A_i \exp(-B_i/kT), \quad (5)$$

where K_{in} is the respective coefficient (k_{in} , D_{in} or S_{in}), k is the Boltzmann constant, and A_i and B_i are the different numerical coefficients for the indicated processes respectively. As seen from equation (5) the coefficients of segregation, diffusion and solubility increase with increasing temperature. Moreover, these coefficients can greatly exceed the equilibrium values under laser annealing conditions because of the action of laser-induced stress and shock waves [11–14]. These coefficients and the In donor electronic state are strongly affected by the presence of intrinsic defects, particularly V_{Cd} [2]. An increase in V_{Cd} results in a drastic rise of velocities of the segregation and diffusion of In atoms in CdTe [2, 8].

The discussed changes in the PL spectra have supported the assumption that irradiation of CdTe crystals with nanosecond KrF excimer laser pulses resulted in the dissociation of defect complexes ($V_{Cd}-Cl_{Te}$) and formation of V_{Cd} as well as laser-stimulated incorporation of In atoms and increase in the In_{Cd} donor concentration in the case of samples with a deposited In film. This implied that the electrical properties changed from p -like high resistivity to n -type low resistivity [4, 5]. Using KrF excimer laser annealing as a doping technique for CdTe crystals, it was shown that the electron concentration of $\sim 10^{19} \text{ cm}^{-3}$ in the near-surface region was achieved [5]. The thickness of the indium diffused thin layer was estimated as $\sim 100 \text{ nm}$ [5].

Thus, the laser-stimulated doping of CdTe crystals coated with an In film was realized in the following stages: (1) melting of both the In coating film and thin surface CdTe layer and mixing of the liquid phases of In and CdTe; (2) laser-stimulated solubility of liquid In in the molten surface layer of the CdTe crystal; (3) formation of a large number of Cd vacancies as a result of the dissociation of (Cd–X) complexes and laser desorption of Cd from the crystal lattice; (4) laser-stimulated diffusion of In atoms at Cd vacancies; (5) fast freezing of a large number of the point donor defects In_{Cd} without forming the compensating acceptor complexes ($V_{Cd}-In_{Cd}$). However, in order to make a strong conclusion about dominating processes during laser-stimulated In doping of CdTe crystals it is necessary to carry out additional investigations.

Thus, it can be concluded that using irradiation of CdTe crystals coated with an In dopant film by nanosecond KrF laser pulses, it is possible to suppress the self-compensation mechanism, to introduce and activate the In impurity of high concentration in a thin layer of the crystals without damaging of the structure and properties of the underlying region. Hence, laser procedure shows promise of producing p - n junctions in CdTe crystals for the design of high-energy nuclear radiation detectors.

Acknowledgment

One of the authors (VAG) appreciates the long-term fellowship provided by the Japan Society for the Promotion of Science in order to visit the Research Institute of Electronics of the Shizuoka University.

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