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Second metastable *DX* center in CdF_2:Ga crystals

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Two metastable centers have been detected in semiconducting CdF_2 crystals, nominally doped only with Ga. One of them has very high metastability temperature, about 250 K, and it has been previously assigned to Ga dopant. The second one, with much lower metastability temperature close to 80 K, has very similar properties to In dopant in CdF_2 host. Absorption, light-induced gratings, and secondary-ion-mass spectroscopy studies show that In ions are present in some CdF_2 crystals nominally doped only with Ga. Therefore we associate this second metastable center in CdF_2 with indium ions. It is also shown that in crystals without In contamination only one metastable Ga center occurs.

Metastable centers in semiconductors recently attracted a lot of attention due to the possibility of application in holographic recording, providing advantages over the classical photorefractive materials such as $LiNbO_3$ and other oxides.[1,2] Various compounds and different dopants have been studied for this application, among them also ionic semiconducting cadmium fluoride crystals doped with indium[3] and gallium.[4–6] The main obstacle for practical application of metastable centers for permanent holographic recording is usually very low metastability temperature, usually below 150 K. CdF_2:Ga is an important exemption here since its metastability temperature is close to 250 K,[4–6] and it is the highest known for metastable centers in semiconductors. Interestingly, properties of metastable dopants (In and Ga) in this ionic material resemble very much the properties of well-known *DX* centers in III-V compounds. For example, metastability in CdF_2 doped with In or with Ga is associated also with noncentrosymmetrical large lattice relaxation[7–9] and population of D^- states displaced from typical cation-substitutional position along [100] axis.[9,10]

Recently has been reported the existence of a second metastable *DX* state in some CdF_2:Ga crystals,[5] which is present simultaneously with the already known state. The authors of Ref. 5 have found that the annealing of the CdF_2:Ga crystals at a temperature of 77 K, that have been previously bleached by light at 5 K, leads to the appearance of an additional absorption band, which they have assigned to a different metastable state, associated with Ga dopant. This state has metastability temperature in the 100-K range, the peak of the photoionization absorption around 3 eV, and the capture energy barrier close to 0.1 eV. These values for the already known ''typical'' metastable state in CdF_2:Ga are equal to 250 K, 4 eV, and about 1 eV, respectively.[4–6] It has been also shown that, most probably, this metastable state has negative Hubbard correlation energy (negative U properties), i.e., it is a D^- state.[5]

The second metastable center in some CdF_2:Ga crystals has been observed also by us in the holographic experiments.[11] Existence of the second metastable state or center, associated with the same Ga dopant, could be of importance since it should inherently affect the process of holographic recording in those crystals, especially at low temperatures. It would also affect the other properties of the material, as, for example, its electrical transport behavior.

The properties of the second metastable state in CdF_2:Ga are surprisingly similar to properties of indium metastable center in CdF_2.[3,12] In fact, accidental indium contamination should result in very much similar effects as described in Ref. 5 since the phototransformation proceeds through delocalized effective mass states. In order to check this hypothesis we performed some additional tests of properties of this second state. Results of absorption, light-induced gratings, and secondary-ion-mass spectroscopy (SIMS) studies of three CdF_2:Ga samples with metastable centers are reported in this communication. The samples have been grown by Bridgman method. CdF_2 raw material used for growing crystals was purified by several passes of melting zone before crystallization. Therefore the undoped CdF_2 crystals prepared from such a material are pure and transparent. Sample 1 is a typical CdF_2 crystal intentionally doped with Ga, having brownish color after annealing at temperature of 400 °C in reducing hydrogen atmosphere for removing charge-compensating interstitial fluorine ions in order to convert the sample into semiconducting state. Sample 1A comes from the same crystal as the sample 1, but it has lower concentration of shallow donors (about three times) than the sample 1 due to annealing at hydrogen at lower temperature (300 °C). This sample has very light brownish color. Sample 2, also doped with Ga, has a slightly green-bluish tint after similar thermal treatment.

The In and Ga metastable dopants in CdF_2 have relatively broad absorption bands in the visible and UV part of the

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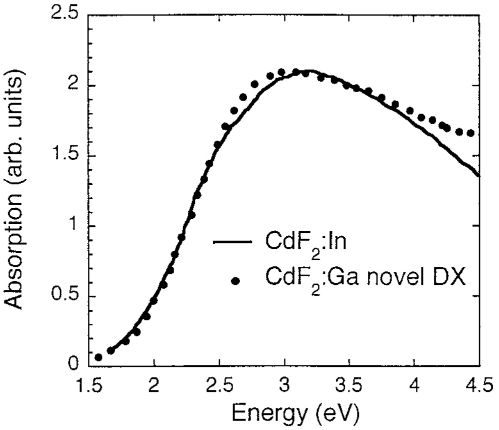

FIG. 1. Comparizon of the differential absorption (photoionization spectrum of deep state of indium donor) of CdF_2:In (Ref. 12) and second *DX* center absorption in CdF_2:Ga (Ref. 5) crystals.

spectrum, associated with the photoionization of the deep states of metastable centers.[3,4,6,12] The crystals cooled in darkness undergo phototransformation at low temperature under the influence of illumination with wavelengths coincident with the photoionization transitions of the deep states.[3,4,6,12] The absorption in the visible and UV decreases and the new absorption bands in the infrared appear at expense of the former ones. This new absorption in the infrared is associated with photoionization of shallow donor levels, populated in the process of phototransformation. The effect is metastable at low temperatures since the energy barrier prevents returning of electrons to the deep, localized states. The number of phototransformed centers depends on the total number of absorbed photons. Subtracting the absorption of the crystal after phototransformation from the absorption before the illumination the photoionization spectra of the deep states (differential absorption) of metastable dopants are obtained.

The low-temperature differential absorption spectrum of the additional *DX* state of Ga reported in Ref. 5 is, in fact, identical (see Fig. 1) with that of the deep state photoionization absorption of the bistable In donor in CdF_2 crystals.[12] It means that the optical ionization energy of this state is identical with that of the deep In donor.

The differential absorption spectra of samples 1 and 2 after illumination at 5 K by the broad-band light from a halogen lamp are shown in Fig. 2. The spectrum of sample 2 has a maximum at energy of 4 eV (line b in Fig. 2). It is a typical spectrum of photoionization of a deep state of Ga metastable dopant in CdF_2 crystal.[4,6] The spectrum of sample 1 (line a in Fig. 2) after total phototransformation is much more extended towards infrared in comparizon with the spectrum of sample 2 with a peak energy at about 3 eV. Actually, absorption spectrum of this sample, doped intentionally only with Ga, is rather similar to the absorption spectrum of CdF_2:In, although the UV part of the spectrum of sample 1 is associated with absorption of deep state of Ga. This is proved by partial phototransformation of the deep states in sample 1 with the light from a halogen lamp. Due to higher quantum efficiency of the centers with the absorption maximum at higher energy, the centers with the peak energy of 4 eV undergo faster phototransformation than the centers with peak energy of 3 eV. Therefore the differential absorption after partial phototransformation is shifted towards the spectrum of centers with peak energy at 4 eV (see line c in Fig. 2).

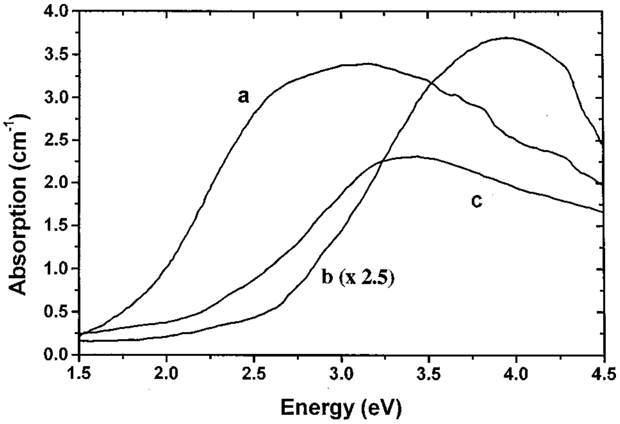

FIG. 2. Differential absorption spectra of CdF_2:Ga crystals: (a) sample 1; (b) sample 2 (multiplied by 2.5); (c) sample 1 after partial phototransformation.

The results of absorption measurements of sample 1A, which are almost the same as in sample 1, but it contains less shallow donors, are presented in Fig. 3. In this sample the differential absorption after phototransformation (see Fig. 3, line a) is dominated by the absorption of the center with a peak at 4 eV, although the contribution of the center with the peak at 3 eV is clearly visible. The differential absorption spectrum of this sample after annealing the previously bleached crystal up to 80 K and subsequent slow cooling to about 10 K (the difference between the absorption spectra recorded after annealing and recorded after bleaching, i.e., before annealing at 80 K) is shown also in Fig. 3 (line b). The spectrum b has a maximum at about 3 eV, and it is very similar to the spectrum of indium metastable dopant and to the spectrum measured in the same procedure in Ref. 5. In contrast to that, this procedure performed on sample 2 does not produce any different spectral feature other than that observed due to the phototransformation process at 5 K.

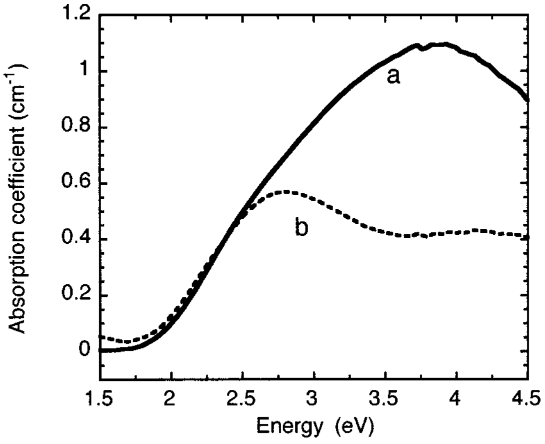

FIG. 3. Differential absorption spectra of CdF_2:Ga crystals, sample 1A: (a) spectrum after phototransformation at 10 K; (b) spectrum after annealing the crystal up to 80 K and subsequent slow cooling to 10 K.

The relative amount of absorption with the peak at 3 and 4 eV depends on the sample and also on the other factors. The spectrum of sample 2 has only the absorption with maximum at 4 eV. In sample 1 absorption with maximum at 3 eV is prevailing and absorption peaked at 4 eV dominates the spectrum in the sample reported in Ref. 5 at low temperatures. Due to two-electron character of the deep states of metastable dopants in CdF_2 (negative Hubbard correlation energy) the deeper centers (i.e., associated with the peak at 4 eV) can absorb all electrons which are released from the shallower ones if the concentration of shallower centers (i.e., associated with the peak at 3 eV) is equal to or lower than the deeper ones. This would result in the lack of the absorption of the shallower centers in the differential absorption spectrum although this spectrum will appear after the annealing procedure, described above. Thus the results of the differential absorption measurements can be the same if the second metastable state is associated with the same center and if this state is related to a different one. On the other hand, the faster cooling rate and/or relatively small concentration of bistable dopants and low mobility of carriers in CdF_2 crystals may prevent of transfer of all electrons to the deeper centers. Thus the shallower centers can be sometimes also visible in the differential absorption without annealing procedure. These are the reasons for slightly different results of the shapes of differential absorption (measured before annealing the crystals at 80 K) observed in samples, measured in Ref. 5 and in this work. Therefore the results of the differential absorption measurements alone cannot distinguish unequivocally between cases whether the second metastable state is associated with the same or with a different center. Very broad overlapped absorption bands associated with both states additionally make this task even more difficult.

The different complex polarizabilities of deep and shallow states of the metastable centers allow us to use them for the hologram recording. The similarity of the energy barrier and also capture cross section of the second Ga state to In center also results in the possibility of cw recording of holographic gratings at similar temperatures in indium doped crystals and the samples 1 and 1A. The cw light-induced gratings were recorded in the crystals with use of a 488-nm argon-ion laser line. A helium-neon laser was used for grating detection. In Ga doped sample 1 two maxima in the temperature dependence of the diffraction efficiency are observed, shown in Fig. 4. The same behavior exhibits the sample 1A (but with lower scattering efficiency due to smaller number of metastable centers in this crystal as compared with sample 1). A broad low-temperature peak (100 K temperature range) is at the same temperature as that observed in In doped crystals. The origin of the peaks in this experiment is associated with the destruction mechanism of the light-induced gratings. At higher temperatures the gratings are destroyed by the thermal recovery of electrons from the excited states to the deep ones. At low temperatures the permanent phototransformation of the deep states to the shallow ones in the full crystal volume prevails mainly due to incoherent illumination (light scattering from the optical elements of the optical setup, sample surfaces, etc.) or due to nonequal intensity of the beams that create the grating. This destroys the cw light-induced gratings at low temperatures. The peak of the scattering efficiency occurs when the rates of both processes are equal. The temperature at which the peak occurs depends on the intensities of the writing beams, concentration of active centers and a degree of incoherent background, but a major factor is the energy of the barrier separating the deep and shallow states of the metastable center. Therefore cw light-induced grating measurements can be used as a tool for identification of metastable centers (for a detailed discussion of the mechanism of writing cw holographic gratings in crystals containing metastable centers, see, for example, Ref. 3).

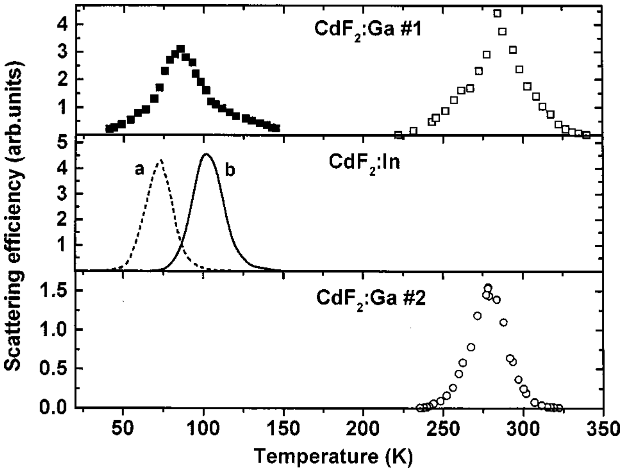

FIG. 4. Dependence of the diffraction efficiency of the holographic grating on temperature in CdF_2:In (two samples with different In concentrations: 0.1 mol % (a) and 0.5 mol % (b) and CdF_2:Ga crystals (samples 1 and 2).

Temperature proximity of the holographic signal associated with the second state in CdF_2:Ga (samples 1 and 1A) and in indium doped crystals indicates that also barrier causing the metastability is practically the same. Detailed analysis of temperature erasure of the photoinduced holographic grating indicates that also the values of the capture cross sections are very close. In contrast to that there is no light-induced grating signal in 100 K temperature range in sample 2, although there is a signal at the 300-K temperature range, as it is in samples 1 and 1A at the same temperature. The signal at the 300-K temperature range has been associated with ''typical'' Ga metastable dopant in CdF_2.[4,6]

Our observations, presented above, made us suspect that some of the CdF_2 samples (as for example, samples 1 and 1A, but *not* sample 2), although doped intentionally only with gallium, may also contain nonintentional indium ions. In order to check this we performed chemical analysis of both our samples using secondary-ion-mass spectroscopy (SIMS) technique. The CAMECA IMS 6*f* equipment has been used for the SIMS measurements.

Indium is relatively easy detectable in mass spectroscopy due to ^{115}In isotope that has abundance of 95.7%. Cadmium, adjacent to indium in the periodic table, has several isotopes: ^{106}Cd, ^{108}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, and ^{116}Cd. Therefore ^{115}In signal is in between the signals of two Cd isotopes: ^{114}Cd and ^{116}Cd. The results of SIMS measurements of our samples, presented in Table I, show that sample 1 contains about two orders of magnitude more indium than sample 2. It is possible to estimate the concentrations of In in the samples using abundance of all cadmium isotopes in our

TABLE I. The SIMS signals for Cd, In, and Ga various isotopes for CdF_2:Ga samples 1 and 2.

Isotope	Natural abundance %	SIMS Signal sample 1 (10^7 counts/s)	SIMS Signal sample 2 (10^7 counts/s)
^{69}Ga	60.11	1.0×10^{-2}	3.2×10^{-3}
^{71}Ga	39.89	7.4×10^{-3}	1.9×10^{-3}
^{106}Cd	1.25	0.4	0.4
^{108}Cd	0.89	0.3	0.3
^{110}Cd	12.51	3.9	4.0
^{111}Cd	12.81	4.0	3.9
^{112}Cd	24.13	7.5	7.0
^{113}Cd	12.22	4.0	3.5
^{114}Cd	28.72	8.9	8.6
^{116}Cd	7.47	2.3	2.1
^{115}In	95.7	8.1×10^{-4}	9×10^{-6}

samples as a reference, assuming that in the presence of highly electronegative F atoms ionization probability of both Ga^+ and In^+ secondary ions is close to unity. It is equal to approximately $6\times10^{17}\,cm^{-3}$ and $7.1\times10^{15}\,cm^{-3}$ in sample 1 and in sample 2, respectively.

In contrast to that, SIMS measurements show that the concentration of Ga is approximately only about three times higher in sample 1 than in sample 2. In this case the total signal from Cd ions cannot be used as a reference for estimation of the concentration of Ga in the sample. From the absorption measurements in the infrared we estimate the number of phototransformed shallow donors as equal to $2.9\times10^{17}\,cm^{-3}$, $1\times10^{17}\,cm^{-3}$, and $1.4\times10^{17}\,cm^{-3}$ in samples 1, 1A, and 2, respectively. These shallow donors are associated with In and Ga ions in samples 1 and 1A and only Ga ions in sample 2. The final number of In and Ga metastable centers (and shallow donor associated with them) does not have to be proportional to the total concentrations of these dopants and it is usually lower than these since it depends also on the conditions of annealing in reducing atmosphere, that removes compensating F^- ions, and also other factors.[13] This can be seen also in the results of absorption measurements of our samples. The absorption measurements show that the concentration of In donors in sample 1 is most probably higher than concentration of Ga donors. The concentration of In metastable centers in sample 1A is about a half of concentration of Ga-related metastable centers. The concentration of In in sample 2 is almost two orders of magnitude lower than in sample 1, below the detection limit of absorption or light-induced grating experiments.

Indium contamination could be a result of using not pure enough materials for synthesis of CdF_2, or, what is even more possible, from contaminated GaF_3 used for doping of the crystals, since CdF_2 raw material was carefully purified before crystallization. It is well known that Ga contains very often some In contamination. Doping of CdF_2 with gallium is difficult for two reasons. Solubility of Ga in CdF_2 is low due to quite different ionic radius of Ga (0.78 Å)[14] as compared with ionic radius of Cd (1.175 Å),[14] which Ga substitutes in CdF_2 host (ionic radius of In is equal to 1.06 Å).[14] Based on differences of ionic radii, Ryskin and Fedorov have estimated that the theoretical maximum level of doping of CdF_2 with In is about 17.5 mol %, in contrast to only 1.6×10^{-2} mol % for Ga.[14] Therefore In and Ga do not dissolve in CdF_2 with the same proportion as they occur in the material used for doping. Thus the process of certain ''enrichment'' of CdF_2 with In as compared with doping with Ga occurs if GaF_3 contains some InF_3 contamination. The second problem is related to low sublimation temperature of GaF_3 (about 800 °C), which causes evaporation of GaF_3 from substrate materials since the melting point of CdF_2 is equal to 1050 °C. Doping with InF_3 does not present such a problem. These are the most probable reasons for increased In nonintentional doping of CdF_2. It may also happen that this process is quite accidental and may change from sample to sample if different materials (for example, from different sources) are used for crystal doping. Although precautions were taken in order to use the purest materials for every crystal-growth process, the most probably GaF_3 substrate used for doping samples 1 and 1A, contained some nonintentional InF_3.

In summary, we show that a possible source of the second metastable *DX* state in CdF_2:Ga crystal could be indium contamination of substrate materials used for crystal growth. Therefore it is possible to obtain the CdF_2:Ga crystals without the second metastable state. This might be more difficult to achieve if the second metastable state is associated with Ga dopant.

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