

PHOTOSTRICTION OF CdF<sub>2</sub>:In CRYSTALSA. SUCHOCKI, J. RAULUSZKIEWICZ, J.M. LANGER  
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Lattice relaxation accompanying phototransformation of In bistable centers from the ground, deep state to the shallow state in CdF<sub>2</sub> crystal has been measured with the use of scanning tunnelling microscope. It is shown that relatively small macroscopic changes of the crystal length in the order of  $1.8 \times 10^{-6}$  accompany the phototransformation of In ions. Lattice expansion upon the influence of population of shallow donor levels in CdF<sub>2</sub> explains the observed small changes of lattice constant during the process.

PACS numbers: 61.16.Ch, 61.72.Hh, 74.62.Dh

The nature of lattice relaxation related to bistability of dopant centers in semiconductors has attracted a lot of attention for many years [1, 2]. In impurity in CdF<sub>2</sub> crystals was among the first characterized bistable centers in semiconductors. Its ground state is localized with a thermal ionization energy about six times smaller than the optical ionization energy (about 2 eV) [3, 4]. The hydrogenic effective mass bound state of the In impurity (about 110 meV deep) is separated by a large vibronic barrier from the ground state. Photoionization of the two impurity states occurs in different spectral regions. At room temperature two strongly asymmetric bands are seen. The absorption band in the visible range (VIS) is caused by the photoionization of the localized In ground state, while the infrared (IR) band, peaked at  $\lambda \approx 8 \mu\text{m}$ , is due to photoionization of a hydrogenic, extended state of the impurity. At low temperatures the IR band disappears, unless the crystal is first illuminated by light resonant with the VIS photoionization band. Such illumination causes metastable bleaching of the VIS absorption and simultaneous appearance of the IR band. The localized ground state is only a fraction of an eV thermally deeper than the hydrogenic state, but it exhibits an enormous 2 eV, Stokes shift [3, 4]. The shift is caused by large lattice relaxation (LLR) around the impurity during photoionization. It has been postulated that the LLR in In impurity is caused by the local lattice collapse upon the photoionization of the localized In<sup>2+</sup> deep state. This intuitive model has been recently supported by theoretical studies of In and Ga impurities in CdF<sub>2</sub> [5]. The photoinduced local lattice collapse should affect the macroscopic dimensions of the crystal and detection of such changes may provide a direct proof of the existence of the LLR in CdF<sub>2</sub>:In and

thus its role in the bistability of this defect. This communication reports on the first successful attempt to detect such changes by using a custom-made scanning tunnelling microscope as a dilatometer.

The  $\text{CdF}_2:\text{In}$  crystal with concentration of In donors of about  $2.3 \times 10^{18} \text{ cm}^{-3}$  (determined by the independent SQUID measurements [6]) has been used in the experiment. The sample of dimensions of  $5 \times 3 \times 2 \text{ mm}^3$  was not crystallographically oriented.

Traditional methods of measuring the dilatation as X-ray diffractometry, capacitance dilatometer and also stress sensors turned out to be inadequate for our measurements. The experimentally observed changes of crystal dimensions were smaller than expected. Therefore finally a custom-made scanning tunnelling microscope (STM), capable of working at liquid helium was used as dilatometer. The STM was working in a constant current regime with very minute lateral scanning — only about  $2 \text{ \AA}$ , in order to assure a proper operation of the device. The samples were partially covered by an evaporated gold layer in order to assure good electrical conductivity necessary for the proper operation of STM. The device was immersed in liquid helium for measurements at  $4.2 \text{ K}$  temperature. The samples were cooled in darkness and afterwards illuminated uniformly through an optical fiber by the light from the argon-ion laser (multiline: mainly  $488 \text{ nm}$  and  $514.5 \text{ nm}$ , coinciding with the absorption of the deep donor state). The vertical movements of the sample surface, induced by the illumination, scanned by the STM tip, were reflected in the voltage signal and recorded by a computer. The STM has been calibrated with the use of the known pattern.

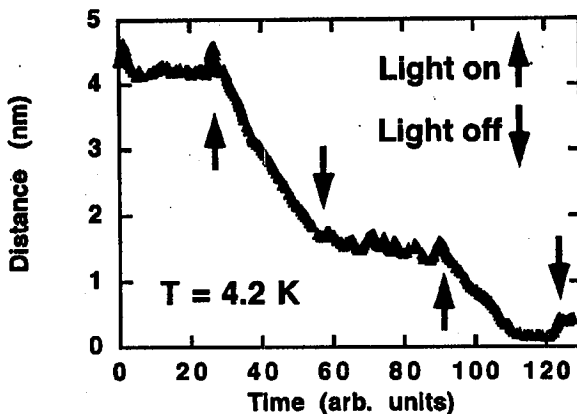


Fig. 1. Photostriction of the  $\text{CdF}_2:\text{In}$  crystal upon illumination by argon-ion laser light at  $4.2 \text{ K}$ , measured by STM.

Figure 1 presents one of the measurements runs of the STM experiment carried out liquid helium temperature, illustrating metastable character of the photoinduced changes. The crystal contracts when illuminated by the light. When the light is switched off the crystal size remains unchanged. After prolonged illumination the saturation occurs when the crystal contracts vertically by about

9 nm ( $\Delta l/l = 1.8 \times 10^{-6}$ ). Further illumination does not cause any changes of the crystal length.

Measurements of another  $\text{CdF}_2:\text{In}$  sample with a much smaller concentration of bistable In centers reveals a much weaker effect. The crystal contracts by about 1 nm, which is close to the resolution of our system.

The contribution of the local lattice relaxation ( $\Delta a/a_0$ ) to the macroscopic changes of the crystal dimension ( $\Delta l/l$ ) can be expressed as

$$(\Delta l/l)_{\text{size}} = (\Delta a/a_0)(N_{\text{In}}^*/N_{\text{cation}}), \quad (1)$$

where  $N_{\text{In}}^*/N_{\text{cation}}$  is the ratio of concentration of ionized centers to the total concentration of cations. Our experiment gives as a result of relative shortening the value of  $\Delta l/l = 1.8 \times 10^{-6}$ . If concentration of phototransformable indium centers is equal to  $2.3 \times 10^{18} \text{ cm}^{-3}$ , then the effective local lattice relaxation around ionized In ions should be about 2.3% only. This value is about 3 times smaller than that obtained either from early empirical estimation of Langer et al. [4] or from the recent calculations made by Cai and Song [5]. According to their results the symmetric lattice relaxation around the In equals 7.9%.

The situation is even worse, since the recent results indicate that In is in fact a negative- $U$  system [6, 7]. Then the local lattice relaxation for the 2-electron ground state would be 4.6%. The difference in the ionic radii between  $\text{In}^{1+}$  and  $\text{In}^{3+}$  is six times larger than between  $\text{In}^{2+}$  and  $\text{In}^{3+}$ , hence a symmetric relaxation in this case is most unlikely.

A proper description of the total lattice dimension must however include an opposite contribution coming from a local weakening of the local bonds after photopopulation of the hydrogen-like In metastable states. The effects is roughly the same as the lattice expansion by the presence of the free carriers [8–11]. For  $n$ -type of semiconductors the effects is described by the formula

$$(\Delta l/l)_{\text{el}} = (-D_n/3B)n, \quad (2)$$

where  $D_n$  is the deformation potential,  $B$  is the bulk modulus and  $n$  is the concentration of electrons. In our case  $n$  should be replaced by the concentration of shallow donors as the concentration of free electrons in  $\text{CdF}_2$  at low temperatures is negligible. It is safe to assume that the deformation potential of the shallow donor level in  $\text{CdF}_2$  is the same as the deformation potential of the conduction band minimum. Thus the population of shallow donor level leads to the electronic contribution to global lattice dilatation of the  $\text{CdF}_2$  through the electron-phonon coupling, described by the deformation potential.

Unfortunately, we are not aware of any accurate estimation of the deformation potential of the bottom of the conduction band in  $\text{CdF}_2$ . It is actually a very complicated problem both theoretically and experimentally [10–12], and very often we have only very crude estimation of it. Therefore we decided to calculate the deformation potential for  $\text{CdF}_2$  from our data of lattice dilatation, assuming that total dilatation of the crystal  $(\Delta l/l)_{\text{tot}}$  is a sum of size  $(\Delta l/l)_{\text{size}}$  and electronic  $(\Delta l/l)_{\text{el}}$  effects

$$(\Delta l/l)_{\text{tot}} = (\Delta l/l)_{\text{size}} + (\Delta l/l)_{\text{el}}. \quad (3)$$

The first term has been estimated from Eq. (1) and substituting  $\Delta a/a_0$  either from the Cai and Song theory for  $U > 0$  or from the difference in ionic radii for  $U < 0$  model. Substituting the known values of the elastic constants of  $\text{CdF}_2$  [13], we get for the value of deformation potential of the shallow donor level in  $\text{CdF}_2$  values of  $D_n^{U>0} = -4.6$  eV and of  $D_n^{U<0} = -10$  eV, depending on the adopted model of the deep-shallow donor phototransformation, "classical" ( $\text{In}^{2+} \rightarrow \text{In}^{3+}$ ) or "negative- $U$ " ( $\text{In}^{1+} \rightarrow 2\text{In}^{3+}$ ), respectively.

A more accurate procedure should take into account the extended character of the local lattice dilatation (not only the nearest neighbor movement, especially when the defect becomes charged, as it is in the case there).

This work was supported in part by the contract No. 8 T11B 017 09 from the Committee for Scientific Research. We would like to acknowledge comments by J. Adamowski, M. Baj and A.M. Stoneham on the problem.

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