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Evidence for metastable behavior of Ga-doped CdTe

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In this paper, we report for the first time on persistent photoeffects in gallium doped CdTe. Persistent photoconductivity and photoinduced persistent absorption were observed at 77 K. Both effects quenched above 120 K. The photoeffects have been attributed to the metastable behavior of gallium in CdTe.

Keywords: semiconductors, semiconducting compounds, CdTe, DX centers, persistent photoeffects.

1. Introduction

CdTe based mixed crystals have been widely applied in semiconducting devices with gallium commonly used as the *n*-type dopant. However the operation of the devices is seriously affected by the deep–shallow metastability of gallium. According to the large lattice relaxation model of DX centers introduced by Park and Chadi, gallium dopant in CdTe and CdTe based $Cd_{1-x}Mn_xTe$ semiconducting alloys forms DX centers [1]. The experimental findings concerning the material are comparable to the well-known DX behavior of, *e.g.*, Si in $Al_xGa_{1-x}As$ [2]. When the atom of Ga-dopant replaces Cd in the lattice it behaves as a shallow donor. At low temperature, after capturing an electron the dopant passes to the interstitial position. Along with this new position, another deep, localized state of the DX center appears. Thus, the different charge states of the DX center are related to the different locations in the crystal lattice. The transition from one state to another is accompanied by a very significant lattice reconfiguration, the so-called large lattice relaxation. At low temperature, the photoionization of the DX center accompanies the deep–shallow transition and return to the "dark" ground state is not possible unless the system possesses enough energy. This energy is called the capture barrier.

The photoionization of DX centers is accompanied by an increase of excess carrier density in the conduction band followed by the conductivity rise. The presence of the barrier for capture prevents electrons from returning to the DX center and the higher value of conductivity persists even after termination of light excitation. This phenomenon is called persistent photoconductivity. Persistent photoconductivity has

been commonly recognized as a finger print for the presence of metastable defects in the materials under study.

Another effect related to the existence of metastable defects is the persistent photoinduced change of the absorption coefficient. The photoinduced absorption related to the materials with DX centers has been reported only in a few papers [3–6], the most significant effect being found in CdF_2 [4] and AlSb [6].

One of the crucial parameters for the operation of semiconducting devices such as photodiodes, lasers, *etc*., is their time constant. The devices are expected to be very fast with the time constants on the order of nanoseconds and less. Obviously, the presence of metastable defects strongly affects this parameter, making the devices useless. Therefore, there is a strong need to study the properties of the defects responsible for the degradation of the devices.

So far the DX behavior of gallium was confirmed only for gallium doped $Cd_{1-x}Mn_xTe$ [7–10], mostly by persistent photoconductivity and photocapacitance. In this paper, we report for the first time on persistent photoeffects in gallium doped CdTe. Persistent photoconductivity and photoinduced persistent absorption were observed at 77 K. Thus, the presence of DX centers in the material has been proved.

2. Experiment

2.1. Samples and experimental methods

Experiments were performed on the samples of gallium doped CdTe grown by the Bridgman method. Prior to the measurements the samples were annealed at 600 °C in cadmium vapor for one week to reduce the level of compensation in the material due to cadmium vacancies. Slices of the material were prepared by mechanical polishing followed by the chemical etching in 2% Br_2 in methanol solution to remove the remaining damaged surface layer. The Au-CdTe Schottky diodes were realised by evaporation of gold in the vacuum of 10^{-6} torr on the chemically prepared surface and were situated on the front side of the samples. Ohmic contacts were produced by soldering indium onto the fresh backside surface.

For the conductivity measurements a four point method was applied. A Keithley constant current source was used and the voltage drop across the sample measured at constant current was equal to 10 μA. The temporal kinetics of conductivity was measured at 77 K. The samples were initially cooled down in the darkness to the low temperature to achieve the ground state of the DX centers. The conductivity transients were recorded in the darkness, after illumination, until the conductivity saturated and until the equilibrium state was reached. A shutter was used to turn the light on/off. The monochromatic light beam coming out of the monochromator was focused with the help of a fiber optic onto the sample, mounted in the sample holder immersed directly in the liquid nitrogen. The conductivity transients were recorded by means of multimeters and a computer. The monochromatic light of photon energy equal to 1.24 eV was chosen.

Absorption measurements were made at room temperature and at 77 K. Persistent photoinduced absorption was investigated at 77 K. Persistent photoinduced absorption was observed for the 77 K measurements run for 10 min after terminating a 30 min halogen light excitation.

2.2. Characterization of the samples

The results of optical measurements run at room temperature and at 77 K for the samples under study are given in Fig. 1. In the figure, the square of the absorption coefficient α^2 as a function of photon energy $h\nu$ is shown. CdTe is a direct band gap material, therefore the value of energy gap can be determined from the linear part of the $\alpha^2 = f(h\nu)$ plot. The values of energy gap obtained from the linear fit of the solid line slopes in Fig. 1 are equal to 1.38 eV at 300 K and 1.45 eV at 77 K. Both, of the obtained

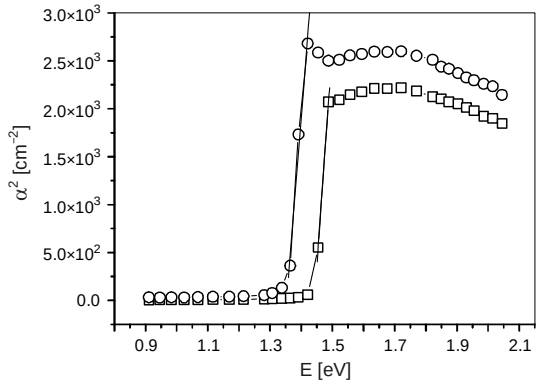

Fig. 1. The square of the absorption coefficient α^2 as a function of photon energy $h\nu$ for CdTe:Ga at room temperature (open circles) and at 77 K (open squares). The solid lines are the best square linear fits to the experimental data.

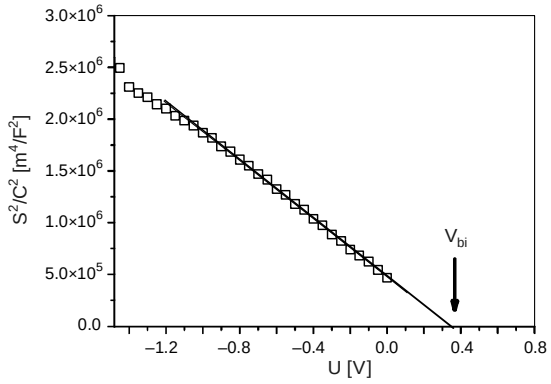

Fig. 2. Capacitance–voltage characteristic for CdTe:Ga measured at 300 K. The solid line is the best square linear fit to the experimental data. The fit yields the value of built in voltage equal to 0.33 eV and donor net concentration equal to 10^{17} cm^{-3}.

values of energy gap and linear behavior of the dependence show good quality of the CdTe samples [11].

The donor net concentration in the samples was estimated from the capacitance–voltage measurement. A sample capacitance–voltage characteristic taken at 300 K is shown in Fig. 2. The solid line is the least square linear fit to the experimental data. The room temperature net donor concentration found from the fit is equal to 10^{17} cm^{-3}.

3. Results and discussion

In the gallium doped CdTe under study, persistent photoeffects were observed at low temperatures. A typical PPC behavior is presented in Fig. 3. In the figure, a sample temporal kinetic of photoconductivity measured at 77 K for photon energy equal to 1.24 eV is shown. Both the conductivity build-up after turning on the light and its

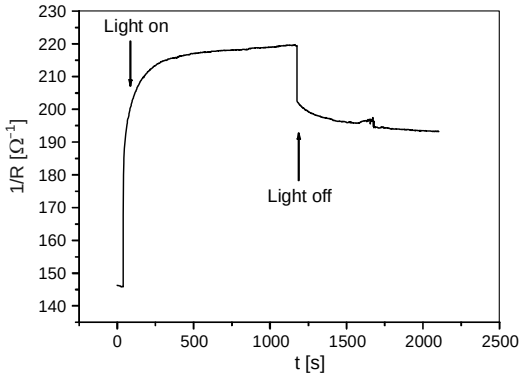

Fig. 3. Conductivity build-up and decay for CdTe:Ga at 77 K. The sample was illuminated with photons of energy equal to 1.24 eV.

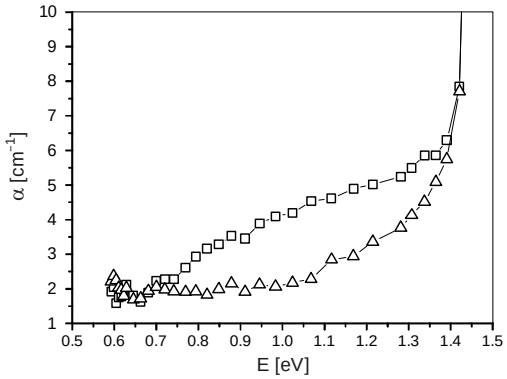

Fig. 4. Optical absorption for CdTe:Ga at 77 K (open triangles) and after preliminary 30 min illumination with halogen light (open squares). The latter measurements were performed 10 min after termination of light.

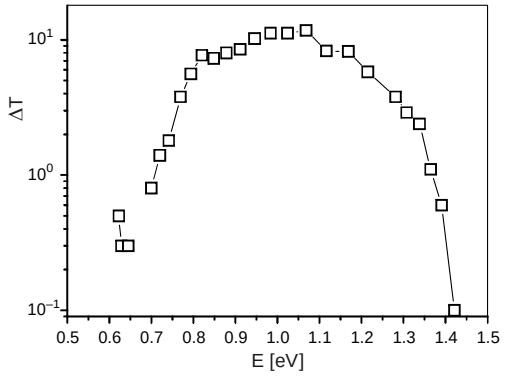

Fig. 5. The difference ΔT between the transmission spectra measured in darkness and after illumination at 77 K, related to the data shown in Fig. 4.

decay after turning off the light exhibit slow kinetics. After light termination the conductivity of the sample does not return to the value it had before illumination. The higher value persists for a long time after termination of light.

A spectrum of photoinduced absorption is shown in Fig. 4. Illumination at temperatures less than 120 K produced an increase in the optical absorption over a spectral range extending from about 0.62–1.4 eV. In Figure 5, the difference between the dark and illuminated transmission spectra corresponding to those given in Fig. 4 is shown. A well defined maximum corresponding to the energy equal to 1 eV can be observed. The photoinduced absorption is persistent, *i.e.*, it remains almost unchanged after terminating the light.

It has been found that both persistent photoconductivity and photoinduced persistent absorption are quenched for temperature above 120 K, approximately.

The results shown in Figs. 3–5 give direct evidence for the presence of metastable defects in the material under investigation. As regards the temporal kinetics of photoconductivity shown in Fig. 3, it can be explained by the presence of DX centers in the material. Upon cooling, the sample DX centers get occupied by electrons and undergo a shallow–deep transformation. Illumination at sufficiently low temperature (here, 77 K) leads to the photoionization of DX centers if the photon energy exceeds their photoionization energy. The photoionization energy of DX centers for Ga doped $Cd_{0.99}Mn_{0.01}Te$ was found to be equal to 1.1 eV [11]. It may be expected that the photoionization energy for the DX centers in CdTe is close to this value. The kinetics presented in Fig. 3 was taken for photon energy equal to 1.24 eV, higher than 1.1 eV, we may therefore assume that the DX centers have become photoionized. Once photoionized, the DX centers undergo a deep–shallow transformation. As a result the occupation of deep levels decreases, and subsequently, the density of electrons in conduction band increases leading to an increase in conductivity.

After termination of light initial fast kinetics is followed by a very slow decay. The barrier for capture prevents DX centers from returning to their ground state. At low temperature the electrons have not got enough energy to surpass the barrier.

Warming above 120 K leads to the quenching of the photoeffect as electrons are provided with energy to overcome the barrier for capture.

The presence of the barrier for capture between the shallow, metastable state and the deep ground state of DX center does not explain however the observed photoinduced persistent absorption increase. Usually, in materials with DX centers a photoinduced persistent decrease in absorption is observed within the energy range corresponding to the DX photoionization energy and simultaneous increase in the infrared range [3–6]. The former is due to the lack of electrons which already left the photoionized DX ground state. The latter is the result of absorption by electrons occupying the shallow metastable hydrogenic Ga donor level. In Figure 5, the difference between the transmissions measured in darkness without and with preliminary illumination is shown. In this way, a broad absorption band with maximum around 1 eV was found. There is a possibility that as in the case of $Al_xGa_{1-x}As$:Te the band may be associated with another metastable state of DX center [3], the DX^0 state or a new kind of metastable defect created during iluminaton. This is an open question and needs further investigation. The photoinduced absorption has undoubtedly its origin in a metastable state.

4.Conclusions

The presence of metastable defects in gallium doped CdTe was confirmed by the observation of persistent photoconductivity and photoinduced persistent absorption at 77 K. It was found that both effects are quenched at temperatures above 120 K, approximately. The two-fold nature of DX centers with deep–shallow transformation accompanied by large lattice relaxation explains the persistent photoconductivity effect. As for the photoinduced persistent absorption it cannot be understood within the frame of this model. There has to be another metastable state responsible for the effect. No matter whether the origin of the observed persistent photoeffects is the DX center or any other metastable defect, its formation in the material is undesirable. Metastable defects act as carrier traps and thus may seriously affect, *e.g.*, carrier densities. Their presence is a crucial factor which may deteriorate parameters of semiconductor devices made of the gallium doped CdTe material.

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