PHYSICAL REVIEW B **83**, 241201(R) (2011)

Persistent light-induced change in the effective band gap and reversible control over the effective band gap in bulk semiconductor crystals

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(Received 4 May 2011; published 16 June 2011)

We demonstrate that the effective optical band gap of bulk semiconductor CdZnTe:V crystals can be varied and controlled by dual application of light and electric field, both at moderate strengths. When the combined effect of light intensity and applied field exceeds a threshold, the effective band-gap shift persists even after the light is turned off, as long as the electric field is applied. The persistent effective band-gap shift is accompanied by persistent photocurrent and persistent change in the (220) *d* spacing of crystalline lattice. However, all persistence effects can be reset to their original values when the applied field is turned off.

DOI: 10.1103/PhysRevB.83.241201 PACS number(s): 71.55.Gs, 72.40.+w

Finding an efficient way to tune the electronic band gap in semiconductors could open new horizons in microelectronics and optoelectronics. However, varying the band gap requires large dc electric fields (the static Franz-Keldysh effect, in which the effective band gap is modified by field-assisted electron tunneling[1,2]) or magnetic fields,[3] or exposing the material to high pressure or temperature.[4] These methods are greatly limited in their usefulness, since the effect on band gap is very small. For example, electric fields of several tens of kilovolts per centimeter[1,2] or magnetic fields of several Tesla[3] lead to a just tiny shift of a few meV in the optical band gaps of GaAs or InSb (1.43 and 0.17 eV, respectively). For many applications, it is highly desirable to tune the band gap by light, in real time and in a reversible way. Unfortunately, light-induced reversible effective band-gap shift based on the dynamic (ac) Franz-Keldysh effect[5] requires very high intensities ($>5\times10^9$ W/cm^2).

Here we demonstrate experimentally that the effective optical band gap of a bulk semiconductor with deep impurity levels can be varied by light and electric field, both at moderate strengths. The observed effective band-gap shift is the largest ever reported in any bulk material, and cannot be explained in the framework of any previously known effect.[1–5] We use moderate field ($\sim$2 kV/cm) and moderate light intensity ($\sim$1 W/cm^2) to modify the absorption edge[6] of a V-doped CdZnTe crystal (CZT:V) by as much as 60 meV, which is nearly 4% of its original value (1.56 eV). The band-gap change is induced by a laser beam at photon energies far below band gap. It is devoid of any thermal effects and is fully reversible: a few seconds after the field and the light are turned off, the band gap returns to its initial value. When the light intensity and electric field exceeds some threshold values, the band-gap shift becomes persistent, remaining unchanged as long as the electric field is applied, even after the light is turned off. Under the same conditions we also find persistent relative change ($\sim$0.04%) of the (220) lattice *d* spacing. We believe that this method of controlling the band gap of semiconductors by light can be extended to other materials, and can be used to enhance nonlinear material properties for THz generation and control nonlinear ultrafast effects, such as two-photon absorption and self-phase modulation.

Our bulk $Cd_{1-x}Zn_xTe$:V single crystals were grown by the modified horizontal Bridgman technique,[7] with nominal Zn concentration $x = 0.01$, and nominal V doping of $\sim10^{17}$ cm^{-3}. In our experiments [Fig. 1(a)] the crystal is illuminated uniformly with a 980 nm wavelength laser beam, corresponding to photon energies much smaller than the band gap. We denote this beam as the "control beam." We apply a dc field E along the crystalline $\langle001\rangle$ direction, while the control beam is propagating along the $\langle110\rangle$ direction. The transmission of the sample is probed by a weak light source [see Fig. 1(a)] in the wavelength range 800–1000 nm.

First, we investigate the light-induced change in the absorption spectrum. At moderate fields ($E < 2.2$ kV/cm), increasing the control-beam intensity in the range 0.1–1.3 W/cm^2 results in a remarkable shift of the absorption edge toward longer wavelengths [Fig. 1(b)]. The effective band gap decreases linearly with light intensity [Fig. 1(c)], with a maximum band-gap shift of 64 meV, at $I_l = 1.3$ W/cm^2 and $E = 2.2$ kV/cm.

It is worth comparing the magnitude of the observed effect to the Franz-Keldysh and quantum-confined Stark effects in similar materials. The theory of the Franz-Keldysh effect[4] yields a band-gap shift of 10 meV at $E = 50$ kV/cm. In practice, the Franz-Keldysh effect in bulk crystals is even smaller, for example, in ZnS the band-gap shift due to the Franz-Keldysh effect is 3.8 meV at $E = 50$ kV/cm,[8] while in GaAs this shift is 200 μeV at $E = 5$ kV/cm.[9] Evidently the values observed by us are much higher than those ever reported for the Franz-Keldysh effect. In fact, the band-gap shifts observed in our bulk crystals are comparable to the quantum-confined Stark effect in quantum-well structures. For example, in Ge/SiGe quantum wells, an absorption peak shift by 48 nm (30 meV) was found at $E = 80$ kV/cm.[10] The band-gap shift we measure is twice as large at $E = 2.2$ kV/cm, that is, at 36 times smaller electric field, despite that we conduct experiments with bulk crystals. These facts lead us to conclude that our effect, being much stronger, has a different origin than the Franz-Keldysh effect.

Having demonstrated huge light-induced shift in the effective band gap, we now show that this shift is fully reversible. We measure the absorption spectrum as a function of time, upon turning on simultaneously the control beam and E [black hollow circles in Fig. 2(a)], and upon turning both of them off blue solid circles in Fig. 2(a)]. Figure 2(a) displays that the band-gap shift is indeed fully reversible, and that the response time for the shift is $\sim$10 s.

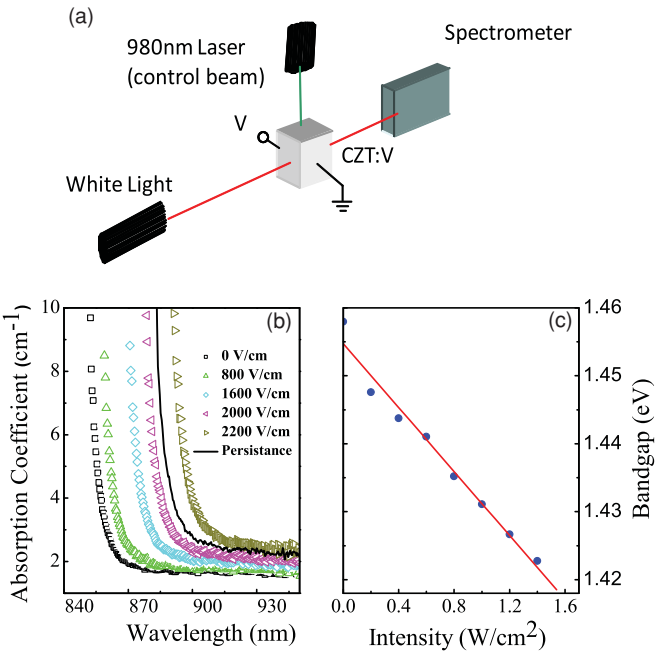

FIG. 1. (Color online) Experimental setup and experimental results demonstrating light-induced shift of the absorption edge of CZT:V crystals. (a) Setup. (b) Shift of the absorption spectrum as a function of applied field (at $I_l = 1.3$ W/cm^2). (c) Shift of the band-gap energy as a function of the control-beam intensity (at $E =$ 1.8 kV/cm). Blue solid circles are the experimental data and the red solid line is the linear fit.

It is essential to check that the observed effective band-gap shift does not arise from thermal effects. For this purpose we test the temperature dependence of the band gap by measuring the absorption spectra at different temperatures, and find that a band-gap reduction of 64 meV requires raising the sample temperature by 70 K above room temperature up to 363 K [due to rather low Debye temperature of CdTe, $\Theta_D = 141$ K (Ref. 11)]. This finding completely rules out the possibility that the observed band-gap shift originates from sample heating, since the directly measured maximum temperature increase of the sample in our experiments is less than 5 K. Another major difference between the light-induced and the thermal effects is the response time: When we heat the crystal (or when its temperature is decreased) it takes several minutes for the band gap to reach its new equilibrium value. In a sharp contrast to that, the time scale in the light-induced effective band-gap shift is only ~10 s [Fig. 2(a)].

It is now natural to examine the dependence of the light-induced band-gap shift on the applied field, under fixed control-beam intensity [Fig. 2(b)]. We fix the intensity of the control beam to its highest available value (1.3 W/cm^2), and gradually increase E. For $E < 2.2$ kV/cm, the band gap is monotonically decreasing with increasing E [Fig. 2(b)], and the effect is fully reversible: when we turn the control beam off, the band gap returns to its initial value [Fig. 2(a)]. However, when the E exceeds 2.2 kV/cm, the band-gap shift becomes persistent: it persists for many hours after the control beam is turned off [Fig. 3(a)]. The persistent shift can be completely terminated by turning E off. After that, the crystal returns back to its original state in ~30 s [Fig. 3(b)]. The very large light-induced, reversible, effective band-gap shift and the persistence effects above some threshold cannot be explained in the framework of any known model. It is therefore natural to ask whether the band-gap shift is accompanied by other effects, which up to some threshold are reversible, and above threshold become persistent. We first investigate the photocurrent. To do that we monitor the electric current through the crystal simultaneously with the variation in the absorption spectrum, as a function of E [Fig. 2(c)], when the control beam intensity is set to its highest value ($I_l = 1.3$ W/cm^2). As shown in Figs. 2(a)) and 2(c), when the band-gap shift is smaller than 20 meV (absorption edge above 1.445 eV), the current depends linearly on voltage. At larger shifts (absorption edge in the range 1.445–1.430 eV), the current exhibits a nonlinear voltage dependence with a slope smaller than unity. When E is set to 2.2 kV/cm, a sharp transition occurs: the photocurrent jumps abruptly to a value more than twice larger than that just below the transition. That is, the conductivity of the crystal changes dramatically at this transition point.[12] This abrupt increase in conductivity coincides with the jump in the band-gap shift [Fig. 2(b)], and like the band-gap shift, the increased photocurrent also becomes persistent [Fig. 3(a)]. In other words, if we turn the control beam off both the band-gap shift and the increased conductivity retain their high values [Fig. 3(a)], that is, they survive with no light, as long as the electric field is applied. Importantly, both persistent effects can be reset by turning E off: as shown in Fig. 3(b), after turning E off the band gap returns to its initial value within 30 s.

The optical measurements of large intensity-dependent band-gap shift and photocurrent, in both the reversible regime and in the persistence regime, call for experiments that could test whether these effects could be correlated with significant changes in the crystalline structure. We carried out high-resolution x-ray diffraction experiments similar to Ref. 13. We measure the (220)-d spacing at control beam intensity of $I_l =$ 0.7 W/cm^2, with E applied perpendicular to the [110] direction and at 24° with respect to the [001] direction (dictated by actual crystal shape). The experimental results [Fig. 4(a)] show relative change in lattice d spacing (i.e., strain ε), which increases with E, reaching $\varepsilon \approx 4\times10^{-4}$ at $E = 1.75$ kV/cm. When E is increased above this value, the strain jumps to $\varepsilon = 5.5\times10^{-4}$ and becomes persistent (fluctuating around $\varepsilon = 3\times10^{-4}$) for 5 h after turning off the control beam [Fig. 4(b)]. After switching off E, the crystal returns to its initial state $\varepsilon = 0$ [last two points in Fig. 4(b)]. This transition to the persistence regime, signified by the abrupt increase in strain, correlates with the jumps in the effective band-gap shift [Fig. 2(b)] and the current [Fig. 2(c)].

Explaining the observed very large effects is of major importance. However, many questions are still open. Our findings cannot be explained within the free-carrier injection model[4] because the concentration of charge carriers in our experiments is too small. The same conclusion is drawn with respect to the classical Franz-Keldysh theory, since the effects we observed are too large. That is, attempting to explain our findings through the Franz-Keldysh theory, by suggesting that the local electric field is higher than the applied field, results in a calculated local field much larger than the dielectric breakdown field of CZT crystals. What we observe is therefore a new effect, awaiting a theoretical model.

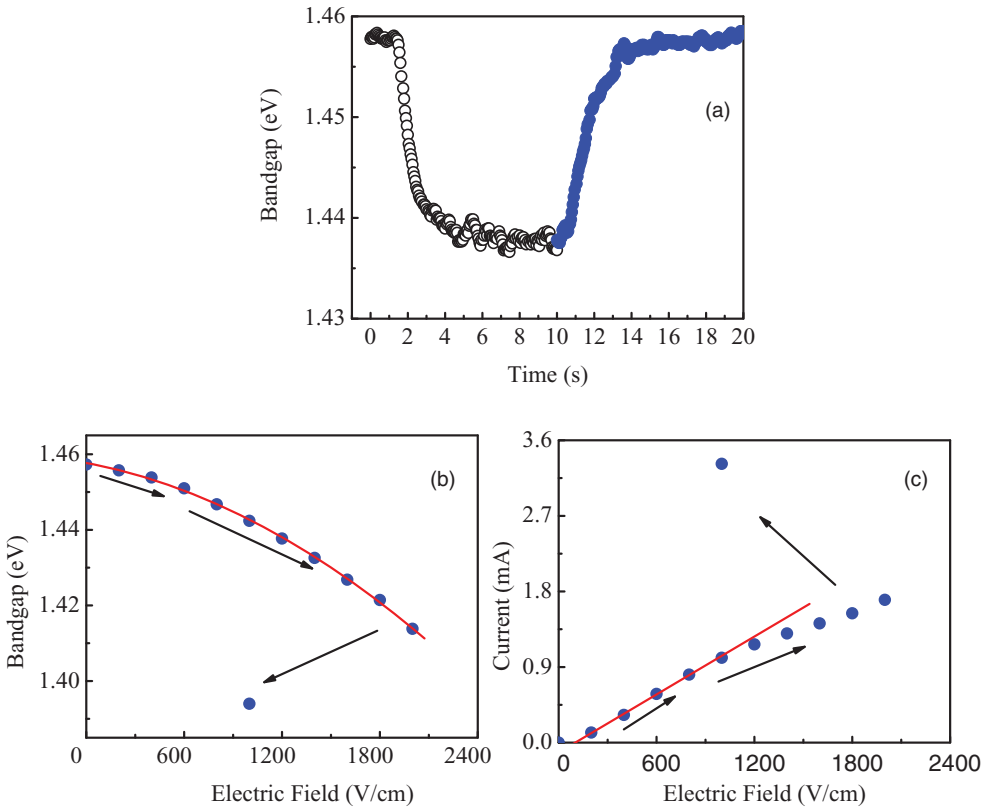

FIG. 2. (Color online) Reversibility and persistence of the light-induced effective band-gap shift and the photocurrent. (a) Time evolution of the band-gap value when the control beam and the applied electric field are turned on (black hollow circles), and upon turning both off (blue solid circles), simultaneously. When the maximum band-gap shift is smaller than ∼40 meV, the change in the crystal properties (band gap and photoconductivity) is fully reversible. (b) Band gap vs electric field under fixed control beam intensity ($I_l = 1.3$ W/cm^2); blue circles are the experimental data and the red line is a parabolic fit. When the applied field is increased beyond 2 kV/cm, the band-gap energy abruptly jumps to a value smaller than 1.4 eV (a shift larger than 58 meV), and becomes persistent: it persists for many hours after the control beam is turned off. (c) Current flowing through the crystal vs applied field, under fixed control-beam intensity ($I_l = 1.3$ W/cm^2); blue circles are the experimental data and the red line is a linear fit. At applied fields lower than 1 kV/cm, the current obeys Ohm's law. In the range 1–2 kV/cm, the dependence of the current on the electric field is nonlinear. At 2 kV/cm, the current jumps to a value more than twice larger, which persists for many hours after the control beam is turned off. That is, at 2 kV/cm the material undergoes a transition into the "persistence regime," where both the band-gap shift and the photocurrent remain unchanged for many hours after the control beam is turned off. The maximum effective band-gap shift displayed in (b), 64 meV, is larger than any band-gap shift ever measured in any bulk material. Note that, after the abrupt jump in the current, the applied voltage drops due to the current limit of the power supply. For this reason, in (b) and (c) the applied field after the jump is smaller, yet the variation in the effective band gap holds under the lower applied field.

In the absence of a model explaining our experimental observations, we note the essential role of the vanadium (V) doping. First and most important, we do not observe any persistence effect in samples with no V. Second, in the absence of deep traps, CZT crystals are very sensitive photoconductors for photon energies just below the band gap. Thus even when the intensity of the probe beam is very low (below the sensitivity of the detector of the spectrometer) and the applied field is smaller than 200 V/cm, the current through the sample exceeds the current limit of the power supply (3.3 mA). This is apparently the reason why the high current in samples with no V hampers the large effects we observe in samples with V doping. Third, in V-doped CZT crystals, the electric field of the ionized V atoms is very strong and cannot be screened by free carriers. This is because the energy level of V impurities is located deep within the band gap, which makes the V atoms efficient traps for both electrons and holes. Hence, the density of charge carriers in CZT:V, in the dark and under moderate light intensities, is much smaller than the density of the ionized impurities (V and intrinsic).[14] Under these conditions the screening of ionized traps (V ions) by free carriers is negligible (screening length is larger than average distance between neighboring impurities). Thus the strong electric field generated by the ionized V atoms deforms both the conduction and the valence bands, according to their local distribution. Since the V atoms are randomly distributed across the sample, the spatial modulation of both bands is also random. An important outcome of the random modulation of the bands is the presence of the Urbach's tail:[15,16] the absorption coefficient for photon energies below band gap contains an exponential tail, lagging deeply into the band gap. The Urbach's rule is clearly revealed in Fig. 1(b): without illumination and external field, the absorption spectrum indeed has an exponential tail. Since the classic Franz-Keldysh effect is also due to the "penetration" of the electron wave function into the band-gap region under electric field, we do see one common feature

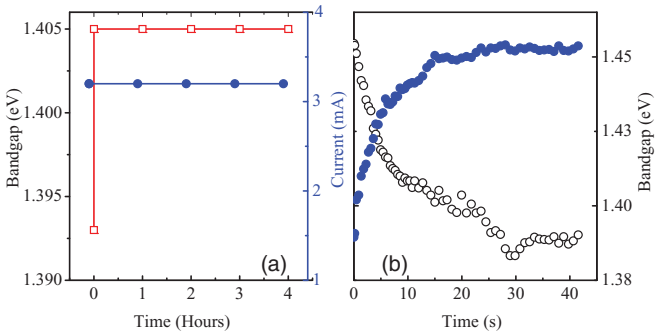

FIG. 3. (Color online) Persistence of the effective band-gap shift and the photocurrent, and the ability to reset the effects electrically. (a) Persistence of band-gap shift (red hollow square) and photocurrent (solid blue circles): after the band-gap shift reaches its maximum value (red square at $t = 0$, band gap $= 1.382$ eV), we turn the light off; the band gap slightly increases (reducing the shift) to 1.405 eV. The magnitudes of the band gap and the photocurrent persist for 4 h after the control beam is turned off (solid lines are a guide for the eye). (b) The persistent band-gap shift can be reset to its initial value by turning also the bias field off. Black hollow circles: buildup of the band-gap shift when the crystal is subjected to electric field $E = 2.2$ kV/cm, and control beam intensity $I_l = 1$ W/cm^2. Blue solid circles: resetting the band gap to its initial value. When both the electric field and control beam are turned off, the band-gap shift decays and the initial band gap is restored.

between our effect and the Franz-Keldysh effect. One might be tempted to think that perhaps our observations could be explained through the local electric field generated by the deep traps shifting the band gap through the Franz-Keldysh effect. However, as was already mentioned, the Franz-Keldysh effect is too small to account for the large shifts displayed in Figs. 1 and 2. Our experiments suggest that the spatial modulation of the bands greatly increases upon illumination and applied field.

In conclusion, we demonstrated very large light-induced changes in the effective band gap of bulk CZT crystals: up to 64 meV, a 4% change. The observed band-gap shift greatly exceeds the expected magnitude of the Franz-Keldysh effect. The effect occurs under the combination of an applied electric field and illumination, both at moderate strengths. When the applied field and control-beam intensity exceed a threshold, the band-gap shift and photocurrent become persistent: one can turn the control beam off and the band-gap shift and

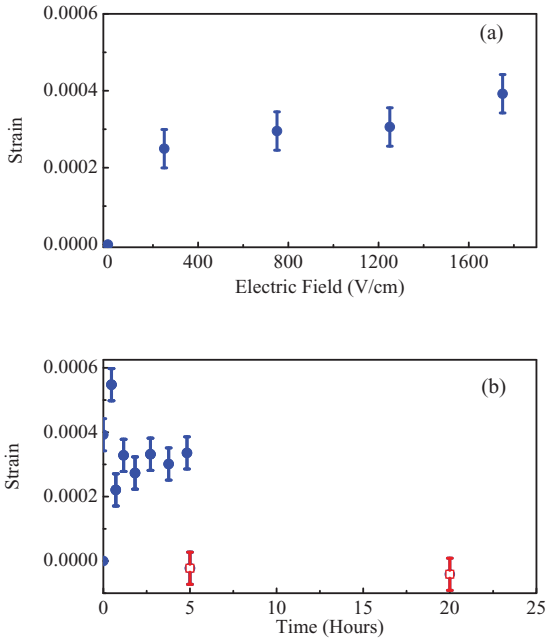

FIG. 4. (Color online) High-resolution x-ray diffraction measurements showing substantial change in the (220) lattice d spacing correlated with the band-gap shift and photocurrent induced by the control beam, in both the reversible regime and at persistence. (a) Light-induced strain, that is, relative change of the (220) lattice d spacing vs electric field at fixed control beam intensity of 0.7 W/cm^2. (b) Persistence of strain over time for nearly 5 h (blue solid circles) and its relaxation after switching off the applied electric field (red hollow square).

photocurrent persist for as long as the field is on. Our x-ray diffraction measurements reveal simultaneous build up of considerable lattice strain (up to 5.5×10^{-4}), which also displays persistence effects, and is correlated with the persistent band-gap shift and current. We find that the presence of deep level impurities is essential for the observation of the large effects we report in this work. Our findings provide a powerful tool for controlling the electrical and optical properties of bulk semiconductors. We anticipate that the light-induced effective band-gap shift can be used to control ultra-fast optical nonlinear processes such as two-photon absorption and THz generation.

[1]W. Franz, Z. Naturforsch. Teil A **13**, 484 (1956).
[2]L. V. Keldysh, Sov. Phys. JETP **6**, 763 (1958).
[3]F. Burstein, G. S. Picus, H. A. Gebbie, and F. Blatt, Phys. Rev. **103**, 826 (1956).
[4]K. Seeger, *Semiconductor Physics: An Introduction*; 8th ed. (Springer, Berlin, 2002).
[5]A. H. Chin, J. M. Bakker, and J. Kono, Phys. Rev. Lett. **85**, 3293 (2000).
[6]We define the effective optical band edge as the photon energy at which the absorption coefficient is 10 cm^{-1}.
[7]See supplemental material at [http://link.aps.org/supplemental/10.1103/PhysRevB.83.241201] for technical details.
[8]B. G. Yacobi and Y. Barda, Phys. Rev. B **10**, 665 (1974).
[9]T. S. Moss, J. Appl. Phys. **32**, 2136 (1961).
[10]Y. Kuo, Y. k. Lee, Y. Ge, S. Ren, J. E. Roth, T. I. Kamins, D. A. B. Miller, and J. S. Harris, Nature (London) **437**, 1334 (2005).
[11]R. D. Horning and J.-L. Stauderman, Phys. Rev. B **36**, 2873 (1983).
[12]In fact, the jump of electric current might be much higher since the measured current value is limited by the power supply.
[13]S. Shwartz, R. Weil, M. Segev, E. Lakin, E. Zolotoyabko, V. M. Menon, S. R. Forrest, and U. El-Hanany, Opt. Express **14**, 9385 (2006).
[14]We estimate the density of V atoms to be 10^{17} cm^{-3}, whereas the density of the free carriers never exceeds 10^{12} cm^{-3} (using the values of the dc current observed in our experiments and electron mobility of 1000 cm^2/Vs).
[15]F. Urbach, Phys. Rev. **92**, 1324 (1953).
[16]F. Moser and F. Urbach, Phys. Rev. **102**, 1519 (1956).