

Effect of X radiation on the plastic deformation of II-VI compounds

V. F. Petrenko, N. N. Khusnatdinov, and I. Baker

Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire 03755

(Received 7 March 1996)

This paper examines the effects of x rays on the plastic deformation of single crystals of II-VI semiconductors. It was found that x-ray excitation of CdTe, CdS, ZnS, and ZnSe causes significant hardening, with a decrease in the rate of plastic deformation up to two orders of magnitude, and an increase in the resolved shear stress up to 90%. The hardening is almost completely reversible. The dependencies of the phenomenon on the slip systems, plastic strain, and the current and voltage of the x-ray source are reported along with results on the x-ray conductivity and dislocation currents which were recorded simultaneously with the stress and strain diagrams. [S0163-1829(96)02524-6]

The motivation for this study was twofold. First, since x radiation significantly affects the electric conductivity of II-VI compound semiconductors,¹ one may ask can x radiation cause an x-ray plastic effect similar to the effect of optical excitation, which significantly changes the electric conductivity (photoconductivity, PC) (Ref. 2) as well as the plastic properties (photoplastic effect, PPE) of all II-VI semiconductors?^{3,4} Second, since these materials are widely used in both x- and γ -ray detectors, and are exposed to such radiation during the process of x-ray lithography, it is important to know whether or not x radiation affects their mechanical properties.

The PPE has been observed in a narrow spectral interval close to the fundamental absorption band of the material being studied.⁴ It has been demonstrated that photoconductivity alone cannot account for the photoplastic effect, because the wavelength dependencies of the PPE and PC are different.⁴⁻⁷ Thus it was not obvious that x rays, while changing the conductivity, can also affect plastic deformation of II-VI compounds.

The experiments were performed on pure undoped single crystals of CdTe, CdS, ZnSe, and ZnS, all grown from the melt. Due to nonstoichiometry all the materials had *n*-type conductivity. CdS had a hexagonal wurtzite structure, while the other materials were cubic with the sphalerite structure. Although ZnS had the sphalerite structure it contained a large number of stacking faults, giving it pseudo-hexagonal symmetry and a single {111} slip plane. Samples measuring $6 \times 4 \times 1.5 \text{ mm}^3$ or $6 \times 4 \times 1 \text{ mm}^3$ were cut from the crystals with a diamond saw, ground with abrasive powders, polished with diamond paste, and finally chemically polished at room temperature with a concentrated solution of CrO_3 in concentrated hydrochloric acid and washed in distilled water. The (111) or (0001) slip plane was oriented at 45° to the compression axis, as shown in Fig. 1. For measurements of dislocation currents,⁴ conductivity and photoconductivity, Ohmic indium electrodes were deposited over the entire 6×4 -mm faces (for dislocation currents and conductivity) or the 4×1.5 -mm faces (conductivity only) using an ultrasonic soldering iron. The specimens were compressed at room temperature at a fixed strain rate of 2.5×10^{-5} or $5 \times 10^{-5} \text{ s}^{-1}$ between the parallel fused-quartz plates of a special compression cell mounted in a testing jig. Electrical mea-

surements were made with a Fluke multimeter (model 45) and a Keithley electrometer (model 616). During the tests, data on stress, dislocation current, and/or conductivity were recorded.

White light from a fiber-optic illuminator with a quartz-iodine lamp was used to produce both a photoplastic effect and photoconductivity. As an x-ray source we used a Siemens Kritaloflex 710/710h x-ray generator with a copper target. The tube anode was 15 cm from the test specimens. The specimens were placed in the center of the x-ray beam; the width of the x-ray beam, 30 mm, exceeded the specimens' dimensions.

The linear density of the electric charge of dislocations can be determined from a dislocation current produced in II-VI compounds by the predominant motion of dislocations of one mechanical sign.⁴ For the orientations shown in Fig. 1, a charge q per unit length of 60° dislocations (screw dislocations are not charged) can be calculated from Eq. (1),

$$q = \frac{b_z I_d}{d i_p}, \quad (1)$$

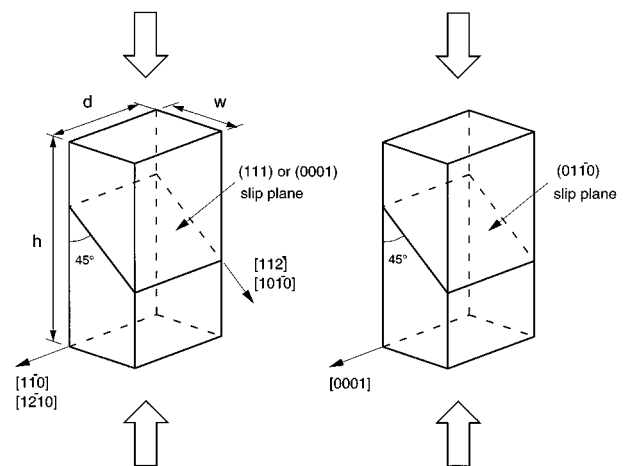


FIG. 1. (a) Orientation of crystals with the sphalerite and wurtzite structures, showing the (111) and (0001) planes. (b) Orientation of a crystal with the wurtzite structure for prismatic slip. $h = 6 \text{ mm}$, $d = 4 \text{ mm}$, $w = 1.5$ or 1 mm .

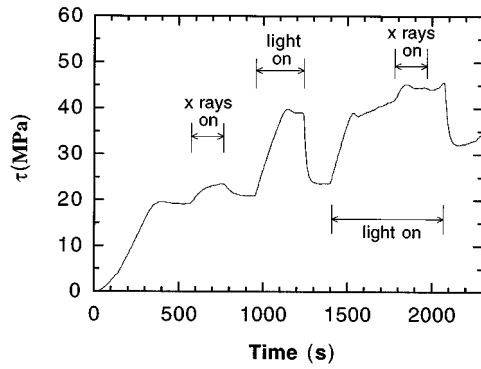


FIG. 2. Graph of resolved shear stress on the slip plane (111) τ vs time for ZnS crystal compressed at a strain rate of $5 \times 10^{-5} \text{ s}^{-1}$. $T=295 \text{ K}$. The x-ray tube current and voltage were 30 mA and 40 kV, respectively. See text for details. The light intensity was lower the second time the light was turned on.

where b_z is the projection of the Burger's vector on the compression axis, I_d is the dislocation current, d is the width of the electrodes (4 mm), and \dot{l}_p is the plastic rate of change of the length of the specimen.^{6,7}

We found that x rays strongly affected plastic properties of all the II-VI crystals. That is, x rays cause significant and almost reversible hardening of these materials. Figure 2 shows a typical graph of stress, τ , versus time recorded during compression of a ZnS specimen. The actuator speed of $18 \mu\text{m}/\text{min}$ corresponds to a strain rate $\dot{\epsilon}=5 \times 10^{-5} \text{ s}^{-1}$. The initial part of the graph shows a characteristic elastic deformation with $\tau \propto \epsilon \propto \dot{\epsilon} \cdot t$ from 0 to 300 s (Hooke's law), followed by a region of plastic deformation from 300 to 600 s in which τ is approximately constant. Illumination of the sample either with x rays or white light caused hardening and a drop in the plastic strain rate $\dot{\epsilon}_p$. The relative hardening caused by the x rays, $\Delta\tau/\tau$, depends on many factors (described below) and reached 90% for CdS and 60% for ZnSe when the wide ($6 \times 4 \text{ mm}$) side of the specimen was illuminated. The magnitude of $\Delta\tau/\tau$ varied for specimens cut from different crystals of the same material. Since for these materials the rate of plastic deformation, $\dot{\epsilon}_p$ ($\dot{\epsilon}_p \neq \dot{\epsilon} = \text{const}$), depends exponentially on stress τ ,^{4,8} the corresponding change in $\dot{\epsilon}_p$ was even more dramatic. For example, in ZnSe the x rays produced a drop in $\dot{\epsilon}_p$ of two orders of magnitude. The hardening caused by the x rays is mostly reversible; i.e., the stress τ at which a sample deformed plastically returned to its initial magnitude after the x rays were shut off. The small difference in τ before and after the x radiation is due to strain hardening. When both x rays and white light were turned on, their action was additive as long as both effects were far from saturation; see Fig. 2.

We checked whether the hardening caused by x rays diminishes with accumulation of plastic deformation ϵ_p . Figure 3 depicts the dependencies of $\Delta\tau/\tau_0$ on ϵ_p , measured in ZnSe and CdS. While in ZnSe and CdTe the effect noticeably decreases as plastic deformation increases, in ZnS and CdS the accumulation of plastic deformation produced little change, at least within the tested range of ϵ_p from 0% to 8%.

During most of the compression tests both conductivity and photoconductivity of the specimens were measured. A sample plot of conductivity current versus time is shown in

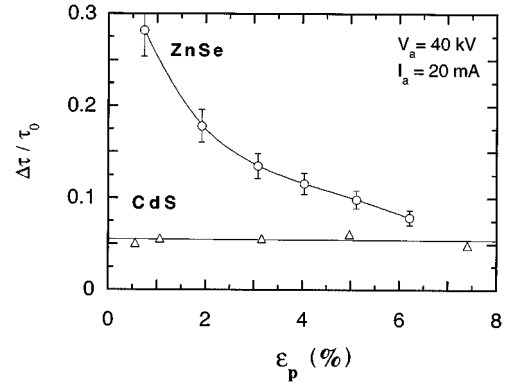


FIG. 3. Graph showing dependence of the relative magnitude of the x-ray plastic effect $\Delta\tau/\tau_0$ on plastic deformation ϵ_p in ZnSe and CdS. $T=295 \text{ K}$, anode voltage $V_a=40 \text{ kV}$, and anode current $I_a=20 \text{ mA}$.

Fig. 4. In such tests the conductivity current exceeded by one or two orders of magnitude the dislocation current, which was oriented perpendicular to the latter to prevent interference between the currents. As one can see in Fig. 4, both photocurrents, excited by the x rays and by white light, were comparable in magnitude. The rise and decay times of both the photocurrents were also very similar. Although the x rays excited weak visible fluorescence in CdS, ZnS, and ZnSe, the intensity of this fluorescence was several orders of magnitude less than the intensity of light capable of generating any noticeable photoplastic effect. Hence the fluorescence cannot account for the x-ray-stimulated hardening of the materials.

Although the actions of both the x rays and the white light on dislocation motion in (111) and (0001) planes were similar, their actions on prismatic slip in CdS were opposite. That is, during compression of CdS specimens oriented by prismatic slip, the x rays caused 1% hardening, while the white-light illumination caused 15% softening, in accordance with the negative photoplastic effect observed earlier.⁶ This difference in the reactions of the basal and prismatic dislocations on both the x-ray and optical excitations may be because in the wurtzite structure dislocations in these two planes have different core structures and carry different electric charges.^{4,9}

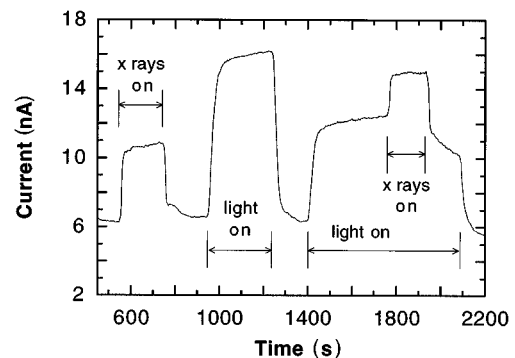


FIG. 4. Graph showing the time dependence of the conductivity current through a ZnS sample during the compression test shown in Fig. 2. The applied voltage was 70 V.

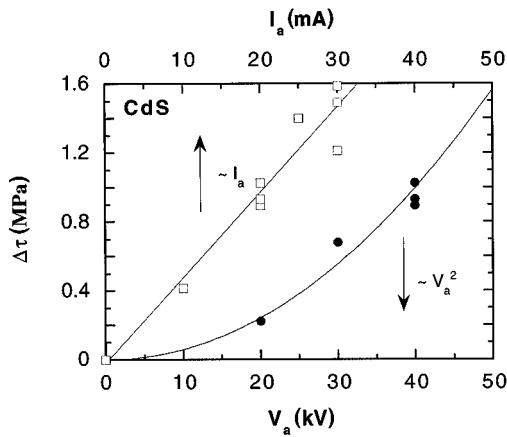


FIG. 5. Graph showing the dependence of x-ray-stimulated hardening of CdS, $\Delta\tau$, on the x-ray tube current I_a at a constant tube voltage $V_a=40$ kV, and voltage V_a at constant tube current $I_a=20$ mA.

The dependencies of the magnitude of the x-ray plastic effect (XPE), $\Delta\tau$, in CdS on the anode current I_a and voltage V_a are shown in Fig. 5. As one can see from this figure, $\Delta\tau \propto I_a V_a^2$. Since the total intensity of bremsstrahlung radiation is also proportional to $I_a V_a^2$,¹⁰ this observation indicates indirectly that in the tested photon energy range $h\nu < 40$ keV the effect is not sensitive to x-ray wavelength. At the same time the x-ray absorption coefficient of CdS varies from $5 \times 10^2 \text{ cm}^{-1}$ at 10 keV to 11.8 cm^{-1} at 40 keV.¹¹ That means that most of the radiation was absorbed in a thin layer about 0.1 mm thick when V_a was 10 kV, while at 40 kV the excitation was spread over the 1.5-mm-thick sample quite uniformly. When indium electrodes were parallel to the x-ray beam and did not shield the specimens the x-ray plastic effect was the same as without electrodes.

The value of q was determined in ZnSe from measurements of dislocation currents I_d using Eq. (1). It was found that q increases under x-ray illumination in the same manner as it does under optical excitation.^{4,7,8,12} In our experiments q was 1.74×10^{-10} , 2.18×10^{-10} , and $3.28 \times 10^{-10} \text{ C m}^{-1}$ in darkness, under x radiation (40 kV, 30 mA), and under visible illumination, respectively.

While the findings presented in this paper are not yet sufficient to define a physical mechanism for this phenomenon, we are still able to make several useful conclusions. First, the reversible hardening of II-VI semiconductors under x-ray il-

lumination was not due to such a trivial effect as heating of the samples, since heating would cause the materials to soften.⁴ Neither can the effect be explained in terms of excitation of the photoplastic effect generated by x-ray-stimulated fluorescence.

While in many respects the actions of optical illumination and x-ray illumination on the flow stress were similar, in the case of prismatic slip in CdS their actions were opposites. Possible generation of point defects by x rays can hardly explain this difference because the threshold energy for x-ray damage of CdS lies between 250 and 300 keV,¹³ while we used $h\nu \leq 40$ keV. Another possible origin of the difference between PPE and XPE is the difference in spatial absorption of x rays and that of visible light, which has a wavelength adjacent to the fundamental absorption band (the light mainly responsible for the generation of the photoplastic effect⁴). Such light has a much larger absorption coefficient in the vicinity of a dislocation core, while x rays are absorbed more uniformly in the bulk.

On the basis of our knowledge of the plastic and electrical properties of II-VI semiconductors, we can suggest several mechanisms for the XPE.

(1) Decrease in mobility of dislocations under x radiation as a consequence of the following.

(a) An increase of activation energy (the height of the Peierls barrier) for either the formation and/or the motion of kinks. This may happen if charge carriers are captured by a dislocation core changing its electric charge.

(b) Pinning of dislocations by intrinsic ionized centers.

(c) Pinning of dislocations by radiation damage produced defects, such as vacancies, interstitials, etc., if any are generated.

(2) X radiation inhibits dislocation multiplication.

(3) X radiation reduces the mean free path of the dislocations before they become pinned.

These mechanisms are similar to the possible mechanisms of the PPE discussed by Osip'yan *et al.*⁴ It is worth noting here that the debate on the mechanism of the PPE itself is not yet concluded, and a future parallel study of the PPE and XPE may shed some light on the nature of both of these phenomena.

We think that the strong action of x rays on the plastic properties of II-VI compounds should be taken into account in such technological processes as x-ray lithography.

This work was supported by the National Science Foundation under Grant No. DMR-9413362.

¹M. Fiederle, D. Ebling, C. Eiche, D. M. Hofmann, M. Salk, W. Stadler, K. M. Benz, and B. K. Meyer, *J. Cryst. Growth* **138**, 529 (1994).

²*Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967).

³Yu. A. Osip'yan and I. B. Savchenko, *Zh. Eksp. Teor. Fiz. Pis'ma Red.* **7**, 130 (1968) [*JETP Lett.* **7**, 100 (1968)].

⁴Yu. A. Ossipyan, V. F. Petrenko, A. V. Zaretskii, and R. W. Whitworth, *Adv. Phys.* **35**, 115 (1986).

⁵Yu. A. Ossipyan and V. F. Petrenko, *Zh. Eksp. Teor. Fiz.* **63**, 1735 (1972) [*Sov. Phys. JETP* **36**, 916 (1972)].

⁶Yu. A. Osip'yan and M. Sh. Shikhsaidov, *Fiz. Tverd. Tela (Leningrad)* **15**, 3711 (1973) [*Sov. Phys. Solid State* **15**, 2475 (1973)].

⁷V. F. Petrenko and R. W. Whitworth, *Philos. Mag. A* **41**, 681 (1980).

⁸Yu. A. Ossipyan and V. F. Petrenko, *Zh. Eksp. Teor. Fiz.* **75**, 296 (1978) [*Sov. Phys. JETP* **48**, 147 (1978)].

⁹A. V. Zaretskii, Yu. A. Osip'yan, V. F. Petrenko, and G. K. Strukova, *Fiz. Tverd. Tela (Leningrad)* **19**, 418 (1977) [*Sov. Phys. Solid State* **19**, 240 (1977)].

¹⁰C. Giacomazzo, H. L. Monaco, D. Viterbo, F. Scordari, G. Gilli,

- G. Zanotti, M. Catti, in *Fundamentals of Crystallography*, edited by C. Giacovazzo (Oxford University Press, New York, 1992), p. 230.
- ¹¹ *Handbook of Spectroscopy*, edited by J. W. Robinson (CRC Press, Cleveland, Ohio, 1974), Vol. I, p. 28.
- ¹² Yu. A. Ossipyan and V. F. Petrenko, Dok. Akad. Nauk SSSR **226**, 803 (1976) [Sov. Phys. Dokl. **21**, 87 (1976)].
- ¹³ K. W. Boer and J. C. O'Connell, in *Proceedings of the International Conference on Luminescence*, edited by G. Szigetti (Akademiai Kiado, Budapest, 1968), p. 1063.