Photomechanical effect in p-type zinc telluride

M. Nagabhooshanam*

Departamento de Física, Universidade Federal do Paraná, CP 19081, 81531 Curitiba PR (Brazil)

C. Veerender

Department of Physics, Osmania University, Hyderabad 500 007 (India)

V. R. Dumke

Departamento de Física, Universidade Federal do Paraná, CP 19081, 81531 Curitiba PR (Brazil)

Abstract

The photomechanical effect in p-type ZnTe single crystals was observed via a study of the microhardness variation with and without IR photoexcitation ($\lambda = 790$ nm). The surface softening was found to increase with increasing intensity of radiation. At all intensity levels, the surface softening was seen to decrease slowly up to 8 gf load and thereafter to decline rapidly towards zero. The strain energy acting on the covalent bonds was determined as 0.27 eV. The results are explained on the basis of ionization of photosensitive defect centres.

1. Introduction

The photomechanical effect (PME) in semiconductors has been studied by several workers [1–3]. It was found that the plastic properties of germanium are considerably altered by photoexcitation with 200–400 nm radiation; in particular, the microhardness of the germanium surface falls by 40%–60%. The same reduction in surface hardness was observed on introducing minority carriers by injection from a point contact. From the results obtained it was concluded that the strength of germanium depends to a great extent on its electronic properties. In particular, a change in carrier density in the conduction band alters the mobility of dislocations and this accounts for the reduction in hardness of germanium. The PME was found to occur in germanium only on photoexcitation with radiation in the region of its fundamental absorption [1]. At the fundamental absorption the photons, particularly in covalently bonded crystals, raise the bottom of a square potential well, cause a dislocation to move out of the potential well and cause dislocation motion. This suggests

---

*Permanent address: Department of Physics, Osmania University, Hyderabad 500 007, India.

that other semiconductor materials excited at their fundamental absorption band may possibly exhibit the PME. Recently, one of the authors has observed changes in Hall coefficient and mobility of the carriers in p-type ZnTe by exciting the photosensitive defect centres using IR radiation [4]. The effect of temperature on the photoconductivity of ZnTe was studied by Blount et al. [5], who showed that the photoexcited carriers have an insignificant influence on conductivity. However, the effect of these excited carriers on the motion of dislocations and the mechanical properties of p-type ZnTe single-crystal surfaces was not studied.

The aim of the present work was to observe the PME in p-type ZnTe single crystals by studying the microhardness variation with and without IR radiation of different intensities and of energy less than the band gap of ZnTe. The effect of high temperature on microhardness was also studied and the results are explained in terms of dislocation mobility due to photoexcitation.

2. Experimental details

Single crystals of p-type ZnTe were obtained from the Department of Physics, University of Hull, U.K. Freshly cleaved (110) planes of the crystals without additional mechanical treatment such as grinding or polishing were used for hardness measurements. An Amplival polarizing microscope (Carl Zeiss Jena) with a Vickers microhardness attachment was used to create indentations and to measure the diagonal of the indented impression. The Vickers microhardness was calculated using

$$H = 1854.4 \, \frac{P}{d^2} \quad (\text{kgf mm}^{-2}) \tag{1}$$

where P (kgf) is the load on the indenter and d (mm) is the length of the average diagonal of the impression on the crystal surface. The surface of the sample was excited with two IR ($\lambda = 790$ nm) lamps positioned such that the light rays fell at an angle of about 45° on the surface. The light from these samples was focused on the specimen surface by means of fused quartz lenses. To reduce the surface temperature, a small sample was used, held in a massive copper clamp inside which water was circulated. The lamp circuit was closed 10 s before the indenter touched the specimen surface and was opened 20 s after the indenter had left the surface. These precautions reduced the sample temperature rise during photoexcitation to 2–3 °C. The sample temperature during hardness measurements was approximately 20 °C. The distance between the IR lamp and the specimen surface was altered in steps to cause a change in intensity of the light (22, 14 and 18 W m^{-2}) on the surface. The hardness at temperatures higher than room temperature was measured using a small heater under the top plate of the copper clamp placed on the stage of a Tukon hardness tester. The entire arrangement was mechanically isolated from vibrations. At least eight indentations were made

at each load–temperature combination and an average diagonal of them was taken to calculate the hardness. The time of each indentation was 10 s. The standard deviation of each measurement is as shown in the figures.

3. Results and discussion

The dependences of the sample hardness on the load applied to the indenter in the dark and under different photoexcitation intensities are given in Fig. 1. It is clear from the figure that:

(i) the hardness number of photoexcited samples is less at all loads than that of the dark sample;

(ii) in excited samples the decrease in hardness is more at low loads than at high loads;

(iii) the hardness number at a particular load decreases with increasing intensity of photoexcitation;

(iv) in both dark and photoexcited samples the hardness increases with decreasing load.

The PME is generally assumed to be a surface phenomenon. This is clear by the fact that the hardness numbers both with and without photo-excitation vary similarly with increasing load. The PME (percentage of softening) in photoexcited samples is shown in Fig. 2. The figure shows that the PME decreases slowly up to 8 gf of load and then declines rapidly
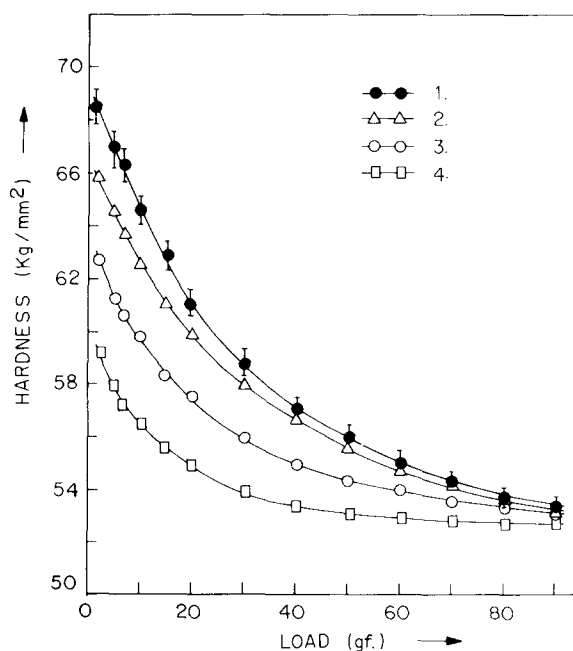

Fig. 1. Variation of microhardness with load in p-type ZnTe: 1, without excitation; 2–4, with IR photoexcitation of surface energy density equal to 8, 14 and 22 W m^{-2} respectively.
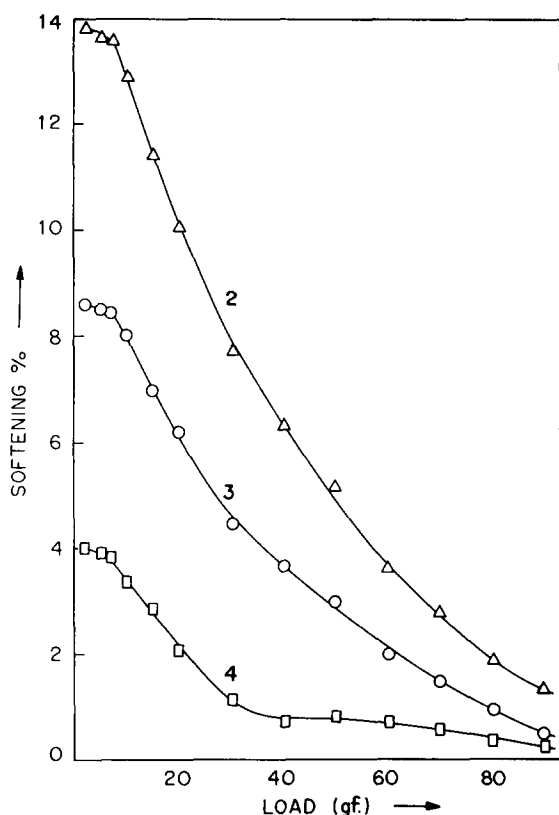
Fig. 2. Percentage variation of softening (PME) with load in photoexcited samples. The radiation intensities are as given in Fig. 1.

towards zero at higher loads. The slow decrease in the PME may be due to a lack of good contact between the specimen surface and the indenter. The rapid decrease in softening caused by photoexcitation may be a reason for the observations (i)–(iii) in Fig. 1.

The possibility of softening of the surface due to heat generated during the excitation should not arise, since the observed rise in temperature is only 2–3 °C. To ascertain whether heating of the crystal on photoexcitation is the cause of the change in its mechanical properties, the temperature dependence of the hardness of p-type ZnTe was studied in the dark (Fig. 3(a)). This dependence shows that the hardness number of ZnTe begins to fall with heating at about 50 °C. During the excitation and indentation the sample temperature did not exceed 20 °C. Consequently the PME in ZnTe cannot be due to heating of the sample.

It has been found in many single crystals that the microhardness value increases with decreasing load [6–14], but proved that this is in no way associated with instrumental error or the preparative treatment of the surface. Several explanations have been offered for the observed phenomenon. Mott [7] has suggested that the indentation hardness of a given material will be
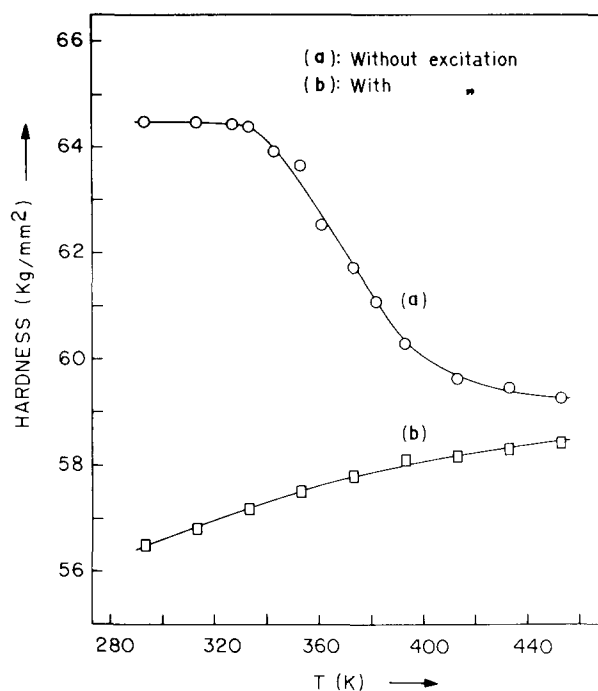
Fig. 3. Effect of temperature on microhardness with a load of 10 gf: (a) without photoexcitation; (b) with photoexcitation of surface energy density equal to 22 W m^{-1}.

constant above a critical size of impression, but below this size a steady increase in hardness will occur as the load is decreased. Theoretical justification for this has been given on the basis of Orowan's [15] model of work hardening. On the other hand, Buckle [6] has suggested that it is the presence of 'coherent regions' in the material that is responsible for the observed increase in hardness with decreasing load. Furthermore, it has been suggested that when the size of the indentation falls below the size of these coherent regions, there is no further increase in hardness, Yoshino [8] has proposed that the observed load dependence of micro-indentation hardness is due to inhomogeneity of the deformation produced by the indenter penetrating the material, *i.e.* the impressions are heterogeneous. Gane and Cox [12] have put forward an alternative explanation suggesting that the increase in hardness at small indentation sizes is due to an increase in the stress necessary to operate dislocation sources. Such a mechanism supposes that the stress required to operate a dislocation source is dependent on work hardening. The flow stress of the material sampled by the indenter is then a sum of work hardening and source hardening. It is apparent that whatever the detailed mechanism for such an indentation hardness–load dependence, it is associated with the movement of dislocations introduced by the indenter. In semiconductors such as that of the present study the PME may be due to a change in the number of electrons in higher energy states (which are produced by photo-

excitation), which causes an increase in dislocation mobility [16]. Particularly at low loads the surface receives less plastic deformation (work hardening) and a smaller number of fresh dislocations are introduced. Their number being less, these fresh dislocations have less interaction with themselves and have higher dislocation mobility. A bunch of fresh dislocations introduced at higher loads may cause low dislocation mobility and lead to a gradual decrease in hardness number with load.

The increase in the average length of the diagonal of the indented impression with increasing load implies an increase in the depth of impression. It is also apparent that the intensity of photoexcitation decreases with increasing depth, so that its effect ultimately becomes small. Basically, absorption and internal scattering prevent the penetration of radiation. This may be the reason for $\Delta H = H_d - H_e$, where H_d and H_e represent the hardness numbers without (dark) and with excitation respectively, decreasing with increasing load. If still higher loads are applied, the two curves may even coincide.

As the temperature of a semiconductor increases, the number of charge carriers increases. Because charge carriers act to absorb transmitted light, the effectiveness of photoexcitation should decrease. From Fig. 3(b) one can observe that this is so, because the hardness number vs. temperature increases with increasing temperature while the PME decreases. It is apparent that further increases in temperature will cause the two curves to coincide, thus eliminating the PME. Replotting the data given in Fig. 3 as $\ln(\Delta H/H_d)$ vs. $1/T$ (Fig. 4), the slope of the curve will give an energy value of 0.27 eV. This value can be considered to be a strain energy acting on the covalent bonds during the deformation process.

In semiconductors, photoexcitation with photons having an energy equal to or greater than the bandwidth will excite the electrons from the valence band into the conduction band. Increasing the temperature will cause thermal excitation and thus increase the density of charge carriers and the number of broken covalent bonds in semiconductors. The movement of dislocations in a covalently bonded crystal requires the breaking of covalent bonds [16]. Any bonds broken by thermal means should soften the crystal. Figure 3 confirms this hypothesis by the decrease in hardness of an excited sample with increasing temperature. It is clear from the experimental observations that IR radiation of photon energy 1.57 eV (790 nm) produces the PME. Trefilov and Milman [17] have proposed that the movement of a dislocation in a covalently bonded crystal involves the raising of the dislocation out of a square potential well in order for it to move. Photons should rise from the bottom of the potential well and thus make it easier for the dislocation to move. In the process the photons would assist the breaking of covalent bonds already under stress. The sum of the strain energy (0.27 eV) and the photon energy (1.57 eV) will give 1.84 eV, which is not sufficient to excite electrons into the conduction band (the energy gap of ZnTe at 300 K is 2.1 eV). However, the photon energy is high enough to excite the holes from the defect centres in p-type ZnTe. The same conclusion was also drawn from
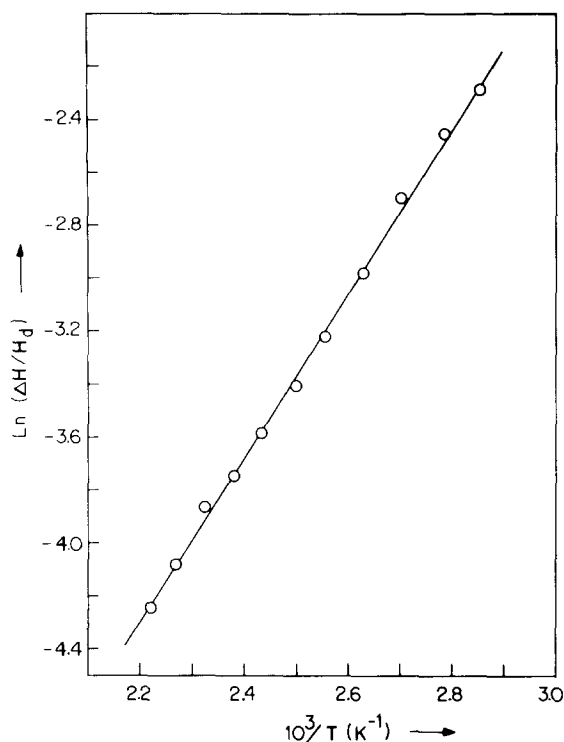
Fig. 4. Dependence of $\ln(\Delta H/H_d)$ on reciprocal of absolute temperature.

Hall effect studies on IR-photoexcited p-type ZnTe [4]. Since the hole mobility is usually low, it will not cause much hindrance to the movement of dislocations and breaking of covalent bonds. The most commonly accepted defect centre in ZnTe is due to copper impurity with an energy of 0.6 eV [18]. This is nearly one-third of the total energy available (1.84 eV). Therefore almost all defect centres near the surface are excited instantly and develop some complex defects [4] with further increase in intensity. The decrease in softening with increasing intensity implies that these complexes could be of negative charge, so that some holes are annihilated, and causes the flow of dislocations. Thus on ionization of the photosensitive defect centres the PME can be observed and it increases with increasing photoexcitation energy in semiconductors such as p-type ZnTe.

4. Conclusions

(1) The photomechanical effect is observed in p-type ZnTe with IR radiation of photon energy 1.57 eV via ionization of photosensitive defect centres.

(2) The surface softening increases with increasing intensity of radiation.

(3) The strain energy of the covalent bonds in p-type ZnTe is nearly 0.27 eV.

(4) IR radiation creates complex defects in p-type ZnTe. The charge of these complexes may be negative.

Acknowledgments

References

1 M. S. Ablova, L. A. Mozgovaya and E. P. Berdnikov, *Sov. Phys. — Solid State, 11* (1968) 1168.
2 V. N. Lange and J. S. Lange, *Sov. Phys. — Solid State, 6* (1964) 942.
3 N. Ya. Gorid'ko, P. P. Kuz'menko and N. N. Novikov, *Sov. Phys. — Solid State, 3* (1961) 2652.
4 M. Nagabhooshanam, *J. Less-Common Met., 163* (1990) 63078.
5 G. H. Blount, A. C. Sanderson and R. H. Bube, *J. Appl. Phys., 38* (1967) 4409.
6 H. Buckle, *Met. Rev. (Lond.), 4* (1959) 737.
7 B. W. Mott, *Micro-indentation Hardness Testing*, Butterworths, London, 1956.
8 T. Yoshino, *Bull. JSME, 8* (1965) 291.
9 G. P. Upit and S. A. Varchenya, *Izv. Akad. Nauk SSSR Met., 2* (1969) 737.
10 G. V. Vanicheva, M. I. Babicheva, E. V. Kulmanen and O. N. Shivrin, *Fiz. Metall. Metalloved., 17* (1964) 234.
11 V. M. Dolize, *Fiz. Metall. Metalloved., 8* (1959) 268.
12 N. Gane and J. M. Cox, *Philos. Mag., 22* (1970) 881.
13 M. Nagabhooshanam and V. Hari Babu, *Cryst. Res. Technol., 20* (1985) 1399.
14 A. Fissel, M. Schenk and A. Engel, *Cryst. Res. Technol., 24* (1989) 557.
15 E. Orowan, *Nature, 147* (1941) 452.
16 H. P. Leighly Jr. and R. M. Oglesbee, in J. H. Westbrook and H. Conrad (eds.), *The Science of Hardness Testing and Its Research Applications*, American Society for Metals, Metals Park, OH, 1973, p. 445.
17 V. I. Trefilov and Yu. V. Milman, *Sov. Phys. — Dokl., 8* (1964) 1240.
18 T. L. Larsen, C. F. Varotto and D. A. Stevenson, *J. Appl. Phys., 43* (1972) 172.