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Cathodoluminescence studies of dislocation motion in II_b–VI_b compounds deformed in SEM

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Continuous observation of dislocation motion on the specimen surface of II_b–VI_b semiconducting compounds (CdS and CdTe) has been made using a scanning electron microscope (SEM) with the cathodoluminescence (CL) by use of a deformation apparatus installed in the SEM chamber. With the application of stress, SEM–CL patterns revealed an increasing density of dark spots that formed dark stripes along slip traces. For both CdS and CdTe crystals, regardless of the slip system involved, the dark spots corresponding to individual dislocations appeared in the SEM field without displaying their moving state and seldom disappeared, indicating that dislocations are immobilized after they travel a certain distance from the source with a high velocity. The investigation of slip-band growth in CdS showed that screw bands on the basal plane exhibit the photoplastic effect, whereas those on the prismatic plane do not, in accordance with the macroscopic deformation tests.

1. Introduction

The plasticity of semiconductors such as II_b–VI_b compounds is strongly influenced by the electrical or optical conditions to which the material is subjected. For such peculiar behaviour of dislocations in semiconductors to be investigated, it is essential to observe the motion of individual dislocations microscopically.

Chemical etch-pitting is the method most commonly used to reveal dislocation sites on semiconductor surfaces and to measure the dislocation mobility by tracing the etch pits. In some cases, however, there is difficulty in finding a reproducible dislocation etchant suitable for a specific surface, and even if an etchant is available, it is troublesome or sometimes almost impossible to repeat the procedure of deformation and etching for the same specimen to measure the dislocation mobility.

For the past few years many studies have been made on observation of defects in semiconducting materials using a scanning electron microscope (SEM) with an electron beam-induced current (EBIC) and/or cathodoluminescence (CL) [1–11]. Etch pit and transmission electron microscope (TEM) studies have shown that the dark spots or lines observed in SEM–CL and SEM–EBIC micrographs correspond to individual dislocations [5, 9, 11–14]. In comparison with conventional techniques the SEM technique has the following advantages: (a) the SEM technique does not need a thinning process, which is essential for TEM observation; (b) the SEM–CL or SEM–EBIC technique has a resolution of ~ 1 μm, which is higher than that of X-ray topography (~ 10 μm) and, furthermore, the magnification can be changed over a wide range from a few tens to a few thousands times; and (c) SEM needs no special

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etchant as in the etch-pitting method nor does it need the decoration of dislocations with impurities or the selection of the orientation of the surface to be investigated. Merit (a) enables us to estimate reliable values of the applied stress which are necessary to obtain dislocation mobility data. Merit (b) makes it possible to pursue the development of the dislocation distribution during deformation of specimens up to relatively large plastic strains. Merit (c), the non-destructive nature of SEM, further allows us to make a continuous observation of dislocation motion on the same specimen.

One of the aims of the present report is to describe an application of the SEM to an *in situ* study of dislocation motion in semiconductors by use of a deformation apparatus installed in the microscope chamber. Another aim is to describe characteristics of the motion of dislocations in II_b–VI_b semiconducting compounds to give an insight into the photoplastic effect i.e. the reversible hardening caused by illumination with light, observed in these crystals [15]. In the present work, CdS and CdTe single crystals were used. Since a p–n or a Schottky junction, which must be fabricated on the specimen surface, in the case of observation with the EBIC mode, might affect the motion of dislocations, only the CL-mode was employed in the present investigation.

2. Experimental procedure

CdS specimens were prepared from a vapour-phase grown ultra-high purity grade n-type ingot purchased from Eagle-Pitcher Co. Ltd (undoped, $n = 2.5$ to $25 \times 10^{21}\ m^{-3}$, $\mu_e = 0.25\ m^2\ V^{-1}\ sec^{-1}$), and CdTe fron an n-type ingot grown by the Bridgman method in the authors' laboratory (undoped, $n = 4.5 \times 10^{20}\ m^{-3}$, $\mu_e = 0.11\ m^2\ V^{-1}\ sec^{-1}$).

Plate-shaped specimens of $\sim 0.5\ mm \times 3\ mm \times 7\ mm$ for bending deformation were cut using a multi-wire saw, then mechanically polished with lapping film and finally chemically polished with concentrated H_3PO_4 at 573 K followed by a rinse with $H_2O(50\ cm^3) : H_2SO_4\ (20\ cm^3) : K_2Cr_2O_7(6.5\ g)$ at 373 K for CdS and with the E-reagent [16], $H_2O(10\ cm^3) : HNO_3(5\ cm^3) : K_2Cr_2O_7(2\ g)$, at room temperature for CdTe. The duration of chemical polishing was determined by monitoring the lapping damage with the SEM–CL micrographs and it was found that 2 to 3 min were sufficient in both crystals. The specimen must be optically flat to avoid fictitious contrast in SEM micrographs due to unevenness of the surface.

CdS crystallizes in the wurtzite lattice and CdTe in the zinc-blende lattice. Because of the polarity of AB compounds along the [0 0 0 1] or ⟨1 1 1⟩ axes, there are two types of edge dislocations, α- and β-dislocations in which the extra half plane of the dislocation, if assumed to be a shuffle set (regardless of the actual core structure [17–19]), ends on a row of A atoms or B atoms, respectively. In the case of hexagonal CdS, glide dislocations were further classified according to the slip system, i.e. basal slip or prismatic slip.

In the present work, for CdS crystals α- and β-dislocations on the basal plane (orientation No. 1 in Fig. 1 and Table I), screw dislocations on the basal plane (orientation No. 2) and mixed (edge component is dominant) dislocations on the prismatic plane (also orientation No. 2) were examined; for CdTe crystals, edge (both α- and β-) dislocations (orientation No. 3) and screw dislocations (orientation No. 4) on the (1 1 1) plane were examined.

For *in situ* observation of dislocation motion, two types of apparatus were used to deform the specimens, as shown in Fig. 2: (a) for constant strain rate testing a SEM-U3 (JEOL Ltd) was used and (b) for constant stress test (creep test) a CSM-501 (Comtec Inc.) was used. The former type was used for CdS and the latter for CdTe. The plate specimens were placed between the upper and lower edges and subjected to deformation in the four-point bending mode. A combination of a motor and gears in the case of (a) or a moving coil in a speaker magnet in the case of (b) drove the lower edges upwards with respect to the upper edges fixed in the chamber. The load applied to the specimen could be controlled by adjusting the electric current through the motor or the moving coil, the latter allowing us to apply stress pulses of short duration down to 1 msec on the specimen. The edges could be heated up to 550 K using an electric heater wound around the edge support.

The tension surface was examined using the SEM operated at 10 to 30 kV with an electron beam diameter of 0.5 to 1.0 μm and an electron beam current of 10^{-7} to 10^{-6} A. The excited cathodoluminescence from the specimens was collected by an optical system consisting of two concave mirrors shown in Fig. 2 for case (b) or

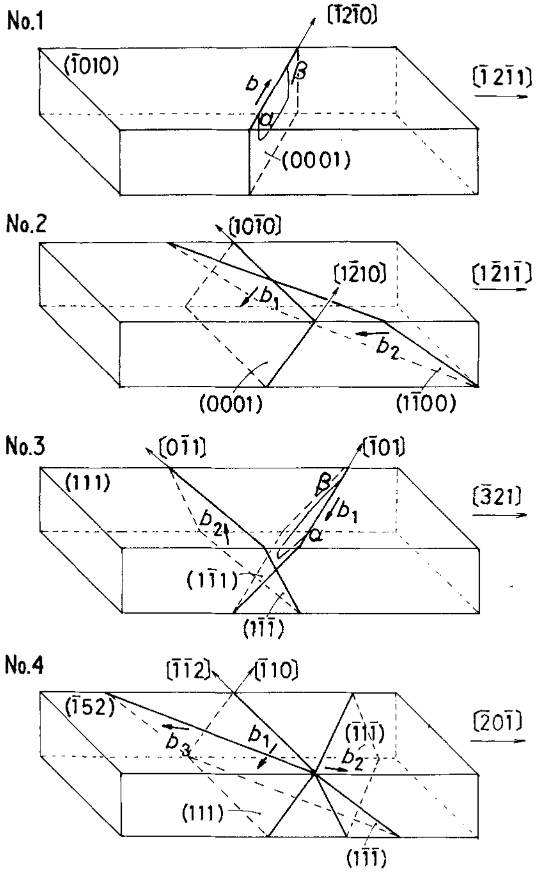

Figure 1 Orientations of bent specimens; 1 and 2 are for CdS and 3 and 4 for CdTe.

simply by an optical pipe directly contacted with the head of a photomultiplier for case (a). The light signal was detected by photomultipliers R268 (300 to 650 nm, max 450 nm) for CdS and R316 (S-1 type) (400 to 1200 nm max 800 nm) or R712 (185 to 900 nm, max 650 nm) for CdTe. In a previous paper [20] by two of the present authors it was reported that electron-beam irradiation can affect the dislocation motion in a similar way to the photoplastic effect. However, if the electron beam intensity is low enough, this "cathodoplastic effect" has been found to be negligible, and continuous observation is possible without being affected by the electron beam irradiation. In the present experiments, for the study of the effect of light illumination, the load was applied only while the beam was turned off.

3. Results

A general feature of SEM–CL micrographs after plastic deformation is exemplified for CdTe (Fig. 1, orientation No. 3) in Fig. 3 exhibiting dark stripes which lie in the crystallographic directions. These dark stripes correspond well to the slip traces expected from a geometrical consideration of the possible slip systems for this orientation. Rotating the specimen with respect to the photodetector confirmed that the contrast of the dark stripes is not associated with the slip steps on the step surface; in fact dark stripes were still observed for the slip system $a/2\ [\bar{1}\,0\,1]\ (1\,\bar{1}\,1)$ which has a Burgers vector parallel to the specimen surface and hence does not give rise to steps.

When the spacings between the spots were larger than the resolution of the microscope, the dark stripes were resolved to dark spots lying along the slip traces as seen in the enlarged photograph in Fig. 3b. As deformation proceeded the dark spots increased in number and grew to the dark stripes. Fig. 4 shows a sequential increment of dark spots on the CdS crystal surface (Fig. 1, orientation No. 1) which is oriented to observe edge dislocations on the basal plane. There seems to be a dislocation source below the field. It should be noted that most of individual dark spots did not change their positions while the number increased. This is the case with the dark spots

TABLE I

Crystal	Orientation	Slip system	Dislocation observed
CdS	Number 1	$b = (a/3)[\bar{1}\,2\,\bar{1}\,0]\ (0\,0\,0\,1)$	Edge dislocation on basal plane
CdS	Number 2	$b_1 = (a/3)[\bar{1}\,2\,\bar{1}\,0]\ (0\,0\,0\,1)$	Screw dislocation on basal plane
		$b_2 = (a/3)[1\,1\,\bar{2}\,0]\ (1\,\bar{1}\,0\,0)$	Mixed dislocation on prismatic plane
CdTe	Number 3	$b_1 = (a/2)[1\,0\,\bar{1}]\ (1\,\bar{1}\,1)$	Edge dislocation
		$b_2 = (a/2)[1\,0\,1]\ (1\,\bar{1}\,\bar{1})$	Mixed dislocation
CdTe	Number 4	$b_1 = (a/2)[\bar{1}\,\bar{1}\,0]\ (1\,1\,1)$	Screw dislocation
		$b_2 = (a/2)[\bar{1}\,\bar{1}\,0]\ (\bar{1}\,1\,\bar{1})$	Mixed dislocation
		$b_3 = (a/2)[1\,0\,1]\ (1\,\bar{1}\,\bar{1})$	Edge dislocation

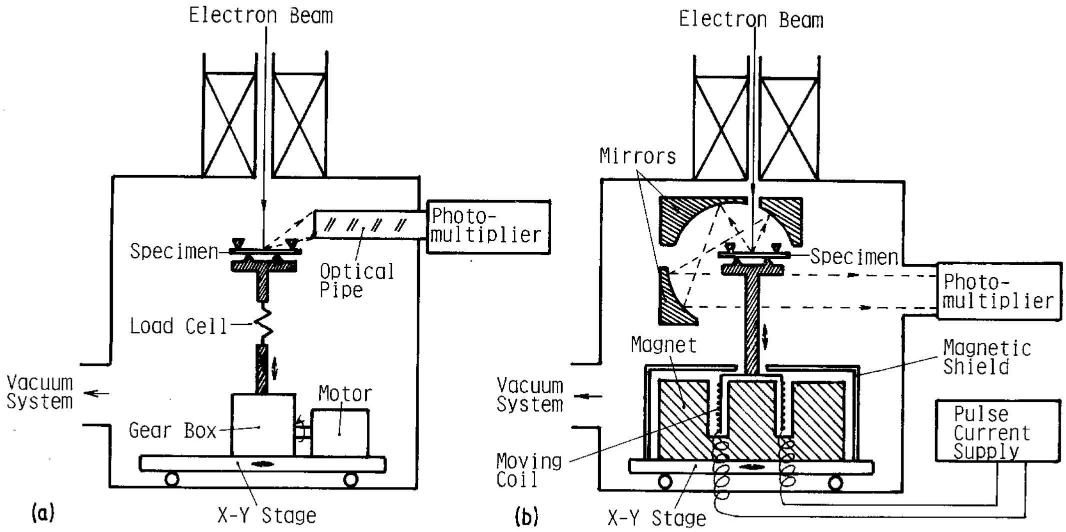

Figure 2 Schematic illustration of apparatus for *in situ* observation of dislocation motion in the SEM (a) is for JOEL-U3 and (b) for CSM-501.

obtained on all the specimens investigated in the present study. Such behaviour of the dislocations is unusual for semiconducting crystals; in Si, Ge and III_b–V_b compounds chemical etch pits corresponding to dislocations change their positions as the specimens are stressed with a sufficient load. However, it still happened that some of the dark spots disappeared, as indicated by arrows in Fig. 4.

Since we could not recognize the moving state of dark spots, probably due to high velocities, it was not possible to obtain the dislocation mobility by tracing the individual dislocation motions. Nevertheless, when the top of the stripes or the leading dislocations in the stripes could be well defined, the velocity of slip-band growth could be investigated by tracing the slip band lengthening in a similar way to that often used in dislocation mobility measurements.

Fig. 5 shows the sequence of growth of a slip band on the CdS specimen (Fig. 1, orientation

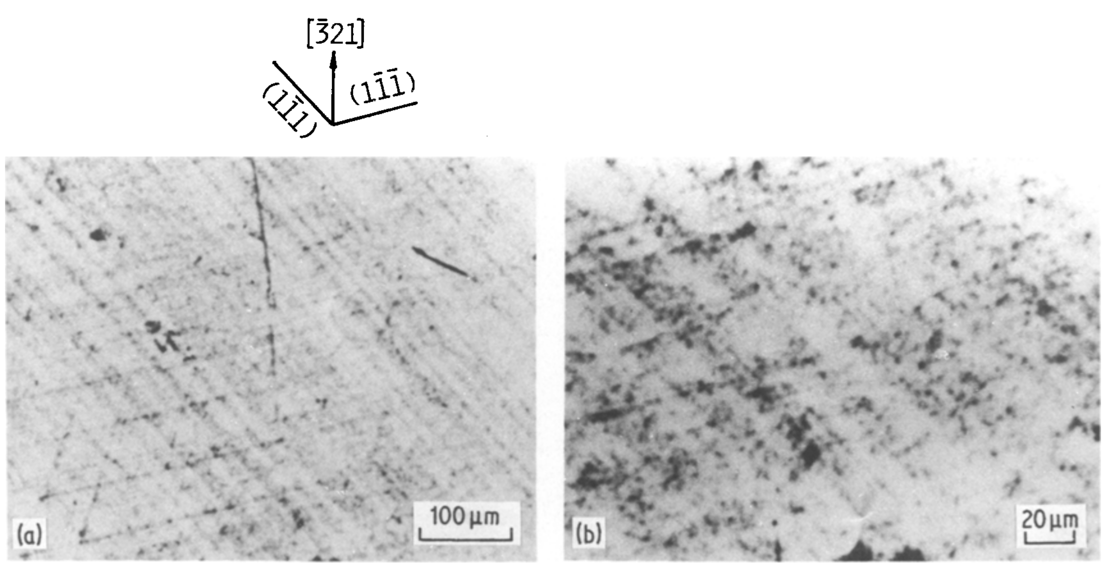

Figure 3 SEM-CL micrographs of CdTe specimen (Fig. 1, orientation No. 3) deformed at room temperature, (b) is a magnification of a part of (a).

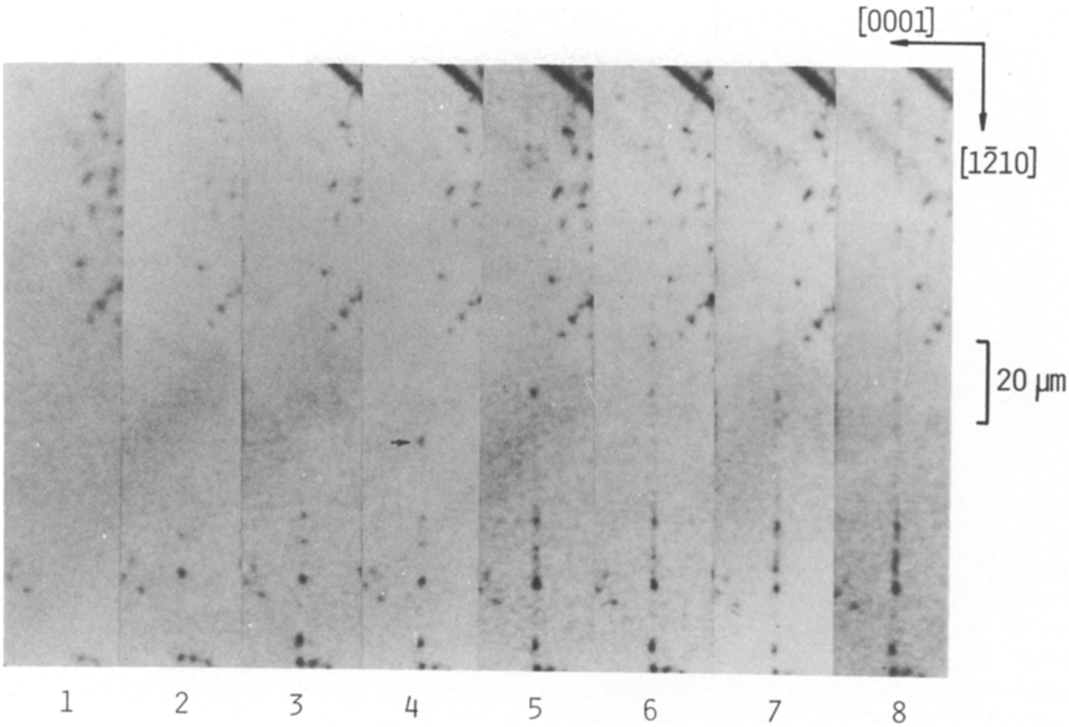

Figure 4 Sequential development of dark spots along a slip trace in CdS (Fig. 1, orientation No. 1) deformed at 345 K and with tensile surface stress $\sigma_s = 18\ \text{MN mm}^{-2}$.

No. 2) oriented to observe screw dislocations on the basal plane. Dark spots were generated at several places, then increased in number along the slip traces, thickened the width perpendicularly to the bands and grow until the bands overlapped with each other.

In Fig. 6 the travelling distances of the top of several different slip bands are plotted as a function of the loading time. In order to examine the effect of light illumination, the specimen was kept in darkness at an early stage of deformation, then illuminated with visible light and again kept in darkness. The growth rate or the slope of the curves changed according to whether the specimen was illuminated or not: the growth rate of the slip bands was suppressed by illumination of light as expected from the macroscopic photoplastic effect. It should be noted, however, that even under illumination some of the slip bands grew at almost the same rate as that in darkness.

An effect of light illumination on the growth of slip bands was also investigated for the CdS specimen (Fig. 1, orientation No. 2) oriented to observe mixed dislocations on the prismatic plane. In this orientation no appreciable effect of light illumination on the growth rate of the slip band was observed.

Fig. 7 shows the growth of α-dislocation bands (filled points) and screw dislocation bands (open points) in the CdTe specimens (Fig. 1, orientation No. 4). The growth of β-dislocation bands is not shown in the figure because the growth rate was too low to be measured compared with the other two types of slip bands. The investigation of growth rate of the dislocation bands on the basal plane in CdS for orientation No. 1 in Fig. 1 was not very successful because the top of the slip bands could not be well defined. However, a rough estimate showed that the growth rate of the edge dislocation bands was more than three times higher than that of the screw type.

4. Discussion

It has been established by many studies that dark spots observed in SEM micrographs correspond to individual dislocations [5, 9, 11–14]. The present observation that some of the dark spots disappeared after application of stress provides additional evidence for the identification of the dark spots with dislocations. Dark spots in SEM–CL micrographs associated with dislocations introduced by plastic deformation have so far been observed in GaP [7] and GaAs [8]. The deformation temperature employed in these studies was

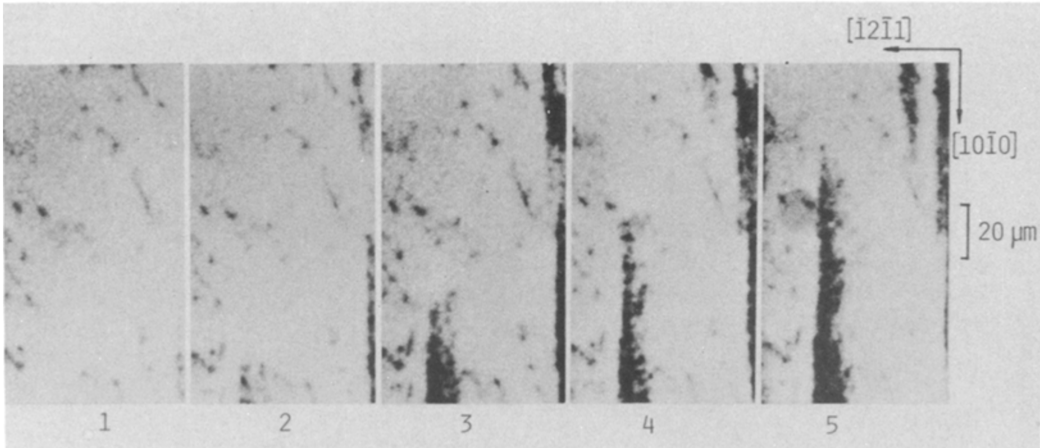

Figure 5 Growth behaviour of slip bands in CdS (Fig. 1, orientation No. 2) deformed at 345 K and $\sigma_S = 16$ MN mm^{-2}.

so high (973 K) that the possibility of decoration of dislocations with impurities could not be ruled out. In the present study, however, the deformation temperatures were so low (from room temperature for CdTe to 380 K for CdS) that long-range diffusion of impurities to decorate dislocation lines was unlikely to take place. Therefore, it is probable that the dark spots introduced by deformation, regardless of whether moved or not in the later stage, were all associated with fresh dislocations. This result also means that decoration with impurities is not necessary for dislocations to be revealed as dark spots in SEM–CL micrographs.

Although attempts to observe the dynamical motions of dislocations were not successful, there still remains a possibility that the present technique may be applied to following the motion of dislocations with a high velocity if one makes use of a high-speed video scan. In order to do this it is necessary to achieve a high signal to noise (S/N) ratio which is essential to obtain clear contrast. The S/N ratio could be improved by increasing the intensity of the electron probe beam; however, it should be kept in mind that this cannot be done immoderately because of the cathodoplastic effect that might be brought about by the irradiation of intense electron beams. An alternative way to enhance the contrast was found to be to focus the electron beam as small as possible with the total intensity being fixed, which optimizes the resolution as well. This would be achieved partly by

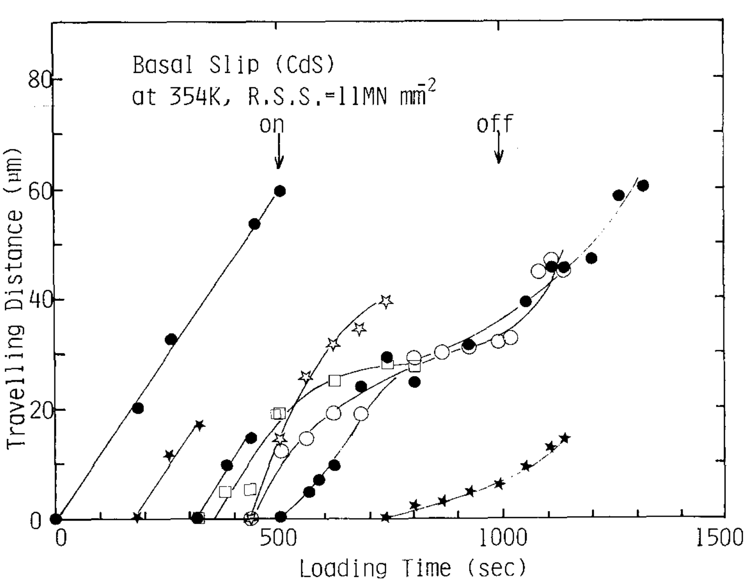

Figure 6 Growth of slip bands of screw type on the basal plane of CdS (Fig. 1, orientation No. 2) as a function of loading time.

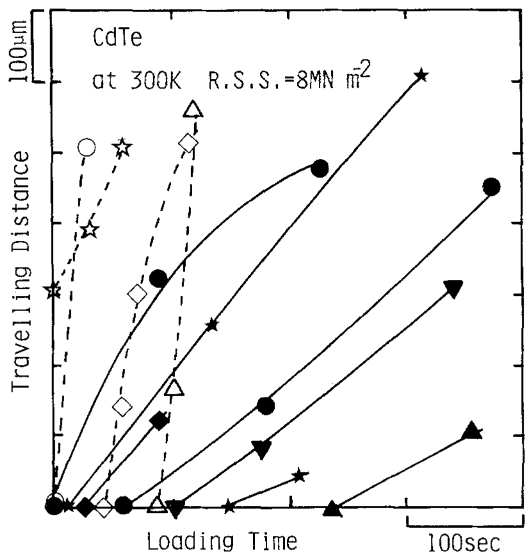

Figure 7 Growth of slip bands of screw type (solid lines) and of α-edge type (broken lines) in CdTe (Fig. 1, orientation No. 4).

making the working distance shorter than the present value of 30 mm, though some modification in the light collecting system would become necessary.

The characteristic feature of the motion of dislocations in CdS and CdTe single crystals is that most of the dislocations are immobilized after they have travelled a certain distance from their sources. Such behaviour seems to be in common with other II_b–VI_b compounds, since similar behaviour of dislocations has also been found in ZnSe [21]. On the other hand, the small activation volumes experimentally estimated, $\sim 30\,b^3$ for CdS [21] and several b^3 for CdTe [22, 23], suggest that the Peierls mechanism is operating in the thermally activated motion of dislocations. This was further confirmed by *in situ* observation of dislocation motion in CdTe and CdS by TEM [24]. Such facts may appear to be inconsistent with the result of the present SEM–CL study where no such smooth motion of dislocations was observed as expected from the Peierls mechanism. This contradiction is not serious however, if one considers the difference in the distance scale of dislocation motion investigated by the two methods; the dislocation motion observed in TEM studies at the distance scale of several microns is considered to be a direct manifestation of the thermally activated dislocation motion on an atomic scale; whereas, the dislocation motion observed in the SEM–CL study is in the intermediate distance scale and rather directly related to the macroscopic plastic behaviour, which is not necessarily determined by the short-range velocity of individual dislocations.

Thus, it is not quite appropriate to regard the growth rates of the slip bands simply as the mobilities of individual dislocations, which is sometimes assumed in the dislocation mobility measurements. Instead they should be regarded as representing microscopic strain rates borne by the individual slip bands. Since the slip bands have their own character depending on the slip system and the type of dislocations involved, it is still possible by the present method to discriminate the contribution of a specified system to the macroscopic deformation from those of others. For example, the effect of light illumination could be investigated separately for the different slip system, as demonstrated by the present results, where the effect of light illumination of CdS was observed on those of the basal system with screw dislocations but not on the slip bands of the prismatic system. This observation is in accordance with the macroscopic deformation tests conducted by Osip'yan and Savchenko for CdS [25], where the crystals oriented to prohibit basal slip did not show the photoplastic effect.

A recent *in situ* observation of dislocation motion by TEM [24] showed that dislocation motion in the TEM scale is not affected by light illumination. This observation rules out the assertion that the cause of the photoplastic effect is the decrease of the individual dislocation mobility due to illumination by light. Another observation that the photoplastic effect is drastically reduced in small-size specimens [26] suggests an important role for the dislocation mean free path which can be affected by light illumination. In the present investigation, on the other hand, it was frequently observed that the slip bands grew in length in a jerky manner and then the dispersed dark spots were bridged with more spots. If the growth rate of a slip band is equal to a creation rate of dislocation sources (probably formed by double cross-slips) along the slip bands times the dislocation mean free path, it would also be affected by light illumination through a change in the mean free path. Concerning the mechanism of the photoplastic effect, details will be described elsewhere [27].

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