JOURNAL OF MATERIALS SCIENCE 16 (1981) 1167–1170

Dislocation activity in single crystal HgI_2

TIMOTHY W. JAMES*, FREDERICK MILSTEIN
Department of Mechanical and Environmental Engineering, University of California, Santa Barbara, California 93106, USA

An etchant of 5% alcohol in trichloroethylene (TCE) allows greater resolution of dislocation etch pits in vapour-grown single crystals of HgI_2 than the "traditional" alcohol etches. The improved etchant has made possible the identification of etch pits, on the (0 0 1) faces of single-crystal HgI_2, that are associated with dislocations on {1 0 0}-type slip planes. The evidence for this conclusion includes (a) the geometric and crystallographic features of the etch pits, (b) the manner in which they are induced by deformation, and (c) their regularity in passing through the crystal, perpendicular to the (0 0 1) plane.

1. Introduction

In recent years there has been considerable interest in mercuric iodide (HgI_2) for applications as a room-temperature nuclear radiation detector [1–3]. Although it is well known that electronic properties of semiconductors are very sensitive to crystal defects, relatively little work has been done to characterize the nature of dislocations in HgI_2. A number of authors [4–7] have observed etch pits on the (0 0 1) surface of HgI_2 single crystals by using various alcohol etches; the pits have been attributed to the presence of dislocations. In the present work we have been able to delineate etch pits more clearly on the (0 0 1) surface owing to the development and application of an improved etchant, consisting of 5% alcohol in trichloroethylene (TCE). Comparison of the pits formed after alcohol etches with those formed after etching in the improved etchant, 5% alcohol in TCE, suggests that the former do not result from single dislocations, but instead occur at the intersections of two perpendicular arrays of dislocations. Furthermore, as a direct consequence of the new etching techniques, it has been possible to clearly demonstrate that there are etch pits on the (0 0 1) surface of HgI_2 that are associated with dislocations, based on their motion under deformation. (Dislocation motion could not be observed using the alcohol etches employed by earlier investigators.)

Ponpon *et al.* [4] observed etch pits on the (0 0 1) face of vapour-grown HgI_2 single crystals. Their etching technique consisted of solution polishing using a 20% KI aqueous solution and then etching for a few minutes with either methanol or ethanol alcohol. They reported dislocation densities of the order of $10^4 cm^{-2}$. In 1975, Schieber [5] observed etch pits on both (1 1 0) and (0 0 1) as-grown faces of vapour-grown crystals. The etchant used was 2% bromine in ethanol. Defect densities were reported to be in the range of 10^3 to $10^7 cm^{-2}$. Randtke and Ortale [6] observed etch pits on the (0 0 1) face of vapour-grown HgI_2 (using ethanol as an etchant) and reported dislocation densities of the order of 10^3 to $10^6 cm^{-2}$. Nicolau and Joly [7] observed square etch pits on the (0 0 1) face of HgI_2 single crystals grown from DMSO solutions and associated the pits with screw dislocations normal to the (0 0 1) face. They also observed etch pits on the (0 1 1) and (1 1 0) faces. The former were attributed to the same dislocations that are seen on the (0 0 1) face and the latter to edge dislocations.

2. Experimental techniques

The single crystals used in the present study were

---

*This work is based upon part of the Ph.D. dissertation of T. W. James.

0022–2461/81/051167–04$02.40/0

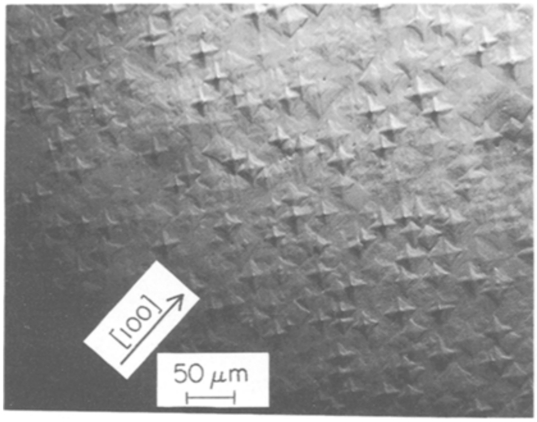

Figure 1 An example of etch pits produced by a 5 second etch with 100% methanol on a (0 0 1) face of HgI_2. Similar results are obtained with 100% ethanol etches.

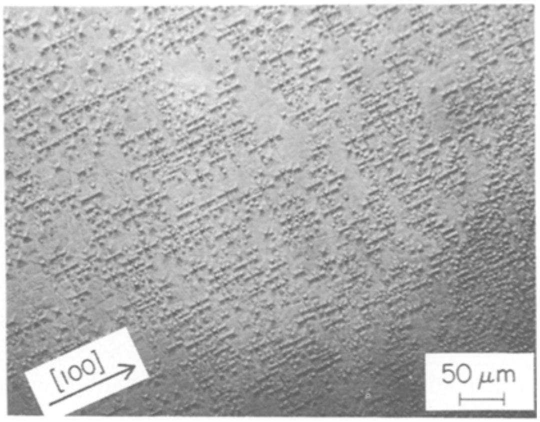

Figure 2 An example of the etch pits produced on the (0 0 1) face using the 5% ethanol–95% TCE etchant. The photomicrographs shown in Figs 1 and 2 were taken at the same magnification and in the same region of the (0 0 1) face of the same single crystal.

vapour-grown by W. F. Schnepple and L. van den Berg† using the temperature oscillation method [1, 8]. Before etching, the crystals were cleaved parallel to the (0 0 1) surfaces. In our initial work, chemical solution etching was performed using both methanol and ethanol at room temperature. However, it was found that these etchants acted very quickly (with etching times of less than 10 sec). This prompted a search for a more controllable etchant that would not attack the crystal as rapidly. The combination of 5% ethanol/95% TCE was selected after experimenting with a variety of etchants (e.g. acids, bases, salt solutions, aqueous alcohol solutions). The alcohol–TCE solution can be applied effectively with a cotton swab held on the surface of the crystal or by immersing the specimen in solution for approximately 10 seconds. The etch pits were observed using an oblique illumination metallurgical microscope with magnifications in the range × 50 to × 200.

Figs 1 and 2 illustrate the difference between the results of the alcohol etches and the dilute alcohol–TCE etch. The photomicrographs in these figures were both taken at the same magnification and in the same region of the (0 0 1) face of a particular single crystal. Specifically, a cleaved region of a (0 0 1) face was etched with alcohol and Fig. 1 was taken; the (0 0 1) surface layer was then cleaved again, the freshly cleaved surface was etched with the TCE solution and the pattern of Fig. 2 was then observed. This process was then repeated several times, alternating between the alcohol etch and the TCE solution etch; in each case, the former gave the results of Fig. 1 and the latter the results of Fig. 2. It is readily apparent that the straight alcohol etches produce an over-etched condition in a very short period of time. The alcohol–TCE etch reveals many individual, closely spaced, etch pits (which we associate with dislocations) existing in intersecting line patterns. By comparison, after an alcoholic etch, large individual pits appear in place of such pairs of line patterns. The TCE diluted etchant always produced a properly etched surface after about 15 seconds. We presume that in previous studies, where straight alcohol etches have been employed, the crystal surfaces were like-wise heavily etched; Fig. 9 of [7] shows an example of such a surface.

The crystallographic orientation of individual pits on the (0 0 1) faces was determined by etching a fresh, as-grown crystal which had large and easily identifiable (0 0 1) and (1 1 0) growth faces.

3. Results and discussion

The TCE etchant was used to examine the (0 0 1) faces of many different vapour-grown single crystals. Since this etchant provided greater resolution than the previously used alcohol etchants, it was possible to reveal microstructural features that have not previously been observed.

In the present study, the etch pits on the

---

† At E.G. and G., Inc., Santa Barbara Operations, Goleta, CA, USA.

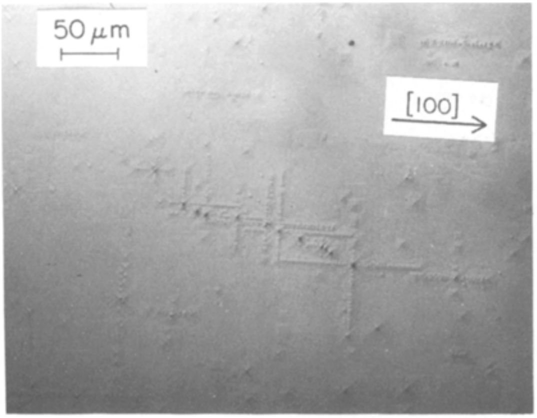

Figure 3 An example of intersecting linear arrays of etch pits associated with (approximately) centrally located darker pits. The linear arrays extended from the darker pits, forming crosses that are aligned with the [1 0 0] and [0 1 0] crystallographic axes.

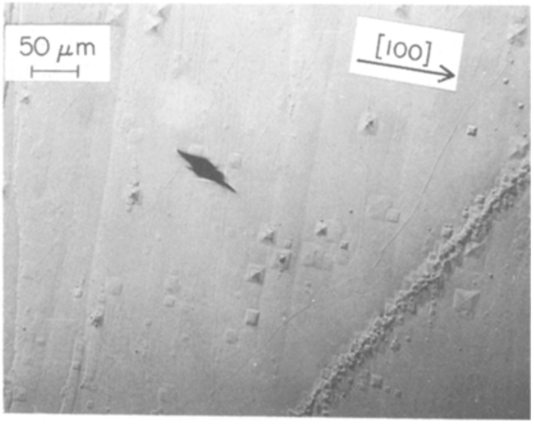

Figure 4 Knoop microhardness indentation made on an etched (0 0 1) face of low dislocation density HgI_2. The band of dislocations passing diagonally across the lower right hand corner results from the cleavage process.

(0 0 1) surfaces were found to be square with their edges parallel to the ⟨1 0 0⟩ directions (in agreement with earlier investigations [4–7]). The size of the pits varied from about 1–15 μm; the pit density varied from about 10^2–$10^5\,cm^{-2}$. The pits occurred either individually (in a random distribution) or in linear arrays that are aligned with the ⟨1 0 0⟩ directions. For reasons to be discussed below, the linear arrays of etch pits are interpreted as resulting from dislocations on slip planes that intersect the (0 0 1) surface in ⟨1 0 0⟩ directions. (By contrast, the pits observed after the alcohol etches were always randomly distributed.) A commonly occurring feature is illustrated in Fig. 3; here, pairs of linear arrays are seen to be extending (in [1 0 0] and [0 1 0] directions) from centrally located defects that appear as darker spots at the locations of the intersections of the arrays. These darker spots generally coincide with intersections of curvilinear distributions of micrometre-sized inclusions that pass through (and are visible in) the interior of the crystal. Such inclusions have been reported in vapour-grown HgI_2 crystals by Schieber *et al.* (Figs 10–13 in [9]).

In order to investigate further the specific nature of the linear arrays of etch pits visible in Figs 2 and 3, the effect of deformation by microhardness indentation on the (0 0 1) surface was examined. In particular, it was sought to determine whether or not such arrays could consist of mobile dislocations resulting from crystallographic slip. The results of these investigations are illustrated in Figs 4 and 5. Fig. 4 shows the region of a crystal that was cleaved on a (0 0 1) plane, etched with 5% alcohol in TCE (in order to reveal the initial etch pit locations), and deformed with a 10 g Knoop microhardness indentation. Fig. 5 shows the same region of the same crystal, but after a final alcohol–TCE etch (in order to reveal changes in etch pit locations resulting from the indentation). In Fig. 5, linear arrays of etch pits protrude, in ⟨1 0 0⟩ directions, from the indentation. These etch pits can clearly be interpreted as dislocations that were introduced by the indentation, i.e. plastic deformation, and are present on slip bands that intersect the (0 0 1) planes in the ⟨1 0 0⟩-type directions. Similar conclusions have been drawn from etching–deformation studies of

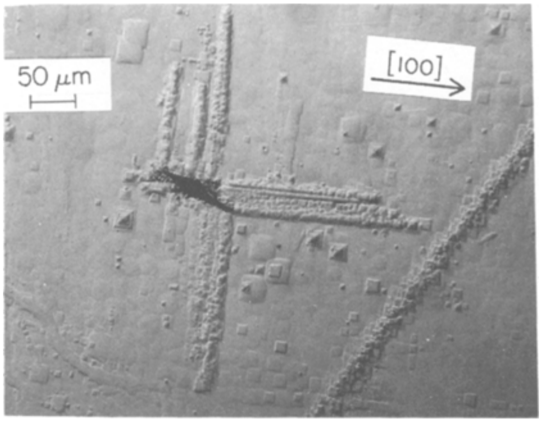

Figure 5 The same Knoop microhardness indentation as that shown in Fig. 4, re-etched after indentation in order to show changes in dislocation structure occurring as a result of the indentation.

single crystals of MgO [10] and LiF [11]. While these results do not show conclusively that the linear arrays of defects in Figs 2 and 3 are mobile dislocations, the comparison with such arrays in Fig. 5 is highly suggestive.

In addition, experiments were carried out in which the (0 0 1) surface was progressively etched deeper and deeper. This procedure did not result in any substantive change either in the shape of the etch pits or in their positions (e.g., relative to the indentation in Fig. 5), showing, first, that the defects that cause the etch pits exist on {1 0 0} planes and, second, that they are perpendicular to the (0 0 1) surface. (The latter conclusion is also consistent with the etch pits being square rather than rectangular.)

In summary, owing to improved etching techniques, it has been possible to identify etch pits on the (0 0 1) faces of single crystal HgI_2 that are associated with dislocations on {1 0 0}-type slip planes. The evidence for this conclusion includes (a) the geometric and crystallographic features of the etch pits, (b) the manner in which they are induced by deformation, and (c) their regularity in passing through the crystal, perpendicular to the (0 0 1) plane.

Acknowledgement

The authors are very grateful to E.G. and G., Inc., Santa Barbara Operations, Goletta, CA, for supplying the single crystals used in the present study and for a research grant that supported this work. We wish to express particular appreciation to Dr M. Schieber, Dr L. van den Berg, Mr. W. Schnepple and Mrs. C. Ortale for many helpful discussions and invaluable assistance.

References

1. M. SCHIEBER, W. F. SCHNEPPLE and W. VAN DEN BERG, *J. Crystal. Growth* **33** (1976) 125.
2. M. SCHIEBER, *Nucl. Inst. and Methods* **144** (1977) 469.
3. R. C. WHITED and M. M. SCHIEBER, *ibid.* **162** (1979) 113.
4. J. P. PONPON, R. STUCK, P. SIFFERT, B. MEYER and C. SCHWAB, *IEEE Trans. Nuc. Sci.* **NS-22** (1975) 182.
5. M. M. SCHIEBER, in Proceedings of the Workshop on Mercuric Iodide Nuclear Radiation Detectors, Centre de Recherches Nucléaires, Strassbourg, June 11, 1975, edited by P. Siffert, J. P. Ponpon, I. Zschokke-Granacher and B. Schwab.
6. P. T. RANDTKE and C. ORTALE, *IEEE Trans. Nuc. Sci.* **NS-24** (1977) 129.
7. I. F. NICOLAU and J. P. JOLY, *J. Crystal Growth,* to be published.
8. H. SCHOLZ, *Akta Electronica* **17** (1974) 69.
9. M. SCHIEBER, I. BEINGLASS, G. DISHON and A. HOLZER, in "Crystal Growth and Materials", edited by E. Kaldis and H. J. Scheel (North-Holland Publishing Co, 1977) Chap. 1; 8.
10. A. S. KEH, *J. Appl. Phys.* **31** (1960) 1538.
11. W. G. JOHNSTON, in "Progress in Ceramic Science" Vol. 2, edited by J. E. Berke (Pergamon Press, Oxford, 1962) Chap. 1.

Received 14 August and accepted 15 September 1980.