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# Deformation and fracture of germanium single crystals

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Diamond-pyramid indentations, made with loads of 1 to 100 g at room temperature on {111}, {110} and {112} faces of germanium crystals, were studied by scanning electron microscopy. The Vickers-hardness number, which was highest for {111} faces, increased with the square root of the load by a factor of about 10 on any given surface, ranging from values as low as 60 to about 850, the latter corresponding to the VHN reported in the literature. The lengths of major cracks, generally seen on the surface of the crystal as an extension of the indentation diagonals, were found to be proportional to $d - d_0$, where $d_0$, equal to about 3 μm, represents a lower limiting value of the indentation diagonal $d$, below which cracks do not seem to form. The increase of the VHN and of the crack-lengths with load is explained in terms of a tentative model involving the formation and the stress-induced growth of laminar "plastic" patches in a volume surrounding the indentation.

## 1. Introduction

Below a certain temperature, which in the case of germanium is about 300°C [1-3], crystals with the diamond or sphalerite structures are generally regarded as brittle. Although the differentiation between brittle and plastic behaviour lacks precision [2], the former is characterized by the rather limited mobility of dislocations and a relatively low temperature-dependence of the hardness as conventionally determined. Dislocations, if formed, tend not to move over significant distances, and the defect structures with which they are associated remain spatially confined, and are difficult to resolve by microscopy, e.g. on using etch-pit methods. Consequently, most studies of the micro-plasticity of such crystals have been restricted to the "plastic" region, at relatively high temperatures, e.g. in the early work of Churchman *et al.* [4] on Ge, Si, GaSb and InSb, in the more recent studies of Eremenko and Nikitenko [5] on Si, and in that of Wagatsuma *et al.* [6] on Ge.

Although at room temperature cracking at the base of diamond-pyramid indentations is observed in silicon even at loads as small as 2 g [5], there is evidence of the occurrence of damage, other than cracks, in a volume of linear dimensions several times larger than that of the "plan" of the indentation. This observation, based on the use of the Borrmann effect [6], supports the inference advanced by M. E. Fine in the discussion of the paper by Sumino and Hasegawa [2] on germanium that, as a well-defined hardness-impression is left after an indentation test, some dislocation movement must have taken place to account for the implied plastic deformation.

The principal object of the present work was to re-examine the problem of the low-temperature plasticity of germanium, in particular to study the topography near indentations, made with a wide range of loads, by means of scanning electron-microscopy, to investigate the hardness of different crystal "faces", and to search for a possible dependence of the Vickers-hardness number (VHN) on the load applied to the indentor.

The possibility that the VHN of germanium crystals may be load-sensitive is suggested by measurements of the VHN in the range 20 to 300°C included in the results of Sumino and Hasegawa [2], which show a trend towards lower hardness-values with the smallest loads used by them (50 g), compared with the VHNs obtained with 100 and 300g loads. In any case, with the complex process of deformation and cracking, known to accompany indentation of germanium in the brittle range, independence of the VHN on load could not be assumed *a priori*. Any significant dependence, if clearly established, was considered to be of potential diagnostic value in the elucidation of the "micro-plastic" processes in germanium, as well as in other materials with a similar crystal structure.

## 2. Experimental method and results

The germanium crystals used in the experiments came from the same batch as those described in [7]. They were Sb-doped, with $7 \times 10^{13}$ donors per $cm^3$, with an initial dislocation density of $3 \times 10^3$ $cm^{-2}$, and measured $0.4 \times 0.4 \times 1.0$ $cm^3$. The rectangular sides were of $\{111\}$ and $\{112\}$ type, the square base of $\{110\}$.

The crystals were polished mechanically down to the finest diamond-paste finish, and about 1 μm of the surfaces to be indented was then removed by etching with CP-4. As an added precaution the crystals were further stress-relieved by heating them for 3 h at 600°C in a tungsten-wound refractory furnace in a vacuum of $10^{-5}$ Torr and then cooling them slowly *in situ*. The surfaces remained mirror-like, free from tarnish or discolouration. The good surface quality obtained in this manner is apparent from the areas around indentations viewed at magnifications of up to about 8000. (Figs. 1 to 3).

Indentations were made with a GKN micro-hardness tester at room temperature on the three crystallographically different surfaces shown in Fig. 4, and the VHN as well as the lengths of the diagonals of the indentations, and any cracks emanating from the centre of the indentation were measured, i.e. the lengths as appearing in projection on the crystal surface, allowance being made for any foreshortening in scanning electron micrographs.

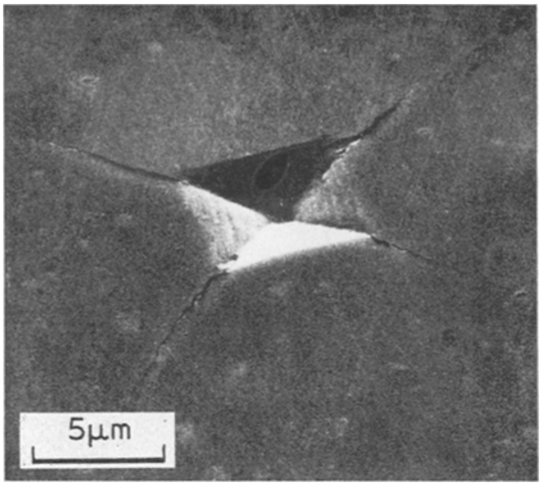


*Figure 2* Indentation of the $(1\bar{1}0)$ surface. $L = 30$ g.

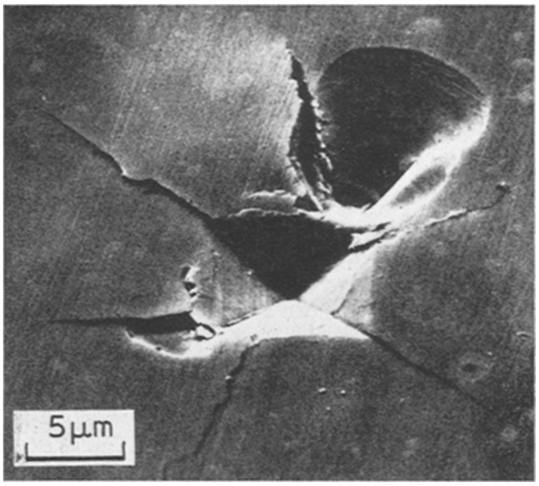


*Figure 3* Indentation of the $(1\bar{1}0)$ surface. $L = 100$ g.

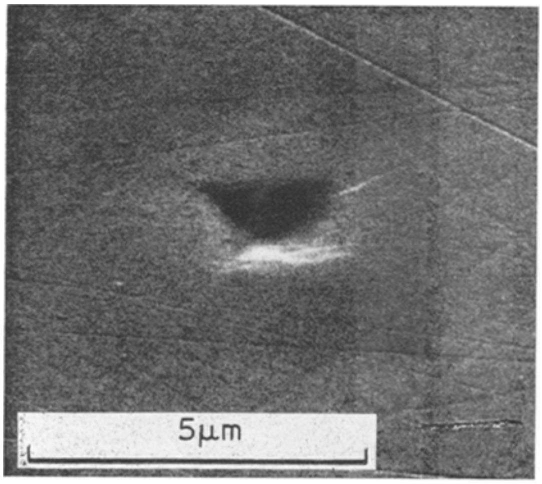


*Figure 1* Indentation of the (111) surface. $L = 1$ g.

The indentations sketched in Fig. 4 are assumed to refer to loads of 1, 3, 10, 30 and 100 g respectively. The pattern of indentation-alignment indicated for the (111) plane was also used on the $(11\bar{2})$ and $(1\bar{1}0)$ surfaces of the crystal, with the side "*a*" of the triangle parallel to the edges AB and BC respectively. Centres of neighbouring indentations were not less than 50 μm apart; tests with fully isolated indentations showed that with this separation parameters determined in the present study were not influenced by proximity effects.

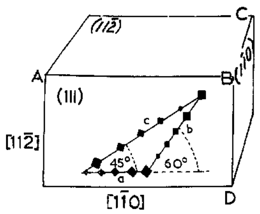


*Figure 4* Crystal planes indented, and the pattern of indentor orientations used, illustrated on the (1 1 1) plane only.

In Fig. 4 diagonals of indentations lying on the sides "*a*" and "*b*" of the triangle are parallel to traces of (1 1 1) cleavage planes; this would also be the case, for example, with indentations on the (1 $\bar{1}$ 0) face having diagonals parallel to the edge BD of the crystal. With similar variations of the indentor orientation, using however a rectangle-based Knoop pyramid, Chin *et al.* [8] detected a directional anisotropy of the Knoop hardness in ionic crystals having NaCl and fluoride structures. Although, in the present results, there appeared to be a tendency to lower hardness values for "cleavage" orientations of the indentor on all the faces, the effect was not sufficiently pronounced to establish its occurrence and magnitude unequivocally with the available data. The "points" in the correlation of the VHN with the length $d$ of the "projected" indentation diagonal, shown in Fig. 5, were drawn of sufficient size to encompass hardness variations arising from the use of the three indentor-orientations illustrated for the (1 1 1) plane by the triangle in Fig. 4.

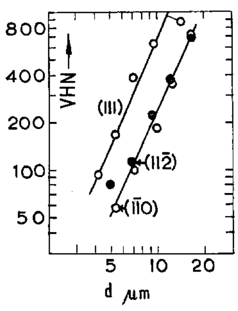


*Figure 5* Dependence of the VHN on the length $d$ of the projection of the indentation diagonal onto the crystal surface.

Relatively large cracks in the crystals, which appeared in micrographs as continuations of the diagonals of the indentations, were invariably present, except on using 1 g loads. In the latter case the indentation diagonal $d$, i.e. as projected onto the crystal surface, measured approximately 3 μm (Fig. 1). By contrast, with the high (100 g) load, cracks other than those seen to emanate from the indentation corners were also formed, and chipping was frequently observed (Fig. 3).

Step-like protuberances on the surface, close to the indentation, such as have been ascribed to micro-twinning [4] or to the formation of a new, martensitic, phase [5] in germanium indented above 300° C, were not detected. The (projected) crack-length, $c$, was in all cases taken equal to the distance between the "projected" apex of the indentation and the sometimes not-too-well-defined crack tip, generally as seen in scanning electron-micrographs. Results for all three crystal faces correlated well with the relation

$$c = d - d_0\,,\ d > d_0 \qquad (1)$$

over the entire range of indentation diagonals used, extending up to $d \approx 15$ μm. The limiting value of $d$, i.e. $d_0$, was about 3 μm, suggesting that with loads lower than about 1 g cracking at the indentation would not, as a rule, occur. Fig. 1 supports this conclusion.

## 3. Discussion

The VHN of germanium crystals, as determined by Sumino and Hasegawa [2] by indentation of {1 1 1} planes with loads of 50 to 300 g, is about 860 ± 40 kg mm$^{-2}$ at room temperature. Under similar conditions, using a 234 g load, Trefilov and Milman [3] obtained a value about 10% lower. These results are in reasonable agreement with the present VHN of 800 to 900 kg mm$^{-2}$ obtained with the highest loads used (100 g). It is also apparent from the tendency to "flattening" of the uppermost curve in Fig. 5, which appears to set in at the highest $d$-values, why the strong load-dependence of the VHN observed with rather low loads in the present work previously escaped attention. This load-dependence appears to be pronounced only in the "brittle" region, as may be inferred from the data of Sumino and Hasegawa [2], which cover the temperature range from about 20° C to close to the melting point of germanium. At temperatures within the "plastic" region the effect is absent or not pronounced; similar conclusions were reached by the present authors in preliminary work with InSb crystals in the range of 20 to 300°C [9].

The increase in the severity of cracking with increasing load, as indicated by Figs. 1 to 3, and the absence of evidence of other forms of damage resolvable with the available means, suggests that the plastic deformation referred to by Fine, and commented on above, consists of a distribution of "small", unresolved "plastic patches", distributed over a volume centred on the indentation, in which a limited amount of plastic deformation has taken place. The dominant form of the deformation process cannot be ascertained at present, i.e. whether it involves, for example, micro-twinning associated with the movement of partial dislocations, such as is known to lead to the formation of stacking-faults in germanium [10] and silicon [11], or to other variants of dislocation displacement and generation.

However, a phenomenological model of the plasticity, which takes into account the growth of plastic "patches" with the dimensions of the indentation and, through the linking up of such patches, could account indirectly, for the enhanced cracking under large indentor-loads will be outlined. It also involves the assumed formation of an envelope of distorted "plastic" material in a substantial volume around an indentation; as this envelope appears to grow in thickness with the depth of the indentation [6], the volume will be taken to be proportional to $d^3$.

We consider that an increment of work, $\delta W$, done by the indentor, expressed in terms of the instantaneous value of the diagonal, $d$, is proportional to the incremental change in the length of the diagonal, i.e.

$$\delta W \propto L(d)\,.\,\delta d\,, \qquad (2)$$

where $L(d)$ is the instantaneous value of the load, as it increases from zero to the final level $L$. Equation 2 is general; no specific functional form of $L(d)$ is assumed.

Further, if in a layer of thickness proportional to $d$, adjacent to the indentation, there are $N$ "dislocated" or "plastic" patches of constant thickness per unit volume, then the indentation will be surrounded by material containing a number of such patches proportional to $Nd^3$. If they are imagined to be penny-shaped, the diameter of each growing with the deformation, being proportional to $d$, also taking the energy of formation per unit area of patch to be constant, then the energy of formation of the patches will be proportional to $Nd^3\,.\,d^2$, i.e. to $Nd^5$. The patches can be regarded as crack embrya, and within the framework of the present, rather tentative model, cracks will be regarded as similar "patches". The fact that coarse cracking is observed only above a certain load suggests that a linking-up of "plastic" patches may, in fact, facilitate cracking at "large" deformations. If now an increment of this energy is equated to $\delta W$, as given by Equation 2, one has

$$\delta W \propto Nd^4\,.\,\delta d\,, \qquad (3)$$

and, on using the definition

$$\mathrm{VHN} = 2L/d^2 \qquad (4)$$

in conjunction with Equations 2 and 3, one finds that $L(d) \propto d^4$, and the

$$\mathrm{VHN} \propto d^n\,,\ n = 2$$

for the present model. A direct correlation of $L(d)$ with $d$, including all the experimental results except for the highest load (100 g) used on the (111) plane, yielded, in conformity with the slopes of the lines in Fig. 5,

$$n = 2.1 \pm 0.2\,, \qquad (6)$$

which agrees quite well with the requirement of the model. Equations 3 and 4 also show, on eliminating $d$, that the

$$\mathrm{VHN} \propto L^{\frac{1}{2}}\,. \qquad (7)$$

## 4. Conclusions

The present measurements show that a simple physical significance cannot be ascribed to the VHN when related to brittle materials. With low loads, i.e. 1 to about 100 g, the VHN of germanium crystals is approximately proportional to the square of the "projected" diagonal $d$ of the indentation. As shown in Fig. 5, the (111) plane is more resistant to indentation than the less "close-packed" ones: $(11\bar{2})$ and $(1\bar{1}0)$.

The above model, based on the assumed growth of the dimensions of plate-like "plastic" micro-volumes, as the depth of the indentation is increased, is reconcilable with the observed existence of a "damage zone" around indentations in germanium, and with the lack of evidence of slip or twinning resolvable by scanning electron-microscopy on the crystal surface. Although the model is highly tentative, it may be potentially useful in the study of further results on the micro-plasticity of brittle crystalline materials.

The tendency to the formation and growth of relatively large "corner cracks", provided the indentation exceeds a certain critical size, suggests that cracking may be facilitated by the linking-up of such plastic patches, as the latter grow in the course of the penetration of the indentor into the material.

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