term $\frac{1}{2} q^2$ discussed above and for the incident wave-front curvature multiplies the argument of the cosine term by a factor which amounts to

$$(1+2.2\times10^{-3})+(2.8\times10^{-3}) \quad =1+5\times10^{-3}$$

in the case of silicon, and

$$(1+2.5\times10^{-3})+(10.4\times10^{-3})=1+13\times10^{-3}$$

in the case of germanium. Hence these revisions of the formulae which have been accepted as the basis for interpreting the fringe spacing measurements imply a reduction in the calculated central fringe spacing by 0.5% in the case of silicon, and by 1.3% in the case of germanium. Such changes are significant when compared with the standard errors, $\pm 0.2\%$ for silicon and $\pm \frac{1}{3}\%$ for germanium, reported in the structure factor determinations [1, 2].

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Dislocation-free Silver Single Crystals Grown by the Czochralski Method

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Dedicated to Professor G. Borrmann on the occasion of his 65th birthday

Single crystals of pure silver have been grown by the Czochralski technique and Borrmann X-ray topography has been used to study the perfection of the as-grown crystals. Conditions have been found under which dislocation-free growth takes place and crystals of about 1 cm length and 1 mm diameter have been grown free from dislocations.

1. Introduction

While large, dislocation-free crystals of semi-conducting materials have been available for many years [1, 2], it is only recently that relatively large volume metal single crystals have been grown free from dislocations. Following earlier work on copper, which showed that crystals grown by the Czochralski technique had lower dislocation densities than similar crystals grown by the Bridgman method [3], both Fehmer and Uelhoff [4], and Sworn and Brown [5] used the Czochralski method to pull dislocation-free copper crystals. Both pairs of authors took great care to minimise thermal gradients, the only major difference in technique being that while Sworn and Brown grew their crystals under an argon atmosphere, Fehmer and Uelhoff grew crystals under high vacuum. In the latter situation, the elimination of heat loss by convection enables much larger diameter crystals to be grown dislocation-free under otherwise similar conditions.

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Borrmann X-ray topography was used by the present author [6] to establish the perfection of copper crystals grown by the method of Sworn and Brown. The technique of anomalous transmission X-ray topography, first employed to reveal dislocations by Borrmann et al. [7], is ideally suited to studying nearly perfect copper (and silver) crystals of about 1 mm thickness. In this situation, for Mo $K\alpha$ radiation, $\mu t \sim 40$ and unless the crystal is very nearly perfect, no transmitted intensity will be detected.

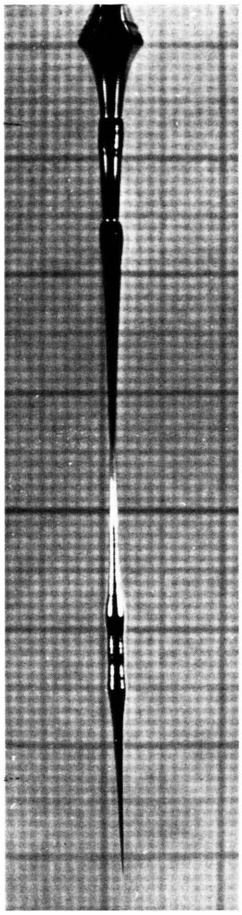

Fig. 1

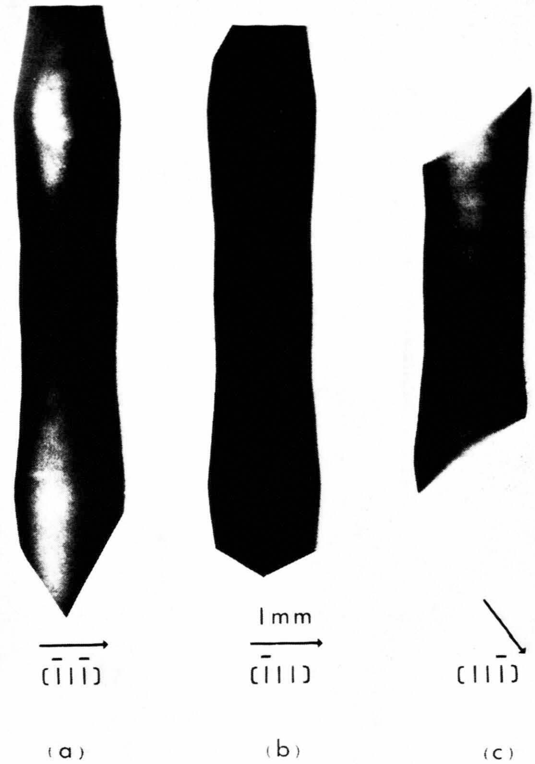

Fig. 3

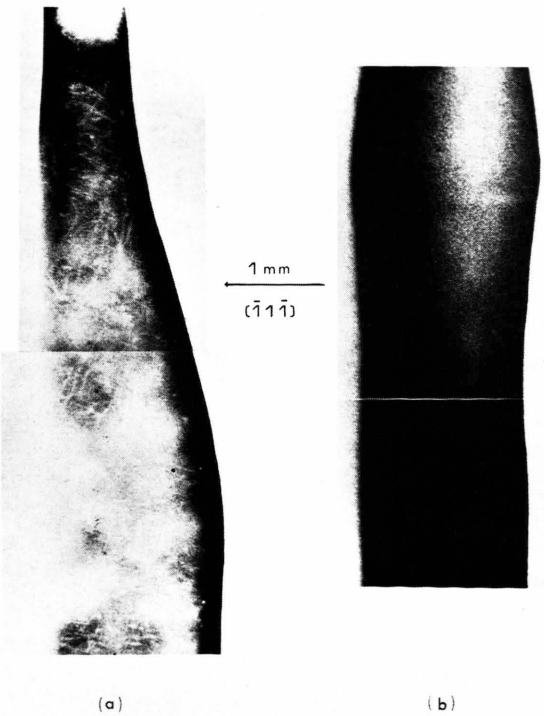

Fig. 2

Fig. 1. Photograph of typical Czochralski grown silver single crystal (each small gird square is of side 1 mm).

Fig. 2. [110] orientation silver crystals. $\bar{1}1\bar{1}$ reflection. (a) Pulling rate 1.5 cm/hour. Ag Kα radiation. μt ~20. (b) Pulling rate 0.85 cm/hour. Mo Kα radiation. μt ~35.

Fig. 3. Dislocation-free silver crystal. Mo Kα radiation. μt ~35. (a) $\bar{1}1\bar{1}$ reflection, (b) $\bar{1}11$ reflection. (c) $11\bar{1}$ reflection.

When appreciable intensity is transmitted, dislocations may be seen clearly as white shadows on the darker background. A further advantage of the technique is that no sectioning of the crystal is required and a crystal typically 1 cm long and 1 mm diameter may be studied as a whole. From Borrmann topographs, using three non co-planar diffraction vectors, it was shown that the copper crystals were free from dislocations and, in particular. free from axial screw dislocations [6]. It is interesting to note that while Fehmer and Uelhoff [4] did not obtain dislocation-free growth when the growth direction was ⟨110⟩, both Sworn and Brown and the present author have obtained dislocation-free growth in specimens of this orientation.

However, it was felt to be important to establish whether dislocation-free growth could be produced in other metals, or whether copper was a unique metal system. In this paper, the growth of dislocation-free silver single crystals is reported. Borrmann topography, utilizing the scanning arrangement of Lang [8], has been used to monitor the crystal perfection.

2. Experimental Details

Single crystals of 99.999% purity silver (Metals Research) were grown in a high purity argon atmosphere in a Metals Research 265 crystal furnace fitted with a Czochralski puller. Seed crystals of about 5 mm diameter were grown by the Bridgman technique. The melt was contained in a high purity graphite crucible which was surrounded by an alumina sheath to act as an after-heater. Details of crucible design and discussion of the effects of the after-heater may be found in Sworn and Brown's paper [5]. Power was supplied by an r.f. coil surrounding the crucible.

The same basic technique as that used for growing dislocation-free copper crystals has been applied to growing silver crystals. Below the seed, the crystal diameter was reduced to a very fine neck of less than 0.3 mm diameter and several millimetres in length. The crystal diameter was controlled by varying the r.f. power applied to the melt while the pulling speed was kept constant. Once the fine neck had been produced, the crystal diameter was increased to pull a specimen of the required shape. It is, however, most important to reduce the specimen diameter before removing the crystal from the melt, or dislocations generated by the subsequent thermal shock may extend back into the crystal. In all these experiments, the crystal was rotated slowly, at about 3 – 4 rev/min. Pulling speeds varied from 3 to 0.85 cm/hour. A typical crystal, still attached to its seed, is shown in Figure 1 *.

The crystals were detached from their seeds and mounted for X-ray topography. It is important that the crystals are handled and mounted only by the necks and that nothing touches the specimen, as it is very easy to introduce dislocations into these fragile crystals. X-ray topographs using Mo $K\alpha$ and Ag $K\alpha$ radiations were taken in anomalous transmission through the whole specimen using a Lang camera. As an Elliott GX6 rotating anode generator was employed, exposures from $\{111\}$ diffracting planes were of the order of 2 hours/mm when recorded on Ilford G5 emulsions.

3. Results

When silver single crystals were pulled from the melt under conditions in which copper grew dislocation-free, high densities of dislocations were produced. No anomalous transmission could be obtained from silver crystals pulled at a rate of 3 cm/hour, even with necks of less than 0.3 mm diameter. Reduction of the pulling speed to 1.5 cm/hour produced crystals with a much lower dislocation density. Figure 2 (a) shows part of a [110] orientation crystal pulled at this speed, and sufficient anomalous transmission is present to enable dislocations to be individually identified. Further reduction of the pulling speed to 0.85 cm/hour enabled crystals of about 1 mm diameter to be grown which gave good anomalous transmission and in which no dislocations were visible, Figure 2 (b).

However, one topograph is not enough to establish the absence of dislocations and three reflections with non co-planar diffracting vectors are required. Figures 3 (a) and (b) show the $\bar{1}1\bar{1}$ and $\bar{1}11$ reflections from the crystal shown in Fig. 2 (b) whose growth direction is parallel to [110]. Good anomalous transmission is observed and no dislocations are visible (except in a thinner region not shown where a few dislocations were accidentally introduced during handling). The only possible Burgers vector of any dislocations present is then parallel to [110]. Although growth bands are visible, presumably resulting from slight fluctuations in melt temperature, no such dislocations are visible in the $11\bar{1}$ reflection shown in Figure 3 (c). It is thus concluded that the crystal is dislocation-free.

* Figures 1 – 3 on page 676 a.

4. Discussion

It has been shown in this experiment that it is possible to grow silver single crystals which are free from dislocations using the Czochralski technique. This statement must, of course, be qualified in so far as one cannot rule out the presence of small dislocation loops resulting from vacancy condensation. Such loops, on a sub-micron scale, would neither be visible in the X-ray topographs nor appreciably destroy the anomalous transmission. (It must be stressed, however, that in both copper and silver crystals grown under the conditions described above, "black spot" defects such as those found by Young [9] and Fehmer and Uelhoff [4] were never observed.) Nevertheless, the absence of long dislocation tangles such as found in Bridgman grown crystals is definitely established. In copper, it has been found that the deformation behaviour of dislocation-free crystals and crystals containing a few dislocations is markedly different. In particular, a large and sharp yield drop has been observed in dislocation-free crystals, though never in crystals containing dislocations [10].

As in copper, for a given neck diameter there seems to be an inverse relationship between pulling speed and the maximum diameter of dislocation-free growth. In the case of silver, while a growth speed of 0.85 cm/hour enabled crystals of about 1 mm diameter to be pulled dislocation-free, at 1.5 cm/hour only crystals less than about 0.5 mm were dislocation-free. The exact dependence of the maximum diameter of dislocation-free growth on pulling speed and neck diameter is clearly a subject for further study. Also, as in copper, dislocation-free growth may be re-established after this critical diameter has been exceeded simply by reducing the crystal diameter below the critical value. No second neck is required. A further interesting point is that dislocation-free crystals of $\langle 110 \rangle$ orientation have been successfully grown, substantiating the result on copper.

5. Conclusions

By means of Borrmann X-ray topography it has been shown that relatively large volume crystals of pure silver may be grown free from dislocations using the Czochralski technique. While there are many similarities between copper and silver, these experiments do show that copper is not a unique system and is not the only metal to exhibit dislocation-free growth.

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