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Dislocation Content in Epitaxially Vapor-Grown Ge Crystals

The process of growing single crystals of germanium[1] by epitaxial deposition onto seeds during disproportionation of GeI_2 to Ge and GeI_4 raised a number of interesting questions concerning the perfection of these crystals. The preliminary results of a study of the dislocation content of such crystals are reported here. It was found that the perfection of the crystals is principally controlled by the condition of the surface of the seed crystal, and that the perfection of the seed significantly affects the dislocation content of the deposit only in certain cases to be described. These results, though not unexpected, are in contrast to the results of perfection studies on melt-grown crystals, where it has been shown that the perfection of a growing crystal is influenced by the perfection of the seed, as well as growth conditions that include thermal stresses and impurity distributions.[2-7]

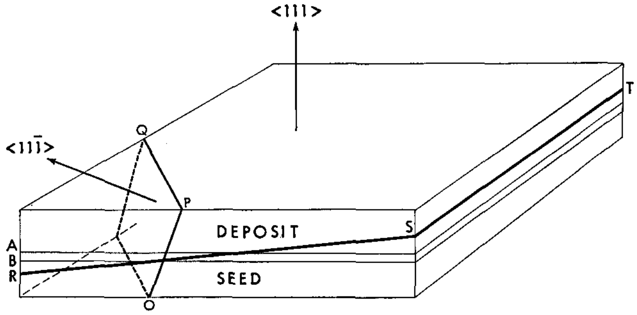

Figure 1 **Section of a crystal showing the interface region *AB* between Ge seed and deposit.** *Figs. 2 and 3 are taken in plane RST. Fig. 4 is taken in plane OPQ.*

Experiment

Most of the crystals were grown according to the "closed-tube" technique described by Marinace.[1] The (111) seeds were wafers of melt-grown germanium. These were etched with white etch[8] which was stopped by dilution with cold water. According to Green,[9] such treatment probably leaves an oxide film several atomic layers thick. Epitaxial deposits of Ge were obtained at about 400°C from the disproportionation of GeI_2 into Ge and GeI_4. Growth rates of approximately 1 to 10 μ/hr resulted in deposits up to several millimeters thick. Some deposits were doped, and neither this nor the growth rate had any apparent effect on the results presented here. Other crystals were grown in an "open tube"[10] on seeds which were initially exposed to an atmosphere of hydrogen and iodine. After this initial treatment, the usual vapor-growth procedure was followed.

The vapor-grown crystals were lapped and polished (a) parallel to the (111) face, (b) at a slight angle to the (111) face, and (c) parallel to the (11$\bar{1}$) face (Fig. 1). These surfaces were etched in CP_4 to produce etch pits which are assumed to correspond to the intersection of dislocations with the surface.[11] Continued lapping and etching in 100μ intervals permitted dislocation densities on (111) faces to be determined in successive layers.

Importance of interface

Etch pit counts on the (111) face in seed and deposit are summarized in Table 1 and show no apparent correlation between dislocations in seed and deposit. Etch pit densities, taken at random over a given surface, varied by a factor of 3, excluding small clusters of pits that will be discussed below.

A continuous increase in etch pit density across interface regions was observed on surfaces exposed by lapping at 1° to 3° angles to the interface. In Fig. 1 the lapped surface is shown by plane *RST* and the interface region by the area *AB*. A typical example of such a surface is shown in Fig. 2 and an extreme case is shown in Fig. 3. The interface is characterized by an increase in the numbers of dislocations and by the presence of flat bottom pits. In addition, Baker and Compton[12] have observed the enhanced incorporation of impurities, including iodine, in these imperfect interface regions. Thicknesses of the interface regions were up to 100μ. The dislocation density usually reached a maximum near the interface and then decreased slightly to a density in the deposit that was still higher than that of the seed. This systematic variation was consistent and the small differences in the data shown in Fig. 3 are significant.

Fig. 4 is a photomicrograph of a crystal grown on a (111) face and sectioned on a (11$\bar{1}$) face as shown by plane *OPQ* in Fig. 1. Dislocations lying nearly parallel to the interface produce etch pits on this face. The seed (*C*) is separated from the deposit (*B*) by an interface region which appears as a heavy dark line. The deposit dislocation density observed on the (11$\bar{1}$) face is 300 times higher than that of the seed. The density is highest near the interface and decreases to a constant lower value

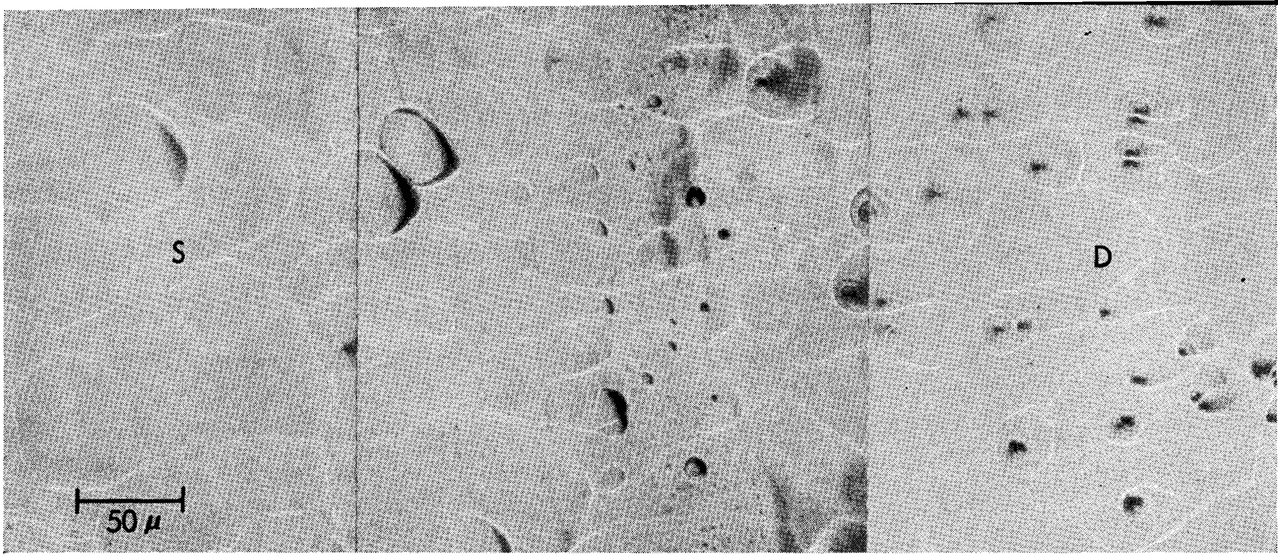

Figure 2 **Photomicrograph of the surface of a beveled Ge crystal showing typical interface between seed (S) and deposit (D). This surface is shown by plane *RST* in Fig. 1.**

away from the interface region.

Vapor growth on seeds which were initially exposed to hydrogen and iodine did not contain the imperfect interface region described above, and the etch pit densities in the deposits were comparable to those in the seeds. Initial exposure to iodine only did not produce these results, although much of the seed could be etched away. Deposit that was nearly dislocation-free (up to 10^2 cm^{-2}) was obtained on a hydrogen-treated, dislocation-free seed. This emphasizes the importance of the perfection of the interface in determining the dislocation content of deposits on untreated seeds.

Observations have been made which indicate that not all dislocations originate at the interface. Etch pits on faces etched successively across the interface have indicated that dislocations in the seed extend into the deposit. These interface regions were less imperfect than usual, although they were not hydrogen treated. These results are preliminary but are definite and pertinent. It appears that the number of dislocations contributed by the seed is ordinarily insignificant because of the large number of dislocations initiated at the interface.

The necessity of using hydrogen to eliminate the interface region suggests that even the very thin oxide layer left by the white-etch treatment prevents perfect epitaxy. It is possible that the initial deposition takes place at pin holes in the oxide layer and the deposit then grows over the surface. A poor match of the deposit with this layer results in high dislocation densities. There is direct evidence of pin hole growth in other work in which epitaxial deposits have been made on thick oxide layers.[13,14] Investigations on the nature of the interface are being continued.

Table 1 **Summary of etch pit data.**

	Density in cm^{-2}		
Crystal	*Seed*	*Deposit*	*Interface*
1	dislocation-free	7×10^4	
2	2×10^3	3×10^5	7×10^5
3	2×10^3	1×10^5	1×10^6
4	7×10^5	5×10^5	
5		5×10^3	2×10^6
6	5×10^3	7×10^3	

Other characteristic features

Preliminary results indicate that dislocations loop or bend over in the deposit, as has been observed in melt-grown crystals.[15] As previously mentioned, Fig. 4 is a photomicrograph of a crystal sectioned and etched on a $(11\bar{1})$ face, as shown by plane *OPQ* in Fig. 1. The density in region (*B*) of the deposit is approximately twice that of region (*A*). This result is compared with results from Fig. 3, which illustrates that on (111) faces the greatest changes in etch pit densities are near the interface. It is possible that dislocations which produce etch pits on the (111) face bend over so as to produce etch pits on the $(11\bar{1})$ face. Most of this bending occurs near the interface, and the dislocations may either loop over or extend approximately parallel to the interface to the edge of the crystal.

Growth pyramids are generally observed on (111) faces.[16] The Frank theory of crystal growth[17] requires screw dislocations along the axes of such pyramids. In order to associate dislocations with the pyramids, the positions of peaks on deposits on seeds not treated with hydrogen were determined with a vernier micrometer stage. In this way, the area where the axis of the pyramid intersected the surface was accurately relocated each time photomicrographs were taken. Observations of these surface areas often revealed clusters of as many as 3500 etch pits in circular areas 200-350μ in diameter. As lapping and etching was repeated, the high density persisted, indicating that in the deposit there were cylindrical regions of high dislocation density along the axes of pyramids which disappeared either before or near the interface and were not found in the seed. The average dislocation density for the circular areas was 4×10^6 cm^{-2} as compared to 1×10^5 cm^{-2} for the deposit. As the crystals were lapped and etched, high-density regions not associated with surface pyramids were uncovered, but these disap-

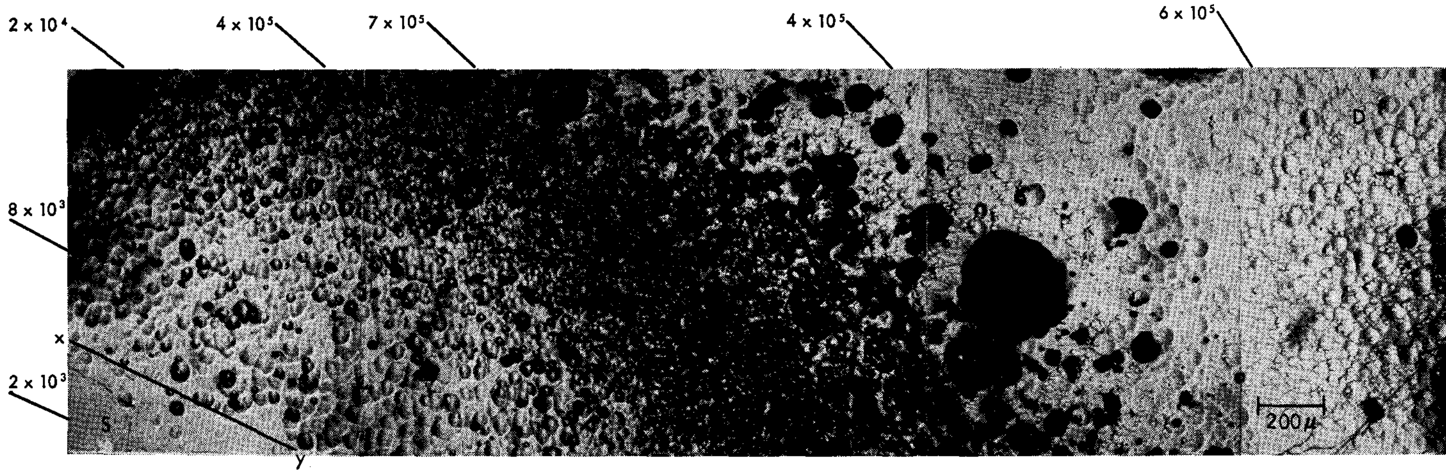

Figure 3 **Photomicrograph of the surface of a beveled crystal showing seed (S), interface and deposit (D). This surface is shown by plane *RST* in Fig. 1.**
The dislocation etch pit concentration per cm² is designated for various areas of the crystal.

peared before or near the interface. These were probably due to pyramids which were covered during growth. Observations of crystals during growth revealed the burying of many pyramids. The existence of dislocations near the axes of pyramids is consistent with the Frank growth mechanism, or, since etch pits do not distinguish between predominantly edge- or screw-type dislocations, there exists the possibility of an edge dislocation mechanism for pyramid growth. The fact that pyramids are not observed on deposits made on hydrogen-treated, dislocation-free crystals further establishes the importance of the dislocations in pyramid growth. In this case neither the seed nor the interface supplied the dislocations necessary for the pyramids.

From these observations we have concluded that the surface condition of the seeds has been the controlling factor in determining dislocation density of the deposit. Further studies are being made on deposits with interface regions eliminated, including observations on the extent to which dislocations carry through the interface from the seed and their effect on growth patterns.

Acknowledgments

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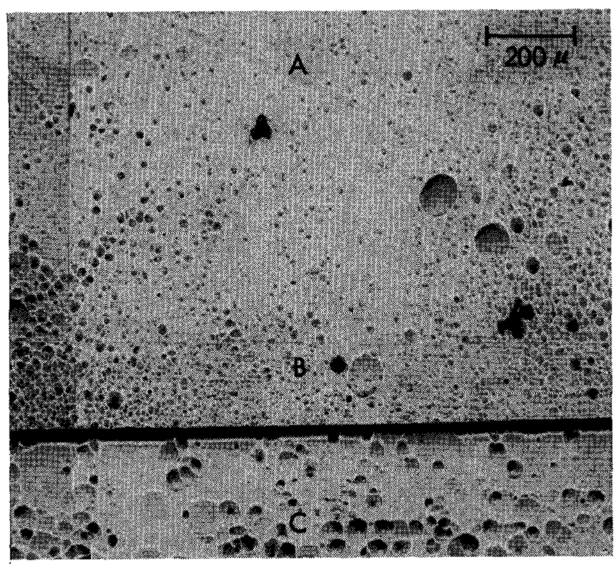

Figure 4 **Photomicrograph showing etch pits on the $(11\bar{1})$ face of a crystal grown in the [111] direction. The dark interface line separates the seed (C) from the deposit (A, B).**
The etch-pit concentrations in the three regions are (A) 6×10^6/sq cm; (B) 1×10^7/sq cm; (C) 2×10^4/sq cm.

References and Footnotes

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