Any additional change due to shift of E_v relative to E_v' should be small, as already discussed. We also expect δ to be small because the effective mass at E_v' should be no smaller than that at E_c. Thus we can account for the smallness of the shift of $(E_v-E_v'+\delta)$ with doping.

In the last column we have included an estimate of the Burstein shift to give a better comparison of the effects of donors and acceptors. Based on the effective mass of pure germanium, we expect the Fermi level to be 0.06 ev above the conduction-band edge for 3×10^{19} As/cm^3. This gives a thermal gap shrinkage of 0.12 ev for the arsenic-doped sample which greatly exceeds the total change $\Delta(E_c-E_v')$ for p-type germanium with 2×10^{20} Ga/cm^3 in agreement with the perturbation theory argument.

Note added in proof. A slight error has been found in the origin of the energy scales for the 4.4-ev peak in Figs. 2 and 3. The scales should be shifted by the amount required to bring the maxima to the energy values given in Fig. 5.

ACKNOWLEDGMENTS

We wish to acknowledge the help of Heinrich Meier in assembling the equipment and processing the data. The samples were prepared by the Materials and Device Technology section of the Radio Corporation of America Laboratories in Princeton, New Jersey.

PHYSICAL REVIEW VOLUME 122, NUMBER 5 JUNE 1, 1961

Electron Microscope Observation of Precipitates on Grown-In Dislocations in MgO†

J. D. VENABLES
Parma Research Laboratory, Union Carbide Corporation, Parma, Ohio
(Received January 30, 1961)

The defect structure of undeformed, single-crystal, Norton MgO has been examined by transmission in the electron microscope. It is observed that precipitate particles in the form of 0.2-μ diam spheres and short rods are present in large numbers on as-grown dislocations. By using special etching and optical techniques which are described, the concentration of the precipitate spheres is shown to average 10^9 "balls"/cc (but range from 10^7 to 10^{10} "balls"/cc) for a large number of samples examined. Qualitative evidence is presented which indicates that these precipitates are the origin of Tyndall scattering frequently observed in MgO.

MAY and Kronberg,[1] on the basis of experiments concerned with the temperature dependence of the yield stress of Norton Company MgO, have concluded that the material contains precipitate particles which give rise to prominent macroscopic effects on the mechanical properties of the crystals. The purpose of this paper is to present direct microscopic evidence of the existence of many such particles.

The defect structure of undeformed MgO has been examined by transmission in the electron microscope. Samples obtained from the Norton Company have been shaped in the form of 0.010-in. thick slabs by rapid cleaving (to introduce a minimum of fresh dislocations) and then chemically thinned by a method similar to that of Washburn *et al.*[2] with a jet stream of hot phosphoric acid. Examination in the electron microscope of a large number of samples prepared in this manner has shown that grown-in dislocations invariably take the form shown in Fig. 1. The dislocation does not appear as a smooth line, but rather is seen to be bogged down with precipitate particles in the form of rods and spheres arranged in a "ball and chain" configuration. The "balls," which range in size from 0.1 to 0.3 μ in diameter occur rather evenly spaced along the dislocation at intervals of ~1 μ. The "balls" may, in some instances, be joined with an otherwise undecorated dislocation; however, it is also found that rodlike precipitates, which have the dislocation as their axis, occur on the dislocation between the "balls." They are usually <500 A in diameter and between 0.2 and 0.8 μ long In addition to isolated dislocations, several very low-angle boundaries have been examined and reveal the same structure, i.e., the dislocations which make up the boundary are weighted down with "ball and chain" precipitates.

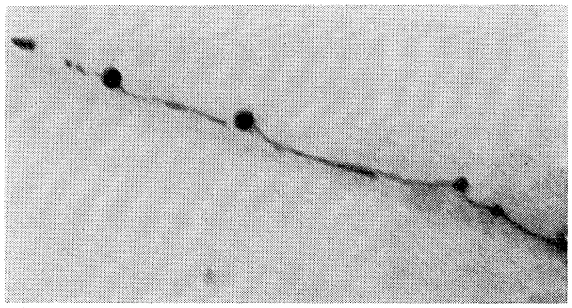

FIG. 1. Electron micrograph of grown-in dislocation in MgO showing precipitates distributed along its length (×10 000).

† This work was performed under the auspices of Advanced Research Projects Agency and Army Rocket and Guided Missile Agency.

[1] J. E. May and M. L. Kronberg, J. Am. Ceram. Soc. **43**, 525 (1960).

[2] J. Washburn, G. W. Groves, A. Kelly, and G. K. Williamson, Phil Mag. **5**, 991 (1960).

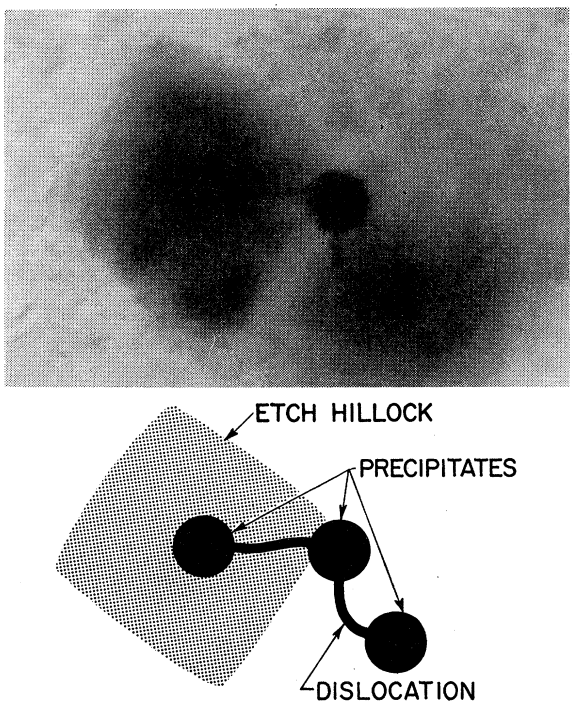

FIG. 2. Three precipitate particles and the dislocation upon which they have condensed are shown in this electron micrograph (×75 000). Surrounding one of the particles is a large dark area, an etch figure, which, by the nature of the contrast, is believed to be a "hillock" (not a pit). These "hillocks," which average ~1 μ in size, may also be seen in the optical microscope at high magnification. Line drawing of photograph included for clarity.

Associated with some of the spherical precipitates are small etch figures which are formed during the thinning operation. One of these may be seen in Fig. 2 as a dark square surrounding one of three precipitates on the dislocation that runs from the front to back surface of the sample. Since the image of the figure is dark (on a positive print), it is believed to be an "etch hillock" (not a pit), somewhat reminiscent of those observed in Ge by Allen and Smith[3] with the reflection electron microscope and in Fe by van Wijk and van Dijck[4] using surface replication. The "hillocks" are usually of the order of 1 μ across and so are just visible in the optical microscope. A study of the distribution of these "hillocks" with the optical microscope has revealed that dislocations which run parallel with and very close to the etched surface may be delineated, since each of the precipitates along its length produces a "hillock." It has also been noticed that the "hillocks" are present in large numbers at known grain boundaries, consistent with the electron microscope observations mentioned above.

When a sample is not jet-etched, but simply etched by immersion in phosphoric acid at ~130°C, the "hillocks" are no longer formed. Nevertheless, it is still possible to detect the presence of precipitates optically, since those which break the surface may be seen as tiny points of light when examined at high magnification with dark-field illumination. That these points of light correspond to precipitates has been inferred from the similarity of their distribution with that of the "hillocks." Furthermore, examination in the electron microscope of surface replicas of immersion-etched samples has revealed many protuberances which are the same size and shape as the precipitate particles shown in the accompanying figures.

In as-grown MgO there are approximately 10^5 cm of dislocation/cc which, our observations show, contain ~10^4 precipitates/cm of length so that altogether there are 10^9 particles/cc existing in the form of precipitates on dislocations. The concentration of particles determined by counting the points of light on an etched surface average about 10^9/cc (but range from 10^7 to 10^{10}/cc) in good agreement with the calculated number. It is concluded, therefore, that the technique provides a valid means of studying the precipitate concentration and distribution in MgO. It must be emphasized that these are order-of-magnitude figures and are not meant to imply that *all* precipitates form on dislocations. Indeed, isolated precipitates have been observed in the electron microscope, but no attempt has been made to determine their relative abundance since it is never clear that they were not at some time associated with a dislocation.

When a strong beam of light is passed through Norton MgO, it is observed that some samples exhibit Tyndall scattering, an effect which is produced when light is scattered from particles or voids small compared with the wavelength of light. Although this effect has been observed in MgO by many workers in the field, it has never (to the author's knowledge) been established whether the scattering is due to small cavities such as vacancy clusters, for instance, or to precipitates. By using the counting technique described above, we have established that samples with a high precipitate concentration always exhibit pronounced Tyndall scattering and those with low concentration show decidedly less scattering. This qualitative correlation suggests that the scattering is due to precipitates but this cannot be put on a more quantitative basis until the composition of the precipitate particles is known. This is so because the intensity of Tyndall scattering is a function of the relative index of refraction between the matrix and the scattering centers.

It has been impossible thus far to obtain a selected-area diffraction pattern of the precipitates due to their small size and their opacity to electrons so that the identification of the precipitate material is as yet undetermined; however, work is continuing on this phase of the problem.

ACKNOWLEDGMENTS

The author wishes to thank R. L. Cummerow, R. G. Lye, R. Sprague and R. Bacon for their assistance and helpful comments.

[3] J. W. Allen and K. C. Smith, J. Electronics **1**, 439 (1956).
[4] F. van Wijk and J. van Dijck, Acta Met. **4**, 659 (1956).

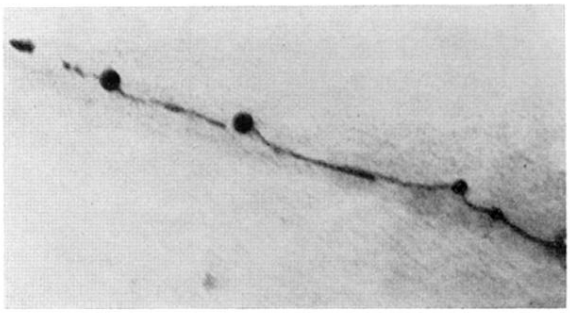

FIG. 1. Electron micrograph of grown-in dislocation in MgO showing precipitates distributed along its length ($\times 10\,000$).

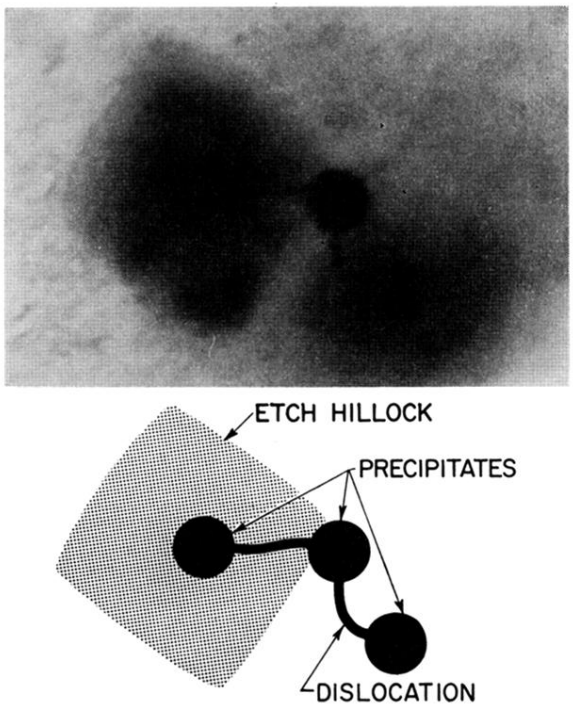

FIG. 2. Three precipitate particles and the dislocation upon which they have condensed are shown in this electron micrograph (×75 000). Surrounding one of the particles is a large dark area, an etch figure, which, by the nature of the contrast, is believed to be a "hillock" (not a pit). These "hillocks," which average ~1 μ in size, may also be seen in the optical microscope at high magnification. Line drawing of photograph included for clarity.