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THE NON-EQUILIBRIUM VAPORIZATION RATES OF SINGLE
CRYSTAL ZINC OXIDE BASAL FACES

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This communication reports the initial results of a study of the vaporization of basal faces of ZnO single crystals. An unpublished contemporaneous independent study yields somewhat different results which are interpreted similarly.¹

We observe a dependence of the vaporization rate on the atomic asymmetry along a crystal axis, a phenomenon which has not been previously reported to our knowledge for a congruently vaporizing compound. Different vaporization rates for the Ga(111) and As($\bar{1}\bar{1}\bar{1}$) faces have been observed for GaAs,² however this compound vaporizes non-congruently and liquid gallium remains on the surface.

The ZnO hexagonal wurtzite structure is non-centrosymmetric and pairs of zinc-oxygen layers are stacked normal to the c-axis (Fig. 1). Hence, opposite basal faces are not equivalent. The different sides of the zinc-oxygen layers are identifiable either by x-ray analysis or by etching.³ Etching with 20 v/o HNO₃, as described by Mariano and Hanne-
man,³ produces large hexagonal pits on a Zn face and roughened surface with no distinct features on an O-face.

The single crystals used were wafers (3M Company) cut perpendicular to the c-axis and were 1 mm thick and 6 mm in diameter. For Langmuir vaporization rate measurements a crystal wafer was held in an alumina cell so that only the chosen face was exposed. The cell was suspended from a semi-micro balance into a vertical quartz tube heated by a Kanthal coil.

The system was evacuated to 4×10^{-6} torr, but the pressure rose to 10^{-5} torr upon heating to the vaporization temperature of 1107°C . The weight loss was then monitored until a constant vaporization rate was obtained.

Figure 2 shows the results for eight crystals used in ten vaporizations (both sides of crystal one and three were vaporized). The steady state vaporization rate from the Zn-face is about three times higher than from the O-face. The surface morphologies of the two faces were completely different after the steady state had been reached. The O-face exhibited a large number of hexagonal pits (300 microns in diameter and smaller) while the Zn-face exhibited a surface covered with peaks (approximately 10 microns high) and spikes (approximately 80 microns high) separated by narrow valleys with no hexagonal pits. Examination with a scanning electron microscope showed that the sides of the hexagonal pits on the O-side had steps and ledges while no steps or ledges could be found on the features on the Zn-face at magnifications up to 11,000X.

We have found that vaporization rates and surface morphologies are alike for opposite prismatic faces which do have atomic symmetry and hence are equivalent to each other. Accordingly, the difference in rates found for the basal faces is clearly associated with the atomic asymmetry.

It should be noted that the atomic asymmetry may influence the observed vaporization behavior in an indirect manner. Namely, one face may be more susceptible to reaction with residual gases in the system (e.g. H_2O) or one face may more strongly adsorb impurities, which in turn could alter the rate of vaporization. Studies are continuing in an attempt to determine the influence of stoichiometry, impurities and residual gases and to see if similar behavior is found for other compounds with the wurtzite structure.

Acknowledgements

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Fig. 1. Zinc and oxygen basal faces showing zinc-oxygen layers stacked normal to the c-axis.

Fig. 2. Total weight loss vs. time for the zinc and oxygen basal faces of ZnO single crystals.

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