Lawrence Berkeley National Laboratory

Recent Work

Title

THE VARIATION OF VAPORIZATION RATES WITH ORIENTATION FOR BASAL PLANES OF ZINC OXIDE AND CADMIUM SULFIDE

Permalink

<https://escholarship.org/uc/item/5ks8b7r5>

Authors

Leonard, Ralph B.
Searcy, Alan W.

Publication Date

1971

C. 2

THE VARIATION OF VAPORIZATION RATES WITH
ORIENTATION FOR BASAL PLANES OF ZINC OXIDE
AND CADMIUM SULFIDE

Ralph B. Leonard and Alan W. Searcy

January 1971

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-20392

C. 2

25

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE VARIATION OF VAPORIZATION RATES WITH ORIENTATION
FOR BASAL PLANES OF ZINC OXIDE AND CADMIUM SULFIDE

Ralph B. Leonard and Alan W. Searcy

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
Department of Materials Science and Engineering, College of Engineering,
University of California, Berkeley, California

ABSTRACT

The metal (0001) basal faces of hexagonal (wurtzite) modifications of both zinc oxide and cadmium sulfide are shown to vaporize at higher rates than the non-metal ($000\bar{1}$) faces. The difference in rates has been measured for cadmium sulfide as a function of temperature. Surface morphologies also differ between opposite basal faces of both kinds of crystals. The data suggest that desorption may be rate limiting.

Recently we reported the observation that opposite basal faces of zinc oxide in its hexagonal (wurtzite) crystal modification vaporize in vacuo at rates that differ from each other by approximately a factor of three at 1100°C.¹

A difference in chemical etching behavior between (0001) and (000 $\bar{1}$) planes of wurtzite-type crystals and between (111) and ($\bar{1}\bar{1}\bar{1}$) planes of zinc blend-type crystals was already well established,^{2,3,4} and Miller, et al.⁵ showed that gallium arsenide, which decomposes to liquid gallium and As₂ gas and As₄ gas displays a difference in behavior between (111) and ($\bar{1}\bar{1}\bar{1}$) faces. But our results and those obtained in an independent study of zinc oxide that was concurrent with ours⁶ are the first observations of different vaporization rates for (0001) and (000 $\bar{1}$) faces of a substance that vaporizes by a congruent reaction. For zinc oxide the reaction is⁷

Certainly the anisotropic vaporization behavior of zinc oxide must reflect the anisotropic packing of alternate zinc and oxygen layers in the crystallographic c direction. In Fig. 1 it is apparent that zinc atoms that are exposed by vaporization toward the top of the figure would have three oxygen atom nearest neighbors in the layer below, while zinc atoms that are exposed by vaporization of the lower face of the crystal would have only single oxygen atom nearest neighbors. With oxygen, the situation is exactly reversed so that a crystal oriented like that in Fig. 1 can be expected to have lower free energies when zinc atoms predominate in its upper surface layer and when oxygen atoms

predominate in its lower surface.

The anisotropic surface concentrations might affect the vaporization rate either directly or indirectly:

(1) There might be an intrinsically different steady state rate for opposite basal faces.

(2) Differential adsorption of impurities on the opposite faces might cause the different vaporization rates.

(3) Residual gases in the system might react with the Zn-face at a higher rate than with the O-face.

One of the purposes of this paper is to report the effects of increasing the concentration of common vacuum system background gases and the effects of silicon (probably present as silicon carbide) and aluminum (probably present as Al_2O_3) on basal plane vaporization behavior.

Our furnace was unsuitable for a study of the temperature dependence of zinc oxide, and while Wolff, et al.⁶ did study the effect of temperature, their results that we have so far seen are ambiguous in that an apparent effect of container material on zinc oxide vaporization rates is difficult to separate from the inherent properties of zinc oxide. Accordingly, we have extended our study to include a determination of the effect of temperature on the rate of vaporization of opposite basal surfaces of cadmium sulfide, which also has the wurtzite structure and which has a high enough vapor pressure for ready study in our furnace. The temperature dependence of vaporization of cadmium sulfide basal faces had been studied previously by Somorjai and Jepsen⁸ and by Munir,⁹ who

did not note a difference in vaporization rates for opposite faces.

The congruent vaporization reaction is

We have correlated our vaporization study with the morphologies developed by the vaporizing surfaces. This information will be presented and discussed.

EXPERIMENTAL

The zinc oxide crystals were grown by Minnesota Mining and Manufacturing Co. by a vapor phase process which yielded hexagonal needles up to 10 mm long with a maximum diameter of 8 mm.* The company provided basal slices 1 mm thick and 8 mm in diameter, and prismatic slices 2 mm thick with faces which were 5 mm by 6 mm. Total impurities, as measured by emission spectroscopy, were less than 25 ppm.

The as-received basal slices were examined with an electron beam microprobe, and large concentrations of Si and Al were found. The Si and Al, which were present in lesser amounts after extensive etching with nitric acid, probably were left by polishing operations with SiC and Al_2O_3 . A batch of basal slices that were not polished showed no Si or Al. No difference in vaporization behavior was found for the crystals whether or not they initially had Si or Al on the surface.

A Laue back-reflection X-ray photograph showed that the crystals were within $1/2^\circ$ of the c-axis orientation.

An ultra-high purity cadmium sulfide single crystal with a face cut perpendicular to the c-axis was obtained from Eagle-Picher Industries. A Laue back-reflection X-ray photograph showed that the face was within 1° of the desired orientation. The stated impurities of the crystal were (in parts per million): Ag, .01; Mg, .10; Si, .90; Cu, .22.

Basal slices 0.8 to 1.4 mm thick were cut from the crystal using a wire saw and a 1:1 water:glycerol slurry of 600 grit silicon carbide.

Warekois et al.² have investigated the crystallographic polarity of

* Zinc oxide crystals are no longer available from the 3M Co.

cadmium sulfide by X-ray analysis and by studies of chemical etching behavior, and the crystallographic polarity of zinc oxide has been investigated by Mariano and Hanneman.³ An etchant of 20 Vol. % HNO_3 produces hexagonal pits on the $\text{Zn}(0001)$ face but hillocks on the $0(000\bar{1})$ face; the prismatic faces develop triangular pits, with the apexes pointing toward the $\text{Zn}(0001)$ face. A nitric acid-acetic acid-water etch as described by Warekois, et al.² produces hexagonal pits on the $\text{Cd}(0001)$ face of cadmium sulfide and hillocks on the $S(000\bar{1})$ face.

Annealing the zinc oxide crystals wrapped in platinum foil for 30 hours at $1000^\circ\text{--}1100^\circ\text{C}$ in an evacuated quartz container turned the crystals a light yellow. Annealing a cadmium sulfide crystal wrapped in platinum foil for three days at 700°C in an evacuated quartz container produced no visible change in the crystal color. No observable difference in vaporization behavior from un-annealed crystals was observed for either zinc oxide or cadmium sulfide.

Some zinc oxide crystals were annealed for 2 to 3 h at 800 to 900°C in zinc metal vapor in an evacuated and sealed quartz tube. Each crystal was loosely wrapped with platinum foil so that it did not come into contact with the quartz. After these anneals, the crystals were a bright red-orange throughout the entire bulk.

For vaporization rate measurements the crystal wafer was held in a 99.5% aluminum oxide cell designed so that only the chosen face was exposed. Essentially no vaporization was observed from the rear face, which was masked by a tight fitting plug which fit against the crystal. From available thermodynamic information alumina was expected to be unreactive toward either zinc oxide or cadmium sulfide. Anthrop and

Searcy⁷ found no reaction when alumina was used as a container for zinc oxide at 1150°C. No physical change was observed in the cell after use with either zinc oxide or cadmium sulfide.

The aluminum oxide cell orifice had a channel length to radius ratio of 0.54. No correction was made for reflection at the channel walls for either zinc oxide or cadmium sulfide because their condensation coefficients are low.

The apparatus is shown in Fig. 2. The cell was suspended by a 0.077 mm platinum wire from a quartz semi-micro balance so that the crystal vaporized downward. A vertical fused silica tube heated by a Kanthal coil surrounded the cell.

The quartz tube, which had an i.d. of approximately 50 mm, was cooled at each end by a water cooling collar. A control thermocouple kept the temperature constant to $\pm 2^\circ\text{C}$ over a length of 3.5 cm at 1100°C. A platinum tube 15 cm long, 4 cm in diameter and 0.5 mm thick was inserted into the hot zone for the cadmium sulfide vaporizations. This arrangement produced a 5 cm long temperature zone where the temperature was constant to $\pm 1/2^\circ\text{C}$ at 650°C.

The system could be pumped to 4×10^{-6} torr, but the pressure rose to 2×10^{-5} torr during vaporization. The pressure was read with an ion gauge at the top of the system. Since this was at the opposite end of the system from the pumping port, the measured pressure was a maximum value.

A leak valve at the bottom of the system allowed the introduction of various gases. The stainless steel tube aimed the incoming gases directly at the vaporizing surface. The gas inlet system was flushed

for an hour with a gas before it was introduced into the furnace. Carbon monoxide and methane were supplied by the Matheson Company and oxygen by the Pacific Oxygen Company. Typical impurities in parts per million, as stated by the suppliers were:

For CO	CO ₂ ,	200;
	O ₂ ,	20;
	N ₂ ,	75.
For CH ₄	N ₂ ,	< 50;
	O ₂ ,	2;
	CO ₂ ,	110;
	C ₂ H ₆ ,	30.
For O ₂	N ₂ ,	< 500;
	CO ₂ ,	2;
	Ar,	2000.

A single measurement was made of the effect of water vapor on the rate of vaporization of an O(000 $\bar{1}$) face. This was accomplished by fitting a coil of copper tubing containing distilled water to the gas inlet system. The coil was then packed in dry ice so that the vapor pressure of the water was approximately 4×10^{-4} mm Hg.

RESULTS

A. Vaporization from ZnO Basal Faces

Figure 3 shows ten basal face vaporizations of eight crystals (both sides of crystals one and three were vaporized). The zinc face vaporized at a rate about three times as great as did the oxygen face at 1107°C. The oxygen flux from the vaporizing surface was approximately 0.01 times the flux from an equilibrium surface.¹⁰ There was no observable effect on the rates from a change in the order of vaporization of the two faces or from use of chemically etched or non-etched crystals.

Vaporizations 4, 5, 7 and 8 in Fig. 3 were performed on crystals that had previously been doped with enough zinc to give them a distinct red-orange color. When heated in vacuum at 1107°C, the crystals lost the red color within 20 minutes or less and showed no apparent difference in subsequent vaporization rates from the rates of undoped crystals. Attempts at doping the crystals with oxygen were unsuccessful.

Figure 4 is a typical SEM photograph of the Zn(0001) steady-state surface. This surface looks like sharp mountain peaks separated by narrow valleys.

Figure 5 is an SEM photograph of the O(000 $\bar{1}$) face steady-state morphology, showing hexagonal pits.

B. Effect of Added Background Gases on Zinc Oxide Vaporization

Additions were made of about 8×10^{-4} torr of gases that might be expected to be in the furnace. This pressure would produce a flux of about 10^{17} molecules/cm²-sec onto the surface as compared to a vaporization flux of about 10^{16} O₂ molecules/cm²-sec at the vaporization temperature of 1107°C. Results for methane and carbon monoxide on both

the Zn-face and the O-face are shown in Fig. 6. The dashed lines indicate the maximum and minimum slopes found for vaporizations in the absence of added gases. No apparent change in the vaporization rate of either the zinc-face or the oxygen-face is produced by either of these two gases.

The vaporization of zinc oxide under an increased pressure of oxygen was measured both with a single crystal and with powder samples held in a platinum basket. The introduction of 7×10^{-4} torr of oxygen produced no measurable change in vaporization rate either for the powder samples or for the single crystal. Results for the zinc face are shown in Fig. 7.

Because increased water vapor pressures have a very adverse effect on the vacuum system only a single run with increased water pressures was made. The exact pressure is unknown, but it was high enough to cause a rise in the measured ionization gauge pressure.

The vaporization curves (Fig. 3) exhibit induction periods during which the rate slowly changes before a constant rate is reached for (0001) faces and a nearly constant rate is reached for $O(000\bar{1})$ faces. For crystals that had not been previously vaporized, part of the induction effect may have arisen because of differences in initial surface morphology from the steady state morphology. However, induction periods are also observed for crystals which had reached the steady state morphology but had been stored in air in glass containers.

To determine if oxygen pick-up during cooling or storage might be responsible for the induction periods, a crystal that had been heated to steady state was twice allowed to cool in 700 torr of oxygen and

stored overnight in the furnace before reheating. In each case the rate of vaporization was unchanged from that shown before the oxygen treatment. Next, the same crystal was cooled in the system under the vacuum produced by a mechanical pump and removed for approximately one hour for examination. This procedure produced a small induction period.

Figure 8 shows the vaporization of an as-received crystal with the typical initial induction period. After 260 minutes it was removed and stored in air in a glass container for twelve weeks. The subsequent vaporization exhibits a pronounced induction period typical of a long exposure to lab air. A quench in argon followed by reheating without exposure to laboratory air also eliminates any induction period as did nitrogen quenches.

These results strongly suggest that the cause of the induction periods is adsorbed water. Hence, after 500 minutes, the crystal was nitrogen quenched, quickly removed from the system, and stored for one week at room temperature in a vessel that contained air which was saturated with water vapor. The subsequent vaporization exhibited the most pronounced induction period which was observed. At the conclusion of this vaporization, the crystal was stored for ten days in a dessicator that contained fresh phosphorous pentoxide. This storage still produced an induction period, although much shorter (Fig. 8). Repetition of these experiments with wet and dry storage yielded similar results.

C. Zinc Oxide Prismatic Face Vaporization

The six prismatic planes of the wurtzite structure are all crystallographically equivalent. Hence one should get similar vaporization rates and similar morphologies when a prismatic slice is vaporized in opposite directions normal to a prismatic face. Figure 9 shows vaporization rates of two prismatic slices. The slice used for the A vaporization was cut from the center of a crystal and hence the surfaces were produced by the diamond saw. The B curve was obtained by vaporization of an as-grown prismatic face.

The prismatic slice that yielded the A curves was first vaporized for 660 minute (open circles). The opposite face was then vaporized for 620 minutes (solid circles). Finally, vaporization of the first side was continued (open circles) for an additional 640 minutes.

The vaporization rates for opposite directions on a prismatic slice (A curves) are almost identical for the first one hundred fifty minutes, when the B slice was removed for examination. The B slice showed an induction period following its first removal (first arrow, Fig. 9, probably due to water adsorption such as was found for the basal faces, but showed little change in slope resulted from subsequent removals. Rates of vaporization of the prismatic surfaces are about the same as those of the oxygen basal face, but prismatic vaporization rates show greater increases at longer times.

Explanations for the increase in rates with time and for the divergence of curves at long times are found from examination of prismatic surfaces. Two main surface features were evident: large, irregular, shallow pits and deep pits which appear to be slits.

Figure 10 shows a typical large irregular pit and Fig. 11 shows an area containing several of the slit pits. These slit pits are parallel to the c-axis. More slit pits seemed to develop as the vaporization continued (Fig. 12). A series of slit pits would occasionally lie very close together and develop into a larger pit. The increase in depth of penetration of the slit pits with time should increase the effective area for vaporization and give rise to an increased rate of vaporization. The variation in fractions of the surface in which the pits occur accounts for the divergence of vaporization rates at longer times.

Opposite faces of prismatic slices showed similar morphologies. At this time there is no explanation as to why some areas of the prismatic faces develop thermal pits that are irregular and other areas nearby develop the slit pits. In contrast, the entire Zn-face developed the mountain-like features, while the entire O-face developed the array of hexagonal pits.

D. Cadmium Sulfide Basal Face Vaporizations

Total pressures for the reaction $2\text{CdS(s)} \rightarrow 2\text{Cd(g)} + \text{S}_2\text{(g)}$ were calculated from the slopes of the total weight loss versus time plots. The data shown in Fig. 13 were collected in a random temperature sequence for each run. Crystals were not annealed prior to the runs, but a more limited series of measurements collected for both basal faces of a crystal that had been wrapped in platinum foil and annealed for three days at 700°C gave results not significantly different from those shown.

The rate of vaporization of the Cd(0001) surface is the higher in the temperature range studied, but shows a lesser temperature dependence.

Cd(0001) vaporization data were more reproducible than S(000 $\bar{1}$) data. Data points collected for the Cd-faces of the different crystals can be fit to a single curve while the S-faces pressures show somewhat different magnitudes and slopes in each separate run.

Surprisingly, while basal surface structures are similar to those observed for zinc oxide, it is the Cd(0001) face that develops hexagonal pits (Fig. 14) while the S(000 $\bar{1}$) face has a morphology that resembles rounded mountain peaks separated by narrow valleys (Figs. 15 and 16). In zinc oxide, the Zn(0001) face steady state morphology resembled rather sharper mountain peaks and the O(000 $\bar{1}$) face had the hexagonal pits (Figs. 4 and 5).

Apparent equilibrium constants were calculated for the congruent vaporization and the slopes were determined by least squares analysis (Table 1) (errors are one standard deviation). Munir⁹ reports a vaporization rate equation which yields $\Delta H^\ddagger = 175.3$ kcal for the same reaction in the temperature range of measurement.

The S(000 $\bar{1}$) faces can be seen in the higher magnification of Fig. 1b to have very fine particles dispersed over the surface. A yellow powder was obtained when the S(000 $\bar{1}$) steady state surface was brushed or rubbed. Some powder was removed by pressing masking tape against the surface. Semi-quantitative microprobe measurements of the powder that adhered to the tape showed the powder to contain cadmium and sulfur in approximately a one to one ratio. Probably the ready detachment of this loosely adhering powder from our downward directed vaporizing surfaces accounts, at least in part, for the low reproducibility of S face vaporization behavior.

DISCUSSION

Since steady state rates of vaporization of the basal planes of zinc oxide were not measurably affected by the increased pressures of oxygen, methane, carbon monoxide or water vapor, or by silicon- or aluminum-containing impurities on the surface, it seems probable that the difference in vaporization rates between (0001) and (000 $\bar{1}$) surfaces is an inherent property of the pure crystals and not the indirect result of selective adsorption. Conclusive proof of this point will require studies at much lower background pressures.

The relatively linear plots of weight losses for zinc faces with time in comparison to curved plots for the oxygen faces and the greater reproducibility of the plots of $\log P_T$ versus temperature that characterized the cadmium faces of cadmium sulfide in comparison to the sulfur faces are noteworthy. As already mentioned, the sulfur faces of cadmium sulfide are lightly covered with a loose powder, a fact that probably accounts at least in part for the lower reproducibility of data for the sulfur face.

The progressive increase in weight losses of the oxygen faces of zinc oxide crystals cannot be similarly accounted for; significant concentrations of loose powder could not be discerned on either the zinc or oxygen basal faces. Examination of the oxygen basal faces, however, revealed that the area of vaporized surface was larger than the area of the orifice and increased with time. This increase in actual vaporization area over that assumed in plotting Fig. 1 is almost certainly responsible for the increasing slope of the oxygen weight loss data. In marked contrast, the area vaporized from the

zinc face was essentially that defined by the orifice. The effective area of Cd(0001) faces of cadmium sulfide, but not the S(000 $\bar{1}$) faces, similarly increased with time. Because heating periods were kept short for cadmium sulfide measurements this area increase did not appear to seriously influence our Cd(0001) vapor pressure measurements.

A somewhat surprising observation is that thermal etching produces for zinc oxide a reversal in the characteristic appearances of the metal and non-metal basal surfaces from that produced by etching with nitric acid, while for cadmium sulfide thermally etched surfaces are similar in appearance to the chemically etched surfaces (Table II). For both solids the metal basal faces show the higher vaporization rates, although the steady state morphology of the oxygen face of zinc oxide is similar to the morphology of the cadmium face of cadmium sulfide.

Munir and Hirth¹¹ have recently interpreted the vaporization kinetics of cadmium sulfide and zinc sulfide in terms of the terrace-ledge-kink model, which predicts that near equilibrium concentrations of self-adsorbed atoms can be expected in regions with closely spaced ledges and low concentrations can be expected in regions of widely spaced ledges. The pressures and temperature dependences reported by Munir⁹ and the micrographs displayed by Munir and Hirth¹¹ are similar to those shown in the present paper to be characteristic of Cd(0001) faces. There is, however, a difference in observed surface structure for cadmium faces in the two studies that is pertinent in view of the interpretation of the kinetic data given by Munir and Hirth. They found their cadmium face pits to be characteristically flat bottomed with steep walls and argued that the vaporization coefficient for the flat regions must be negligibly

small and for the walls must be about 0.35.

This interpretation seems to require the assumption that most atoms are desorbed from the surface before they diffuse distances greater than the spacings between adjacent ledges. But if this assumption is made, it is difficult to understand how the surfaces of Munir and Hirth could be steady state surfaces. With time the steep walled regions, which are assumed to be the only active regions for vaporization, should be eliminated by selective vaporization leaving only the flat surfaces.

The pits on some (but not all) of our Cd(0001) faces had distinctly sloping central regions, although the steepness of the walls increases toward the edges of the pits (Fig. 14). Yet vaporization rates for our Cd(0001) faces differed by only about 30% from those of Munir. A possible explanation of these observations is that the surface morphology during vacuum vaporization is relatively strongly influenced by small variations in impurity adsorption but the rate of vaporization is not.

The morphology of the S(000 $\bar{1}$) face is completely different from that of the Cd(0001) face, but the vaporization rates for our Cd(0001) and S(000 $\bar{1}$) faces, while clearly not identical over most of our range of study, are only slightly different. The specific surface free energies of the opposite faces probably are considerably different because of the anisotropic packing along the C-axis.

We think that the steady state surface morphologies of the different crystal faces of cadmium sulfide and zinc oxide may be produced by thermal faceting for which the principal driving force is reduction in total surface free energy through development of planes of lower specific surface free energies.¹²

This interpretation of the data suggests that atoms in the self adsorbed layer may be at near equilibrium concentrations, since relatively long range diffusion would be required to develop the lower energy surfaces at the expense of higher energy surfaces. If the self adsorption layer is near equilibrium, desorption must be the rate determining step of vaporization.

It has been shown elsewhere¹³ that approximate coincidence of the value of an apparent entropy of vaporization with the entropy of the equilibrium vaporization reaction is circumstantial evidence, though it certainly is not conclusive proof, that desorption is rate determining. Data for the sulfur faces are not sufficiently reproducible to give clear evidence, but the cadmium face data allow calculation of an apparent entropy of sublimation by the second law method. The value obtained for the apparent entropy of vaporization from the data of Fig. 13 is 95.4 eu for Eq. (2), compared to 91.6 eu, which is calculated for the equilibrium from known entropies at 1000°K for S_2 ¹⁴ and $Cd(g)$ ¹⁵ and from the estimated entropy¹⁶ and heat capacity¹⁷ of $Cd(s)$. Desorption may well be rate determining.

We see no conflict between the evidence found by Somorjai and coworkers¹⁸ for effects on cadmium sulfide vaporization rates of light¹⁹ and of a sulfur vapor flux⁸ and the hypothesis that desorption may be rate determining. The effect of light may be to increase the population of atoms in the self-adsorption layer that have sufficient energy to overcome the barrier to desorption, and a sulfur flux from the vapor may decrease the concentration of sulfur atoms that can be transferred from the bulk crystal to the self-adsorption layer.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Eric Kay, Dr. David Meschi, Professor Zuhair Munir and Professor Gabor Somorjai for many helpful comments and discussions. The scanning electron microscope, which was provided through NSF Grant No. GB-6428 and NIH Grant GM 15536, was kindly made available by Professor Thomas Everhart. This work was performed under the auspices of the Metallurgy and Materials Branch of the U. S. Atomic Energy Commission.

REFERENCES

1. Leonard, R. B. and Searcy, A. W., J. Chem. Phys. 50, 5419 (1969).
2. Warekois, E. P., Lavine, M. C., Mariano, A. N., and Gatos, H. C., J. Appl. Phys. 33, 690 (1962).
Errata, J. Appl. Phys. 37, 2203 (1966).
3. Mariano, A. N. and Hanneman, R. E., J. Appl. Phys. 34, 384 (1963).
4. Wolff, G. A., Frawley, J. J., and Heitanen, J. R., J. Electrochem. Soc. 111, 22 (1964).
5. Miller, D. P., Harper, J. G., and Perry, T. R., J. Electrochem. Soc. 108, 1123 (1961).
6. B. N. Das, C. B. Lamport, A. A. Menna, and G. A. Wolff, Tyco Labs., Inc., Waltham, Mass., Tech. Report AFML-TR-69-13 (1968).
7. Anthrop, D. F. and Searcy, A. W., J. Phys. Chem. 68, 2335 (1964).
8. Somorjai, G. A., and Jepsen, D. W., J. Chem. Phys. 41, 1389 (1964).
9. Munir, Z. A., High Temperature Sci., 2, 58 (1970).
10. Coughlin, J. P., U. S. Bur. Mines Bull. 542 (1954).
11. Munir, Z. A. and Hirth, J. P., J. Appl. Phys. 41, 2697 (1970).
12. Searcy, A. W., in Chemical and Mechanical Behavior of Inorganic Materials, edited by A. W. Searcy, D. V. Ragone and V. Colombo; Wiley-Interscience, N. Y., 1970, Chapter 6.
13. Herring, C., Phys. Rev. 82, 87 (1951).
14. Stull, D. R., et al., JANAF Thermochemical Tables, Dow Chemical Co., Midland, Mich. Various dates.
15. Hultgren, R., Orr, R. S., Anderson, P. D., and Kelley, K. K., Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley, New York, 1963.

16. Freeman, R. D., Thermodynamics of Binary Sulfides, Oklahoma State University Research Foundation, 1962.
17. Kelley, K. K., U. S. Bureau of Mines Bull. No. 584, 1960.
18. G. A. Somorjai and J. E. Lester in Progress in Solid State Chemistry Vol. 4, Edited by H. Reiss, 1968, p. 1.
19. G. A. Somorjai and J. E. Lester, J. Chem. Phys. 43, 1450 (1965).

Table I. Apparent emthalpies of vaporization for 2CdS(s) (kcal) =

Crystal Face	Crystal No. 1	Crystal No. 2	Sum of points of Crystals No. 1 and 2
Cd(0001)	172.2 ± 2.8	168.0 ± 3.7	170.8 ± 2.2
S(000 $\bar{1}$)	206.1 ± 7.1	183.2 ± 8.0	193.3 ± 6.8
		$190.2 \pm 7^{\sim 2}$	

Table II

Crystal face	Surface after chemical etch	Surface after steady-state vaporization	Relative vaporization rate
Zn(0001)	hexagonal pits	sharp mountain peaks separated by narrow valleys	higher
O(000 $\bar{1}$)	steep hillocks	hexagonal pits	lower
Cd(0001)	hexagonal pits	hexagonal pits	higher
S(000 $\bar{1}$)	rounded hillocks	rounded mountain peaks separated by narrow valleys	lower

XBL693-2169

Fig. 1.

XBL695-2625

Fig. 2.

XBL693-2170

Fig. 3.

XBB701-429

Fig. 4.

XBB701-422

Fig. 5.

XBL698 - 3585

Fig. 6.

XBL701-2082

Fig. 7.

XBL698-3584

Fig. 8.

XBL695-2623

Fig. 9.

XBB 701-416

Fig. 10.

Fig. 11.

XBB701-417A

Fig. 12.

XBL 7012-7236

Fig. 13.

XBB7012-5404

Fig. 14.

XBB703-1346

Fig. 15.

XBB703-1348A

Fig. 16.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720