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THE SUBLIMATION OF BASAL SURFACES OF ZINC OXIDE
SINGLE CRYSTALS UNDER ULTRAVIOLET ILLUMINATION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Donald Albert Carey, B.S., M.S.

The Ohio State University
1976

Reading Committee:
Professor Rudolph Speiser
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Professor John P. Hirth

Approved By
Advisor
Department of Metallurgical Engineering
DEDICATION

This work is dedicated to the United States Air Force with my gratitude for being permitted to pursue an advanced education. A special tribute is due my wife, Christa, for her patience and understanding which made this investigation more enjoyable.
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Studies in Evaporation. Professor John P. Hirth
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INTRODUCTION

Zinc oxide is a relatively simple AB crystalline compound which has seen a wide variety of applications throughout history, starting with its initial employment in the making of brass. Modern day applications include use as a pigment in spacecraft paints and as an activator in the vulcanization of rubber. Zinc oxide exhibits a wide spectrum of solid-state properties. Its behavior in catalysis and as a semiconductor represents that of a class of materials, which permits a generalization of ZnO behavior to the entire class known as II-VI compounds. Some of its properties can be markedly changed by the introduction of imperfections, making zinc oxide a candidate for study into the basic knowledge of matter.

Recent advances in energy conversion technology indicate that employment of heterojunction devices may offer greatly improved efficiencies. Junctions made of Cu₂O or Cu₂S and CdS, another II-VI compound, may someday find application in photovoltaic arrays constructed in space. It is of great interest, therefore, to investigate the stability of zinc oxide in a simulated space environment which promotes decomposition, i.e., high vacuum with high temperature due to solar radiation. The particular portion of the solar radiation spectrum investigated in this study is the high energy, short wavelength regime of the ultraviolet (UV).
The type of decomposition that can occur under the above conditions is termed Langmuir nonequilibrium dissociation, or free vacuum vaporization. ZnO is one of a number of substances which dissociate congruently, i.e., the A-B ratio in the crystal remains approximately the same during vacuum vaporization. For zinc oxide

\[ \text{2ZnO} \rightarrow \text{2Zn(v)} + \text{O}_2(v) \] (1)

Studies by Pourbaix and Brewer indicate that no ZnO molecules are detectable in the vapor phase, only zinc atoms and oxygen molecules in approximately the same ratio as the original zinc oxide. To maintain congruency, for each mole of zinc which leaves the crystal, one half mole of \( \text{O}_2 \) must leave, or

\[ J_{\text{Zn}} = 2J_{\text{O}_2} \] (2)

where \( J_i \) is the flux (molecules/cm\(^2\)-sec) of the i-th species leaving the surface. Langmuir, in his study of the evaporation of high-purity tungsten wires, deduced that

\[ J_i = \alpha_P^c/(2\pi M k T)^{1/2} \] (3)

where \( P^e \) is the equilibrium vapor pressure of the condensed tungsten, \( M \) is the molecular weight, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( \alpha_P \) is the evaporation coefficient. The term \( P^e/(2\pi M k T)^{1/2} \) also represents the flux \( (J_i^e) \) of species i leaving the surface under equilibrium conditions, as in a Knudsen cell. Therefore,
The value of $\alpha_v$ ranges from one where equilibrium conditions exist, to $10^{-6}$. In general, then, free vacuum vaporization fluxes are less than equilibrium fluxes. Hirth and Pound\textsuperscript{8,9} attribute this to contamination, or "poisoning", of evaporation surfaces which retards atomic or molecular desorption. Somorjai and Jepsen\textsuperscript{10} interpret this lower vacuum evaporation rate as being the result of a higher activation energy barrier, $\Delta G_v$, than in the case of equilibrium evaporation. In both interpretations, an impediment to vaporization is evident. To better understand the kinetics of evaporation, a multistep process due to Volmer\textsuperscript{11} is considered as depicted in Figure 1. Here the crystal surface is a low-index crystallographic plane with ledges present. The sequence of steps leading to evaporation is as shown. Atoms or molecules in different surface sites have different binding energies due to the differing number of neighbors to which they bond. The surface states are therefore of highest importance as are the energetics of moving from one surface position to another. In addition, if surface atoms, molecules, or ions must associate, dissociate, or transfer charge at the vaporizing surface, the sequence becomes more complicated.\textsuperscript{12} The focus upon surface sites lead to the development of the terrace-ledge-kink (TLK) mechanism by Burton\textsuperscript{13} \textit{et al}. This surface sequence involves: (a) removal from a kink site to a ledge site; (b) diffusion along the ledge; (c) removal from ledge site to an adsorbed site; (d) diffusion of the adsorbed species on the surface; and (e) desorption into the

\[ \alpha_v = \frac{J_v}{J_e} \]

(4)
Figure 1 Legend

1. Bulk
2. In crystal
3. In ledge
4. Kink
5. At ledge
6. Adsorbed on surface
Figure 1. Schematic view of possible sequential atomic or molecular sites occupied in the terrace-ledge-kink (TLK) sublimation model.
vapor. The slowest of any of the steps (a)-(e), or any required association, dissociation, or charge transfer process prior to (e), will be rate controlling.

Numerous investigations have been conducted in an attempt to determine the rate limiting step. Hirth and Pound\(^9\) showed that the dissociation of atoms from ledges, followed by desorption, were rate limiting in many pure metals at equilibrium. Munir and Hirth\(^{14}\) and Short \textit{et al}.\(^{15}\) demonstrated that charged defects, specifically kinks, can influence the evaporation rate through an induced surface charge which results from a difference in the concentration of such oppositely charged kinks. The surface charge follows an earlier theory proposed by Frenkel\(^{16}\) that ionic crystals with internal point defects at thermal equilibrium have a charged surface and compensating space charge beneath the surface resulting from differences in formation energies of the internal point defects. A mathematical theory by Short \textit{et al}.\(^{15}\) predicts the sign and magnitude of the surface/space-charge dipole.

McVicker\(^{17}\) and McVicker \textit{et al}.\(^{18}\) extended the theory by changing the concentration of internal points through a controlled oxygen atmosphere. An increase in the partial pressure of oxygen in the atmosphere would predict an increased surface charge and thereby reduce the evaporation rate, but more significant effects were shown by changed defect formation energies, kink formation energies, and ledge separation distance. Somorjai and Lester\(^{12,19}\) propose that charge transfer is the controlling mechanism.
in the sublimation of cadmium sulfide single crystals. They reached this conclusion after observing that ultraviolet illumination of the proper intensity produced sufficient electron multiplication at the surface to cause a five-fold increase in the evaporation rate of high resistivity crystals over that achieved in the dark. More recently, Hirschwald and Stolze propose that charge transfer is a rate-limiting partial step in the dissociation of ZnO, though they had no experimental data to support the theory, even after illumination experiments were conducted. The purpose of this investigation is to resolve the charge-transfer controlled theory of ZnO sublimation.
THEORETICAL DEVELOPMENT

Illumination Effects

High purity zinc oxide is an ionic crystal which exhibits n-type semiconductor behavior with a moderate room temperature band gap energy of 3.2 eV.\textsuperscript{21} The increase in electrical conductivity of ZnO with increased temperature is due to the higher concentration of conduction band electrons and valence band holes. The increased electronic energies which enable electrons to jump the band gap from the valence to conduction bands may be supplied thermally or by light excitation.\textsuperscript{21,22} This process of charge transfer is illustrated schematically in Figure 2. Illumination must be of sufficient frequency to satisfy Planck's Law

\[ E = h\nu = \frac{hc}{\lambda} \]  

(5)

where \( h \) is Planck's constant, \( \nu \) is the wave frequency, \( c \) is the speed of light and \( \lambda \) is wavelength. In addition, the intensity of illumination must provide sufficient photon flux if measurable increases in conductivity are to be achieved.

The magnitude of the band gap is temperature dependent, the relationship according to Kröger\textsuperscript{21} is given by

\[ E_{\text{gap}} = 3.5 - 10^{-3}T \text{ (eV)} \]  

(6)
Figure 2. Schematic of electron-hole pair production in a semiconductor during UV illumination.
Therefore, light of the proper intensity and wavelength will generate electronic defects, holes and electrons, which could influence evaporation behavior. The absorption of the light is fundamental to this process. For short wavelength (UV) light, ZnO exhibits high absorptance for $\lambda < 400 \, \text{nm}$. The depth of absorption is $\approx 10^{-5} \, \text{cm}$, so reactions are primarily surface phenomena.\textsuperscript{23} Light in this wavelength range is best provided by a high pressure mercury source. The calculated output from such a lamp selected for this study is detailed in Appendix B.

**Defect Structure**

The defect structure of ZnO remains a topic of conjecture. Though the open nature of the wurtzite crystal structure suggests that the metal excess nonstoichiometry could be provided by zinc interstitial atoms, some studies indicate that oxygen vacancies may predominate.\textsuperscript{24} Calculations by McVicker\textsuperscript{17} show that singly ionized cation vacancies, $V'_O$, and free electrons are the dominant defects in ZnO crystals which indicates Schottky-Wagner type disorder in the experimental conditions of this study. Conductivity studies\textsuperscript{25,26} in this range of temperature and $P_{O_2}$ show that electron concentration is proportional to $P_{O_2}^{-\frac{1}{6}}$. The electroneutrality condition reduces to $[V'_O] = n$, where the brackets indicate the concentration of oxygen vacancies having a single positive charge (denoted by $'$) relative to bulk position anions of charge $-2$, and $n$ represents the concentration of free electrons. For these conditions, the
concentration of singly ionized cation vacancies, \([V'_{\text{Zn}}]\), where the ' indicates a negative charge with respect to normal bulk cation positions of charge +2, is much less than \([V'_{\text{O}}]\), i.e., \([V'_{\text{O}}]\gg [V'_{\text{Zn}}]\). This indicates that the standard Gibbs free energy of formation, \(\Delta G^0\), is less for the anion vacancies than for the cation vacancies. At a specified temperature and \(P_{O_2}\), an equilibrium number of vacancies of each species may exist. We therefore assume a Schottky-Wagner defect structure, where unequal numbers of vacancies of each species exist due to a difference in formation energies.

**Surface Charge Density**

The difference in formation energies of cation and anion vacancies creates what is known as a Debye-Hückel space charge. Since the bulk crystal has an unbalanced electrical charge, compensation must occur to achieve overall crystal neutrality. This is accomplished by the formation of charged kinks on the crystal surface which have a charge \(\pm e\) depending on whether the site is occupied by an anion or cation. The formation of the kinks is coincident with the bulk vacancies which they electrically compensate. For example,

\[
K^X_{\text{Zn}} + O^X_0(z) + K'_{\text{O}} + V'_{\text{O}}(z) + \text{Zn}^X_{\text{Zn}}
\]

represents the transformation of a neutral cation zinc site and an oxygen ion a distance "z" below the surface into a singly-charged oxygen kink and a singly charged anion vacancy in the bulk. Mechanistically, an oxygen ion and a free electron have been removed from
the bulk and placed on the surface, creating the anion vacancy and negatively charged kink, $K'_0$. The standard Gibbs free energy of formation for this reaction is

$$\Delta G^0 = -kT\ln \frac{[K'_0][V'_0]}{[K^x_{Zn}]} - e\phi(z) \quad (8)$$

where the brackets denote concentrations and $\phi$ is a potential developed over the depth $z$. Kink positions are sometimes termed as being of "half-crystal" character and thus are charged $\pm \frac{1}{2}$ the value of bulk sites. The neutral $K^x_{Zn}$ mainly ionize further, so the following reaction can be substituted into equation (7). We write

$$K^x_{Zn} \rightarrow K^*_z + e' \quad (9)$$

where $e'$ represents a single free electron. Again, from the law of mass action

$$\Delta G^0 = -kT\ln \frac{[K^*_z][n]}{[K^x_{Zn}]} + e\phi(z) \quad (10)$$

Combining equations (7) and (9)

$$O^x_{0}(z) + K^*_z + e'(z) = K'_0 + V'_0(z) + Zn^x_{Zn} \quad (11)$$

The overall $\Delta G^0$ is, then

$$\Delta G^0 = -kT\ln \frac{[K'_0][V'_0(z)]}{[K^*_z][n]} - 2e\phi(z) \quad (12)$$

Thus, the formation of bulk anion vacancies is inextricably linked to the change in sign of surface kinks and the formation energy must take this into account. A similar analysis for the removal
of a bulk Zn ion to the surface yields

\[ K_0^X + Zn_0^X \rightarrow K_{Zn}^- + V_{Zn}^1(z) + O_0^X \]  \hspace{1cm} (13)

\[ \Delta G_{13}^O = -kT \ln \frac{[K_{Zn}^-][V_{Zn}^1(z)]}{[K_0^X]} - e\phi(z) \]  \hspace{1cm} (14)

\[ K_0^X \rightarrow K_0^1 + h' \]  \hspace{1cm} (15)

\[ \Delta G_{15}^O = -kT \ln \frac{[K_0^1][h']}{[K_0^X]} + e\phi(z) \]  \hspace{1cm} (16)

where \( h' \) designates holes and \([h']\) the concentration of holes.

Combining equations (13) and (15),

\[ K_0^1 + h' + Zn_0^X \rightarrow K_{Zn}^- + V_{Zn}^1(z) + O_0^X \]  \hspace{1cm} (17)

results in an overall formation energy of

\[ \Delta G_{17}^O = -kT \ln \frac{[K_{Zn}^-][V_{Zn}^1(z)]}{[K_0^1][h']} - 2e\phi(z) \]  \hspace{1cm} (18)

Since Schottky-Wagner disorder has been assumed, \( \Delta G_{11}^O < \Delta G_{17}^O \) and once again \([V_0^1] >> [V_{Zn}^1]\). This also implies an imbalance in the numbers of oppositely charged surface kinks, which leads to a formulation of the surface charge, \( Q \), the charge density per unit of surface. Short et al.\(^{15}\) derived an expression for \( Q \) for the case of Schottky-Wagner disorder which is

\[ Q = -8\{[V_0^1](\infty) + [h'](\infty)\}^{1/2} (2\rho\kappa\varepsilon_0 kT)^{1/2} \times \sinh (e\phi(\infty)/2kT) \]  \hspace{1cm} (19)
where \([V'_0]^{(\infty)}\) and \(p^{(\infty)}\) are the bulk concentrations of singly
ionized anion vacancies and holes in the bulk, respectively, \(\kappa\)
is the dielectric constant for ZnO, \(\varepsilon_0\) is the permittivity of
free space, \(e\) is the unit electric charge, \(\phi^{(\infty)}\) is the electric
potential in the bulk crystal, \(k\) is Boltzmann's constant, and \(T\)
is the absolute temperature.

For the case of thermally induced \(V'_0\) and \(K'_0\) formation con-
sidered by McVicker\(^17\) and McVicker et al.,\(^18\) where \([V'_0]^{(\infty)} \approx n^{(\infty)}\),
\(\Delta G^0_{11}\) has a finite positive value, assuming that \(\Delta G^0 > \Delta G^0_{11}\). This
can be interpreted as the free energy of formation of singly-ionized
anion vacancies in the bulk exceeding the energy required for
electron production at kink sites. Estimates of \(\Delta G^0_{11}\) by Burton
et al.,\(^13\) in which nearest neighbor bonds only are considered, result
in a value of 3.75 eV. Using the band gap relationship derived from
the optical work of Mollwo,\(^24\) at 1000°C, \(\Delta G^0\) is 2.23 eV. Thus, the
assumption of positive values of \(\Delta G^0_{11}\) seems valid. From equation
(12), rearranging

\[
[[V'_0](z)[K'_0]/[K'_0/Zn]n(z)] = \exp \left\{ -\Delta G^0_{11} - 2e\phi(z)/kT \right\} \quad (20)
\]

and

\[
e\phi^{(\infty)}/kT = - \Delta G^0_{11}/4 T + \ln([K'_0/[K'_0/Zn]])^{-k} \quad (21)
\]

Substituting this result into the expression for surface charge
density, \(Q\), we have

\[
Q = 8([V'_0]^{(\infty)} + [h'^{(\infty)}])^{1/2} (2\rho e\kappa_0 kT)^{1/2}
\]

\[
\times \sinh \left\{ \Delta G^0_{11}/4kT + \frac{k}{2} \ln([K'_0/[K'_0/Zn]]) \right\} \quad (22)
\]
This expression predicts a positive value of surface charge which means the compensating bulk charge due to defect structure is negative.

The surface charge density expressed above is a result of the defect structure of the ZnO crystal. Superimposed upon this charge density is a difference in the surface charge of the (0001) and (0001) surfaces due to the intrinsic dipolar arrangement of these planes. The total surface charge densities, then, become

\[
Q_{\text{Zn}}^T = Q_{\text{Zn}}^i + Q_{\text{Zn}}^d \tag{23}
\]

and

\[
Q_{02}^T = Q_{02}^i + Q_{02}^d \tag{24}
\]

where \( Q_{\text{Zn}}^N \) and \( Q_{02}^N \) represent the total surface charge density for the (0001) and (0001) surfaces, respectively, \( Q^i \) is the intrinsic surface charge density and \( Q^d \) is the surface charge density due to crystal defects, as shown by equation (22). The total surface charge term represents a barrier against atom surface movement which leads to evaporation. \( Q_{\text{Zn}}^i \) and \( Q_{02}^i \) can be considered as equivalent but of opposite sign: that is, \( Q_{\text{Zn}}^i = -Q_{02}^i \). McVicker and others\(^{17,18}\) have shown that evaporation rates from Zn surfaces are two to three times those measured from oxygen surfaces. This implies that \( Q_{02}^d > Q_{\text{Zn}}^d \), which is possible if the energy to form a kink-vacancy pair and/or the formation energies of kink sites (and therefore \( [K_0] \) and \( [K_{\text{Zn}}^*] \)) are greater for the oxygen surface.
Discussion of Theoretical Implications

We now consider the effect of ultraviolet illumination upon the surface charge, and hence on the evaporation rate. The initial influence of the illumination is to produce excess electrons and holes in the surface layer ions. The balance of \( V'_0 \) and \( n \) then no longer holds, with \( n \gg [V'_0(z)] \). These terms will now not cancel, so equation (22) becomes

\[
Q = 8([V'_0](\infty) + [h^+](\infty))^\frac{1}{2} (2 \rho \epsilon_o kT)^\frac{1}{2} \\
x \sinh(\Delta G_{\infty}^0/4kT + \frac{1}{2} \ln \left( \frac{[K'_0][V'_0(\infty)]}{[K'_Zn][n(\infty)]} \right)
\]

As \( n \gg [V'_0(z)] \), \( Q \) due to the defects is decreased which would increase the vaporization rates from both (0001) and (000{1}) surfaces. The electrons and holes could also play a role in the evaporation mechanism. For example

\[
K'_Zn \rightarrow Zn'_ad + K'_0
\]  \hspace{1cm} (26)

and

\[
K'_0 \rightarrow O'_ad + K'_Zn
\]  \hspace{1cm} (27)

are possible reactions as a result of kink movement to adsorbed ion positions. These adsorbed ions might then combine with electrons or holes producing neutral atoms in the last crystal position prior to desorption. We can write

\[
Zn'_ad + e^+ \rightarrow Zn(v)
\]  \hspace{1cm} (28)
and
\[ \text{O}_\text{ad}^+ + \text{h}^+ \rightarrow \text{O}_\text{ad}^X \]  \hspace{1cm} (29)

followed by
\[ \text{O}_\text{ad}^X + \text{O}_\text{ad}^X \rightarrow \text{O}_\text{ad}^X \rightarrow \text{O}_2(v) \]  \hspace{1cm} (30)

Another possible sequence is
\[ \text{Zn}_\text{ad}^+ + \text{O}_\text{ad}^+ \rightarrow \text{Zn}_\text{ad}^X + \text{O}_\text{ad}^X \]  \hspace{1cm} (31)

followed by (30). These are examples of charge transfer processes as implied by Somorjai and Hirschwald and Stolze. These equations indicate that vaporization rates will be increased by the UV illumination, while the surface charge density equation predicts a decreased rate due to increased $Q^\alpha$. 
EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental Apparatus

The experimental apparatus utilized in this investigation is the same as was previously used by McVicker17 with slight modifications and additions. A schematic layout is shown in Figure 3 with details of the specimen and thermocouple capsules and the evaporation chamber illustrated in Figures 4, and 5, respectively. Major components are as follows:

1. High intensity grating monochromator
2. Evaporation chamber
3. Vacuum recording microbalance
4. Vacuum pumping system
5. Radiant heating lamps
6. Movable thermocouple
7. Specimen capsule
8. Oxygen pump.

1. High-Intensity Grating Monochromator.

A Bausch and Lomb high-intensity monochromator with selective UV wavelength capability was used as an illuminator. The housing utilized (Cat. #33-86-07) had a range of UV through the visible
wavelengths (200-700 millimicrons) by the use of a diffraction grating with 1200 grooves per millimeter. A corrector lens (Cat. #33-86-28) provided optimum performance in the UV range, with the peak efficiency of the grating being at 220 millimicrons. The light source was a 200 watt (Cat. #33-86-36-01), short arc, super pressure mercury lamp having a quartz envelope. A quartz flourite achromatic condenser was employed at the exit slit of the monochromator. It had a working distance of 26 cm to infinity with an iris diaphragm which acted as a field stop. A typical spectral output plot with calculated intensity values is shown in Appendix B. This monochromator was restricted to horizontal positions, so a quartz prism was required to direct the beam upon the specimen.

2. Evaporation Chamber.

The chamber in which the specimen was heated was constructed of Pyrex glass as shown in Figure 5. Each end of the evaporation chamber was fitted with a glass to metal vacuum adaptor (Varian 952-5018). The 13.3 cm offset in the design facilitated the monochromator position and use of the prism. The window through which the beam impinged the crystal specimen was a quartz flat of optical quality which necessitated a graded seal. To insure Langmuir evaporation conditions, the glass walls were cooled by using three Universal Electric fans (Model AA2CLH2). The interior of the chamber in locations out of the path of the incident radiation became coated with zinc as evaporation progressed. This was a particular problem on the quartz window which necessitated frequent cleaning.
Figure 3 Legend

A. Ultraviolet light source
B. Quartz prism
C. Evaporation chamber
D. To vacuum pumps
E. Focused radiant heating lamps
F. Ionization gauge
G. To potentiometer
H. Oxygen pump
I. Vacuum recording microbalance
Figure 3. Schematic diagram of the evaporation system.
Figure 4. Cross section of specimen capsule.
Figure 5. Evaporation chamber.
3. Vacuum Recording Microbalance.

The primary data collection equipment was a Cahn R-100 microbalance. The specimen weight change was input to a Brown strip chart recorder (Model 153X12V-X-30) set for a three inch per hour chart speed. The chart thus gave a weight loss against time record of the evaporation process. A weighing range of one milligram for full deflection of the microbalance was selected for this study. Since the microbalance had a sensitivity of one in a thousand ($10^{-3}$) parts of full deflection, weight losses of 0.001 milligrams were detected.


The mechanical forepump was a Hitachi type 4VP-C3 with a pumping speed of 100 liters per second. An Edwards model E02 oil diffusion pump utilizing Silicone 705 oil was used to achieve vacuum in the $10^{-6}$ torr range. The vacuum system employed a liquid nitrogen cold trap (Granville-Phillips series 244) and thermoelectrically cooled baffles (Edwards model DCB2B) to minimize backstreaming.

5. Radiant Heating Lamps.

Three MRC model L-85 radiant energy heat lamps were used to heat the crystal specimens to the 950-1050°C range. External heating sources were utilized to minimize back fluxes to the evaporating surface and to insure that no contaminants due to internal heating were introduced into the system. The focal points of the lamps were adjusted to insure equivalent heating of both the specimen and
thermocouple capsules when in the temperature monitoring position. This procedure is illustrated in Figure 6. The three lamps were arranged approximately 120° apart on the same horizontal plane about the evaporation chamber. Power to each lamp was controlled by individual NRC model 2-82-102A variable voltage sources. Each lamp incorporated a squirrel-cage blower for cooling.


Temperature measurement was accomplished by utilizing a Pt/Pt-10%Rh thermocouple positioned in a movable thermocouple capsule. The capsule itself was constructed of alumina and was approximately the same mass and shape as the specimen capsule. The thermocouple bead was established in the same relative position as the evaporating crystal face had in the specimen holder. The capsule was coated with platinum (Engelhard unfluxed platinum paste No. 6926) to promote uniform heating. A double-bore alumina tube was rigidly attached to the capsule as shown in Figure 6. The tube carried the thermocouple leads which also served as a flexible suspension for the tube-capsule arrangement. An iron vane was attached to the top of the tube. A permanent magnet properly placed on the external surface of the evaporation chamber could thereby attract the vane, swinging the thermocouple capsule into position beneath the evaporating crystal. Care was taken to locate the vane well above the band of radiant heating so as not to produce "hot spots" on the glass chamber.
Figure 6 Legend

A. Specimen capsule
B. Movable thermocouple
C. Zone of radiant heating
D. Double bore alumina tube
E. Microbalance hang-down wire
F. Vane support
G. Vane
H. Movable permanent magnet
Figure 6. Thermocouple in temperature measuring position beneath specimen capsule.
External connection to the temperature sensing equipment was facilitated by a Varian model 954-5021 instrumentation feed-through. Actual temperature measurements were made from millivolt readings taken from a L&N potentiometer (No. 8686) utilizing a distilled water/ice cold junction as reference. Preliminary experiments demonstrated an accuracy of ±2°C in the temperature range of 900-1100°C for a period of several days.

7. Specimen Capsule.

The crystal was held in an alumina tube approximately 15mm long with 8mm OD and an original inside diameter of 4.8mm. The tube was drilled with a 6.35mm flat bottom drill so as to leave a 0.78mm internal lip at the bottom opening of the tube. The crystal was supported upon the lip so as to expose the lower surface in the circular 4.8mm diameter opening. The outer cylindrical surface of the holder was platinized in the same manner as the movable thermocouple. A platinum disc was placed upon the top crystal surface and the tube was sealed by an alumina plug of 6.35mm OD. The capsule was held closed by a platinum wire clip which also served as an attachment point for the platinum microbalance chain. When suspended from the microbalance, the evaporation surface was exposed horizontally to the vertical UV beam. The crystal surface was thus not in direct line with the radiant heating lamps. Heating was accomplished by conduction through the specimen capsule and across the platinum disk behind the crystal.
8. Oxygen Pump.

Though the oxygen pressure was varied on relatively few experimental runs to check the effect on evaporation behavior, a short description is warranted. The pump consisted of an electrically heated, closed-end silver tube, with the open end of the tube attached to the vacuum system. By varying the voltage to a Nichrome wire about the tube, the temperature was closely controlled. Increased tube temperature permitted increased flow of oxygen by diffusion into the system. Other atmospheric components were selectively excluded, so essentially pure oxygen was admitted.


The system was supported within a metal strut framework which was placed on rubber pads to minimize building vibrations. The microbalance was placed atop the structure. The oxygen pump access was into the support plate of the microbalance dome. The oxygen pump and the microbalance dome used Viton "O" rings to insure vacuum. The ionization gauge (NRC-563P) was located beneath the microbalance table but 35 cm above the evaporating crystal surface. Gauge attachment was by using Conflat flanges and copper gaskets. The upper portion of the apparatus also utilized an electrical heat tape for prerun bakeout of the ion gauge and thermocouple feed-through assembly. The glass evaporation chamber was connected by Conflat flanges and copper gaskets which facilitated specimen retrieval and replacement. New gaskets were installed each time the chamber was
removed. The glass chamber also was subjected to bakeout by the use of a removable oven which utilized resistance-heated Nichrome wires.

System oxygen pressure was monitored by an NRC-763 ionization gauge control. This control also had a thermocouple gauge monitoring station which indicated system pressure in the early pumpdown phases. The system had an ultimate vacuum capability of $7.6 \times 10^{-7}$ torr with no specimen in the chamber at 1000°C.

Sample Preparation

The zinc oxide crystals used in this study were cut from hexagonal rods supplied by the 3M Company. The cutting was done by a Buehler Isomet precision diamond saw using distilled water as coolant. The resulting crystal wafers were approximately 2mm in thickness. A typical chemical analysis is given in Table 1.

The cut faces of the crystal specimens were successively polished with 260, 400, and 600 grit silicon carbide paper. Each surface was then etched for 90 seconds with 20 volume % nitric acid for identification as (0001) Zn or (000\overline{1}) O faces. Etching was stopped by immersing the crystal in 250 ml of distilled water. This procedure, as previously outlined by Mariano and Hanneman,\textsuperscript{29} results in characteristic hexagonal pits on the Zn surface and hillocks on the O surface as shown in Figures 7 and 8. The crystal faces were examined at 250X on the metallograph for positive identification. The crystal was placed in the specimen capsule with the selected surface facing downward.
Table 1. Typical Analysis of the Zinc Oxide Single Crystals Supplies by the 3M Company as Determined by the Emission Spectrograph.

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<th>Analysis (ppm)</th>
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</tr>
<tr>
<td>Na</td>
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<td>3</td>
</tr>
</tbody>
</table>

*Ground with a $B_4C$ mortar and pestal.
Figure 7. Optical micrograph of the (0001) surface of a zinc oxide single crystal etched for 90 seconds in 20 volume % HNO₃. (500X)
Figure 8. Scanning electron photomicrograph of the (0001) surface of a zinc oxide single crystal etched for 90 seconds in 20 volume percent HNO$_3$. (1000X, 30° tilt)
Experimental Procedure

The specimen capsule with the prepared surface was suspended from the microbalance hang-down wire. The evaporation chamber was put in place using new copper gaskets at the Conflat flanges. The position of the capsule and the thermocouple were carefully checked for vertical separation while in the temperature measuring position. The space between capsules was also aligned at the focal point of the radiant heating lamps. With room lights off, the ultraviolet lamp was aligned so that the beam impinged the entire exposed crystal face. The UV beam was turned off and an aluminum plate placed at the exit slit of the monochromator. Room lights remained off and the curtains closed for the duration of the experimental runs.

The mechanical forepump was started and allowed to run until a reading of 25 microns was indicated on the thermocouple gauge. At this point, the diffusion pump and cooling baffles were turned on. The removable bakeout oven was put in place around the evaporation chamber and the bakeout initiated for 8 hours at 250°C. The upper portions of the system were simultaneously baked at 200°C with the heating tapes. The ambient conditions about the microbalance indicated it was heated to approximately 100°C by conduction and convection. When the ionization gauge indicated a system pressure of $1.0 \times 10^{-5}$ torr, liquid nitrogen was introduced to the cold trap and was continuously provided until the end of the experimental run. After trapping for approximately one hour, system pressure would drop to the mid $10^{-6}$ torr range. The bakeout tapes were then turned off
and the oven removed. After cooling for 20-30 minutes, system pressures in the mid $10^{-7}$ torr range were achieved.

The radiant heating lamps were turned on and the thermocouple swung into position to monitor the temperature. The voltage settings of the lamps were individually controllable so that specific temperatures could be realized ($\pm 2^\circ$C). When a stable temperature was indicated for three minutes on the strip chart recorder, the potentiometer reading (mv) was taken and converted to temperature. The thermocouple was then swung away from the specimen capsule and the experiment begun. Temperature constancy was monitored by the strip chart recorder.

Initial weight loss measurements indicated a very high rate and were attributed to desorption of molecules remaining after bakeout. Approximately three hours were required for this transient behavior until the desired steady-state evaporation was detected. For higher temperatures, three hours of constant weight loss measurements were required to measure an evaporation rate. This rate was then compared to data taken by McVicker under the same conditions. The ultraviolet lamp was then turned on and allowed a five-minute warmup period. The desired wavelength setting was checked and the aluminum plate removed from the exit slit of the monochromator, thus allowing the UV beam to illuminate the crystal. Changes in weight-loss rate were recorded on the strip-chart recorder. The weight loss with the UV light on was allowed to achieve a constant rate for three hours. At this point, the UV lamp was turned off and the weight-loss rate
allowed to stabilize once again. This latter step was often deleted, particularly if morphological surface changes under UV were of interest. Lower temperature experiments took longer time periods, some up to sixteen hours, before constant weight loss could be measured.

Crystal specimens were removed for morphological examination with the scanning electron microscope. Frequent system shutdown was necessitated by a film of Zn which was deposited on the inner surface of the evaporation chamber, particularly on the UV port.
RESULTS AND DISCUSSION

Results of Evaporation Experiments

The initial experimental run provided some interesting morphological information though the system was imploded due to the attraction of the specimen holder to the chamber walls, as described in Appendix C. The incoming room temperature air thermally shocked the crystal such that a fracture surface formed diagonally across the crystal face. Figure 9 shows a view of the (0001) face of the crystal with the fracture face at the bottom of the photomicrograph. The irregular depth of evaporation is evident, as well as the spires which are characteristic of evaporation of Zn surfaces. Figure 10 is a closeup of the fracture -(0001) face intersection showing the fracture surface extending to spire tips. The initiation point of the fracture was most likely at the bottom of the photo, with final separation at the spire tips. A normal view of this (0001) surface (Figure 11) shows the distribution of the spires, which are generally separated by valleys of greatest evaporation depth. These valleys may correspond to dislocation sub-cell locations. The crosssections of the spires themselves only remotely suggest the hexagonal symmetry characteristic of ZnO.

Figure 12 shows spire formation in the early stages of evaporation of a (0001) surface. The gross hexagonal formations in the upper portion of the figure are etch pits characteristic of
Figure 9. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 8 hours at 980°C with the system $P_{O_2} = 1.6 \times 10^{-6}$ torr. (200X, 45° tilt)
Figure 10. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 8 hours at 980°C with the system $P_{O_2} = 1.6 \times 10^{-6}$ torr. (1000X, 45° tilt)
Figure 11. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 8 hours at 980°C with the system $P_{O_2} = 1.6 \times 10^{-6}$ torr. (1000X, 0° tilt)
Figure 12. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 3 hours at 995°C with the system $P_0 = 1.6 \times 10^{-6}$ torr. (1000X, 45° tilt)
those used to identify the surface prior to evaporation. It is clear that the spires have formed generally in a uniform distribution over the entire surface, etch pitted and unpitted alike. This establishes that etch pits are not exclusive nucleation sites for evaporation pits. The random arrangement of the valleys has no apparent relationship to original etch pit configuration, so the dislocation substructure seems more plausible for the valley formation.

Figure 13 illustrates the result of the evaporation of (0001) under UV illumination. It is believed that the material connecting spire tips is at the original crystal surface. The holes in this material are definitely hexagonal (see Figures 14 and 15), which suggests that the mechanism of evaporation on the Zn surface is also by nucleation and growth of hexagonal pits. As these pits insect one another, the spires result with their random distribution and irregular crosssections. Figure 14 also shows ledges and steps on the sides of the spires, a structure previously unreported.

Figures 16 and 17 show the hexagonal pits characteristic of evaporation of (000\overline{1}) faces. Upon illumination, the surface film is again in evidence, as shown in Figures 18, 19, and 20, though the evaporation has gone well beyond the initial stages and any interpretable structure is presumed to be missing after 20 hours of evaporation. Figure 21 shows the result of evaporating the (000\overline{1}) surface under UV with increased \(P_{O_2} = 2.2 \times 10^{-5}\) torr. The increased evaporation rate seems largely due to accelerated loss at the pit bottoms.

Discussion of Results

Figure 22 is a graphical presentation of the data for evaporation of basal surfaces resulting from the calculations outlined in Appendix D. The evaporation rates of the (0001) and
Figure 13. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 3 hours, UV illumination (300 nm) for 2 hours at 1020°C with the system $P_{O_2} = 1.6 \times 10^{-6}$ torr. (1000X, 45° tilt)
Figure 14. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 3 hours, UV illumination (300 μm) for 2 hours at 1020°C with the system $P_{O_2} = 1.6 \times 10^{-6}$ torr. (2000X, 20° tilt)
Figure 15. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 3 hours, UV illumination (300 nm) for 2 hours at 1020°C with the system $P_0 = 1.6 \times 10^{-6}$ torr. (4000X, 10° tilt)
Figure 16. The (000\overline{1}) surface of a zinc oxide single crystal after free vacuum evaporation for 26 hours at 1010°C with the system $P_{O_2} = 3.7 \times 10^{-6}$ torr. (2000X, 45° tilt)
Figure 17. The (000\bar{1}) surface of a zinc oxide single crystal after free vacuum evaporations for 26 hours at 1010°C with the system $P_{O_2} = 3.7 \times 10^{-6}$ torr. (2000X, 0° tilt)
Figure 18. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 20 hours, UV illumination for 5 hours (300 μm) at 990°C with the system P_{O_2} \approx 1.7 \times 10^{-6} \text{ torr.} \ (1000X, \ 45^\circ \text{ tilt})
Figure 19. The (000$\bar{1}$) surface of a zinc oxide single crystal after free vacuum evaporation for 20 hours, UV illumination for 5 hours (300 μμ) at 990°C with the system $P_{O_2}$ $\approx$ 1.7 x 10$^{-6}$ torr. (2000X, 45° tilt)
Figure 20. The (0001) surface of a zinc oxide single crystal after free vacuum evaporation for 20 hours, UV illumination for 5 hours (300 mJ) at 990°C with the system $P_{O_2} = 1.7 \times 10^{-6}$ torr. (10000X, 45° tilt)
Figure 21. The (000\overline{1}) surface of a zinc oxide single crystal after free vacuum evaporation for 11 hours, UV illumination (300 m\mu) for 5 hours at 990\textdegree C with the system $P_{O_2} \approx 2.2 \times 10^{-5}$ torr. (1000X, 45\degree tilt)
Figure 22. Experimental data for free vacuum evaporation of ZnO; $P_{O_2} = 2.2 \times 10^{-6}$ torr with UV illumination.
(0001) surfaces without illumination agree well with the previously published results of other researchers. With UV illumination, the faster evaporating (0001) surface has a decreased evaporation rate. The (0001) surface has a slightly increased evaporation rate under illumination. The magnitude of the increase and decrease in evaporation rates for the O$_2$ and Zn faces, respectively, is $+3.5 \pm 1.3\%$ and $-5.5 \pm 0.75\%$, as shown in Tables 2 and 3.

The fact that the O$_2$ face shows increased rates while the Zn face shows decreased rates demonstrates that the charge transfer theory of evaporation rate control does not apply for ZnO. Both faces should exhibit increased rates under UV illumination were charge transfer rate controlling. Looking at equation (25), and recalling that illumination increases $n$, we see that $Q$ is decreased, which should result in increased evaporation rates. Furthermore, the defects and atmosphere equilibrate in accordance with

$$\frac{1}{2} O_2 + [V_0^\ast] + n \rightarrow O_0^x$$  \hspace{1cm} (32)

for which an equilibrium constant can be written

$$K_{32} = \frac{P_{O_2}^{-\frac{1}{2}}}{[V_0^\ast]^n}$$  \hspace{1cm} (33)

from the law of mass action. This means that as $n$ increases, $[V_0^\ast]$ must decrease to maintain the relationship in equation (33). This also would reduce $[K_0']$, since the anion vacancies and negatively charged kinks are paired as described by equation (12). All of these factors reduce $Q$, which should produce increased evaporation rates on both surfaces. The concentration profiles of these defects are shown in Figure 23.
TABLE 2: Summary of experimental data for (0001) surface with no oxygen added to the system.

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<th>W(mg/hr)</th>
<th>ΔW(%)</th>
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<th>ln(P^*Zn(P^*O_2)_k)</th>
<th>System Pressure (torr)</th>
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<td>UV(mg)</td>
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<td>1253</td>
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<td>-</td>
<td>-</td>
<td>0.7981</td>
<td>-26.42</td>
</tr>
<tr>
<td>1268</td>
<td>0.356</td>
<td>-</td>
<td>-</td>
<td>0.7886</td>
<td>-25.95</td>
</tr>
<tr>
<td>1293</td>
<td>0.583</td>
<td>0.548</td>
<td>-6.0</td>
<td>0.7734</td>
<td>-25.19</td>
</tr>
</tbody>
</table>

ΔW = -5.5 ± 0.75%

ΔH* = 123.968 cal/mole

ΔS* = 47.692 eu
### TABLE 3: Summary of experimental data for (0001) surface with no oxygen added to the system.

(*denotes increased system P_{O_2})*

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>W(mg/hr)</th>
<th>ΔW(%)</th>
<th>10^3 ln(P^<em>_{O_2}+P^</em>_{O_2})</th>
<th>System Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no UV</td>
<td>UV(my)</td>
<td>T No UV</td>
<td>UV</td>
</tr>
<tr>
<td>1263</td>
<td>0.089</td>
<td>0.092(300)</td>
<td>+3.4</td>
<td>0.7918</td>
</tr>
<tr>
<td>1277</td>
<td>0.115</td>
<td>0.121(300)</td>
<td>+5.2</td>
<td>0.7831</td>
</tr>
<tr>
<td>1285</td>
<td>0.168</td>
<td>0.172(372)</td>
<td>+2.4</td>
<td>0.7782</td>
</tr>
<tr>
<td>1298</td>
<td>0.218</td>
<td>0.221(300)</td>
<td>+1.4</td>
<td>0.7704</td>
</tr>
<tr>
<td>1298</td>
<td>0.209</td>
<td>0.218(300)</td>
<td>+4.3</td>
<td>0.7704</td>
</tr>
<tr>
<td>1298</td>
<td>0.218</td>
<td>0.221(300)</td>
<td>+1.4</td>
<td>0.7704</td>
</tr>
<tr>
<td>1263</td>
<td>0.079</td>
<td>0.082(300)</td>
<td>+3.8</td>
<td>0.7918</td>
</tr>
<tr>
<td>1263</td>
<td>0.075</td>
<td>0.079(300)</td>
<td>+5.3</td>
<td>0.7918</td>
</tr>
<tr>
<td>1263</td>
<td>0.079</td>
<td>0.082(300)</td>
<td>+3.8</td>
<td>0.7918</td>
</tr>
<tr>
<td>1283</td>
<td>0.125</td>
<td>-</td>
<td>-</td>
<td>0.7794</td>
</tr>
<tr>
<td>1263</td>
<td>0.083</td>
<td>0.086(300)</td>
<td>+3.6</td>
<td>0.7918</td>
</tr>
</tbody>
</table>

ΔW = +3.5±1.3%

ΔH* = 134,980 cal/mole
ΔS* = 51.432 eu
Figure 23. Concentration profiles of $n$ and $V_0^*$ in dark and during illumination.
SUMMARY AND CONCLUSIONS

The primary conclusions as a result of this study are:

1) It was confirmed that the free vacuum evaporation rate for the Zn face is two to three times that of the O\textsubscript{2} face for temperatures in the 950-1050\degree C range.

2) The evaporation rate of the O\textsubscript{2} face was demonstrated to increase by 3.5% and that of the Zn face to decrease by 5.5% under illumination with ultraviolet light of 372 m\u or less.

3) Because of the dissimilar changes in evaporation rates for the opposite basal surfaces, the charge transfer theory is proved to be inapplicable to ZnO.

4) Increased P\textsubscript{O2} is found to further increase the evaporation rate of (0001) surfaces under ultraviolet illumination.

5) The proposed mechanism of spire formation on the (0001) surface is one of nucleation and growth of hexagonal pits.
APPENDIX A

ZnO PHYSICAL PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure: wurtzite</td>
<td>3</td>
</tr>
<tr>
<td>$a = 3.24 \text{ Å, } c = 5.19 \text{ Å}$</td>
<td>32</td>
</tr>
<tr>
<td>Magdelung constant : 5.99413</td>
<td>33</td>
</tr>
<tr>
<td>Space group : P6$_3$mc</td>
<td>33</td>
</tr>
<tr>
<td>Packing density : 44%</td>
<td>3</td>
</tr>
<tr>
<td>Density : 5.6 gm/cm$^3$</td>
<td>32</td>
</tr>
<tr>
<td>Band gap : 3.2 eV at 20°C</td>
<td>32</td>
</tr>
<tr>
<td>Natural color : white</td>
<td>3</td>
</tr>
<tr>
<td>Refractive index : 2.00</td>
<td>3</td>
</tr>
</tbody>
</table>
APPENDIX B

CALCULATION OF THE LIGHT INTENSITY

An important consideration in determining the effect of the UV illumination is to assure sufficient electron-hole pair production such that measurable changes in dark evaporation rates are detected. This is accomplished by selecting a light source of sufficient intensity and having photon energies which exceed the band gap value of ZnO. This latter parameter is reported by Kröger\textsuperscript{21} to be

\[ E_{\text{gap}} = 3.5 - 10^{-3} T \text{ eV} \]  \hspace{1cm} (B-1)

where \( T \) is absolute temperature (°K). For the 950–1050°C temperature range of this investigation, the corresponding band gap range is 2.28 to 2.18 eV. The photon wavelengths, \( \lambda \), corresponding to this energy range may be calculated using

\[ E = \frac{hc}{\lambda} \]  \hspace{1cm} (B-2)

c and \( h \) being the speed of light and Planck's constant, respectively.

Rearranging and substituting the appropriate values

\[ \lambda = \frac{hc}{E} = \frac{(6.625 \times 10^{-15} \text{ eV}\cdot\text{sec})(3\times10^{10} \text{ cm/sec})}{E(\text{eV})} \]

\[ = \frac{1.9875 \times 10^{-6} \text{ cm}}{E} \]  \hspace{1cm} (B-3)

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Therefore, the wavelength range was determined to be between 871 and 911 μm, since 1 cm = 10^7 μm. Since photon energies greater than the band gap are desired, values of λ < 871 μm should produce the desired effect. A transparency cutoff exists at 400 μm, which explains why ZnO is white in visible light and black in ultraviolet light.

The radiant flux output as a function of λ is shown in Figure 24 for the monochromator with a high pressure mercury arc source. This diagram is accurate to ±5% for a typical new bulb and indicates the spectral output at the exit slit of the monochromator. Bulb performance remains constant up to 80% of bulb lifetime (estimated at 120 hours) after which slight degradation occurs. To check for any possible variances in electron-hole production rate as a function of λ, three selected wavelengths less than 400 μm were chosen. An arbitrarily selected radiant flux output of 75 mW corresponded to λ's of 300, 354, and 372 μm. The 75 mW output was then converted to an energy flux impinging the specimen surface.

The 75 mW radiant flux output represents the integrated power uniformly dispersed over the cross section of the beam. At the crystal surface, the beam cross section is measured to be 1.91 cm x 2.22 cm or 4.24 cm^2. The exposed surface area of the crystal is 0.18 cm^2. The crystal is therefore capturing 0.18/4.24 or 4.24% of the beam power. The beam power striking the crystal surface is 3.18 mW distributed over the surface with a power density of 75 mW/4.24 cm^2 = 17.69 mW/cm^2. The conversion of spectral output to energy flux is
Figure 24. Radiant flux output of B&L monochromator with Hg super pressure lamp.
The molecular density of ZnO is $4.21 \times 10^{22}$ molecules/cm$^3$ which corresponds to $1.21 \times 10^{15}$ molecular sites per cm$^2$ of surface. The beam incident energy is thus of the same order of magnitude and, assuming reasonable quantum efficiencies, the desired electron-hole pair production should result. Beam intensity losses due to travel in quartz, air, and vacuum are negligible.
APPENDIX C
EXPERIMENTAL PROBLEMS

The use of radiant lamps as a heating source for evaporation studies of specimens in a glass chamber has several advantages. Primary among these is the visibility of the specimen - thermocouple proximity and the capability of close control of temperature through adjustment of lamp position and voltage. Though subject to heating externally by the lamps and internally by radiation from the specimen holder, the glass could be effectively cooled by proper placement of air blowers. The chamber temperatures at experimental conditions thus permitted touching with bare fingers. This condition promoted the free evaporation condition required in this study. This was confirmed by the presence of a metallic deposit on the inner surface of the chamber in the vicinity of the specimen.

The use of Pyrex 7740 as a chamber material also presented a problem as any condition which caused a local thermal overload softened the chamber wall. This occurred experimentally through two distinct mechanisms worthy of reporting:

1) Electrostatic effect - The specimen holder was observed to swing on the platinum hangdown chain when the exterior glass chamber
wall was stroked with cotton containing acetone. Vigorous rubbing could cause the specimen holder to become electrostatically attached to the inner chamber wall. Close examination of the position of the specimen holder against the wall indicated that the contact points, and therefore the charged attractive component, was the platinum wire clip. Gentle tapping broke the attraction and the specimen holder returned to the centerline of the chamber after several oscillations.

This apparent electrostatic effect was a true hazard during high temperature runs. In the event the platinum wires became attached to the wall, localized softening was assured. If this condition advanced to localized melting, the wires became embedded in the glass and an immediate, carefully controlled lowering of temperature was necessitated. If the temperature reduction was too slow, the platinum-glass hot spot caused melting with subsequent system implosion. If temperature letdown was too rapid, the difference in thermal conductivities and coefficients of thermal expansion between platinum and Pyrex 7740 cracked the glass and again lead to system implosion.

The apparent charging of the platinum wire was thought to be caused by airflow friction during system evacuation. The glass chamber was periodically removed for cleaning of the zinc deposits and specimen replacement. Cleaning was facilitated by using acetone as a cleanser with a laboratory bottle brush. After rinsing with acetone, the glass was air dried. After reinstallation of the chamber, use of cotton balls and acetone facilitated removal of
external chamber fingerprints. It is theorized that attraction of the wire was due to friction on the glass and a residual charge on the chain from prior experiments. Air friction could subsequently add additional electrostatic charge to both wire and glass during pumpdown and experimental runs.

2) Radiation - Particular care must be applied to the position of wires in the hot zone of the chamber. The platinum wires attached to the specimen holder were evidently of small enough diameter and such high thermal conductivity that hot spots did not develop. However, a larger support wire for the thermocouple was exposed to radiation in close proximity to the chamber wall. This wire was observed to glow very rapidly at a point in line with incident radiation from one lamp. Reradiation in accordance with the Stephan-Boltzmann relationship lead to local wall melting and system implosion. Relocation of the support wire prevented subsequent reoccurrences.
APPENDIX D
DATA REDUCTION

This appendix describes the method of converting the weight loss information from the raw data (mg/hour) into the \( \ln\left(\frac{p_{\text{zn}}^*}{p_{O_2}}\right) \) expression for sublimation rate. Determination of the best data fit using least squares analysis and calculations of \( \Delta H^* \) and \( \Delta S^* \) are also included.

The Hertz - Langmuir expression describes the loss rate from an evaporating surface. This equation can be expressed in terms of grams/cm\(^2\)-sec as

\[
R_v^e = \frac{p_i^e}{\pi} \left(\frac{M_i}{2\pi RT}\right)^{\frac{1}{2}}
\]  

(D-1)

\( R_v^e \) is the vaporization loss rate per unit area of surface, \( M_i \) is the molecular weight in grams/mole, \( R \) is the gas constant in ergs/mole-degree and \( p_i^e \) the vapor pressure of the \( i \)-th component in dynes/cm\(^2\).

The experimental data was obtained for free vaporization conditions, so the evaporation calculations must be made for those same conditions (denoted by superscript *).

Since the composition of ZnO stays nearly constant, the evaporation is termed congruent and

\[
J_{\text{zn}} = J_0 = 2J_{O_2}
\]  

(D-2)
This can be rewritten in terms of the vaporization rates for nonequilibrium conditions

\[ \frac{R^*}{M_{\text{zn}}} = \frac{R^*}{M_{\text{zn}}} = \frac{2R^*}{M_{\text{zn}}} = \frac{2R^*}{M_{\text{zn}}} \]  

Therefore,

\[ R^* = 2R^* \frac{M_{\text{zn}}}{M_{\text{zn}}} \]  

If

\[ R^*_{\text{tot}} = R^*_{\text{zn}} + R^*_{\text{zn}} \]  

Then

\[ R^*_{\text{tot}} = 2R^* \frac{M_{\text{zn}}}{M_{\text{zn}}} + R^*_{\text{zn}} \frac{R^*}{M_{\text{zn}} + M_{\text{zn}}} \]

\[ = R^*_{\text{zn}} (2M_{\text{zn}} + 1) \]

\[ = R^*_{\text{zn}} (2M_{\text{zn}} + M_{\text{zn}}) / M_{\text{zn}} \]  

Similarly, \( R^*_{\text{tot}} = R^*_{\text{zn}} (2M_{\text{zn}} + M_{\text{zn}}) / 2M_{\text{zn}} \)  

Using (D-1) for nonequilibrium conditions,

\[ R^*_{\text{tot}} = (2M_{\text{zn}} + M_{\text{zn}}) / 2M_{\text{zn}} (M_{\text{zn}} / 2RT)^{\frac{1}{2}} P^*_{\text{zn}} \]  

and

\[ R^*_{\text{tot}} = (2M_{\text{zn}} + M_{\text{zn}}) / M_{\text{zn}} (M_{\text{zn}} / 2RT)^{\frac{1}{2}} P^*_{\text{zn}} \]

For the vaporization reaction

\[ \text{ZnO (s)} = \text{Zn (v)} + \frac{1}{2} \text{O}_2 (v) \]

the equilibrium constant is given by

\[ K = \frac{p^e_{\text{zn}}}{p^e_{\text{zn}}} \left( \frac{1}{2} \right) \]
so

$$\Delta G^0_v = -RT \ln K$$

$$= -RT \ln (P^{e}_{zn} P^{e}_{O_2}) = H^0_v - T S^0_v$$

This leads to

$$\Delta H^0_v = -R \{ \ln (P^{e}_{zn} P^{e}_{O_2}) \} / \Theta (1/T)$$

(D-10)

and

$$\Delta S^0_v = H^0_v / T + R \ln (P^{e}_{zn} P^{e}_{O_2})$$

(D-11)

For the free vaporization case, the total change in free energy is

$$\Delta G_T = G^0_v + RT \ln (P^{e}_{zn} P^{e}_{O_2})$$

$$= -RT \ln (P^{e}_{zn} P^{e}_{O_2}) + RT \ln (P^{e}_{zn} P^{e}_{O_2})$$

$$= RT \ln [A]$$

(D-12)

where

$$A = (P^{e}_{zn} P^{e}_{O_2}) / (P^{e}_{zn} P^{e}_{O_2})$$

and

$$\Delta G_T = \Delta H_T - T \Delta S_T$$

(D-13)

Therefore

$$\Delta H_T = R \{ \Theta \ln (A) / \Theta (1/T) \}$$

(D-14)

and

$$\Delta S_T = \Delta H_T / T - R \ln (A)$$

(D-15)

where \( \Delta H_T \) and \( \Delta S_T \) are the enthalpy and entropy changes, respectively, for the vaporization. For the free vaporization case, we can write

$$\Delta H^* = \Delta H^0 - \Delta H_T$$
\[ \Delta H^* = -R \delta \ln \left( \frac{P^e}{P^e_0} \right)^{1/2} / \delta (1/T) \]  

Therefore

\[ \Delta S^* = \Delta H^*/T = R \ln \left( \frac{P^e}{P^e_0} \right)^{1/2} \]  

Similarly,

\[ \Delta S^* = \Delta H^*/T = R \ln \left( \frac{P^e}{P^e_0} \right)^{1/2} \]  

Now \( \Delta H^* \) and \( \Delta S^* \) are expressed in terms of \( \ln \left( \frac{P^e}{P^e_0} \right)^{1/2} \) which can be calculated from experimental results.

Equation (D-8) can be rewritten as

\[ P^e_{zn} = \frac{(8\pi RM_{zn})^{1/2}}{(2M_{zn} + M_{02})} (T)^{1/2} R^*_{tot} \]  

and (D-9) can be rewritten as

\[ P^e_{02} = \frac{(8\pi RM_{02})^{1/2}}{(2M_{zn} + M_{02})} (T)^{1/2} R^*_{tot} \]  

Substituting values in (D-19) and (D-20) for each of the constants shown \((\pi = 3.142, M_{zn} = 65.37 \text{ grams/mole}, M_{02} = 31.99 \text{ grams/mole}, R = 8.314 \times 10^7 \text{ ergs/mole-degree})\) yields

\[ P^e_{zn} = 2,271.06 T^{1/2} R^*_{tot} \]  

and

\[ P^e_{02} = 794.46 T^{1/2} R^*_{tot} \]  

where \( R^* \) expresses the free vaporization rate in grams/cm\(^2\)-sec.

The measured data is in terms of mg/hr so a conversion is necessary.

The measured diameter of the opening exposing the crystal surface is 4.8mm or a circle of 0.180956 cm\(^2\). Converting,
\[ R_{\text{tot}} = W(\text{mg/hr}) \times \frac{1}{0.180956 \text{ cm}^2} \times \frac{1 \text{ hr}}{3600\text{sec}} \times \frac{1\text{gm}}{10^3\text{mg}} \]

\[ = 1.535 \times 10^{-6} \text{ W gm/cm}^2 \text{ } \text{sec} \]  

(D-23)

Now, (D-21) and (D-22) can be written as

\[ p^*_{\text{zn}} = 3.486 \times 10^{-9} W T^{\frac{1}{2}} \]  

(D-24)

and

\[ p^*_{O_2} = 1.204 \times 10^{-9} W T^{\frac{1}{2}} \]  

(D-25)

To complete the conversion in terms of atmospheres of pressure, which corresponds to the experimental readings, (D-24) and (D-25) must be divided by 1.01325 \times 10^6 \text{dynes/cm}^2 \text{ per atmosphere.}

Therefore,

\[ p^*_{\text{zn}} = 3.44 \times 10^{-9} W T^{\frac{1}{2}} \text{ ATM} \]  

(D-26)

and

\[ p^*_{O_2} = 1.204 \times 10^{-9} W T^{\frac{1}{2}} \text{ ATM} \]  

(D-27)

The results of the above calculation were used to determine

\[ \ln(p^*_{\text{zn}} (p^*_{O_2})^{\frac{1}{2}}) \]  

for experimental conditions for this study. Values of enthalpy and entropy change were calculated using Equations (D-17) and (D-18). A least squares fit of the data \( \ln(p^*_{\text{zn}} (p^*_{O_2})^{\frac{1}{2}}) \) against \( 10^3/T \) was determined using a preprogrammed polynomial regression technique on a Hewlett-Packard 9830 computer. The results of the calculations are summarized in Tables 2 and 3.
REFERENCES


