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EFFECTS OF LIGHT AND OXYGEN CONTENT ON
THE EVAPORATION RATE OF ZINC OXIDE

Ralph Beaumont Leonard

(M.S. Thesis)

December, 1966

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EFFECTS OF LIGHT AND OXYGEN CONTENT ON
THE EVAPORATION RATE OF ZINC OXIDE

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December, 1966

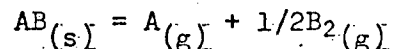
ABSTRACT

High intensity ultraviolet light of energy greater than the band gap was used to illuminate the evaporating surface of single crystals of zinc oxide in an attempt to determine if an electron-transfer mechanism was the rate limiting step. The influence of the oxygen content on the evaporation rate was studied by annealing the crystals in oxygen and observing the subsequent evaporation behavior.

No influence of light was found on the evaporation rate at 1365°K but excess oxygen caused the evaporation rate to drop sharply. The evaporation rate slowly increased to a constant rate as the oxygen diffused out. The activation enthalpy for the {1000} face, which is crystallographically stable during evaporation, was found to be 85 ± 8 kcal/mole.

I. INTRODUCTION

A compound which dissociates upon evaporation, i.e., undergoes a reaction of the type:



may have a rate limiting step involving surface reactions, desorption of surface atoms or diffusion of a species to the surface. A specific type of surface reaction that may limit vaporization is electron transfer between the surface cations and anions. Somorjai and Lester¹ have reviewed such phenomena.

Somorjai and Lester² found that light of greater than band gap energy increased the evaporation rate of the (1000) face of high resistivity cadmium sulfide. Such illumination is believed to change the free carrier concentration at the vaporizing surface by creation of hole-electron pairs. The rate of the hypothesized charge transfer rate-limiting step would increase because of the increased free electron concentration.

This work was undertaken to determine whether the rate of evaporation of zinc oxide, which, like cadmium sulfide, is a II-VI semiconductor, is also increased by high intensity ultraviolet light.

Anthrop and Searcy³ have reported that a mass spectrometer study of the vapor in equilibrium with zinc oxide revealed no species other than zinc atoms and oxygen molecules. They observed no detectable change in the lattice parameters and no significant systematic change with composition in the equilibrium constant for the dissociation of solid zinc oxide. Hoenig⁴ measured Knudsen effusion pressures for

zinc oxide that agree with values calculated from thermochemical data but his Langmuir studies indicated that an upper limit to the evaporation coefficient is 10^{-2} to 10^{-3} . He calculated an enthalpy of activation ($\Delta H^* = 93 \pm 3$ kcal/mole) which is approximately 23% higher than the equilibrium enthalpy. The $(10\bar{1}0)$ prismatic faces used in Hoenig's Langmuir studies were found to be unstable during evaporation as evidenced by preferred evaporation from other crystallographic planes. Hence it was deemed desirable in this work to determine the activation enthalpy of the (1000) basal face which was expected to be stable during evaporation.

Brewer⁵ and Anthrop³ both report zinc oxide to vaporize under neutral conditions at a composition that is close to stoichiometric. However, one can expect to find small differences, usually less than 10^{-4} mole/cm³, between the composition of a solid when it is evaporated under equilibrium and vacuum conditions.⁶ These small differences are undetectable by ordinary analytical methods,^{7,8} but can have a large influence on the evaporation rate and mechanism. Accordingly, crystals were annealed in oxygen in order to observe the effect of a change in stoichiometry on the evaporation rate and hence to obtain additional insight into the evaporation mechanism.

Zinc oxide crystallizes in the hexagonal wurtzite structure which has close packed oxygen ions with the zinc ions occupying one-half of the tetrahedral interstitial sites. Comprehensive reviews have been published on the electronic processes⁹ and surface characteristics¹⁰ of zinc oxide.

Zinc oxide is known to be an n-type semiconductor with negligible hole conduction as indicated by the Hall effect and Seebeck emf.¹¹ The band gap is approximately 3.2 eV which corresponds to 3875Å.^{10,12,13} The energy levels at 3.2 eV are usually considered to be due to singly ionized interstitial zinc atoms, however, Thomas⁷ has investigated interstitial zinc in single crystals of zinc oxide grown by the Sharowsky method and has concluded that unless the crystals have undergone some special treatment such as rapid quenching from an atmosphere of nearly saturated zinc vapor they will contain little interstitial zinc. He suggests that either oxygen vacancies or chemical impurities are the donors in ordinary zinc oxide.

II. EXPERIMENTAL

The single crystals that were used were grown by vapor deposition at the Electrical Products Division of the Minnesota Mining and Manufacturing Company. They were wafers 1 mm in thickness and approximately 6 mm in diameter and cut so that the flat face was the (1000) basal plane. The orientation was verified by means of back-reflection Laue x-ray photographs. A list of impurities found in the crystals by spectrographic means is included in the appendix.

The evaporation cell was fabricated from 99.5% pure aluminum oxide, the design and dimensions of which are shown in Fig. 1. A groove was cut around the cap so that the cell could be held securely by platinum wire to a thermocouple tube. A platinum disc and washer separated the crystal from the cell during evaporations and the snugly fitting cap could be easily removed to permit weighing of the crystal.

The thermocouple was made from .5 mm diameter platinum and platinum-10% rhodium wire and was calibrated against freezing copper where it checked within $1/2^{\circ}\text{C}$.

Evaporations were carried out in a 38 mm i.d. Morganite recrystallized alumina tube heated by a Burell high-temperature silicon carbide resistance furnace with a 35 mm zone in which the temperature was constant to $1-1/2^{\circ}\text{C}$.

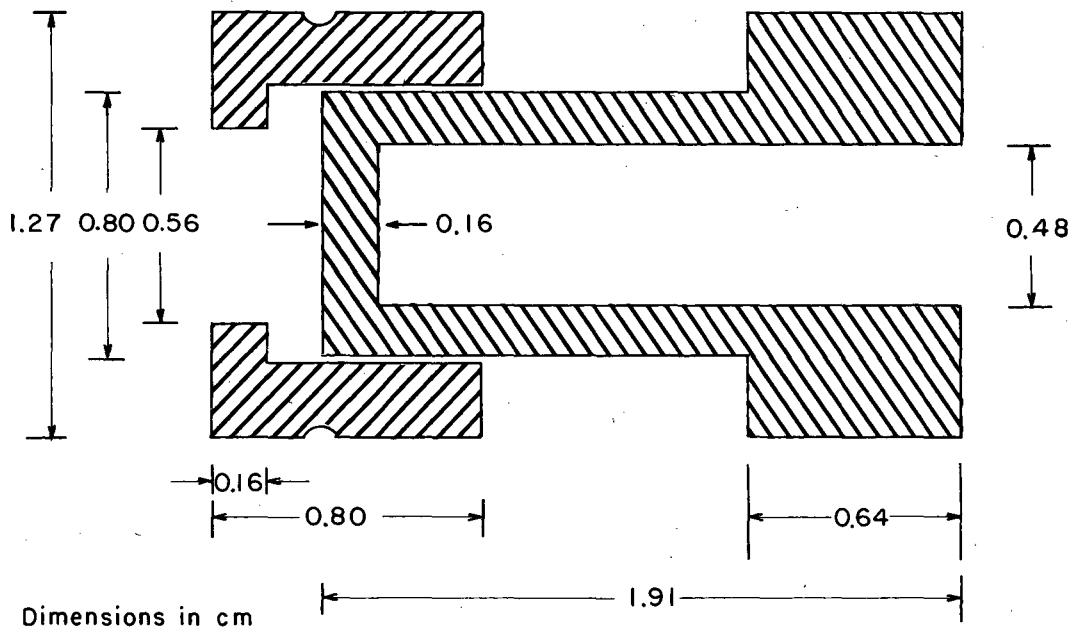
High intensity ultraviolet light was supplied by a PEK Labs., Inc., #110 high pressure mercury arc lamp in conjunction with a first-surface coated concave mirror. A spectrum of the lamp is given in Fig. 8. Distilled water contained in a cell with quartz windows served as an infrared filter to prevent heating of the crystal surface. This cell had an ultraviolet transmission coefficient of .98. The filtered beam of light was admitted into the furnace tube through a quartz window which was kept free from condensed zinc vapor by a series of tantalum shields in the cold zone. Even though no condensed zinc vapor was visible, the window was washed with hydrochloric acid between experiments in which light was used. The beam produced, at the sample, a 1.25 cm diameter spot of uniform high intensity light. Since the evaporating area was .55 cm in diameter, the entire evaporating surface could be bathed in the light. The intensity of the filtered light was approximately one watt/cm² as was determined by means of a thermopile calibrated at the Eppley Laboratory, Newport, Rhode Island (see appendix).

In order to prepare samples for use in the assessment of the influence of composition on evaporation kinetics, some crystals were

placed in a platinum basket and heated at 1365°K for 24 to 36 hours in an oxygen stream. The oxygen was dried by U-tubes filled with Drierite (calcium sulfate). The oxygen was stated to be 99.6% O₂, .3% Ar, and .1% N₂.

The crystals used for studies summarized in Fig. 3 were all from the same lot and batch, and all were sealed in an evacuated quartz tube and annealed at 1190°C for 35 hours. This treatment changed the color of the crystals from a light gray to light yellow but they remained transparent. They retained the light yellow color during all subsequent evaporations. The crystal surfaces were not polished or disturbed in any way between evaporations because the physical and chemical changes produced by such treatment might drastically change the evaporation rate.¹⁴

Evaporations were carried out by withdrawing the thermocouple and the attached cell into the cold zone, pumping the system to 3×10^{-5} torr and then quickly inserting the cell into the constant temperature zone. Evaporation times of 240 minutes at the lowest temperature and 15 minutes at the highest temperature were found to give convenient weight losses and yet permit a single crystal to be used for many evaporations. Crystals were quenched at the end of the runs by withdrawing them into the cold zone. Weight loss was determined by using an Ainsworth semi-micro balance. Crystals used in the determination of ΔH^* were brought to steady-state evaporation rates at each temperature before data points were taken.



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Fig. 1. Alumina evaporation cell.

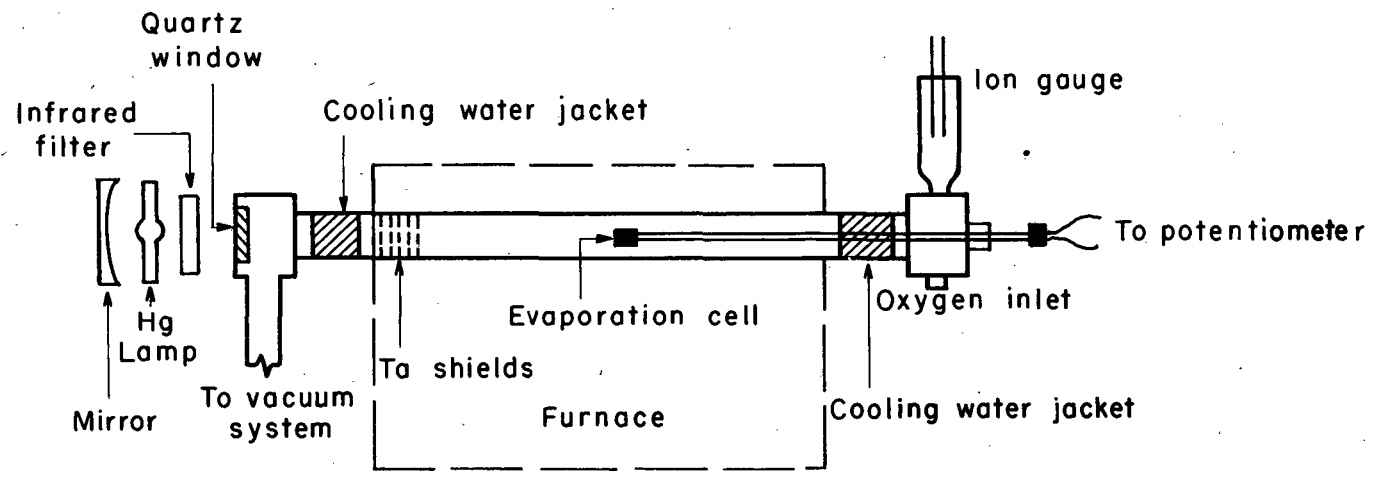


Fig. 2. Furnace assembly.

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III. RESULTS AND DISCUSSION

Figure 3 shows the evaporation of three different crystals from the same lot, after having been annealed in the evacuated quartz tube as explained in the experimental section. An anneal of this kind could not have changed the stoichiometry significantly from that of the unannealed crystals since the tube was sealed and was held in a uniform temperature region of the furnace. No cold zone existed in which vapor could condense.

Crystal a was brought to a constant evaporation rate at 1365°K under illumination. When the light was turned off, the crystal continued to evaporate at the same rate. Crystal b was annealed in oxygen before being brought to a constant evaporation rate at 1365°K under illumination. Its behavior was similar to that of crystal a both before and after the light was turned off. Crystal b was then re-annealed in oxygen, turned over and evaporated from the opposite side in the dark. Following the second oxygen anneal, the evaporation rate dropped sharply and then slowly returned to a slightly higher constant rate. After annealing in oxygen, crystal c was brought to a constant evaporation rate at 1365°K in the dark. It was then re-annealed in oxygen and evaporated from the opposite side under illumination. Its evaporation rate dropped sharply and slowly returned to a slightly higher constant rate.

Any effect of illumination would be most noticeable during the initial low evaporation rate since the ratio of incident photons to evaporating species would be highest. For the lowest evaporation

rates measured in light the ratio of incident photons to the number of evaporating ZnO units exceeded 100. At steady state the ratio exceeded 10. This contrasts with findings of Somorjai for cadmium sulfide for which the ratio of photons to evaporating cadmium sulfide units was approximately one to one. We can conclude that the excitation of electrons above the band gap in zinc oxide does not limit the rate of vacuum sublimation.

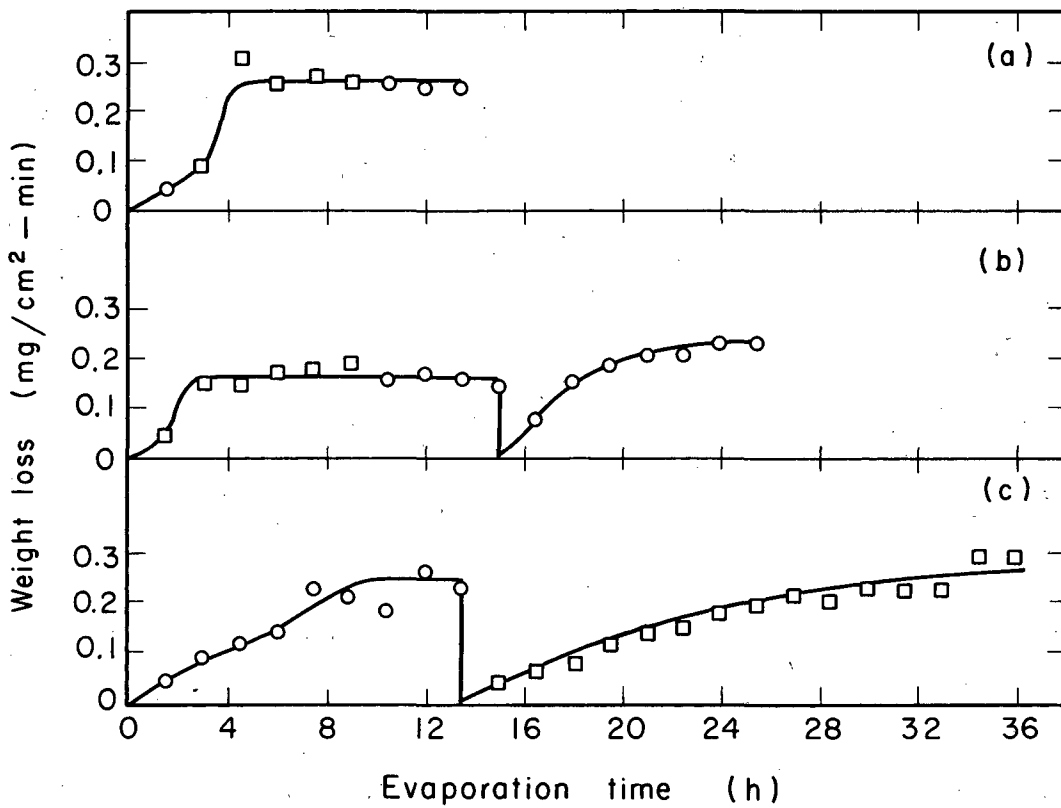
The initial increase with time of the evaporation rate must be due either to a change in impurity content or of the oxygen content with time. If it is due to an impurity effect, then once a constant evaporation rate has been reached the subsequent oxygen anneal would probably have no effect, but the sharp drop in evaporation rate following an oxygen anneal indicates that the evaporation kinetics depend upon the oxygen content and that the out-diffusion of the excess oxygen or escape of oxygen from the surface controls the evaporation rate until the crystal reaches its steady state composition. Crystal a, which was not annealed in oxygen, probably had a low initial evaporation rate because the oxygen content of the as-received crystal was higher than for congruent free surface sublimation.

Each crystal seemed to have some evaporation behavior peculiar to itself such as the time needed to reach a constant evaporation rate and the value of this rate. Crystal b reached a constant evaporation rate much faster than did crystal c both when initially evaporated and when re-evaporated following its second oxygen anneal. Crystals that had an evaporation rate of $.25 \text{ mg/cm}^2 - \text{min}$ (crystals a and c) or higher

produced a surface that looked like Fig. 5. This surface was very even with no large pits. The "orange peel" appearance was produced by pits of approximately 20 to 30 micron diameter and similar depth with no planar surfaces visible. On the other hand, crystals that had constant evaporation rates lower than $.25 \text{ mg/cm}^2 - \text{min}$ (crystal b) or crystals during their initial evaporation following an oxygen anneal exhibited surfaces that were deeply pitted as in Fig. 6 where the largest pit showing is about .3 mm in diameter. Many areas of such surfaces showed hexagonal pits of about 2 to 5 micron diameter. These various pits probably developed because of preferential evaporation from defects such as impurities or dislocations.

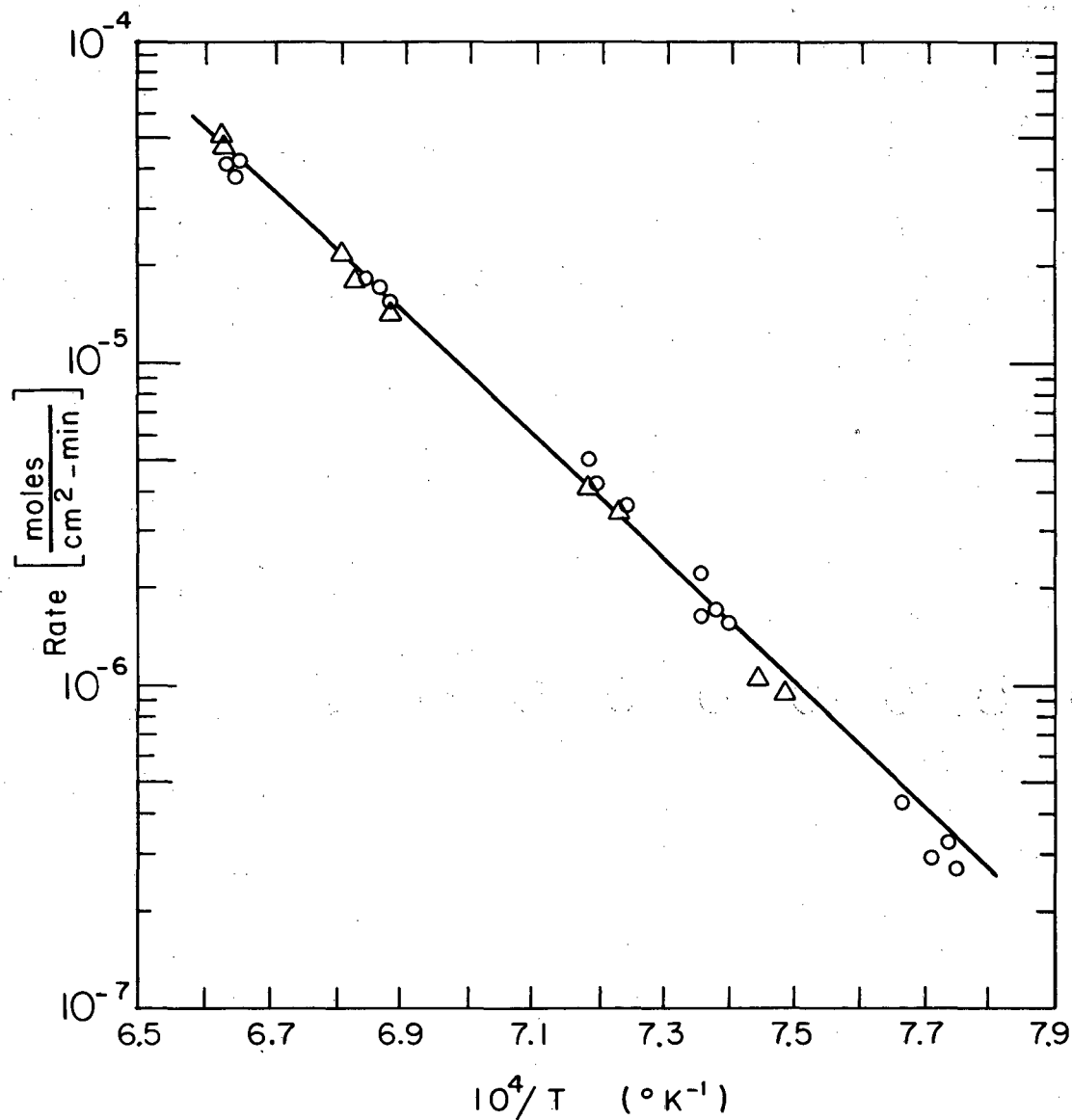
Two different crystals from the same lot were used in the determination of the activation enthalpy. At 1350°K ($10^4/1350 = 7.4$) the pressure of the oxygen from the zinc oxide becomes approximately equal to the background pressure in the system ($4 \times 10^{-8} \text{ atm}$). At this temperature and below all the data points fall slightly below the straight line established by the higher temperature points. If one assumed that the background gas was air, then the background pressure of oxygen would be approximately $8 \times 10^{-9} \text{ atm}$. If the evaporation kinetics do depend upon the concentration of oxygen at the vaporizing surface, then one would expect that the evaporation rate might be influenced by impinging oxygen molecules.

A least squares line including all points gives $\Delta H^* = 89.44 \text{ Kcal/mole}$, while if the six data points from temperatures lower than 1350°K are excluded, then $\Delta H^* = 85.13 \text{ Kcal/mole}$.



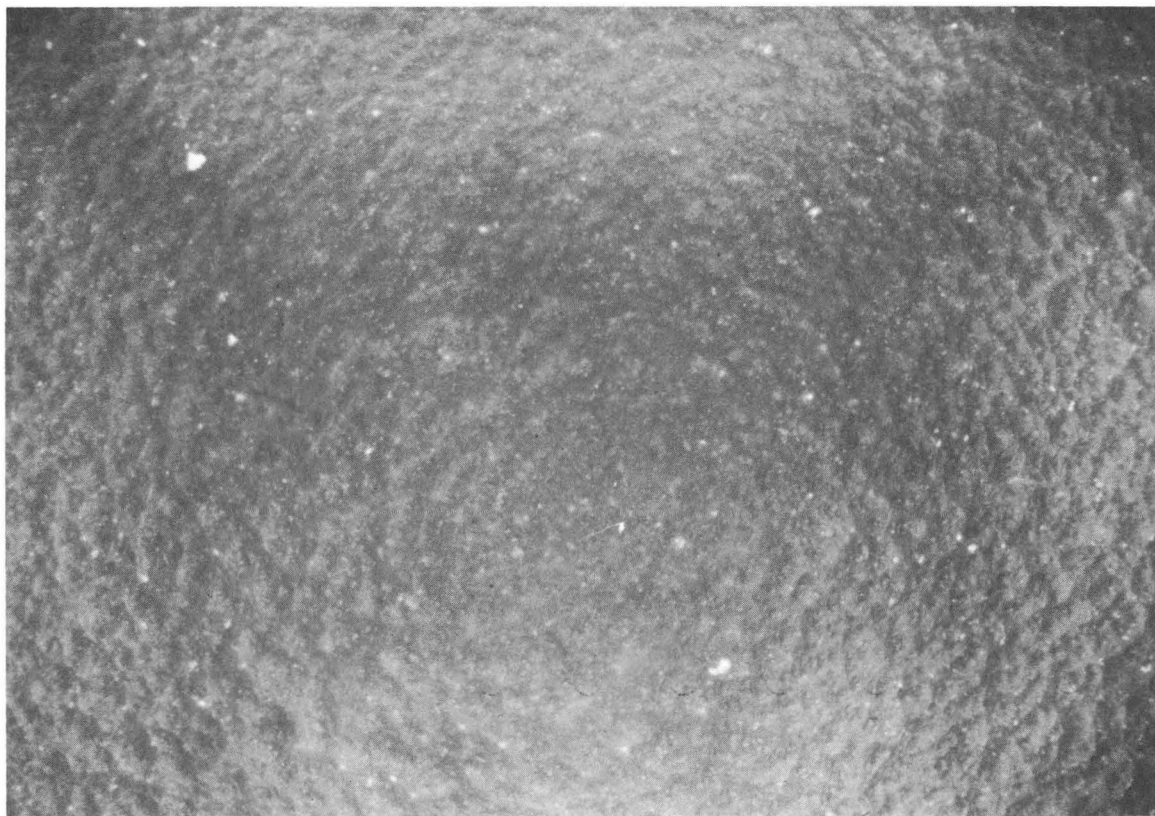
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Fig. 3. Weight loss vs time for (1000) face of three ZnO single crystals at 1365 K.
□ illuminated ○ dark



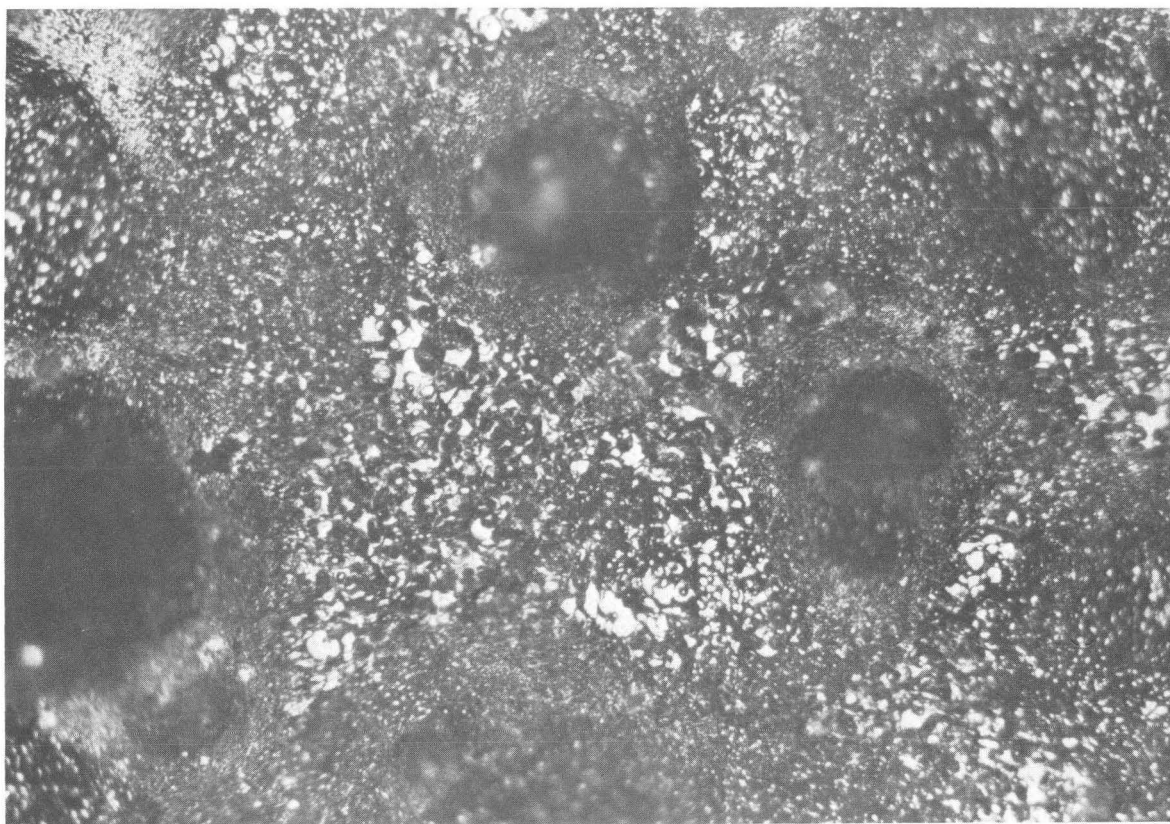
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Fig. 4. Rate of evaporation of two ZnO single crystals from (1000) face as a function of reciprocal temperature.



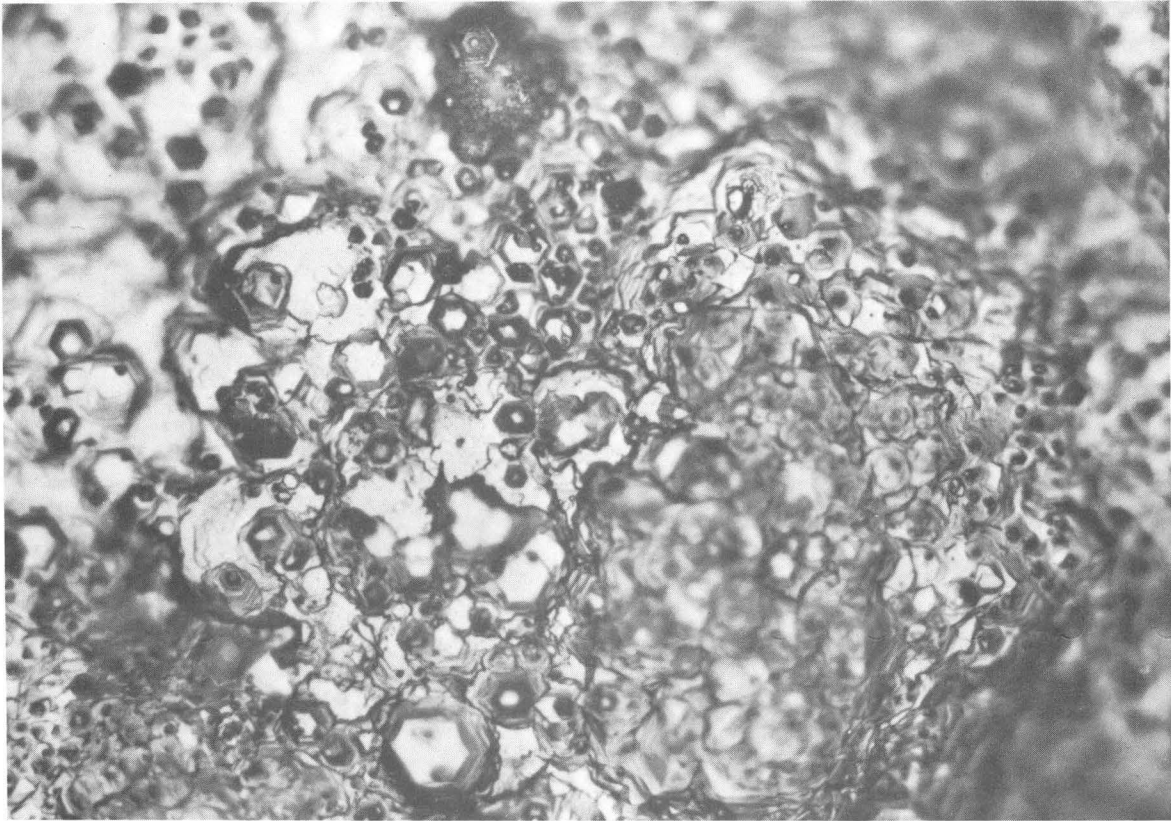
ZN-6038

Fig. 5. Surface of (1000) face of zinc oxide single crystal with a high evaporation rate ($> .25 \text{ mg/cm}^2 - \text{min}$) X88.



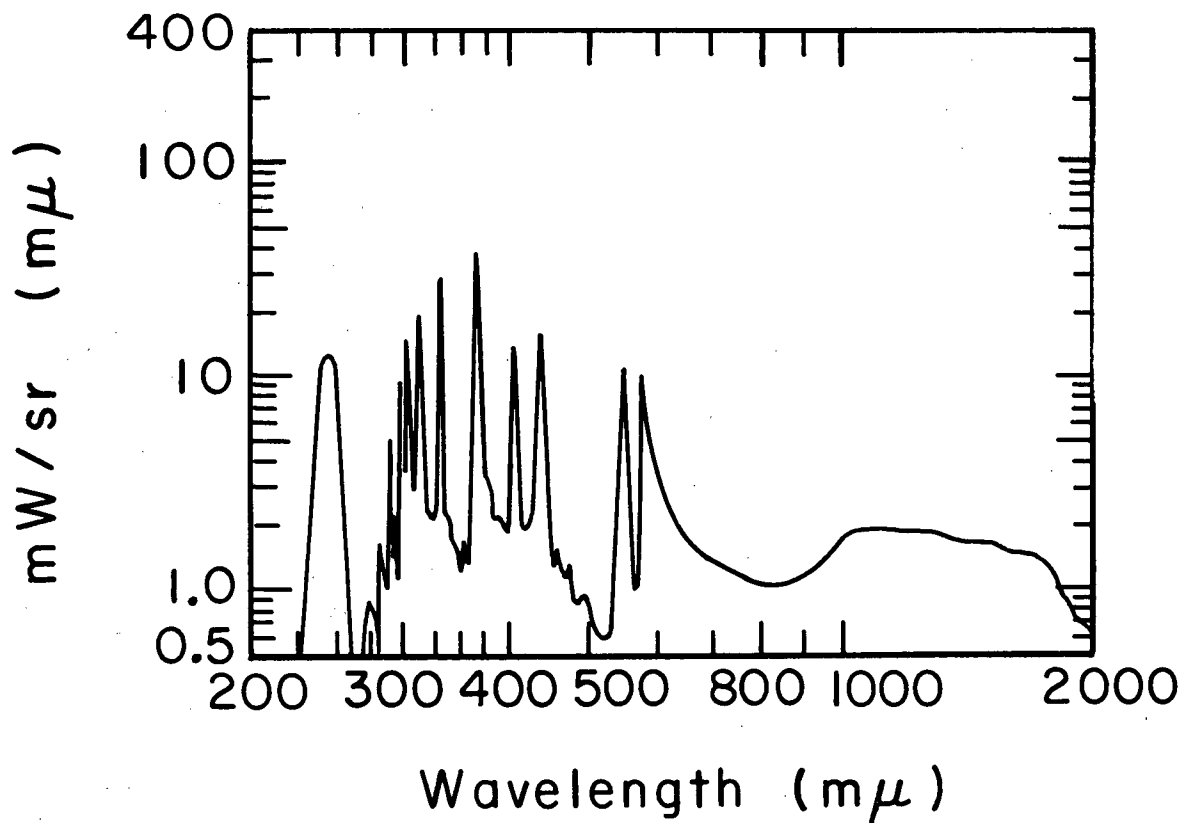
ZN-6039

Fig. 6. Surface of (1000) face of zinc oxide single crystal with a low evaporation rate ($< .25 \text{ mg/cm}^2 - \text{min}$) X140.



ZN-6040

Fig. 7. Detail of evaporation pits of (1000) face of ZnO single crystal X250.



MUB-14129

Fig. 8. Spectrum of PEK #110 high-pressure mercury arc lamp.

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APPENDIX

Impurities as found by emission spectrographic means for the crystals used in Fig. 3.

<u>Measurement Limit</u>	<u>Amount Detected</u>	<u>Measurement Limit</u>	<u>Amount Detected</u>
Sr < 1.0 ppm	-	Fe < 1.0 ppm	< 1
Co 3	-	Cr < 1.0	< 1
Zr 3	-	Ni < 1.0	-
Ag < 1.0	< 1	Si 5	< 5
Cu < 1.0	8	Sb 10	-
Cd 3	-	Mg < 1.0	< 1
Ti < 1.0	-	Pb 3	-
V < 1.0	-	Mn < 1.0	-
Ca < 1.0	< 1	B < 1.0	15
Sn < 1.0	< 1	Te 10	-
Mo < 1.0	-	As 10	-
Be < 1.0	-	Ba 3	-
Al 3	< 3	Li < 1.0	< 1
Bi < 1.0	-	K 3	< 3
In 3	-	Na < 1.0	8
Ge < 1.0	-		

Calculation of the Ratio of Photons to Evaporating Species

The average λ is certainly greater than 1000\AA , so that $\nu_{\text{ave}} = 3 \cdot 10^{15} \text{ sec}^{-1}$

$$E = h\nu = 6.63 \cdot 10^{-34} \text{ joule} \cdot \text{sec} \cdot 3 \cdot 10^{15} \text{ sec}^{-1} = 20 \cdot 10^{-19} \text{ joule/photon}$$

$$1 \frac{\text{watt}}{\text{cm}^2} = \frac{1 \text{ joule}}{\text{sec} \cdot \text{cm}^2}$$

$$\frac{\# \text{ photons}}{\text{cm}^2 \cdot \text{min}} = \frac{60}{20 \cdot 10^{-19}} \frac{\text{photons}}{\text{cm}^2 \cdot \text{min}} = 3 \cdot 10^{19} \frac{\text{photons}}{\text{cm}^2 \cdot \text{min}}$$

$$\text{Molecular weight of zinc oxide} = 81.37 \frac{\text{g}}{\text{mole}}$$

$$\frac{2.5 \cdot 10^{-5} \text{g} \cdot 6.02 \cdot 10^{23} \frac{\text{molecules}}{\text{mole}}}{\text{cm}^2 \cdot \text{min} \cdot 81.37 \frac{\text{g}}{\text{mole}}} = 2 \cdot 10^{17} \frac{\text{ZnO molecules}}{\text{cm}^2 \cdot \text{min}}$$

$$\frac{\# \text{ photons}}{\# \text{ evaporating ZnO molecules}} = \frac{3 \cdot 10^{19}}{2 \cdot 10^{17}} = 100$$

MEASUREMENT OF LIGHT INTENSITY

A bismuth-silver surface type Eppley Thermopile (Serial #6142) with a 1 mm LiF window was used for light intensity measurements. The thermopile was calibrated by the Eppley Laboratory, Inc., Newport, Rhode Island, using a standard lamp which had been calibrated by the National Bureau of Standards. The thermopile developed .061 microvolts per microwatt per cm^2 .

The beam of light was focused on the thermopile and the voltage developed measured by a microvoltmeter. Neutral density filters of known absorbance were used so that the thermopile would not be overloaded by the high intensity light.

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