UCRL-16067

University of California

Ernest O. Lawrence Radiation Laboratory

CHARGE TRANSFER CONTROLLED VAPORIZATION OF CADMIUM SULFIDE SINGLE CRYSTALS: I. EFFECT OF LIGHT ON THE EVAPORATION RATE OF THE (0001)-FACE

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

Berkeley, California

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.

Submitted to J. Chemical Physics

UCRL-16067

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory

AEC Contract W-7405-eng-48

CHARGE TRANSFER CONTROLLED VAPORIZATION OF CADMIUM SULFIDE SINGLE CRYSTALS: I. EFFECT OF LIGHT ON THE EVAPORATION RATE OF THE (0001)-FACE.

G. A. Somorjai and J. E. Lester

MAY 1965

Charge Transfer Controlled Vaporization of Cadmium Sulfide Single Crystals: I. Effect of Light of the Evaporation Rate of the (0001)-Face.

G. A. Somorjai and J. E. Lester*

Department of Chemistry, University of California, [illegible]
Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California 94720

ABSTRACT

Light of greater than band gap energy was found to change markedly the vacuum evaporation rate of the (0001)-face of cadmium sulfide single crystals. Evaporation temperatures of 680-740°C and light intensities of 5.0×10^3–2.0×10^5 μwatt/cm^2 were used. The results were interpreted assuming that charge transfer is the rate determining step in the sequence of vaporization surface reactions. An evaporation mechanism in terms of charge transfer has been proposed. Light (1) changes the free carrier concentrations at the vaporizing surface, and (2) under proper conditions, changes the composition of the crystals. High resistivity crystals showed a five-fold increase of their evaporation rate under illumination due to the increase by light of both electron and hole concentrations. In low resistivity crystals in which illumination can only significantly increase the minority free carrier concentration above the dark equilibrium value effects which are due to the change of the crystal composition dominated.

Introduction

The evaporation mechanism of cadmium sulfide single crystals has been studied recently by several techniques. Dependence of the evaporation rate on temperature,[1,2] surface concentration,[1] crystal orientation,[3] and minute excesses of the crystal constituents, cadmium and sulfur, in the crystal lattice,[4] have been investigated. In most of the investigations the vacuum evaporation rate of one face of the single crystal has been studied. From these results, a tentative mechanism for the rate determining surface reaction has been proposed[1] and the bulk diffusion rate of sulfur vacancies has been measured.[4] It was found that the evaporation rate is a sensitive function of small excesses of cadmium or sulfur in the cadmium sulfide crystal lattice. The solubility of either cadmium or sulfur in cadmium sulfide is so low,[5] however, that, by heating the crystals at the highest temperature and dopant pressure (1200°C, 20 atm. cadmium or sulfur), less than one in 10^3 surface atoms/cm^2 can be substituted.[4] For the presence of such small concentrations of surface sites to have such a drastic influence on the evaporation rate makes it improbable that any atomic surface step could play a rate controlling role in the vaporization process.[6] A small excess of either cadmium or sulfur in cadmium sulfide, however, changes the equilibrium free carrier concentration of the crystals by more than ten orders of magnitude by shifting the Fermi level, thus, it also drastically changes

the free carrier concentration at the surface.[7] It was then thought that the charge density at the surface may play an all important role in the evaporation surface reactions.

In order to investigate whether charge transfer is the rate limiting surface step in the evaporation of cadmium sulfide we have varied the carrier concentration at the crystal surface in two ways: (1) Illumination of the crystal surface by light of greater than band gap energy, (2) doping the crystal with copper impurity. In this paper we shall describe the effect of light on the vaporization rate of the (0001)-face of cadmium sulfide single crystal while the effect of copper doping is described in the following paper.

In order to perturb the equilibrium carrier concentration at the surface by light, the electron-hole pair concentration produced by illumination should be larger than its equilibrium value in dark, at the evaporation temperature.[7] This criterion was met by using light intensities in the range of 5.0×10^3–2.0×10^5 μwatt/cm^2.

Experimental

Cadmium sulfide single crystals of the highest available purity[8] were used in all of the experiments. The crystals were n-type, with high room temperature conductivity (1 mho cm), and mobility (~200 cm^2/volt sec). The high conductivity

indicates[1] the presence of cadmium in excess of the steady state concentration at the evaporation temperatures (680-760°C).[9] This excess could be removed by annealing the crystals at 700°C for 48 hours.[1] After annealing the conductivity decreased to 10^{-4}–10^{-3} mho cm^{-1}. This treatment was necessary to obtain reproducible evaporation rates.

Doped crystals were prepared by doping with cadmium or sulfur in a sealed, evacuated quartz chamber at an elevated temperature (1200°C) and dopant pressure (10-20 atm. sulfur or cadmium). The crystals remained n-type after any of the doping treatments. The room temperature conductivity changed, however, to about 10^{-10} mho cm^{-1} for sulfur doped, and to about 2.0 mho cm^{-1} for cadmium doped specimens.

High pressure mercury and/or xenon lamps were used as light sources. Intensities of 5.1×10^3–2.0×10^5 μwatt/cm^2 were used in the light experiments. For wavelength dependence studies, either a Bausch and Lomb grating monochromator, or cutoff filters were employed.

Studies of the orientation dependence of the vacuum evaporation have shown that the (0001), or c-face, is stable under free evaporation conditions;[3] i.e., its surface area remains unchanged. Hence, the c-face was used in all the present studies. The crystals (3x3x6 mm) were polished, etched (6N HCl), then wrapped in platinum foil such that only the c-face was exposed. Several crystals were used in each experiment (10-20).

The apparatus has been described elsewhere.[7] Care was taken that the vapor species could not condense on the quartz window through which the sample was illuminated. No heating of the surface due to light could be detected at the intensities employed. Since light changes the rate of vacuum evaporation of CdS markedly, care had to be taken to insure uniform illumination [i.e., photon flux (photon/cm^2 sec)] over the entire vaporizing c-face. Under non-uniform illumination the crystal surface became irregular.

Evaporation rate measurements were carried out in the temperature range 680-740°C. Temperature measurements were corrected[2] to give the true surface temperature. The ambient pressure was $5x10^{-7}$–$5x10^{-6}$ torr in the reaction chamber in most of the experiments, after it has been established that the evaporation rates were independent of the ambient pressure in the $5x10^{-9}$–$7x10^{-5}$ torr range.

Results

Evaporation of Sulfur Doped Cadmium Sulfide Crystals in Light.

Sulfur doped cadmium sulfide crystals are n-type, have high room temperature resistivities ($\approx 10^{10}$ ohm cm), i.e., their equilibrium ionized vacancy and free carrier concentration in the dark is small.[10] Calculations which were made to estimate the charge concentration near the crystal surface in the dark and in light at the evaporation temperatures by using reasonable estimates for the position of the Fermi level ($E_c - E_F \simeq 0.95$ eV),[11] density of states ($\simeq 10^{19}$ cm^{-3}), photon flux ($\simeq 3.4x10^{17}$

photons/cm^2 sec) and free carrier lifetime ($\leq 10^{-6}$ sec),[10] show that for these crystals the free carrier concentration can, indeed, be increased by light.

Figure I shows the effect of light of intensity I = 2.0×10^5 μwatt/cm^2 on the evaporation rate. At 696°C the evaporation rate in light is five times that in the dark. The increased rate remains constant for hours at a given light level. The dependence of the evaporation rate on intensity at a constant temperature, is shown in Fig. II. The rate increases linearly with the light intensity in the studied intensity range, within the accuracy of the experiments (5%).

Studies of the wavelength dependence of the light effect yield a cutoff at $\lambda \leq 6400$ Å ± 200 Å. Longer wavelength light had no effect on the vacuum evaporation rate. The cutoff wavelength corresponds to the optical band gap of cadmium sulfide at the temperature of evaporation, 700°C.[10] The large uncertainty is due to the substitution of filters for the monochromator in the measurements at these high light intensities. From the known light intensities and evaporation rates one can estimate the quantum efficiency of the light effect, i.e., the charge transfer process. It was found to be ≥0.7 atom/photon for all of the crystals used in these experiments.

Evaporation of Cadmium Doped Cadmium Sulfide Crystals in Light.

The cadmium doped n-type crystals of cadmium sulfide have low room temperature resistivities (≈2.0 ohm cm) indicating a large electron to hole concentration ratio ($n \gg p$) in the

dark. This is believed to be due to the presence of a large excess of ionized sulfur vacancies which are donors. These crystals show a transient vaporization behavior in the dark.[4] The initial low rate is followed by an exponential increase of the evaporation rate as it approaches the steady state value at a given temperature. The evaporation rate in dark, is controlled by the out-diffusion of the dopant from the bulk of the crystal.[4] Steady state is finally reached when the excess dopant is removed and the steady state composition is attained.

Figure III shows the evaporation rate of cadmium-doped crystals in dark and in light ($I = 2.0 \times 10^5$ μwatt/cm^2) at T = 715°C. It is seen that the low evaporation rate remains virtually unchanged as long as the crystal vaporizes under illumination. Once light is turned off, the vaporization rate begins to increase as expected. Light apparently prevents the out-diffusion of excess cadmium from the vaporizing cadmium sulfide crystal.

Evaporation of Annealed Cadmium Sulfide Crystals in Light

The undoped crystals of cadmium sulfide after annealing are n-type, and have room temperature resistivities $\approx 10^4$–10^5 ohm cm ($n \gg p$).[4] When evaporated in dark they show steady state evaporation rate.[1] Calculations made to estimate the carrier concentration of the undoped crystal at the evaporation temperature revealed that, unlike the high resistivity sulfur doped crystals, one would not expect to be able to increase the electron concentration appreciably with respect to its dark

equilibrium value. The hole concentration however, could probably be increased.

Illumination by light of the highest intensity $I \simeq 2.0 \times 10^5$ μwatt/cm^2 was found to increase the evaporation rate of annealed cadmium sulfide crystals. This increase is about 20% to 50% over the steady state dark value depending on the evaporation temperature (smaller increase at higher temperatures). It was also found that the effect of light depends somewhat on the crystal lot which was used in these experiments. The dependence of the results on the crystal lots was especially pronounced in experiments at low light intensities ($\leq 2.0 \times 10^4$ μwatt/cm^2). For several crystal lots (5-25 samples were prepared from each crystal lot) the evaporation rate was found to decrease exponentially from its dark steady state value to a new, lower steady state rate (lower by 30%).[7] The lower steady state rate once established, could be maintained indefinitely under illumination. When light was turned off the evaporation rate started to rise and returned slowly (about two hours) to its higher dark steady state value.[7] For other samples however, from different crystal lots, illumination by low intensity light had no effect on the evaporation rate in the temperature range of interest.

The annealed single crystal samples for the different crystal lots differed only in their trace impurity concentrations. Their carrier concentrations and mobilities in the dark were the same within 20%. For one lot of undoped crystals for which spectroscopic analysis showed the presence of $\geq 10^{16}$ cm^{-3} copper

impurity, the evaporation rate was found to be insensitive to illumination at the intensities and wavelengths used in the experiments. It was concluded that the observed irreproducibility in the evaporation characteristics of undoped crystals in light, was due to the presence of uncontrolled impurities in the different crystal lots.

The trace impurities (Pb, Si, Fe, Ag) do not seem to effect the electrical properties of CdS in the dark, although they may have an effect on the trapping lifetime and recombination kinetics of free carriers which were produced by light at the vaporizing surface. The effect of one impurity copper, will be discussed in the following paper.

For sulfur and cadmium doped crystals the presence of trace impurities had no effect on the experimental results. Our doping treatment apparently swamped any effect due to uncontrolled impurities.

The wavelength dependence of all of the light effects on the undoped crystals was the same as was found for the sulfur doped cadmium sulfide crystals. There is a cutoff at the high temperature optical band edge[10] of cadmium sulfide (λ = 6400 Å ± 100 Å at 700°C). At longer wavelengths light had no effect on the evaporation rate of the undoped crystals.

It was found that under non-vaporizing conditions, cadmium particles could be precipitated out on an illuminated surface of undoped cadmium sulfide.[7] This surface reaction took place at 280-450°C in an oxidizing atmosphere. No precipitation occurs in the absence of light of larger than band gap energy.

X-ray and electron diffraction measurements were used to identify the precipitated cadmium particles.

Discussion

Light of greater than band gap energy and intensities $I = 5.0\times10^{3}-2.0\times10^{5}$ μwatt/cm^2 was found to affect the evaporation rate of cadmium sulfide single crystal c-face. The results can be explained in terms of (a) charge transfer controlled evaporation and (b) light induced change of the composition of cadmium sulfide crystals.

The following statements summarize the informations deduced from experiments which will be used in the analysis of the data.

(a) Cadmium sulfide is n-type, which is believed to be due to excess of singly ionized sulfur vacancies, V_S^+ ($V_S^+ >> V_{Cd}^-$). All vacancies can be considered to be ionized at the evaporation temperature.[10] The crystals remain n-type after all of the doping treatments. The crystal constituents, cadmium and sulfur, are assumed to be doubly ionized.

(b) The bulk diffusion rate of sulfur vacancies (D_{700} - 6.5×10^{-6} cm^2/sec) is greater[4,12] than the vacuum evaporation rates of the (0001)-face of cadmium sulfide throughout the experimental temperature range.[13]

(c) The evaporation rate of sulfur doped high resistivity cadmium sulfide crystals is greatly increased by light over the steady state value in the dark. A quantum efficiency near unity was found from studies of the intensity dependence of

the evaporation rate. Illumination of the vaporizing surface of cadmium doped high conductivity cadmium sulfide single crystals apparently prevents the out-diffusion of excess cadmium which would occur in the absence of light.

(d) The net reaction for vacuum evaporation is assumed to be the same as the dominant vaporization reaction in equilibrium[14]

$$CdS_{(solid)} \rightarrow Cd_{(vapor)} + \frac{1}{2} S_{2(vapor)} \qquad (1)$$

At the vacuum evaporation steady state, cadmium sulfide vaporizes congruently,[1] that is

$$\frac{dCd_{(vapor)}}{dt} = 2\frac{dS_{2(vapor)}}{dt}$$

(e) Particles of cadmium can be precipitated out on the illuminated cadmium sulfide surface by light of greater than band gap energy under non-vaporizing conditions.[7] This is taken as a direct evidence of the composition change which occurs in CdS under the influence of light, absorbed at the crystal surface.

The evaporation mechanism of the c-face of cadmium sulfide single crystals is described in the Appendix. Here, we consider only the effect of light on the evaporation rate. Light of greater than band gap energy creates electron-hole pairs in a surface layer of thickness ($\leq 10^{-3}$ cm)[15] small compared to the crystal dimensions. The concentrations of free carriers at the vaporizing crystal surface for a given light intensity, can be expressed as

$$n_{light} = n_{dark} + \Delta n$$

$$p_{light} = p_{dark} + \Delta p$$

where n_{light}, n_{dark}, p_{light} and p_{dark} are the electron and hole concentrations in light and in the dark, respectively. The rate controlling charge transfer steps for vaporization under illumination (Eqs. 2A and 3A in the Appendix) may be written as

$$CdS_{(surface)} + 2(p+\Delta p) \underset{k_2^a}{\overset{k_1^a}{\rightleftharpoons}} (S+\Delta S)_{(surface)} + (V_S^+ + \Delta V_S^+)_{(surface)} + (n+\Delta n) \quad (2)$$

$$CdS_{(surface)} + 2(n+\Delta n) \underset{k_2^b}{\overset{k_1^b}{\rightleftharpoons}} (Cd+\Delta Cd)_{(Surface)} + (V_{Cd}^- + \Delta V_{Cd}^-) + (p+\Delta p) \quad (3)$$

where S, Cd, V_S^+, and V_{Cd}^- are the steady state concentrations of sulfur and cadmium atoms and ionized vacancies at the surface, in the dark, ΔS, ΔCd, ΔV_S^+, and ΔV_{Cd}^- are the concentrations of sulfur and cadmium atoms, ionized sulfur and cadmium vacancies, respectively, in excess of their steady state concentrations. We shall now consider experimental conditions which are of special importance to our studies.

(I) $n_{dark} \approx p_{dark}$; $n_{dark} < \Delta n \approx \Delta p > p_{dark}$

These conditions are fulfilled for high resistivity sulfur doped cadmium sulfide crystals and may also have been partially met by undoped crystals at high light intensities. It is seen from Eqs. (2) and (3) that in this case both reactions are

accelerated at an equal rate. If charge transfer is the rate determining step in the sequence of surface reaction steps leading to evaporation, an increase in the overall evaporation rate of cadmium sulfide single crystals would be expected. This has been observed for the sulfur doped crystals for many hours of evaporation as shown in Fig. I. Under these conditions at constant illumination, Eqs. (2) and (3) are indistinguishable and can be expressed as

$$CdS_{(surface)} + n_{light} + p_{light} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (S+\Delta S)_{(surface)} + (Cd+\Delta Cd)_{(surface)} + (V_S^+ + \Delta V_S^+)_{(surface)} + (V_{Cd}^- + \Delta V_{Cd}^-)_{(surface)} \quad (4)$$

(II) $n_{dark} >> p_{dark}$; $n_{dark} >> \Delta n \approx \Delta p >> p_{dark}$

These conditions were met in the experiments with cadmium doped crystals for the light intensities employed, and probably for undoped cadmium sulfide samples at low light levels ($I \leq 2.0 \times 10^4$ μwatt/cm^2). These crystals are strongly n-type ($n_{dark} >> p_{dark}$) hence, only the minority carrier concentration could be increased by illumination. Under these conditions Eqs. (2) and (3) can be rewritten and added to give,

$$CdS_{(surface)} + \Delta p + n \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (S+\Delta S)_{(surface)} + Cd_{(surface)} + (V_S^+ + \Delta V_S^+)_{(surface)} + V_{Cd}^-{}_{(surface)} \quad (5)$$

Thus, the ionized sulfur vacancy concentration becomes increasingly larger at the vaporizing surface, until the solubility limit of cadmium in cadmium sulfide, $(V_S^+)_{solubility}$ is reached.

The surface cadmium which is produced in excess of its solubility $(V_S^+ + \Delta V_S^+)_{(surface)} - (V_S^+)_{(Solubility)}$ in CdS at the evaporation temperature, cannot precipitate under vacuum vaporization conditions since metallic cadmium has very high vapor pressure in the temperature range of interest and would vaporize instantly.[16] Excess cadmium at the vaporizing surface could, however, also diffuse rapidly into the bulk of the crystal due to the large diffusion rate for sulfur vacancies in CdS and the concentration gradient for sulfur vacancies which was established between the surface and the bulk under these conditions. Hence, the crystal becomes cadmium-rich by the indiffusion of excess sulfur vacancies from the illuminated, vaporizing surface.

This model explains why the low vaporization rate of cadmium doped crystals is maintained in light. Excess cadmium which could diffuse out of the cadmium sulfide crystal in dark via the vaporizing surface cannot be removed effectively under illumination. The constant generation of excess cadmium at the vaporizing surface of the cadmium sulfide crystal in light, prevents the establishment of a concentration gradient between the bulk and the surface.

The observed precipitation of cadmium on the illuminated surface of CdS in an oxidizing atmosphere also indicates that the crystal composition shifts to the cadmium rich side in light, with respect to the dark steady state composition.

The exponential decrease of the evaporation rate of undoped cadmium sulfide crystals at low light levels, and subsequent slow return of the dark rate to its steady state value[7] can only be explained by a diffusion controlled composition change of the illuminated single crystals. Cadmium-rich crystals have lower evaporation rates than undoped crystals, as shown recently.[4] This result, however, cannot be taken as evidence of the light induced composition change due to the observed irreproducibility. Work is in progress to further purify the CdS single crystals for continued investigation of the effect of light on the vaporization of undoped crystals.

Further experiments are needed to determine the nature of the electron and hole trapping centers in CdS which are responsible for the efficient charge transfer observed at these elevated temperatures.

Appendix

The diffusion of ionized vacancies between the bulk of the cadmium sulfide single crystal and its vaporizing surface may be represented by the equation

$$V^{+}_{S(bulk)} + V^{-}_{Cd(bulk)} \xrightleftharpoons{\text{diffusion}} V^{+}_{S(surface)} + V^{-}_{Cd(surface)} \quad (1A)$$

where the symbols are the corresponding ionized vacancy concentrations in the bulk and at the surface.

The charge transfer surface reaction steps which control the vaporization in the dark, may be written as

$$CdS_{(surface)} + 2p \underset{k_2^a}{\overset{k_1^a}{\rightleftharpoons}} S_{(surface)} + V^{+}_{S(surface)} + n \quad (2A)$$

$$CdS_{(surface)} + 2n \underset{k_2^b}{\overset{k_1^b}{\rightleftharpoons}} Cd_{(surface)} + V^{-}_{Cd(surface)} + p \quad (3A)$$

Thus, the surface ions capture electrons and/or holes and the resulting neutral atoms diffuse to surface sites which are removed from their original lattice positions within the trapping lifetime of the free carriers. Charge transfer controls the vaporization only if surface diffusion rates of neutral atoms from their original lattice sites and the rates of subsequent surface steps are greater than the recombination rates of trapped electrons and/or holes. Slow surface diffusion would lead to equilibrium in Eqs. (2A) and (3A). Silver salts[17]

also show the conditions which we seem to have encountered in cadmium sulfide. The vacancy at the surface which was left behind, becomes ionized. We have separated the electron and hole transfer steps since under certain experimental conditions (2A) or (3A) may be rate controlling.

Once the neutral atoms have been created, their vaporization occur as a result of a sequence of rapid reactions,

$$Cd_{(surface)} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Cd_{(gas)} \tag{4A}$$

$$2S_{(surface)} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} S_{2(surface)} \tag{5A}$$

$$S_{2(surface)} \underset{k_8}{\overset{k_7}{\rightleftharpoons}} S_{2(gas)} \tag{6A}$$

Under steady state conditions in dark, at a given temperature, Eqs. (2A) and (3A) are indistinguishable since the vaporization is congruent. Therefore, we should write instead of (2A) and (3A)

$$CdS_{(surface)}+n+p \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S_{(surface)}+Cd_{(surface)}+V^{+}_{S(surface)}+V^{-}_{Cd(surface)} \tag{7A}$$

At any temperature, in steady state, the ratio V^{+}_{S}/V^{-}_{Cd} is constant.[18] Any change in this ratio at the same temperature brings about a lowering of the evaporation rate. This was proven by doping the cadmium sulfide single crystals with cadmium and/or sulfur, and is due to the large changes in the free carrier concentrations produced by the doping treatments.[4]

Studies of the surface concentration dependence[1] of the cadmium sulfide evaporation using a molecular beam of sulfur, would yield the following rate equation assuming steady state in (4A) and equilibrium in (5A) and (6A)

$$-\frac{dCdS_{(surface)}}{dt} = \frac{k_1 np}{1+(k_1/k_4\ K)[V_{S(surface)}^{+}][V_{Cd(surface)}^{-}]S_{2(gas)}^{1/2}} \tag{8A}$$

instead of Eq. (3) of reference (1). Using atomic beam of cadmium the cadmium surface concentration dependence of the evaporation rate for large cadmium fluxes is given by [instead of Eq. (5) in reference (1)]

$$-\frac{dCdS_{(surface)}}{dt} = \frac{k_1^2 k_3^2 k_5 n^2 p^2}{k_2^2 k_4^2 (V_S^{+})^2 (V_{Cd}^{+})^2} \frac{1}{(Cd_{gas})^2} \tag{9A}$$

Here, we assumed steady state for (5A) and (6A) and equilibrium in (4A). Since under steady state conditions the surface concentrations of vacancies and of free carriers are fixed the introduction of charge transfer into the rate equations of reference (1) have no effect on the validity of its conclusions. It explains, however, why the predicted cadmium pressure dependence of the evaporation rate was not observed in the experiments.[1] The small cadmium vacancy concentration in the n-type ($V_{Cd}^{-} << V_S^{+}$) undoped cadmium sulfide in which the cadmium concentration is already close to its solubility limit, renders the evaporation rate independent of cadmium pressure.

Footnotes and References

* National Science Foundation Graduate Fellow

1. G. A. Somorjai and D. W. Jepsen, J. Chem. Phys., 41, 1389 (1964).

2. G. A. Somorjai, Condensation and Evaporation of Solids, Ed., E. Rutner, P. Goldfinger, and J. P. Hirth (Gordon and Breach Science Publ. New York) 1964.

3. G. A. Somorjai and N. R. Stemple, J. Appl. Phys., 35, 3398 (1964).

4. G. A. Somorjai and D. W. Jepsen, J. Chem. Phys., 41, 1394 (1964).

5. F. A. Kroger, H. J. Vink, and J. von der Boomgaard, Z. Physik. Chem., 203, 1 (1954).

6. W. K. Burton, N. Cabrera, and F. C. Frank, Phil. Trans. Roy. Soc. London, A243, 299 (1951).

7. G. A. Somorjai, Surface Science, 2, 298 (1964).

8. Cadmium sulfide single crystals were prepared by Eagle-Picher Company, Miami, Oklahoma.

9. F. A. Kroger, H. J. Vink and J. von der Boomgaard, Physica, 20, 950 (1954).

10. R. H. Bube, Photoconductivity of Solids (John Wiley and Sons, Inc.) 1960.

11. G. A. Somorjai and R. S. Title, J. Phys. Chem. 68, 3907 (1964).

12. In order to compare the steady state rate of evaporation of the c-face of cadmium sulfide with the time dependent diffusion rate of sulfur vacancies in cadmium sulfide, it is convenient to calculate the crystal thickness, x_V, which is removed by vacuum evaporation in one hour, and

Footnotes (Continued)

the mean displacement of ionized sulfur vacancies, x_D, during the same period. In the temperature range 680-730°C $x_V = 5.2 \times 10^{-2}$ cm - 9.9×10^{-2} cm while x_D - 3.0×10^{-1} cm at 700°C.

13. H. H. Woodbury, Phys. Rev., 134, 492 (1964).

14. M. Jeunehomme, Ph.D. thesis, Universite Libre de Bruxelles (1962).

15. The penetration depth of the photoelectrons can be estimated from the free carrier lifetime at the evaporation temperature and the electronic mobility.

16. R. E. Honig and H. O. Hook, RCA Rev., 21, No. 3 (1960).

17. J. W. Mitchell, J. of Photographic Science, 5, 49 (1957).

18. G. A. Somorjai and J. E. Lester, "Composition Change of Binary Compounds Under Conditions of Equilibrium and Vacuum Vaporization", J. Chem. Phys. (to be published).

Acknowledgment

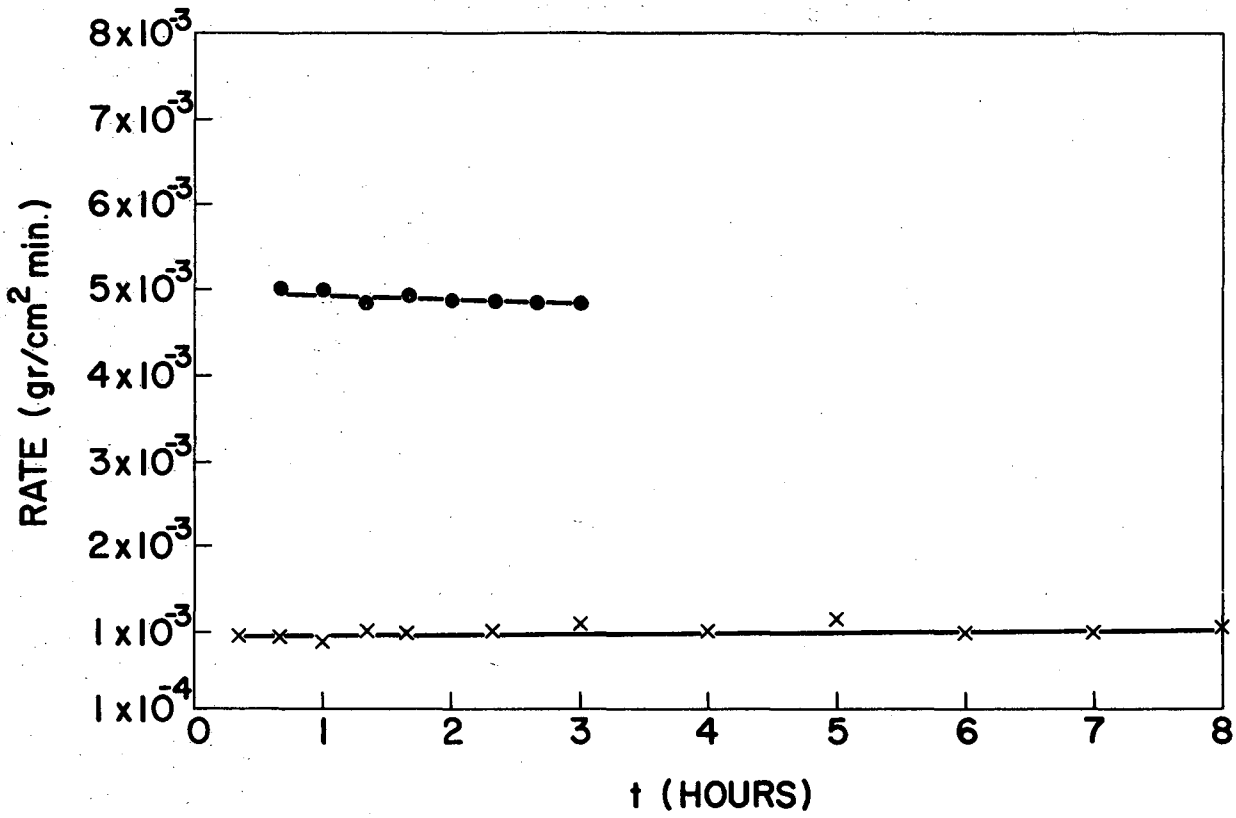
This work was performed under the auspices of the U. S. Atomic Energy Commission.

Figure Captions

Figure I. The evaporation rate of sulfur-doped (1200°C, 20 atm) CdS single crystal c-face, x - in dark and o in light at 696°C.

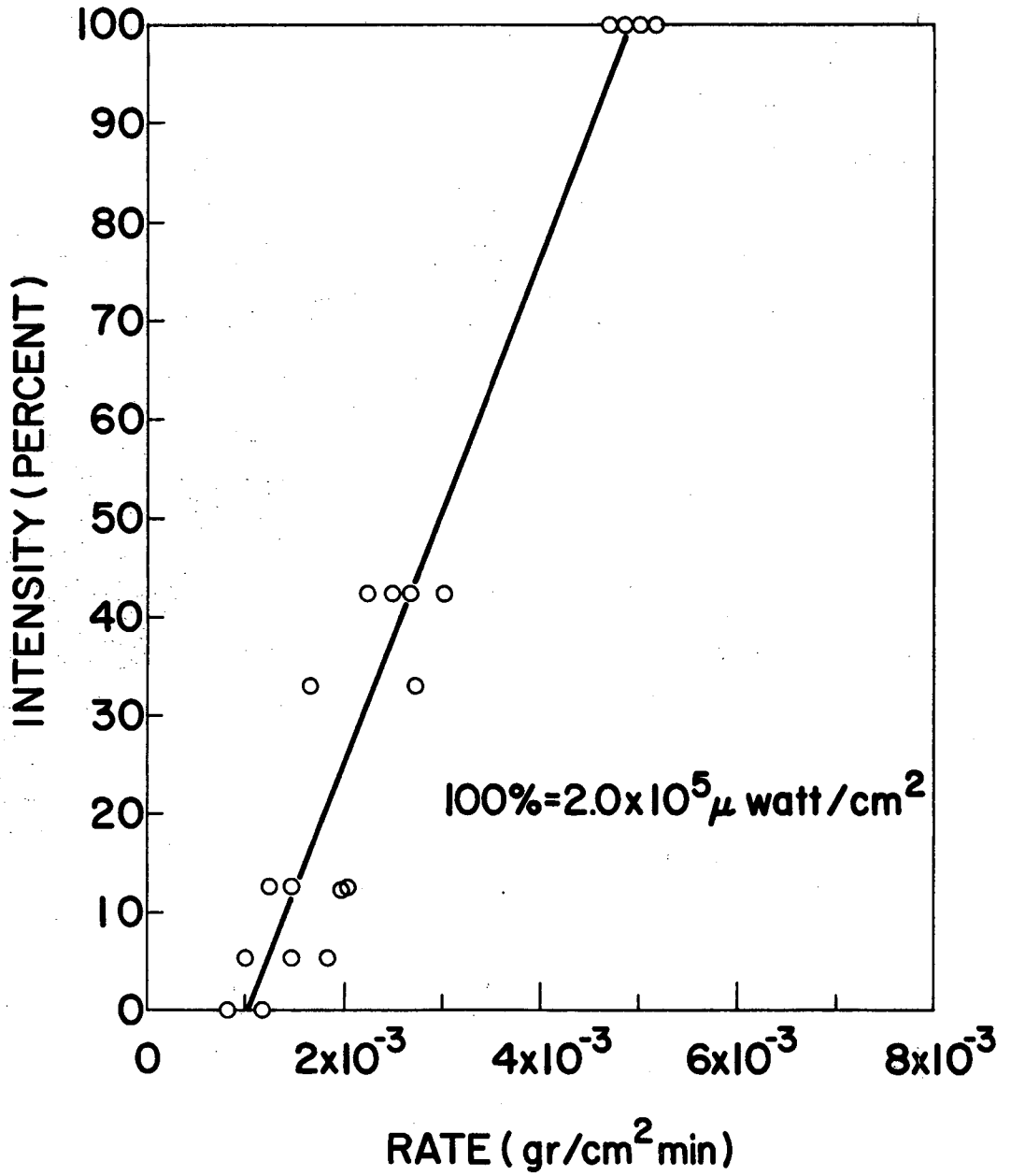
Figure II. Light intensity dependence of the evaporation rate of sulfur-doped (1200°C, 20 atm) CdS single crystal c-face at 696°C. 100% = 2.0×10^5 μwatt/cm^2.

Figure III. The evaporation rate of cadmium-doped (1200°C, 10 atm) CdS single crystal c-face, x - in dark and o - in light at 715°C as a function of time.



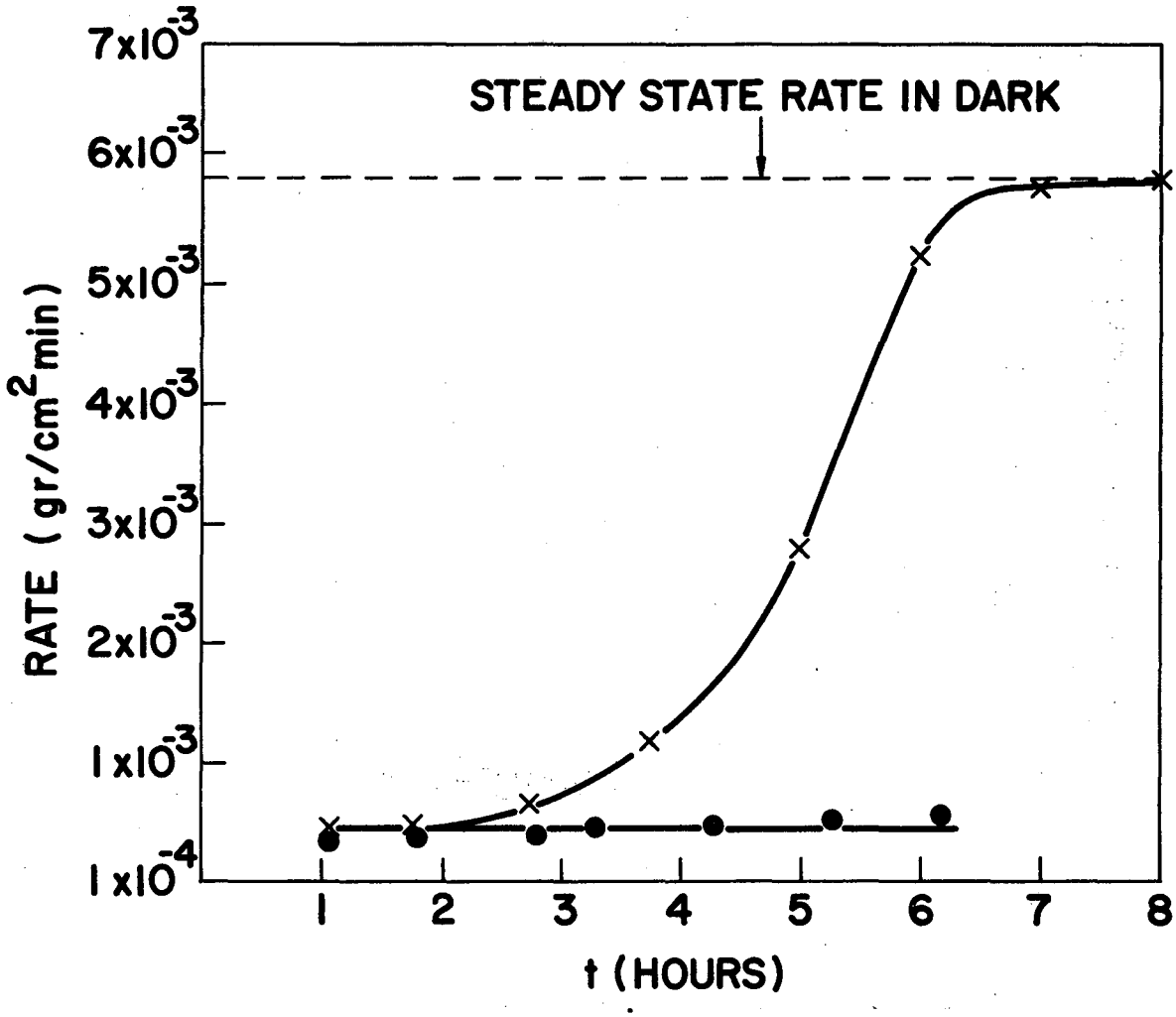
MUB-5946

Fig. 1



MUB-5947

Fig. 2



MUB-5945

Fig. 3

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.