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MAY 1965

Charge Transfer Controlled Vaporization of Cadmium Sulfide Single Crystals: II. Effect of Copper Doping on the Evaporation Rate of the (0001)-Face.

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ABSTRACT

The evaporation rate of copper doped CdS single crystal c-face was measured in the temperature range 680-740°C. The evaporation rate was decreased markedly with respect to that of the undoped crystals. The copper surface concentration dependence of the vaporization rate was studied by simultaneous diffusion of copper into, and vaporization of the crystal at the $(000\bar{1})$ and (0001) crystal-faces, respectively. The presence of copper impurity in the bulk of the crystal was found to also have an effect on the evaporation rate of CdS. The results were interpreted in terms of self-compensation in CdS via sulfur vacancy formation, copper and sulfur vacancy diffusion toward the vaporizing surface. Copper doping rendered the crystal vaporization insensitive to light.

Introduction

The charge transfer model of the vacuum vaporization of cadmium sulfide single crystal has many implications. It suggests that ionized impurities which act as acceptors or donors in the cadmium sulfide crystal lattice may have influence on the evaporation rate. The effects of cadmium and/or sulfur excesses[1] which have reduced the evaporation rate of cadmium sulfide have been taken as an indication of the validity of this deduction. It also points to the possibility that the charge transfer controlled vaporization may not be a unique property of the IIB-VIA compounds but could be the rate determining step for the vaporization of other groups of compounds as well.

In order to investigate the effect of impurities on the evaporation rate of cadmium sulfide we chose copper. Copper is a well known acceptor[2] in cadmium sulfide, it has a large diffusion coefficient[3] and solubility[4] in the cadmium sulfide crystal lattice. These properties made this impurity attractive for the evaporation studies. The purpose of this paper is to describe the effect of copper doping on the evaporation rate of cadmium sulfide single crystal c-faces and to provide further proof of the validity of the charge transfer controlled vaporization model.

Experiment and Results

The n-type ultra-high purity cadmium sulfide single crystals were cut (3x3x6 mm) perpendicular to the c-face (3x3 mm) and were annealed in vacuum at 700°C for 10 hours in order to attain the steady state composition, characteristic of cadmium sulfide at that temperature.[5] Copper was evaporated onto all faces of the crystals and diffusion was carried out in vacuum sealed quartz tubes at 700°C for 24 hours. The yellow cadmium sulfide crystals (room temperature band gap: 2.4 ev)[2] turned black as a result of copper diffusion due to absorption by the copper acceptor centers at $\approx$ 0.6-1.0 ev above the valence band.[2,4] Due to this effect, copper diffusion into cadmium sulfide can conveniently be studied by optical absorption measurements along the diffusion profile.[6] The room temperature resistivity of the crystals before copper diffusion was $R \simeq 10^3$ ohm cm and that after copper diffusion $R \simeq 10^6$ ohm cm. For many of the crystals however, copper was vacuum deposited only onto the $(000\bar{1})$-face for reasons described below. The apparatus and the experimental procedure used in these experiments has been described previously.[7]

The evaporation rate of the (0001)-face of a cadmium sulfide single crystal at 700°C is shown in Fig. I as a function of time. This crystal had previously been uniformly copper doped at 700°C. The evaporation rate decreased by more than 50% relative to the vaporization rate of the pure crystal at the same temperature. The rate remains independent of time throughout the experiment in the temperature range 680-740°C.

In order to investigate the dependence of the cadmium sulfide evaporation rate on the surface concentration of diffused copper, the following experiment was performed. Copper was vacuum deposited on only the $(000\bar{1})$-face of the undoped crystals prior to wrapping the specimen in platinum foil.[5] During the vacuum evaporation experiments the (0001)-face was allowed to vaporize while copper diffuses into the crystal from the back surface. This way the vaporizing surface retreats while the copper diffusion front moves toward the vaporizing face.[8] As the copper profile reaches the vaporizing (0001)-face, a rapid change in the copper surface concentration occurs which, according to Fig. I should give rise to a time-dependent lowering of the evaporation rate. Figures II, III, and IV are representative data showing this effect at three different temperatures. There is an exponential decrease of the evaporation rate due to the increasing copper surface concentration. The rapid decrease of the rate begins earlier the higher the evaporation temperature and consequently, the temperature of copper diffusion. The surface concentration of copper increases at the vaporizing cadmium sulfide surface until it reaches a maximum, which corresponds to the solubility of copper in cadmium sulfide at that temperature. The copper concentration at this point becomes uniform throughout the crystal. A new lower steady state evaporation rate is then established which is characteristic of the constant surface concentration of copper ions in the CdS crystal.

For all the cadmium sulfide crystals for which both copper diffusion from the back-face (0001) and evaporation from the front-surface (0001) takes place simultaneously (25-30 samples) the evaporation rate increases at first significantly above its steady state value for the pure crystal. This increase occurs shortly after the beginning of the evaporation experiment (within minutes) and the evaporation rate remains higher than the steady state value <u>until</u> the copper diffusion profile reaches the vaporizing surface. Then, the rate drops exponentially to attain its new, lower steady state value.

In order to investigate the effect of light on copper diffused crystals, the uniformly doped samples were illuminated by light of energy greater than band gap energy and intensities 10^3-10^5 μwatt/cm^2. Light was found to have no detectable effect on the vaporization of copper doped cadmium sulfide single crystals in the temperature range 680-740°C.

Discussion

The following statements summarize the experimental informations obtained on the vaporizing copper doped cadmium sulfide single crystals.

(1) Copper is an acceptor in the cadmium sulfide crystal lattice, has a diffusion coefficient parallel to the (0001)-face D_{11} (cm^2/sec) = $1.6 \times 10^{-3} \exp(-17{,}800/RT)$ in the temperature range of interest, 680-740°C.[3]

(2) The vacuum evaporation rate of pure cadmium sulfide is decreased by about 50% in the presence of copper in the <u>vaporizing surface</u>. The evaporation rate decreases exponentially with increasing copper surface concentration until finally a lower steady state rate is attained. This rate is reached when

the surface concentration of copper corresponds to that of its solubility in cadmium sulfide at the evaporation temperature.

(3) The vacuum evaporation rate of pure cadmium sulfide is increased by the presence of copper in the bulk of the single crystal but not at the vaporizing surface. This was observed by the simultaneous evaporation of and copper duffusion into the cadmium sulfide single crystals at the (0001) and $(000\overline{1})$ crystal faces, respectively. The fact that the presence of bulk impurity appears to have an effect on the evaporation surface reaction indicates rapid "communication" between the bulk and the surface.[1,9]

(4) Light of same wavelengths and intensities which had effected the evaporation rate of cadmium sulfide single crystals in the absence of copper, had no effect on the evaporation rates of uniformly copper doped samples.

The rates of copper diffusion in cadmium sulfide and the rates of vaporization of cadmium sulfide are of the same order of magnitude as can be seen from Table I. Here, we have tabulated that thickness of the pure crystal which is removed by vacuum evaporation in one hour at different temperatures, and compared it with the mean displacement of diffusing copper atoms during the same period. During the evaporation of CdS with simultaneous copper diffusion, the dopant concentration in the crystal increases continuously until its solubility limit is reached throughout the crystal.

Undoped cadmium sulfide is strongly n-type which is attributed to the large excess of ionized donor sulfur vacancies, V_S^+, over the ionized acceptor cadmium vacancies, $V_{Cd}^-(V_S^+ >> V_{Cd}^-)$.[10,11] Hence, for pure cadmium sulfide the charge neutrality condition gives $(V_S^+)_{pure} \simeq n$, where n is the majority free carrier concentration and $(V_S^+)_{pure}$ is the sulfur vacancy concentration in the undoped cadmium sulfide. At first, copper diffuses into the crystal lattice by filling up cadmium vacancies. The solubility of copper in cadmium sulfide however, is much larger than (V_{Cd}^-)[4] hence, it must find another mechanism to enter the crystal.

It is well known that the large band gap IIB-VIA compounds including cadmium sulfide show self-compensation[12-14] under conditions of charged impurity diffusion. That is, for every ionized acceptor (or donor) which enters the crystal an ionized donor vacancy (acceptor vacancy) is generated.[12] Thus, for every copper ion, Cu_{CdS}^-, in the cadmium sulfide lattice an ionized sulfur vacancy is created:

$$Cu_{external} \longrightarrow V_S^+ + Cu_{CdS}^-.$$

Therefore the charge neutrality condition for the copper doped CdS lattice can be written

$$(V_S^+)_{doped} + p \approx (Cu^-)_{CdS} + n$$

where $(V_S^+)_{doped}$ is the sulfur vacancy concentration in the copper doped cadmium sulfide. This way, the concentrations of both ionized donor vacancies and of ionized copper acceptors in the cadmium sulfide crystals increase as a function of increasing copper concentration in the crystal.

Sulfur vacancies have much larger diffusion rates ($D_{700} \geq 6.5\text{x}10^{-6}$ cm^2/sec) in cadmium sulfide[1] than the copper ions ($D_{700} = 1.6\text{x}10^{-7}$ cm^2/sec).[3] Therefore, they diffuse more rapidly toward the vaporizing surface from the bulk where they were created. Thus, due to the larger separation between the copper acceptors and donor vacancies at the early stages of copper diffusion, direct charge transfer between these two centers is improbable. Ionization occurs via the valence band (for copper) and the conduction band (for sulfur vacancy) with a corresponding increase in the free carrier concentration over that of their equilibrium value in the pure crystal. The mobile free carriers thus created, give rise to an increased charge concentration at the vaporizing surface, i.e., the evaporation rate increases. This way copper ions, far removed from the surface could have an accelerating effect on the evaporation surface reaction as observed in the experiments.

All available experimental evidence, obtained from electrical measurements indicate, that cadmium sulfide cannot be made p-type by copper diffusion or by the introduction of other acceptors. This is thought to be due to self-compensation.[4,12] Our observation of the increased evaporation rate of copper doped cadmium sulfide confirms the occurrence of self-compensation by excess sulfur vacancy formation. Self compensation is the only model we found to explain the observed increased initial evaporation rate.

As the copper diffusion profile reaches the surface, direct charge recombination between the copper centers and the sulfur vacancies could take place. The free carrier concentration is therefore reduced at the vaporizing surface. The evaporation rate drops sharply to a new lower steady state value which is characteristic of the low charge concentration found in the copper doped crystals.

A similar model was proposed by W. M. Anderson et al. to explain the behavior of the photocurrent and the mobility of photoexcited carriers in highly Cu-doped CdS crystals.[15] This physical picture of sensitized photoconductor with two recombination centers was also considered by Bube.[2]

Light of same band gap energy and intensities which have effected the evaporation rate of undoped cadmium sulfide crystals was found to have no effect on the evaporation of copper doped samples. The crystal resistivity was increased by the presence of copper sufficiently that, the production of electron-hole pairs in excess of their equilibrium concentration in the dark, could be achieved. Thus, the absence of the light effect would indicate that either free carrier life time has decreased sharply in the copper doped samples or, that cadmium vacancies play an important role in the rate determining charge transfer step. Charge recombination, via copper sites may occur before charge transfer to the cadmium and sulfur ions at the surface and subsequent evaporation can be completed, according to the proposed evaporation mechanism in the preceding paper. Copper doping which renders the evaporation rate insensitive to light also reduces V_{Cd}^{-}, while sulfur doping which increases V_{Cd}^{-} increases the photosensitivity as well.

The effect of bulk copper on the evaporation surface reaction is due partly to the generation and rapid diffusion of excess sulfur vacancies and free carriers. In turn, the diffusion rate of copper will likely be effected by change of the sulfur vacancy concentration of the cadmium sulfide crystal. Continuous illumination of the cadmium sulfide crystal by light of effective wavelength and intensity at the (0001)-face while copper diffusion takes place from the $(000\bar{1})$-face, could have an effect on the diffusion rate of copper.

It is interesting to speculate which groups of compounds besides those in the IIB-VIA group could show charge transfer controlled vaporization. Insulators with reported low vaporization coefficients are the primary suspects.[16-18] Good communication between the bulk and the vaporizing surface via a rapid diffusion mechanism may also be a necessary condition for charge transfer to be rate determining. The reason that most metals fulfill the Langmuir condition of vaporization[19] (with evaporation coefficient near unity) may only be due to their large concentration of free electrons at the evaporation temperature. The experimental verification of these questions is within the realm of present techniques and will be attempted.

Acknowledgment

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Table I

T°C	$\bar{x}_D$ (cm)	$\bar{x}_V$ (cm)
680	$4.38\text{x}10^{-2}$	$5.23\text{x}10^{-2}$
700	$4.80\text{x}10^{-2}$	$6.97\text{x}10^{-2}$
715	$5.16\text{x}10^{-2}$	$8.34\text{x}10^{-2}$
740	$5.52\text{x}10^{-2}$	$9.95\text{x}10^{-2}$

Figure Captions

Fig. I. o-Evaporation rate of the (0001)-face of CdS at 700°C. The crystal was copper doped at 700°C. Dotted line shows the evaporation rate of undoped crystal.

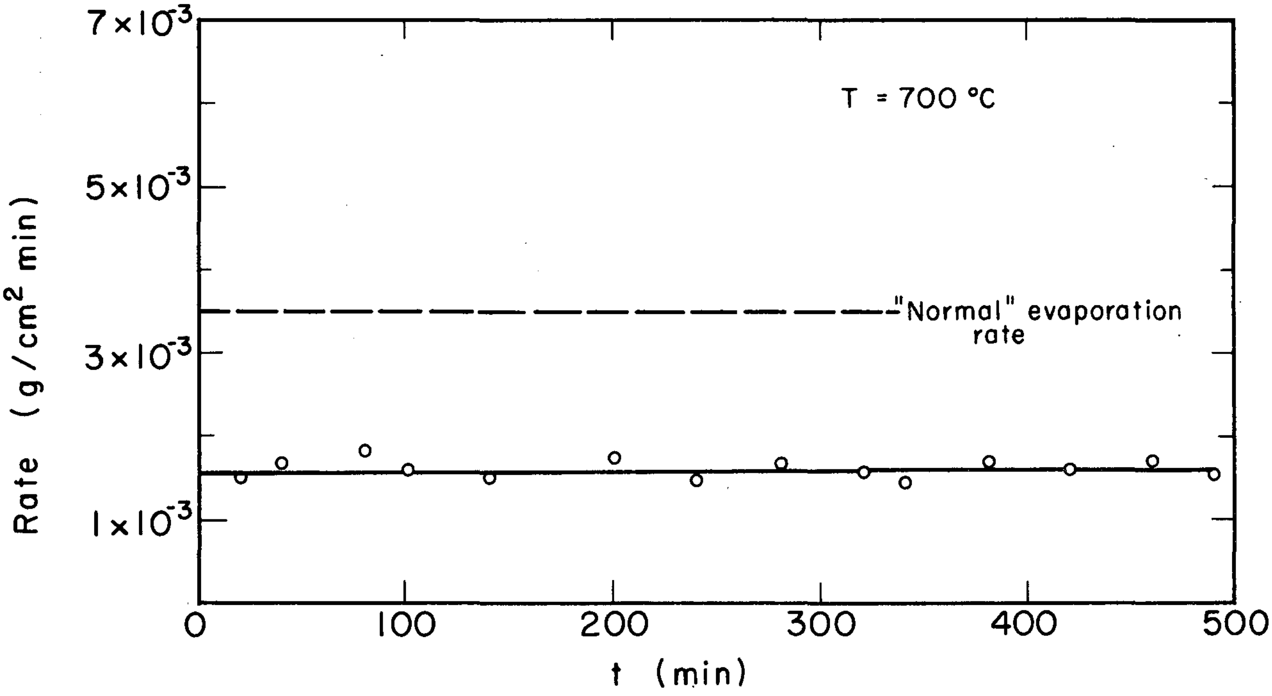
Fig. II. Evaporation rate of the (0001)-face of CdS at 700°C while copper diffuses into the crystal from the $(000\bar{1})$-face.

Fig. III. Evaporation rate of the (0001)-face of CdS at 715°C while copper diffuses into the crystal from the $(000\bar{1})$-face.

Fig. IV. Evaporation rate of the (0001)-face of CdS at 729°C while copper diffuses into the crystal from the $(000\bar{1})$-face.

Table Caption

Table I. x_D, the mean displacement of copper in CdS in the direction of the (0001)-face in one hour and x_V, the crystal thickness removed by vacuum evaporation of the (0001)-face in one hour.



MUB-5954

Fig. 1.

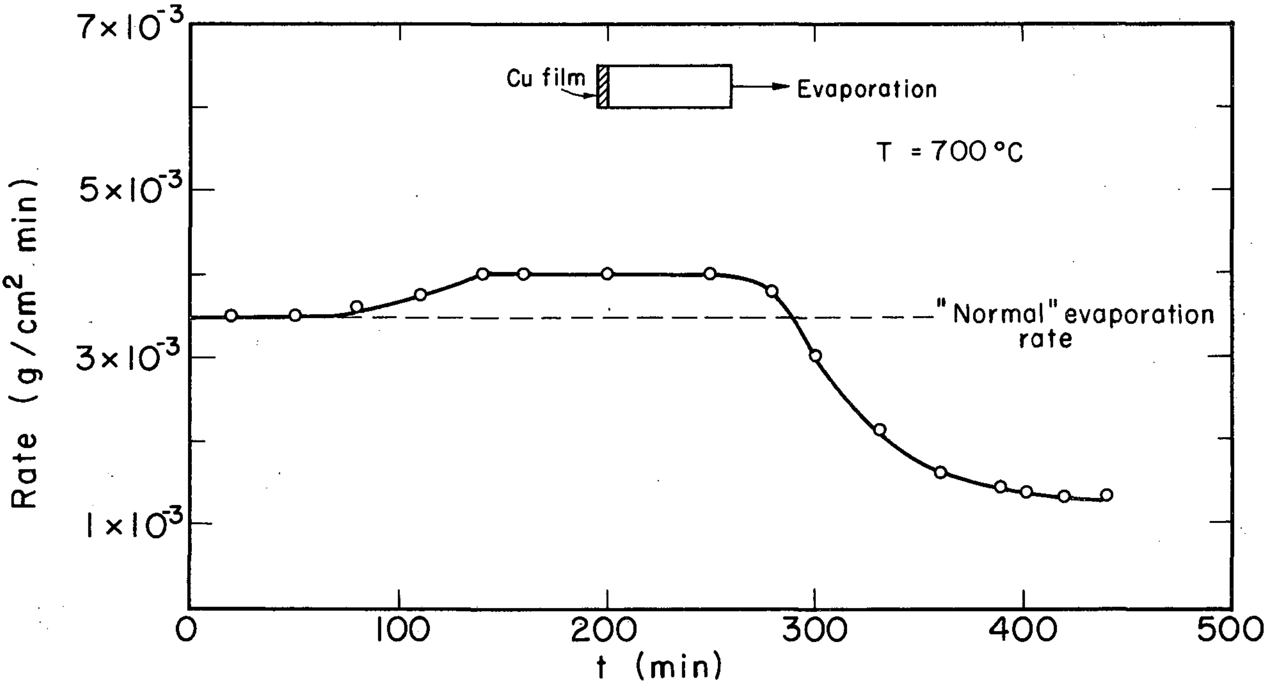


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Fig. 2.

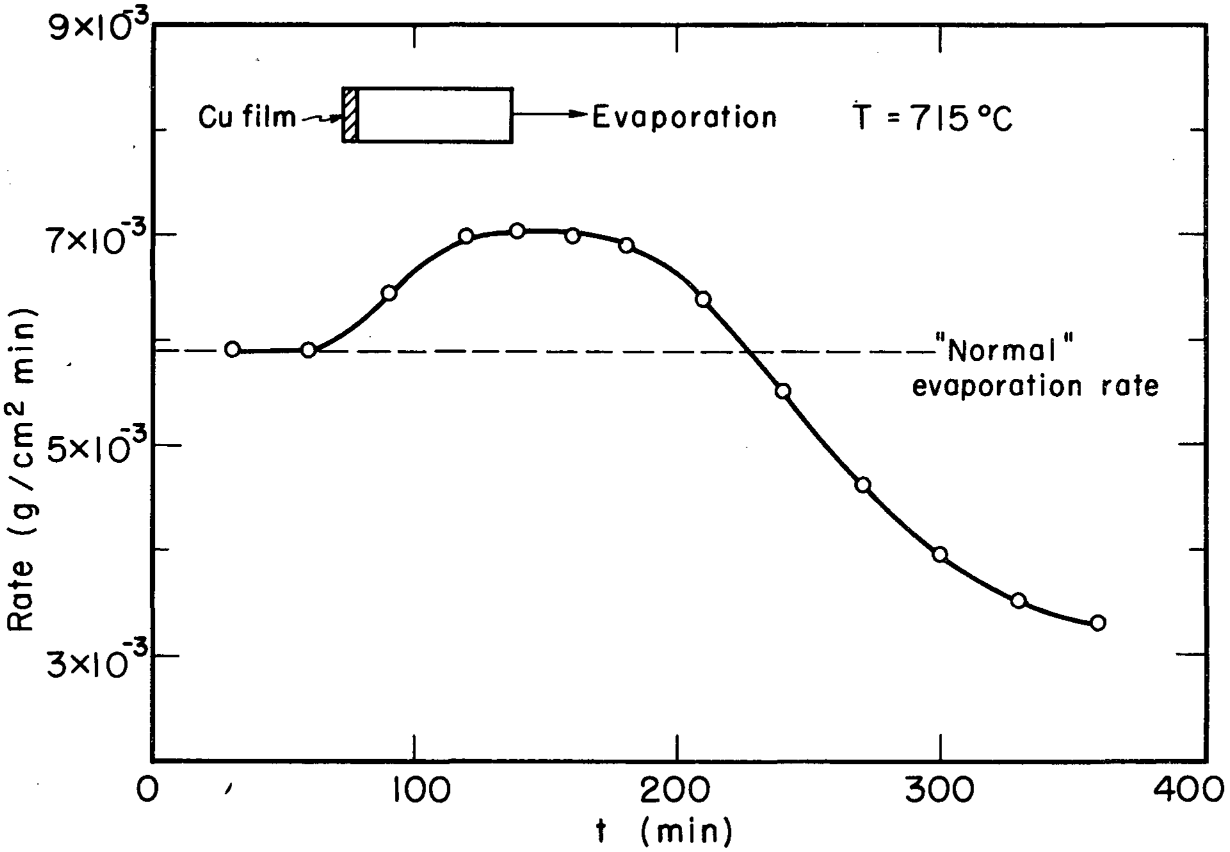

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Fig. 3,

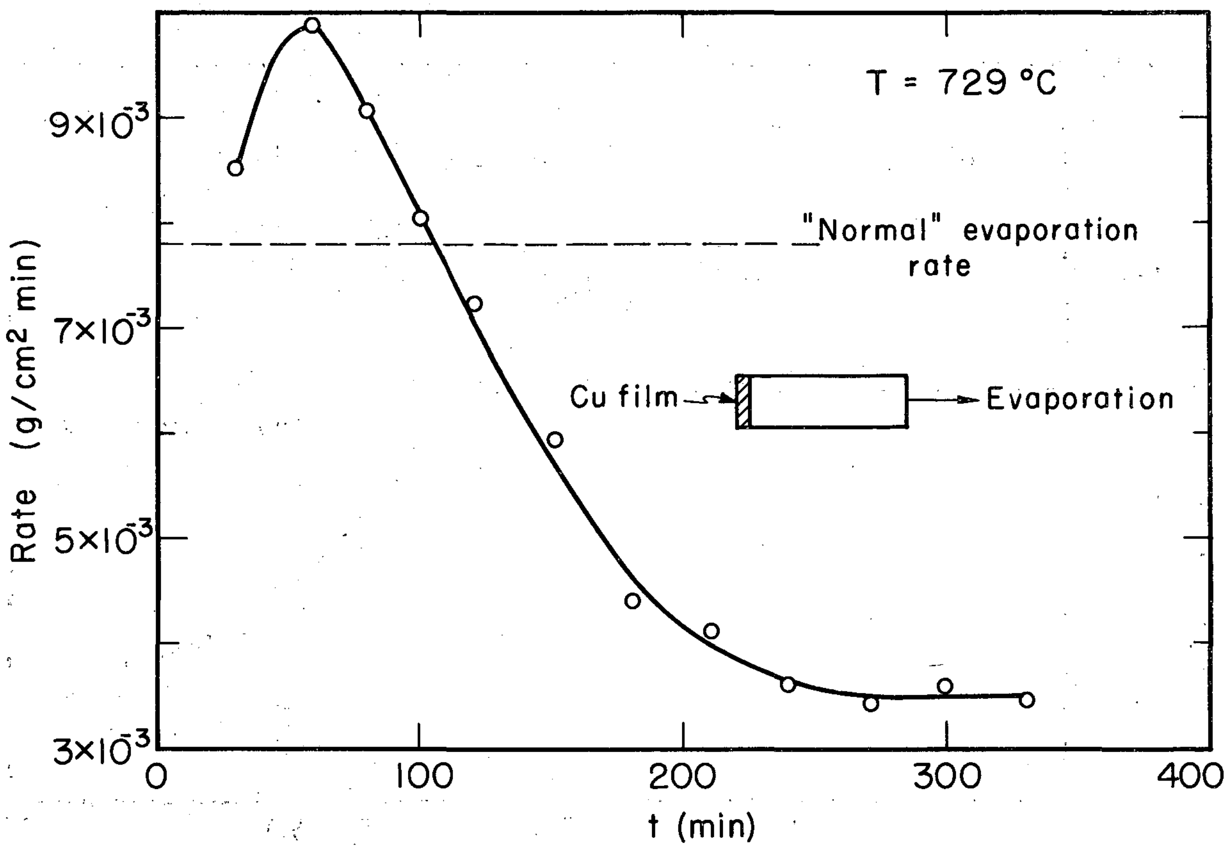

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Fig. 4.