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STUDIES OF THE VAPORIZATION MECHANISM OF GALLIUM ARSENIDE SINGLE CRYSTALS

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ABSTRACT

The kinetics of vaporization of gallium arsenide single crystals into vacuum have been investigated using microbalance and mass spectrometric techniques in the temperature range 700°-900° C. Although gallium arsenide vaporized incongruently to yield liquid gallium and arsenic vapor molecules, initial steady state evaporation rates can be obtained in the temperature range of study. The total evaporation rates and the activation energies of vaporization were found to be the same for both (111) and ($\bar{1}\bar{1}\bar{1}$) faces. The initial vacuum vaporization rates of gallium arsenide single crystals are lower than the maximum rates calculated from equilibrium vapor pressures by about a factor of two and the activation energy of vaporization is $\Delta H^* = 90 \pm 3$ kcal/mole. When excess gallium liquid was placed on top of the vaporizing surface, the rate increased (by a factor of two) to that of the calculated maximum rate, while the activation energy remained virtually unchanged. Both Te-doped and Zn-doped GaAs samples have lower evaporation rates than the pure gallium arsenide crystals. The activation

energy for Te-doped samples is 90 kcal/mole, the same as that found for pure samples. However the activation energy of vaporization is lower for the Zn-doped samples (76 kcal/mole). When excess gallium liquid was placed on top of the surface of these doped samples, the vaporization rate was found again to have increased to the maximum rate, with the activation energies remaining the same as those without excess liquid gallium. The vapor compositions for the (111) and ($\bar{1}\bar{1}\bar{1}$) faces were found to be different by mass-spectrometric studies. Vaporization of the (111) face yielded only tetramers (As_4). However, during the vaporization of the ($\bar{1}\bar{1}\bar{1}$) crystal face both the tetramers (As_4) and the dimers (As_2) were detected. Excess gallium liquid on top of the crystal surfaces does not seem to affect the vapor compositions significantly. Based on these experimental results at least two reaction steps in the sequence of reactions leading to vaporization of gallium arsenide single crystals can be distinguished. 1) The availability of arsenic vacancies V_{As} or divacancies $V_{As}V_{Ga}$ at the vaporizing surface appears to control the rate of sublimation. 2) Once these defects are created the vaporizing arsenic molecules break away from the lattice in a subsequent rapid reaction step which does not control the rate, but establishes the vapor compositions over the two different crystal surfaces.

INTRODUCTION

The compounds made up of elements in groups IIIA and VA in the periodic table have a broad spectrum of interesting physical and chemical properties. These compounds are semiconductors with varying electronic band gaps and crystallize into either cubic (zinc-blende) or hexagonal (wurtzite) structures. They vaporize dissociatively near equilibrium or into vacuum according to the net reaction

$$AB(\text{solid}) \rightarrow A(\text{solid or liquid}) + (1/X)B_X(\text{vapor}) \qquad (1)$$

where $X = 1$, 2, or 4 in most cases.[1] Often, more than one type of vapor molecules are found. For aluminum nitride[2] and gallium nitride[3] the vacuum (Langmuir) vaporization rates were found to be lower than the maximum rates calculable from the equilibrium vapor pressure data. It has been shown that the vacuum evaporation rates of gallium nitride increase markedly in the presence of excess liquid gallium or indium on the vaporizing surface.[3,4]

Vaporization of solids is a process which involves a complex series of reaction steps. The rate-limiting step may involve bulk-diffusion, charge transfer, bond-breaking, rearrangement, association, or dissociation of the vaporizing surface atoms.[5] It may also involve the transport of these atoms along the crystal surface. The purpose of a kinetic study of vaporization is to find out which of these steps can be rate-controlling in the complex mechanism of evaporation. It should be noted that as the conditions of vaporization change (e.g., change of surface composition, temperature, etc.) the rate-limiting step may also change, thus perhaps

giving rise to different vaporization rates and different activation energies of vaporization. In recent years the detailed vaporization kinetics of several solids which undergo chemical rearrangements,[7,8] association,[9] or dissociation[10,11] have been investigated.

In order to explore the vaporization mechanism of IIIA-VA compounds, we have studied the vacuum vaporization rates of gallium arsenide single crystals (cubic zinc-blende structure) in the temperature range of 700°C-900°C. Along the [111] direction, gallium arsenide crystals have alternate layers of two types of atoms, as shown in Figure 1. Both the (111) and ($\bar{1}\bar{1}\bar{1}$) faces were used in the investigations. These two low index faces are composed of predominantly one type of atoms and have been shown to have different surface structures,[12] oxygen adsorption and desorption behavior, etching[13] and crystal growth rates[14] under a variety of experimental conditions. The (111) face will be referred to as the gallium face and the ($\bar{1}\bar{1}\bar{1}$) face as the arsenic face.

The vaporization studies were carried out using both microbalance and mass spectrometer. Microbalance studies yield the absolute vacuum vaporization rate by monitoring the weight loss of the single crystal sample with known surface area as a function of time. Mass spectrometric studies allow one to determine the vapor composition over the vaporizing specimen. When these investigations are carried out as a function of temperature, the mass spectrometric measurements yield activation energies of vaporization of each vapor species whereas the microbalance studies given an average activation energy of vaporization of all species.

Near equilibrium gallium arsenide vaporizes incongruently (i.e., its vapor composition is different from the crystal composition) according to the dominant net reaction:[15]

$$GaAs(solid) = Ga(liquid) + (X/2)As_2(vapor) + (1-X/4)As_4(vapor)$$

in the temperature range of 700°C-900°C. In order to establish the sublimation mechanism, in addition to measuring the vacuum vaporization rates and the vapor compositions of both the gallium and arsenic faces as a function of time and as a function of temperature, the vacuum vaporization rates of these faces covered with excess liquid gallium were also monitored. Mass spectrometric measurements of the vapor compositions over the liquid gallium covered surfaces were performed. GaAs samples doped with tellurium and zinc were used to correlate evaporation rates with the defect concentrations and electrical properties of the crystals. Again, vaporization rates with excess liquid gallium on top of these doped samples were determined. From these studies, a mechanism for the vaporization of gallium arsenide single crystals is proposed. It is likely that this mechanism is applicable to most other IIIA-VA compound semiconductors as well.

EXPERIMENTAL APPARATUS AND PROCEDURES

Gallium arsenide has zinc-blende structure and a melting point of 1238°C.[16] High purity gallium arsenide single crystals (purchased from Cominco American Inc., Spokane, Washington) were used in the experiments.

These crystals were n-type, had room temperature resistivities of 0.1-0.2 ohm-cm and mobilities of about 5×10^3 cm^2/volt-sec. Single crystals were also obtained from Bell and Howell Corp. in Pasadena, California along with samples doped with zinc and tellurium. The pure single crystals were again n-type but with room temperature resistivities of 0.027 ohm-cm and mobilities of 5,000 cm^2/volt-sec. Zinc-doped crystals (p-type) had room temperature resistivities of 0.0045 ohm-cm and mobilities of 71 cm^2/volt-sec. Tellurium doped samples (n-type) had room temperature resistivities of 8.4×10^{-4} ohm-cm and mobilities of 2410 cm^2/volt-sec. Electronic grade gallium metal used in the experiments (obtained from Eagle-Picher Co.) had a minimum purity of seven 9's.

The GaAs crystals were X-ray oriented, cut into 3x3x6 mm pieces, polished, and etched with 5% Br_2-methanol solution. Triangular etch pits for the gallium face and mirror finish for the arsenic face were obtained. These differences in the etching behaviors could then be used as identification for the two crystal faces.[17] The samples were then rinsed in methanol solution and wrapped in W foil to expose only the gallium or the arsenic face.

The microbalance used for weight loss measurements was made after a design by Honig and Czanderna[18,19] and was described in detail elsewhere. The restoring force for a change in sample weight was produced by the coupling of a magnet and a solenoid. Both magnet and sample were supported by quartz fibers with hooked ends. With a weight of 500 mg, the sensitivity of the balance is about 1μ gram. The thermocouple monitoring the the sample temperature was placed outside the quartz vaporization chamber

and was calibrated in reference to another thermocouple placed inside the quartz tube in the position where the sample should be.

The sample was mounted on the supporting fiber with the vaporizing surface facing downward. Experiments were carried out to determine the effect of the direction of vaporization (i.e., vaporizing surface facing either upward or downward) and no observable differences were found in the evaporation rate. The ambient pressure during the runs was usually in the range of 10^{-7} torr so that the recondensation rates were orders of magnitude lower than the vaporization rates. The furnace, with a well known temperature profile, was heated to the desired temperature, and the temperature was then stabilized to within ±1°. Once steady state temperature was reached, the sample was lowered into the furnace and hooked over the balance pivot wire. Weight loss measurements were then taken at this temperature as a function of time. After the evaporation rate was determined, the sample was removed from the hot zone and the furnace was heated to another temperature. Again the sample was lowered and weight loss measurements were taken. Measurements were also made both while increasing and while decreasing the temperatures. Optical micrographs were taken of all sample surfaces before and after each vaporization run.

For vaporization experiments with excess liquid metal (~ 0.04 gm) on top of the evaporating surface, the exposed face of the sample was placed in the vaporization chamber facing upward. Excess liquid metal was then put on to cover the entire surface area and the vacuum vaporization experiment was carried out.

Studies of the vapor composition over the vaporizing GaAs surfaces were carried out in a separate vacuum system using a quadrupole mass spectrometer (Electronic Associates, Inc. (EAI) Model No. 200). This system is shown in Fig. 2. The sample was wrapped in W foil and then placed in a high density graphite sample holder with the vaporizing surface facing upward. In the case of the mass spectrometer system, the thermocouple junction was placed in contact with the wrapping foil of the sample. The system was then evacuated first with sorption pumps, then with a VacIon pump to a pressure of $\leq 4 \times 10^{-7}$ torr, and baked out at 300°C. After bake-out, the ambient pressure was in the range of about 10^{-9} torr. The furnace was then turned on to heat the sample to the desired vaporization temperature. Simultaneously, the chamber walls were chilled with liquid nitrogen to decrease the diffuse scattering of arsenic molecules from the walls.[20] After the temperature was stabilized (about 30 min.) the intensities of the ion fluxes were measured for each of the ions of interest (As^+, As_2^+, As_3^+, As_4^+) with the slit moving in line and out of alignment with the ion source and the ionizer so as to account for the background contributions. The mass spectrometer was operated using the following ionization parameters: electron energy = 50 eV, emission = 0.2 ma, electron trap voltage = 30 eV, ion energy = 6 eV, and focus voltage = -23 eV. These measurements were repeated at different temperatures. During a typical experiment, measurements were made both while increasing and while decreasing the temperatures between intensity measurements, as was done in the microbalance experiments.

RESULTS

Studies of Surface Morphology

Optical micrographs of the crystal faces were taken after vaporization at different temperatures. We found two types of distinctly different topography for the two opposing faces. These are shown in Fig. 3a and 3b.

At temperatures below 800°C, various triangular thermal pits were observed on the gallium face, with gallium droplets covering part of the vaporizing surface. These triangular pits intersect each other and form terraced macroscopic ledges, giving the appearance of a very rough surface. Mechanical damages on surface and edges of the sample seem to serve as nucleation sites for vaporization. At temperatures above 850°C, vaporization was rapid; consequently, bigger gallium droplets were formed.

On the arsenic face, liquid gallium droplets were observed after vaporization even at the lower temperature (750°C) of our microbalance studies (Fig. 3b). This surface, however, appears to be smooth when compared to the vaporized gallium face. The surface regions of the arsenic face that are not covered by gallium were flat and showed no pitting similar to that of the gallium face. For both orientations, when liquid gallium droplets were physically removed from the surface, flat regions were found underneath.

Microbalance Studies of the Vacuum Vaporization Rates

The weight loss of the sample was measured as a function of time at a given temperature. From these data and the geometric surface area, the

evaporation rate (mg/cm^2-sec) was calculated. During the vaporization, the surface was of course not flat, as has been discussed previously, so that the geometric surface area is the lower limit of the total vaporizing area. However, Melville[21] has shown that the evaporation rate may not be appreciably larger from a rough surface than from a crystal with a smooth geometrical surface area. Thus the error involved in the estimation of surface area is expected to be within the experimental accuracy (± 5%). As a check on the calibration of our system, sodium chloride single crystals with high dislocation densities ($\sim 6 \times 10^6/cm^2$) were vaporized and the rates were found to be the same as those reported by Lester and Somorjai.[9]

Since gallium liquid droplets were readily discernible on both crystal faces after vaporization, it was concluded that gallium arsenide vaporizes incongruently to give gallium liquid and arsenic vapor molecules. The presence of liquid gallium, as we shall show below, increases the evaporation rate of gallium arsenide surfaces. Since liquid gallium is accumulating on top of the vaporizing surface as a function of time, the question can be raised as to whether one could attain a steady state evaporation rate at all at a given temperature under these conditions. In order to test this an exhaustive vaporization was performed during which a small crystal was evaporated completely at a given temperature and the vacuum vaporization rates were continuously monitored. The results are shown in Fig. 4. The vaporization rates remain constant for more than five hours at T = 849°C. A simple calculation of the surface area covered by the liquid gallium droplets shows that the liquid gallium coverage of the vaporizing surface remains relatively constant

during the initial period (approx. 5 hrs) of vaporization. Due to the large contact angle of gallium droplets on the gallium arsenide surface they assume a semispherical shape. Thus, their volume increases without appreciable spreading on the surface. When the accumulated liquid gallium was then spread over the entire surface by violently shaking the sample a few times, the evaporation rates suddenly increase to that value which is equal to the evaporation rate where excess gallium was added. As the crystal continues to vaporize over a long period (hours), finally a decrease in rate was observed, corresponding to a depletion of the vaporizing material from the crystal holder. Thus, from this experiment we can conclude that an initial, virtual steady state vaporization rate of gallium arsenide can be obtained in our temperature range of study even though gallium arsenide single crystals vaporize incongruently.

With the limit of sensitivity of our apparatus ($\pm$ 1μ gm), reproducible initial steady state vaporization rates were found at any temperature in the range of our study. However, there is a short induction period of slow transient evaporation before the steady state vaporization is obtained. The length of this transient period depends strongly on the history of the sample, e.g., preparation, etching, heat treatment. Unetched crystals usually have longer transient periods. Furthermore, the initial transient period is, in general, longer for the arsenic face than for the gallium face.

The steady state vacuum vaporization rates were measured for both crystal faces of gallium arsenide as a function of temperature. The data obtained using several samples is shown in Fig. 5.[22] Within our

experimental accuracy the steady state rates are the same for both gallium and arsenic faces. The thermal history of the sample appeared to have no effect on the vaporization rates. The activation energy of vaporization is 90 ± 3 kcal/mole and the evaporation coefficient, α_v is about 0.5 in the studied temperature range (700-900°C). Crysals (undoped) with slightly different electron carrier concentrations were found to have the same vaporization rates and the same activation energies. When excess liquid gallium was placed on top of the vaporizing face so as to cover the entire surface, evaporation rates were increased by a factor of two (Fig. 5) to that of the maximum rate ($\alpha_v \sim 1.0$). Both crystal faces gave the same evaporation rates and the activation energy was found to be 86 ± 5 kcal/mole.

There is considerable disagreement in the literature concerning the exact equilibrium vapor composition of gallium arsenide. Arthur[23] has studied the equilibrium vapor pressures of GaAs using a mass spectrometer and has reported the equilibrium vapor to consist mainly of As_2 molecules. He has also found the heat of dissociation of $As_4(g) \rightarrow 2As_2(g)$ to be 62.5 kcal. De Maria et al.[15] has also studied the equilibrium vapor pressure over GaAs using a mass spectrometer. However, he has found comparable intensities for As_2 and As_4 in the vapor phase and a heat of dissociation ($As_4 \rightarrow 2As_2$) of 73.5 kcal. Recently Hudson,[24] using electron impact ionization, has reported 68.5 kcal for the heat of dissociation of As_4. After corrections for the entropy factor in the data reported by De Maria, we found similar values for the heat of dissociation as that reported by Hudson. Based on these observations, we shall use

the equilibrium vapor pressures reported by De Maria in our calculations of the evaporation coefficient α_v. Table I gives the equilibrium vapor pressures of GaAs and the corresponding maximum evaporation rates. It should be pointed out that the absolute vaporization rates and the ratio of As_2/As_4 found for vaporization of the arsenic face of GaAs with excess Ga(ℓ) on top of the surface are similar to the maximum rates calculable from the equilibrium data reported by De Maria et al.[15]

In order to investigate the effect of impurities in the GaAs crystal on the kinetics of vaporization, the vacuum vaporization rates of crystals heavily doped with tellurium and zinc were measured (impurity concentrations $\sim 10^{18}/cm^3$). The vaporization rates of the Te-doped samples were found to be about one-half of that of the pure samples ($\alpha_v \sim 0.29$), as shown in Fig. 6a. Within our experimental accuracy, the activation energy remains the same, i.e., 90 ± 3 kcal/mole as that for pure GaAs. The conductivity of the doped samples did not change during vaporization. The diffusion rate of Te in gallium arsenide is low enough so that the out-diffusion of tellurium from GaAs during vaporization is improbable.[25,26] When excess liquid gallium was placed on top of Te-doped crystals, again, the maximum vaporization rates were obtained. The activation energy was found to be 87 ± 3 kcal/mole (Fig. 6a).

The vacuum vaporization rates of Zn-doped GaAs crystals are shown in Fig. 6b, as a function of temperature. The evaporation coefficient is the lowest of all, $\alpha_v \sim 0.1$-0.2, in the temperature range of our study. In addition, the activation energy also decreases to 76 ± 3 kcal/mole (Fig. 6b). As one continues to vaporize either crystal face of the

same sample, there is a progressive increase in the vaporization rates. Conductivity measurements before and after vaporization and diffusion data indicate that zinc does not diffuse out of the crystal during vaporization. Fig. 6b clearly shows that the evaporation rates are gradually increasing. When excess gallium was placed on top of these p-type crystals, rates comparable to the maximum rates of undoped gallium-arsenide were measured. However, the activation energy of vaporization for zinc-doped samples with Ga(liquid) on top remains the same as that without liquid gallium, i.e., 76 ± 3 kcal/mole.

Since liquid gallium catalyses the vaporization of GaAs, an attempt was made to investigate the possible catalytic effect of other liquid metals. Liquid tin has low vapor pressures ($\approx 10^{-8}$ torr) at the temperatures of our studies (700-900°C). When Sn(liquid) was placed on top of undoped GaAs the absolute vaporization rates were found to be lower than that for GaAs with excess Ga(liquid) on top and the activation energy of vaporization was found to be 76 ± 3 kcal/mole. This is shown in Fig. 7.

Mass Spectrometric Investigation of the Products of Vaporization

The ions which were readily detected in the mass spectra of vaporizing gallium arsenide are As^+, As_2^+, As_3^+, and As_4^+. The dimer and tetramer ion peaks had the largest intensities and they were of comparable magnitude in the temperature range of our study.

The experimental geometry has the advantage of allowing one to sample directly the vapor composition which emanates from the vaporizing gallium arsenide surface. Thus, any association reaction which may take place on

the heater or chamber walls would only change the background intensity which can be measured independently and then subtracted from the signal. Interactions of the arsenic molecules with the hot thorium coated tungsten ionizer filament (most likely dissociative reactions) can also change the vapor composition. However, we have found no observable change in the ion intensity ratios upon changing the emission current, thereby changing the temperature, of the ionizer filament. Xenon isotope spectra were used to calibrate the mass-transmission of the quadrupole mass spectrometer. Due to the lack of accurate ionization cross section data and the experimental uncertainties in calibrating the mass spectrometer, we shall not attempt to compute the absolute vaporization rates of the different vapor species from the ion intensities, but rather use the intensity changes as a function of temperature to monitor changes in intensity ratios and calculate the activation energies of each vaporizing species.

Appearance potential curves for all the ions were determined, and were found to be comparable to the literature values shown in Table II along with the dissociation energies and electron affinities of the different arsenic molecules.[24] As it can be seen, all ions appear at electron energies below 15 eV. Since the practical lower limit for the energy of the ionizing electron beam in the quadrupole mass spectrometer is about 20 eV, it would be difficult to employ electron energies low enough to eliminate molecular fragmentation by electron impact. In order to determine the fragmentation pattern of the arsenic molecules, pure arsenic crystals were vaporized at 500°K where the vapor was shown to consist mainly of tetramer molecules.[8] In the vaporization of GaAs single

crystals, both As and As_3 molecules can be identified as fragmentation products of electron impact ionization of As_2 and As_4 molecules. Corrections for fragmentations of As_4 to As_2 molecules were also made in the intensities detected for As_2 and As_4. The method for these corrections is discussed in detail elsewhere.[25] Since As_4 is a monoisotopic molecule, one may not easily identify the contribution of As_4^{++} to the intensities detected for As_2^+. However, comparing the ionization potential and the dissociation energies of As_4^+ to form As_4^{2+} and $As_2^+ + As_2$ molecules, respectively, it can be shown that the contribution of As_2^{++} to As_2^+ intensities will be small as compared to other contributions due to fragmentation of As_4 and the ionization of neutral dimer molecules. The same argument may also be used to disregard the contribution of As_2^{2+} to As^+.

No gallium ion peak was detected as coming from the vaporizing gallium arsenide crystals in the temperature range of our study (700-900°C). Inspection of the high density graphite sample holder and the stainless steel vaporization chamber did not reveal the occurrence of any possible solid state reaction with gallium. Thus we have been unable to monitor the vaporization of gallium as a function of temperature and to calculate its activation energy of vaporization.

The intensities, which were corrected for fragmentation, of As_2^+ and As_4^+ peaks from the vaporization of GaAs single crystals for both gallium (111) and arsenic ($\bar{1}\bar{1}\bar{1}$) faces are plotted as a function of temperature in Fig. 8a and 8b. During the vaporization of the gallium face of GaAs, after correction for fragmentation, only tetramers were found, with an average activation energy of 92 ± 5 kcal/mole. However, during the

vaporization of the arsenic face, one finds both the dimer and the tetramer vapor molecules with activation energies of $\Delta H^*(As_2) = 88 \pm 5$ kcal/mole and $\Delta H^*(As_4) = 98 \pm 5$ kcal/mole (Fig. 8b) respectively.

When excess liquid gallium was placed on top of the vaporizing surface, again different vapor compositions were found for the two opposing faces. For the vaporization of gallium face, only tetramers (As_4) were found, just as for the vaporization of the same face without liquid gallium on top (Fig. 8a). For arsenic face, both the dimers (As_2) and the tetramers (As_4) were found. However, the ratio As_2^+/As_4^+ seems to be slightly higher in this case than for the pure crystals without gallium liquid on top. These intensities were plotted as a function of temperature and the activation energies calculated. Within experimental accuracy, the activation energies were indistinguishable from that observed during the vaporization of GaAs surfaces without excess liquid metal placed on the vaporizing surface.

DISCUSSION

The following statements summarize those results of our vaporization studies that should be helpful in uncovering the vaporization mechanism of gallium arsenide:

1) The morphology of the vaporizing gallium and arsenic faces are different. Liquid gallium droplets are detectable on both crystal faces, the gallium face is roughened and exhibits triangular etch pits while the arsenic face is relatively smooth.

2) Vaporization of gallium arsenide samples for long times (~ 5 hrs) at constant temperature showed that steady state vaporization rates could be attained and maintained after a brief induction period in the temperature range of study (700°-900°C).

3) Vacuum vaporization rates of pure GaAs crystals were found to be lower by about a factor of two than the calculated maximum rate ($\alpha_v \sim 0.46$). Within experimental accuracy the vaporization rates and activation energies of vaporization are the same for both gallium (111) and arsenic ($\bar{1}\bar{1}\bar{1}$) crystal faces ($\Delta H^* = 90 \pm 3$ kcal/mole).

4) Liquid gallium, when placed on the vaporizing surfaces, increases the evaporation rates to that of the maximum rates (for both (111) and ($\bar{1}\bar{1}\bar{1}$) crystal faces) without significantly changing the activation energies of vaporization.

5) Only tetramers (As_4) were found to vaporize from the gallium face whereas both dimers (As_2) and tetramers (As_4) were found to vaporize from the arsenic face. Excess liquid gallium on top of the vaporizing surface does not change significantly the vapor composition emanating from the two different crystal faces.

6) The vaporization rates of tellurium-doped GaAs samples are decreased ($\alpha_v \sim 0.29$) when compared to the vaporization rates of undoped crystals. The activation energy of vaporization however, remains unchanges ($\Delta H^* = 90 \pm 3$ kcal/mole). Liquid gallium on top of the vaporizing surface increases the evaporation rates to that of the maximum rates.

7) The vaporization rates of zinc-doped GaAs samples is decreased ($\alpha_v \sim 0.15$) with respect to the vaporization rates for undoped crystals.

The activation energy of vaporization is also lowered ($\Delta H^* = 76 \pm 3$ kcal/mole). Liquid gallium on top of the vaporizing surface increases the rates to near that of the maximum rates but the activation energy of vaporization remains unchanged (76 kcal/mole) in the presence of liquid gallium.

8) Liquid tin, when placed on top of the vaporizing gallium arsenide surfaces does not increase the evaporation rates significantly ($\alpha_v \sim 0.49$) as does liquid gallium, but changes the activation energy of vaporization similar to that for zinc-doped samples ($\Delta H^* = 76 \pm 3$ kcal/mole).

Liquid gallium droplets are discernible after evaporation on top of every gallium arsenide surface that was studied. Mass spectrometric studies of the vapor composition over the vaporizing samples revealed the presence of As_2 and As_4 molecules but gallium atoms were not detected in the vapor phase in the temperature range of our vaporization studies. Therefore, one may conclude that far from equilibrium gallium arsenide single crystals vaporize incongruently according to the equation:

$$GaAs(solid) \rightarrow Ga(liquid) + X/2\ As_2(vapor) + (1-X/4)As_4(vapor) \quad (2)$$

From exhaustive vaporization experiments, it was found that even though evaporation rates increase slowly with increasing coverage of gallium liquid on the crystal face, virtual steady state rates can be obtained for more than five hours at 850°C, a time span that is much longer than needed to complete a rate measurement. This indicates that the liquid gallium coverage can be assumed to stay constant for the usual experimental time of 0.5 2.5 hours. Thus the initial vaporization rates are reproducible

and one could obtain an activation energy of vaporization. From the microbalance studies, one obtains the average activation energy of vaporization, $\Delta H^* = 90 \pm 3$ kcal/mole. The absolute vaporization rates and the average activation energies of vaporization were identical for both (111) and ($\bar{1}\bar{1}\bar{1}$) crystal faces.

The vapor compositions emanating from the vaporizing Ga face and As face were found to be different. For the vaporization from Ga face, one finds predominantly As_4 molecules whereas the vaporization of As face yields both As_2 and As_4 molecules in comparable quantities. Liquid gallium does not seem to affect the vapor compositions significantly, i.e., one still observes only the As_4 molecules over the vaporizing Ga face and both As_2 and As_4 molecules over the vaporizing As face. Thus the vapor compositions emanating from the two crystal faces do not change with increasing concentrations of liquid gallium on the surfaces even though excess liquid gallium increases the evaporation rate by a factor of two.

In spite of the different vapor compositions found for the two crystal faces, the fact that the initial steady state rates and the activation energies of vaporization are the same for both Ga and As faces, with and without excess liquid gallium on top of the vaporizing surface, indicates that the rate-limiting step for evaporation into vacuum is the same for both faces. This rate-limiting step must then be followed by another more rapid reaction step that establishes the different vapor compositions of the two opposing faces. The latter step is different for the two faces and must depend on the different surface structures of the (111) and ($\bar{1}\bar{1}\bar{1}$)

crystal faces. Thus we can distinguish at least two steps in the sequence of reactions leading to vaporization.

In order to identify the rate-limiting step let us review those experimental parameters that influence the absolute vaporization rates and/or the activation energy.

First of all, liquid gallium increases the vaporization rates without changing the activation energy. This catalytic effect of liquid metals or evaporation has been observed before (Tl(ℓ) on As[27] and Ga(ℓ) and In(ℓ) on GaN[4]). Catalysis by liquid metals is also well documented in the reverse process, i.e., in condensation or crystal growth. This catalytic effect may be attributed to one of the following reasons: (1) the liquid metal provides electrons at the surface that facilitate charge transfer during vaporization or condensation, (2) liquid metal dissolves the vaporizing or the condensing species and thus provides an alternate route for evaporation or crystal growth, (3) the liquid metal changes the defect concentrations at the surface that might play an important role in vaporization or condensation. Since the liquid metal increases the absolute evaporation rates of gallium arsenide and arsenic crystals, the concentrations of these surface defect sites must be increased by the liquid metal if the latter effect is the cause of this catalytic behavior.

Secondly, both Zn or Te when present in the GaAs crystal lattice, (in substitutional sites[28]), decreased the vaporization rates. Furthermore, the activation energy of Zn-doped samples are lowered in comparison to that of pure samples (ΔH^*(Zn-doped) = 76 ± 5 kcal/mole and ΔH^*(pure) = 90 ± 3 kcal/mole). Due to the low concentrations of these impurities

in the crystal ($\approx$ 0.1 atom %) it is very unlikely that the lowering of the vaporization rates is caused by the blocking of the GaAs surfaces by foreign atoms. Both Zn and Te could form compounds in the GaAs lattice, e.g., Zn_3As_2 and Ga_3Te_2. However, these compounds have higher vapor pressures and are also likely to have higher vacuum vaporization rates than GaAs. In addition, in the temperature range of our study, the bulk diffusion rates of both Zn and Te in GaAs are much lower than the evaporation rates of gallium arsenide so that the impurity concentrations throughout the crystal would remain virtually constant, as indicated by the conductivity measurements before and after each experiment.

Te-impurities in GaAs produce electron donor states (ionization energy = 0.02 eV) while Zn impurities introduce electron acceptor states (ionization energy = 0.08 eV). Dopeing the crystals with these elements will change the free carrier concentrations and the type of majority free carriers (electrons or holes). In addition, these impurities also change the vacancy concentrations of GaAs crystals. Both Te and Zn are known to enter into the crystal lattice substitutionally,[28] i.e.,

$$V_{As} + Te_{(surface)} \rightarrow Te_{As} \qquad (3)$$

$$V_{Ga} + Zn_{(surface)} \rightarrow Zn_{Ga} \qquad (4)$$

where the subscripts denote the sites being occupied by the atoms and V_{As} and V_{Ga} are the un-ionized arsenic and gallium vacancies, respectively. In effect, doping the GaAs crystals with impurities will decrease the concentrations of one of the two types of vacancies. Since these impurities

are introduced during crystal growth at high temperatures, equilibria among defects can easily be established.

Charge transfer has been found to be the rate-limiting step in the evaporation of pure CdS single crystals.[10] The activation energy for vaporization (~ 50 kcal) was found to be similar to the band gap energy (2.41 eV). However, if this were also the rate-limiting step in the evaporation of GaAs one would expect an activation energy similar or equal to the band gap energy (1.4 eV or 32 kcal). The observed activation energy (90 kcal) is much greater than the band gap energy. It seems unlikely that the rate-limiting step for vaporization would be related to the electronic properties of pure GaAs. Furthermore, the difference in activation energies of vaporization between Te-doped and Zn-doped GaAs samples is much too great (~ 15 kcal or 0.6 eV) to be attributed to the difference in the position of the donor and the acceptor levels within the band gap or any other electrical properties of these impurities in the GaAs crystal lattice. At the temperatures of our studies (700-900°C) most of the impurities are expected to be ionized because of their low ionization energy in the gallium arsenide crystal lattice. In addition, crystals with different charge carrier concentrations have been found to have the same vaporization rates. Therefore, we conclude that Ga(ℓ), Te and Zn in the GaAs crystal lattice do not influence the vaporization rates by changing its electronic properties.

The vapor compositions over the vaporizing gallium and arsenic crystal faces remained unchanged when liquid gallium was placed on top of the surface. Also liquid gallium has not changed the activation

energies of vaporization of the different Zn and Te-doped crystal samples. Thus, it appears that liquid gallium does not change the reaction path, i.e., does not provide alternate route for the vaporization reaction. Therefore we conclude that Ga(ℓ), Te and Zn in the GaAs crystal lattice influence the evaporation rate by changing the defect concentrations at the surface. While the arsenic atoms associate and are subsequently removed into the vapor phase the gallium atoms precipitate out in the form of liquid at the surface due to their low vapor pressure.

There is only incomplete experimental information available on the nature of point defects in gallium arsenide. Self-diffusion studies[26] revealed very high and different activation energies for the migration of arsenic (235 kcal/mole) and gallium (129 kcal/mole) atoms in the bulk GaAs crystal. Due to these large energy requirements and the large pre-exponential terms it was proposed that diffusion occurs substitutionally in the arsenic and in the gallium sublattices. [This model is further supported by the observation that impurities which occupy substitutional sites in the gallium sublattice (Zn, Cd and Sn) have nearly identical activation energies of diffusion in GaAs. The same holds for the diffusion of impurities in the arsenic sublattice (S,Se).] Part of the activation energy of self-diffusion is the energy of arsenic or gallium vacancy formation. However, for another IIIA-VA compound, indium antimonide, InSb, the activation energies of self-diffusion are the same for both indium and antimony.[29] In this case a divacancy mechanism is proposed. The migration of $V_{In}V_{Sb}$ divacancy is thought to be primarily responsible for the diffusion of both indium and antimony.[29] The enthalpy of formation for the divacancy is estimated to be about 74 kcal/mole and that of

the single vacancies 40.5 kcal/mole. The heat of atomization of InSb has been reported as 127 kcal/mole. Thus the formation energy for divacancies is about 58% of the heat of atomization. The heat of atomization of GaAs is reported to be 156 kcal/mole. Therefore the activation energy of vaporization (90 kcal/mole) could be a likely value also for the heat of divacancy formation.

Most of the experimental data can be rationalized by assuming that the rate limiting step in the vaporization of gallium arsenide is either the formation of divacancies of the surface, $V_{Ga}V_{As}$, or the formation of the minority vacancies V_{As} or V_{Ga}. It is likely that in an undoped gallium arsenide single crystal the gallium vacancies V_{Ga} predominate.[30] The vaporization of gallium arsenide would then be limited by the rate of formation of arsenic vacancies at the surface. In this case the heat of formation of V_{As} should be approximately 38% of the activation energy of self-diffusion of arsenic in the gallium arsenide lattice.

Decreased vaporization rates were found for crystals doped with Te or Zn. Te in GaAs reduces the (V_{As}) concentration. If the rate of vaporization is controlled by the rate of formation of V_{As} in pure samples the evaporation rate would indeed be reduced for the Te-doped crystals without any change of activation energy of vaporization, as observed. For Zn-doped samples not only the evaporation rates decreased but the activation energy of vaporization has also changed. For these p-type samples the gallium vacancy concentration (V_{Ga}) might be reduced below that of (V_{As}) and its rate of formation becomes rate determining.

These results can also be rationalized assuming that the rate of formation of divacancies controls the evaporation rate since a reduction in either the (V_{As}) or (V_{Ga}) concentration can shift the equilibrium between single vacancies and divacancies and reduces the divacancy concentration. However, if this mechanism is operative the change of activation energy of vaporization for Zn-doped GaAs crystals indicate that Zn atoms associate with divacancies in the GaAs crystal lattice.[31]

Koster and Thoma have made extensive studies of the phase diagram of the gallium-arsenic system.[32] It was found that GaAs does not dissolve significantly in liquid gallium. The diffusion of Ga into the crystal lattice is extremely slow; consequently, during the time that is required to measure vaporization rates, little or no gallium is expected to be incorporated into the lattice. In our experiments, we have observed that excess liquid gallium on top of the vaporizing surface increases the rates with the activation energies remaining the same as for those samples without the excess gallium. This effect could be explained that even though GaAs does not dissolve in liquid gallium to any great extent, the small but finite solubility (ppm) of the molecular GaAs in Ga(liquid) increases the surface concentration of both vacancies (V_{As}) and (V_{Ga}) or divacancies ($V_{Ga}V_{As}$) thereby increasing the rates of evaporation.

Studies of the condensation of gallium arsenide using arsenic molecular beams have shown that the sticking probability of As_2 molecules has increased markedly in the presence of liquid gallium on the GaAs surface.[33] Thus, the surface concentration of arsenic vacancies is likely to be increased in the presence of liquid gallium. It would be

important to change the surface concentration of As_4 or As_2 molecules at the vaporizing GaAs surface using molecular beam techniques in order to further elucidate the mechanism of vaporization of gallium arsenide. If the slow step in the vaporization process involves the formation of arsenic vacancies excess arsenic molecules at the surface should decrease the sublimation rate.

The diffusion rates of Sn in GaAs have been studied and were found to be similar to that of Zn.[28] The activation energies for diffusion of Sn or Zn in GaAs are very similar ($E_D \approx 57.5$ kcal/mole). Thus it is not surprising that one finds the same activation energies of vaporization of GaAs in the presence of excess liquid tin on the vaporizing surface as those found for the vaporization of Zn-doped GaAs crystals (~ 76 kcal/mole). It appears that Sn atoms, when entering the GaAs crystal lattice at the vaporizing surface, affect the vacancy concentrations of the host lattice the same way as do Zn atoms.

Since the (111) and ($\bar{1}\bar{1}\bar{1}$) faces of IIIA-VA compounds are known to behave differently under a variety of experimental conditions, e.g., chemical dissolution, adsorption and desorption of molecules, LEED studies, one might suspect that the surface structural differences will also play an important role in their mechanisms of vaporization. The fact that one obtains the same evaporation rates for both the gallium face and the arsenic face implies that the surface configurations do not influence the rate-limiting step. However, different vapor compositions were found over the two opposing faces. This suggests that the surface structures do influence the formation of vapor molecules even though this

step is not rate-limiting. For evaporation from the Ga-face one can see from the model in Fig. 1 that all the As atoms that would form the tetrahedral unit are available for vaporization (i.e., none of the As atoms are blocked by Ga atoms on top). When an As_4 molecule finally forms, it could then desorb immediately. This is not the case for the As-face. Three of the As atoms that would form the tetrahedral unit have Ga atoms directly on top of them so that the formation and subsequent removal of the As_4 molecule is difficult. Consequently, some of the surface As atoms would have the opportunity to form As_2 units and vaporize. Thus, the effect of steric hindrance for the formation of As_4 molecules in the As-face could then provide a clue for the cause of the different vapor compositions from the different crystal faces.

It might be interesting to speculate how the As_4 molecules form at the surface. In the vapor phase, the bond angle and bond distance for the tetrahedral As_4 molecules are 60° and 2.44 Å, respectively. In the gallium arsenide crystals, the As_4 unit has bond angles and bond distances of 60° and 3.99 Å, respectively. Thus the bond distances of As_4 units in the crystal lattice have to change markedly at the vaporizing surface to form gaseous As_4 molecules. This process may require a certain configuration of neighboring vacancies, thereby breaking up the regular arrangement of surface bonds and making it easier for the As atoms to vibrate into the tetrahedral configuration which is required for vaporization.

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TABLE I. Equilibrium Vapor Pressures and the Corresponding Maximum Vaporization Rates of GaAs Single Crystals

T(°K)	$10^4/T$ (°K)	$P_{As_2} \times 10^6$ (atm)	$P_{As_4} \times 10^6$ (atm)	$P_{total} \times 10^6$ (atm)	$J_{max} \times 10^2$ (mg/cm^2-sec)
1106	9.04	0.76	0.94	1.70	1.02
1119	8.94	0.01	1.04	1.05	0.55
1121	8.92	0.93	1.00	1.93	1.16
1122	8.91	1.05	1.07	2.12	1.29
1129	8.86	1.45	1.71	3.16	1.89
1131	8.84	1.45	1.65	3.10	1.86
1135	8.81	1.86	2.34	4.20	2.49
1151	8.69	3.76	5.46	9.22	5.36
1152	8.68	3.88	5.55	9.43	5.46
1162	8.61	4.43	5.65	10.1	5.92
1163	8.60	4.70	6.00	10.7	6.26
1163	8.60	4.72	6.05	10.8	6.32
1174	8.52	6.84	6.26	13.1	7.85
1186	8.43	7.32	6.68	14.0	8.33
1194	8.38	7.32	6.80	14.1	8.33
1195	8.37	7.34	6.86	14.2	8.42
1197	8.35	8.15	7.20	15.4	9.12

TABLE II. Ionization Potentials, Dissociation Energies, and Electronic Affinities of Arsenic Molecules

Ionization Potentials	
As	9.88 eV
As_2	9.86 eV ± 0.16 eV
As_4	8.84 eV ± 0.16 eV
Dissociation Energies at 0°K	
As_2 - As_2	2.98 eV ± 0.18 eV
As - As	3.94 eV ± 0.12 eV
As_3 - As	4.22 eV ± 0.20 eV
As_2 - As	2.70 eV ± 0.20 eV
As_3^+ - As	2.59 eV ± 0.32 eV
As_2^+ - As	5.35 eV ± 0.32 eV
As^+ - As	3.89 eV ± 0.16 eV
Electron Affinities	
As	0.74
As_2	0.35±0.2
As_3	1.1± 0.2

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20. Both the dimer and the tetramer arsenic molecules are known to have low condensation coefficients and can undergo multiple scattering. The association of dimers to form tetramers on the chamber walls was the probable reason for the discrepancy of the reported vapor compositions over GaAs in different effusion cell studies.[15,23] Our system was designed in such a way that only molecules which come directly from the vaporizing surface can contribute to the detector signal after a correction to the background intensity is made.

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Figure Captions

1. Cubic zinc-blende structure of gallium arsenide single crystals.
2. Mass spectrometer system.

3a. Ga-face of GaAs after vaporization at 800°C.

3b. As-face of GaAs after vaporization at 750°C.

4. Exhaustive vaporization of a gallium arsenide single crystal at temperature T = 870°C.
5. Total vacuum evaporation rates of pure GaAs crystals.

6a. Total evaporation rates of Te-doped GaAs crystals.

6b. Total evaporation rates of Zn-doped GaAs crystals.

7. Total evaporation rates of undoped GaAs crystals with excess liquid tin placed on top of the surface before vaporization.

8a. Vapor composition over the gallium face of gallium arsenide single crystals.

8b. Vapor composition over the arsenic face of gallium arsenide single crystals.

List of symbols used in figures.

○ vaporization rates of gallium face upon heating.

◐ vaporization rates of gallium face upon cooling.

△ vaporization rates of arsenic face upon heating

▲ vaporization rates of arsenic face upon cooling.

⊕ vaporization rates of gallium face with excess gallium placed on top of surface before evaporation (heating)

● vaporization rates of arsenic face with excess gallium placed on top of surface before evaporation (cooling).

△ vaporization rates of arsenic face with excess gallium placed on top of surface before evaporation (heating).

▲ vaporization rates of arsenic face with excess gallium placed on top of surface before evaporation (cooling).

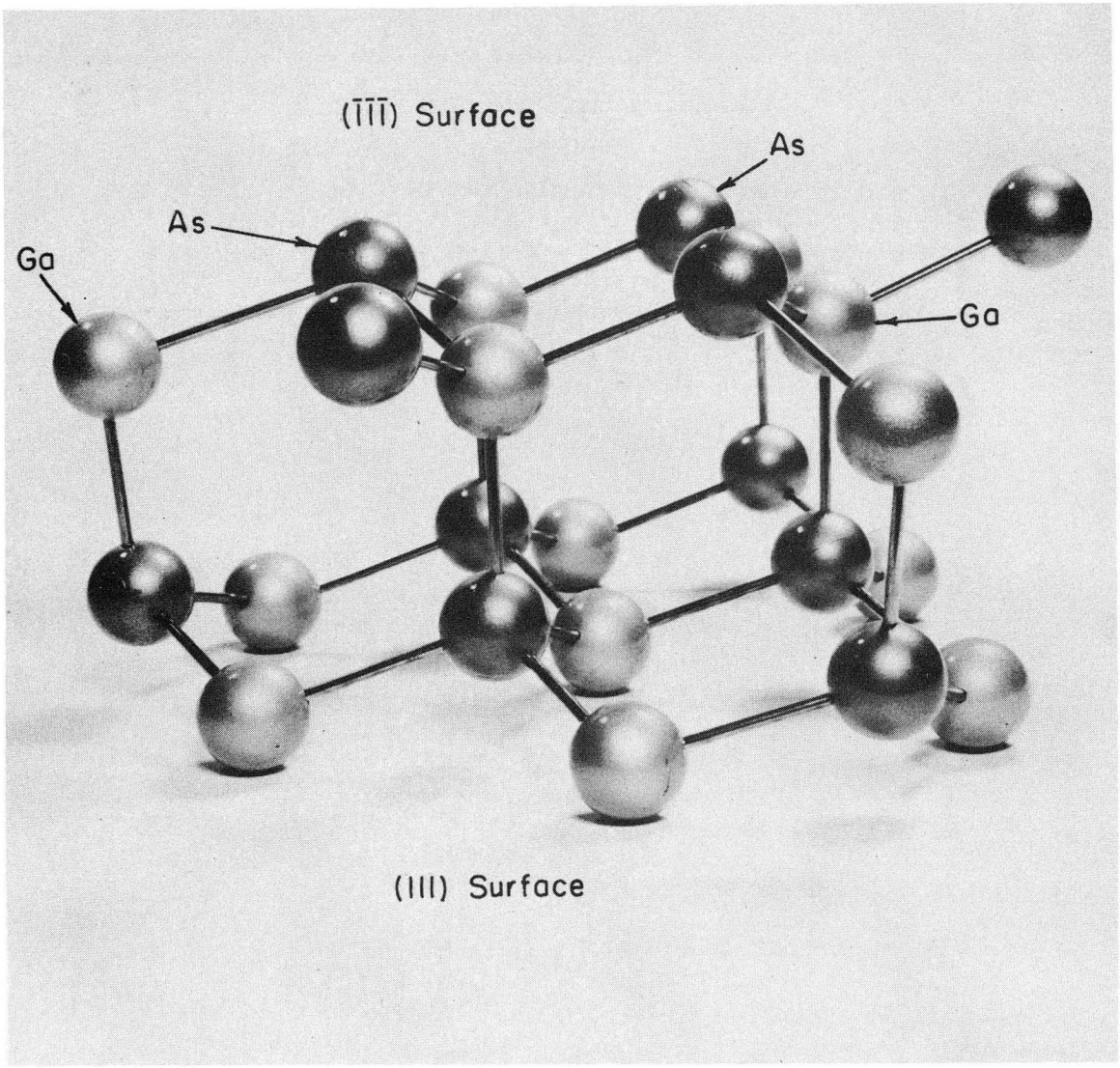
⊘ vaporization rates of gallium face with excess tin placed on top of surface before evaporation (heating).

◐ vaporization rates of gallium face with excess tin placed on top of the surface before evaporation (cooling).

△ vaporization rates of arsenic face with excess tin placed on top of surface before evaporation

1. The first time the crystal face was being vaporized.
2. The second time the crystal face was being vaporized.

The data points are taken from one representative experiment whereas the slope drawn through these points is the average value of all experiments that were carried out under the identical conditions.



XBB 708-3837A

Fig. 1

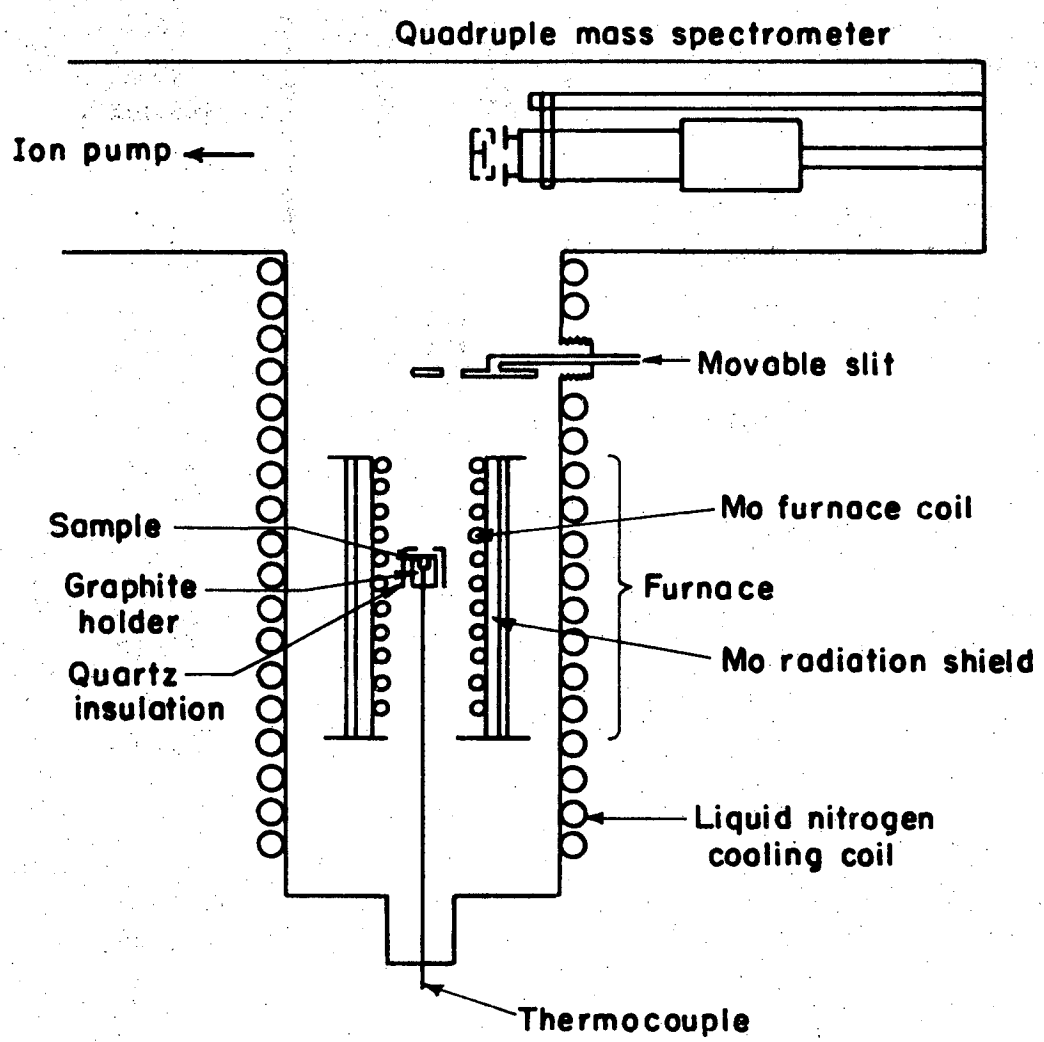


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Fig. 2

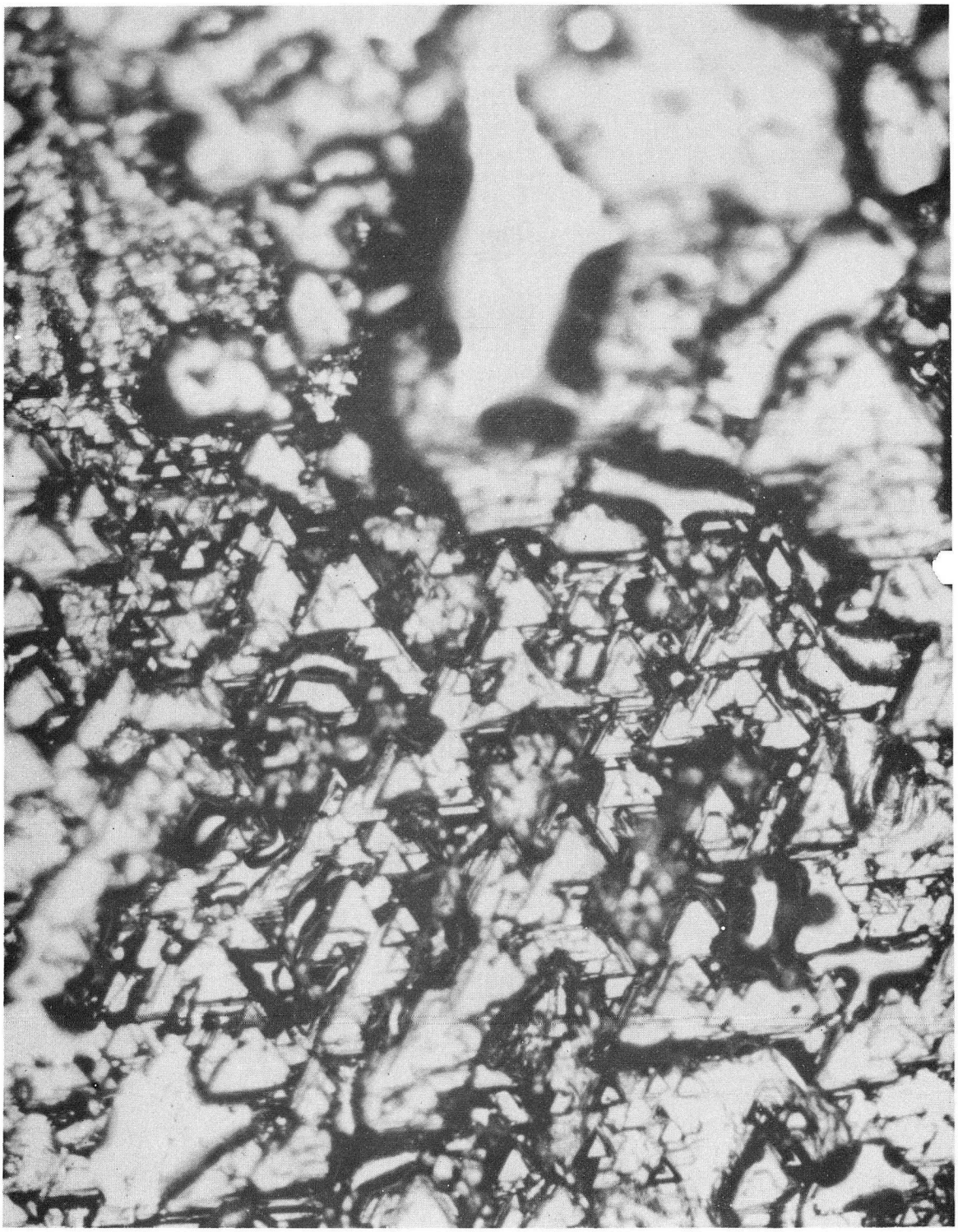

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Fig. 3a

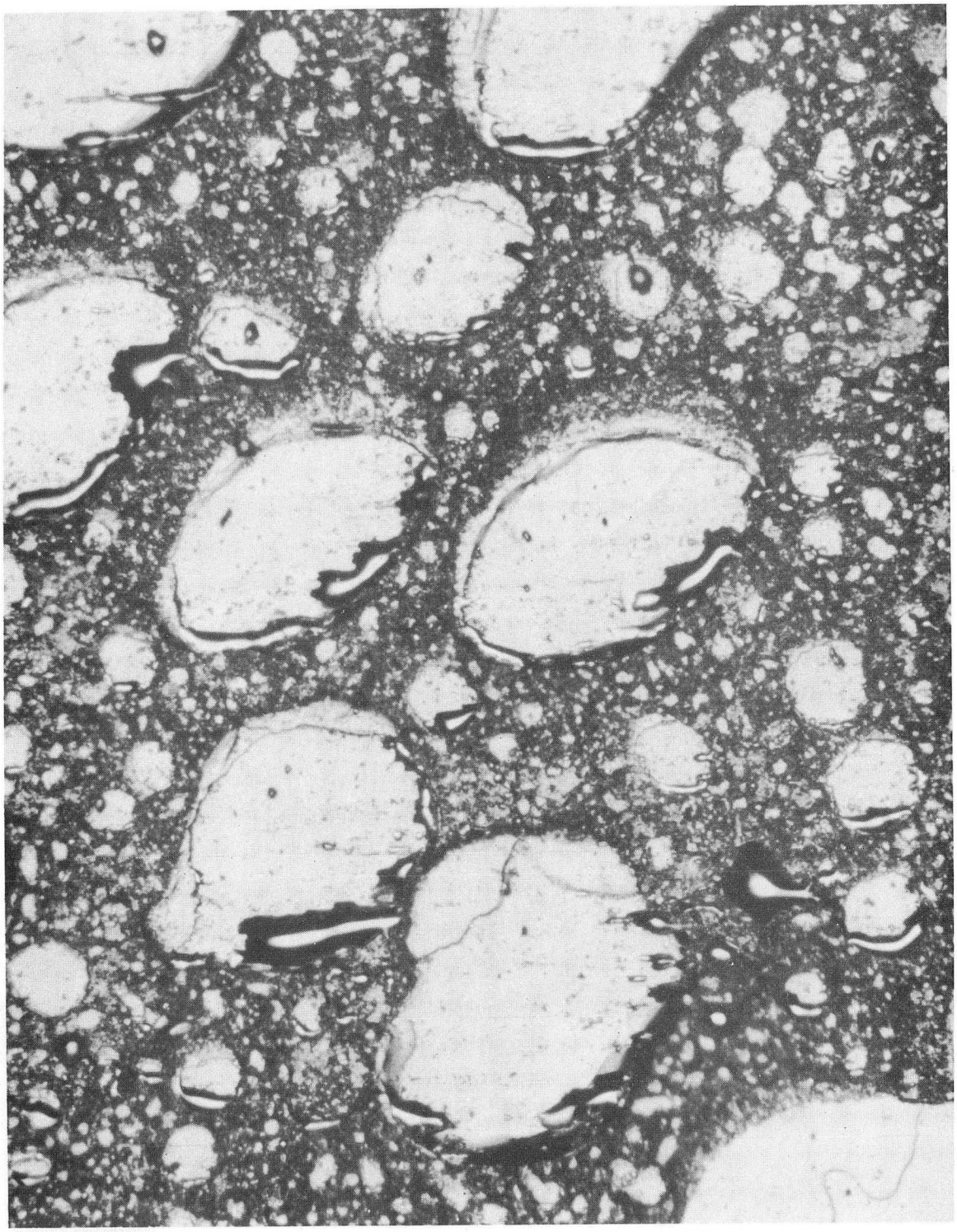

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Fig. 3b

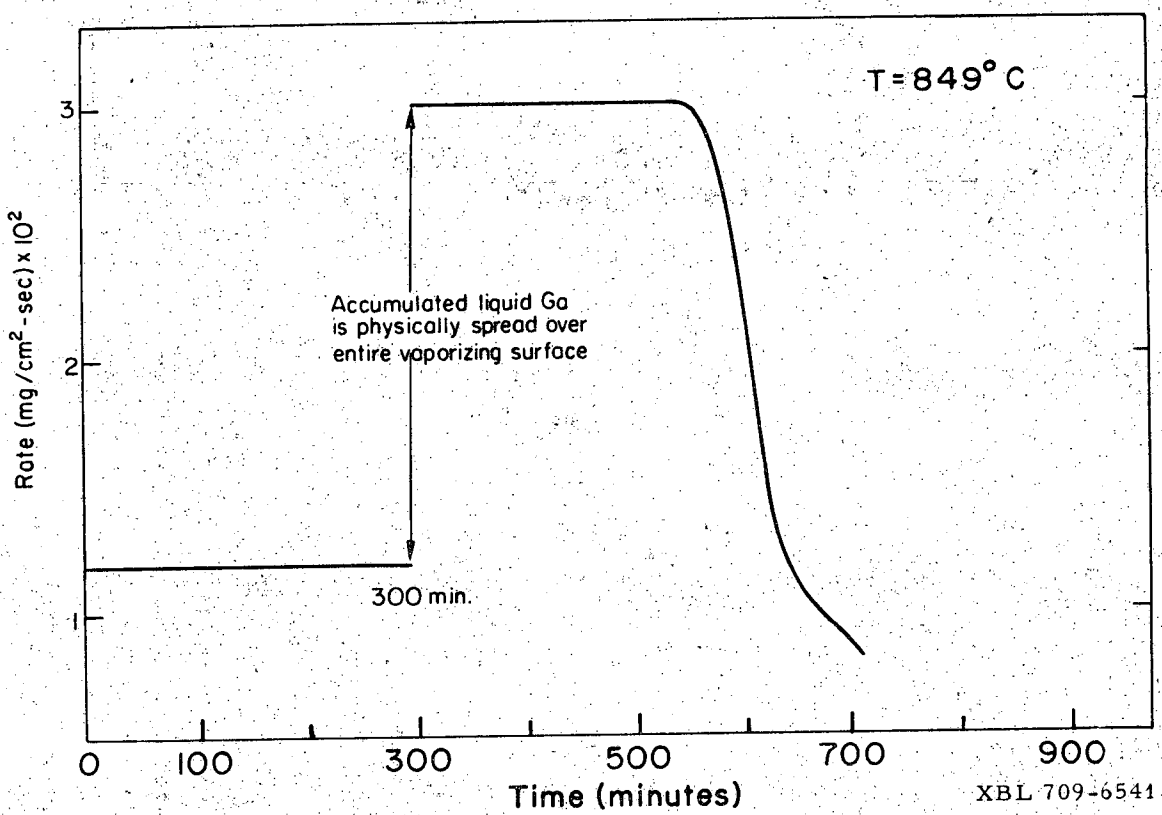
T = 849° C
Accumulated liquid Ga
is physically spread over
entire vaporizing surface
300 min.
Rate (mg/cm²-sec) x 10²
3
2
1
0
100
300
500
700
900
Time (minutes)
XBL 709-6541

Fig. 4

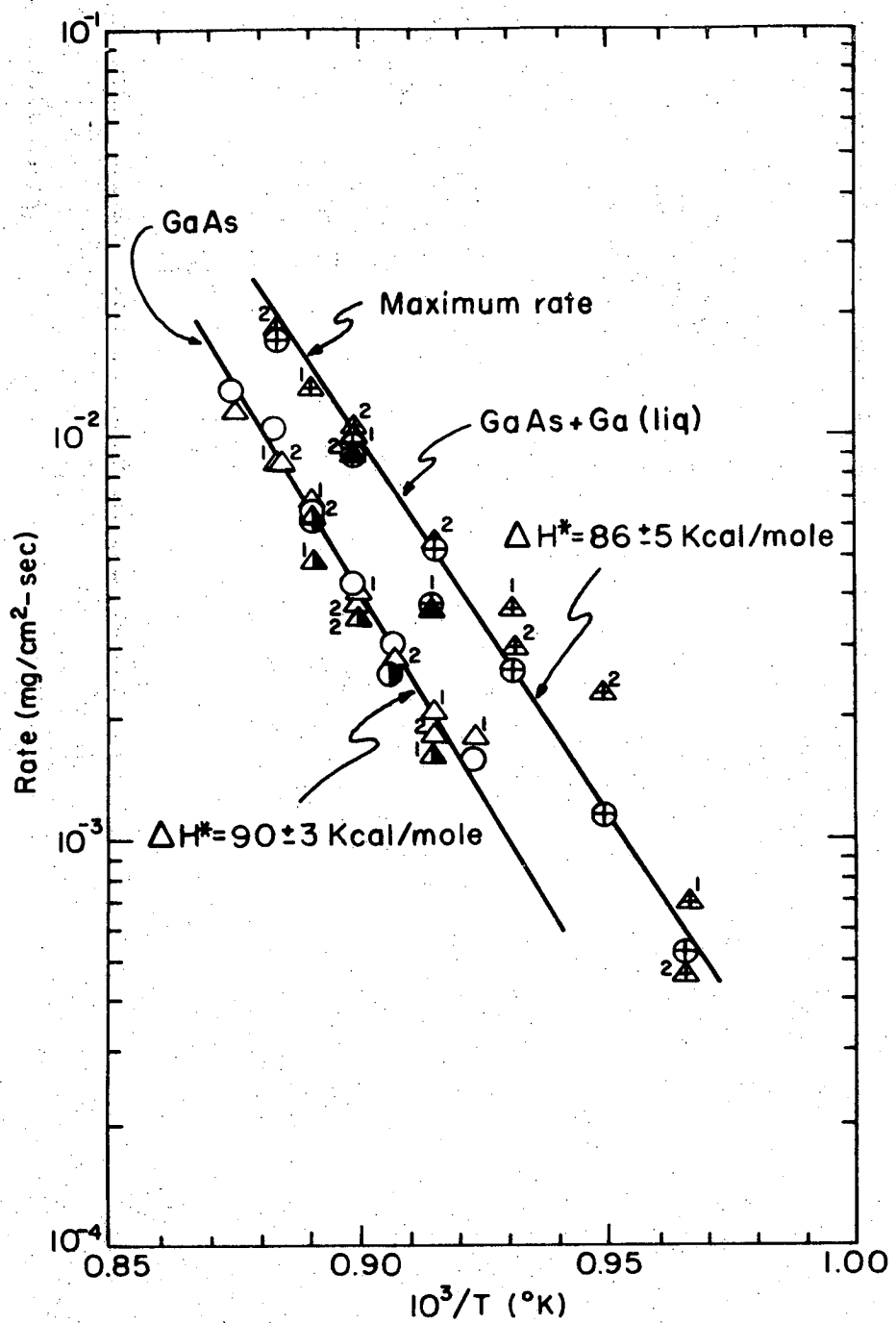

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Fig. 5

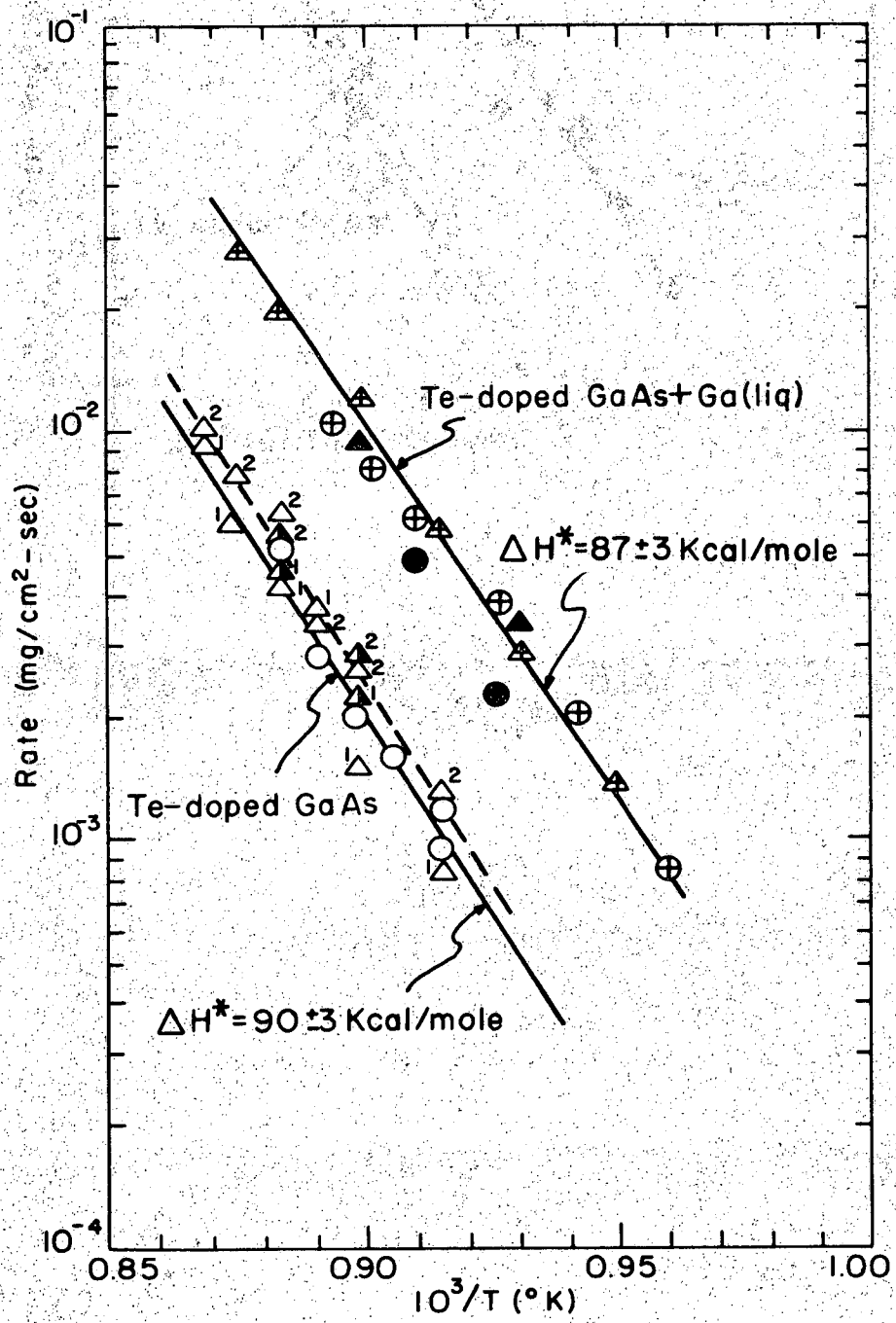

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Fig. 6a

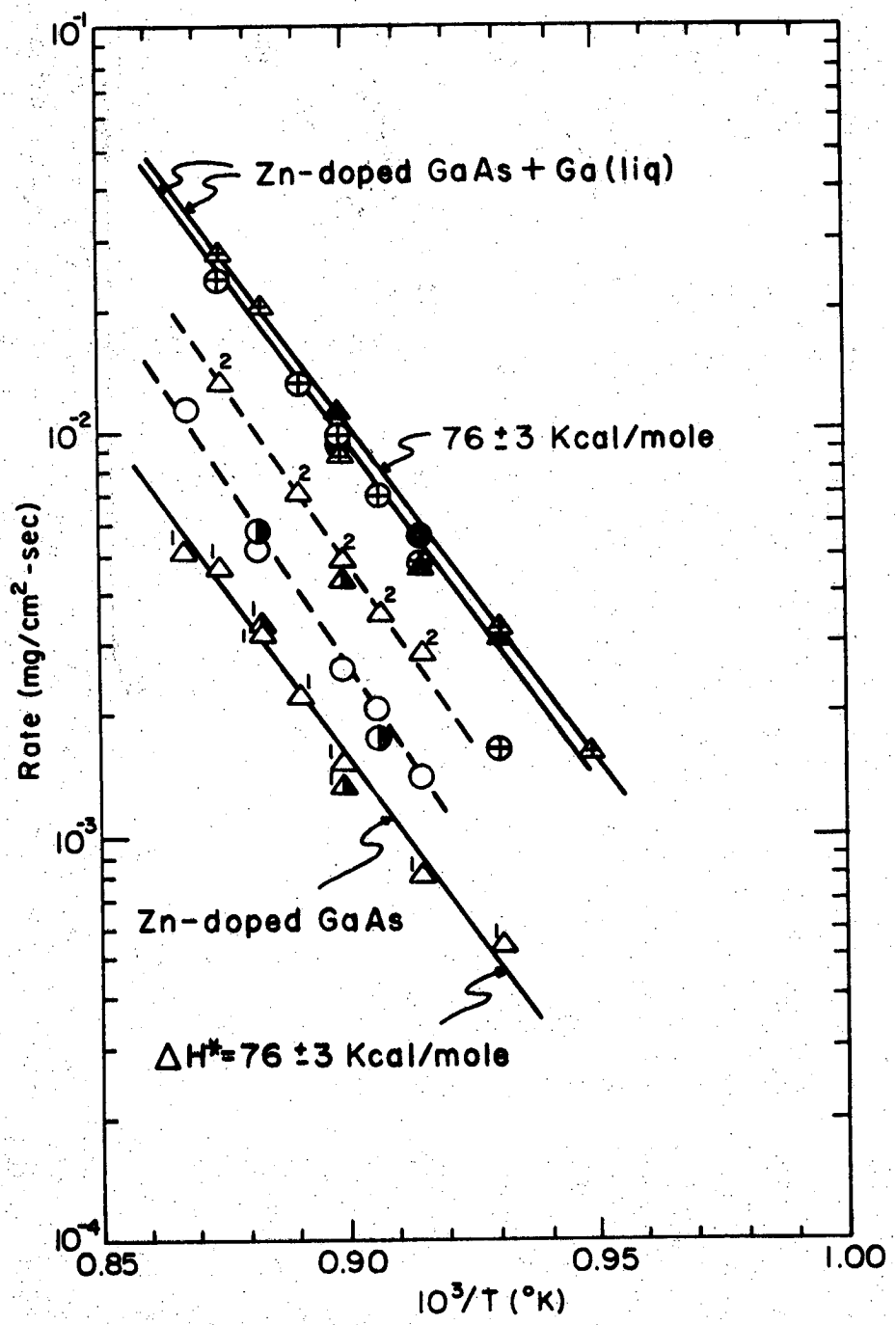

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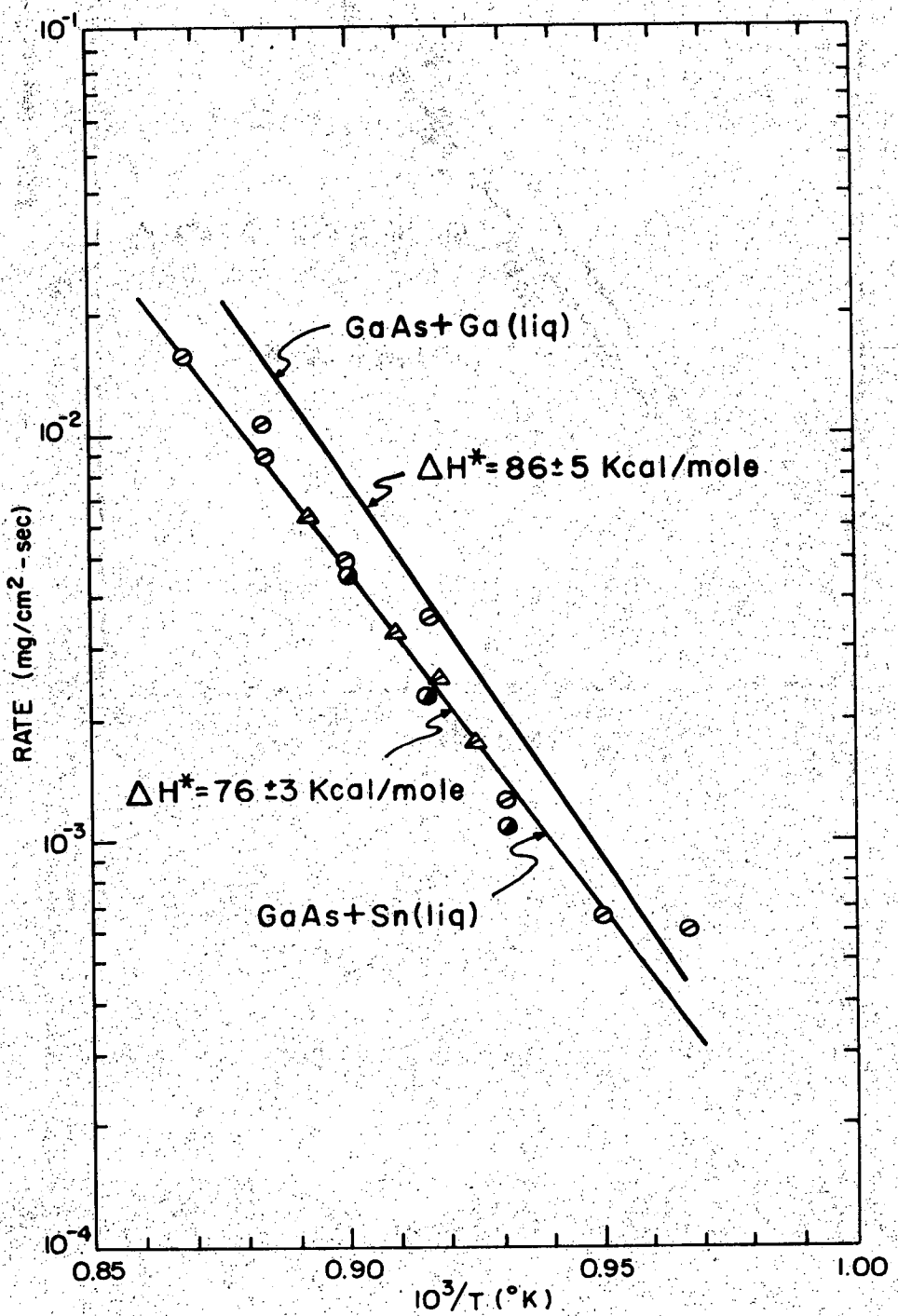
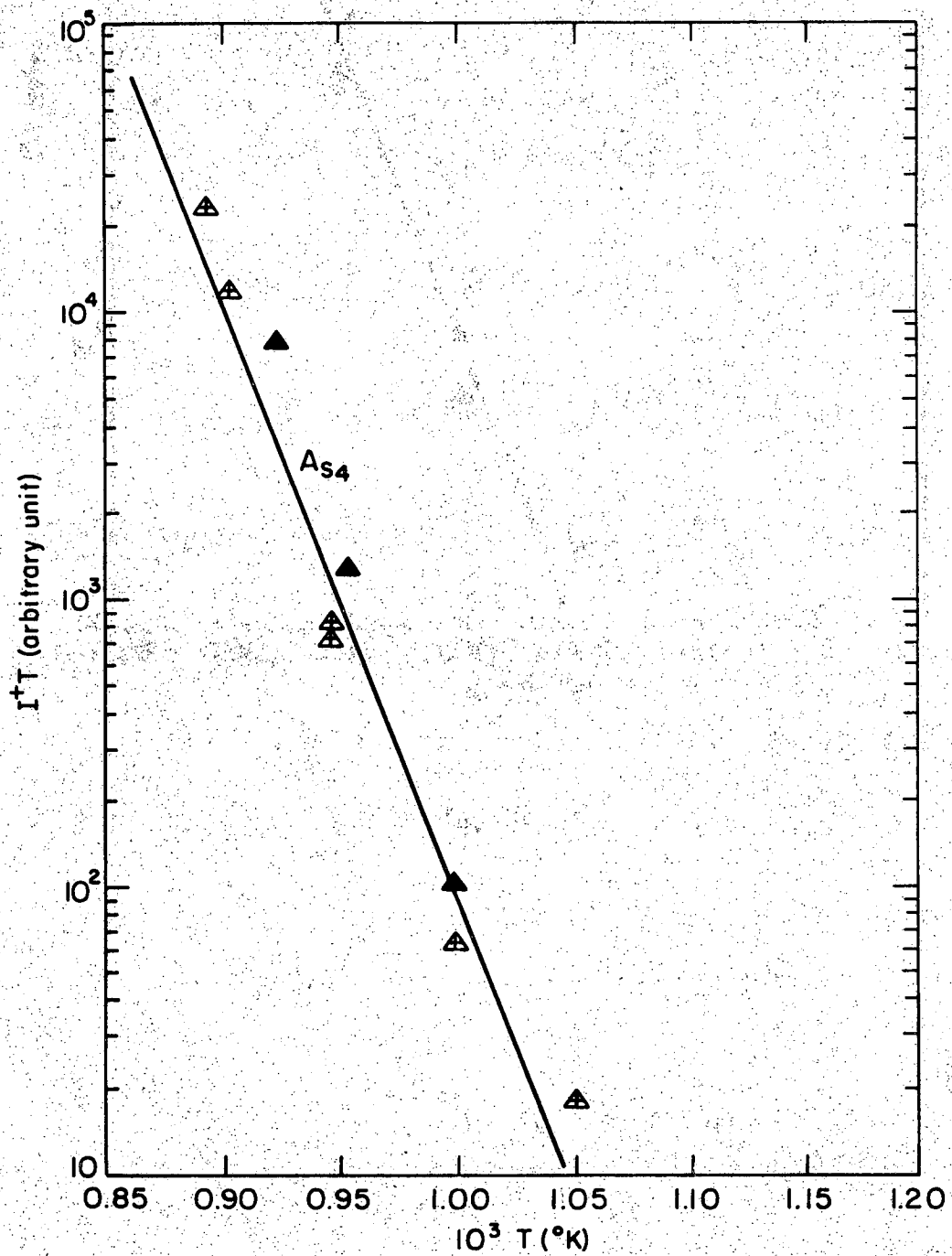
Fig. 6b



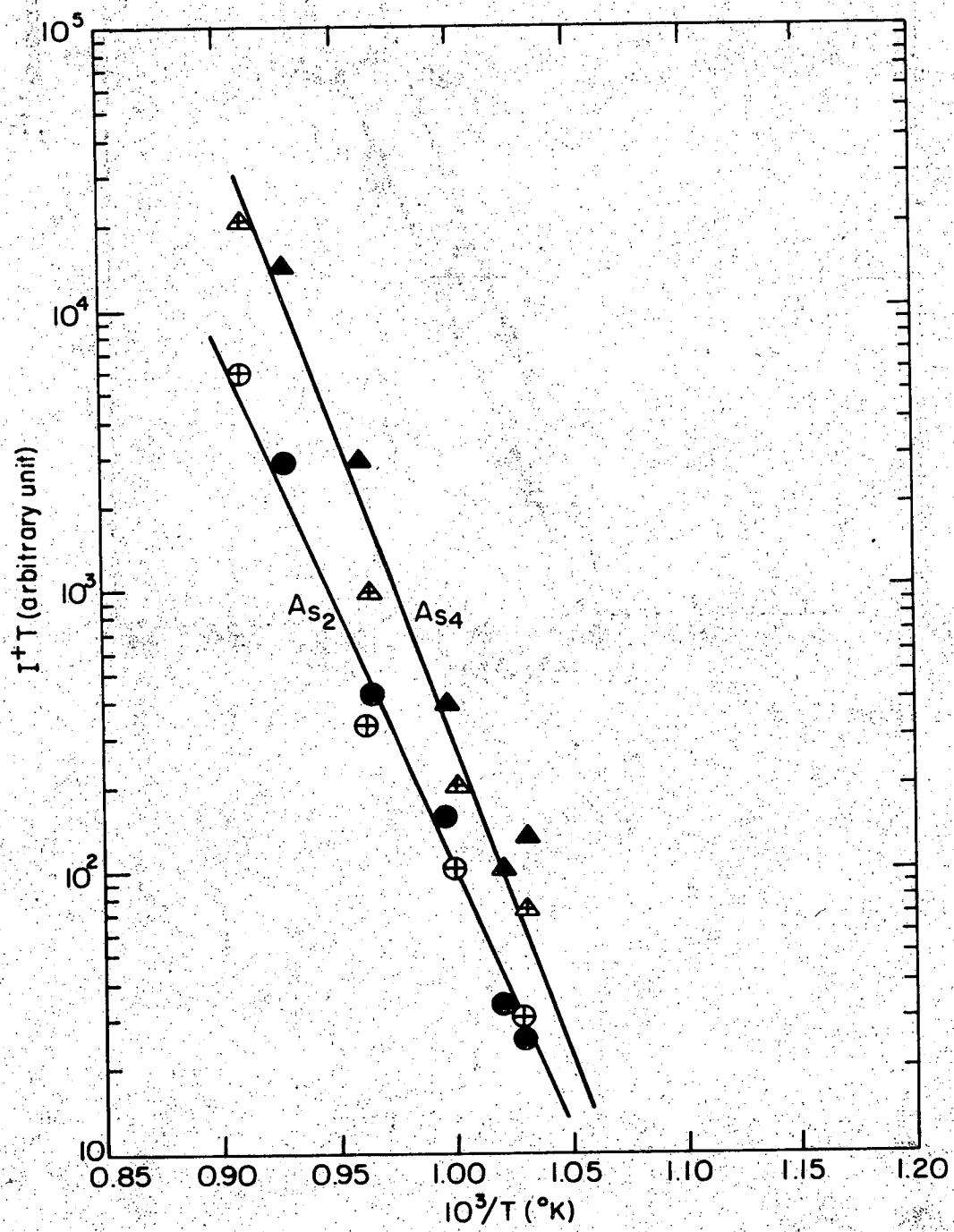
XBL 709-6623

Fig. 7



XBL 709-6550

Fig. 8a



XBL 709-6546

Fig. 8b

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