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T. Sakata, J. Block, M. Naschitzki, W. Schmidt. THE TEMPERATURE DEPENDENCE OF FIELD EVAPORATION OF GaP (111) SURFACES IN THE PRESENCE OF HYDROGEN. Journal de Physique Colloques, 1987, 48 (C6), pp.C6-239-C6-244. 10.1051/jphyscol:1987639 . jpa-00226844

**HAL Id: jpa-00226844**

**<https://hal.science/jpa-00226844>**

Submitted on 4 Feb 2008

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## THE TEMPERATURE DEPENDENCE OF FIELD EVAPORATION OF GaP (111) SURFACES IN THE PRESENCE OF HYDROGEN

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### Abstract

Quantitative measurements on the field evaporation of GaP(111) planes in the presence of hydrogen have been carried out using a field ion microscope. Below room temperature, the evaporation rate was found to decrease with increasing temperature, while above room temperature it steeply increased. The evaporation voltage was found to increase with increasing temperature up to room temperature and decreased slightly with further temperature rising. The evaporation rate was proportional to the hydrogen pressure in the investigated temperature range of 80-330 K. Based on the assumption that surface hydride formation is rate-determining for the field evaporation process, two kinds of hydrogen supply to the kink site atoms of the GaP(111) plane are considered to explain the unusual temperature dependence of the evaporation rates at low temperatures. One supply is only within the (111) plane, and, additionally, the other one is by diffusion over the steps between (111) planes. At  $T > 300$  K the thermally activated evaporation is promoted by hydrogen without having an observable precursor of molecular hydrogen.

### 1. Introduction

Field evaporation, which is the removal of surface atoms as positive ions due to high electric fields, has been studied extensively because of its importance in field ion microscopy and atom probe mass spectroscopy<sup>1,2</sup>. Only a few of these studies, however, have been carried out on semiconducting materials in particular silicon<sup>3-6</sup>. In the case of metals, field evaporation has been considered to be a thermally activated process over a field reduced surface potential. Sakata and Block recently found that field evaporation of silicon in the presence of hydrogen was rate-determined by surface hydride formation rather than by a thermally activated process. Later on, Kellogg<sup>6</sup> reported that in ultrahigh vacuum field evaporation of silicon is qualitatively that of metals. There is experimental indication that the interaction of hydrogen greatly changes the field evaporation process of silicon.

Field ion microscope studies of semiconductors have generally been carried out using whiskers as samples. However, it has proved recently that semiconductor samples can be readily prepared from commercially available wafers by cutting them into the shape of a rod<sup>7</sup>. With this improvement of sample preparation, it has become easier to examine various semiconductors such as Ge, GaAs and GaP as well as Si. The ordered field ion images of these

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semiconductors have generally been obtained by field evaporation in hydrogen imaging gas, where the presence of hydrogen is known to reduce greatly the evaporation field. With this increased applicability of field ion microscopes, there have been also increasing applications with the atom probe in studying various semiconductor surfaces and their interfaces formed with metals<sup>8-10</sup>. The atom probe have frequently been carried out in the presence of hydrogen to promote field evaporation. Therefore, it is important to get more information about field evaporation of semiconductors in the presence of hydrogen.

In the present work, we studied field evaporation of GaP(111) surfaces in the presence of hydrogen. The evaporation rate and the evaporation voltage have been measured as a function of temperature. We have also examined the hydrogen pressure dependence of the evaporation rate. The results obtained are discussed in comparison with previous results of Si(111)<sup>4,5</sup>.

## 2. Experimental

GaP specimen were fabricated by cutting commercially available GaP wafers of n-type, resistivity about 0.1 ohm-cm, into square rods of 0.35x0.35 mm<sup>2</sup>, the [110] direction being along the rod axis. Such rods were squeezed into a Pt tube of 1.0mm inner diameter and were etched chemically to form sharp needles. A mixed solution of HNO<sub>3</sub> and HCl was used. The specimen temperature was controlled by ac currents passing through a Mo heating loop on which the Pt tube was spot-welded. A Ni-NiCr thermocouple spot-welded to the Pt tube was used to measure the tip temperature. The field ion microscope used was a conventional UHV system, equipped with a 2 inch diameter channelplate for ion image intensification.

The field evaporation rate was determined by measuring the time needed to remove freshly formed GaP(111) planes - Ga side exposed -layer by layer, as described in the previous work<sup>4,5</sup>. During the measurements of the evaporation rates and the evaporation voltages, the tip radius gradually increased due to continuous field evaporation, causing a gradual decrease of the effective field strength at the surface and a gradual increase of the (111) plane size. Taking into account these tip blunting effects, all the data presented in this paper were corrected after each experimental run by evaluating the dependences of the evaporation rate and the evaporation voltage on the number of (111) planes already evaporated.

## 3. Results and discussion

The temperature dependence of the evaporation rate is shown in fig. 1. Since the variable range of temperature is limited by the observable range of ion image brightness for counting the number of planes evaporated, the measurable range of evaporation rate was typically limited to between 0.01 to 0.5 planes per second. Therefore, in order to cover a wide range of temperature, the measurements were carried out in three temperature ranges, 80-105K, 150-200K, and 249-336K. During each experimental run, the hydrogen pressure and the evaporation voltage were kept constant. Up to about 295K, the evaporation rate decreased with increasing temperature. However, further increase of temperature led to a steep increase of the evaporation rate. To be more precise, in the temperature range, 80-250K, the evaporation rate increased exponentially with increasing the reciprocal of temperature, while, above 310K, it decreased exponentially with the same. The exponential increase was already observed for Si(111) surfaces in a limited range of temperature, 80-103K<sup>4,5</sup> and has been explained by assuming that surface hydride formation is the rate-determining process since field-adsorbed hydrogen desorbs successively increasing temperature. The same explanation is applicable to the present result obtained below 250K, but is not consistent with the result obtained above 310K. An alternative explanation must be invoked to the reverse temperature dependence above 310K.

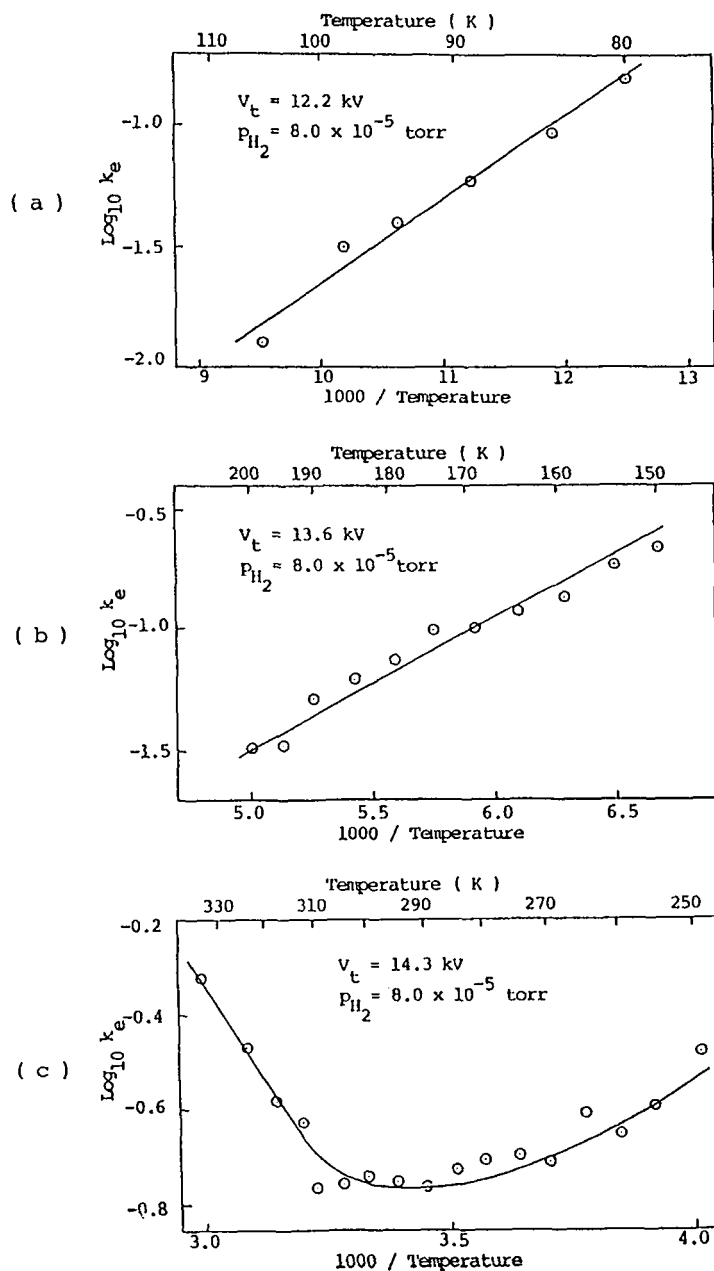


Fig. 1 Temperature dependence of the field evaporation rate,  $k_e$ , of GaP (111) surface in the temperature ranges, (a) 80-105K, (b) 150-200K and (c) 250-336K. During measurements, hydrogen pressure,  $p_{H_2}$ , and evaporation voltage,  $V_t$ , were kept constant as described in each figure.

The temperature dependence of the evaporation voltage is shown in fig. 2 where the evaporation rate and the hydrogen pressure have been kept constant.

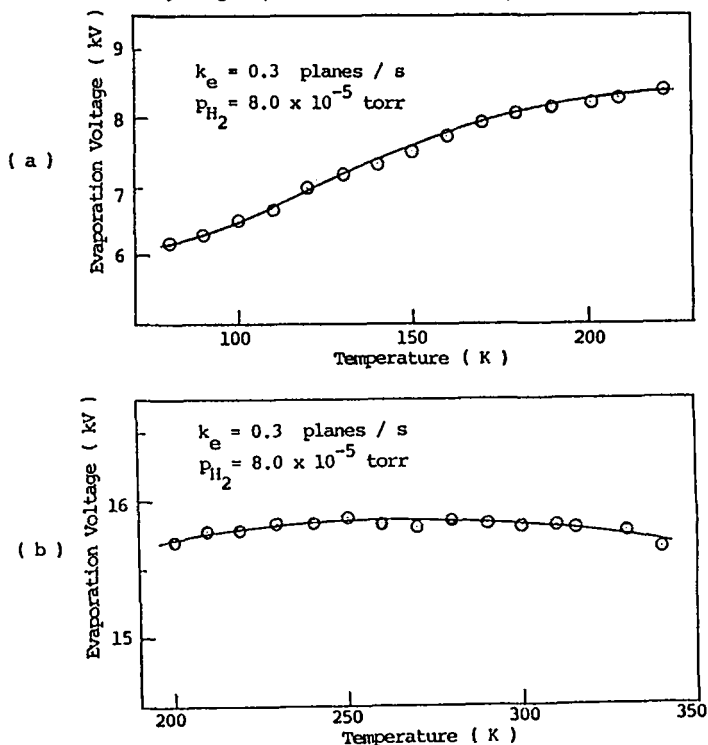


Fig. 2 Temperature dependence of the evaporation voltage of GaP (111) surface in the temperature ranges, (a) 80-222K and (b) 200-340K. During measurements, evaporation rate,  $k_e$ , and hydrogen pressure,  $p_{H_2}$ , were kept constant as described in each figure.

In order to avoid experimental errors due to tip blunting, the measurements were carried out in two temperature ranges, 80-210K and 200-340K, where the tip radii were different. Therefore, the evaporation voltages are not comparable for these two experimental runs. The evaporation voltage increased with increasing temperature in the range 80-250K, and became saturated above 250K followed by a slight decrease above 270K. A similar temperature dependence was also observed in the case of Si<sup>4,5</sup>, where the evaporation voltage increased with increasing temperature in the range 80-300K. This unexpected temperature dependence was explained by the depletion of adsorbed hydrogen with increasing temperature. The evaporation voltage then must be increased to keep the evaporation rate constant. The same explanation may be applicable to the present result obtained below 250K. The saturation and the following slight decrease of the evaporation voltage observed above 250K, however, is not consistent with the above explanation.

In fig. 3 the hydrogen pressure dependence of the evaporation rate is shown. The temperature and the evaporation voltage were kept constant during the measurement. It can be seen that in the investigated range of 80-320K, the evaporation rate increased linearly with increasing pressure. In the case of Si<sup>4,5</sup>, where the measurement was carried out only at 80K, the linear pressure dependence was also observed and explained by the linear increase of hydrogen supply rate to the kink site Si atoms. It was assumed that surface hydride formation is rate-determining in the field evaporation process. In the present case, the same explanation may be true but it should be noted that the linear pressure dependence was observed even at temperature higher than room temperature. This fact definitely indicates that the surface hydride formation is still rate-determining even above

room temperature, but the results shown in figs. 1 and 2 suggest that different processes are apparently taking place below and above room temperature:

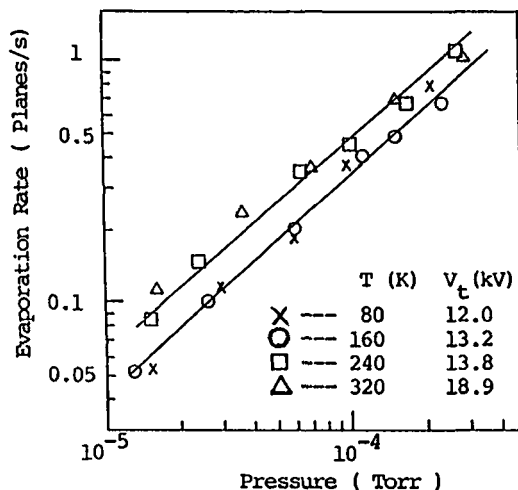


Fig. 3 Hydrogen pressure dependence of the field evaporation rate of GaP (111) surface. During measurements, tip temperature,  $T$ , and the evaporation voltage,  $V_t$  were kept constant as described in the figure.

In order to explain the results of the entire examined temperature range, we will discuss the hydrogen supply to the kink site atoms of the topmost GaP(111) layer. As observed in the field ion images, field evaporation of a freshly formed GaP(111) plane always proceeds through the evaporation of kink site atoms at the periphery of the plane. Hydrogen molecules impinging on the surface from the gas phase are thermally accommodated and migrate to the kink site atoms where they form surface hydrides. We assume that the kink site atoms field-evaporate at the instant of the hydrides being formed, which was assumed also in the previous work<sup>4,5</sup>. This assumption is consistent with the observation in fig. 3, where the evaporation rate increased linearly with increasing hydrogen pressure. The topmost (111) plane is positioned on another larger (111) layer, so additionally an atomic terrace is present, separated from the toplayer by a step. Each terrace is terminated, and its periphery appears as a ring structure in the field ion image. Therefore, we must consider two kinds of hydrogen supply to the kink site atoms of the topmost (111) plane. One is the supply of hydrogen within the topmost layer, the other one is the supply from (111) terraces by jumping over the respective atomic steps. Surface diffusion is of course a thermally activated process. Since the activation energy for surface diffusion over a step is higher than that within a terrace or within the topmost plane, at sufficiently low temperatures hydrogen is supplied to the kink site atoms only within the terraces or the plane. At higher temperatures, hydrogen is also supplied from other terraces to the topmost layer. So a larger surface area which accommodates hydrogen is then available. Hydrogen arriving at the kink site atoms reacts with them to form hydride in a reaction time proportional to

$$\exp\left(\frac{1}{2} \alpha F^2 / kT\right)$$

as discussed in the previous work<sup>4,5</sup>, where  $\alpha$  is the polarizability of hydrogen,  $F$  the field strength,  $k$  the Boltzmann's constant and  $T$  the tip temperature. The supply rate of hydrogen to kink site atoms is proportional to  $\exp(-E_d/kT)$ , where  $E_d$  is the activation energy for surface diffusion on a flat plane. Thus, the supply rate decreases exponentially with increasing the reciprocal of the temperature, while the reaction time increases exponentially with the same. Based on the above discussion, at low temperatures the hydride formation rate can be considered to be proportional to

$$\exp\left[\left(\frac{1}{2} \alpha F^2 - E_{dt}\right) / kT\right],$$

where  $E_{dt}$  is the activation energy for surface diffusion over a flat plane. At high temperatures it should be proportional to

$$\exp \left[ \left( \frac{1}{2} \alpha F^2 - E_{ds} \right) / kT \right],$$

where  $E_{ds}$  is the activation energy for surface diffusion over steps. If the polarization energy,

$$\frac{1}{2} \alpha F^2,$$

satisfies the relation,

$$E_{dt} < \frac{1}{2} \alpha F^2 < E_{dt},$$

the hydride formation rate increases exponentially with increasing the reciprocal of the temperature at low temperatures, while at high temperatures, it decreases exponentially with the same. Since we assume that the rate of evaporation and hydride formation are proportional, we can expect the same temperature dependence of the evaporation rate over the entire temperature range as shown in fig.1. Since at high temperature the evaporation rate increases with increasing temperature, the evaporation voltage must be lowered to keep the evaporation rate constant. This is consistent with the experimental result observed above room temperature which are shown in fig. 2.

In summary, field evaporation of the GaP(111) plane has been studied in the presence of hydrogen. The temperature dependences of the evaporation rate and the evaporation voltage were quite different below and above room temperature. Below room temperature, the evaporation rate decreased with increasing temperature and of the evaporation voltage increased with increasing temperature. Above room temperature, the evaporation rate increased with increasing temperature and increased linearly with increasing hydrogen pressure. The linear pressure dependence suggests that field evaporation is rate-determined through the process of hydride formation within the entire range of temperature being examined from 80-330K. The change in the temperature dependence of evaporation rate and evaporation voltage above room temperature was attributed to two different kinds of hydrogen supply to the kink site atoms of the GaP(111) plane.

### Acknowledgements

One of us (T. S.) thanks for a fellowship of the Max-Planck-Gesellschaft. Financial support by the Deutsche Forschungsgemeinschaft (SFB 6, Berlin) is gratefully acknowledged.

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