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FIELD EVAPORATION OF n-Ge (111) IN HYDROGEN AND DECOMPOSITION OF GeH_4 IN HIGH ELECTROSTATIC FIELDS

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Abstract -Using a field ion microscope, the field evaporation rate of Ge(111) in hydrogen at pressures ranging fron 10^{-4} to 10^{-6} mbar was determined. From 80 to 300 K the evaporation rate decreases, keeping the field strength constant (~1.5 V/Å), or vice versa at a constant rate the needed evaporation voltage increases. Above 300 K the temperature dependence reverses, the evaporation rate increases strongly with increasing temperature. Effective binding energies for the hydrogen promoting field evaporation were determined to range from 32 meV to 97 meV with increasing field strength. The evaporation rate is shown to have $\sqrt{p_{H_2}}$ -dependence regardless of temperature or field strength.

The observed anomalous temperature dependence agrees with earlier FIM-experiments performed on Si (110) and GaP (111). It is well established that adsorbed hydrogen plays an important role in the field evaporation process of semiconductors. The observed pressure dependence is an indication that the dissociation of $H_2 \rightarrow 2H$ is involved in the rate determining step, which is discussed in the light of a field evaporation model.

Field ionization and field desorption of GeH_4 results in the formation of GeH_3^+-ions from surface interactions, GeH_2^+ from gas phase surface interactions GeH_2^+ from gas phase decomposition during the field ionization, and Ge^+ from the thermal decomposition of germane. Kinetic energy distribution measurements indicate that germane is ionized out of a thermally activated state of GeH_4 at $T > 400$ K.

1 - INTRODUCTION

Field evaporation is a thermally activated process with an activation energy which normally decreases with increasing field strength. An exception in the temperature dependence of field evaporation rates was found for semiconductors if hydrogen is used as imaging gas. For silicon, Sakata and Block /1/ found that at $T < 300$ K the evaporation voltage increased when the temperature was raised. Accordingly, the field evaporation rate decreased with increasing temperature. This behavior is just opposite to that of metals and that of silicon without hydrogen imaging gas /2/. This unexpected temperature dependence is explained by a field induced surface reaction of hydrogen which forms surface hydrides with low evaporation fields. A field-adsorbed molecular hydrogen precursor state is depleted with increasing temperature and responsible for the overall temperature coefficient of the field evaporation process. Similar observations have been made for GaP /3,4/. In connection with the field evaporation of Ge in hydrogen, it is interesting to learn about the properties of GeH_x^+-ions. This is achieved by mass spectrometric investigations of field ionized and field desorbed of germane.

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2 - EXPERIMENTAL

For field-evaporation experiments of Ge, wafers of n-conducting material were cut into rods. These were mechanically squeezed into Pt-tubes and electrochemically (≈ 20 V a.c.) etched in a HF/HNO_3 mixture. The Pt-tubes with Ge-tips were mounted to a Mo-heating loop to which a thermocouple was also connected. The tip was cooled by a liquid nitrogen trap and heated by regulated current.

The field ion microscope was equipped with a channel plate and reached pressures as low as 4×10^{-10} Torr (for details see /5/). Evaporation experiments were recorded with a video camera. Evaporation rates, dN/dt, were determined by measuring the times required to remove N single layers from the top of the Ge-tip.

3 - RESULTS AND DISCUSSION

a) Morphological changes of tips

The field evaporated Ge-surface clearly displayed the (111) poles when hydrogen was used as imaging gas. The field evaporation of the germanium tip can be seen in the field ion microscope layer by layer. The measured quantity $k_V = dN/dt$ in layers/s is linearly decreasing over a limited range of removed layers in advancing field evaporation, as shown in fig. 1. The value of $\Delta k_V/\Delta N$ ($\approx 2.2 \cdot 10^{-4}$ layer/sec/layer in this case) is used for correction of constant rate measurements. For constant field measurements the applied tip voltage is increased by a value derived from $(\Delta V/\Delta N)k_{V=const}$, which gives in fig. 1 a value of 20 V/layer. These correction factors gradually decrease for a wider range of removed layers (N>200). All reported data were corrected accordingly.

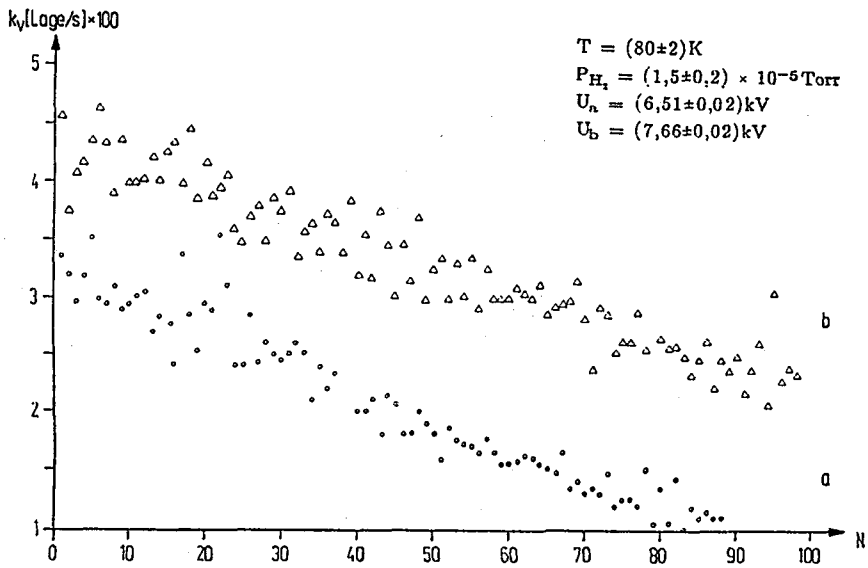

Fig. 1 - The field evaporation rate $k_V = dN/dt$ at two constant evaporation voltages, T = 80 K, $p_{H_2} = 1.5 \cdot 10^{-5}$ Torr.

b) Evaporation voltages

For these measurements the evaporation rate is kept constant (k_V = 0.047 layers /s) . The results (fig.2) show that fromT = 120 K to T = 320 K an increase of U_V about 40 % is required. At low temperature (T ≈ 100 K), U_V -values are independent of temperature. This behaviour resembles the observations of field evaporation of silicon in hydrogen.

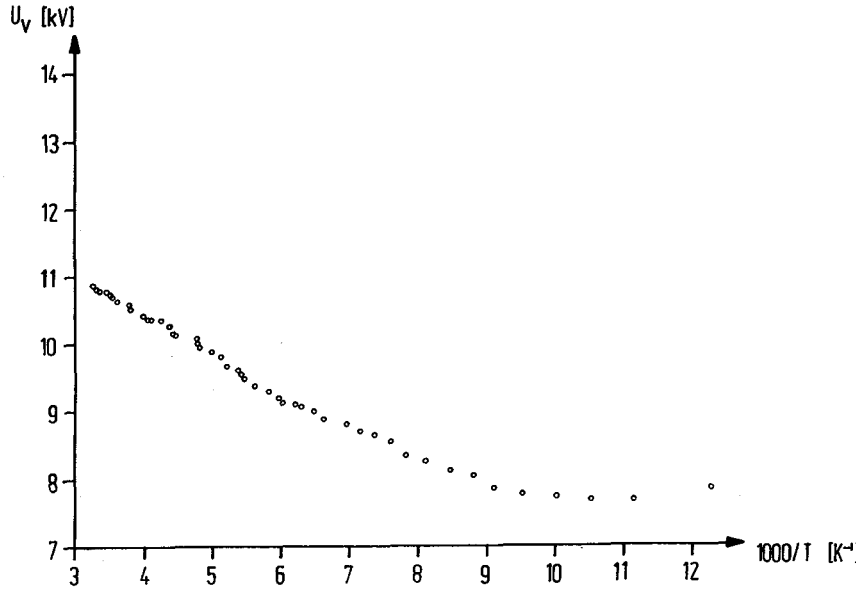

Fig. 2 - The dependence of evaporation voltage U_V on temperature at constant evaporation rate $k_V = 4.7 \pm 0.2 \times 10^{-2}$ layers /s, $p_{H_2} = 2.3 \cdot 10^{-5}$ Torr.

c) The temperature dependence of field evaporation rates

The field evaporation rates k_V were measured between 80 and 300 K. One experimental difficulty arose due to the diminishing brightness of the field ion images with increasing temperature (H_2 imaging gas). The experiments therefore had to be made at different imaging voltages (fig. 3 a-c). Between 80 K and ≈307 K a negative temperature coefficient of the field evaporation rate is observed. The slopes in the ln k_V versus 1/T diagram (fig. 3) are 32 meV (U_V = 8.42 kV), 77 meV

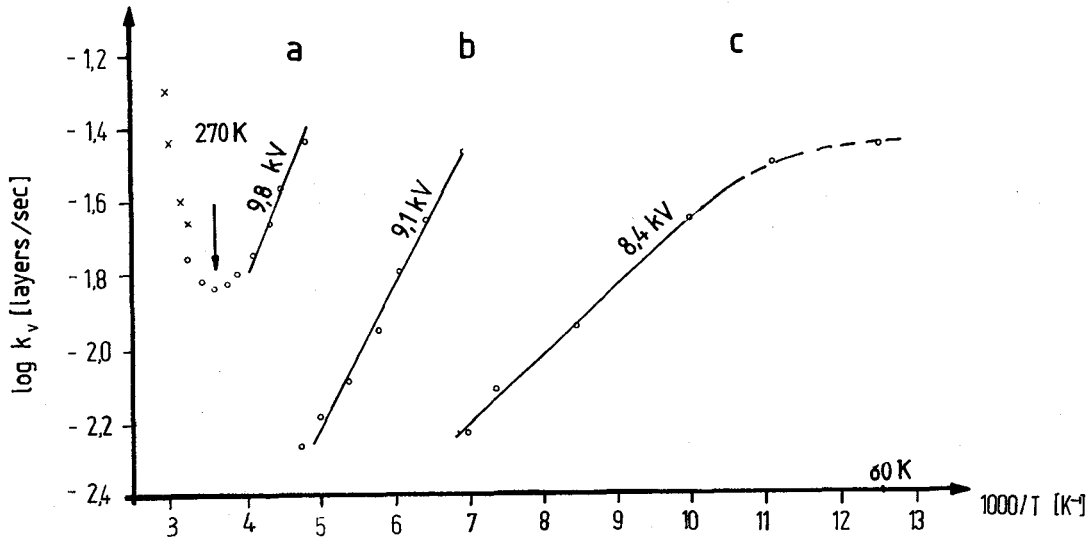

Fig. 3 - The temperature dependence of evaporation rates at constant p_{H_2}: T = 80-144 K (c), U_V = 8.42 ± 002 kV; T = 144-210 K (b), U_V = 9.14 ± 00.2 kV, T = 207-307 K, UV = 9.85 00.2 kV; and T = 307- 337 K, U_V = 11.80 ± 00.2 kV (a). The points x are not corrected for tip radius changes.

($U_V = 9.14$ kV) and 95 meV ($U_V = 9.85$ kV). These energies reflect the field adsorption energies of molecular hydrogen. As before (fig. 2) a temperature independent behaviour is observed at $T \approx 100$ K. At temperatures above 307 K, the field evaporation rate increases rapidly with temperature. The temperature coefficient could not be measured in this region.

d) The evaporation rate at different hydrogen pressures

The p_{H_2}-dependence of k_V has been measured at different evaporation voltages and temperatures (fig. 4). In the region of measurement, T = 80 K to 207 K and U_V = 11.5 to 13.3 k_V, the field evaporation rate increases with increasing hydrogen pressure. The best fit of the data follow a lag $k_V = \sqrt{2} \log p_{H_2}$ dependence. This relationship differs from observations with Si /1/, where $k_V \alpha\, p_{H_2}$ was found. The findings at Ge suggest that a dissociation of H_2 occurs and that atomic hydrogen is involved in the rate determining step of field evaporation.

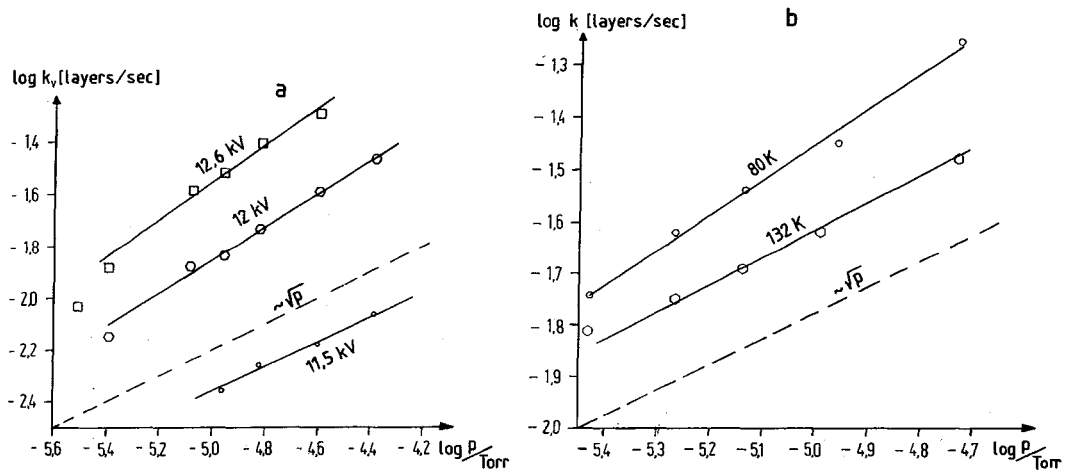

Fig. 4 - The dependence of field evaporation rates k_V on hydrogen pressure at different evaporation voltages (a) with T = 80 K and temperatures (b)with U = 12.63 kV.

e) Conclusions for the field evaporation process of Ge in hydrogen

The anomalous temperature dependence of field evaporation voltage and field evaporation rate is caused by a field induced surface reaction of hydrogen, which results in the formation of surface hydrides. The Ge-H bond strength (289 kJ /mol) is higher that for the Ge-Ge bond (188 kJ/mol). Molecular hydrogen is field adsorbed at the Ge-surface with field dependent binding energies (fig 2). This precursor state is reponsible for the anomalous temperature dependence of k_V. The low field evaporation field strength of Ge in hydrogen, which was reported earlier /6/, can be related to three facts

1. The field induced dissociation of molecular hydrogen is enhanced by the formation of surface hydride Ge-H or Ge- H_2.
2. The formation of Ge-H_x-surface bonds reduces the back-bonding of Ge-surface atoms to the bulk.
3. The formation of surface Ge-H_x-bonds removes an unoccupied electronic surface state. As a consequence the field penetration into the bulk increases and weakens chemical bonds /7/.

The same mechanism, that has been discussed earlier for Si /1/ can be applied to be with the exception that a square root p_{H_2}-dependence of k_V was found for Ge (and not k_V proportional p_{H_2} as for Si). This would suggest that hydrogen interacts in atomic form, whereby GeH^+-ions are formed. In order to learn about the stability of GeH_x in the high electric field, field desorption experiments have been performed using GeH_4 as imaging gas.

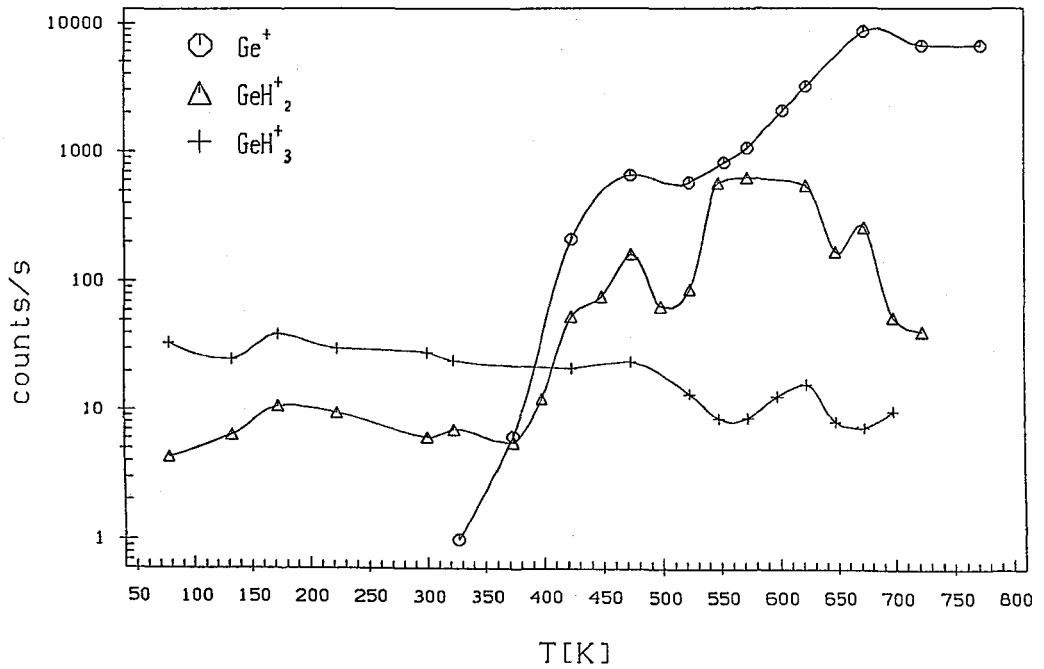

Fig. 5 - Field ionization and - desorption of GeH_4: fragment ions as function of emitter temperature. The tungsten emitter was coated by a Ge-layer, GeH_4-pressure $1x10^{-5}$ Torr. Experimental conditions as in /8/.

f) Field ion mass spectrometry of germane

As before for silane /8/, field ion mass spectrometry and appearance spectroscopy was performed for germane. In continuation of earlier studies /9/, appearance potentials of fragment ions were evaluated for different values of field strength and temperature. In the field ionization mass spectrum GeH_2^+ and GeH_3^+ are the most abundant ions, GeH^+ is observed only in small quantities and the parent molecular ion could only be detected if Ge-emitter surfaces were used. Appearance potential measurements demonstrated that GeH_3^+ is a surface reaction product whereas GeH_2^+ is formed during fragmentation in the gas phase. Interesting results have been obtained in the temperature dependence of ionic species of germane. In fig. 5, ion intensities of GeH_2^+, GeH_3^+ and Ge^+ are given as function of the tip temperature. In the temperature region ($T>300$ K) where the normal field evaporation temperature coefficient (fig. 3) is reached, decomposition products of GeH_4^+, i. e. GeH_2^+ and Ge^+, display increasing intensities. This temperature region coincides also with the start of thermal decomposition of germane /10/. Another interesting observation concerned the appearance potentials, A of fragment ions. Above 350 K the A-values of GeH_2^+ decrease by 1.5 eV (fig. 6). This can be considered as due to an internal excitation which reduces the energy for ion formation. Since there are no electronic states in GeH_4 in this energy range, we have to assume a vibrational excitation is the cause. Such excitations have been observed optically as vibrational overtones in photoacoustic measurements /11/.

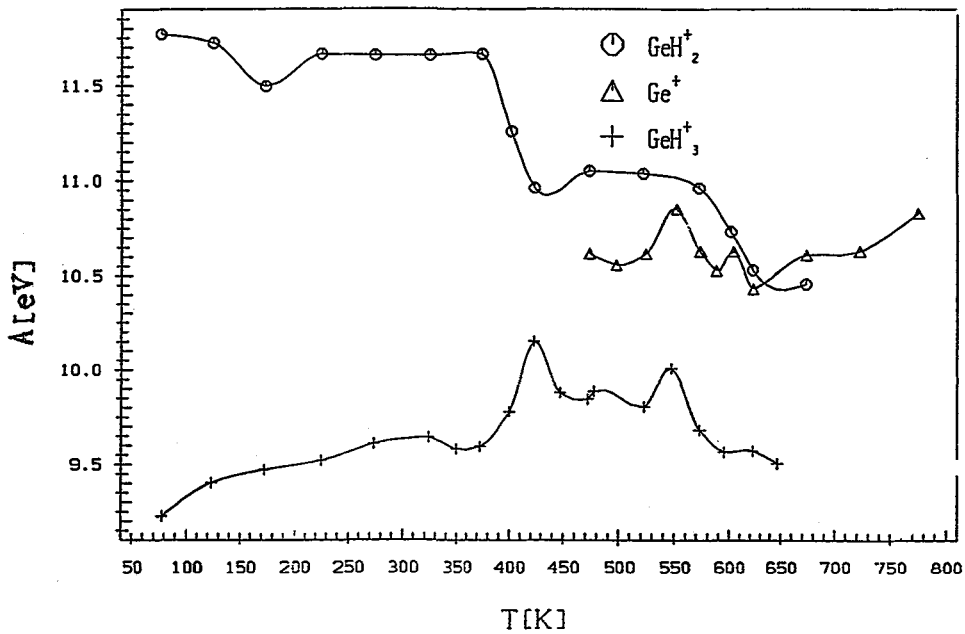

Fig. 6 - Field ion appearance energies, A, of fragmentation products of germane: Temperature dependence of A-values. Experimental conditions as in /8/.

4 - CONCLUSIONS

The field evaporation of Ge in hydrogen is determined by the formation of hydride ions via a field-adsorbed precursor state of molecular hydrogen at temperatures $T<300$ K. Above $T>350$ K field ion mass spectra of germane display fragmentation products, i.e. GeH_2^+ and Ge^+. Thus the temperatures where the anomalous field evaporation of Ge in hydrogen changes into a normal thermally activated evaporation process coincides with the temperature region of beginning instabilities of GeH_x^+-ions.

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