Hydrogen adsorption on GaAs(110) studied by temperature-programmed desorption

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GaAs(110) was cleaved in ultrahigh vacuum and exposed to atomic and to molecular hydrogen. After exposure at 250 K to molecular hydrogen neither H nor H_2 is found desorbing up to 670 K. Upon adsorption of atomic hydrogen, use of the temperature-programmed-desorption technique reveals a second-order process for the desorption of molecular hydrogen ($E_d = 13.8$ kcal/mole, T_{max} near 450 K), with no desorption of atomic hydrogen. Desorption of AsH_3 ($T_{max} = 340$ K) precedes the desorption of H_2. Further H chemisorption induces an additional amount of Ga atoms to desorb above 700 K. Preadsorption of hydrogen decreases the As_2 evaporation rate. An energy scheme with the equilibrium and an excited adsorbate state is derived from the combination of the temperature-programmed-desorption data and the high-resolution electron-energy-loss spectroscopy data of Lüth and Math [Phys. Rev. Lett. 46, 1652 (1981)].

I. INTRODUCTION

In the last few years the study of the adsorption of gases on clean, well-defined semiconductor surfaces has attracted a lot of interest. One intention of these studies is to learn about the surface states of the clean semiconductor surface using the adsorbed gas to perturb the surface.

There exists strong activity in studies of the formation and chemistry of the metal-semiconductor interface on GaAs.[1] Fermi level pinning positions are close in energy for low coverages of oxygen,[2] germanium,[3] various metal adsorbates,[4] and hydrogen[5] on GaAs(110). Spicer has concluded that this behavior is due to defect states which do not depend on the electronic features of the adatom. The energy required to initiate defect formation may be provided by the heat of adsorption.[6,7]

Another intention is to learn something about the binding of the gas to the semiconductor surface. In particular, investigations of hydrogen interaction with GaAs are of relevance for some topics of current interest, e.g., a problem of ion implantation in GaAs is to prevent dissociation during the necessary high-temperature anneals. The compound semiconductor must either be covered with a protective layer or the anneal must be performed under a controlled atmosphere.[8] In the latter case the changes of the sublimation by previous gas adsorption are of interest. This influence is discussed in Sec. IV C.

In this paper we report temperature-programmed desorption (TPD) studies of the adsorption and reaction of atomic hydrogen on the cleaved GaAs(110) face; molecular hydrogen does not adsorb[9,10] (see Sec. III A).

TPD gives information about the kinetics of desorption. The method allows very low initial coverages. In TPD results breaking of adsorbate bonds, and possibly migration and reactions during heating (e.g., formation of H_2 from H atoms or the formation of Ga or As hydrides) and the related energies show up. Temperature-programmed desorption complements the methods of surface spectroscopy. The spectroscopical tools provide information about adsorption sites, induced changes in the local density of states, and the corresponding strength of the binding state.

The reaction kinetics of hydrogen is of practical importance, e.g., in gas phase epitaxy. The influence of macroscopic parameters like partial pressures, temperature, etc., has been widely investigated. But not so much is known about processes on an atomic scale except for recent investigations of a metalorganic chemical vapor deposition system (MOCVD).[11] In this system hydrogen and compounds containing hydrogen [$Ga(CH_3)_3$, AsH_3] have been used.

II. EXPERIMENTAL METHOD

The measurements were performed on ultrahigh vacuum- (UHV) cleaved GaAs(110) faces of n-type material (Te doped, $n = 4\times10^{17}$ cm^{-3}, $\mu = 3000$ $cm^2 V^{-1} s^{-1}$; Wacker Chemitronic). The crystals were orientated by x-ray diffraction and cut into prisms 5 mm$\times$5 mm$\times$12 mm in size. Grooves 2 mm in depth were cut on the 5 mm$\times$5 mm faces for cleavage in UHV by the double-wedge technique.

A precision manipulator with a liquid-nitrogen tank and electrically isolated copper jaws held the sample. Copper stripes clamped the sample and served as current contacts to the GaAs bulk for resistive heating. The jaws were always kept at 150 K.

The stainless-steel chamber of the UHV system was equipped with an ion/sublimation pump, a cryogenic pump, and a turbomolecular pump. A retractable pair of pliers was provided to cleave the sample.

The crystal temperature was monitored with a pressure bonded Ni-Au thermocouple at the back of the sample. Heating rates between 1 and 40 K/s were used.

A quadrupole mass spectrometer (Extra Nuclear Laboratory) identified and recorded the desorption products. The sample was positioned 10 mm in front of the ionizer aperture (9 mm in diameter). Six preselected masses were recorded simultaneously. The mass spectrometer signal

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could be calibrated by a capacitance manometer and an ionization gauge.

Molecular hydrogen was admitted to the whole UHV chamber. Atomic hydrogen could be formed at a hot tungsten filament (2200 K) placed without any baffle 5 cm in front of the cleaved face. The sample was kept at 250 K during adsorption to avoid precocious desorption of arsenic hydrides (see Fig. 3) (jaws still at 150 K). Doses of atomic hydrogen were not calculated. In the following we choose the expression "3×10^4 L hydrogen" to describe an exposure to 3×10^4 L H_2 *with* the hot filament on (1 L$\equiv10^6$Torr s). After hydrogen exposure the gas was pumped off. The pressure recovered to below 10^{-9} Torr within 15 minutes.

III. EXPERIMENTAL RESULTS

A. Adsorption of hydrogen

In order to get reproducible conditions for repeated hydrogen adsorption (desorption) cycles some experimental observations have been decisive for the preparation applied later on: Immediately after cleavage we did not observe any desorption of Ga, GaAs, As, As_2, As_3, or As_4 below 670 K. Hydrogen desorbed completely below 670 K. Further heating resulted in a stationary sublimation above 730 K.

We prepared six samples. The pretreatment consisted of cleavage and heating to 670 K in UHV before the first exposure to hydrogen. The temperature-programmed heating was terminated at 670 K in the desorption experiments.

The faces were exposed up to 5×10^7 L H_2 (5×10^{-2} Torr) with all filaments turned off, but no H or H_2 appeared in TPD. To obtain atomic hydrogen, molecular hydrogen between 1×10^{-6} and 5×10^{-2} Torr was admitted to the UHV chamber and a filament was turned on. Each exposure was finished after 900 s. Molecular hydrogen appeared as the main desorption product. Exposure to atomic hydrogen formed out of molecular hydrogen at pressures below 5×10^{-5} Torr leads to a single maximum of the desorption curves (Nos. 1 to 4 of Fig. 1). The maximum shifts to lower temperatures with increasing hydrogen pressures during adsorption. A second set of curves for the calculation of a desorption energy was recorded with a constant initial coverage of 1×10^{13} cm^{-2} (conditions of curve 2 of Fig. 1). The heating rate was varied from 1 to 40 K/s, and the results are given in Fig. 2. Higher pressures during adsorption lead to an additional desorption maximum at about 500 K. Integration of the desorption flux given in curve 7 (Fig. 1) yields a coverage of about 3×10^{14} cm^{-2} hydrogen atoms. This may be

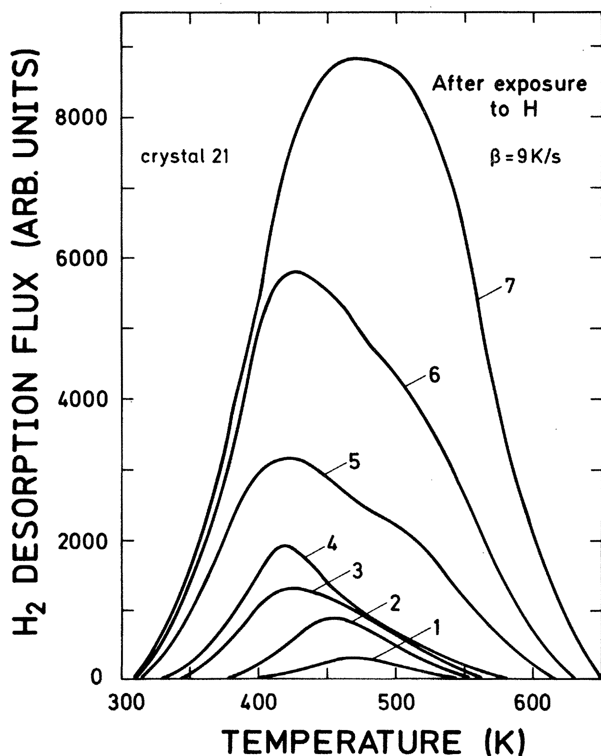

FIG. 1. H_2 desorption curves after exposure to different amounts of atomic hydrogen at 250 K. (Atomic hydrogen was produced by dissociation of H_2 at a hot tungsten wire.) Only the H_2 doses can be given. Curve 1, 3×10^3 L; curve 2, 9×10^3 L; curve 3, 5×10^4 L; curve 4, 5×10^5 L; curve 5, 6×10^5 L; curve 6, 9×10^5 L; curve 7, 3×10^7 L hydrogen.

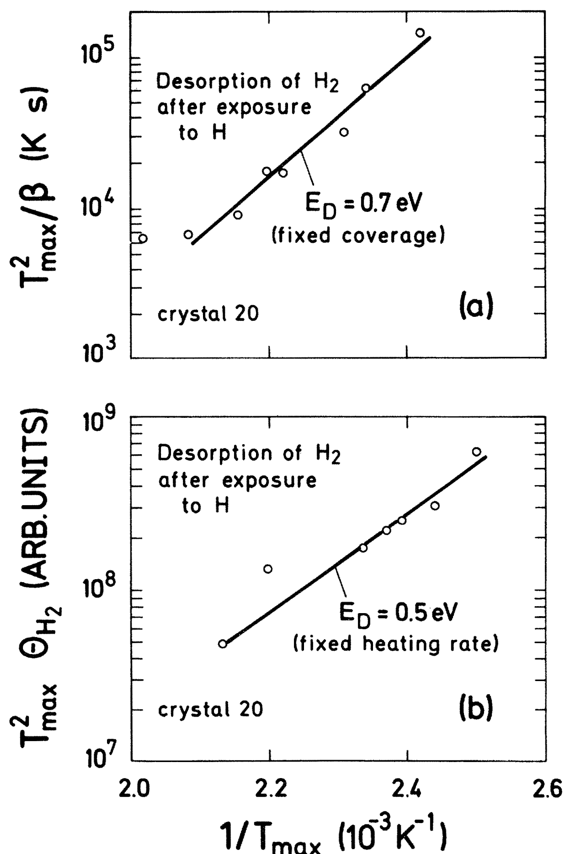

FIG. 2. Determination of the H_2 desorption energy after adsorption of atomic hydrogen. (a) Arrhenius plot derived from a variation of heating rate. ($\beta=1$–40 K/s; H_2 dose $=9\times10^3$ L.) (b) Arrhenius plot derived from a variation of coverage (exposure to 3×10^3–5×10^6 L hydrogen; $\beta=9$ K/s).

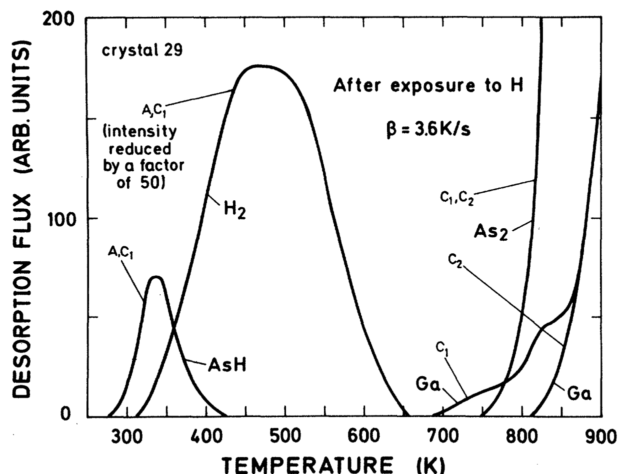

FIG. 3. TPD spectra after adsorption of atomic hydrogen at 250 K (3×10^7 L hydrogen). Curves A are obtained during adsorption-desorption cycles below 670 K. Curves C_1 are obtained during adsorption-desorption cycles up to 970 K. Then curves C_2 are obtained without prior H adsorption (no sensitivity corrections).

compared to the number of Ga atoms in the uppermost layer: 4.4×10^{14} cm^{-2}. The peak height ratio H/H_2 of 3% does not change during desorption and is due to cracking in the ionizer.

At high H coverages peaks at $m/e=78$, 77, and 76 emerged simultaneously. They can be identified with AsH_3, AsH_2, and AsH (curve A of Fig. 3 shows AsH, temperature range 250 to 670 K). These three peaks have about the same magnitude; the latter ones are probably formed by removal of hydrogen from AsH_3. Three to five desorption runs per sample did not show significant deviation in the spectra.

B. Sublimation of Ga and As

Treatment with hydrogen affects the surface stoichiometry. One indication is the occurrence of arsenic hydrides. Therefore sublimation has been studied in an extended temperature range. The last desorption cycle with temperatures up to 670 K was followed by a linear heating from 250 K to 970 K without prior exposure to hydrogen. The sublimation products Ga and As_2 are labeled B_1 in Fig. 4. As_4, As_3, and As were also found with the ratios $[As_4]:[As_3]:[As_2]:[As]=0.03:0.02:1:0.4$. Then the heating to 970 K was repeated; compare the curves labeled B_2. The ratios $[As_4]:[As_3]:[As_2]:[As]$ changed to 0.08:0.02:1:0.7. These ratios remained constant within each of the heating cycles given in Fig. 4. Another heating reproduced the last set of curves. The proportionality within each heating cycle seems to be easily explained by a desorption of As, As_2, As_3, and As_4 straight from the surface. However, the sublimation from (100) faces was thoroughly investigated by Foxon[12] using a chopper between the sample and the ionization chamber. He found that arsenic, a polymeric gas, can undergo both associative and dissociative reactions on the walls of the vacuum

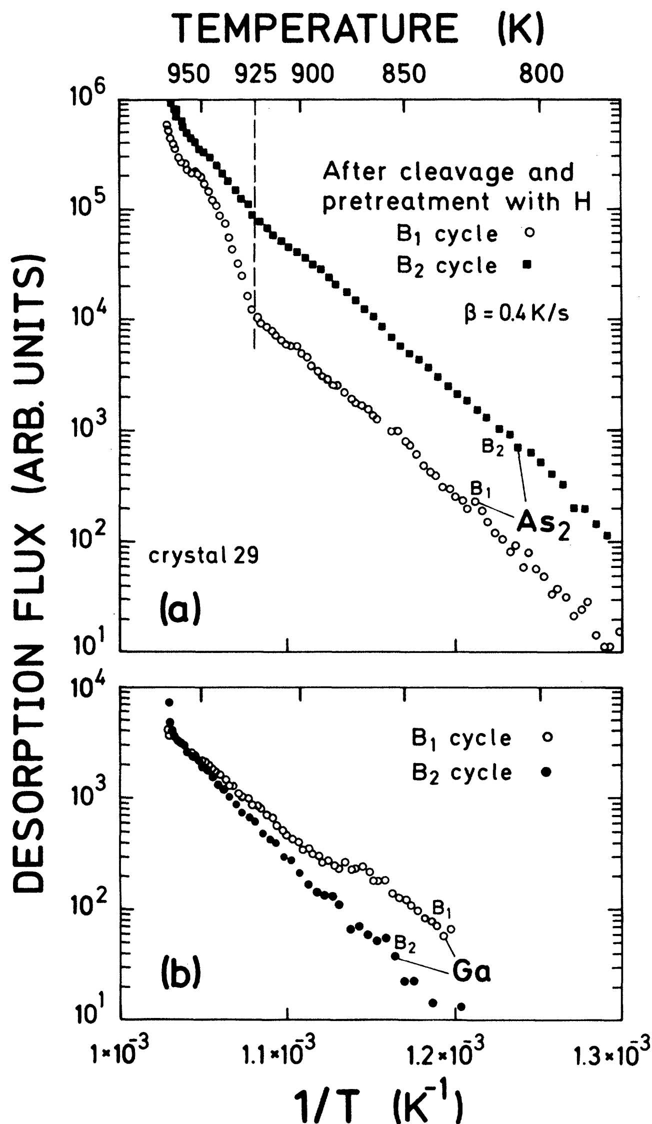

FIG. 4. Evaporation rates of GaAs(110). The last H_2 desorption cycle with temperatures up to 670 K is followed by a linear heating from 250 to 970 K, curves B_1. Then in a second heating the curves B_2 are obtained. (a) Evaporation rates of As_2. (b) Evaporation rates of Ga.

system. The modulated beam technique as well as the use of a cryotrap[13] reduced the As_4/As_2 ratio from about 1 to 0.01. The background pressure so established increases with the specimen temperature. The polymerization to As_4 may to a small extent be effective in our case, too. However, the use of a chopper changes the $[As_2]:[As]$ and the $[As_4]:[As_3]$ ratios only insignificantly.[12] Arsenic atoms and As_3 molecules may be formed by cracking in the ionization chamber.

Influence of adsorbed H on the sublimation. The samples were exposed again to hydrogen, and the desorption as well as sublimation products were monitored in a temperature range from 250 K to 970 K. Up to 670 K the desorption spectrum for H_2 and arsenic hydrides, given in Fig. 3, was reproduced (curves C_1). At 680 K gallium

($m/e = 69,71$) sublimation appeared, curve C_1.

Bringans and Bachrach[14] suggested a possible sublimation of gallium hydrides after H adsorption at 300 K on epitaxially grown GaAs(100) and $(\bar{1}\bar{1}\bar{1})$ faces to explain an increase of the [As]/[Ga] ratio in their soft-XPS study. But peaks at $m/e = 70$, 72, and 73, characteristic of gallium hydrides, did not occur in our mass spectra.

Sublimation of arsenic starts at 750 K (curves C_1 and C_2 of Fig. 3). Then the heating to 970 K was repeated without prior exposure to hydrogen. Only gallium and arsenic were observed, curves C_2 of Fig. 3.

The excess of Ga showing up in the difference between curves C_1 and C_2 (Fig. 3) is formed during a single hydrogen exposure, whereas the difference between curves B_1 and B_2 [Fig. 4(b)] is due to the complete set of treatments described in Sec. III A.

IV. DISCUSSION

A. Adsorption of hydrogen

Molecular hydrogen does not adsorb on cleaved GaAs(110) (see Sec. III A). In photoemission studies by Gregory and Spicer[9] exposure to 2×10^4 L H_2 did not change the electron distribution curves (EDC's). Also on polished and chemically etched (110) faces an exposure to 3×10^5 L H_2 did not change the EDC's in He^+ neutralization experiments.[10] Bonding may be restrained by steric conditions or an activation barrier at the surface. In contrast atomic hydrogen is adsorbed at 250 K. The desorption peak of molecular hydrogen shifts to lower temperatures with increasing coverage whereas atomic hydrogen does not appear. A plot of $\ln T_{max}^2\theta$ versus $1/T_{max}$ shows a constant slope [Fig. 2(b)]. For a second-order process an activation energy of 12 kcal/mole (0.5 eV) is derived. Further an activation energy for constant coverage (0.02 ML) is determined by varying the heating rate: 16 kcal/mole (0.7 eV), data from Fig. 2(a).

Table I shows published values of stretching vibration frequencies and bond energies for the As-H and the Ga-H bond in molecules and for hydrogen adsorbed on GaAs. There are only small deviations in the frequencies between molecular and chemisorption bonds. The similarity encourages us to start the discussion with a Morse potential[15] for the AsH_3 molecule, Fig. 5(a). The energy levels of the ground state and the first excited state of a hydrogen atom are labeled by E_0 and E_1. As an approximation we use the same Morse potential to give a picture of chemisorbed hydrogen above an arsenic site of the (110) face, Fig. 5(b). The system "H + GaAs" and the system "$\frac{1}{2}H_2$+GaAs" are separated by one half of the dissociation enthalpy: $\frac{1}{2}\Delta H = 52$ kcal/mole (2.25 eV). The calculated potential curve for a van der Waals–type interaction of molecular hydrogen at a distance of 2.5 Å from

TABLE I. Energy values for hydrogen bound to As and Ga.

Activation energy for H_2 desorption from GaAs(110) (after adsorption of H)		
TPD: variation of heating rate 16 kcal/mole =0.7 eV from Fig. 2(a)		
TPD: variation of coverage 11 kcal/mole =0.5 eV from Fig. 2(b)		
Stretching vibrations[a]		
	HRELS data of H on GaAs(110)	Reference
As—H bond	2150 cm^{-1} = 0.27 eV	18
As—D bond	1660 cm^{-1} = 0.21 eV	18
Ga—H bond	1890 cm^{-1} = 0.24 eV	18
Ga—D	1380 cm^{-1} = 0.17 eV	18
	HRELS data of H on GaAs(100)	
As—H bond	2110 cm^{-1}[b] = 0.26 eV	26
Ga—H bond	1875 cm^{-1} = 0.23 eV	26
	IR data of molecules	
As—H bond in *A*	2116 cm^{-1} = 0.262 eV	27
As—D bond in *B*	1523 cm^{-1} = 0.189 eV	27
Ga—H bond in *C*	1819—1949 cm^{-1} = 0.226—0.242 eV	28
Ga—D bond in *C*	1324—1393 cm^{-1} = 0.164—0.173 eV	28
Bond energy of As-H in *A*	58.6 kcal/mole = 2.55 eV	29
Bond length of As-H in *A*	1.12 Å	29
Bond energy of Ga-H in *D*	66 kcal/mole = 2.9 eV	30
Bond length of Ga-H in *D*	1.52 Å	30

A: AsH_3; B: AsD_3; C: trimethylamine-halogenogallanes;
D: Gas mixture of Ga, H_2, and He.

[a]Only the values for the symmetric stretching vibrations are given.
[b]Peak intensity dependent on annealing time; peak disappears on well-annealed samples (Ref. 26).

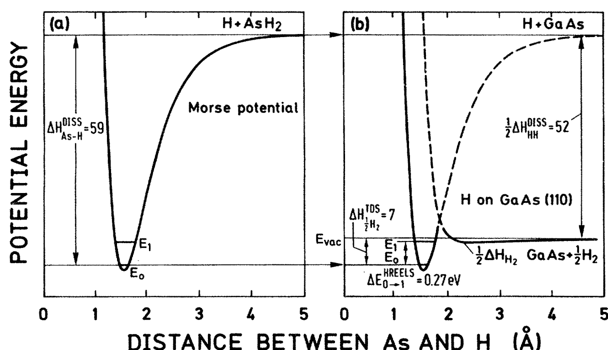

FIG. 5. (a) Potential-energy diagram for the As—H bond in AsH_3 assuming a Morse potential. (b) Potential-energy diagram for the As—H bond of H adsorbed on GaAs(110). The binding energy is assumed to be 2.55 eV. (Data were taken from Table I. All ΔH values are given in kcal/mole.)

the surface exhibits only a relatively shallow minimum of about 0.8 kcal/mole. This curve is a crude approximation because in the calculations the substrate is assumed to be a metal.[16,17] Interaction between the physisorbed and the chemisorbed state lowers the potential energy maximum. The desorption enthalpy ΔH, derived from the TPD measurements, nearly coincides with the difference between the vacuum energy level E_{vac} and the ground-state energy E_0. Therefore, the energy value at the crossing point between the potential curves may only marginally exceed the vacuum energy level. In this model the first excited vibrational level of the chemisorbed hydrogen E_1 is positioned about 1 kcal/mole (0.04 eV) below the vacuum level.

This model is supported by the high-resolution electron-energy loss spectroscopy (HREELS) results of Lüth and Matz.[18] After H adsorption (exposure to "1000 L hydrogen," H doses unknown) on GaAs(110) they found losses at 1890 cm^{-1} (Ga-H) and at 2150 cm^{-1} (As-H). The latter value corresponds to $E_1 - E_0 = 0.27$ eV which comes close to the IR-stretching vibration energy of 0.26 eV for the AsH_3 molecule.

The authors also plotted the integrated intensity of the losses versus annealing temperature (steps: $\Delta T = 10$ K, 5 min). At about 390 K the integrated intensities of both losses decreased to 50% of their initial values. For the lowest heating rate applied in our experiments, $\beta = 1$ K/s [compare Fig. 2(a), H_2 exposure 9000 L], the desorption maximum is found at 410 K. In spite of the differences in the experimental conditions the decrease of the integrated loss intensity corresponds quite well to the observed desorption flux.

Careful UPS studies[9] of atomic hydrogen adsorption (exposure to "6×10^4 L hydrogen") on cleaved *p*-type GaAs(110) at 300 K showed pronounced changes in the energy distribution curves (EDC's): The existence of the tightly bound state for H on GaAs(110) was verified by the observed Fermi level pinning. Recent Kelvin measurements[5] at 300 K reveal a pinning of the Fermi level for *p*- and *n*-doped samples after exposure to "10^3 L hydrogen."

Some of the desorption curves of Fig. 1, especially for medium initial coverage, seem to be composed of two single peaks, at temperatures about 60 K apart. This may be explained by hydrogen desorbing from different sites, e.g., from edge and plane sites or from As and Ga sites with different desorption energies. The differences in the molecular bond energies are given in Table I. But hydrogen from an As and a Ga site can recombine in the desorption process; in the loss spectra mentioned above both the As-H and Ga-H peaks disappear concurrently upon annealing.

B. Reaction of hydrogen with the GaAs(110) face

During repeated runs with high coverages of hydrogen the desorption spectra do not only show H_2 but also a constant amount of arsenic hydrides; below 670 K a desorption of gallium or its hydride has not been found (Fig. 3). As mentioned in Sec. III A even immediately after cleavage Ga or As did not desorb up to this temperature. Above 670 K excess gallium appeared in a reproducible way only after H adsorption (curve C1).

Hydrogen reacts with As already near room temperature to AsH_3 and disappears from the surface below 400 K, Fig. 3. Therefore, the As/Ga ratio has to decrease. Bartels *et al.*[5] reported that the intensity ratio of the surface sensitive As (31 eV) and the Ga(55 eV) Auger-electron spectroscopy (AES) peaks was reduced by 20% after exposure of the cleaved GaAs(110) face to "3×10^4 L hydrogen" at 300 K.

Ga leaving the surface above 700 K increases the As/Ga ratio again. It may desorb as gallium or gallium hydride, the latter would probably be cracked in the ionizer. The source for the repeated desorption of arsenic hydride and gallium cannot be an initial excess of As or Ga atoms after cleavage, but As atoms at special sites, e.g., steps may preferentially react with chemisorbed hydrogen. At higher temperatures gallium atoms (or possibly gallium hydride) near these sites may be more loosely bound and desorb precociously. The amounts of As (as AsH_3) and Ga (shoulder around 750 K) may not be equal and certainly do not coincide if the TPD measurement is terminated at temperatures above 750 K. A net excess of, e.g., As may preferentially react with hydrogen of the next experimental run.

C. The sublimation of Ga and As

The sublimation of Ga was investigated up to a temperature of 970 K. An activation energy of 64 kcal/mole (2.8 eV) was derived from the data of cycles B_1 and B_2, Fig. 4(b). The sublimation of As_2 showed an activation energy of 62 kcal/mole (2.7 eV) below 920 K, Fig. 4(a), curve B_2. But the first run following the investigations below 670 K (Sec. III A) yielded lower evaporation rates, curve B_1. Above a transition region an increased activation energy of 87 kcal/mole (3.8 eV) appeared. The sublimation energies in the low-temperature region coincided for Ga and As and did not depend on the As/Ga ratio, changed by the hydrogen reaction with arsenic, Sec. IV B.

These findings suggest that only one activated process controls both the desorption of Ga and As below 920 K. The As/Ga ratio on the surface, decreased by the hydro-

TABLE II. Activation energies for As_2 evaporation above 920 K from different GaAs surfaces.

Surface	Dopant[a]: concentration of free carriers (cm^{-3})	E_{As_2} (eV)	Surface morphology	Reference
(110)	Te: $n=4\times10^{17}$	3.8		This work
(110)	$p=2\times10^{18}$ $n=4\times10^{17}$		Furrows parallel to the (110) direction exhibiting polar faces	21
(111)	$n=6\times10^{15}$ Zn: $p=2\times10^{19}$	3.9	Triangular pits, mostly terraced macroscopic ledges	25
$(\bar{1}\bar{1}\bar{1})$	$n=6\times10^{15}$ Zn: $p=2\times10^{19}$	3.9	Flat	25
(111)	Te: $n=3\times10^{18}$	3.3		25
$(\bar{1}\bar{1}\bar{1})$	Te: $n=3\times10^{18}$	3.3		25
(100)	Si: $n=5\times10^{17}$	4.2	Rectangular pits with (111) and $(\bar{1}\bar{1}\bar{1})$ facets	12

[a]If the type of dopant is known.

gen reaction with arsenic, may cause the decreased arsenic (1:7) and the increased gallium rate (5:1), see Fig. 4. This process remains responsible for the Ga sublimation at high temperatures, whereas for the As sublimation a process with a higher activation energy becomes rate limiting.

Elementary gallium showed a sublimation energy of 67 kcal/mole (2.9 eV).[19] Nearly the same energy (62 kcal/mole) characterized the sublimation of Ga from polycrystalline GaAs,[20] and from the (110) face (64 kcal/mole, Fig. 4). Therefore, our measured flux of Ga atoms (Fig. 4) may contain contributions from Ga droplets at the surface. During the first heating (curve B_1 in Fig. 4) smaller droplets may join to larger ones with a reduced overall surface. In the following run (curve B_2) the Ga flux shrinks correspondingly. This picture implies a lateral motion of gallium without evaporation.

We see for temperatures below 920 K that the sublimation energy of elementary gallium governs the sublimation of arsenic from GaAs(110) too (Fig. 4). Proix[21] investigated the Auger peak ratio (Ga/As) on (110) faces cleaved in UHV. Isochronous anneals up to 900 K did not change the ratio, the following annealing at 950 K raised the ratio by 10%. This decrease in the density of As atoms at the surface is in agreement with the observed steeper increase above 920 K observed for the As_2 flux but not for the Ga flux in our TPD measurements (TPD results: Fig. 4).

Beyond the temperature range of the present studies, small droplets appeared in electron micrographs on (110) faces, which were cleaved and then annealed at 1050 K in UHV.[21] X-ray fluorescence showed that these droplets consisted of Ga.

The sublimation energy characterizing the temperature range above 920 K on the (110) face (Sec. IV C) deviates only insignificantly from the values found on the (111), $(\bar{1}\bar{1}\bar{1})$, and the (100) face, Table II, as well as on polycrystalline GaAs.[13,22–24] This fact points to a common property of the sublimation processes which is reflected in surface morphology too: $(\bar{1}\bar{1}\bar{1})$ faces appear nearly flat in optical micrographs. The (111) face exhibits flat triangular pits forming terraced macroscopic ledges.[25] Electron micrographs of (110) faces show furrows parallel to the (110) direction which exhibit polar faces.[21] On (100) faces rectangular pits with (111) and $(\bar{1}\bar{1}\bar{1})$ facets have been observed in optical microscopy and scanning electron microscopy.[12] The main contribution to the sublimation at high temperatures seems to arise from polar faces that either already exist or are formed by thermal etching of the (110) and (100) faces.

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