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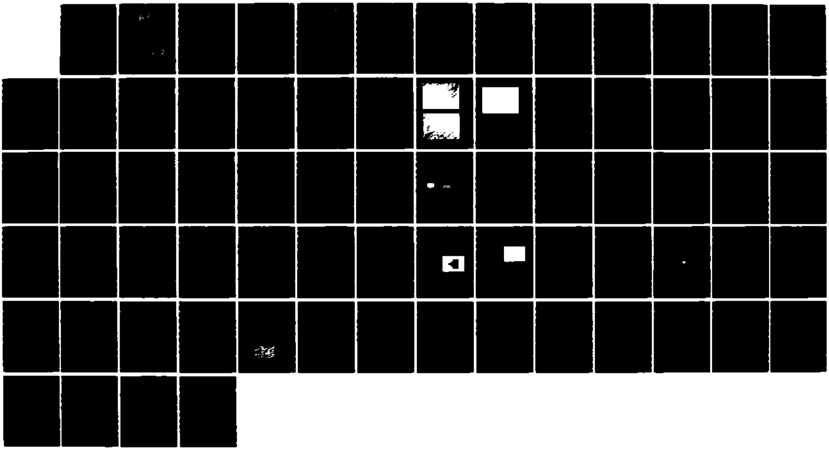

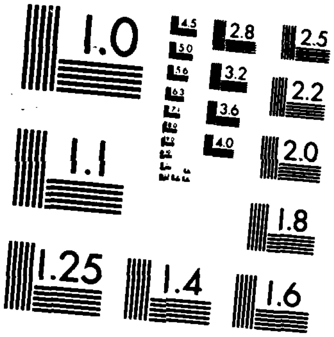

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MICRO-REACTIONS ON METAL CONTACTS ON VARIOUS TYPES OF GaAs SURFACES

Final Technical Report

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Abstract

Results towards an optimization of the GaAs device technology for stable metal contacts are reported. The etch-dependent structure of a surface microroughness has been evaluated by a replica TEM technique. Apart from Al, results are presented for TiPtAu interdiffusion for various types of initial GaAs surface conditions due to the technology applied. At 250°C Ti seems to be exchanged with Ga and becomes a donor under simultaneous current and temperature stressing. The etchant $NH_4OH : H_2O_2 : H_2O$ (ratio 2 : 1 : 300) has been established as possibly one of the best candidates for stable electrodes.

List of Keywords

GaAs, metallization stability, XPS, GaAs surface chemistry, double-replica TEM, Au-Pt-Ti on GaAs, Al on GaAs

CHAPTER I

INTRODUCTION

The subject of the investigations to be undertaken under the above grant concerns an assessment of the metallization behaviour for realistic GaAs surfaces as generally employed for the manufacture of MeSFETs and their IC's, particularly in view of device-life-time optimization. Therefore, this work was started during the 1st year, according to the proposed workplan (point A(i), (iv) and (vi) of Section C-1, of the Award Document), by systematically analyzing GaAs surfaces, after applying the various types of surface treatments, commonly employed by the FET technology/1,2,3/. Here, both XPS and ISS became the most important analytical techniques. Many interesting results were obtained. For example, the chemical surface composition depends strongly on the type of aqueous solutions applied, in particular it was established that acidic etchants gave fundamentally different oxidations of the surface from alkaline solutions. In fact, prior exposure to such processes as plasma bombardment or even long storage in air has a significant effect on the final composition. These surfaces exhibit varying amounts and, at different depths, one or several of the following: Ga_2O_3, As_2O_3, As_2O_5, physically or chemically adsorped oxygen and, of course, usually a cover by a thin layer of carbon.

As a next step, the three important phenomena of material transport in connection with metal electrodes on such GaAs surfaces were investigated during the 2nd year /4/, namely: the electron-wind effect along narrow conductors (point A(ii) of Sect. C-1, Award Doc.); the metal transport between neighbouring, closely-space electrodes (points A(v) and (vii) of Section C-1, Award Doc.); in particular here the formation of narrow, short circuiting metal filaments by field-assisted surface diffusion of metal atoms; and the material transport across the interface metal-GaAs (points A(ii) and (iii) of Section C-1, Award Doc.). It was established that the electron-wind activation energies of narrow conductors on GaAs depend on the treatment which the semiconductor surface experienced before metallization. In fact, at increased temperatures, a rather new failure mechanism became apparent, when strongly interdiffusive effects set in with metallization sandwich structures. Electromigration between neighbouring electrodes was clearly found to be affected by the amount of As_2O_3 present within the first 8 Å of the GaAs surface. And surprising interdiffusive effects in connection with Al electrodes on GaAs were established to occur due to electrical stressing and correlated with changes in the electrical behaviour. These results have also direct relevance for lifetime degradation effects of GaAs devices.

The last period of the grant is described in this Final Technical Report. The electron-wind investigations have now been systematically persued for a good selection of the typical technology processes affecting the GaAs surface before metallization/5,6/. Efforts were undertaken also to assess the quality of GaAs surface uniformity by using a double-replica TEM technique in order to obtain a better understanding of the various effects of current and field stressing on material migration. It was established/7/ that acidically etched GaAs surfaces exhibit a much rougher surface than generally basic solutions, with elongated features (which could be either hills or holes; the TEM photographs do not permit to differentiate between these two possibilities) of around 50 nm long and around 20 nm wide. Since our ESCA studies show also that acidically etched GaAs surfaces exhibit a strong As_2O_3 concentration it can be tentatively suggested that these features are caused by As_2O_3. In any case, they would have a strong influence on the current and field stressing behaviour as generally observed by our various types of electromigration of material.

Material migration between neighbouring electrodes was further explored and a more mature situation has arisen here/8/. For example, an optimized etch solution was found to be $NH_4OH : H_2O_2 : H_2O$ in the ratio 2 : 1 : 300.

Interdiffusive effects were now explored in connection with multilayer metallizations. The new results have shown among other details that Ti remains reasonably stable if operated around room temperature only. However, Ga starts to diffuse out into the metallization and Ti into the GaAs from around 250° C onwards, particularly during electrical stressing, as demonstrated by XPS measurements. Since at the same time, the Schottky behaviour of Au-Pt-Ti contacts goes over into quite good ohmic contacts, as demonstrated by our electrical measurements, it can be suggested that Ti as a group IV element goes onto Ga vacancies and acts there as a donor/9/. It could of course now be tentatively suggested that such high-temperature electrical-stress assisted modification from Schottky into ohmic behaviour can be technically utilized for special device fabrication techniques.

Some of the investigations reported here were again performed by student projects under supervision of the authors of this report. Therefore, a list of these projects is again given in the Appendix IV.

Characterization of Electron-Wind Electromigration Damage in Narrow Aluminium-Schottky Electrodes

As described in the last Annual Report[4] (Chapter III) on the characterization of electromigration damage in current stressed Al-metallizations on different types of substrates we found that the damage parameters which affect the lifetime of the metallization and hence the device strongly depend on the nature of the substrate[5]. It was reported that the electron wind voiding parameters such as the drift velocity v_β of the migrating metal ions, the grain-boundary diffusion activation energy Eg for electrimigration and the contant K which includes the diffusion coefficient D_O at $T \to \infty$ are dependent on the type of the surface treatment given to the GaAs before the evaporation of the metallization. It is believed to be caused by the difference in grain boundary structure for different types of surface quality of GaAs even under identical conditions of evaporation. The subject of surface induced degradation and the investigation of detrimental surface effects on GaAs power MeSFETs has become a field of wide current interest particularly from the device aging point of view[9].

Here, we describe the results obtained since then, which can now be considered to lead to quite a mature understanding. The GaAs wafers of (100) orientation from Sumitomo Electric

Industries Ltd., Japan, were treated first with nearly boiling acetone, trichloroetnylene and methanol successively for 10 minutes in each solution to remove organic contaminants and then etched in the various etchants. Al-metallizations with resistometric structures, as used before, were then evaporated by an electron beam under identical evaporation conditions as described in our last report, and structured by photolithographic lift-off using Shipley's Photoresist 1350. The electrodes were from 850 to 1000 Å thick, evaporated always with exactly the same rate of 4 Å/sec for the first 500 Å and subsequently with 8 Å/sec for the next 500 Å.

If an etch step was applied to the GaAs surface, this was always for one minute. A special example included a Cr interlayer of 200 Å thickness, evaporated with 1 Å/sec.

Electromigration studies were performed on these samples through resistance monitoring experiments performed in the temperature range 80° to 155° C for a current density of $J = 1.8 \times 10^6$ A/cm^2. The rise in temperature of the current-stressed stripe due to Joule heating was taken into account. From the state of resistance increase of zone I of the stripe, the drift velocity v of the migrating Al-ions at different temperatures was determined by using eqn (3) of our last report/4/. The function $\ln \frac{v T}{J}$ vs. 100/T was found to be linear within experimental error limits, indicating that the Arrhenius diffusion law is applicable for this structure.

From the Arrhenius plots, the average values of the electromigration damage parameters have been found. The migrating ion flux density for the transported Al is $J_i = N . \nu_B$ where N - the number of transported ions and ν_B - their drift velocity. The ion drift can be approximated by an equivalent mobility μ_i and the force F exerted by the electron wind so that $\nu_B = \mu_i.F$; F is given by the effective charge of the migrating ion and the electric field $E = J/\sigma$ (J - electric-current density applied to the conductor and σ - the electrical conductivity of the Al film).

The mobility can be expressed by

$$\mu = \frac{D}{fkT}$$

(D - diffusion constant

kF - Boltzmann constant times temperature in K

f - correlation factor, depending on type of lattice)

where

$$D = D_o \exp\left(- \frac{E_A}{kT}\right).$$

Here E_A is the relevant activation energy. Taking all these relations together, one finds that

1) the drift velocity is $\nu_B = \frac{J_i}{N}$, (1)

(ν_B is determined from the measured rate of increase of resistance of the current-stressed conducting line/5/ and

2) that E_A can be found by plotting $\frac{\nu_J T}{J}$ versus 1/T from the slope of the straight lines according to:

$$\ln \left(\frac{\nu_B T}{J}\right) = \ln k - \frac{E_A}{kT}$$

where k is a constant containing all the remaining terms introduced above.

The experimental findings are given in Fig. 1 which shows the activation energy values, the constant k and the drift velocity at 100° C, as presented by Table 1. It is instructive to consider also ν_B versus T (Fig. 2) since it directly indicates which GaAs-surface treatment is recommendable. This appears to be etching with NaOH + H_2O_2; although E_A is not of the highest value of the cases tested, it does have the lowest values of ν_B at temperatures up to around 180° C.

A comparison of this data indicates that the value of the drift velocity v_β in an acidic etch structure is higher than that obtained on a substrate treated with an alkaline etch (for which $v_\beta = 1.9 \times 10^{-10}$ cm/s) and lower than that of an unetched substrate (for which $v_\beta = 7.0 \times 10^{-9}$ cm/s). This means that electromigration damage in the present acidically etched structure is less than that on unetched structures but higher than that of alkaline etched structures. The value of Eg (0.37 eV) has been found to be slightly lower than that for pure grain-boundary diffusion but higher than for oxide free surface diffusion along trapped holes or islands in the film (for which Eg = 0.28 eV/10/). This suggests the presence of appreciable numbers of islands or trapped holes in such a metallization and the electromigration damage seems to be due to mixed diffusion partly along the grain boundaries and partly also along the surfaces of trapped holes or islands. This type of inference is also supported by TEM photographs taken by a double-replica technique on the GaAs surface (Fig. 3) treated with this acidic etch and on the Al-metallization deposited on such a substrate (Fig. 4). These photographs have been taken with a magnification of 61 500 and further enlarged by a factor of about 1.5. In Fig. 3 one finds that acidic etching results in a large number of pits or islands, possibly oriented along the cleavage plane on the (100) GaAs surface. On the basis of our XPS analysis performing on GaAs surfaces etched with this acidic etch (reported in Chapter II of our last Annual Report/4/, Fig. 2), it has been found that such an etch leaves on the GaAs surface primarily arsenic oxide, and dissolves the gallium oxide. These island or grid structures on the GaAs surface may be due to an accumulation of arsenic oxide. Such a GaAs surface inhomogeneity affects also the structure of the Al-metallization evaporated on it, as one can see a similar roughness on the surface of the Al-metallization on it (Fig. 4). The replica photographs only show the surface topography and do not confirm the type of material forming such structures.

By comparing the surface topography of such acidically etched GaAs surfaces with that of alkaline etched surfaces (Fig. 5) one finds that the latter one is more uniform (unfortunately the reproduction of the relevant photographs in this report do not show this difference so clearly as the originals). This makes us to suggest that an alkaline etch dissolves or removes most of the oxide islands.

Table 1: Electromigration damage parameters in Al/GaAs structures (Al-metallizations evaporated on differently-treated GaAs surfaces)

GaAs surface treatment	Temperature range °C	E_A (eV)	k $(\frac{cm^3\ K}{As})$	ν_B at 100°C for $J = 1.8\text{x}10^6$ A/cm^2 (cm/s)
Al/GaAs				
1. GaAs — unetched	60 - 140	0.62 ± 0.05	$2.81\text{x}10^{-4}$	4.63×10^{-9}
2. GaAs etched with NaOH + H_2O_2	100 - 220	0.52 ± 0.02	$4.0\ \text{x}10^{-7}$	1.79×10^{-10}
3. GaAs etched with $H_2SO_3 + H_2O_2 + H_2O$	80 - 155	0.37 ± 0.045	$3.55\text{x}10^{-9}$	1.35×10^{-9}
4. GaAs etched with KOH + H_2O	50 - 150	0.15 ± 0.23	$4.42\text{x}10^{-11}$	2.08×10^{-9}
5. GaAs etched with NH_3 solu^N+H_2O_2+H_2O	45 - 130	0.113 ± 0.015	$2.66\text{x}10^{-11}$	3.86×10^{-9}
Al/Cr/GaAs				
6. GaAs — unetched	20 - 100	0.14 ± 0.03	$1.26\text{x}10^{-10}$	7.96×10^{-9}

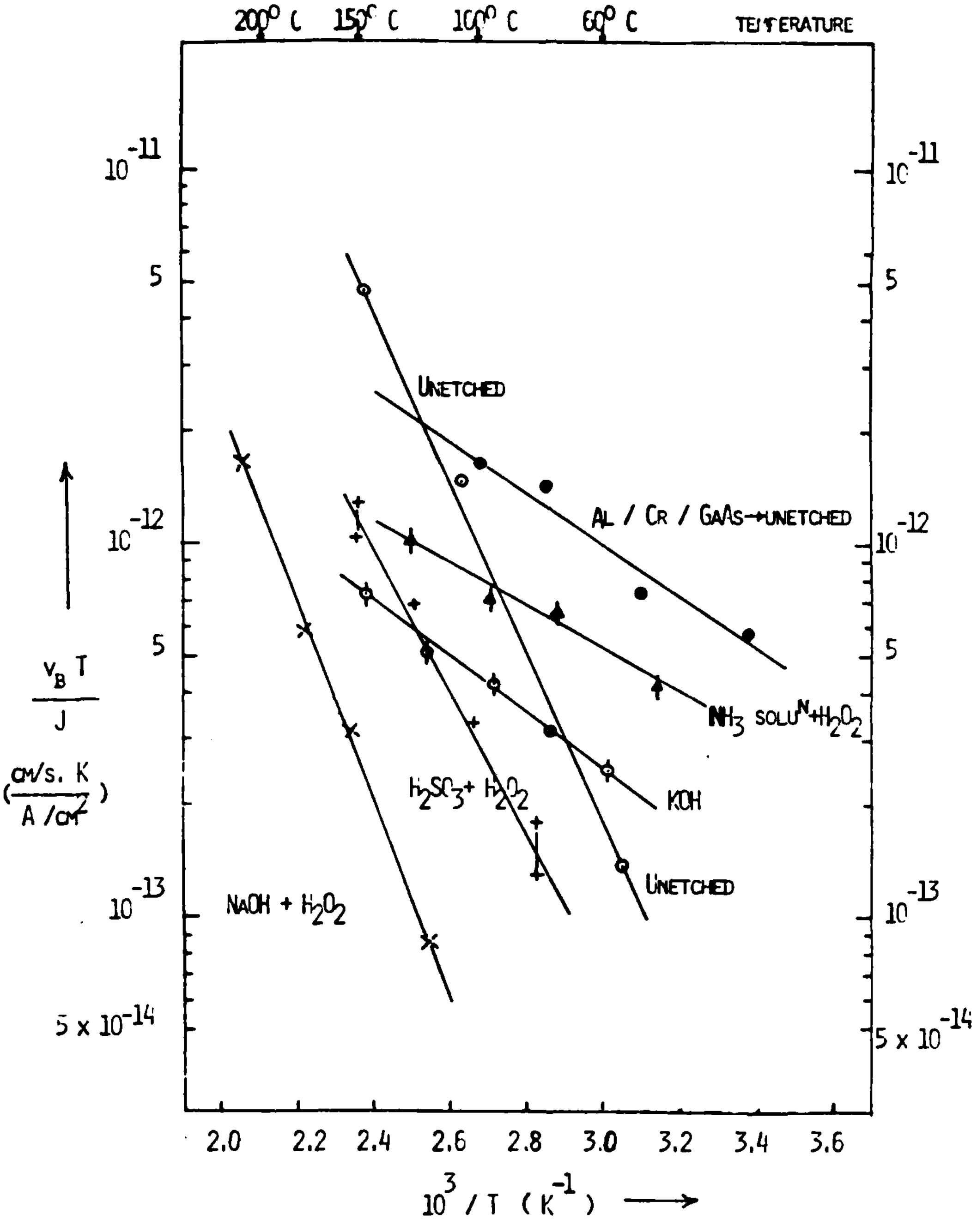

Fig. 1 : Arrhenius plots for electron-wind damage parameters $\frac{\nu_B T}{J}$ from resistometric measurements of Al/GaAs (Al evaporated on differently treated GaAs surfaces, $J = 1.8 \times 10^6$ A/cm^2)

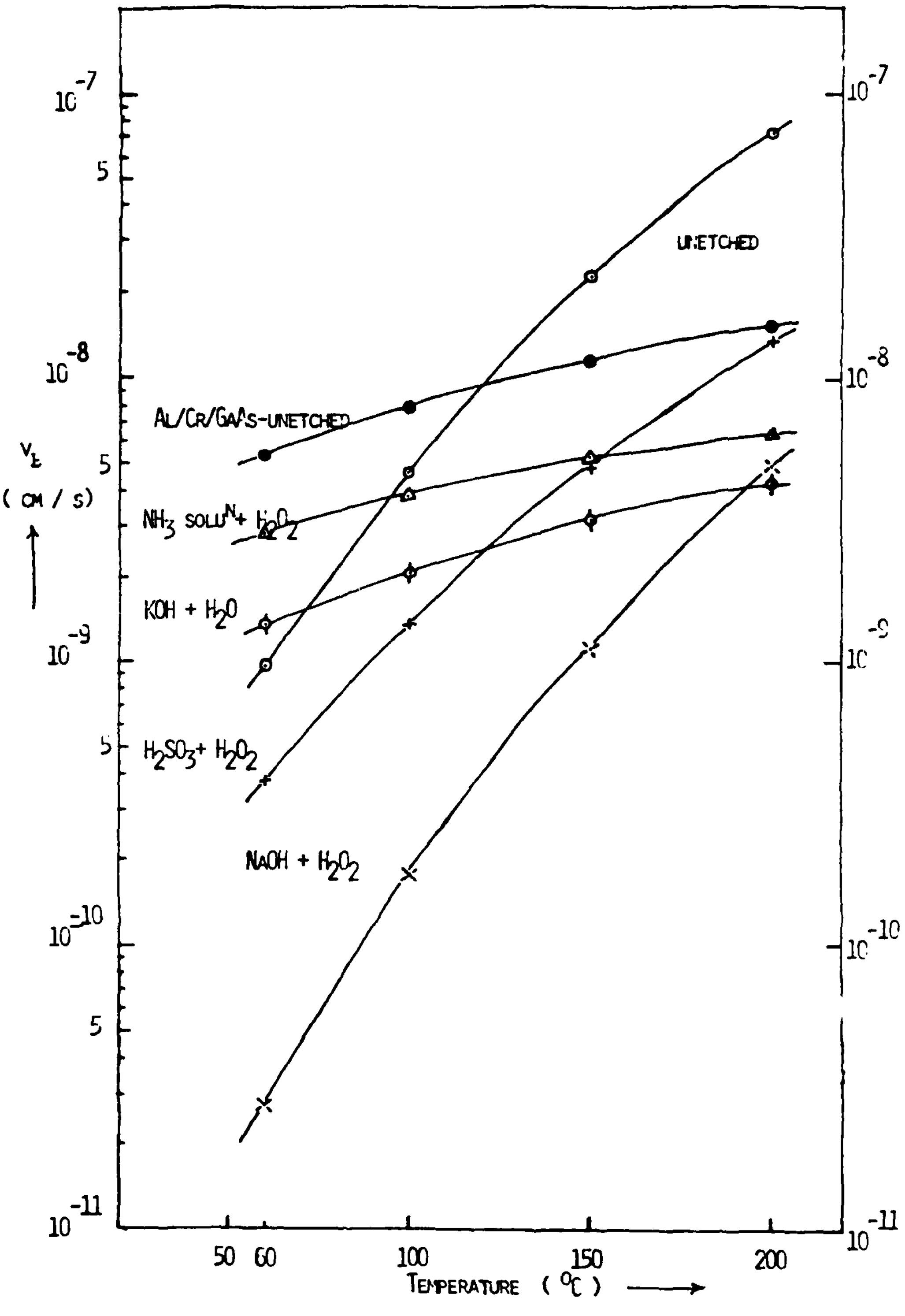

Fig. 2 : Drift velocity v_B of Al-ions at different temperatures (in Al-metallizations evaporated on differently treated GaAs surfaces, $J = 1.8 \times 10^6$ A/cm^2)

Fig. 3 : Double-replica TEM photograph of an acidically etched GaAs surface

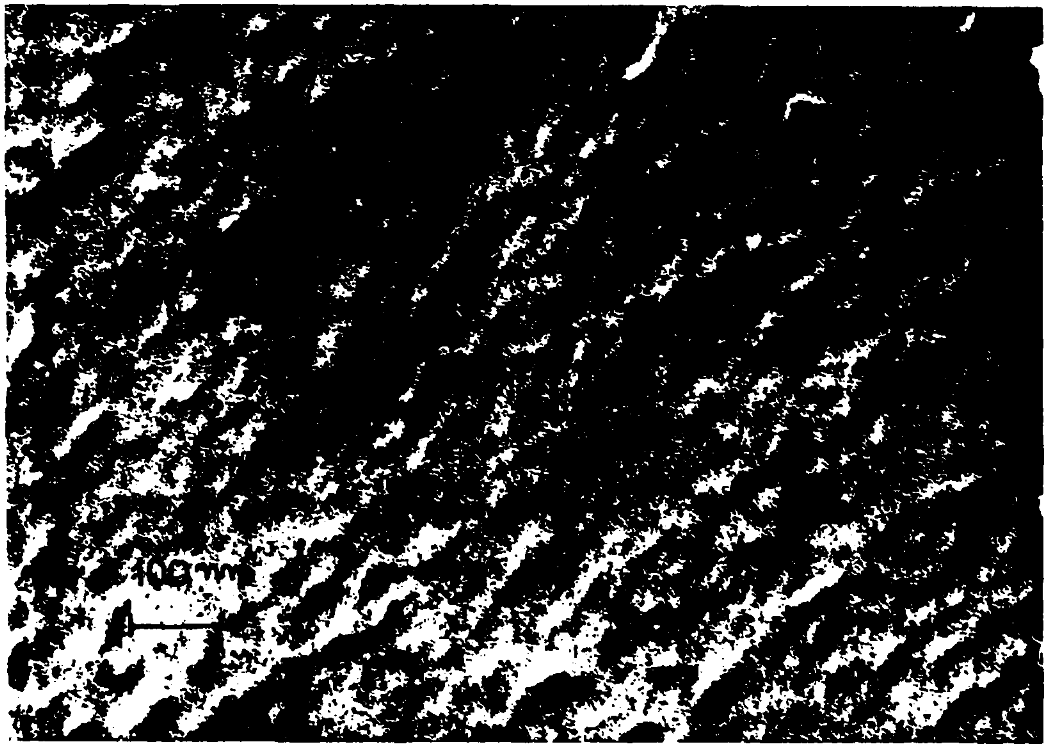

Fig. 4 : Double-replica TEM photograph of an Al-film surface (Al-film is evaporated onto GaAs surface as shown by Fig. 3 ; film thickness 850 Å; same magnification as Fig. 3)

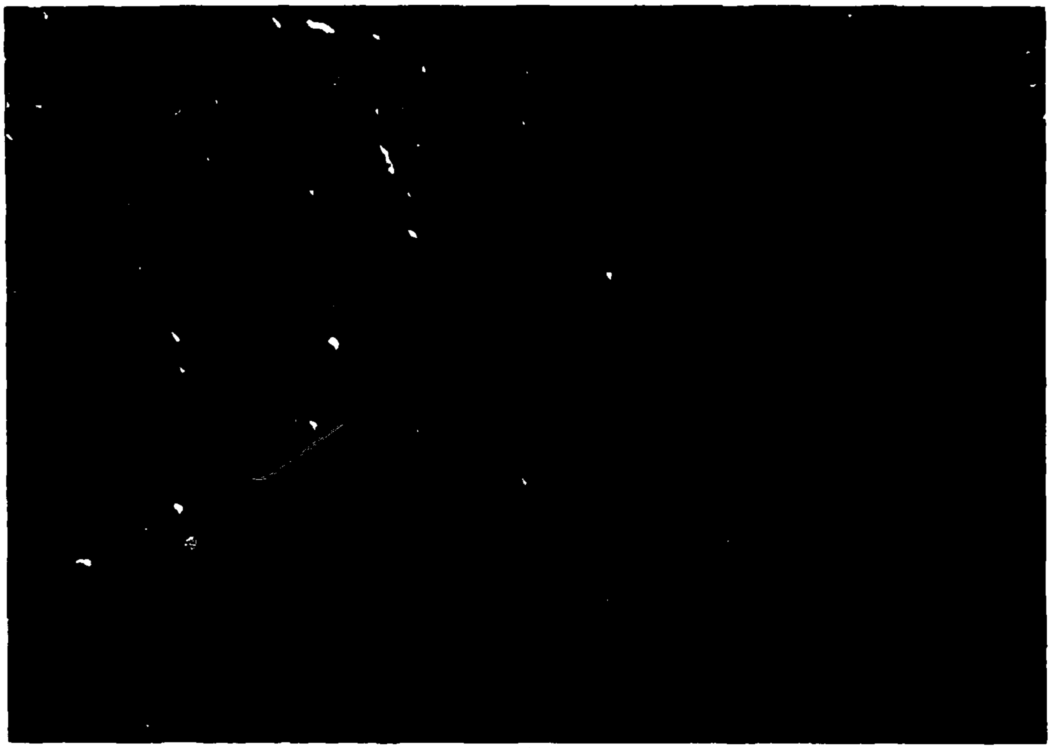

Fig. 5 : Double-replica TEM photograph of a GaAs surface etched by an alkaline etchant

CHAPTER II

Lateral Material Migration

GaAs-surfaces play a major role in production and operation of optoelectronic and microwave devices with GaAs. The stability of metallization contacts and dielectric layers on GaAs are strongly influenced by the GaAs-surface conditions as produced by the various technology processes generally employed.

Therefore, we reported in the last Annual Reports XPS-studies of (100)-GaAs-surfaces, which are treated by various common etchants and cleaning solutions. These XPS-spectra gave detailed information on the type of surface. The resulting "surface-quality" was then correlated with lateral material migration across the GaAs-surface between neighbouring electrodes. We demonstrated that the migration depends very strongly on the amount of arsenic oxide on the surface. Whereas the treatments based on alkaline etchants leave a low arsenic oxide to GaAs-ratio with corresponding high threshold values for material migration, the employed acidic etch solution leads to a strongly increased arsenic oxide component in the surface with unacceptably low threshold voltages. These results were then presented at the International Reliability Physics Symposium, Orlando, Florida, March 26-28, 1985 and published in 23th Annual Proc. Reliability Physics, 1985, pp 45-48.

XPS-Measurements and Experimental Results

Best results were obtained by an etch-solution based on KOH. Unfortunately KOH has a limited application in production processes of GaAs devices because KOH affects also photoresist, which is necessary to define the metallization structure. Using the concept that alkaline etch solutions lead to improved electrode stability, an effort was undertaken, to find other suitable etchants, and it was established that an aqueous solution based on NH_4OH and H_2O_2 was also of high quality. It shows the same good behaviour as the KOH-solution concerning laterial material migration. We finally selected the etchant composition $NH_4OH : H_2O_2 : H_2O$ in the ratio 2 : 1 : 300 and present here results on its GaAs surface as obtained by XPS-measurements. Fig. 6 shows the XPS-spectra of the $2p_{3/2}$ and 3d core level emissions of As and Ga and the 1s level emission of oxygen. These measurements were undertaken with Al K_α radiation (radiation energy: 1486,6 eV). Row 1 corresponds to samples which are only cleaned by organic solvents. Row 2 to 4 show the spectra of the samples which are treated by this above ammonium-solution. Following row 2 to 4 the etch-times are 1/2, 2 and 4 minutes. It is obvious that this etchant removes both the Ga and As oxides even for the short etch-time of 1/2 minute. This is demonstrated by the shift of the spectral line from the position for components bonded to oxygen towards that of components bonded to the semiconductor GaAs. The $2p_{3/2}$ spectra correspond to the near-surface composition of 8 - 12 Å depth, the 3d spectra is obtained from a average depth of 25 Å. So even down to a depth of around 25 Å this good oxygen reduction behaviour of $NH_4OH : H_2O_2 : H_2O$ is present. The O 1s line shows after treatment only a relatively small amount of physically absorbed oxygen. In conclusion the analysis of the treatment of GaAs-surfaces by $NH_4OH : H_2O_2 : H_2O$ with the ratio 2 : 1 : 300 shows that chemically absorbed oxygen could be strongly reduced even by short etch-times. It is worthwhile to mention that the etch-rate is really well controlled within 1/2 to 4 minutes etch-time and is found to be 400 Å/min.

In the last Annual Report/4/ we presented the values for 20 and 40 µm electrodegaps of threshold voltage for lateral material migration, defined as the value required for the onset of a practically instanteneous complete short circuiting of neighbouring electrodes. To study the influence of surface-quality even in the submicron-range, now 5 µm electrode gaps were produced. The measurements of threshold voltage for material migration were undertaken at room-temperature and a vacuum-pressure of 7×10^{-5} mbar. Fig. 7 shows this threshold voltage V_s as a function of electrode distance d in the range of 5 to 20 µm. The parameter is surface-treatment. It is obvious that the surface properties are of significant importance for contact stability, particularly also for 5 µm electrode gaps.

XPS - SPECTRA OF SAMPLES TREATED BY NH_4OH (25%) : H_2O_2(30%) : H_2O (2:1:300)

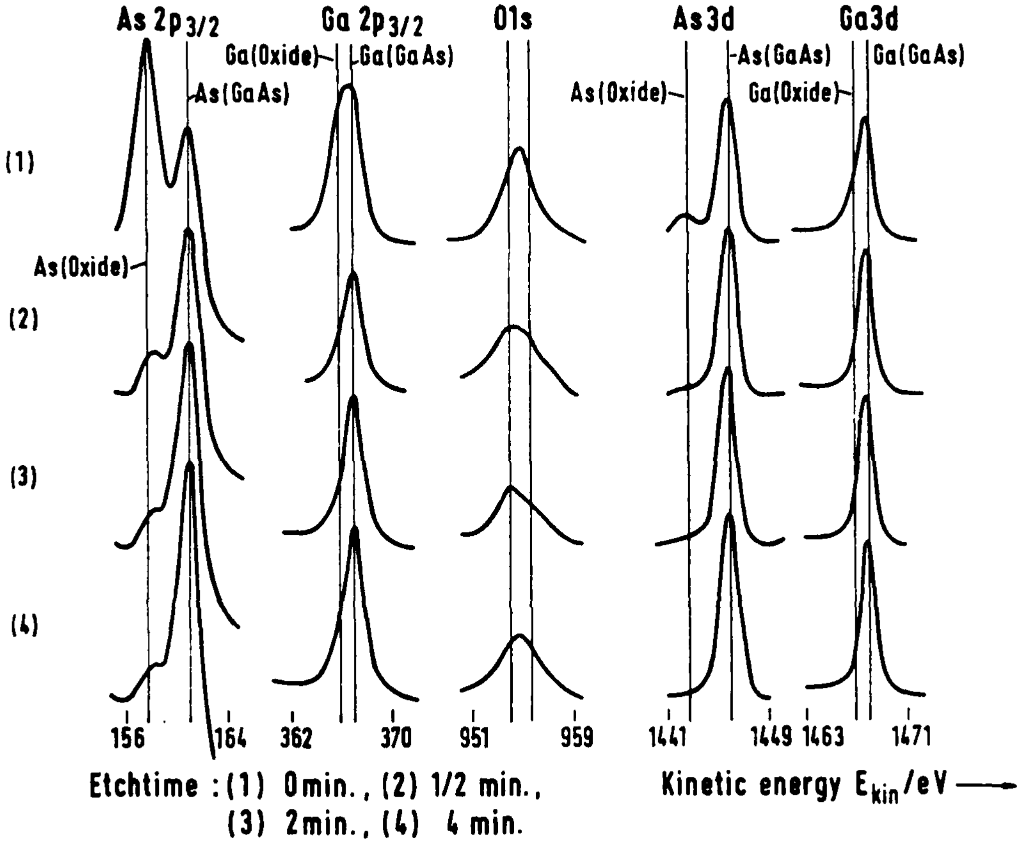

Fig. 6

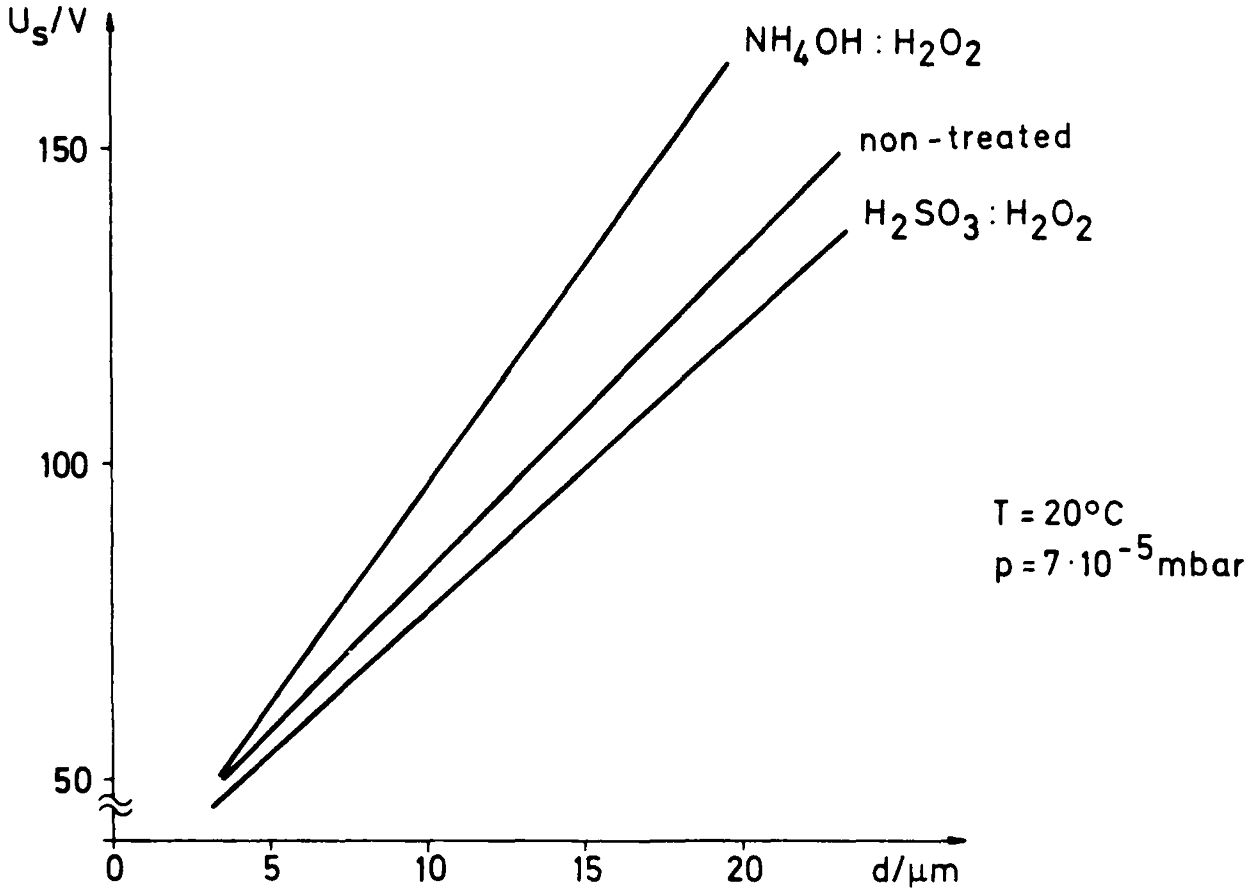

Fig. 7 : U_s versus d for 3 types of GaAs-surface conditions

Discussion

In connection with our XPS-measurements the more bulk like 3d spectra exhibit nearly no arsenic oxide components. This is in agreement with phase diagram calculations for the Ga-As-O-System which were done by Thurmond et al from Bell Labs./11/. They demonstrated that the only stable phases which can coexist in thermodynamic equilibrium with GaAs are Ga_2O_3 and elemental arsenic. Any arsenic oxide in contact with GaAs should react to form Ga_2O_3 and As:

$$As_2O_3 + 2\,GaAs \rightarrow Ga_2O_3 + 4\,As$$

This reaction occurs spontaneously but very slowly. Thus a non-equilibrium surface contains native oxides and free elemental As. Note especially that the initial build up of free As from As_2O_3 will be greatly increased by a processing step involving high temperatures such as contact alloying. Such a step can lead to the complete conversion of any As_2O_3 to free As. The device literature suggests that free As is connected with surface recombination in GaAs solar cells/12/, with interface states in GaAs MOS-devices/13/ and with reliability problems in GaAs power FETs/14/. Therefore, such treatments, which by chemical consideration appear to remove the surface arsenic oxide and free arsenic, reduce at least in part these problems and lateral material migration. On the other hand, etching has to deplete similar group III and V components. Therefore, the main requirements to GaAs etching processes are

1) to remove As_2O_3 and As

and

2) to obtain surface stoichometry.

A possible solution with an applicable wet-etchant is the proposed aqueous solution based on NH_4OH and H_2O_2. The peroxide oxidizes the available free arsenic and both the arsenic- and galliumoxide are soluble in aqueous ammonia. Hence the surface results in an approximately stoichiometric Ga to As ratio, as our XPS-spectra demonstrated.

We have applied the $NH_4OH : H_2O_2$-solution with success in the fabrication of our GaAs-devices, sometimes followed by a $HCl : H_2O$ etch-step which removes the physically adsorbed oxygen part. No lateral material migration was so far observed within the normal operation conditions of such devices.

CHAPTER III

Interdiffusion Effects on Al and TiPtAu Contacts on GaAs

In our preceeding Report/4/ we mainly described results on the contact system Al-Semi-Insulating GaAs. As demonstrated in the last Annual Report field stressing of Al-Si GaAs-Al contact systems results both in changes of the chemical interface properties and changes in the I-V characteristics. To get a more refined understanding of the Al-GaAs contact system our experimental efforts have now been extended to Al-Schottky contacts on n-GaAs (n = 1.7 x 10^{16}). We fabricated structures with Schottky diodes using AuGe/Ni as ohmic back-contacts. The aluminium Schottky contacts were evaporated immediately after the samples were etched in (1 : 1) NaOH + H_2O_2 for two minutes to remove most of the native oxide and to obtain reproducible and comparable surface properties. Each sample consists of two pairs of Schottky diodes, having an electrically active area of 0.5 mm^2 and 0.25 mm^2 repectively, and one large area Schottky diode which is suitable for XPS sputter analysis of the contacts. Two of these samples have been reverse biased with 6 V at a temperature of 150^o C for 50 hours, two other samples have been stored at 150^o C for the same time without biasing. In this way any effects due to biassing can be detected. The same experimental procedure has also been undertaken at room temperature. In the present state of these experiments the results of the severely biased

Schottky diodes at 150^{o} C can be given so far. Fig. 8 shows a typical I - V characteristic of an Al-Schottky diode before and after stressing at 150^{o} C. The average barrier height of the as deposited Al-GaAs contact has been determined to be 0.797 eV with an accuracy of about 1 %. After the 50 hours stress the barrier height increased to 0.835 eV. In the I - V characteristics no extensive differences between biased and unbiased samples could be detected so far. Both sample sets showed nearly the same increase of barrier height after heat treatment independent of the biasing condition. The ideality factor of the Schottky diodes remains constant and has been measured to be 1,05.

The barrier height of the Al-GaAs Schottky contacts is more strongly influenced by heat treatment than by long-time biasing. We believe therefore that any of the small differences noticeable for biasing alone can be considered to lay within the experimental error range. Therefore, no definite statements on the effect of bias stressing can be given yet. We are convinced that the experimental accuracy can be increased satisfactorily now by using bonded contact systems as a next step instead of needle contacts or contacts established with the help of conductive glue. Considerable efforts to improve the reliability of the measuring contacts are being made at the moment. Other experiments were concentrated on the investigations of TiPtAu contacts to n-GaAs.

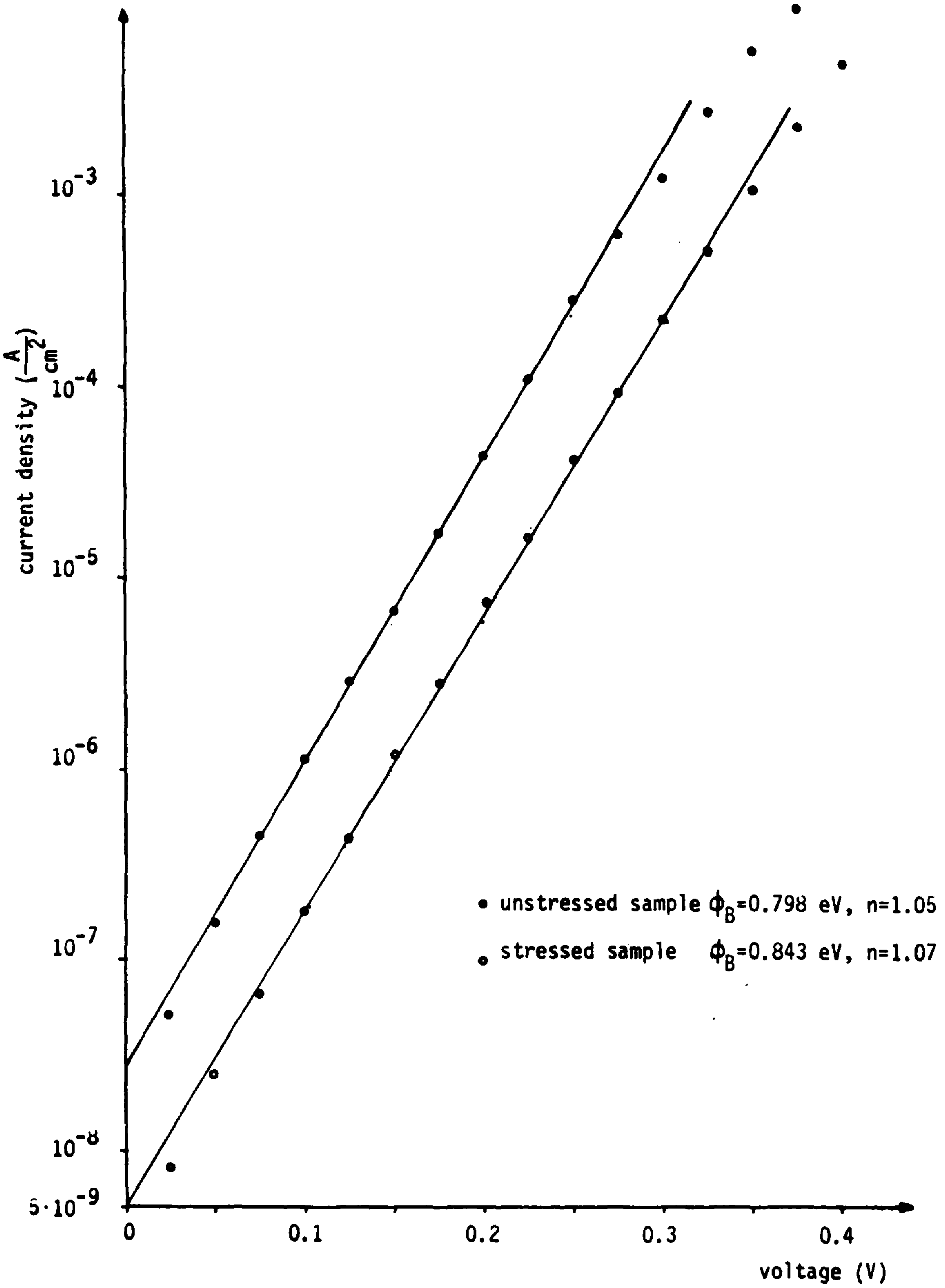

Fig. 8 : Typical I-V characteristic of unstressed samples and of samples stressed at 150 °C

A range of test samples was fabricated according to Fig. 9. The frontside was covered with TiPtAu (40 nm, 80 nm, 200 nm) the backside contact consisted of an AuGe 88/12 ohmic contact annealed at 450° C for 1 min. Before TiPtAu metallization the samples were etched in $NH_4OH + H_2O_2 + H_2O$ (2 : 1 : 200) for 1 minute.

Titanium, which is then deposited immediately onto the GaAs surface, exhibits a much higher affinity to oxygen than aluminium. Therefore, it can be expected that any native oxides on GaAs are reduced during Ti metallization, in a similar manner as in the case of Al. This behaviour has indeed been found by detailed XPS measurements of the Ti-GaAs interface where no oxidized Ga or As could be detected.

The oxygen take-up rate of Ti surfaces was then studied under residual gas pressure down to around 1×10^{-9} mbar by inserting the Ti film deposited on GaAs together with a protective layer of Au and Pt in the UHV system of the XPS chamber. After sputter removal of the protective layers the oxygen take-up rate of the free Ti surface could be monitored. Fig. 10 shows that even at very low pressures of oxygen the relative oxygen intensity increases by a factor of three within 50 min. and remains nearly constant during the subsequent exposure. Higher residual gas pressures of oxygen of course yield higher oxygen uptake rates and higher oxygen saturation for prolonged exposure (Fig. 10). Sinces pressures of about

1×10^{-6} mbar are quite common for metal evaporation, both the titanium evaporation rate and the storing time of any unprotected titanium layer in the evaporation system before continuing the metallization sequence by platinum deposition will affect the oxygen content and thus the reproducibility of these metallizations produced in different runs.

Regarding the stability of TiPtAu contacts on GaAs various sample-sets (fabrication details as described above) have been stressed at room temperature and at temperatures up to 250° C with and without reverse biasing of the AuPtTi-GaAs Schottky contact for about 200 hours. At room temperature the contacts were bias stressed both at - 10 V DC reverse voltage with negligible current flow and in the avalanching region of the contact (about - 12 V DC) where the current density was kept constant at about 3 A/cm^2. At temperatures of 250° C the leakage current of the TiPtAu Schottky contact of course increased in comparison to room temperature conditions so that a leakage current density of 3 A/cm^2 for bias stressing was already obtained at reverse voltages of about 2 Volts. At room temperature the TiPtAu contact was found to be stable over the time of our investigation (200 h) - no degradation of the I/V characterisitic or significant changes of the XPS sputter profiling could be detected after the various stressing conditions at room temperature. However, stressing at temperatures of 250° C yields strong changes of the I/V characteristics and a pronounced variation of the XPS-sputter profiles.

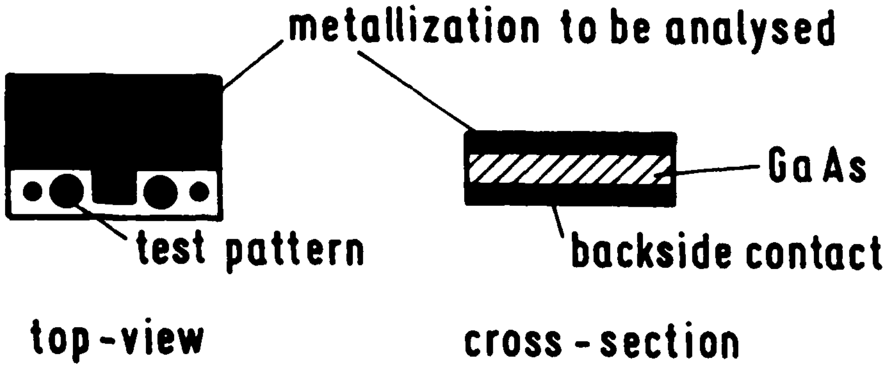

Fig. 9 Sample fabrication

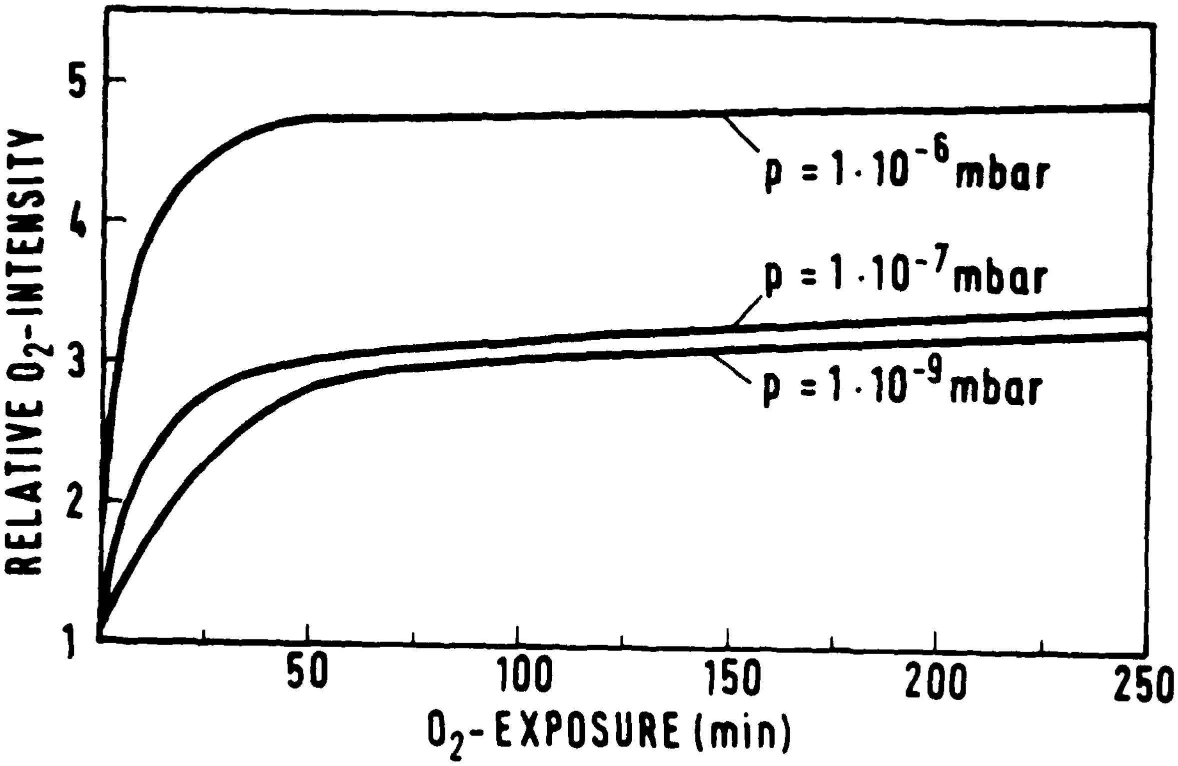

Fig. 1o Ti-oxidation in an UHV-system

Fig. 11 shows the XPS sputter profile of a reference sample, Fig. 12 of a sample stressed only thermally at 250° C and Fig. 13 of a sample that has experienced both thermal and bias stressing. Comparing these sputter profiles several important details can be derived.

1. Both thermal and particularly combined thermal and current stressing produce Ga outdiffusion into Ti and to some extend into Pt, where in the case of current stressing Ga penetrates Pt more deeply. No outdiffusion of arsenic neither during thermal stressing nor during combined thermal and current stressing could be detected. Diffusion of Ga into the contact metal has been observed in many metallizations on GaAs and is commonly considered to be a purely temperature-dependent effect/15/.

2. Interdiffusion Au-Pt and Pt-Ti has taken place, where Pt has diffused through the gold layer towards the surface (Fig. 12, 13).

3. Another interesting dinfing is that the oxygen content in the Ti layer decreases in amplitude and broadens correspondingly during thermal stressing but shows a small increase in amplitude after combined thermal and bias stressing. Since oxygen penetration into the Au layer is much more pronounced in sample-sets, which are bias stressed at 250° C, one can probably assume that unbonded oxygen is transported

into the gold metallization and towards the bulk of the Ti by electron-impulse transfer ("electron-wind")/16/. This means that this current assisted oxygen transport prevents to some degree the oxygen outdiffusion during combined bias and thermal stressing, as was observed. The oxygen inside the Ti is finally largely immobilized due to bonding to titanium. Of course thermal stressing in air enhances surface adsorption of oxygen on the gold surface as can be seen by comparing the relevant figures.

4. As outlined above, thermal and combined thermal and electrical stressing results in a significant outdiffusion of Ga into Ti. This Ga outdiffusion is partly balanced by a subsequent indiffusion of Ti into GaAs particularly during the combined stressing, as careful analysis of the XPS sputter-profiles reveals (Fig. 12 and 13). Obviously the Ti, which is not bonded to oxygen, is pushed into GaAs by the electron wind. Considering the I - V characteristics (Fig. 14) of these samples reveals that simple temperatures stressing causes only relative small changes whereas combined temperature and bias stressing results in a catastrophic degradation of the TiPtAu Schottky contact. The contact becomes nearly ohmic. It is reasonable to assume that Ti is transferred into Ga vacancies during stressing by diffusion and electron wind effects where it acts as a donor level and hence changes the I/V characteristic of the contact in the observed way.

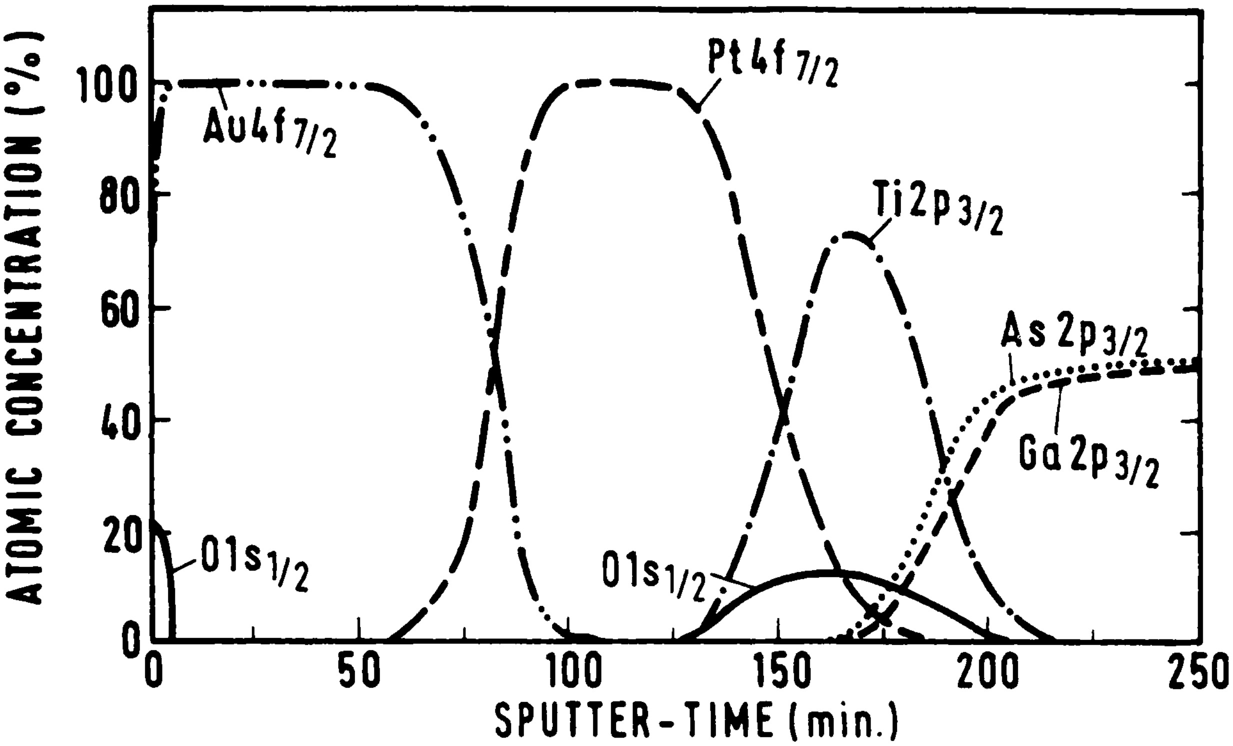

Fig. 11 XPS-sputter-profile of unstressed TiPtAu contacts on GaAs

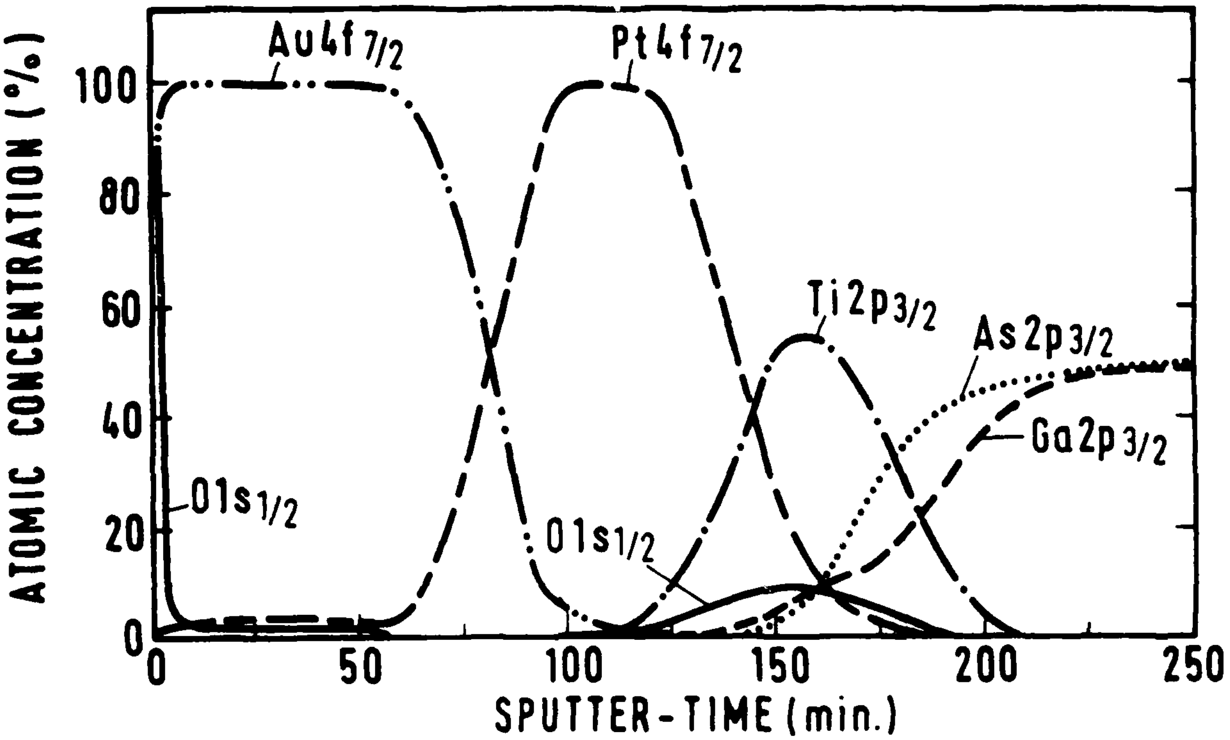

Fig. 12 XPS-sputter-profile of thermally stressed TiPtAu contacts on GaAs

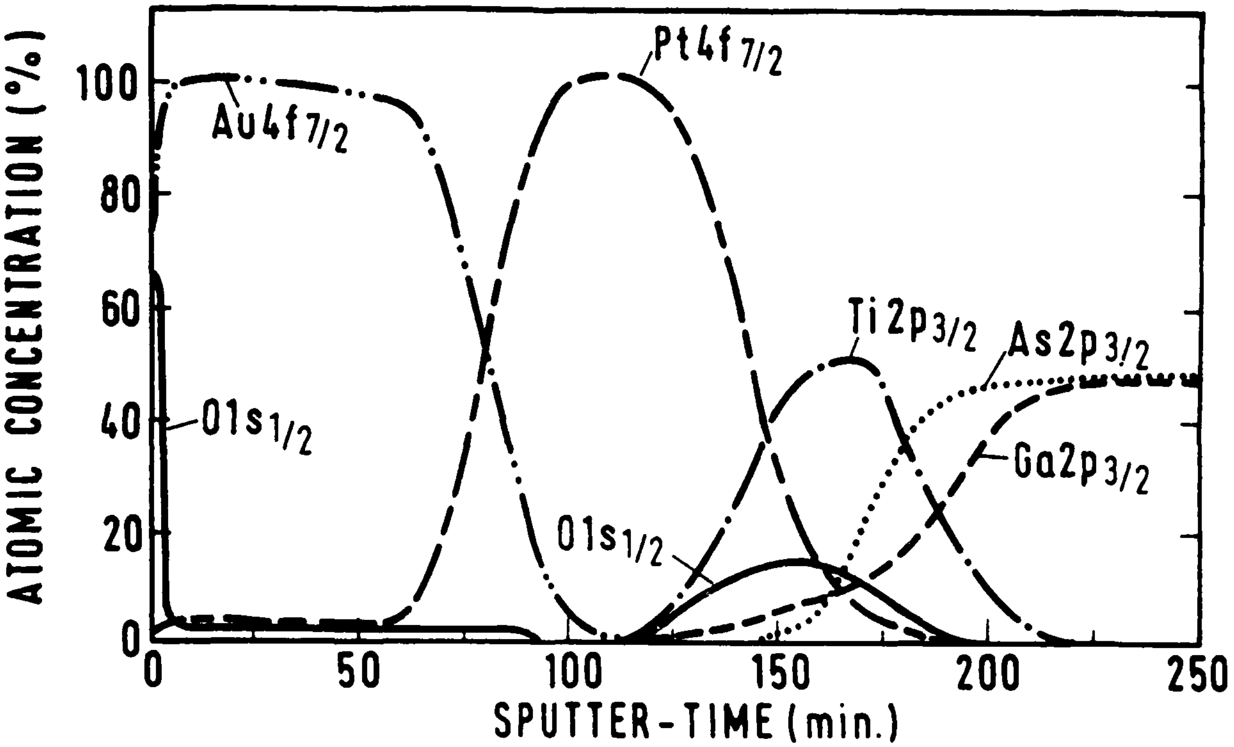

Fig. 13 XPS-sputter-profile of thermally and current stressed TiPtAu contacts on GaAs

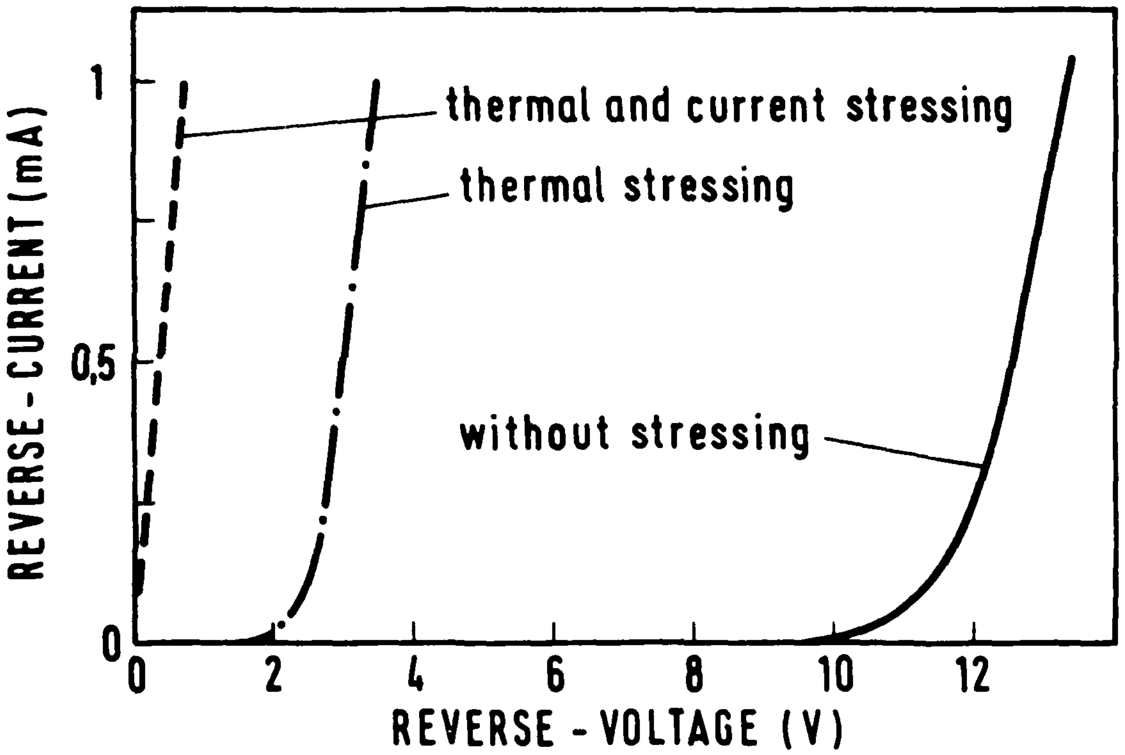

Fig. 14 I/V characteristic (reverse direction) of TiPtAu contacts on GaAs after various stressing conditions

CHAPTER IV

Conclusions

The work supported by the grant of the European Research Office for a period of three years, has now led to a better understanding of the life-time limiting processes of the various metal-electrode structures on GaAs. This new information has therefore also been accepted for presentation at the relevant Conference of such development, namely at the International Reliability Physics Symposium in 1985 in Orlando, USA and in 1986 in Anaheim, USA, and the manuscripts as published in the Proceedings of these Conferences are appended here as Appendices I + II. Additionally, this work has regularly been reported at various International Workshops/17-20/. It can therefore be concluded that the results are of general interest for all those involved with a technology of high-quality MeSFETs and their IC's.

The work has demonstrated that the analysis of the chemical composition of various types of GaAs surfaces is very complex and does affect the stability of metal structures. XPS measurements in connection with the chemical shift information was here particularly useful to establish the chemical reactions which took place. The material composition of complex sandwiches is modified, particularly when both sufficient thermal and electrical stressing occurs. The light emission intensity at places of high surface defects, in particular at edges of metal electrodes, was confirmed to be a good first measure of the GaAs surface quality/3/. The lateral material transfer can be minimized by reducing the surface content of As_2O_3 and many unforseen results have been found such as the surface micro-roughness effect with acidic etchants as recently published/7/. A copy of this paper is attached as Appendix III. Finally, another recently published/21/ report on GaAs surface oxidation rates as relevant for the studies of this project is appended as Appendix V.

Acknowledgements

The help of the relevant technicians of the Institut is gratefully mentioned here, in particular Mr. Heinrich Sturmfels and Mr. Erwin Stromberger. Particularly the competent secretarial and administrative help of Mrs U. Tümmler and the administration of Dr. K. Mayer are to be mentioned here with gratitude.

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APPENDIX I

XPS-ANALYSIS OF GaAs-SURFACE QUALITY AFFECTING INTERELECTRODE MATERIAL MIGRATION

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Abstract

XPS-studies of differently treated (100)-GaAs-surfaces were undertaken and correlated with the threshold for material migration across the GaAs-surface between neighbouring Al-electrodes. 5 surface conditions based on various etching and cleaning processes as commonly employed for the manufacture of GaAs devices have been investigated. The XPS-spectra show that high threshold values can be obtained by treatments resulting in a strongly reduced surface oxygen content.

Introduction

A life-time limiter of planar GaAs devices is given by lateral material migration across the GaAs surface between neighbouring electrodes, which finally leads to an interelectrode short circuiting bridge. The mechanism responsible for this catastrophic failure can be attributed to the existance of high electric surface fields [1]. In recent years the safe applied voltage in GaAs power FETs has been increased by special processing such as introducing n^+ epilayers or recessed gates [2,3,4]. Another case where high electric fields occur is the high-power pulse operation of amplifier stages [5,6]. As these move to more critical applications the material migration has become a serious concern.

In this paper the effect of surface treatment on lateral material migration is examined. Therefore, XPS (X-Ray Photoelectron Spectroscopy) -studies of (100)-GaAs surfaces were correlated with a threshold voltage for material migration. This threshold voltage is defined as the value required for the onset of a practically instantaneous complete short circuiting of neighbouring electrodes (usually within a fraction of a second).

Several surface conditions based on various etching and cleaning processes as commonly employed for the manufacture of GaAs devices have been investigated. The XPS-spectra gave detailed information on the type of surface, (e.g. of the layer very close to the surface, of deeper-lying layers, of the absorbed oxygen etc.) which is also of interest concerning other degradation mechanisms in MeSFETs. They can equally be influenced by surface phenomena [7,8]. The measured threshold values show that the lateral material migration is strongly influenced by the surface oxygen content.

Fabrication and Experimental Procedure

Closely spaced electrode gaps with 20 and 40 µm distances were manufactured to study the field induced material migration. Semiinsolating (s.i.), Cr-doped bulk GaAs with a high resistivity (> 10^8 Ω . cm) was chosen as the substrate so that current-induced heating of the sample does not have to be taken into consideration. After wet-organic cleaning of the substrate, the surfaces were etched for 1 minute with various etching solutions (see Table 1). The first group of samples was treated by a sulfurious acid solution which we commonly employ for mesa-etching. The second group of samples was only cleaned by organic solvents. A pre-evaporation etch was applied to the third group. We found high threshold voltages for the fourth and fifth types, which are basic etchants. The temperature of all etch solutions was 23° C. In all cases subsequent rinsing in H_2O and drying in N_2 gas was applied. Then closely-spaced Al-electrode structures were defined by lift-off technique on the differently treated (100)-GaAs-surfaces. Fig. 1 shows the optical mask with the two closely spaced pairs of electrodes.

Table 1 : Types of surface treatment

no.	solution	remarks
1	H_2SO_3 (conz.) : H_2O_2 (30 %) : H_2O 1 : 10 : 10	Mesa - Etch
2	only cleaning by organic solvents	
3	NaOH (2 %) : H_2O_2 (30 %) (4 Vol %) 1 : 1	Pre-Evaporation - Etch
4	NaOH : H_2O 1 : 5	Etchants with expected higher threshold voltages for material migration
5	KOH : H_2O 5 : 1	

Etch time : 1 minute
Temperature : 23°C

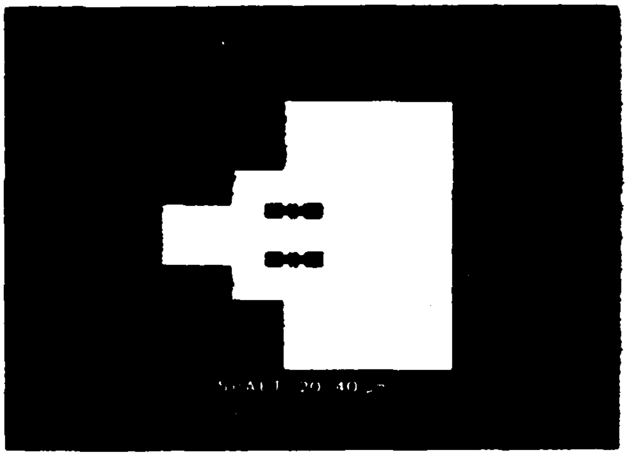

Fig. 1 Photomask of 20 and 40 µm gaps

The free areas on the test chips, which experienced of course the same treatments as the GaAs-surfaces between the electrodes, were then XPS-analyszed to characterize the resulting surface conditions. These measurements were undertaken in a Leybold-Heraeus system with Al K_α radiation (radiation energy: 1486,6 eV). The electron energies were measured by a variable retarding potential and a spherical sector analyser using constant transmission energy which gives constant bandwidths and detection probability for the transmitted electrons.

Accelerated material migration could be observed when applying high voltages between the neighbouring electrodes. The threshold voltage, required for practically instanteneous complete short circuiting of the electrodes by material migration, were measured during standard conditions of 23° C room-temperature and a relative humidity of approximate 65 %.

XPS-Analysis

In connection with the characterization of the differently prepared GaAs samples, the XPS-spectra of As $2p_{3/2}$, Ga $2p_{3/2}$, O 1s, As 3d and Ga 3d surface electrons were employed. Fig. 2 shows these spectra. They are arranged in accordance with the type of surface treat-

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ment by rows 1 to 5. The $2p_{3/2}$ core level emissions of As and Ga are presented in the first two columns. Since the mean free path for the electrons in GaAs without energy loss is energy dependent, the electrons of those lines originate very closely to the surface, typically at a depth of 8 - 12 Å [9]. On the other hand, the 3d XPS lines of As and Ga originate from the 3d electrons of deeper lying atomic layers with an average depth of 25 Å. The 3d core level emissions are given in the two last columns. Additionally the 1s XPS line of oxygen is presented.

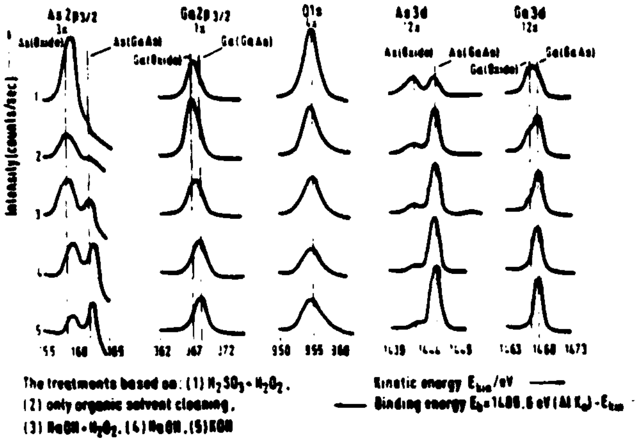

Fig. 2 XPS-spectra of differently treated (100)-GaAs-surfaces

In connection with the $2p_{3/2}$ and 3d lines, two separate levels can be distinguished. The level, representing higher kinetic energies (lower binding energies) originate from those As and Ga atoms which are essentially bonded in connection with the semiconductor GaAs. The level with lower kinetic energies (higher binding energies) are caused by the oxidised forms of As and Ga [10]. The intensity of the maxima with respect to the background noise is a measure of the concentration of the corresponding type of atom.

Using these XPS measurements, the following details can be derived (Fig. 2):

- The non-etched (100)-GaAs surfaces (row 2) exhibit primarily Ga and As oxides. At increased depth the As oxide is reduced rather quickly to As as bonded to Ga. On the other hand the Ga 3d line demonstrates that its oxide penetrates rather more deeply into the bulk material. This is in agreement with [11] where it was established that As_2O_3 in contact with GaAs should react according to the equation

$$As_2O_3 + 2\ GaAs \longrightarrow Ga_2O_3 + 4\ As$$

  yielding Ga_2O_3 and As as the stable phases which can coexist at equilibrium with GaAs.
- When the surfaces are etched in the sulfurious acid solutions (row 1) they exhibit a strong contribution of As oxide. Even down to a depth of about 25 Å such a strong As oxide component is still present (see the As 3d spectrum).
- Following through the three basic solutions NaOH + H_2O_2, NaOH and KOH (rows 3, 4 and 5) both, the As and Ga oxides are removed with increasing extent. The As $2p_{3/2}$ spectra show this particularly clearly by the transfer of intensity to the As which is bonded to Ga. Similarly the Ga $2p_{3/2}$ spectra show this by the shift of the maximum towards the Ga bonded to As. Even at a depth of 25 Å this feature can still be clearly recognized with the Ga 3d line.

Discussion of Results

Material migration from the anode to the cathode could be observed after the application of high voltages to the neighbouring electrode gaps (Fig. 3). The threshold voltages required for quasi-instantaneous complete short circuiting of the electrode by material migration are given in Table 2. It is obviously that great differences exist depending on the GaAs surface conditions as produced by the various treatment processes. Samples where the GaAs surface were etched with H_2SO_3 showed a by 50 % reduced threshold voltage as compared to the non-etched surfaces, whereas the threshold values for the samples treated by the basic etchants was by 35 % higher than those of non-etched surfaces.

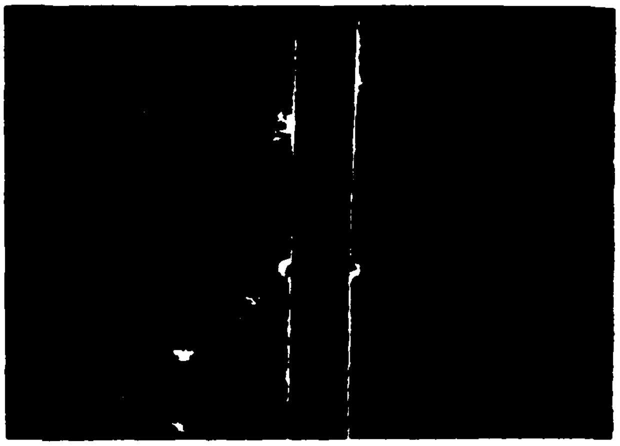

Fig. 3 Photograph of interelectrode metal migration (20 µm gap)

Table 2 : Dependence of threshold voltage on surface treatment

		threshold voltage(typical)	
no.	solution	20µm gap	40µm gap
1	H_2SO_3(conz.) H_2O_2(30%) H_2O 1 10 10	50V	90V
2	only cleaning by organic solvents	100V	200V
3	NaOH(2%) H_2O(30%)(4Vol%) 1 1	150V	270V
4	NaOH H_2O 1 5	160V	300V
5	KOH H_2O 5 1	175V	320V

Temperature 23°C
Rel. humidity 65%

To explain this dependence of material migration on surface conditions, the basic processes of energy exchange at interfaces have to be considered. An atom which is positioned on the GaAs surface is affected by homopolar (exchange-) forces with particular electron exchange or heteropolar (Coulomb-) forces with a full transition of the peripheral electrons to the electron shell of the substrate atom. A further approach of the atom to the substrate surface is prevented by the repulsive forces of the positive core charges. These forces define the probability of finding the atoms on the surface and can be modelled by a surface potential field [12] which is, in the simplest case, of an homogeneous atomic lattice illustrated in Fig. 4a. A particle on the surface oscillates, depending on its kinetic energy about a place, which is determined by a local energy minimum. It migrates on the surfaces if its energy surmounts the energy E_{ch} which is necessary for a site change. Normally at room-temperature the energy of the atom is not high enough to leave the force field of the surface atoms at once. If a high electric field is applied to the surface the function of the potential surface energy will be deformed in such a way that the energy which is necessary for site change decreases (Fig. 4b). A material migration take place in the direction of the electric field.

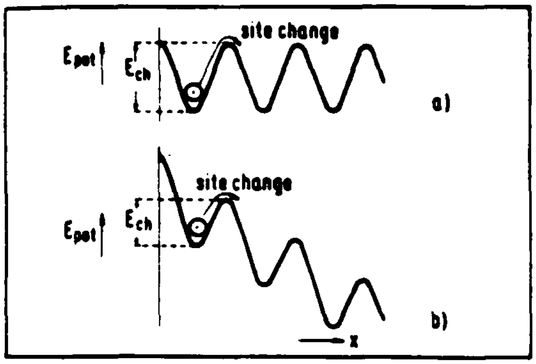

Fig. 4 Mechanism of atomic site-exchange on the surface

If one compares the XPS measurements with the measured threshold voltages for material migration, one can see that the migration depends very strongly on the amount of As_2O_3 on the surface. Fig. 5 shows the correlation of the threshold voltage with the logarithm of the XPS-ratio of As bonded to oxide to As bonded to GaAs. The agreement of the reduction of the oxygen component with the increase in threshold voltage is surprisingly clear. Whereas the treatments based on alkaline etchants leave a low arsenic oxide to GaAs ratio with corresponding high threshold values for material migration, the employed acid etch solutions leads to a strongly increased arsenic oxide component in the surface with unacceptably low threshold voltages.

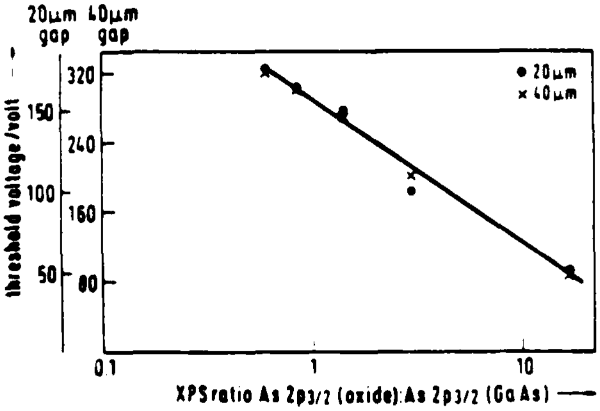

Fig. 5 Threshold voltage for material migration versus XPS-ratio As $2p_{3/2}$ (oxide) : As $2p_{3/2}$ (GaAs)

Very recently, the "gate-recess" etchant NH_4OH (25 %) : H_2O_2 (30 %) : H_2O of the ratio 2 : 1 : 300 has been investigated, which shows the same good behaviour as the KOH etchant.

Summary and Conclusion

We have reported that electric-field induced migration of electrode material along (100)-GaAs-surfaces strongly depends on surface treatment. A direct correlation between "XPS-GaAs-surface quality" and interelectrode material migration has been observed. The XPS-spectra show:

1. Samples cleaned by organic solvents only, exhibit primarily Ga- and As-oxides.
2. Gallium oxide penetrates more deeply into the bulk material.
3. Surfaces treated by the acid etchant $H_2SO_3 + H_2O_2$ exhibit a strong contribution of arsenic oxide even down to the depth of the order of 25 Å. A reduction of threshold voltage up to 50 % have been observed.
4. The treatment with basic etchants removes both As- and Ga-oxides and hence results in an approximately stoichiometric Ga to As ratio. The threshold voltages are more than 35 % higher than the values for the non-etched surfaces. Best results were obtained for the etchants KOH and $NH_4OH + H_2O_2$.

Using this analysis one can conclude that it is necessary to provide as far as possible native-oxide free surfaces between closely-spaced neighbouring electrodes. Since GaAs-surfaces, which are only cleaned by organic solvents, exhibit a high oxygen content, it is desirable to use a suitable surface treatment to achieve a high reliability of GaAs planar devices.

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APPENDIX II

FIELD AND TEMPERATURE DEPENDENT LIFE-TIME LIMITING EFFECTS OF METAL-GaAs INTERFACES OF DEVICE STRUCTURES STUDIED BY XPS AND ELECTRICAL MEASUREMENTS

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Abstract

Typical Schottky contacts for GaAs devices such as Al and TiPtAu metallizations have been accelerated-stress tested under bias at room temperature and at temperatures up to 250° C. The influence of these stress tests on the interface properties were studied by XPS sputter profiling and correlated with electrical measurements. Concerning Al-contacts it has been found that bias-stressing results in a structural change of the Al layer and that the oxygen concentration at the Al-GaAs transition depends both on the polarity of bias stressing and on the GaAs surface treatment before Al-metallization. These effects are quite pronounced even at room temperature. TiPtAu contacts are stable at room temperature over the period of investigation (2oo h) but at elevanted temperatures (200° C) a GaAs diffusion into Ti and a subsequent Ti diffusion into Ga vacancies could be observed. This results in a catastrophic bias dependent degradation of the I/V characteristics.

Introduction

The stability of metal contacts on GaAs devices, e.g. FETs, Gunn-diodes etc., at normal operation conditions is imperative for the performance and the reliability of these devices. Concerning the metallization three different types of failure modes can be observed, electromigration due to electron wind effects/1/ interelectrode, high-field assisted material migration/2/ and interdiffusive effects at the transition metal-GaAs/3/. A great variety of device reliability problems can be attributed to material migration across metal-GaAs interfaces, such as gradual degradation of power amplifications and of noise figure in GaAs FETs or even catastrophic failures due to short circuiting in Gunn-diodes; for example/3,4/. All these failures are affected by high electric fields and currents, and/or high temperatures.

In this paper, a study of these interdiffusive effects on metal-GaAs contacts is presented by selecting two different types of metallization, namely a simple Al-Schottky contact and a TiPtAu contact system on GaAs involving a diffusion barrier. Both metallization types are most widely used in GaAs device technology. The preparation of GaAs surfaces before metal evaporation constitutes a very important aspect concerning stability and interdiffusion properties of metal GaAs contacts. Many workers have shown that the chemical composition of GaAs surfaces that means the amount of oxidized Ga and As, adsorbed oxygen etc. strongly depends on different methods of surface treatment during GaAs device fabrication/2,5/.

Therefore, the experimental efforts have been concentrated on evaluating the influence of both chemical surface preparation before metallization and the bias stressing conditions itself on field or temperature assisted interdiffusion effects at metal GaAs transitions. Among the multitude of metallizations used in GaAs device technology two representative types of contacts have been selected for investigation, namely a simple Al-Schottky contact and a more complex TiPtAu metallization system on GaAs involving a diffusion barrier. Both types of metallizations are widely used in GaAs device fabrication. The contacts have been characterized by XPS (X-Ray-photoelectronspectroscopy) -sputterprofiling and conventional current voltage measurements. It could be shown that both the structure of the Al contact and the oxygen content of the Al-GaAs transition is dependent on GaAs surface preparation and can be modified by electrical stressing even at room temperature. TiPtAu contacts remain stable at room temperature over the period of our investigation (2oo h) but show strong field assisted interdiffusion effects at higher temperatures.

Sample Fabrications And Experimental Details

Special test-structures have been developed to perform both electrical measurements and XPS-sputter profiling on the same sample. Fig. 1 shows the structure of the samples that consists of a large metallized area for XPS analysis and some test pattern for current-voltage measurements. A common backside contact permits high electric fields or current flow across the sample during contact stressing. Before metal evaporation all samples were subjected to a standard wet organic cleaning process consting of successive rinsing in hot acetone, trichlorethylene and methanol for about five minutes in each solvent. Afterwards different types of sample sets were fabricated by etching in various solutions. The fabrication process was finished by the definition of metal contacts using photolithography and lift off techniques.

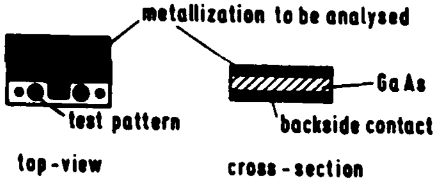

Fig. 1 Sample fabrication

Since XPS-sputter profiling is a destructive way of analysis it is important to fabricate many identical samples and separate them into reference samples and test samples. Only the test samples will be stressed according to the experimental program as outlined later on. Before and after stressing, the current voltage characteristics of the samples were recorded. Comparing XPS sputter profiles of reference samples and stressed samples reveals changes of the physical and chemical composition of the contacts that can be attributed to the corresponding stressing conditions

Stability of Al-Contacts on GaAs

To evaluate the influence of chemical treatment of the GaAs surface before metal evaporation on any interdiffusive effects occuring at the Al-GaAs transition, three sample series were prepared by etching NaOH + H_2O_2 + H_2O, KOH + H_2O and H_2SO_3 + H_2O_2 + H_2O respectively for one minute (Table 1). Firstly, semiinsulating GaAs has been used for sample fabrication because it is then possilbe to employ identical contacts at opposite surfaces of the GaAs in order to study the effect of the type of polarity of the field applied. Additionally, s.i. GaAs permits the use of high electric fields while the current flow across the contacts remains negligible. One is thus able to neglect the current which could increase the temperature at the junction. For each experimental series three identical sample sets were fabricated. One serves as a reference set whereas the other two are biased positively or negatively for about 200 hours. The biasing voltage was 80 Volts. All experiments were carried out at room temperature. The concentration profiles of the Al-layer and the Al-GaAs interface were obtained by XPS-sputter-profiling of both the reference samples and the positively or negatively biased samples after finishing the long-time stressing experiments. The profiles have been computed from the Al $2p_{3/2}$, O $1s_{1/2}$, As $2p_{3/2}$ and Ga $2p_{3/2}$ lines. Comparing the corresponding experimental results, several important conclusions can be drawn.

Table 1: Sample treatment (Al-GaAs contacts)

sample-set	etch-solution	stressing-conditions
1	NaOH(2%) : H_2O_2(30%)(4Vol%) 1 . 1	positive or negative biasing (80V) at room temperature for 200 hours
2	KOH : H_2O 1 : 200	
3	H_2SO_3(conz.) . H_2O_2(30%) : H_2O 1 10 10	

1. Figure 2 shows the XPS sputter profile of the aluminium and oxygen concentration of samples etched in NaOH + H_2O_2 + H_2O before metal evaporation. Although all samples have been carefully checked with regard to the original Al-layer thickness, one can generally observe an apparent "broadening" of the aluminium concentration profile, if presented versus sputter time, irrespectively whether the samples had been biased positively or negatively during the long-time stressing. Obviously, after stressing, the sputter rate is decreased. It might be possible that this effect is caused by a field-assisted aluminium diffusion along grain boundaries so that grain-boundary removal or restructing is taking place and a reduced sputter-rate can therefore be observed. This explanation seems to be supported by the observation that the amount of broadening depends on the GaAs surface treatment before metal evaporation (comparing Fig. 2 to 4). Even the reference samples of the three sample series shown in Fig. 2-4 exhibit different apparent Al-concentration profiles over sputter times although the Al-layer thickness has always been kept the same. Samples etched in sulfurious acid before metallization, for example, have an ion etch rate which is about 17 %* in comparison to samples where the GaAs surface was etched in sodium hydroxide before metal evaporation. It seems reasonable to assume that the observed effects depend on the polycrystalline -structure of the Al-layer because different GaAs etchants of course yield different surface conditions of the semiconductor, which affect the growth processing during metal evaporation/6/. Since the activation energy for diffusion along grain boundaries is smaller than for intra-grain diffusion/7/, any diffusion effects at relatively low temperatures are strongly affected by the grain size, or the number of grain boundaries and therefore by the polycrystalline structure of the film.
2. Another very interesting effect occuring during bias stressing can be observed by considering the amount of oxygen at the interface before and after sample stressing (Fig. 2-4). It is apparent that positive bias causes an increase in oxygen concentration at the interface whereas negative biasing nearly maintains the oxygen concentration or even causes a depletion of oxygen. A systematic analysis of the XPS spectra reveals that oxygen is entirely bonded to aluminium. No gallium oxide or arsenic oxide could be detected. This means that a reduction of the native oxides on the GaAs surface had taken place during aluminium evaporation. It is interesting that aluminium at the interface seems to have another chemical composition than the Al-oxide on free Al-surfaces. This is indicated by the Al $2p_{3/2}$ spectral lines for aluminium surface oxides (energy shift about 0.6 e.V.). It should be mentioned that an increase in aluminium oxide concentration at the interface after positive biasing has been observed in all sample sets, independent on the type of preevaporation etchant that had been used. Both the initial oxygen concentration at the interface and the oxygen accumulation after positive biasing are found to be directly affected by the GaAs surface preparation before Al-metallization. This is in agreement with previous results that different etchants applied to GaAs surfaces change both the type and concentration of native surface oxides/2,5/. Using potassium hydroxide as a preevaporation etchant for example (Fig. 3) only a small initial oxygen concentration at the interface and only small changes of this concentration could be observed after biasing in contrast to the two other etchants used for sample preparation. These changes in oxygen concentration at the interface occur even when the biasing experiments are undertaken in a vacuum system. Since no indiffusion is possible in this case the oxygen accumulation at the interface can probably be considered as a field assisted redistribution of oxygen or aluminium-oxide which is available at the interface or in the grain boundaries of the Al-layer. This redistribution process can be explained in a number of ways; one of them would be a defect mechanism in connection with negatively charged vacancies of oxides in the grain boundaries of the Al-layer or at the interface. These vacancies may be able to move against the direction of the electric field by changing their places with neighbouring neutral atoms.

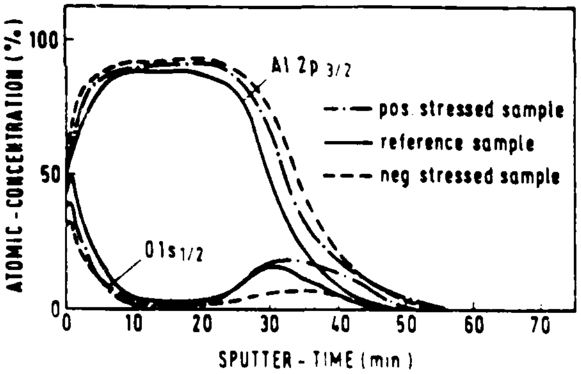

Fig. 2 XPS-sputter-profile of samples etched in NaOH + H_2O_2 + H_2O before Al evaporation

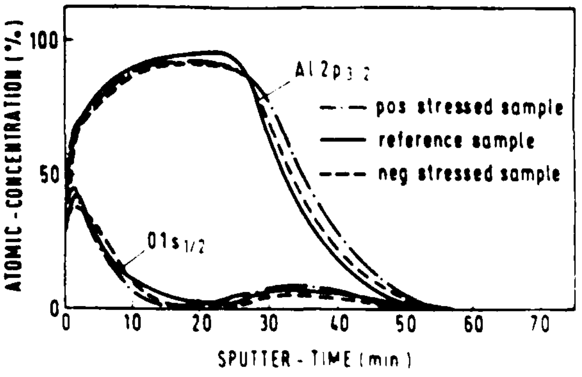

Fig. 3 XPS-sputter-profile of samples etched in KOH + H_2O before Al evaporation

* only 83 %

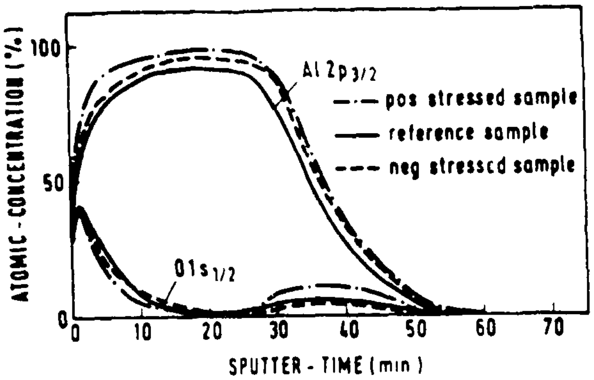

Fig. 4 XPS-sputter-profile of samples etched in $H_2SO_3 + H_2O_2 + H_2O$ before Al evaporation

3. Figure 5 shows the Ga 2p3/2 to As 2p3/2 ratio at the interface of a sample set etched in sodium hydroxide (solution 1 Table 1) for different baising conditions. These diagrams have been computed from the XPS spectra taking into account the shift of the gallium and arsenic concentration profiles that are due to the apparent Al-concentration profile broadening mentioned above. One can easily realize that the Ga to As ratio decreases immediately at the interface. This decrease can be observed in all sample sets and is found to be dependent on the GaAs surface preparation and on the biasing conditions during long-time stressing. An analysis of the XPS spectra reveals that the decrease of the Ga to As ratio seems to be due to an arsenic accumulation at the interface. The magnitude of this accumulation is influenced by both the chemical surface treatment before metal evaporation and the polarity of the bias during long-time stressing. Comparing Fig. 5 and 2 yields a strong correlation between oxygen concentration and the Ga to As ratio at the interface. Positive biasing for example increases the oxygen concentration and the Ga to As ratio at the interface simultaneously. Measurement indicate that this can probably be considered as a field-assisted indiffusion of Ga into oxygen-rich regions of the interface.

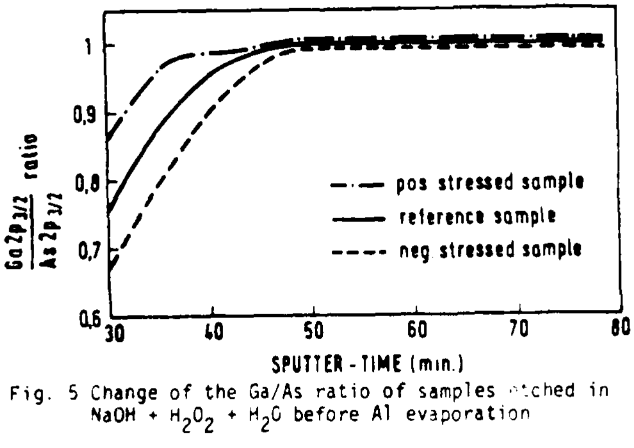

Fig. 5 Change of the Ga/As ratio of samples etched in $NaOH + H_2O_2 + H_2O$ before Al evaporation

4. As mentioned above, current voltage characteristics of the samples were monitored before and after bias stressing. Typical shapes of the I/V characteristics obtained can be explained in connection with Fig. 6 which shows the positive and negative part of the I/V characteristic of a sample treated with pottassium hydroxide (sample ref. 2, Tab. 1) before aluminium evaporation. A relatively steep current increase can be observed at low voltages followed by a region showing very high differential resistance and finally a region with a very steep increase of current at high voltages. According to Kao/8/ this current-voltage characteristic seems to be typical for double injection in solids between two similar oppositely placed Schottky contacts (Al-GaAs-Al). The positive and negative parts of the I-V characteristics show a rather assymetrical behaviour especially with regard to the "breakdown voltage" at the transition from the region with high differential resistivity to the region with very steep current increase. This assymetry is the result of the different surface roughness of the back and the frontside contacts of the samples. (The wafers used for sample preparation have had an unpolished backside and a polished frontside). Increased surface roughness of course leads to locally increased electric fields just underneath the contact, which results in a premature onset of possibly electrons avalanching there if the backside contact serves as a cathode so that electrons can be injected (positive region of the current voltage characteristic). Since Sethi et al/9/ has shown that various etchants applied on GaAs surfaces yields different surface roughnesses it is reasonable to assume that GaAs surface treatment also influences the electrical characteristics of the contact. Indeed the breakdown voltage of samples etched in potassiumhydroxide before metal evaporation has increased for about 50 % in comparison to samples etched in sulfurious acid, since etching in KOH yields a much more smooth surface than etching in sulfurious acid/9/. As mentioned above bias stressing results in a change of polycrystallinity of the Al-layer and the oxygen concentration at the interface which may explain the different breakdown voltages before and after voltage stressing (Fig. 6).

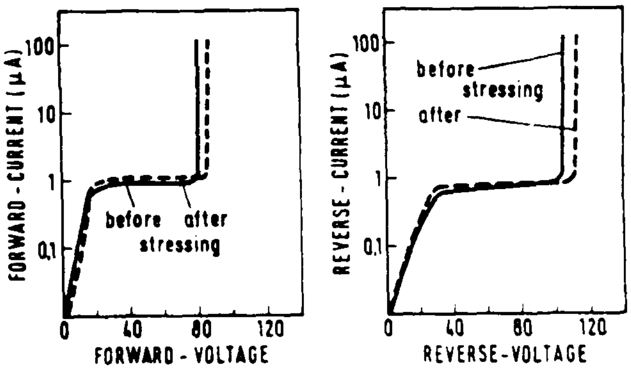

Fig. 6 Typical I-V characteristic before and after field stressing

Besides these experiments on Al-GaAs-Al structures Al-Schottky diodes on n-GaAs ($n = 1.7 \times 10^{16}$ 1/cm^3) have been investigated at room temperature and at temperatures up to 150° C to study the dependence of barrier height on bias stressing conditions. At room temperature no change in barrier height after reverse biasing at 10 V DC for 100 hours could be detected whereas temperature stressing at 150° C with and without biasing increases the barrier height between 5 % and 10 % (Fig. 7). No significant differences in the alteration of the barrier height of field and temperature stressed samples or only temperature stressed samples could be detected.

Stability of TiPtAu Metallization

Apart from metallizations on GaAs consisting of a single metal only (like Al) contact systems involving a diffusion barrier like TiPtAu are widely used in device technology. Since such metallizations can be expected to show basically different bias-stressing behaviour, TiPt-Au contacts were chosen for this investigation to compare these results with those obtained from Al contacts.

Test samples were fabricated according to Fig. 1. The frontside was covered with TiPtAu (40 nm, 80 nm, 200 nm) the backside contact consisted of an AuGe 88/12 ohmic contact annealed at 450° C for 1 min. Before TiPtAu metallization the samples were etched in $NH_4OH + H_2O_2 + H_2O$ (2 : 1 : 200) for 1 minute.

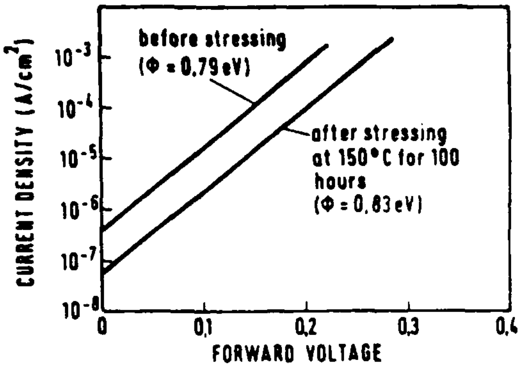

Fig. 7 I/V characteristic of Al-GaAs Schottky diodes before and after thermal stressing

Titanium, which is then deposited immediately onto the GaAs surface, exhibits a much higher affinity to oxygen than aluminium. Therefore, it can be expected that any native oxides on GaAs are reduced during Ti metallization, in a similar manner as in the case of Al. This behaviour has indeed been found by detailed XPS measurements of the Ti-GaAs interface where no oxidized Ga or As could be detected.

The oxygen take-up rate of Ti surfaces was then studied under residual gas pressure down to around I x 10^{-9} mbar by inserting the Ti film deposited on GaAs together with a protective layer of Au and Pt in the UHV system of the XPS chamber. After sputter removal of the protective layers the oxygen take-up rate of the free Ti surface could be monitored. Fig. 8 shows that even at very low pressures of oxygen the relative oxygen intensity increases by a factor of three within 50 min. and remains nearly constant during the subsequent exposure. Higher residual gas pressures of oxygen of course yield higher oxygen uptake rates and higher oxygen saturation for prolonged exposure (Fig. 8). Since pressures of about 1 x 10^{-6} mbar are quite common for metal evaporation, both the titanium evaporation rate and the storing time of any unprotected titanium layer in the evaporation system before continuing the metallization sequence by platinum deposition will affect the oxygen content and thus the reproducibility of these metallizations produced in different runs.

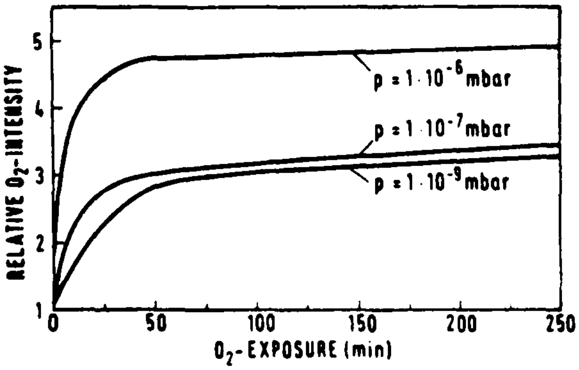

Fig. 8 Ti-oxidation in an UHV-system

Regarding the stability of TiPtAu contacts on GaAs various sample-sets (fabrication details as described above) have been stressed at room temperature and at temperatures up to 250° C with and without reverse biasing of the AuPtTi-GaAs Schottky contact for about 200 hours. At room temperature the contacts were bias stressed both at - 10 V DC reverse voltage with negligible current flow and in the avalanching region of the contact (about - 12 V DC) where the current density was kept constant at about 3 A/cm^2. At temperatures of 250° C the leakage current of the TiPtAu Schottky contact of course increased in comparison to room temperature conditions so that a leakage current density of 3 A/cm^2 for bias stressing was already obtained at reverse voltages of about 2 Volts. At room temperature the TiPtAu contact was found to be stable over the time of our investigation (200 h) - no degradation of the I/V characteristic or significant changes of the XPS-sputter profile could be detected after the various stressing conditions at room temperature. However, stressing at temperatures of 250° C yields strong changes of the I/V characteristics and a pronounced variation of the XPS-sputter profiles.

Fig. 9 shows the XPS sputter profile of a reference sample, Fig. 10 of a sample stressed only thermally at 250° C and Fig. 11 of a sample that has experienced both thermal and bias stressing. Comparing these sputter profiles several important details can be derived.

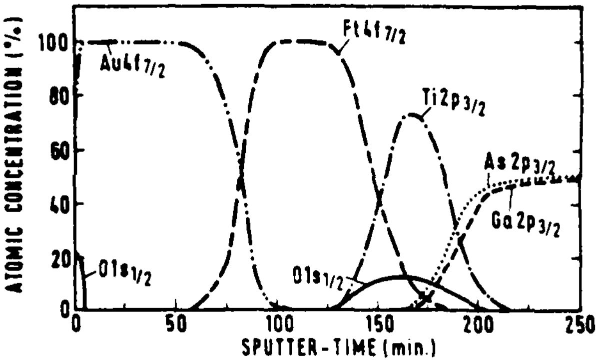

Fig. 9 XPS-sputter-profile of unstressed TiPtAu contacts on GaAs

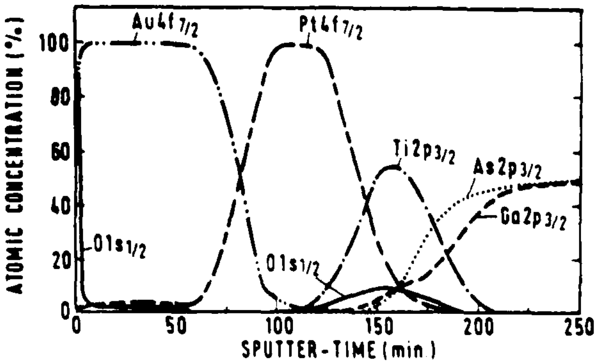

Fig. 10 XPS-sputter-profile of thermally stressed TiPtAu contacts on GaAs

1. Both thermal and particularly combined thermal and current stressing produce Ga outdiffusion into Ti and to some extend into Pt, where in the case of current stressing Ga penetrates Pt more deeply. No outdiffusion of arsenic neither during thermal stressing nor during combined thermal and current stressing could be detected. Diffusion of gallium into the contact metal has been observed in many

metallizations on GaAs and is commonly considered to be a purely temperature-dependent effect/10/.

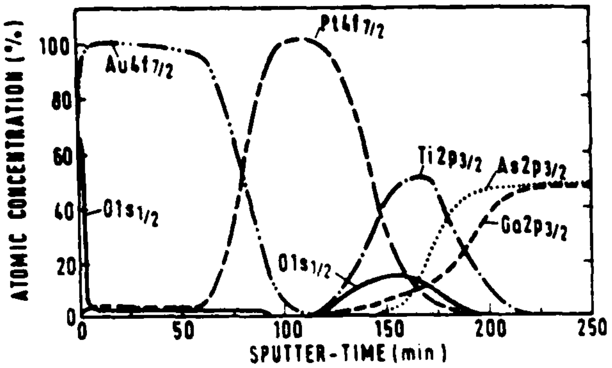

Fig. 11 XPS-sputter-profile of thermally and current stressed TiPtAu contacts on GaAs

2. Interdiffusion Au-Pt and Pt-Ti has taken place, where Pt has diffused through the gold layer towards the surface (Fig. 10, 11).

3. Another interesting finding is that the oxygen content in the Ti-layer decreases in amplitude and broadens correspondingly during thermal stressing but shows a small increase in amplitude after combined thermal and bias stressing. Since oxygen penetration into the Au layer is much more pronounced in sample-sets, which are bias stressed at 25o^{0} C, one can probably assume that unbonded oxygen is transported into the gold metallization and towards the bulk of the Ti by electron-impulse transfer ("electron wind")/1/. This means that this current-assisted oxygen transport prevents, to some degree, the oxygen outdiffusion during combined bias and thermal stressing, as was observed. The oxygen inside the Ti is finally largely immobilized due to bonding to titanium. Of course thermal stressing in air enhances surface adsorption of oxygen on the gold surface as can be seen by comparing the relevant figures.

4. As outlined above, thermal and combined thermal and electrical stressing results in a significant outdiffusion of Ga into Ti. This Ga outdiffusion is partly balanced by a subsequent indiffusion of Ti into GaAs particularly during the combined stressing, as careful analysis of the XPS sputter-profiles reveals (Figures 10 and 11). Obviously the Ti, which is not bonded to oxygen, is pushed into GaAs by the electron wind. Considering the I-V characteristics (Fig. 12) of these samples reveals that simple temperature stressing causes only relatively small changes whereas combined temperature and bias stressing results in a catastrophic degradation of the TiPtAu Schottky contact. The contact becomes nearly ohmic. It is reasonable to assume that Ti is transferred into Ga vacancies during stressing by diffusion and electron wind effects where it acts as a donor level and hence changes the I/V characteristic of the contact in the observed way.

Summary and Conclusion

It has been reported, that electrical and thermal stressing causes degradation of both the physical and electrical properties of Al and TiPtAu contacts on GaAs.

Regarding aluminium contacts on GaAs the following results have been obtained:

1. An apparent broadening of the Al-concentration profile is caused by reduced ion-etching rates due to a configuration of a higher density of the Al-layer during field stressing.

2. The oxygen concentration at the interface depends on stressing conditions and GaAs surface treatment before aluminium evaporation.

3. Stressing conditions and GaAs surface treatment also affect the Ga to As ratio at the interface. This ratio is shown to be strongly correlated with the interface oxygen content.

4. The shape of the I/V characteristic is found to be strongly influenced by GaAs surface treatment before aluminium metallization and on the bias conditions.

5. Thermal stressing of Al-GaAs Schottky contacts increases the barrier height.

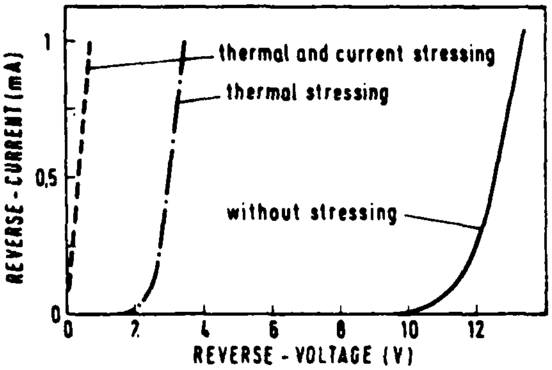

Fig. 12 I/V characteristic (reverse direction) of TiPtAu contacts on GaAs after various stressing conditions

The investigations on TiPtAu contacts showed stable conditions at room temperature over the period of investigation (2oo h), but at elevated temperatures (25o^{0} C) a number of degradation effects could be detected.

1. Both thermal and current stressing produce Ga outdiffusion where in the latter case Ga penetrates Pt more deeply. Ti diffuses into GaAs.

2. Interdiffusion Au-Pt and Pt-Ti was observed.

3. Thermal stressing decreases oxygen content in the Ti layer and enhances surface adsorption of oxygen on the Au surface.

4. Current stressing at elevated temperatures pushes unbonded oxygen towards the bulk of Ti. There oxygen is immobilized due to bonding to Ti. Unbonded Ti is pushed by "electron wind" into Ga vacancies.

5. Thermal stressing alone (25o^{0} C) causes relatively samll changes in electrical behaviour whereas additional current stressing results in nearly ohmic contact behaviour.

Concerning aluminium metallization on GaAs, reliability problems may arise even at room temperature if the oxygen concentration at the Al-GaAs transition is not kept low during device fabrication. Both Al and TiPtAu contacts fail at elevated temperatures. For the development of GaAs devices operating at high temperatures future efforts will have to concentrate on improvements which might include amorphous or even monocrystalline diffusion barriers.

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APPENDIX III

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Surface topography of etched GaAs surfaces

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Double replica TEM of etched (100) GaAs surfaces has shown that acidic etching gives rough island-type features whereas alkaline solutions seem to produce smooth surfaces.

1. Introduction

Recent experimental results on the stability of metal electrodes on GaAs, in view of device-life times, have shown that the initiation of electric-field-assisted metal migration along the semiconductor surface between two neighbouring electrodes (Kretschmer and Hartnagel 1985) and that the electron-wind material transport along narrow high-current carrying conductors (Sethi and Hartnagel 1986) are both dependent on the final etch solution employed with the GaAs before metallization. It has been established by XPS that alkaline etch solutions produce much less As_2O_3 on the GaAs surface than acidic solutions (Kretschmer and Hartnagel 1985). One might therefore be inclined to suggest that As_2O_3 acts like a lubricant for electromigration of metals on GaAs.

In this paper experimental results are presented which appear to give a different explanation for the behaviour observed. Double-replica TEM studies of etched GaAs surfaces have generally given a much rougher surface for acidic-etch cases than for the alkaline ones. Therefore, higher electromigration rates could be caused by the resulting non-uniformity of current densities or field strengths in connection with such metal electrodes on acidic-etched GaAs surfaces.

2. Experimental

Polished semi-insulating GaAs wafers from Sumitomo Electric Industries Ltd., Japan, wafer surface orientation (100), were organic-solvent cleaned using acetone, trichloroethylene and methanol (Sethi and Hartnagel 1985). The etch processes applied are as follows:

(*a*) NaOH (2 %), H_2O_2 (30 % concentration, 4 % by volume), with ratio (1:1);

(*b*) KOH, H_2O (KOH– 0·5 % by weight);

(*c*) NH_3 solution (25 % concentration), H_2O_2, H_2O; and

(*d*) H_2SO_3 (concentrated), H_2O_2, H_2O.

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The solutions (a)-(c) are alkaline, whereas (d) is acidic. The etching time with all these etchants is, in general one minute (while with etchants (a) and (d), it is sometimes also two minutes). Etching is performed at 23° C.

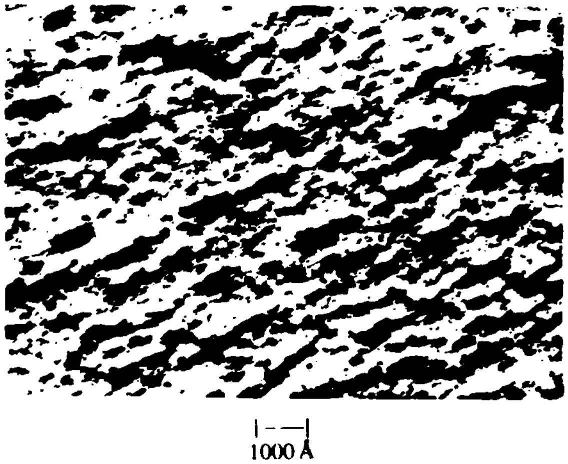
The replica of the resulting surface is taken by applying the transparent organic liquid Tylose, which hardens quickly and which can then be peeled off. This film carries the negative of the GaAs-surface topography. 50–100 Å C Pt is then evaporated, followed by around 500 Å of C forming the base layer. After the deposition of a collodian layer (1 % solution of collodian in n–Butylacetate) to provide strength, the Tylose layer is removed in very hot water by dissolution. The replica, thus produced, is placed on a copper mesh (400 μm hole width) and inserted into the TEM system.

3. Results

The magnifications of the TEM photographs obtained is such that details of less than 100 Å can clearly be seen. Whereas the various alkaline-etched GaAs surfaces did not exhibit any significant features, the surfaces etched with the acidic solution (d) showed the strong characteristic details of the figure. One can clearly see an island pattern which seems to consist of elongated hillocks (although this pattern can also be produced by cavities into the surface). Their longer dimension is several hundred Å. This is clearly below the level of any optical microscope inspection.

4. Discussion

Recently it was reported (Aspnes and Studna 1985) that measurements of the surface roughness using a rotating-analyzer spectro-ellipsometer showed microscopic roughness to occur particularly in strongly acidic solutions. It was suggested that such observations are understandable from the free energy of Ga ions in solution, together with the mechanism by which bifunctional etching groups attack the GaAs bond. It would indeed have been useful to determine the material of our



Double-replica TEM photograph of an acidically etched GaAs surface, 6·1 mm ≙ 1000 Å.

islands in order to establish whether this is caused by the method of Aspnes and Studna (1985), or whether this simply represents clusters of As_2O_3 which such surfaces are found to exhibit strongly (Kretschmer and Hartnagel 1985). Unfortunately, we have not yet succeeded in establishing the island composition owing to the very small dimensions.

Nevertheless, such features can certainly be responsible for the various electromigration effects in metal electrodes by which strong uniformities of current densities or electric fields are established.

ACKNOWLEDGMENTS

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APPENDIX IV

List of Student Projects Related to the Present Project

1. R. Dapper - D 1368 -

   Studie zur Kostenminimierung bei der Entwicklung eines HF-Leistungsgenerators (Ausgangsleistung _ 2 kW im Bereich von 100 kHz bis 1 MHz) zum induktiven Schmelzen von Metall-Legierungen

   High-Frequencyhigh-power generation for inductive melting of metal alloys

2. P. Dworschak - D 1355 -

   Softwareentwicklung für ein 65o2-Mikroprozessorsystem zum Aufbau eines adaptiven, programmierbaren Temperaturreglers

   An adaptive programmable temperature controller

3. K. Steinmetz - D 1354 -

   Elektrische Messungen an Schottky-Dioden auf Indiumphosphid

   Schottky Diodes on InP

4. A. Weitz - D 1350 -

   Experimentelle Untersuchung der Kennlinie ohmscher Kontakte auf Indium-Phosphid

   Ohmic contacts on InP

5. G. Pitz - D 1347 -

   Herstellung planarer Strukturen für GaAs-Höchstfrequenzbauelemente und experimentelle Untersuchung ihrer Zuverlässigkeit

   Planar structures for GaAs microwave devices and reliablity studies

6. P. Ladas, K. Maros - St 1344 -
Herstellung und Untersuchung von Metall-Halbleiterkontakten für GaAs-Höchstfrequenztransistoren

Metal-semiconductor contacts for GaAs microwave transistors

7. B. Meerkötter - D 1341 -
Aufbau eines digitalen Temperaturreglers mit einem Mikroprozessor

Digital control of temperature

8. P. Grambow - D 1364 -
Herstellung coplanarer Strukturen auf GaAs und Messung der Wellenparameter

Fabrication of co-planar structures on GaAs and measurement of the wave parameters

9. H. Hartl - St 1371 -
Aufbau eines GaAs-MeSFET für den Betrieb im Mikrowellenbereich

Fabrication of a GaAs MeSFET for microwave operation

1o. K. Maros - D 1382 -
Herstellung von Metall-Halbleiterkontakten unter Berücksichtigung ihrer Bondbarkeit

Fabrication of metal-semiconductor contacts on GaAs in view of good bondability

11. W. Bay, B. Giese - St 1374 -
Materialwanderung in GaAs MeSFETs

Material migration on GaAs MeSFETs

12. Z. Didoglu, J. Hiotis - St 1384 -
Untersuchung der Materialwanderung in GaAs-Bauelementen mit Siliziumxoid-Passivierung

Material migration on GaAs components with SiO_2-passivation

13. P. Kaiser, A. Lüssem - St 1387 -
    Untersuchung der thermischen und elektrischen Stabilität von Gate-Metallisierungen für GaAs-MeSFET

    Thermal and electrical stability of gate metallizations for GaAs MeSFETs

14. P. Ochs - D 1390 -
    Betrieb von GaAs-Bauelementen bei verschiedenen Umgebungstemperaturen: Untersuchung nichtreversibler Einflüsse auf die Eigenschaften von Au-Ge/Ni-Kontakten auf GaAs

    Operation of GaAs components for various temperatures: The irreversible features of the characteristics of Au-Ge/Ni contacts on GaAs

APPENDIX V

INT. J. ELECTRONICS, 1986, VOL. 60, NO. 6, 663–670

GaAs-surface oxidation in air studied by XPS and ISS

K. RÖHKEL† and H. L. HARTNAGEL†

A study is presented on native air-exposed GaAs' surface composition and the sputter-cleaning transient. These results are based on both XPS and ISS.

1. Introduction

Device manufacturing, based on single-crystal thin-film epitaxy, metal and insulator deposition and other processes, uses air exposed polished and organic-solvent cleaned (100) GaAs surfaces. These are often cleaned by sputter etching several surface layers away. Therefore a study was undertaken to obtain detailed information on the compositional details of such surfaces and on the sequence of material removal by sputtering, in continuation of some previous work (Huber and Hartnagel 1984). The measurements were undertaken by XPS (X-ray photoelectron spectroscopy) and ISS (ion scattering spectroscopy), the latter especially, in order to analyse the very surface layer of the oxidized GaAs' surface, whereas XPS has emission depth ranges from around 5–8 Å for the $2p_{3/2}$ orbitals and from around 20–30 Å for 3d orbitals of Ga and As atoms.

2. Experimental

The (100)*n* GaAs samples were bulk grown material, doped with a carrier density of $10^{16}\,\mathrm{cm}^{-3}$ and delivered, sliced and polished, by the manufacturer Wacker. They had been stored in air for a long period of time. After organic-solvent cleaning in trichlorethylene, acetone and methanol, the samples were mounted on a steel support using conducting silver paint and inserted into the ultra-high vacuum system of a measurement facility of $< 10^{-9}$ mbar. To obtain ISS signals, ions of ^{4}He and ^{20}Ne with a primary energy of 1000 eV were used. The angle of elastic scattering was fixed to 134 degrees. XPS was undertaken with an Al-K$\alpha_{1,2}$ X-ray emitting anode with a line of about 1 eV FHWM. Ion etching was done by Ne$^+$ and Ar$^+$ ions.

3. XPS results

The XPS-spectra are shown in Fig. 1 starting with the lowest row, denoted by 1, with the unsputtered original surface of the GaAs sample. The following rows, up to row 5, show the XPS-spectra after the surface was bombarded with Ne$^+$ ions. The highest row (6) shows the spectra after the surface had been etched for nearly half-an-hour with Ar$^+$ of 3000 eV accelerating potential.

At the initial surface (row 1) a large amount of As$_2$O$_3$ and Ga$_2$O$_3$ is to be seen where the As$_2$O$_3$ occurs, however, only within a thin layer zone, because after a first

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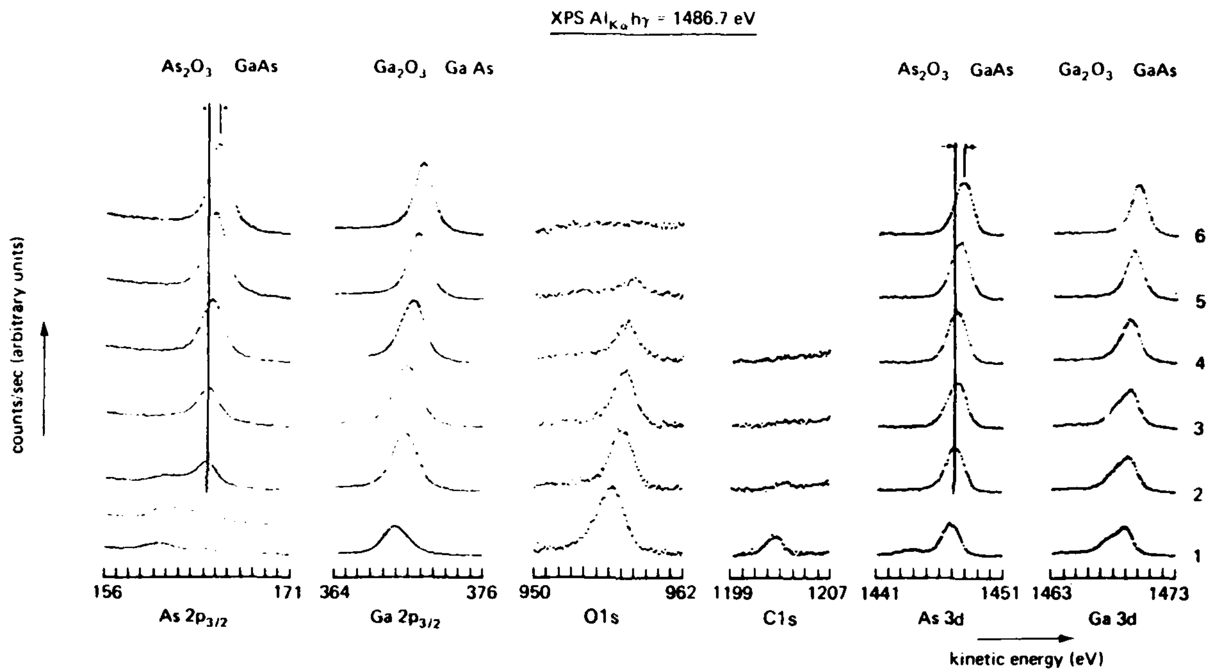

Figure 1. XPS-spectra of sputter-etching compositions of air-oxidized GaAs surface (row 1: original GaAs-sample as inserted into the vacuum system; rows 2–5: subsequent etching with Ne^+ of different intensities and duration; row 6: last etch step when Ar^+ was used (Ar^+ is much heavier than Ne^+)).

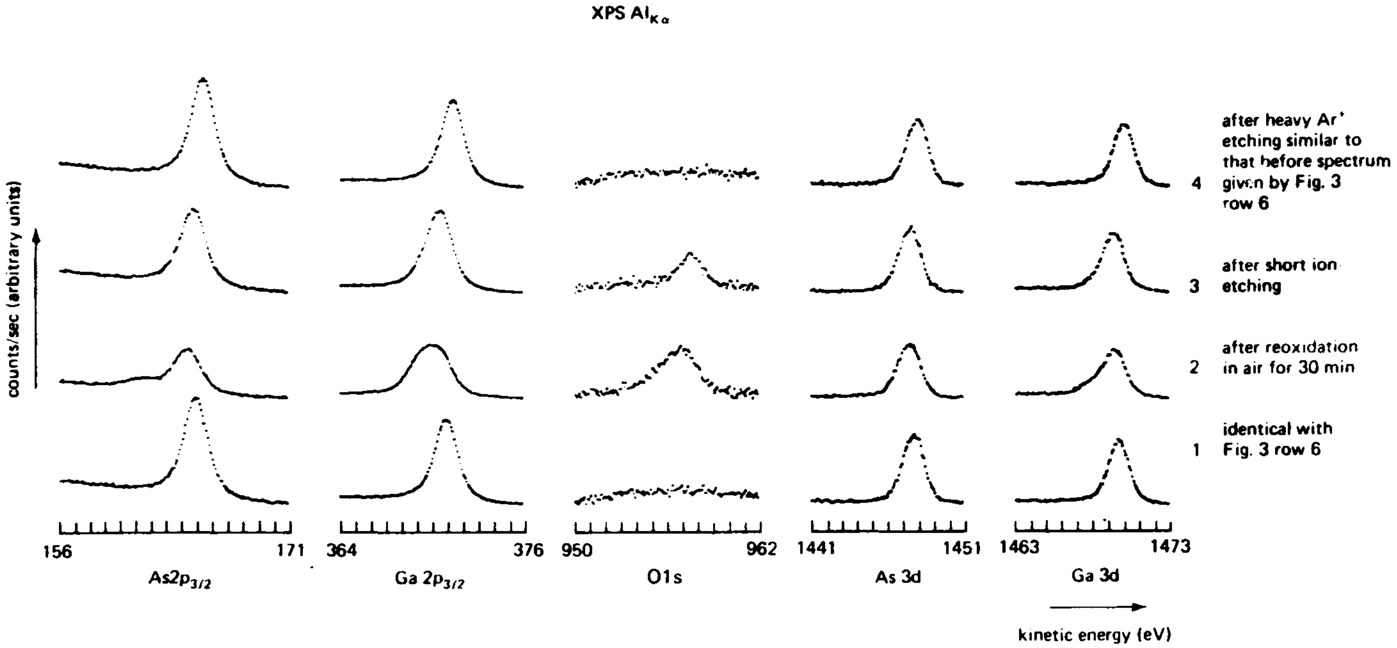

Figure 2. XPS-spectra of re-oxidized GaAs surface after sputter-etch cleaning.

Ne^+ etching, the oxide signal vanishes from the more bulk-sensitive As-3d peak (rows 2 and 3), and is still only detectable within the more surface-sensitive As-$2p_{3/2}$ peak (rows 2 and 3). Ga_2O_3 is much more deeply buried in the GaAs sample as may be seen from the peaks of Ga-$2p_{3/2}$ and -3d (rows 4 and 5). Whereas no As_2O_3 is detectable up to row 4, there still remains a Ga_2O_3 part in the Ga-orbitals and a symmetrical 0 1s peak now occurs.

From the 0 1s spectra it can be seen that the As_2O_3 results in a broadening of the 0 1s peak to higher kinetic energies (i.e. smaller binding energy), which is more pronounced as can be recognized from Fig. 2 which shows the spectra of the same sample after exposure to air for nearly 30 minutes (row 2). The spectra of row 1 represents the data after the last heavy Ar^+ etch. A subsequent first ion-etch (or, what seems to yield the same outcome, namely heating the sample surface by radiation of a filament up to 150°-200 C) takes away all As_2O_3 as can be seen from the As 2p peak (Fig. 2, row 3) and reduces the broadened oxygen 0 1s peak (i.e. two peaks originally overlapping, row 2) into a symmetrical one (row 3), now solely related to Ga_2O_3.

Comparing the initial spectra (Fig. 1, row 1) with those after the last ion-etch with Ar^+ (row 6) there is a significant shift of about nearly 1 eV for all of the peaks, as indicated in Fig. 1, for the As $2p_{3/2}$- and As 3d-orbitals. The shift mainly occurs after the initial As_2O_3 has vanished when Ga_2O_3 remains solely in the GaAs surface. The subsequent etching then causes significant peak-shifts (see Fig. 1, row 4 upwards).

It is likely that this represents a reduction in surface potential starting with etching the Ga_2O_3 zone. Re-oxidizing the etched sample for a short time in air results in a nearly reversible 1 eV shift-back of all peaks (Fig. 2, rows 2, 3) to the original energy positions which had been taken before etching away the last remaining Ga_2O_3 zone (Fig. 1, rows 2, 3). A new heavy Ar^+ etch (etching of Ga_2O_3 zone) again results in nearly a 1 eV shift of all the peaks (Fig. 2, row 4) indicating the surface potential reduction.

A remarkable effect of sputter-cleaning is the accumulation of pure arsenic in the sample surface. Figure 3 shows the more detailed XPS-spectrum of Fig. 1, row 6 of the As 3d-orbital taken after the last heavy Ar^+ bombardment. Because the background is linear and very small, the experimental XPS-signal could be simply fitted

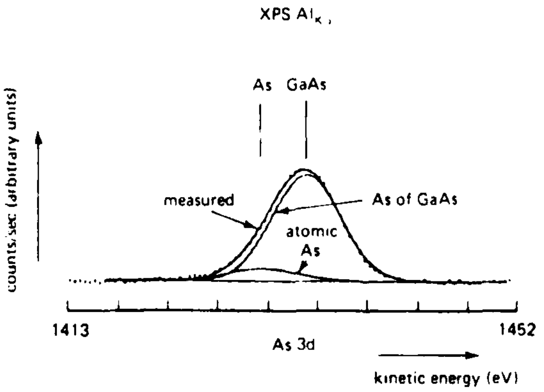

Figure 3. Curve-fitted experimental spectrum of the As 3d-orbital of Fig. 1, row 6.

by two lorentz-gauß lines separated by 0·9 eV, which is just the difference of binding energy for pure As and GaAs-bounded arsenic.

Further, it can be seen that the original unsputtered surface (Fig. 1, row 1) is firstly covered by an extremely thin adsorption-layer (probably a mixture of water film, and a carbon-hydrogen-oxide film), the resulting contamination is due to having air-exposed the sample for a long period of time. The prominent C_1 signal diminishes strongly after the first etch. The contamination itself is easily removed by simply bombarding the surface with the comparatively light He^+ ions of 1000 eV energy as used for ISS analysis. The resulting XPS-spectrum of the surface sensitive As $2p_{3/2}$ orbital (Fig. 1, row 1) shows, after the bombardment, a nearly unaltered ratio of As_2O_3 to As|GaAs| but a more intensive signal. Because of the extremely short free wavelength of the As $2p_{3/2}$ core-electrons, even monolayers contaminating the sample surface result in a strongly reduced signal height. Also the ISS analysis, by elastically scattering ^{4}He, leads to the same conclusions as a first monolayer of contamination.

4. ISS results

Figure 4 shows a typical ISS-spectrum, in this case related to the XPS-spectrum after re-oxidizing the surface for a short time (Fig. 2, row 2). Comparing this ISS-spectrum with that taken just after the sample has been inserted into the vacuum system (Fig. 5, row 1), the following can be found: an extremely reduced signal intensity of Ga and As (which are overlapping each other in the case of ^{4}He), almost no oxygen, and a more pronounced noisy background can be seen, thus indicating a contaminated overlayer on top of the sample surface.

The ISS (^{4}He) spectra of Fig. 5 indicate a reduction of noise and background intensity for further sputter-cleaning of the sample surface. A direct comparison of the O-reduction with the Ga As increase, to obtain possible information of knock-on effects of O due to sputter-cleaning, therefore remains problematic and was not undertaken.

The elastic scattering of the heavier ^{20}Ne ions of the sample surface enables one to distinguish between ions scattered by Ga atoms and those scattered by As atoms

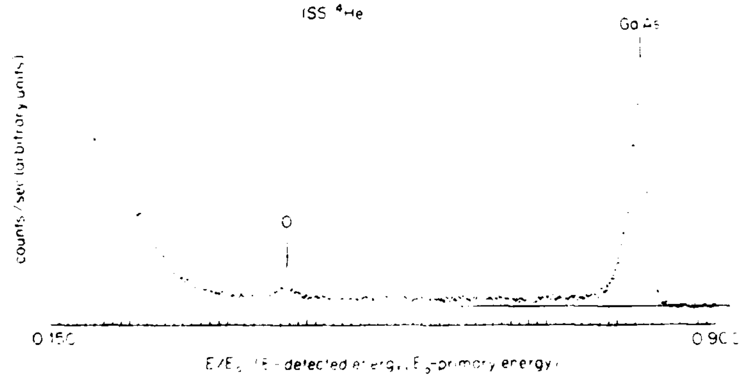

Figure 4. ^{4}He-ISS equivalent to XPS of Fig. 2, row 2.

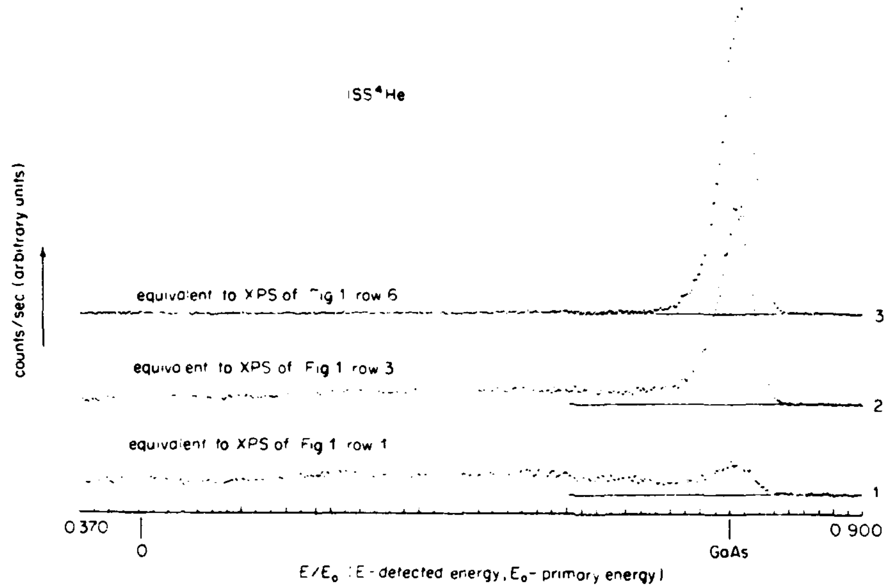

Figure 5. ^{4}He-ISS spectra.

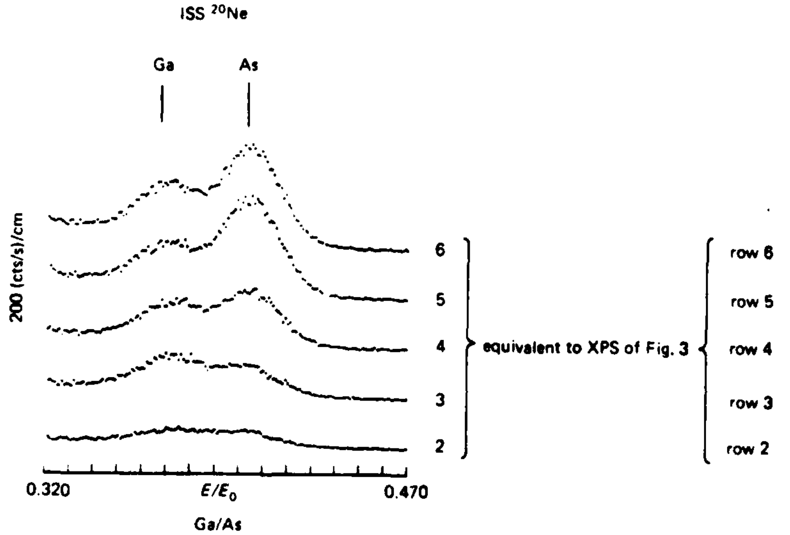

Figure 6. ^{20}Ne-ISS spectra of Ga and As (since the Ga peak is broadened, and thus lowered, due to the existence of two isotopes, row 6 represents a stoichiometric GaAs composition).

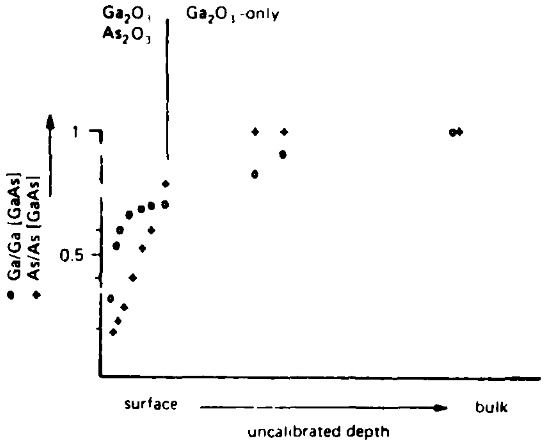

Figure 7. Depth profile of Ga and As by detailed ^{20}Ne-ISS analysis.

Ga|GaAs|	concentration of Ga in GaAs compound
As|GaAs|	concentration of As in GaAs compound
Ga	concentration of Ga after the given etch step
As	concentration of As after the given etch step

(Fig. 6), whereas oxygen, because its mass is smaller than the ^{20}Ne ion used, can no longer be detected. The ISS-spectrum of Fig. 6, row 6 is taken from the heavy Ar^+ etched sample surface related to the XPS-spectra of Fig. 1, row 6. Because the oxidized zones are sputtered away, the stoichiometry of Ga to As is expected to be 1 : 1. Because Ga consists of the two stable isotopes ^{69}Ga and ^{71}Ga, whereas As consists only of ^{75}As, the peak of Ga is lower and broader than that of As. From Fig. 6 it can be seen that during sputter-cleaning significant changes of Ga to As ratios occur.

From more detailed ^{20}Ne ISS measurements a relative depth profile concerning the Ga to As ratios can be obtained (Fig. 7). The calibration of depth for the subsequent etch steps is only very approximate, because the selected changes of current densities and accelerating energies during sputtering cannot be exactly related to the actual etch rates obtained. But from a comparison with the simultaneously performed XPS measurements the following results, shown in Fig. 7, can be found: at the initial surface and as long as there is As_2O_3 to be seen from the XPS-analysis there exists a Ga-enriched phase. After having sputtered away all As_2O_3 (compare Fig. 1, row 4 upwards) a change in the Ga : As ratio takes place. Up to the etch-step where oxygen (and thus Ga_2O_3) is no more detectable, an arsenic-enriched phase of the sample occurs.

These results can be compared with the angle-dependent XPS findings, which also lead to the suggestion of a layered native oxide composition of air-exposed GaAs surfaces (Demanet and Marais 1985).

5. Conclusions

A combination of XPS and ISS analyses has been employed to obtain numerous details on the composition of air-exposure native oxides on GaAs. The advantage of

ISS is the possibility of analysing only the atomic surface layer, whereas XPS probes further down with two different depths due to the two emission lines of 3d and 2p electrons. The dynamics of cleaning such surfaces by ion etching has led to a rather complex sequence of removal details.

6. ACKNOWLEDGMENT

The authors are grateful, for financial assistance of this work, to the European Research Office of the US Army in London in connection with grant number DAJA 45-83-C-0012.

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