CHAPTER II

CHARACTERISATION OF Au,Ge-Au AND Ge-Ga-Au METALLIZATION SYSTEMS ON GaAs

INTRODUCTION

Gold and gold based multicomponent metallization schemes are commonly used for making contacts to GaAs and other compound semiconductors (1-7). As discussed in the section 1.3, the contact formation often involves a brief heat treatment which causes interdiffusion and reactions among elements of the contacting system and the semiconductor (1,5, 8-13). These interactions alter the surface morphology and interface metallurgy (5,10, 13-23) of the alloyed structure and dictate the electrical characteristics of the M-S interface (8-11).

Au, Au:Ge and Au:Ge:Ni films on GaAs have extensively been investigated (5-26) to evaluate their metallurgy after alloying. In these studies, the diffusion of Au and Ge into the semiconductor, out migration of Ga from GaAs, sublimation of arsenic and formation of a variety of intermetallic compounds have been established and correlated to the electrical properties exhibited by the metal-GaAs junctions. Although these results satisfactorily describe the degradation of GaAs-Au contact at elevated temperatures (1,13,20,21,27) but the electrical stability shown by GaAs-Au:Ga Schottky diode (28) has not yet been explained on the basis of metallurgical investigations. Further, the occupation of vacancies created by out diffusing gallium atoms by Ge has been accounted to describe the ohmicity of GaAs-Au:Ge junction (1-4, 8-13) nevertheless the data concerning Ga out diffusion is not available for quantitative analysis of
contact properties. These aspects are not merely important from theoretical viewpoints but also are of great technological interest, particularly for optimising ohmic & Schottky contacts to GaAs.

Therefore, in the present chapter, a systematic investigation of metal-GaAs systems using electron spectroscopy for chemical analysis (ESCA) also known as X-ray Photon Spectroscopy (XPS) is presented. The structural compositions of Au, Ge-Au and Ge-Ga-Au films alloyed to n-GaAs are described to evaluate elemental interdiffusion. The diffusivity of gallium in overlying thin gold film is determined and the role of gallium in a metallization is studied to elucidate the thermal stability of GaAs-Au:Ga contacts. The results are explained with the aid of available phase diagrams. A metallization containing nickel has not been considered since it is not generally preferred in the modern contacts owing to its deep penetration and reliability problems (11, 24-27). We use the convention of labeling films so that the metal deposited on the semiconductor substrate is written first e.g in GaAs-Ge-Ga-Au scheme, the Ge film is on the GaAs substrate and Au is the outermost layer as illustrated in Fig. 2.1.

2.2 EXPERIMENTAL DETAILS

The sample preparation procedure is as follows: The substrate material is n-type GaAs doped with silicon to $10^{16}$ cm$^{-3}$ (supplied by Sumitomo Japan). It is subjected to cleaning in organic solvents and to an MB etch (HCl:HF:H$_2$O :: 1:1:4 with a few drops of H$_2$O$_2$) for 10 seconds just prior to loading in a Balzers coating system evacuated to a pressure of $5 \times 10^{-7}$ Torr.

Germanium is evaporated by electron-beam technique and Au-Ga by resistive heating of tungsten boats. The rate of evaporation and film thickness are monitored with a quartz crystal oscillator mounted on the wafer holder. A Tencor Alpha step is used to establish the thickness
FIG. 2.1 GaAs - METAL STRUCTURES USED FOR ESCA ANALYSIS
of the deposited films. The metallized structures and thickness of the layers, which are involved in the present characterisation are sketched in Fig. 2.1.

The metallized wafer is scribed to obtain 4mm x 6mm samples to facilitate mounting on ESCA holders. The samples are then annealed at various temperatures in a horizontal quartz tube furnace in flowing nitrogen. The temperature of the furnace is regulated by a thermocouple temperature controller and monitored with the aid of a thermocouple attached to the sample boat.

Metallurgical analysis of the metallized surface is accomplished with an ultra-high vacuum ($\sim 10^{-9}$ Torr) Leybold - Heraus ESCA system. ESCA spectra are recorded using anodes emitting Al-K$\alpha$ and Mg - K$\alpha$ radiations. The electron energy is measured with a variable retarding potential and a spherical sector analyser employing a constant transmission energy which gives constant band widths and detection probability for the transmitted electrons. In situ sputter etching by Ar$^+$ ions (3000 eV) is used to obtain depth composition profiles for Ga, As, Au, Ge and O elements. The ESCA depth profiles of as-deposited samples may differ from the true ones since the effects of unintentional temperature rise during metal deposition is not included in the present analysis.

2.3 GaAs-Au SYSTEM

Typical ESCA depth profiles for the GaAs-Au system for various alloy conditions are shown in Fig. 2.2 - 2.4. Following observations may be inferred from the results:

(i) Arsenic is present in the metal layer and increase in its content is detected in case of samples alloyed at high temperatures.

(ii) Gallium out diffusion from GaAs is evident from the figures. It is interesting to note that the accumulation of gallium on the surface
FIG. 2.2 ESCA SPUTTER DEPTH PROFILE OF GaAs - Au SAMPLE AS DEPOSITED.
Fig. 2.3 ESCA sputter depth profile of GaAs - Au sample alloyed at 240°C for 30 min.
FIG. 2.4 ESCA SPATTER DEPTH PROFILE OF GaAs – Au SAMPLE ALLOYED AT 420° C FOR 30 MIN.
is more pronounced compared to increase in its level in the bulk of the metal film, for the sample alloyed at an elevated temperature.

(iii) The presence of oxygen on the surface and at the interface is seen in the profiles. Like gallium, oxygen concentration in the film and on the surface grows substantially with alloying temperature.

(iv) Gold penetration into GaAs is significant in alloyed cases. Depletion in its surface concentration and enhanced penetration with alloying temperatures are indicated by the distribution profiles.

Fig. 2.5 gives the depth profile of gold diffusion into GaAs. Its penetration in case of as-deposited sample may be attributed to combined influence of temperature rise during metal deposition and knock-in effect, which is inherent in an XPS characterisation.

For accurate estimation of gallium distribution in the overlying gold film, the sputtering rate is determined by etching gold film of known thickness on glass plates in the ESCA system. Fig. 2.6 demonstrates the distribution of gallium in a thin gold film (400 Å). Assuming a complementary error function distribution of gallium in gold (11,29), the experimentally obtained gallium concentration at the interface (mentioned in Fig. 2.6) yields the diffusion constant $D_B (240^\circ C) = 1.26 \times 10^{-16} \text{ cm}^2/\text{sec}$. and $D_B (420^\circ C) = 2.1 \times 10^{-14} \text{ cm}^2/\text{sec}$. These data are plotted in Fig. 2.7 to obtain the diffusion activation energy $E_a = 20 \text{ Kcal/mol}$ and pre-exponential factor $D_0 = 4.5 \times 10^{-8} \text{ cm}^2/\text{sec}$ using the Arrhenius relation.

$$D_B = D_0 \exp \left( - \frac{E_a}{KT} \right)$$

Where $K$ is the Boltzmann constant and $T$ is the annealing temperature in Kelvins.

2.4 GaAs-Ge-Au SYSTEM

The XPS sputter profile for the as deposited GaAs-Ge-Au system of Fig. 2.8 shows a layered thin film structure as expected. It is interesting to record germanium signal in and on the top of the gold layer. Also
Fig. 2.5 ESCA SPUTTER DEPTH PROFILE OF GOLD DIFFUSION IN GaAs.
FIG. 2.6 DEPTH PROFILING ESCA ANALYSIS OF GALLIUM OUT-DIFFUSION IN A GOLD FILM 400Å THICK ON GaAs
DIFFUSION OF GALLIUM FROM GaAs IN POLYCRYSTALLINE GOLD FILM

**FIG. 2.7** ARRHENIUS PLOT OF GALLIUM DIFFUSIVITY INTO GOLD
FIG. 2.8 ESCA SPUTTER DEPTH PROFILE OF GaAs - Ge - Au SAMPL AS DEPOSITED.

GaAs-Ge-Au
AS DEPOSITED

Mg-Kα-Line

Ge(3d)

Ga(3d)

As(3d)

SPUTTERING TIME (min.)

0

100

200

300

100

200

300

100

200

300

100

200

300
shown in Fig. 2.8 is contaminant oxygen and out migrated Ga & As from GaAs into the Ge film.

Fig. 2.9 is a typical profile for samples heat treated well below the Au:Ge eutectic temperature (360°C). Ge has rapidly moved through the overlying gold film to such an extent that it appears as if it was the top most layer of the structure. Gold is thus completely covered by out diffused germanium. While the presence of arsenic is detected throughout the alloyed region, out migrated gallium is also found to accumulate below the surface. Note the initiation of Ge & Au penetration into the semiconductor substrate at this temperature.

The composition profiles for samples alloyed at temperatures exceeding 360°C is similar to that of Fig. 2.10. It shows complete intermixing of elements of the system in the alloyed region, together with a strong in-diffusion of Au & Ge. Germanium and gallium peaks still exist near the surface and an excessive incorporation of oxygen is indicated. A significant GaAs dissociation near the original GaAs interface is evident from the figure.

2.5 GaAs - Ge - Ga - Au SYSTEM

Figs. 2.11 - 2.14 are representatives of depth composition profiles for as-deposited and alloyed samples of GaAs-Ge-Ga-Au system. Some of the important salient features which can be extracted from these are:

(i) Quite evidently, arsenic is detected only for sputter time larger than 100 minutes for all the cases. It is interesting to note that the arsenic profiles of alloyed samples appear exactly similar to that of the as-deposited one.

(ii) No definite conclusions can be drawn, directly from gallium distribution since it constitutes one of the component of the deposited layers in the present structure. However, its rapid diffusion through
FIG. 2.9 ESCA SPUTTER DEPTH PROFILE OF GaAs - Ge - Au SAMPLE ALLOYED AT 240°C FOR 30 MIN.
FIG. 2.10 ESCA SPUTTER DEPTH PROFILE OF GaAs - Ge - Au SAMPLE ALLOYED AT 450°C FOR 30 MIN.
FIG. 2.11 ES CA SPUTTER DEPTH PROFILE OF GaAs - Ge - Ga - Au SAMPLE AS DEPOSITED.
FIG. 2.12 ESCA SPUTTER DEPTH PROFILE OF GaAs - Ge - Ga - Au SAMPLE ALLOYED AT 240°C FOR 30 MIN.
**FIG. 2.13** ESCA SPUTTER DEPTH PROFILE OF GaAs - Ge - Ga - Au SAMPLE ALLOYED AT 380°C FOR 30 MIN.
FIG. 2.14 ESCA SPITTER DEPTH PROFILE OF GaAs - Ge - Ga - Au SAMPLE ALLOYED AT 450°C FOR 30 MIN.
the overlying gold film and accumulation on the surface is easily visible even in as-deposited case and this is more so in alloyed samples.

(iii) The profiles of Au & Ge clearly depict the diffusion behaviour of these elements. The gold peak gradually moves towards the interface while that of Ge displaces nearer to the surface. Both shift progressively with diminishing amplitude as alloying temperature is raised. Their tails penetrate deeply into the substrate with alloying.

(iv) The qualitative behaviour of oxygen is similar to that observed in GaAs-Au and GaAs-Ge-Au systems. However, its inclusion is substantial for alloying at 450°C in this case.

2.6 GALLIUM DIFFUSION IN GOLD

The results described in the section 2.3 evince that the heat treatment of GaAs-Au system has mainly been found to cause (i) gallium dissolution in gold (ii) arsenic evolution and (iii) gold penetration into GaAs. There is considerable experimental evidence to suggest that the decomposition of GaAs is enhanced by the contact metal and that it takes place even at room temperature (8,20,30). A few researchers (16,30) have suggested that some kind of non-bulk phenomenon is responsible for this rapid process but the predicted diffusion depths are too great to be explained (30). Recently, Nakahara & McCoy (31) have demonstrated a correlation between the grain size & the diffusion direction in thin metal film couples and concluded that the atoms from a fine grained layer diffuse along the boundaries of large grains in the adjacent layer.

The fabrication of GaAs-Au structures involves the deposition of a polycrystalline gold film on to a single crystal GaAs substrate. The
gold film contains grain of various sizes depending on the evaporation conditions and annealing temperature (32) and thus possesses a high density of grain boundaries. Therefore, in accordance with the prediction of Nakahara and McCoy, arsenic and gallium atoms from GaAs will diffuse along these boundaries.

Arsenic being volatile, escapes out of the system whereas gallium reacts with oxygen and gold to form oxides & intermetallic compounds (1,5,8,20-26). The accumulation of gallium on the surface may be attributed to its strong affinity for oxygen (8). Shifts in the peak position of oxygen & gallium, recorded during ESCA analysis suggests the presence of gallium oxide on the surface and the persistence of some shift in the gallium peak below the surface where no oxygen is recorded, is an indicative of presence of gallium in compound forms, perhaps with gold. A large solubility of gallium in gold (~10%) compared to that of arsenic (~1%) at 300°C (33) also supports the formation of Au-Ga intermetallics. The tie lines in the ternary phase diagrams in Fig.2.15 also predict the stability of gallium oxide and Au-Ga compounds in contact with GaAs (34).

Therefore, it can be concluded that grain boundary diffusion is a dominant mechanism of gallium transport in the GaAs-Au system. Consequently, the Fig. 2.7 provides values of grain boundary diffusion coefficient of gallium in gold. These lie in the range $10^{-16}-10^{-12}$ cm$^2$/sec. which is in good agreement with that determined by Vyas & Sharma (36). However, the grain boundary diffusion activation energy of 20.00 Kcal/mol deduced here is higher than the empirical value of 7.0 Kcal/mol obtained by Nakahara & Kinsborn (30). Further, the pre-exponential factor $D_o = 3.0$ cm$^2$/sec suggested in the study of Nakahara & Kinsborn (30) is enormously greater than our value of $4.5 \times 10^{-8}$ cm$^2$/sec. We believe that this disagreement is due to the different structure considered by them. Their structure consists of evaporated films of gallium & gold whereas the present study concerns polycrystalline gold films on a single-crystal GaAs substrate.
FIG. 2.15  TERNARY PHASE DIAGRAMS OF
(a) Ga–As–Au SYSTEM (Ref. 34)
(b) Ga–As–O SYSTEM (Ref. 35)
Gallium atoms in crystalline GaAs are not as free as unbound atoms in a thin deposited films and perhaps this is responsible for large $D_0$ value obtained by Nakahara & Kinsborn (30). This argument is further supported by the fact that our $D_0$ value is comparable to Robinson's value of $2 \times 10^{-12} \text{cm}^2/\text{sec}$ which he estimated for gallium diffusion in Au:Ge:Ni film on GaAs (11).

2.7 ROLE OF GALLIUM IN A METALLIZATION ON GaAs

The results in sections 2.3 & 2.4 reveal that Ga and As are present in the alloyed region of GaAs-Au and GaAs-Ge-Au samples. Further, the rise in gallium concentration level at high temperatures anneal is seen but arsenic level does not appear to change appreciably. Being a volatile element, perhaps it evaporates out of the system. The observations concur with the reported decomposition of metal coated GaAs substrates on heating (15-17).

The rapid out migration of Ga in GaAs-Au system and that of Ge in GaAs-Ge-Au samples may be attributed to diffusion of these elements through gold grain boundaries as discussed in the preceding section. While gallium forms compounds with gold according to Fig. 2.15a, the formation of GeAs & GeAs$_2$ is expected from phase diagram in Fig. 2.16a (34). The rise in contents of Ga, Ge and oxygen on the surface at a high temperature annealing may be attributed to formation of the metallic oxides & intermetallic compounds as predicted by phase diagrams in Fig. 2.15 & 2.16a. This has also been suggested from the shifts in peak positions of Ga and Ge spectra recorded during XPS characterisation.

From the results discussed in the section 2.5 it is difficult to judge whether or not gallium from GaAs has diffused out in the metal. Nonetheless an important clue can be obtained by comparison of Ga profiles in Fig. 2.11 - 2.14. The disappearance of plateau of Ga distribution of as-deposited sample (Fig. 2.11) on alloying at $240^\circ\text{C}$ (Fig. 2.12) suggests spread
FIG. 2.16 TERNARY PHASE DIAGRAMS OF
(a) Ga-As-Ge SYSTEM
(b) Ga-As-M (Metal-Containing Phase) SYSTEM
(Ref. 34)
of gallium from the deposited film in the adjacent layers. Since the concentration of Ga stays at a constant level (\(\sim 20\%\)) on subsequent annealings (Fig. 2.13 & 2.14) it is expected that no appreciable amount of Ga from GaAs has migrated out. This substantiates the conjecture that Ga saturated gold film on GaAs retards or probably inhibits out diffusion of gallium from the semiconductor (28) and thus precludes decomposition of GaAs. The absence of arsenic in the alloyed region (Fig. 2.12 - 2.14) further strengthens this argument.

The phase diagram of Ga-As-M (metal) system, illustrated in Fig. 2.16b (34), can also be used to explain the above mentioned influence of gallium in the metallization. Beyers et al. (34) suggested that even in case of a stable metal-containing phase on GaAs, metal atoms diffuse from the pure phase into GaAs until the solubility limit is reached. Similarly, Ga & As will diffuse into the pure phase and can cause the formation of a third phase, depending on difference in their solubilities in the contacting phase. If arsenic is less soluble than gallium, the arsenic rich phase adjacent to the metal-containing phase forms and the system composition lies in the M (Ga) - As - GaAs three phase region at equilibrium as depicted in the Fig. 2.16b.

Therefore, to minimise the net exchange of materials between metal-GaAs substrate, the metal-containing phase should be deposited with a maximum solubility of gallium or arsenic already incorporated in it, if it is possible. Since gallium solubility in Au is higher compared to that of arsenic (33), gallium saturated gold film according to this discussion is expected to prevent disintegration of GaAs, as has been observed in the present investigation.

2.8 CONCLUSIONS

In a non-gallium metallization contact to GaAs, Ga atoms from GaAs diffuse out rapidly along grain boundaries in the overlying metal
film. It thus renders behind unbonded arsenic atoms in the crystal which need a lesser amount of energy to escape out of the semiconductor. Thus the presence of As & Ga in alloyed region of GaAs-Au and GaAs-Ge-Au is expected even at a low temperature anneal as has been observed in the present investigation and by many researchers (1,5, 8-25). This effect is primarily responsible for electrical instabilities of the GaAs-Au Schottky diode. The decomposition of gold coated GaAs generates vacancies & defects at the interface. These stimulates elemental interdiffusion and interactions and thus drastically alter the morphology & metallurgy of the alloyed region. Consequently, the electrical performance of GaAs-Au junctions is strongly degraded by thermal treatments (28).

On the other hand, in a gallium based system, the grain boundaries get saturated by gallium atoms of the metallization. This gallium saturated film does not take up any more Ga from GaAs. Hence an early decomposition of GaAs is averted. This accounts for the absence of arsenic in the alloyed region in case of GaAs-Ge-Ga-Au system. Since in a gallium based metal contact to GaAs, elements of the semiconductor are not allowed to evolve out at the interface, the crystal stoichiometry or structure is maintained. Therefore, the interface properties do not change on thermal cycling and thus rationalize the thermal stability exhibited by GaAs-Au:Ga contact (28). The ternary phase diagrams of M-Ga-As provide the simplest, most logical frame work to strengthen the conclusions derived from the experimental results as discussed in the previous sections.
REFERENCES


29. S.D. Mukherjee, in Ref. 1, pp. 1.