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Correlation between solid state reaction and electrical properties of the Rh/GaAs Schottky contact

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The solid state reactions between (100) GaAs substrates and Rh films ~150Å and ~600Å thick, annealed at temperatures between 300 and 800°C, are investigated with conventional and heavy ion Rutherford backscattering spectrometry, and x-ray diffraction. Initiation of interface reactions between the Rh films and the GaAs substrate is observed at ~300°C. Laterally segregated RhGa, RhAs and $RhAs_2$ phases are detected for the 150Å Rh/GaAs contact annealed in the temperature range of 300 to 700°C. For thick Rh film (~600Å) on GaAs, vertical phase separation between the RhGa and the Rh-As phases is observed after annealing. After annealing at 700°C for 20 min., the reaction between the 600Å Rh film and GaAs is complete and a layer sequence of $RhGa/RhAs_2/GaAs$ results. Electrical properties of Rh/n-GaAs diodes are measured using the current voltage (I-V) dependence. A correlation between the electrical behavior and the metallurgical reaction is observed.

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One of the most important current problems in the development of GaAs integrated circuits is the fabrication of stable, reliable and reproducible metal contacts on GaAs devices. In order to solve this problem, basic understanding of the metallurgy of various metal-GaAs interfaces is essential. Contact systems such as Pt-GaAs [1-3], Pd-GaAs [3-8], Ni-GaAs [3, 9-11] and W-GaAs [1, 12-15] have been studied by many investigators. While most studies in this area have been concentrated on a few metal-GaAs systems, many other contact systems which may have great potential in technological applications have been neglected. One such system is the Rh-GaAs Schottky contact. This letter reports on the metallurgical and the electrical characteristics of the Rh/n-GaAs contact after heat treatment. An attempt is also made to correlate the solid state interface reactions with the electrical properties.

Undoped ($\rho > 10^7$ Ω-cm^2) and Te-doped ($n \sim 10^{17}$ cm^{-3}, $\rho \sim 10^{-2}$ Ω-cm^2) (100) GaAs wafers (Wacker Chemitronic*) were degreased in trichloroethylene (TCE) and then etched in 50% HCl solution for 1 min before being loaded into the evaporation chamber. Rhodium films of thicknesses ~150Å and ~600Å were deposited on the two separate undoped wafers by electron gun evaporation at a pressure below 10^{-6} torr. A metal mask with circular holes (1 mm in diameter) was placed on the Te-doped GaAs wafer so that circular diodes with ~1000Å of Rh were formed under similar evaporation conditions. The samples were then capped with ~1000Å SiO_2 on both sides in order to prevent excessive As loss during heat treatment. Annealing was carried out in flowing N_2 ambient in the temperature range of 300°C to 800°C.

The 150Å Rh/GaAs samples were analyzed by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV $^4He^+$ beam incident at 50° with respect to the specimen normal with a depth resolution of <50Å. Samples with ~600Å Rh were investigated by Heavy Ion Rutherford Backscattering Spectrometry (HIRBS) using

a 20 MeV $^{16}O^{++}$ beam at normal incidence. The improved mass resolution of HIRBS facilitated the identification of the interface reactions between the Rh films and the GaAs substrate [3, 16]. X-ray diffraction (XRD) was also performed as a complementary technique for phase identification. Electrical measurements were performed by the current-voltage (I-V) technique. The Schottky barrier heights of the diodes were obtained by considering the ideal thermionic emission equation

$$J = A^* T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \cdot \left[\exp\left(\frac{qV_a}{nkT}\right) - 1\right]$$

where J is the current density, A* is the effective Richardson constant (taken to be $\approx 8.6\ A/cm^2/K^2$ in this work), k is the Boltzmann constant, V_a is the applied voltage, $q\phi_b$ is the Schottky barrier height of the diode and n is the ideality factor which is ≈1 if the thermionic emission process dominates.

Figure 1(a) shows a series of RBS spectra from 150Å Rh/GaAs samples as deposited and annealed at 300, 400 and 500°C for 20 min. An interface reaction is detected for the sample annealed at 300°C for 20 min. It is estimated from the RBS spectrum that ~45Å of Rh is reacted with ~75Å of GaAs. The ratio of the amount of Rh to that of GaAs in the reacted layer is therefore ≈2.0±0.1. Deconvolution of the RBS spectrum of the sample annealed at 400°C for 20 min is shown in Fig. 1(b). It is observed that the entire 150Å of Rh film is reacted in this sample resulting in the formation of a uniform reacted layer containing all three constituents (Rh, Ga and As). Energy loss and yield ratio analyses of the spectrum give [Rh]:[Ga]:[As]≈2:1:1 for this reacted layer. RBS measurement for the sample annealed at 500°C for 20 min shows that a uniform reacted layer with [Rh]:[Ga]:[As]≈1.6:1:1 is formed. No new feature is detected by RBS for samples annealed at temperatures greater than 500°C. These results

suggest that the intermediate phase(s) formed at temperatures lower than 400°C has an overall Rh concentration higher than that of the final phase(s) of the system.

HIRBS spectra from 600Å Rh/GaAs samples as deposited and annealed at 700°C for 20 min are shown in Fig. 2. Complete reaction of the Rh film with the GaAs substrate is evident for the sample annealed at 700°C for 20 min. Deconvolution of this spectrum shown in Fig. 2 (dashed lines) indicates that two distinct layers of Rh-Ga and Rh-As compounds are formed on GaAs. Yield ratio and energy loss analyses of the HIRBS spectrum suggests that the top layer is primarily a compound of Rh and Ga with [Rh]:[Ga]≈1:1 while the interface layer is composed mainly of Rh and As with [Rh]:[As]≈1:2. The ratio of the amount of reacted Rh to that of GaAs measured from the spectrum is ≈1.5. Therefore the reaction: $3Rh + 2GaAs \rightarrow 2RhGa + RhAs_2$ is consistent with the HIRBS measurement for the sample annealed at 700°C. This is in good agreement with the result of the 150Å Rh/GaAs which gives an end phase(s) with [Rh]:[GaAs]≈1.6:1. In addition to the layered structure detected by HIRBS, as much as 15% of RhGa is found in the $RhAs_2$ layer. Similarly ~10% of As is found in the RhGa layer.

The x-ray diffraction spectrum from the sample annealed at 350°C for 120 min shows the existence of two new phases, namely RhGa (CsCl structure with a_0=3.01Å) and RhAs (orthorhombic structure with a_0=5.62Å, b_0=3.58Å and c_0= 6.00Å) with a large amount of unreacted Rh. Only two phases are detected from the XRD spectrum from the sample annealed at 700°C: RhGa and $RhAs_2$ (monoclinic structure with a_0=6.041Å, b_0=6.080Å, c_0=6.126Å and β=114°20').

The RBS, HIRBS and XRD results on the 150Å and 600Å Rh films indicate that the system starts to react at annealing temperature as low as 300°C. The initial reaction products are RhGa and RhAs. Annealing at higher temperatures (>400°C) results in the nucleation of a new phase $RhAs_2$. The $RhAs_2$ phase

continues to grow at the interface at the expense of the RhAs phase until finally a RhGa/$RhAs_2$/GaAs structure is formed. For thin Rh films (~150Å) these three phases are laterally separated in order to minimize interface energy when the grain size of these phases is larger than the film thickness.

Schottky barrier heights ϕ_b and the ideality factors n as measured by the I-V dependence of the Rh/n-GaAs diodes as deposited and annealed at various temperatures are shown in Fig. 3(a). The leakage current densities of the diodes at -0.4 V bias are shown in Fig. 3(b). From Figs. 3(a) and (b) it is obvious that the diode characteristics undergo improvement after annealing at low temperatures (<300°C), degrade after annealing at temperatures ranging from 350°C to 450°C, recover after annealing in the temperature range of 500°C to 550°C and finally, fail completely after annealing at temperatures higher than 600°C.

After annealing at 300°C for 20 min, the ideality factor n decreases from 1.57 to 1.29 and $q\phi_b$ increases from 0.655 eV to 0.732 eV. A decrease in the leakage current by an order of magnitude is also noted as a result of the annealing. Since RBS analysis on 150Å Rh films detected reaction at this annealing temperature, this improvement in the diode characteristics can be attributed to the formation of a thin layer (~100Å) of RhAs at the interface so that morphologically uniform and defect-free interface is obtained.

Drastic degradation (n increases to higher than 1.7, $q\phi_b$ reduces to 0.6 eV and the leakage current increases by three orders of magnitude) results for the diodes annealed at the temperature range of 400°C and 450°C. This electrical degradation is most probably the result of the nucleation of the new binary phase $RhAs_2$ at the interface leading to a "non-planar" interface morphology. The recovery of diode characteristics (n=1.23 and $q\phi_b$=0.74 eV)

after annealing at 500°C can be explained by the formation of a uniform layer of $RhAs_2$ at the interface so that a uniform interface morphology is restored.

Annealing at temperatures higher than 550°C results in severely degraded diodes. The diode annealed at 700°C becomes ohmic rather than rectifying. Since HIRBS analysis of the sample annealed at 700°C shows a significant amount of Ga and As in the reacted compounds on GaAs, it is expected that this diode failure is the result of the GaAs outdiffusion (and possibly Rh in-diffusion) due to the dissociation of GaAs at the interface at high temperatures.

A similar final morphology of the type: $MGa/MAs_2/GaAs$ has also been observed for the more familiar Pt/GaAs system [1-4]. However, for Pt/GaAs, initial interface reactions at ~350°C result in the formation of a $Pt_3Ga/PtAs_2/GaAs$ structure as compared to RhGa/RhAs/GaAs in the Rh/GaAs case. After annealing at higher temperatures (>400°C), the PtGa phase starts to nucleate at the $Pt_3Ga/PtAs_2$ interface while the morphology of the GaAs interface remains uniform. Therefore, no electrical degradation similar to that of the Rh/GaAs system is observed during the phase transformation.

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FIGURE CAPTIONS

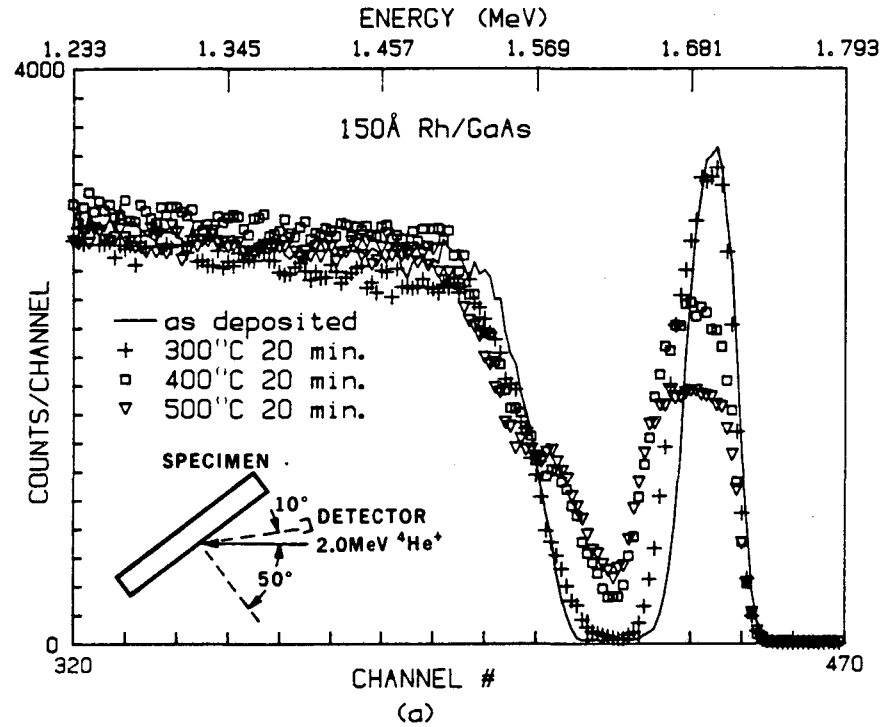
Figure 1(a) High resolution RBS spectra from the 150Å Rh/GaAs samples as deposited and annealed at 300, 400 and 500°C for 20 min. The back-scattering geometry is also shown in this figure.

1(b) Deconvolution of the RBS spectrum from the sample annealed at 400°C for 20 min.

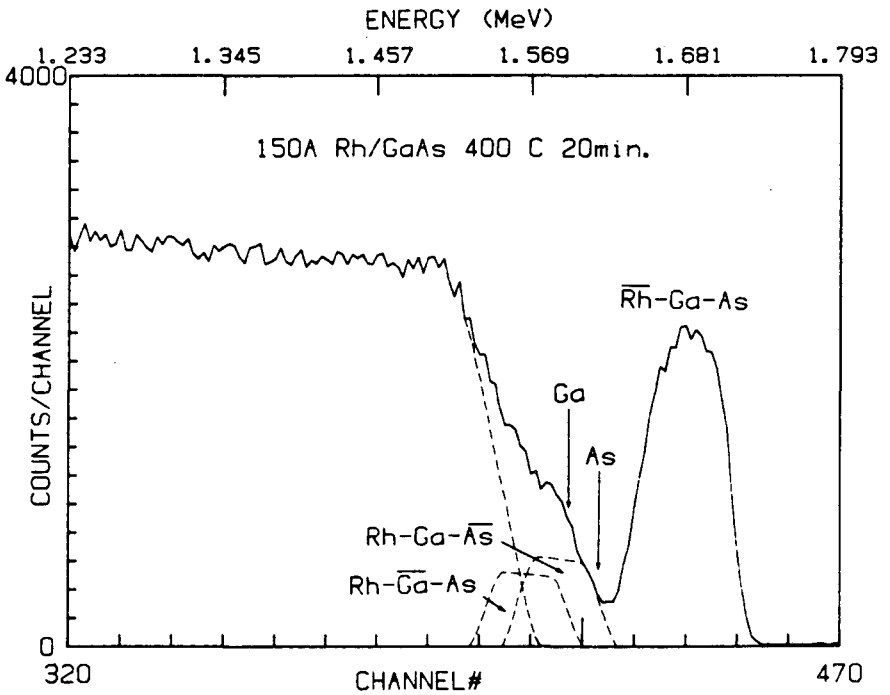
Figure 2 HIRBS spectra from 600Å Rh/GaAs samples as deposited and annealed at 700°C for 20 min. Deconvolution of the spectrum from the annealed sample is also shown (dashed lines).

Figure 3(a) Ideality factor n and Schottky barrier height ϕ_b measured by I-V technique for Rh/n-GaAs diodes as deposited and annealed at different temperatures for 20 min.

3(b) The leakage current density at -0.4 V bias for diodes annealed at different temperatures for 20 min.



(a)



(b)

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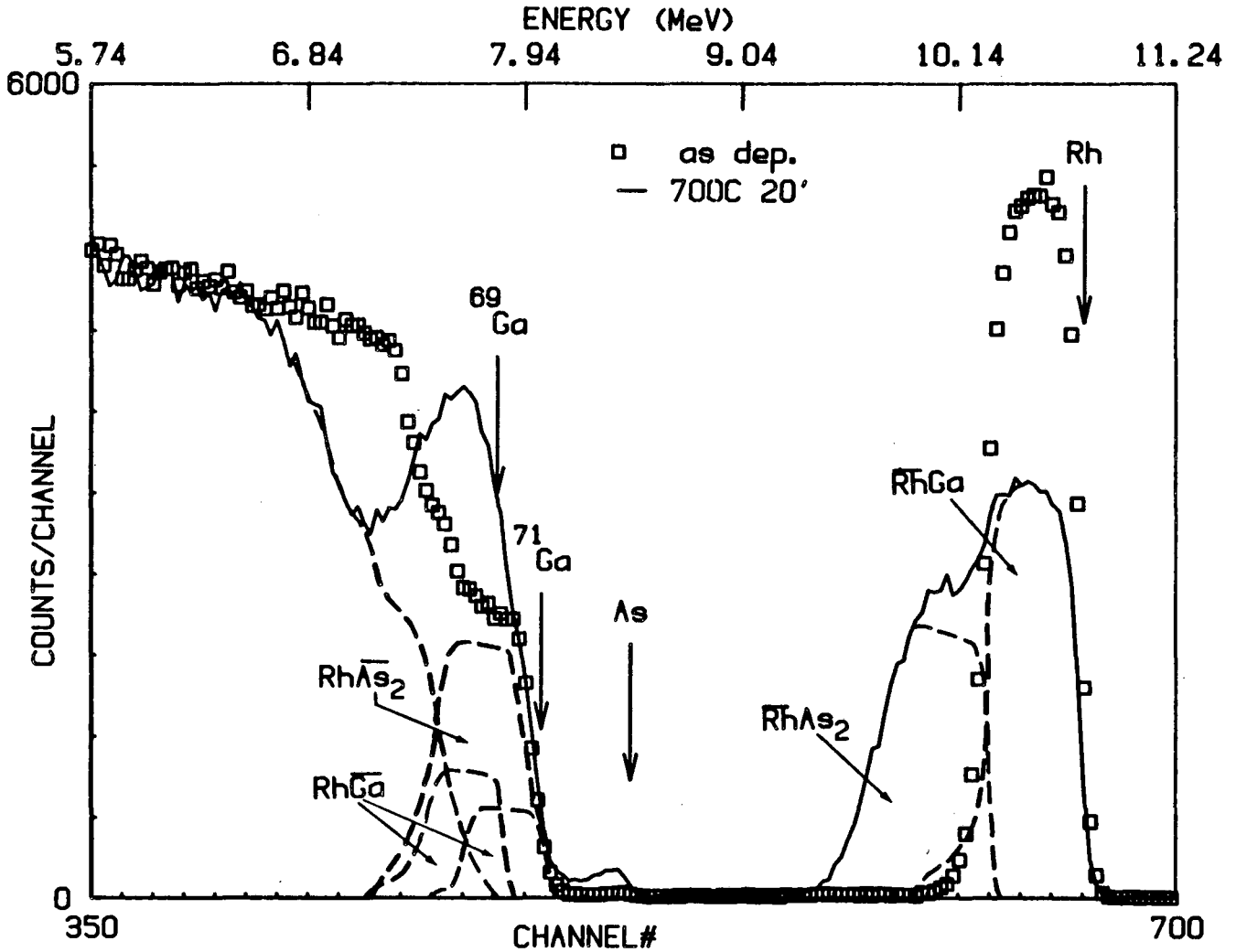
Fig. 1



XBL 863-1067

Fig. 2

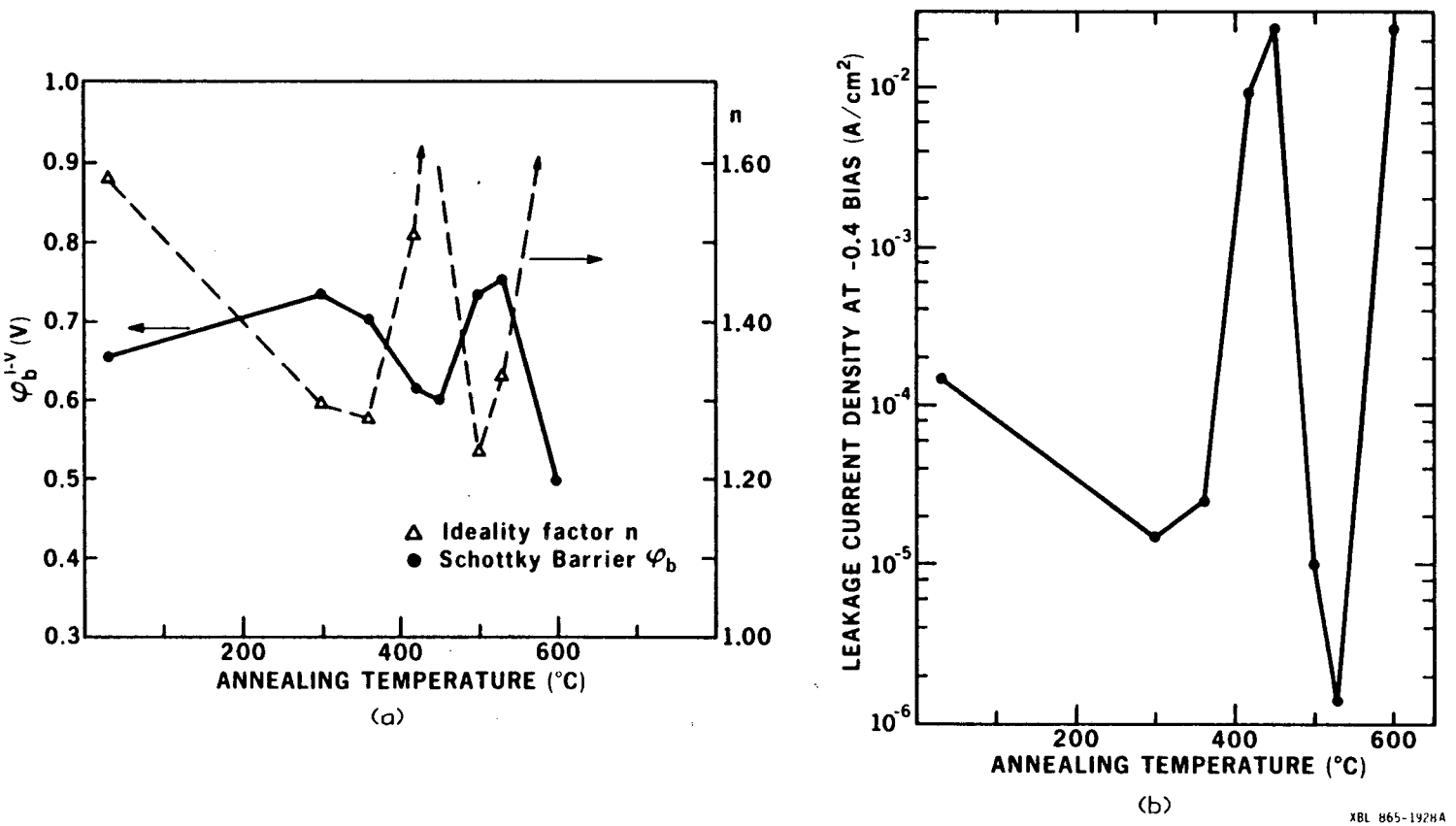

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
φ_b^{I-V} (V)
n
1.60
1.40
1.20
1.00
Ideality factor n
Schottky Barrier φ_b
200
400
600
ANNEALING TEMPERATURE (°C)
(a)
LEAKAGE CURRENT DENSITY AT -0.4 BIAS (A/cm^2)
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
200
400
600
ANNEALING TEMPERATURE (°C)
(b)
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Fig.3

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