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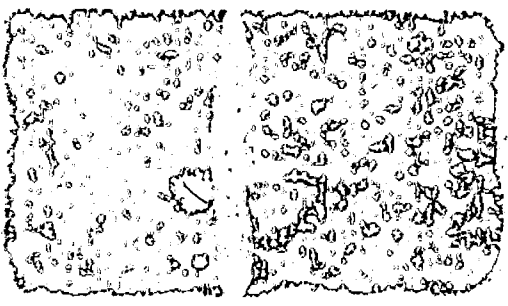
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INVESTIGATION OF METAL/GaAs REACTIONS
BY HEAVY ION RUTHERFORD BACKSCATTERING SPECTROMETRY (HIRBS)

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ABSTRACT

Thermally activated metallurgical reactions between GaAs and various metals of potential importance in contact structures were studied using Heavy Ion Rutherford Backscattering Spectrometry (HIRBS). The improved mass resolution obtained with heavy ions (^{16}O) as projectiles for backscattering measurements facilitated the identification of the various intermetallic compounds formed on GaAs.

The metal/GaAs systems investigated in this study included Pt/GaAs, Pd/GaAs, and Ni/GaAs. Three different binary compounds were formed in the Pt/GaAs system during annealing. Complete reaction between 1200Å of Pt and GaAs was observed after annealing at 500°C for 20 min. Reactions in Pd/GaAs and Ni/GaAs systems were, however, very different from that of Pt/GaAs. Both Pd and Ni formed ternary compounds with GaAs. Detailed information on the various compound compositions of the three systems as measured by HIRBS is presented. Comparisons of results on similar systems obtained by using other analytical techniques are discussed.

I. INTRODUCTION

In recent years, with the development of high speed, high density large scale GaAs integrated circuits, problems associated with the metal-GaAs contacts have attracted much attention. Many of the works done in this area have been directed toward the study of interfacial reactions between metal thin films and GaAs substrates. Owing to the ternary system involved, metallurgical reactions between metal and GaAs are much more complex than the well studied metal-Si reactions.

Near noble metals such as Pt, Pd and Ni are known to be reactive to GaAs [1]. Reactions between GaAs and Pt [2-4], Pd [5-10] and Ni [11-13] thin films have been studied by many investigators. Both binary and ternary phases are reported for the Pd/GaAs and the Ni/GaAs systems while only binary phases are detected in the Pt/GaAs system after annealing. However, disagreements on the compositions and the final distribution of these phases measured by different investigators are still unresolved.

Heavy Ion Rutherford Backscattering Spectrometry (HIRBS) is a powerful analytical technique for the characterization of metal-semiconductor interactions. Analysis of contact structures on Ge and GaAs with HIRBS has been reported [14]. The principal advantage of HIRBS is the improved mass resolution for the analysis of high atomic number targets [15]. Fig. 1(a) shows plots of the 170° backscattering coefficient $K=E_1/E_0$ for the case of ^4He and ^{16}O projectiles where E_1 is the backscattered energy and E_0 is the incident energy of the projectile ions. The increased slope of the ^{16}O curve for target masses $A>50$ clearly indicates the improved mass resolution achieved. The curves in fig. 1(b) show mass resolutions calculated using $\Delta M/\Delta E$ as derived from the relationships of fig. 1(a) combined with a typical experimental ion

detection energy resolution (full width at half maximum) of 20keV for ^4He and 100keV for ^{16}O . Under these assumptions, the ability to resolve adjacent target isotopes extends to $A=150$ for ^{16}O compared to $A=50$ for ^4He .

In this paper, the investigation of thermally activated reactions between GaAs and Pt, Pd and Ni thin films using HIRBS is described. Information on the compositions and the depth distribution of the various phases formed on GaAs is obtained. X-Ray Diffraction (XRD) is also applied as a complementary technique for phase identification. Comparison of results obtained in this study with work reported in the literature is also discussed.

II. EXPERIMENTAL

Undoped semi-insulating (100) GaAs wafers were degreased in trichloroethane (TCA) and etched with a 50% HCl solution for 1 min. to remove the native oxide on the GaAs surface before metal deposition. Pt, Pd and Ni films of thicknesses $\sim 1200\text{\AA}$, $\sim 700\text{\AA}$ and $\sim 600\text{\AA}$ respectively were deposited onto the GaAs wafers in a vacuum of $\sim 1 \times 10^{-6}$ torr using electron beam evaporation. The wafers were then cut into small pieces (4mmX4mm) and capped on both sides with $\sim 2000\text{\AA}$ of SiO_2 using Plasma Enhanced CVD. Annealing was carried out in the temperature range of 200-800°C for various time durations in flowing N_2 ambient. The oxide cap was then removed in a buffered HF solution.

Heavy Ion Rutherford Backscattering Spectrometry (HIRBS) measurements were performed with a 20 MeV $^{16}\text{O}^{++}$ beam generated by the 88" cyclotron at the Lawrence Berkeley Laboratory [14]. A Si surface barrier detector of the annular type with 20keV (FWHM) energy resolution for 5MeV α particles was used for collecting the backscattered ions at a scattering angle of 176° with a

detection solid angle of 16.5msr. Typical beam current was ~30nA and a total charge of ~25 μ C was accumulated for each sample.

III. RESULTS AND DISCUSSION

1. Pt/GaAs

Fig. 2(a) shows a series of HIRBS spectra of a 1200 \AA Pt film on a GaAs substrate as deposited and after annealing at 300, 400 and 500 $^{\circ}$ C for 20 min. Reactions between Pt and GaAs at the interface are observed after annealing at 300 $^{\circ}$ C. Analysis of the spectrum using semi-empirical energy loss data for ^{16}O projectiles indicates that ~250 \AA of Pt reacted with the GaAs substrate. Significant Ga outdiffusion is also noted by HIRBS. The amount of Ga in the unreacted Pt film is estimated to be ~0.8 atomic percent. This outdiffusion of Ga has been reported by Kumar [3]. After annealing at 400 $^{\circ}$ C for 20 min., the Pt film is fully reacted. The high mass resolution of HIRBS unambiguously identifies that the top layer is composed of a compound of Pt and Ga with no detectable amount of As present, while the underlying layer at the GaAs interface is primarily a Pt-As compound. A layer sequence $\text{Pt}_3\text{Ga}/\text{PtGa}/\text{PtAs}_2/\text{GaAs}$ is consistent with the HIRBS results. The presence of these three binary phases is confirmed by X-Ray Diffraction.

Only two distinct layers of PtGa and PtAs_2 are detected by HIRBS and XRD after annealing at 500 $^{\circ}$ C for 20 min. This layered structure is clearly shown in the deconvoluted HIRBS spectrum of this sample in fig. 2(b). It is also noticeable that ~15% of PtGa is present in the PtAs_2 layer while $\sim 10^{19}/\text{cm}^3$ of As is found at the surface of the sample. Except for the As outdiffusion,

which has not been reported, the phase formation mechanism observed here is in good agreement with results obtained by other investigators using various other techniques [2-4,16].

No new phase is detected after annealing at temperatures higher than 500°C. After annealing at 800°C for 20 min. HIRBS measurement shows that a significant amount of Pt ($\sim 10^{20}/\text{cm}^3$) diffuses into the GaAs substrate to a depth $>1700\text{\AA}$. This interdiffusion of Pt and As(Ga) at the interface may be the source for electrical degradation of Pt/n-GaAs Schottky diodes after high temperature annealing ($>500^\circ\text{C}$) [17,18].

2. Pd/GaAs

HIRBS spectra of 700Å Pd on GaAs as deposited and annealed at 350, 400 and 500°C for 10 min. are shown in fig. 3(a). After annealing at 350°C for 10 min., the entire Pd film is reacted with the GaAs substrate forming a layer containing all three constituents (Pd, Ga and As). The deconvolution shown in fig. 3(b) indicates that the HIRBS data are consistent with the interpretation of a uniform reacted layer with a composition of $[\text{Pd}]:[\text{Ga}]:[\text{As}]\approx 4:1:1$. An XRD spectrum of this sample shown in fig. 4 shows that this layer is a ternary phase identified previously by Kuan et. al. [8] and Sands et. al. [9, 10, 16] as $\text{Pd}_x\text{Ga}_{1+y}\text{As}_{1-y}$ (phase II) using Transmission Electron Microscopy (TEM) with x ranging from 2 to 4 and y from 0 to 0.3 depending on the thickness of the Pd film and the annealing conditions [16]. With a relatively thick ($\sim 700\text{\AA}$) Pd film and oxide capping during annealing, our result indicates a nominal composition of Pd_4GaAs . Another ternary phase (phase I) has also been reported [8-10,16] for Pd-GaAs annealed at temperatures below 250°C. A HIRBS measurement

on the sample annealed at 250°C shows a very thin reacted layer (~50–100Å) at the Pd–GaAs interface. However, the composition of this phase cannot be measured due to the limited depth resolution in the present HIRBS system.

The reacted layer becomes less rich in Pd after annealing at 400°C for 10 min. A composition of [Pd]:[Ga]:[As]=3.2:1:1 is measured. The XRD spectrum taken from this sample shows that this layer is still phase II. After annealing at 500°C for 10 min., the three components of the system are still present at the surface layer with [Pd]:[As]=1.4:1. XRD measurement on this sample (fig. 4) identifies three binary phases, namely Pd₂Ga, PdGa and PdAs₂. Since the Pd signal in the HIRBS spectrum seems relatively uniform in height, it can be assumed that the three phases form a mixture in the reacted layer probably in the form of small patches.

Annealing at 600°C for 10 min. results in an increase in the surface Pd concentration ([Pd]:[As]=2.2:1). The XRD spectrum in fig. 4(c) shows that only PdGa and PdAs₂ are present at this temperature. Hence, it can be expected that a certain degree of phase separation starts to occur at high annealing temperatures (>500°C) with the surface region more PdGa rich and the interface region more PdAs₂ rich. It has been reported [5, 7] that only PdGa is detected after annealing at temperatures greater than 500°C. The deficiency of As noted in these studies are mainly the result of excessive As vaporization at high temperatures. Since oxide caps are applied during annealing in our study, no significant As loss occurs and therefore, the end phases of the system are PdGa and PdAs₂.

3. Ni/GaAs

A thin Ni film (~600Å thick) is completely reacted with the GaAs substrate after annealing at 200°C for 10 min. Fig. 5 shows the HIRBS spectra of the Ni/GaAs samples as deposited and after annealing at 200°C for 10 min. A uniformly reacted layer with [Ni]:[Ga]:[As] ≈ 3:1:1 is measured in the sample annealed at 200°C by HIRBS. The XRD spectrum taken from this sample has only two diffraction peaks at $d=2.80\text{Å}$ and 1.40Å . These peaks can be indexed as the $(01\bar{1}1)$ and $(02\bar{2}2)$ peaks of the hexagonal ternary phase Ni_xGaAs with $a_0=3.90\text{Å}$ and $c_0=5.01\text{Å}$. From this XRD pattern, a possible orientation relationship of

$$\{110\}_{\text{GaAs}} // \{\bar{1}012\}_{\text{Ni}_x\text{GaAs}} \text{ and } \langle 001 \rangle_{\text{GaAs}} // \langle 01\bar{1}1 \rangle_{\text{Ni}_x\text{GaAs}}$$

can be established. This relationship agrees well with previous results by other authors [11-13, 16]. The composition of this ternary phase as measured by HIRBS is Ni_3GaAs . This is in good agreement with the results of Sands et. al. [13, 16] but does not match with the Ni_2GaAs phase detected by Ogawa [11] and Lahav et. al. [12] using sputtering Auger Electron Spectroscopy (AES). The non-quantitativeness of the AES technique may be the source of error in the measurements. However, further study would be necessary to resolve this discrepancy.

HIRBS and XRD measurements of the sample annealed at 400°C for 10 min. indicate that the same ternary phase becomes less rich in Ni ($\text{Ni}_{2.4}\text{GaAs}$). This result tends to support the B8 structure for the Ni_xGaAs suggested by Sands et. al. [13] which could possibly tolerate variations in Ni concentration from $x=2$ to $x=4$ [16]. After annealing at 600°C, the [Ni]:[Ga]:[As] ratio in the reacted layer can only be roughly estimated as 2:1:1 due to overlapping of the Ni and Ga backscattering signals. Two binary phases, NiAs and $\beta\text{-NiGa}$ are detected by XRD. Since no macroscopic phase separation is measured by HIRBS, it can be

concluded that the NiGa and NiAs formed after annealing at 600°C tend to mix together in a single layer similar to the reaction products of the Pd/GaAs system annealed at 500°C.

IV. CONCLUSIONS

Reactions between (100) GaAs and Pt, Pd and Ni thin films have been studied with HIRBS and XRD. The results of this study suggest that solid phase reactions between near noble metals and GaAs can be divided into two main groups according to the phases formed after reactions at low temperatures (<300°C). One group of metals, such as Pt and Rh [19], form only binary phases with GaAs upon annealing. The binary phase formation is mainly due to the outdiffusion of Ga and indiffusion of the metal because of the large electronegativity difference between the metal and Ga. As a result, a layered structure with the metal-As phase at the interface and the metal-Ga phase on top is formed after annealing. The other group of metals, such as Pd and Ni, form ternary phase(s) with GaAs at low temperature (<250°C) at which Ga outdiffusion is relatively slow. Although after high temperature (>500°C) annealing the final phases are always binary, phase separation in these systems is usually much less prominent. Instead, a mixture of metal-Ga and metal-As phases in a single layer always results.

This study also demonstrates the strengths of HIRBS as a tool for investigating metal-GaAs reactions. Together with a complementary technique such as XRD for phase identification, HIRBS is capable of playing an important role in the characterization of contact structures on GaAs.

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FIGURE CAPTIONS

Fig. 1(a) Kinematic factor K versus target mass M_2 for ^4He and ^{16}O projectiles calculated for 170° scattering angle.

1(b) Mass resolution versus target mass as calculated from curves in fig. 1(a) assuming energy resolution of 20 keV and 100 keV for ^4He and ^{16}O respectively.

Fig. 2(a) HIRBS spectra from 1200\AA of Pt on GaAs as deposited and heat treated at different temperatures for 20 min.

2(b) HIRBS spectrum from 1200\AA of Pt film on GaAs after annealing at 500°C for 20 min. Deconvoluting the spectrum (---) showing the distribution of the different phases formed.

Fig. 3(a) HIRBS spectra from 700\AA of Pd on GaAs as deposited and after annealing at 350, 400 and 500°C .

3(b) Deconvolution of the HIRBS spectrum from Pd/GaAs sample after annealing at 350°C for 10 min. showing a reacted layer on GaAs with $[\text{Pd}]:[\text{Ga}]:[\text{As}] = 4:1:1$.

Fig. 4 X-Ray Diffraction spectra of Pd/GaAs system after annealing at various temperatures.

Fig. 5 HIRBS spectra from 600\AA Ni on GaAs before and after heat treatment at 200°C for 10 min. The dash line shows the deconvoluted spectrum of the annealed sample.

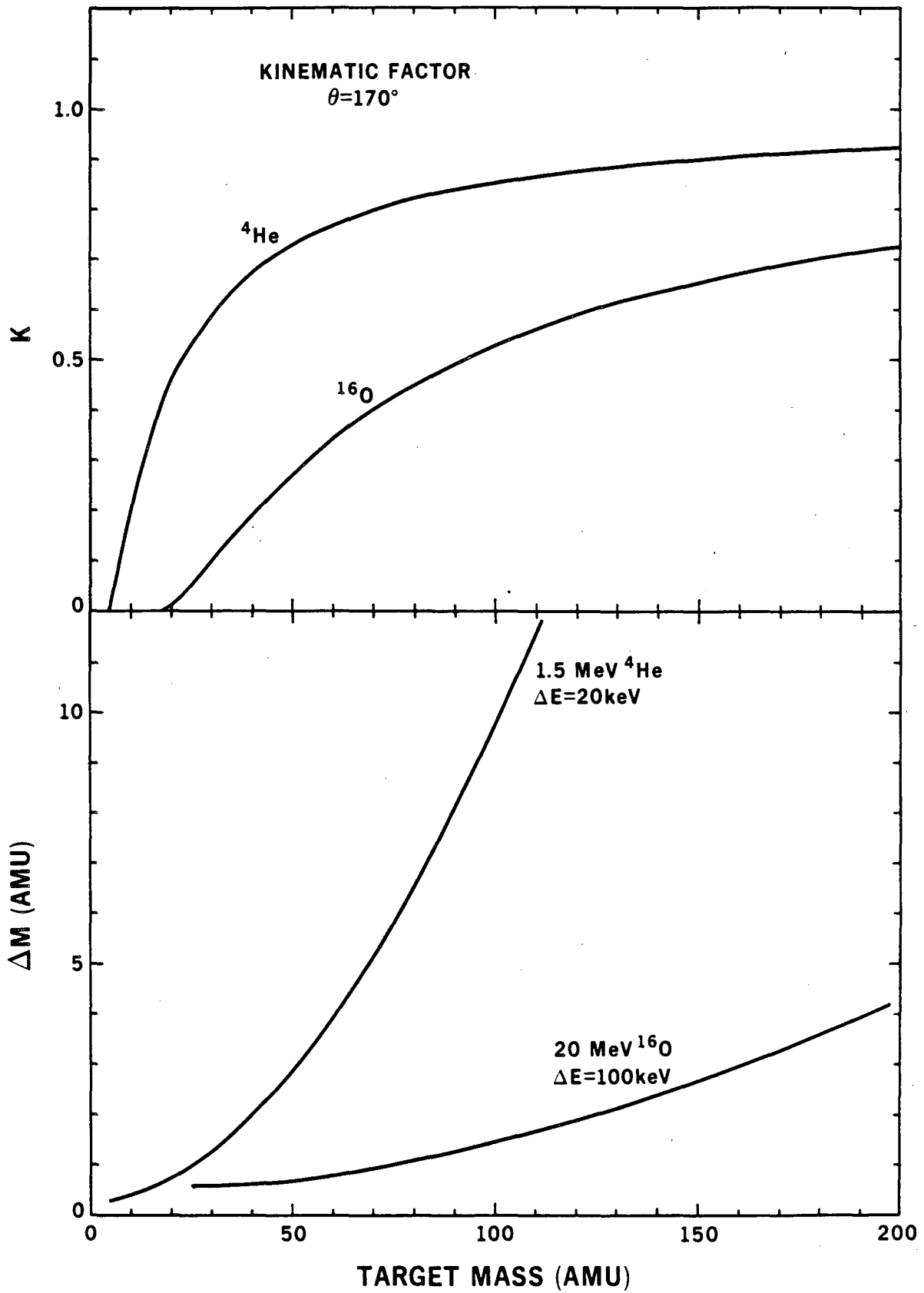
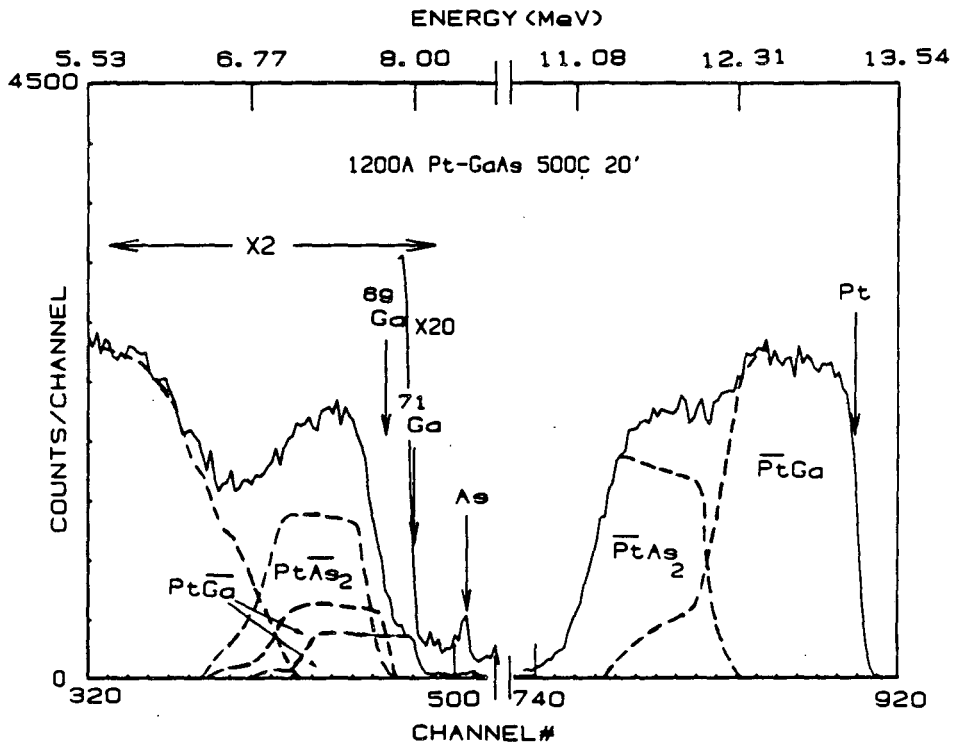
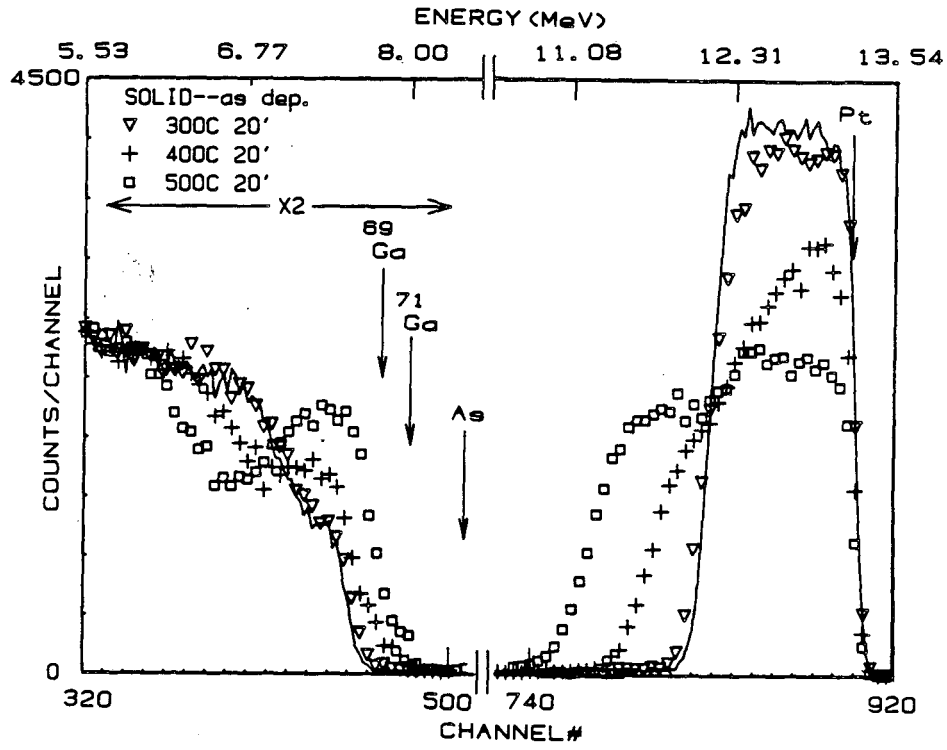
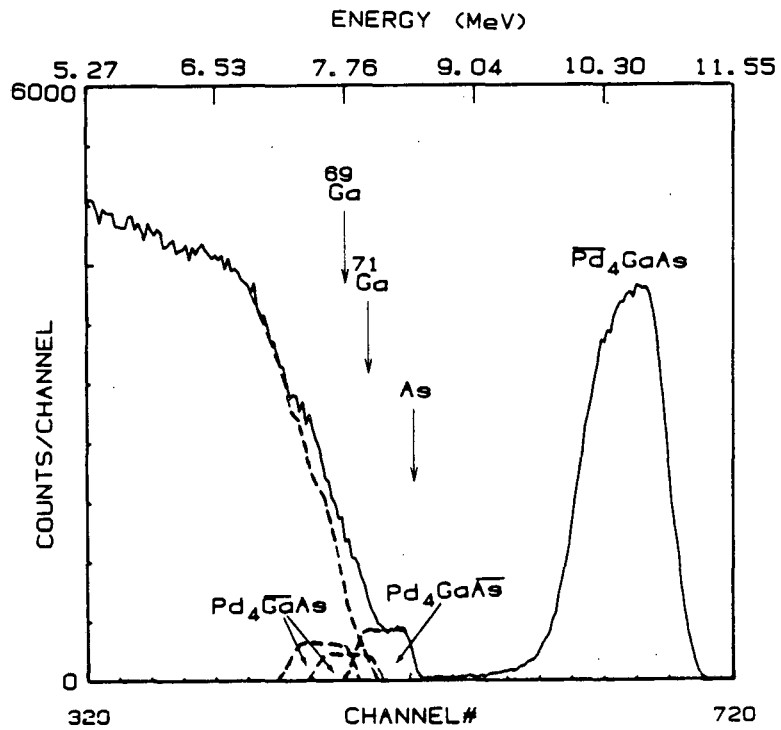
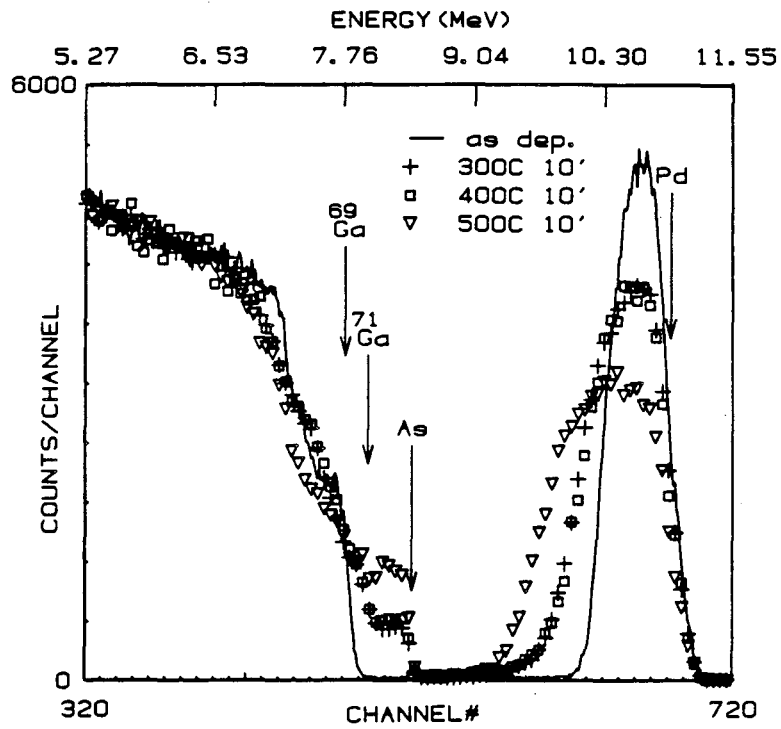


Fig. 1



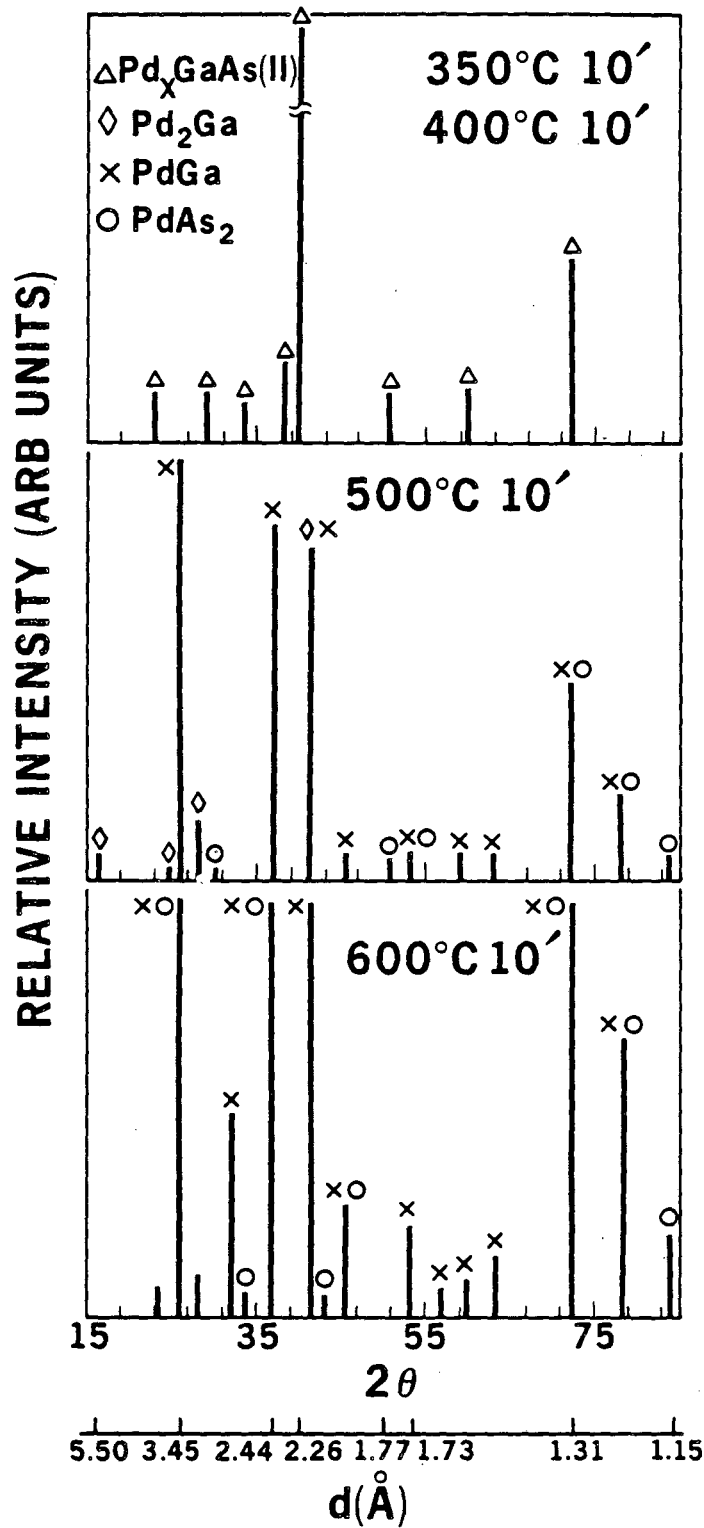
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Fig. 2



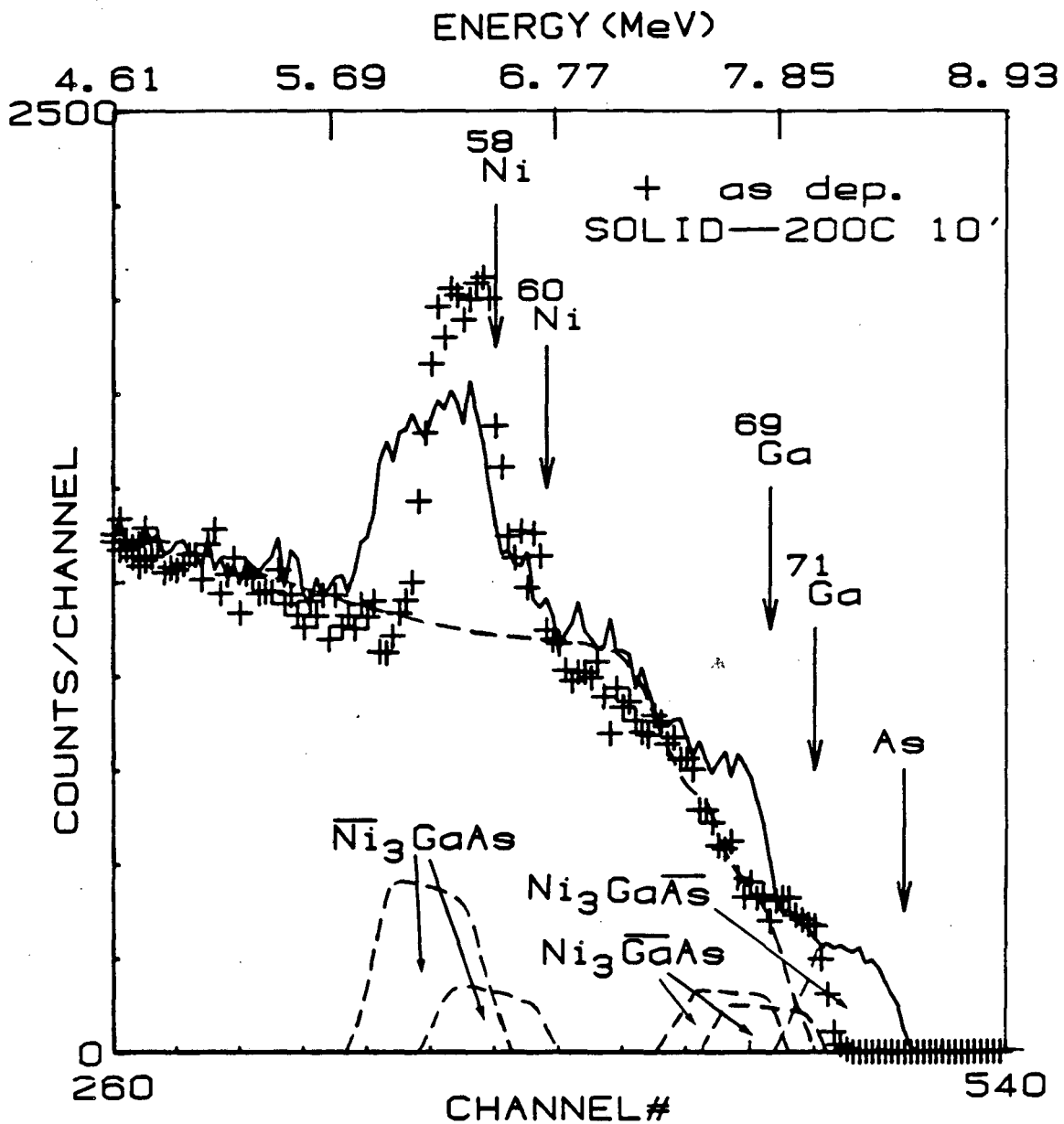
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Fig. 3



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Fig. 4



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Fig. 5

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