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Author
Sands, T.

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T. Sands, V.G. Keramidas, A.J. Yu, K.M. Yu,
R. Gronsky, and J. Washburn

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PHASE FORMATION SEQUENCE IN THE Pd-GaAs SYSTEM

T. SANDS,[*+] V.G. KERAMIDAS[*], A.J. YU[**], K.M. YU[+], R. GRONSKY[#] AND J. WASHBURN[#]

[*] Bell Communications Research, Inc., Murray Hill, NJ 07974
[+] Center for Advanced Materials and [#]Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720
[**] Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853

ABSTRACT

The morphological aspects of ternary phase formation during the Pd-GaAs reaction have been studied by application of transmission electron microscopy (TEM) and Rutherford backscattering (RBS) techniques. The TEM images show that the first product phase, "phase I", forms during deposition of Pd onto (100) GaAs and exhibits the preferred orientation $[0001]_I \sim // [01\bar{1}]_{GaAs}$. In the presence of unreacted Pd, the second phase, "phase II", nucleates at large-angle grain boundaries in the phase I film as the annealing temperature increases above $\sim 250°C$. Energy dispersive analysis of x-rays and RBS suggest the nominal compositions Pd_3GaAs and Pd_4GaAs for phases I and II, respectively.

INTRODUCTION

Miniaturization and integration of compound semiconductor electronic and optoelectronic devices requires the development of rectifying and low-resistance contacts which are adherent, reproducible, stable and laterally uniform. Meeting these criteria demands an understanding of the metallurgical interactions at metal/compound semiconductor interfaces. The metals which react with the AB substrate to form M_xAB compounds are particularly interesting since these reactions should not result in interfacial accumulations of anions or cations [1]. Recent transmission

electron microscopy (TEM) studies have shown that two ternary phases of the type $M_X AB$ are the first product phases of the Pd-GaAs reaction [1-3]. The first phase, "phase I", forms during deposition, even in the presence of a thin (1-2nm) intervening oxide layer [2-4]. Phase I has a hexagonal unit cell (a_0 = 0.672 nm and c_0 = 0.340 nm [4] or a_0 = 0.673 nm and c_0 = 0.338 nm [1]). This phase exhibits a high degree of texture on (100) GaAs with $<0001>_I//<011>_{GaAs}$ and $\{\bar{2}110\}_I$ // $\{100\}_{GaAs}$ [1,4]. Reported compositions for phase I range from Pd_2GaAs estimated by x-ray photoelectron spectroscopy [5] to $PdGa_{\sim 0.3}As_{\sim 0.2}$ measured by energy dispersive analysis of x-rays (EDS) in the TEM [2].

A second ternary phase, "phase II", has been found to form in the presence of unreacted Pd above $\sim 250°C$ [2,3]. The unit cell of phase II is also hexagonal with a_0 = 0.947 nm and c_0 = 0.374 nm [2] or a_0 = 0.92 nm and c_0 = 0.370 nm [1]. Composition estimates for phase II range from $PdGa_{\sim 0.6}As_{\sim 0.4}$ for 15 nm Pd annealed at 350°C in forming gas [2] to Pd_4GaAs for ~ 50 nm Pd annealed at 315°C in forming gas [3].

A third phase has been detected under conditions which promote the sublimation of As. This Pd-Ga phase forms during annealing in ultra-high-vacuum at T $\geq$ 350 °C [2] or during annealing in an inert or forming gas atmosphere at T $\geq$ 400 °C [2,3]. No additional phases have been conclusively identified by a combination of structural and chemical information from the same grain. As discussed by Sands et al [3], glancing angle x-ray diffraction spectra or electron diffraction ring patterns from polycrystalline films are not sufficient to identify phases in this system. Furthermore, the structural data from TEM studies [2,3] suggest that if phases such as $PdAs_2$, Pd_2Ga and Pd_2As are present, they account for only a small fraction of the film volume. In this paper, the

compositional and morphological features of the ternary phase reactions are investigated by application of TEM and Rutherford backscattering (RBS) techniques. Emphasis is placed on the interrelationships between crystallographic texture and the nucleation and growth of phases I and II.

EXPERIMENTAL METHODS

Palladium films were deposited by e⁻gun evaporation to thicknesses of 19-60 nm onto chemically cleaned (100) SI GaAs (undoped). Uncapped and SiO_2 - capped samples were annealed at temperatures up to 500 C in flowing forming gas. Both plan-view and cross-sectional TEM specimens were imaged in a top-entry JEOL JEM 200 CX at 200 keV. Compositional data were obtained from the same specimens by acquiring EDS spectra in a JEOL 200 CX TEM/STEM equipped with an ultra-thin-window x-ray detector. The concentration ratios of [Ga] to [As] were calculated using spectra from the GaAs substrate for calibration. Since reliable Pd-Ga standards are not available, the [Pd] to [Ga] ratios were estimated from the theoretical formula, $[Pd]/[Ga] = k (I_{PdL}/I_{GaK_\alpha})$ [6], which relates the ratio of concentrations of Pd and Ga to the ratio of total counts (intensities) in the L-series of Pd and the K_α peak of Ga for a thin-foil specimen. In addition, reacted films which were shown by TEM to consist of a single phase were analyzed by RBS. Measurements were performed using both 2 MeV ^{4}He and 20 MeV ^{16}O projectiles. The heavy-ion RBS (20 MeV ^{16}O) allowed the separation of the Pd signal from the substrate signal for the thicker films (60 nm Pd).

RESULTS AND DISCUSSION

Nucleation and growth of phase I

The cross-sectional TEM micrograph in Fig. 1 reveals the thin layer

of phase I which forms during deposition. Palladium is the primary diffusing species as indicated by the position of the native oxide. In this specimen the grains of phase I are $\sim$6nm thick by $\sim$18nm wide with $<0001>_I\sim//<011>_{GaAs}$ and $\{\bar{2}110\}_I \sim// \{100\}_{GaAs}$. Adjacent grains are typically misoriented by 5-10°.

In order to determine the orientation relationship uniquely (recall that [011] and [01$\bar{1}$] are not equivalent in the (100) surface), samples were etched in $Cl_2:CH_3OH$. Etchpits at pinholes in the Pd film displayed the characteristic rectangular projected shape with the long axis parallel to [01$\bar{1}$] such that the exposed gallium planes ((111)A and (1$\bar{1}\bar{1}$)A) intersect along [01$\bar{1}$] at the bottom of the pit [7-9]. This information allowed the unique determination of the orientation of cross-sectional TEM specimens. Diffraction patterns recorded with the electron beam parallel to [011] and [01$\bar{1}$] (Fig. 2) show that $[0001]_I//[01\bar{1}]_{GaAs}$. Grains with $[0001]_I//[011]_{GaAs}$ were not observed. During the reaction at higher temperatures (e.g. 200-250°C) the grains of phase I grow and coarsen until the orientation relationship above is clearly established. In these thicker phase I layers ($\sim$20 nm), adjacent grains are misoriented by $\lesssim$3° about [0001]. As will be discussed below the few large-angle grain boundaries that remain play an important role in the subsequent reaction.

These data suggest that the observed phase I - (100) GaAs orientation relationship may result from the preferential growth of grains with the fastest growth direction of phase I (assumed in this argument to be the c-axis) parallel to the fastest etching direction in the (100) GaAs surface (i.e. [01$\bar{1}$]). Nuclei with other orientations would be consumed by these fast growing grains as the reaction continued. Furthermore, the observation

that $\{03\bar{3}0\}_I$ // $(022)_{GaAs}$ is not surprising since the misfit between these planes is ∿3%.

Nucleation and growth of phase II

The series of cross-sectional images in Fig. 3 illustrate the development of the film morphology above 250°C. In Fig. 3(a) only phase I and unreacted Pd are present. Note the formation of voids in the Pd due to the fact that Pd is the primary diffusing species. Figures 3(b)-(d) show deep penetrations of phase II in different stages of development. The cross-sectional TEM image in Figure 4 reveals the nature of the deep penetrations. This image suggests that phase II has nucleated at a large-angle grain boundary (∿20° rotation about $[0001]_I$) in the phase I film. After annealing 45 nm Pd/GaAs at 315°C for 10 min, most of the Pd is concentrated in these thick patches of phase II (Fig. 3(d)). Only a thin skin (20-30 nm) of phase I remains between the deep penetrations.

The growth of phase I is probably limited in these thin (nominally monocrystalline) regions by the diffusion of Pd through the "bulk" of the phase I film. Unreacted Pd then moves by surface diffusion to large-angle grain boundaries which act as fast diffusion paths for the reacting species. After nucleating at these grain boundaries, phase II spreads laterally by transformation of phase I. At temperatures $\gtrsim$ 350°C the phase I layer is completely consumed leaving only phase II and possibly some Pd-Ga phases [3], depending on the annealing ambient.

Compositions of the ternary phases

The compositions of phases I and II formed during annealing 45 nm Pd on (100) GaAs were investigated by combining phase identification by electron diffraction with EDS analysis (Table 1). The size of the probed

area was dictated by the reacted film morphology. For instance, spectra from the sample annealed at 275°C were acquired with a small probe (10-20 nm diameter) incident on a cross-sectional specimen since unreacted Pd would have introduced ambiguities into the interpretation of spectra from plan-view samples. Note that the nominal compositions of phase I and phase II are ∿ Pd_3GaAs and Pd_4GaAs, respectively. As expected, the [Ga] to [As] ratio becomes greater than one as the annealing temperature is increased. The results of Kuan et al [2] show that the sublimation of As is even more significant for thinner films.

Since the EDS analysis presented above involved standardless quantitation for the calculation of [Pd]:[Ga], we attempted to verify these results by independent means. Two samples (19 nm Pd annealed at 250°C for 20 min. plus 350°C for 20 min. and 60 nm Pd capped with SiO_2 and annealed at 400°C for 10 min.) which were found by electron diffraction to consist entirely of phase II were subjected to RBS analysis. Spectra from both films suggest a nominal composition of Pd_4GaAs for phase II (Fig. 5), in agreement with the EDS results. The EDS data, however, indicate that the compositional range of phase II may be quite broad.

Based on the above compositional and morphological data, the formation of phase II during annealing of ∿ 19 nm of Pd on GaAs must involve one or both of the following reactions (assuming no net loss of arsenic and the presence of excess Pd as the sample temperature increased above ∿250° C). (1) $4Pd + GaAs \rightarrow Pd_4GaAs$ and 2) $Pd + Pd_3GaAs \rightarrow Pd_4GaAs$. If Pd is completely consumed during the reaction to form phase I, one might expect $4Pd_3GaAs \rightarrow 3Pd_4GaAs + GaAs$. If reaction (3) occurs it would most likely be observed by annealing a film of phase I with no excess Pd at T>250°C

under conditions which do not result in excessive As loss. Such an experiment would clarify the relative stabilities of phases I and II and would provide insight into the Pd-Ga-As thin-film phase diagram.

CONCLUSIONS

These results suggest that growth rate considerations may, in part, dictate the observed phase I - (100) GaAs orientation relationship. The degree to which this orientation relationship is established while annealing below 250°C may, in turn, determine the distribution of phase II nucleation sites at higher temperatures (T>250°C). Consequently, one would expect that the lateral uniformity of phase II films on GaAs should be affected by (1) the crystalline quality of the near-surface region of the (100) GaAs substrate (e.g. crystalline, heavily damaged or amorphous) and (2) the length of time spent at temperatures below $\sim$250°C (i.e. the degree to which the phase I grains have coarsened before nucleation of phase II). Such information may prove useful in designing laterally uniform contacts for integrated device applications.

ACKNOWLEDGEMENTS

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Table I.   Compositions of phases I and II as determined by EDS

annealing temp., time	TEM specimen geometry	diameter of area probed	composition of phase I	composition of phase II
275 °C, 10 min.	cross-sectional	10-20nm	$Pd_{3.3}Ga_{1.05}As_{0.95}$	$Pd_{5.1}Ga_{1.1}As_{0.9}$
315 °C, 10 min.	plan-view	100nm	$Pd_{3.2}Ga_{1.3}As_{0.7}$	$Pd_{4.0}Ga_{1.2}As_{0.8}$
480 °C, 10 min.[a]	cross-sectional	20nm	-----	$Pd_{4.0}Ga_{1.25}As_{0.75}$

[a] This specimen also contained $Pd_{3.3}Ga_{1.8}As_{0.2}$ as a major phase

FIGURE CAPTIONS

Fig. 1. Cross-sectional TEM micrograph of phase I layer formed during deposition of Pd onto (100) GaAs.

Fig. 2. Transmission electron diffraction patterns from phase I layer on (100) GaAs. Electron beam is parallel to (a) $[011]_{GaAs}$, $[01\bar{1}0]_I$ and (b) $[01\bar{1}]_{GaAs}$, $[0001]_I$. Indices corresponding to GaAs are underlined.

Fig. 3. Series of cross-sectional TEM images showing development of phase II penetrations. Images (a)-(c) are from different regions of sample annealed at 275°C for 10 min. after deposition of 45 nm Pd. Image (d) is from sample annealed at 315°C for 10 min. Deep penetrations are 1-2μm apart.

Fig. 4. High-resolution cross-sectional TEM image of phase II grain at bottom of deep penetration in sample imaged in Fig. 3(a)-(c). Note that adjacent grains of phase I have different orientations. Electron beam is parallel to $[01\bar{1}]_{GaAs}$, $[0001]_I$ and $[0001]_{II}$.

Fig. 5. 2.0 MeV ^{4}He RBS spectrum and deconvolution from sample annealed at 250°C for 20 min. and 350°C for 20 min. after deposition of 19 nm Pd. Sample was tilted 50°.
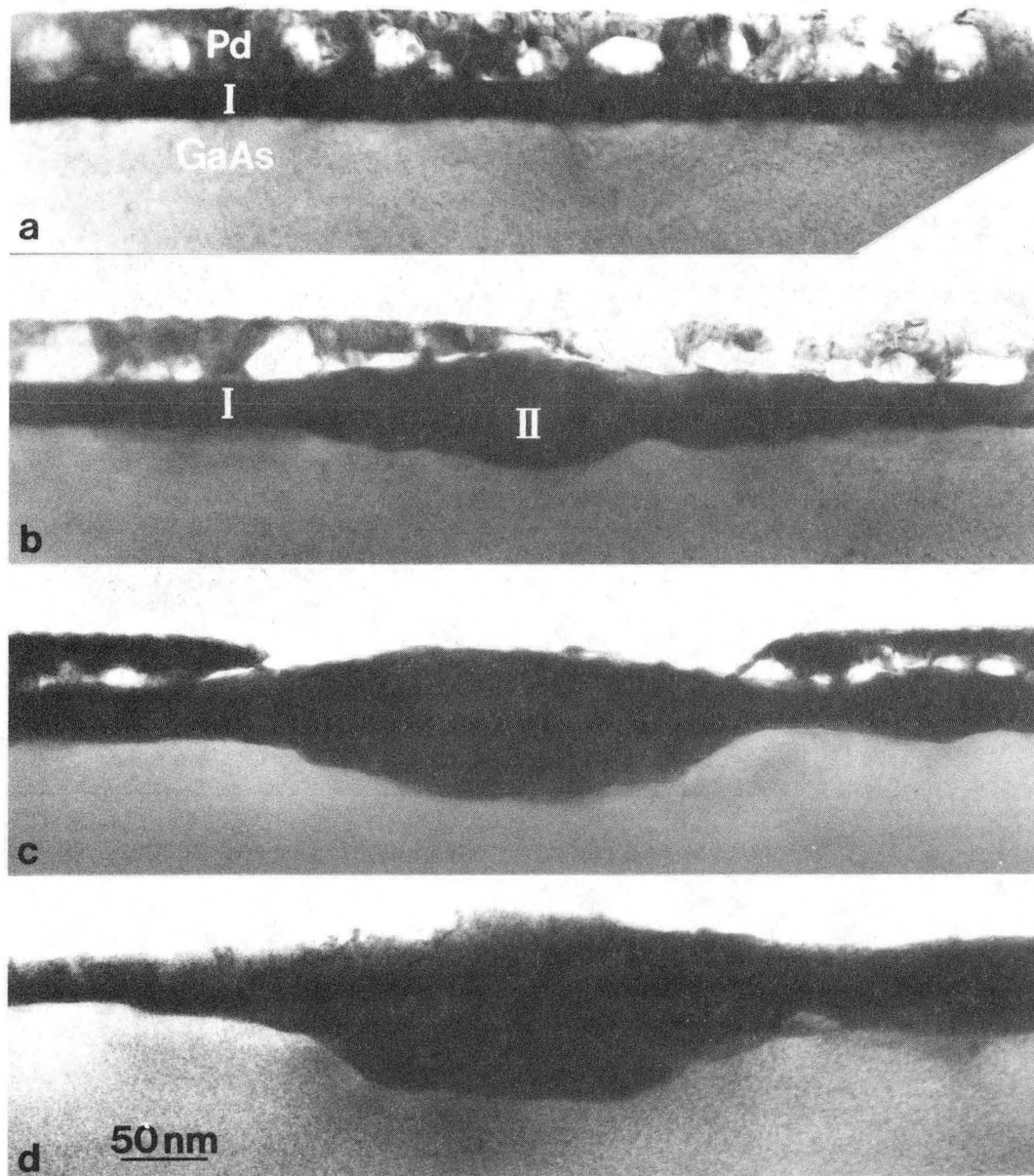
Pd

oxide

phase I
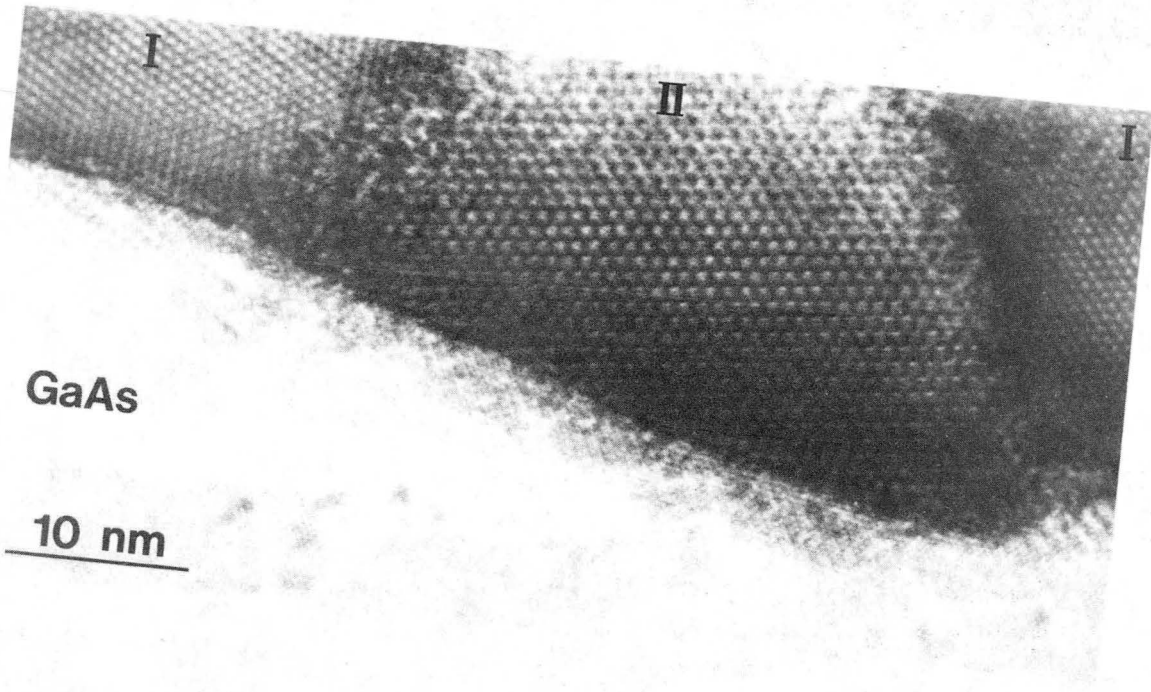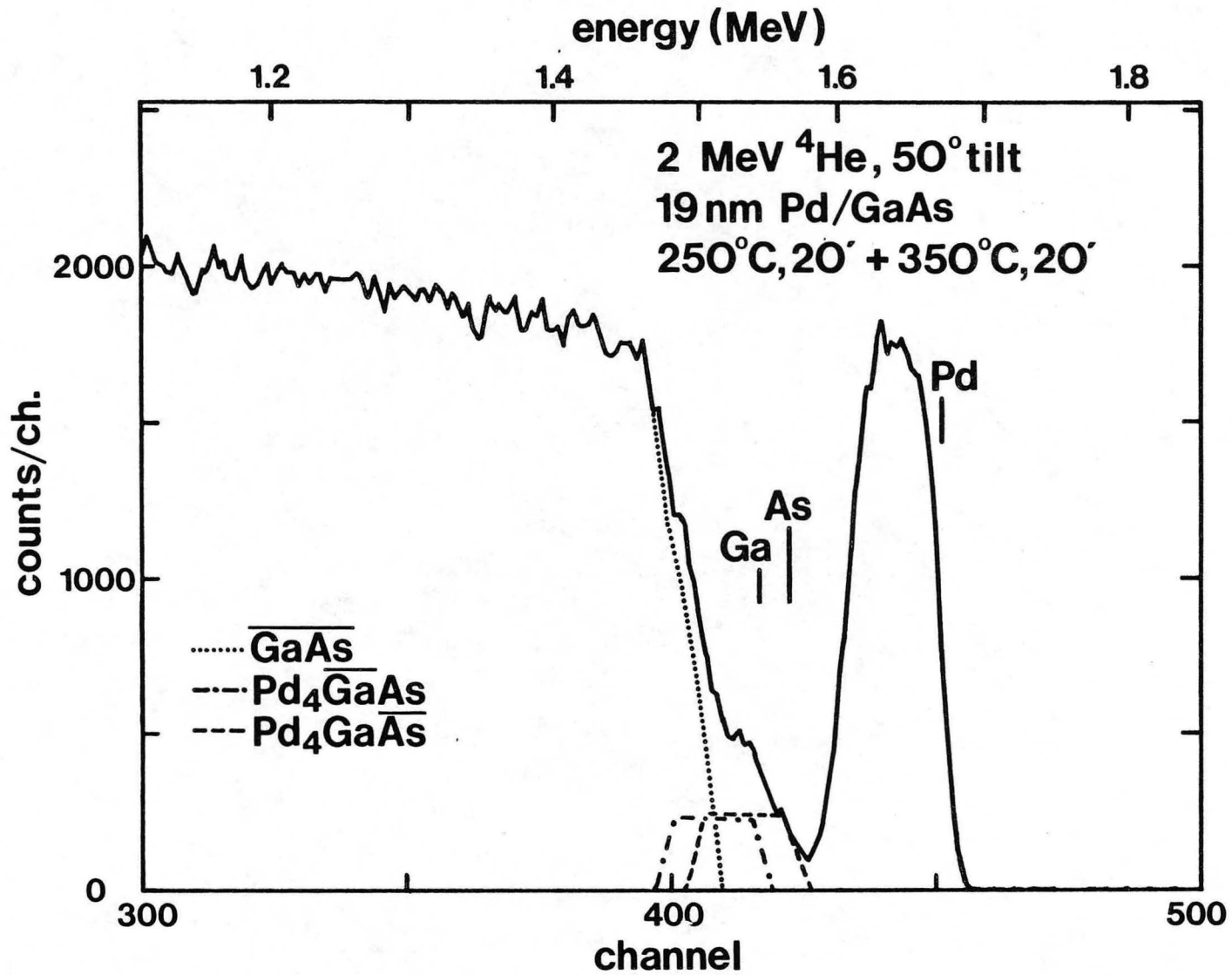
GaAs

as deposited

20 nm

XBB 858-6327

Fig. 1

XBB 850-9417

Fig. 2

50 nm

XBB 850-9419

Fig. 3

GaAs

10 nm

XBB 850-9418

Fig. 4

Fig. 5