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UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Presented at the Spring Meeting of the Materials Research Society on
Chemistry and Defects in Semiconductor Heterostructures,
San Diego, CA, April 24-29, 1989, and to be published
in the Proceedings

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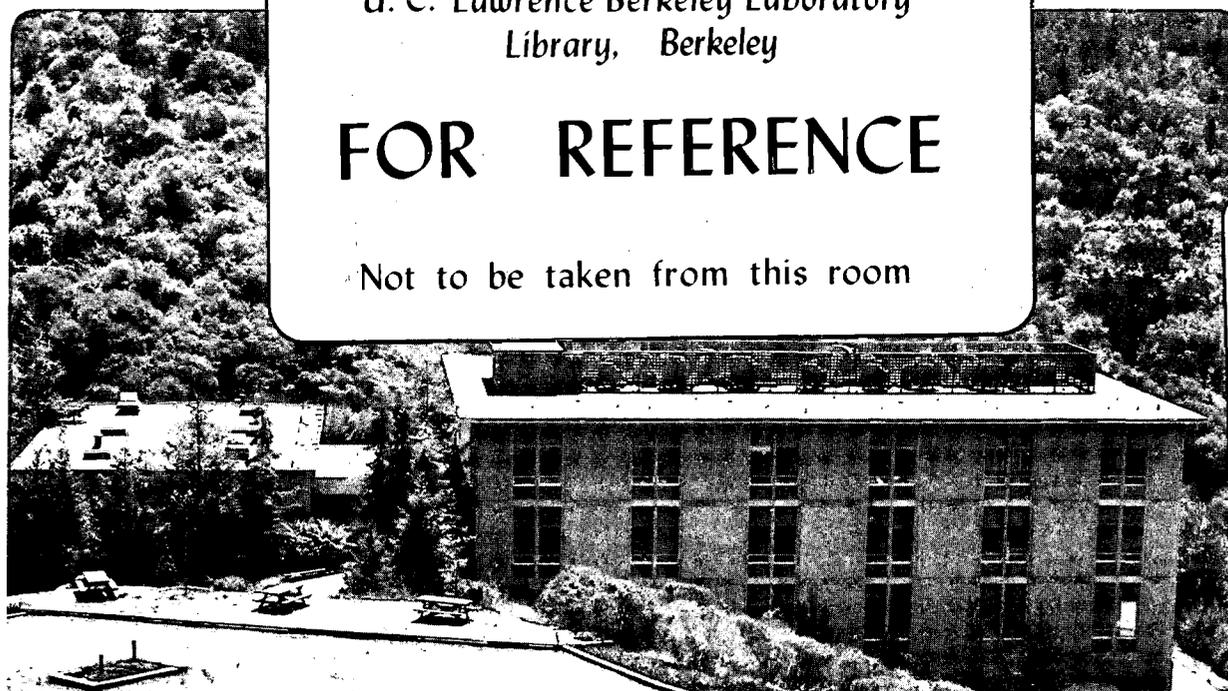
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April 1989

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Phase Formation in the Pt/InP Thin Film System

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PHASE FORMATION IN THE Pt/InP THIN FILM SYSTEM

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ABSTRACT

InP substrates with 40nm metal films of Pt were encapsulated in SiO₂, and isochronally annealed up to 600 °C in flowing forming gas. The composition and morphology of the phases that formed were studied using x-ray diffraction, Rutherford Backscattering, and transmission electron microscopy.

Results show that the Pt/InP system begins interacting at 300 °C. TEM analysis of the 350 °C anneal shows unreacted Pt and an additional polycrystalline phase, with no observed orientation relationship with the substrate. The Pt layer has been completely consumed by 400 °C, with a uniform reacted layer indicated by RBS. At high temperatures (between 500 °C and 600 °C), the reaction products are PtIn₂ and PtP₂. The two phases show a tendency for phase separation, with a higher concentration of PtP₂ at the InP/ reacted layer interface. The phosphide phase also shows a preferred orientation relationship with the substrate.

INTRODUCTION

The metal/semiconductor interface provides electrical contact with the device. These contacts must maintain appropriate electrical characteristics (Ohmic or Schottky) throughout the lifetime of the device. The characteristics are generally dependent on the phases and the morphology of the metal/semiconductor interface [1-6]. If the metal reacts with the substrate, the electrical characteristics of the device may be degraded. Reaction with the metal layer can lead to the formation of electrically active defects in the substrate, or to the formation of new interfacial phases with undesirable electrical properties [1, 2, 3]. If extensive chemical reaction occurs, the definition of the contact dimensions will be difficult to maintain, which is critical for integrated semiconductor devices. A rough interface results in uneven penetration into the substrate, and an unpredictable contact depth [7].

In order to obtain the desired electrical properties of a metal/semiconductor contact, an understanding of the metallurgical behavior of the system is essential. If the metallurgical behavior of the system is known, then the electrical properties of the system can be better controlled. For example, direct deposition of metal-III compounds that are stable in contact with the III-V substrate may inhibit undesirable reactions with the semiconductor [8, 9]. For other systems, annealing may initiate reactions which lead to desirable microstructures [5]. The ideal metal/semiconductor system will be stable at both the fabrication and operation temperatures, or will react to give the most desirable end products and microstructure [9].

Currently, GaAs is the most widely used binary III-V compound, and its interactions with various metal contacts have been extensively investigated [6]. InP is not common as a binary material, although indium and phosphorous are important components of more complex systems. Their interactions with metal contacts have only begun to be studied [10].

The Pt-InP system is the subject of this investigation. Binary phase diagrams (e.g. Pt-In and Pt-P) do not fully describe the nature of possible reaction products in these systems. This study will provide information on the interactions of these III-V elements with Pt overlayers. Using this information, extrapolation to ternary and quaternary III-V materials (e.g. GaInP, GaInAs, and GaInAsP) may be possible.

EXPERIMENT

(100) InP substrates were degreased, etched in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (5:1:1), rinsed in deionized H_2O , and blown dry in N_2 . The Pt overlayers were produced by electron-beam evaporating 40nm of Pt onto the InP substrates. They were encapsulated with SiO_2 prior to annealing to inhibit outgassing of phosphorus. The specimens were heat treated in an (95:5) $\text{Ar}:\text{H}_2$ atmosphere using various annealing schedules, ranging from 200°C to 600°C , and from 30 to 60 minutes. 600°C was chosen as the upper bound for annealing, as decomposition of the compound semiconductor substrate is difficult to control at higher temperatures. The SiO_2 caps were removed with a (10:1) distilled $\text{H}_2\text{O}:\text{buffered HF}$ solution.

The specimens were examined by a combination of X-Ray Diffraction (XRD) using a Siemens Kristalloflex Diffractometer ($\text{Cu K}\alpha$), Rutherford Backscattering Spectrometry (RBS) using a 1.95MeV $^4\text{He}^+$ beam, and Transmission Electron Microscopy (TEM) using Philips 301 and 400 microscopes operating at 100kV.

RESULTS

Pt/GaAs

For comparative purposes, this section summarizes the work of previous investigations on the Pt/GaAs system. Pt begins reacting with the GaAs substrate at $\sim 250^\circ\text{C}$ [11], with an intermediate phase distribution of Pt, Pt_3Ga , PtAs_2 , and GaAs [12]. After annealing at higher temperatures ($>400^\circ\text{C}$, 10-20 minutes), the phase distribution is PtGa, PtAs_2 , and GaAs [11-13]. This phase distribution is also reached for lower temperature, long term anneals (350°C , 20 hours) [13]. The PtAs_2 phase exhibits a preferred orientation relationship with the substrate [13]. Both PtAs_2 and GaAs are cubic structures, with a lattice mismatch of 1.8%; these values are within an acceptable range for a textured or epitaxial relationship [13]. Further annealing leads to a coarsening of the preferred grains, and a roughening of the $\text{PtAs}_2/\text{GaAs}$ interface [14].

Pt/InP

X-ray diffraction indicates that by 500°C , the reaction is essentially complete, with little change evident for 550°C and 600°C anneals. The XRD spectra for these temperatures match the standard powder diffraction spectrum for PtIn_2 ; the extra peaks

can be accounted for by PtP_2 (figure 1).

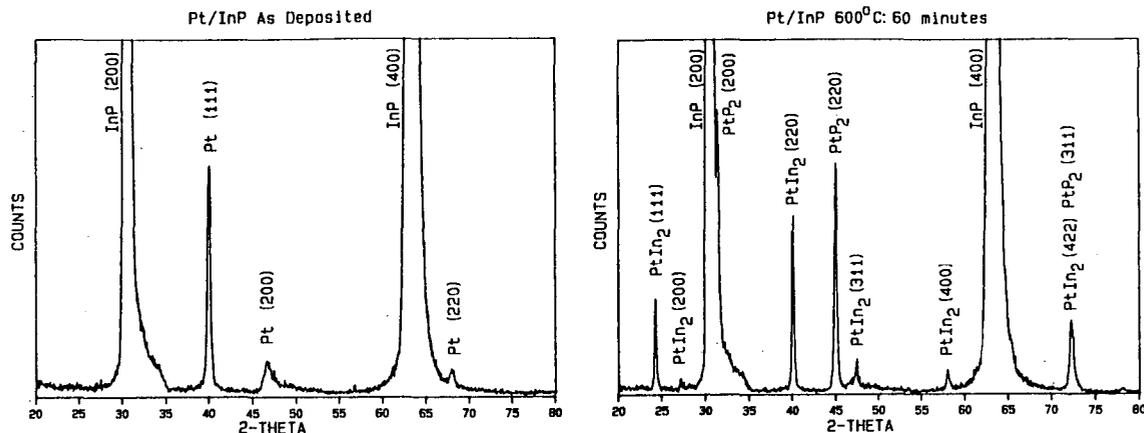


Figure 1. X-ray diffraction spectra for Pt/InP, as-deposited and 600 °C 60 minute anneal.

Rutherford backscattering spectra from these samples indicated that there was some reaction between the Pt and InP for the 300 °C anneal, and that substantial reaction occurred by 350 °C, with approximately 26nm of InP consumed. By 400 °C, the Pt layer had been completely consumed, as indicated by a homogeneous distribution of Pt, In, and P in the reacted layer (figure 2). At temperatures above 500 °C, the ratio of the Pt reacted to InP approaches 1:1, as would be expected for a combination of PtIn₂ and PtP₂.

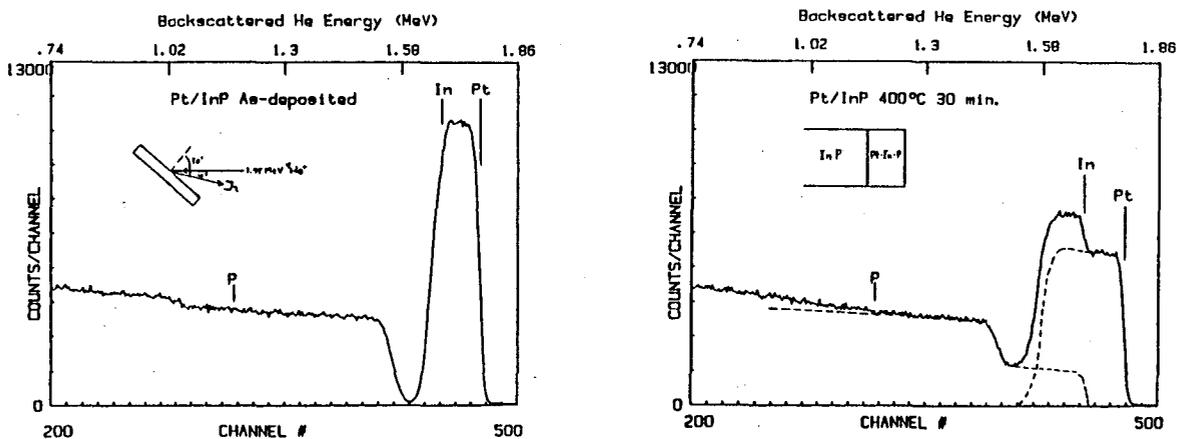


Figure 2. RBS spectra of Pt/InP, as-deposited and 400 °C 30 minute anneal.

TEM studies after the 350 °C anneal showed a polycrystalline microstructure with an average grain-size of 10nm, as compared to 20nm for the as-deposited Pt layer (figure 3). Electron diffraction indicated the presence of unreacted Pt and additional

polycrystalline phases. In the 400 °C specimen, TEM showed a polycrystalline microstructure, with some large lath-like grains (20nm by 200nm) in a textured polycrystalline matrix. Identification of the phases present is in progress.

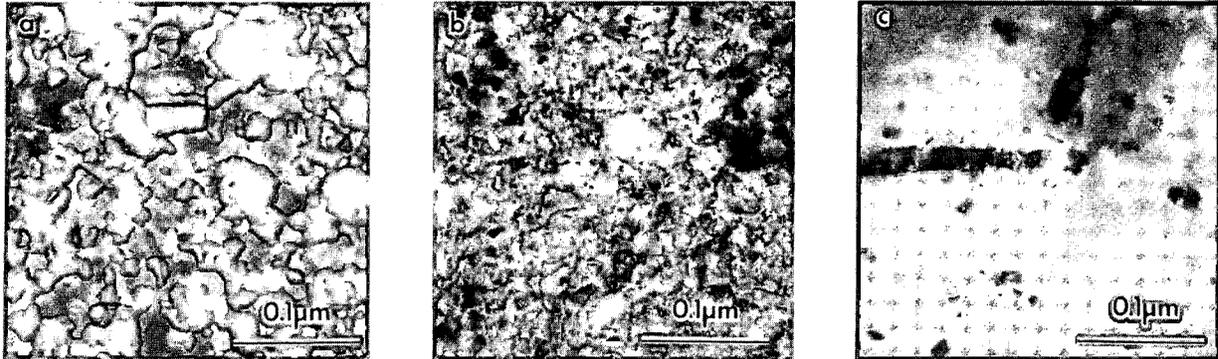


Figure 3: TEM micrographs of plan-view Pt/InP specimens. a) as deposited, b) 350 °C, c) 400 °C:30 minutes.

The XRD results for the 550 °C, 30 minute anneal were corroborated by TEM studies. Microdiffraction patterns confirm the presence of PtP_2 grains. The reacted layer has a coarse-grained, polycrystalline microstructure, with a grain size on the order of 50nm to 70nm (figure 4). The interface with the InP substrate is rough. Selected area diffraction of the 550 °C specimen showed that the PtP_2 phase exhibits a preferred orientation relationship with the substrate. TEM studies of these samples are continuing to determine the morphology of the $PtIn_2$ phase.



figure 4: TEM micrograph of cross-sectional Pt/InP specimen, 550 °C:30 minute anneal.

DISCUSSION

Both the RBS and XRD results for the Pt/InP system indicate that the reactions for this system can be divided into three stages: initial reaction- 300 °C to 350 °C; intermediate stage- 375 °C to 400 °C; and, final stage- 500 °C to 600 °C. At low temperature, InP and Pt react to form polycrystalline phases with no observed preferred

orientation. During the intermediate stage, all three components of the system become intermingled, forming a polycrystalline phase with a preferred orientation with the substrate, and a coarse-grained second phase.

One of the goals in studying the annealing behavior of the Pt/InP system was to determine the stable compounds and their morphology for high-temperature anneals. The stable phases in this system, for the annealing conditions between 500 °C and 600 °C, are PtP₂ and PtIn₂ (figure 5). For this temperature range, the reacted layer has a coarse grained, polycrystalline microstructure, with a grain size between one third to one half the reacted layer thickness. The phosphide layer exhibits a preferred orientation relationship with the InP substrate. Both PtP₂ and InP are cubic structures, with a lattice mismatch of 3%.

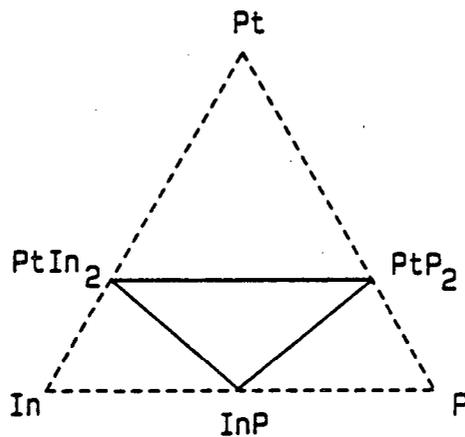


Figure 5. Stable tie-triangle indicated by the results for anneals between 500 °C and 600 °C.

In summary, the Pt/InP and Pt/GaAs systems show similar features after annealing. Both ultimately form layered microstructures, with a Pt-III compound concentrated at the surface, and an intervening Pt-V compound near the substrate. In both cases, the Pt-V compound has a preferred orientation relationship with the substrate. Pt/GaAs begins interacting at a lower temperature (250 °C vs. 300 °C) than does Pt/InP, and attains the final, stable phases earlier (400 °C vs. 500 °C) for similar annealing times and film thicknesses. Additionally, the Pt-Ga and Pt-As phases show a tendency for phase segregation even for the initial reactions, while at intermediate temperatures, the Pt, In and P are completely intermingled.

The phase segregation behavior of these systems indicates which of the elements is the dominant diffusing species. In the case of Pt/GaAs, both Pt and Ga are mobile from low temperature: Ga diffuses into the Pt to form Pt-rich compounds, while Pt diffuses into the substrate to form PtAs₂. The behavior of the Pt/InP system, however, indicates two different stages of atomic mobility: at low to intermediate temperatures, only Pt can diffuse readily, while at higher temperatures, both Pt and In are diffusing. In the first stage, the Pt diffuses into the substrate to form an intermixed layer, while at the higher temperatures, the In diffuses out into the Pt, resulting in phase segregation similar to Pt/GaAs.

ACKNOWLEDGEMENTS

This work was supported by Bellcore, Inc., and the Director, Office of Energy Research, Office of Basic Energy Science, Materials Science Division of the Department of Energy under contract DE-AC03-76SF00098.

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