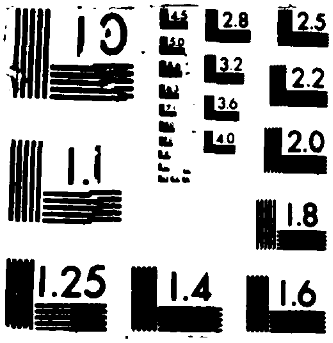
AD-A183 839 CHEMICAL REACTIONS AT THE IN VACUO AU/INP INTERFACE(U) 1/1
CALIFORNIA UNIV LOS ANGELES R S WILLIAMS ET AL
25 JUL 87 N00014-87-K-0014
UNCLASSIFIED F/G 7/4 NL


1.0
4.5
5.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

UN
SEC

DTIC FILE COPY (12)

AD-A183 839 DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED

1b RESTRICTIVE MARKINGS N/A

2a SECURITY CLASSIFICATION AUTHORITY N/A

2b DECLASSIFICATION / DOWNGRADING SCHEDULE N/A

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited

DTIC
CTE
AUG 0 6 19
S
E

4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a NAME OF PERFORMING ORGANIZATION
The Regents of the
University of California

6b OFFICE SYMBOL *(If applicable)*

7a NAME OF MONITORING ORGANIZATION
1) ONR Pasadena - Administrative
2) ONR Alexandria - Technical

6c ADDRESS *(City, State, and ZIP Code)*
Office of Contracts & Grants Administration
U C L A, 405 Hilgard Avenue
Los Angeles, CA 90024

7b. ADDRESS *(City, State, and ZIP Code)*
1) 1030 E. Green Street, Pasadena, CA 91106
2) 800 N. Quincy St., Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)* ONR

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0014

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy Street, 614A:DHP
Arlington, VA 22217-5000

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
UNCLASSIFIED: Tech.Rpt.#5 - CHEMICAL REACTIONS AT THE IN VACUO Au/InP INTERFACE

12 PERSONAL AUTHOR(S)
R. Stanley Williams. C. Thomas Tsai and Eun-Hee Cirlin

13a TYPE OF REPORT Technical

13b TIME COVERED FROM Oct'86 TO Aug'87

14. DATE OF REPORT *(Year, Month, Day)* 25 July 1987

15. PAGE COUNT 7

16 SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
phosphorus escape ; composition shift ; layered islands ; four solid phases ; ternary phase diagram ; intense reflections

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Gold Indium Phosphide

The reaction between a Au film and an InP substrate occurs much more readily in vacuo than under an atmosphere pressure of an inert gas. At high pressures, the compounds Au_2P_3 and the γ intermetallic compound (at times designated Au_7In_3, Au_9In_4, or Au_2In) are formed at 450°C and remain fairly stable even when annealed at 500°C for hours. Under ultra-high vacuum conditions, phosphorus readily escapes from the film when a sample is annealed at 300°C for 15 minutes, and the major reaction products are the ψ phase (Au_3In_2) and an unidentified Au-In intermetallic compound. The presence of an inert gas creates a kinetic barrier for the escape of phosphorus from the surface, and thus Au/InP behaves more like a closed thermodynamic system under pressure than in a vacuum.

Keywords.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED

22a NAME OF RESPONSIBLE INDIVIDUAL R. Stanley Williams

22b TELEPHONE *(Include Area Code)* (213) 825-8818

22c OFFICE SYMBOL UCLA

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

OFFICE OF NAVAL RESEARCH

Research Contract N00014-87-K-0014

R&T Code 413E026---01

Technical Report No.5

CHEMICAL REACTIONS AT THE IN VACUO Au/InP INTERFACE

by

R. Stanley Williams, C. Thomas Tsai

Department of Chemistry & Biochemistry
and Solid State Sciences Center
University of California, Los Angeles, CA 90024-1569

and Eun-Hee Cirlin

Hughes Research Laboratories
3011 Malibu Canyon Road, Malibu, CA 90265

Prepared for publication

in

Materials Research Society Symposium Proceedings (1987)

University of California, Los Angeles
Department of Chemistry & Biochemistry
and Solid State Sciences Center
Los Angeles, CA 90024-1569

July, 1987

87 8 06

CHEMICAL REACTIONS AT THE IN VACUO Au/InP INTERFACE

R. STANLEY WILLIAMS,* C. THOMAS TSAI,* AND EUN-HEE CIRLIN**
* Dept.of Chemistry & Biochemistry and Solid State Science Center
University of California, Los Angeles, CA 90024
** Hughes Research Laboratories, 3011 Malibu Canyon Rd.
Malibu, CA 90265

ABSTRACT

The reaction between a Au film and an InP substrate occurs much more readily in vacuo than under an external pressure of an inert gas. At atmospheric pressure, the compounds Au_2P_3 and the γ intermetallic compound (at times designated Au_7In_3, Au_9In_4, or Au_2In) are formed at 450°C and remain fairly stable even when annealed at 500°C for hours. Under ultra-high vacuum conditions, phosphorus readily escapes from the film when a sample is annealed at 300°C for 15 minutes, and the major reaction products are the ψ phase (Au_3In_2) and another intermetallic compound that is probably AuIn. The presence of an inert gas creates a kinetic barrier for the escape of phosphorus from the surface, and thus Au/InP behaves more like a closed thermodynamic system under pressure than in a vacuum.

INTRODUCTION

The chemical reactions that occur between a deposited Au film and an InP substrate have been the subject of many investigations [1-14], and a brief synopsis of the reported observations may be found in Ref. 15. A major point of interest is that in the investigations in which annealing experiments were performed, roughly half the samples were heated in vacuo [1-7] and the other half under an atmospheric pressure of inert ambient [8-15]. A general observation gained from these studies is that the lower the ambient pressure during annealing, the lower the temperature at which reactions occur.

In a previous study of Au/InP chemistry [15], 550Å Au films were deposited on InP (001) surfaces cleaned in ultra-high vacuum (UHV) and annealed at various temperatures under one atmosphere pressure of flowing nitrogen gas. The samples were removed from the furnace whenever a visibly noticeable change occurred, and they were examined using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), and x-ray diffraction (XRD). The XRD analyses proved to be the most important, since they enabled the compounds that were formed during the various reaction stages to be identified. The reactions proceeded slowly, with days or hours of annealing at different temperatures sometimes being necessary to observe a definite change in the films. The reaction products that were observed, and the sequence in which they were formed, were consistent with the Au-In-P ternary phase diagram [15]. Heating the samples for 25 min. at 450°C produced a surface covered by well separated and preferentially oriented islands of the compounds Au_2P_3 and γ. These are exactly the two bulk phases that would be in thermodynamic equilibrium with InP in a closed system. Heating this sample to 510°C for 40 min. leads to only minor changes as detected by XRD: the γ and Au_2P_3 peaks were still present, but a small reflection from the metastable ψ phase appeared. The presence of this phase on the surface indicated that some phosphorus had sublimed from the sample, and the composition of the sample shifted toward the In-rich side of the phase diagram. In this paper, the above observations are contrasted to the behavior of a thin Au film on InP(001) that was annealed to only 300°C in vacuo.

EXPERIMENTAL PROCEDURE

The InP single-crystal substrates used in this investigation were (001) oriented wafers. They were chemo-mechanically polished with a 2% mixture of bromine in methanol and rinsed in methanol immediately before being mounted in the UHV deposition chamber. The samples were cleaned in vacuo with several cycles that consisted of alternating Ar^+ ion bombardment at 1 keV with annealing to 300°C for 10 minutes. In situ Auger analysis showed that less than 5% of a monolayer of contaminants (primarily O and C) were present at the surface. An Au beam was produced by thermal evaporation from a tungsten basket, and an Inficon (model XTM) micro-balance was used to measure the deposition rate. The base pressure in the chamber was in the the 10^{-10} torr range, rising into the 10^{-9} torr range during the Au evaporation.

For the in vacuo annealing experiment, a 300 Å thick film was evaporated onto a room temperature InP substrate. An Auger spectrum revealed no detectable In or P, which showed that the Au film was continuous. The sample was heated to 300°C by passing a current through a strip heater behind the sample, with the temperature being measured by a thermocouple in direct contact with the side of the InP substrate. During this first annealing cycle, the appearance of the sample surface changed dramatically, so it was removed from the chamber for ex situ analysis by SEM, EDX, and XRD, as discussed previously [15]. The surface of the InP was extremely rough and covered by irregularly shaped islands. A Physical Electronics Model 595 Scanning Auger Microscope (SAM) was used to examine the lateral composition of the islands, and obtain depth profiles in combination with ion beam etching.

RESULTS AND DISCUSSION

After vacuum annealing, visual examination revealed that the sample, which had originally been golden, turned a silvery color. The surface of the sample is shown in the SEM photographs of Fig. 1. The dark regions in the photographs contain no Au, as shown by EDX and SAM analysis, and are thus bare InP. The reaction has left the InP surface heavily fissured and eroded, and the Au-containing compounds have coalesced into well separated but irregular islands that range from 1-50 μ across and less than 0.5 μ high. Close examination of the larger islands reveals a remarkable feature; they all appear to be composed of two different phases, one layered on top of the other. This structure is very clear in the SEM photograph of Fig. 1b, which shows one such island. The lower phase is a darker shade than the upper, and can be seen as "beaches" surrounding the islands as well as through holes in the upper phase.

One clue about the identity of the two phases comes from the XRD pattern shown in Fig.2. This powder pattern shows weak diffraction peaks from the single-crystal substrate, since the sample was not oriented to pick up the <001> reflections. Weak peaks from the Au_2P_3 <110> reflections are observed, as well as a strong (110) reflection from the ψ phase. The three strongest remaining peaks in the XRD pattern appear to belong to the AuIn intermetallic compound, although the identification of this phase is uncertain because the peaks are

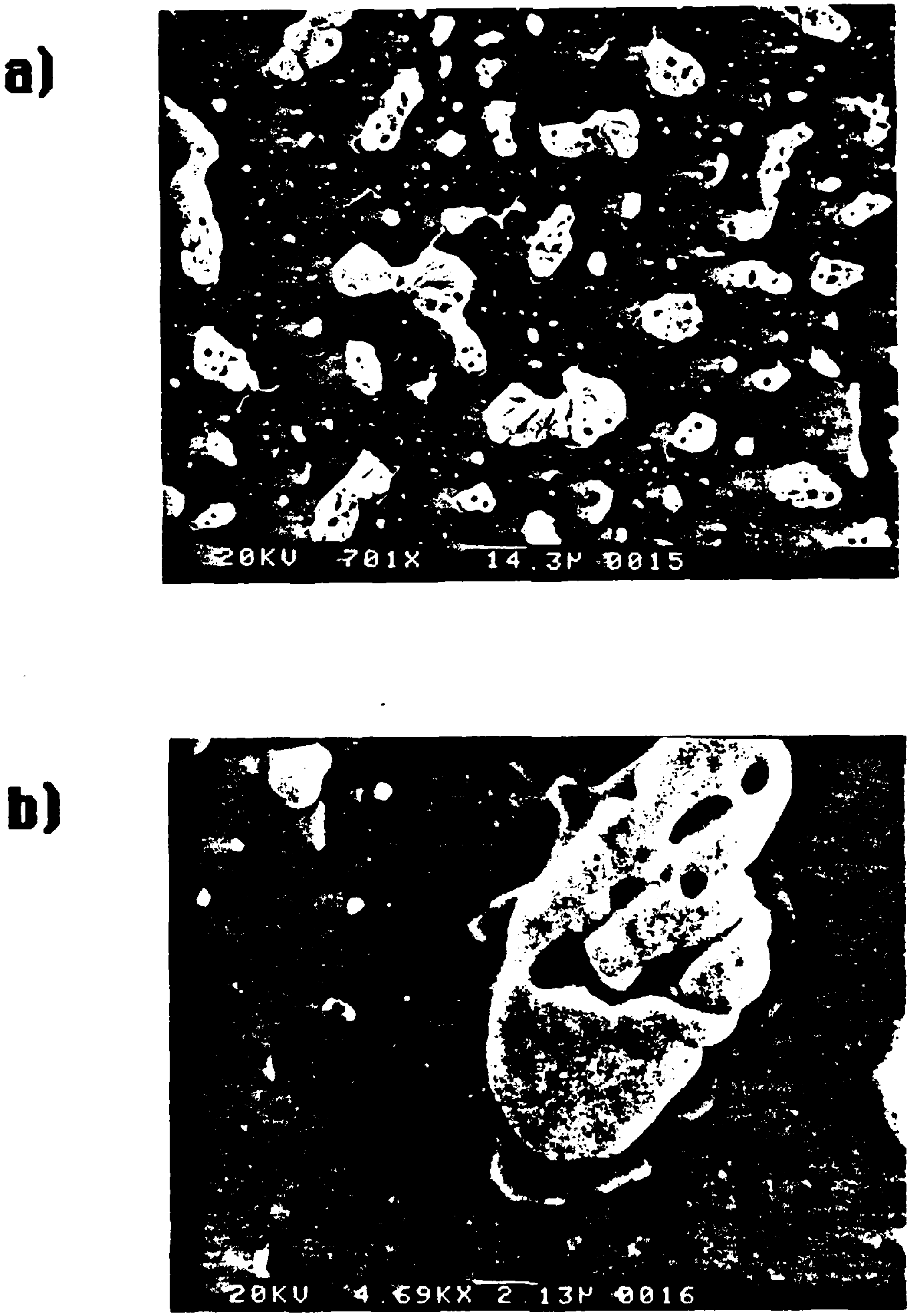


Fig.1 - Two SEM photographs of the sample surface after a 300 Å Au film on InP (001) was annealed at 300°C *in vacuo* for 15 min. The large islands are composed of two different intermetallic compounds of Au and In layered on top of one another. The dark areas are bare InP substrate, which is heavily fissured after the reaction. The length scales are shown at the bottom of each photograph.

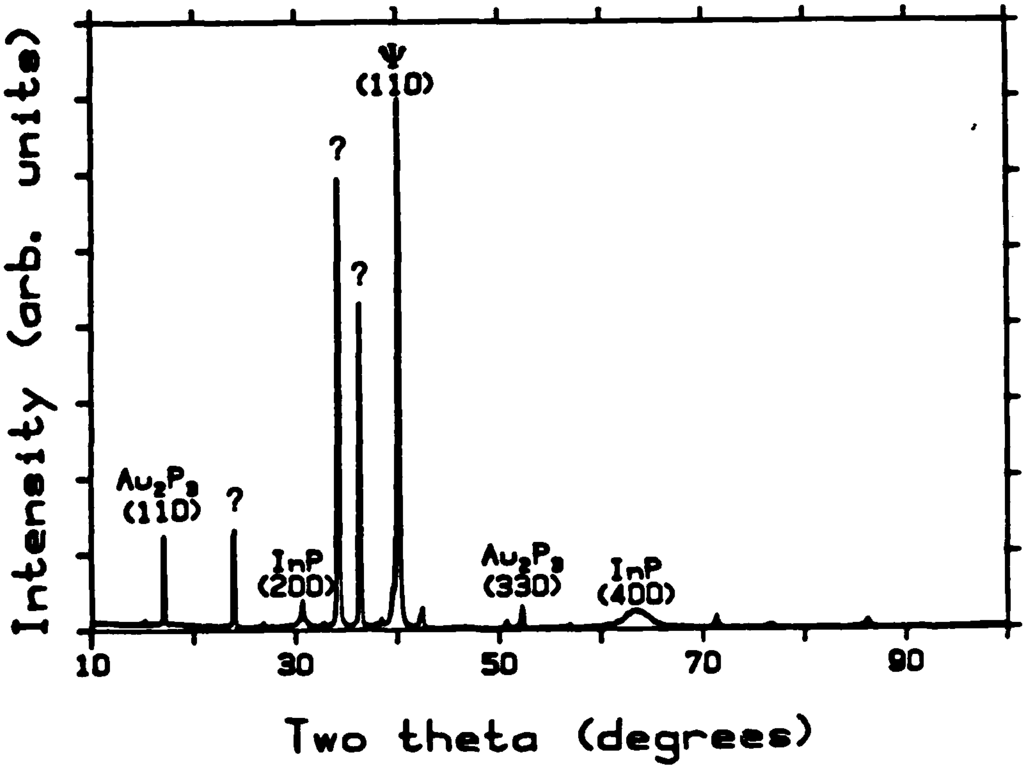


Fig.2 - The XRD pattern of the sample shown in Fig.1. The known reflections are labeled with the compounds and planes that produced them. The intense reflections labeled '?' occur at values of 2θ very close to peaks observed for the AuIn phase.

somewhat shifted from bulk AuIn. This was checked carefully by making all the compounds stable at room temperature and also the Ψ compound, which is stable in bulk form only above 240°C but can be observed by quenching, and examining their XRD patterns [15]. Compounds with other elements were not considered, since no appreciable contamination was observed in either EDX or SAM analyses. The fact that the XRD peaks are shifted may be the result of a stoichiometry difference or stresses in the small islands formed by the chemical reaction.

The composition of various portions of the islands was examined using SAM with sub-micron resolution. Both phases were found to contain only Au and In, the lower in approximately a 2:1 ratio and the upper phase being more Au-rich with a 5:2 ratio. Assigning the two phases to specific Au-In compounds on the basis of the Auger results alone is not possible, since Auger data are not quantitative enough to distinguish among the different compounds with stoichiometries only slightly different from one another. Since the upper phase was more Au-rich than the lower, it is tentatively identified as Ψ, with the lower phase being AuIn. The InP is the source of In for the islands, so the lower phase would be expected to be the more In-rich compound. However, this assignment is somewhat puzzling since the Ψ phase is apparently ordered with only a single orientation, whereas the AuIn-like phase is present with several orientations.

Annealing a 300 Å Au film of InP to only 300°C in vacuum thus leads to major chemical changes of the system. In contrast, annealing a 550 Å Au on InP sample to 300°C under an atmospheric pressure of N_2 gas for 90 min. causes only minor changes in the film [15]. The gold color is retained, the film remains continuous, and a careful examination of the SEM photographs and XRD patterns is required to determine that some solid solution of In in Au has formed. The primary difference between the two surfaces is that the vacuum annealed surface must have lost a large amount of P to form Ψ and AuIn, whereas the P in the sample annealed under pressure ultimately formed Au_2P_3 at the higher annealing temperatures.

At atmospheric pressure, each atom on a surface is struck approximately 10^9 times per second by molecules from the gas. This continual bombardment may act as a kinetic barrier to the surface diffusion and combination of P atoms to form molecules or to the desorption of volatile species such as P_2 or P_4. Thus, the sublimation of P from the sample could be greatly hindered, and the chemical reactions that occur are those that would be expected in a closed thermodynamic system [15]. However, in a vacuum the kinetic bottleneck is removed, and the large increase of entropy available to the system as the gaseous P species expand pushes the system out of the γ-Au_2P_3-InP tie-triangle into the In-rich region of the ternary diagram [16]. Another possible explanation for the kinetic limitation of the reaction on the sample under pressure is the formation of an oxide diffusion barrier at the time when the sample was exposed to the atmosphere. This is unlikely, since the oxide thickness determined during sputter profiling of the vacuum-reacted sample, which was also transferred in air, was only on the order of 10 Å thick, but this possibility should be checked by annealing an air-exposed sample in vacuum.

The reaction is so strong that the system is driven far from equilibrium. When the sample was examined, four solid phases were found to coexist: InP, Ψ, the AuIn-like phase, and a small amount of Au_2P_3. The Au_2P_3 may have formed as an intermediate product, which went on to react with InP to form more Au-In intermetallic compounds and release gas phase P species. The fact that the Ψ compound was observed on the sample after it had cooled to room temperature may be the result of a fairly rapid cooling cycle after the anneal was complete. It may also have gained additional stability by growing epitaxially on the AuIn islands, since only one major crystallite orientation was observed in the XRD pattern of Fig.2.

The Au-In-P ternary phase diagram can be used to illustrate graphically the reaction sequences and products observed in Ref.15 and in this work. As shown in Fig.3, the equilibrium composition of a closed system that originated as an Au film on an InP substrate is represented by the X in the InP-γ-Au_2P_3 tie-triangle. In an open system, P sublimes and the composition become enriched with In, which is represented in Fig.3 by the arrow. The state of the thin film studied in this investigation, after it was annealed <u>in vacuo</u> for 15 minutes, is indicated by the position of the head of the arrow in the InP-γ-AuP tie-triangle. The presence of a small amount of Au_2P_3 shows that the reaction proceeded so rapidly that equilibrium conditions were not fully maintained for the <u>in vacuo</u> thin film reaction.

CONCLUSIONS

If a thin film of Au several hundred Å thick on an InP substrate is annealed under an atmospheric pressure of inert gas at temperatures under 500°C for up to two hours, the chemical reactions that occur are those predicted from the ternary phase diagram for a closed thermodynamic system. The presence of the external gas phase apparently acts as a kinetic barrier to the sublimation of P. Under high vacuum conditions, however, P escapes from the system readily and the accompanying increase in entropy available via the reaction drives the system far from equilibrium. After 15 minutes at 300°C, the major

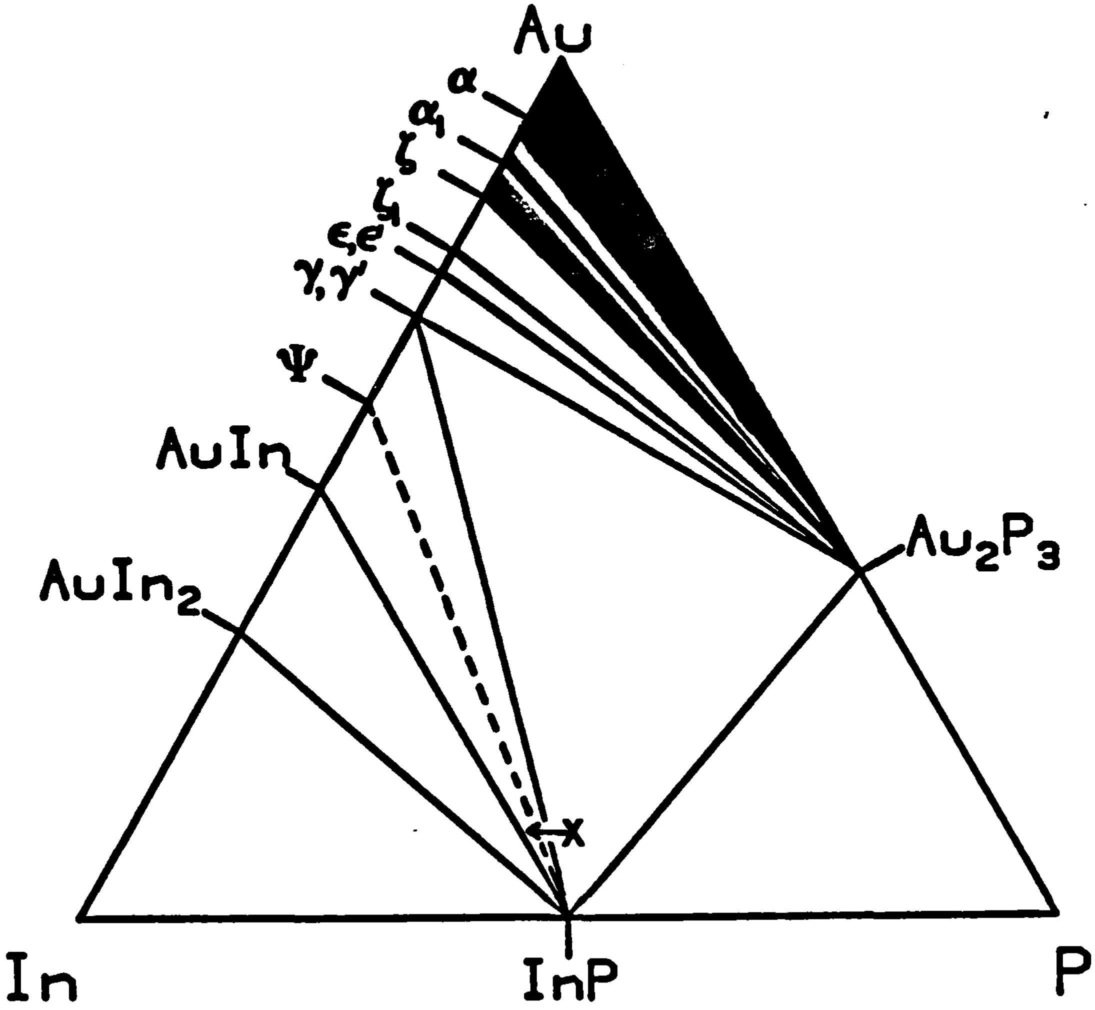


Fig.3 - The Au-In-P ternary phase diagram, after Ref.15. The X shows the initial composition of a system produced by depositing an Au film on InP. In a closed system, the equilibrium phases are InP-γ-Au_2P_3. In an open system, P is lost and the composition of the system evolves as shown by the arrow.

products observed were two Au-In intermetallic compounds, which formed islands with one phase on top of the other. One phase, Ψ, is metastable at room temperature and was produced with a strong preferential orientation with respect to the substrate surface. The other phase is apparently the AuIn compound formed slightly off-stoichiometry or mechanically deformed. A small amount of Au_2P_3 was also observed, which demonstrated that the system was not quite at equilibrium in the InP-Ψ-AuIn tie-triangle. The fact that Au reacts so readily, even in a closed system, makes it unsuitable as a contact metal for InP.

ACKNOWLEDGMENTS

This work was supported by the University of California MICRO program, Hughes Aircraft Corporation, and the Office of Naval Research. RSW received additional support from the Camille and Henry Dreyfus Foundation and the Alfred P. Sloan Foundation. We thank Dr. W. Stanchina of HRL for his assistance during this work.

REFERENCES

1. R.H. Williams, R.R. Varma, and A. McKinley, J. Phys. C: Solid State Phys. **10**, 4545 (1977).
2. A. Hiraki, K. Shuto, S. Kim, W. Kammura, and M. Iwami, Appl.Phys. Letts. **31**, 611 (1977).
3. P.W. Chye, I. Lindau, P. Pianetta, C.M. Garner, C.Y. Su and W.E. Spicer, Phys.Rev. B **18**, 5545 (1978).
4. L.J. Brillson, C.F. Brucker, A.D. Katnani, N.G. Stoffel, and G. Margaritondo, J.Vac Sci.Technol. **19**, 661 (1981).
5. J. M. Vandenberg, H. Temkin, R. A. Hamm, and M. A. DiGiuseppe, J. Appl. Phys. **53**, 7385 (1982); Thin Solid Films **104**, 419 (1983).
6. I. Mojzes, D. Szigethy, and R. Veresegyhazy, Electr. Letts. **19**, 117 (1983).
7. W.G. Petro, T. Kendelewicz, I.A. Babalola, I. Lindau, and W.E. Spicer, J.Vac.Sci.Technol. **A 2**, 835 (1984).
8. H.B. Kim, A.F. Lovas, G.G. Sweeny and T.M.S. Heng, Inst.Phys.Conf., Ser. No. **33b**, 145 (1977).
9. B. Tuck, K.T. Ip, and L.F. Eastman, Thin Solid Films **55**, 41 (1978).
10. N. Szydlo and J. Olivier, J.Appl.Phys. **50**, 1445 (1979).
11. V.G. Keramidas, H. Temkin and S. Mahajan, Inst. Phys Conf., Ser. No. **56**, 293 (1980).
12. A. Piotrowska, P. Auvray, A. Guivarc'h, G. Pelous, and P. Henoc, J.Appl.Phys. **52**, 5112 (1981).
13. I. Camlibel, A.K. Chin, F. Ermanis, M.A. DiGiuseppe, J.A. Lourenco and W.A. Bonner, J.Electrochem.Soc.: Solid-State Sci. & Technol. **129**, 2586 (1982).
14. D. Brasen, R.F. Karlicek and V.M. Donnelly, J. Electrochem. Soc.: Electrochem Sci. and Technol. **130**, 1473 (1983).
15. C.T. Tsai and R.S. Williams, J.Mats. Res. **1**, xxx (1986).
16. J.H. Pugh and R.S. Williams, J.Mats Res. **1**, 343 (1986).

END

9-87

DTIC