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M. Ben-Tzur, K.M. Yu, and E.E. Haller

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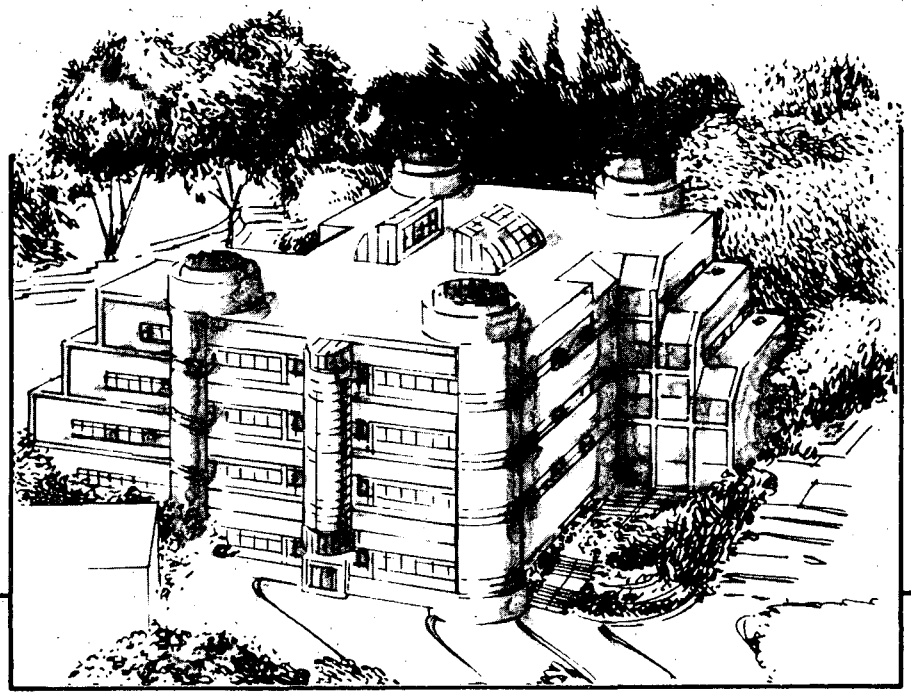

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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INTERFACIAL REACTIONS BETWEEN THIN FILMS OF Co AND InP (100)

M. BEN-TZUR*, K. M. YU, AND E. E. HALLER
Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

* Present Address : Cypress Semiconductor, 3901 North First St., San Jose, California 95134-1599

ABSTRACT

The interfacial reactions between thin films of Co and single crystal InP have been studied. The reaction between the Co and the InP substrate already start in the as-deposited state to form In and P rich compounds. During annealing at 250^0C for 30 min., phase separation takes place. In addition to unreacted Co, we find Co rich compounds, a Co-P compound in contact with the substrate, and Co-In compound in contact with the metal layer. The general morphology appears to be stable up to 500^0C. At higher temperatures ($500\text{-}600^0$C) P is released from the substrate. CoP_4, Co_2P, $CoIn_2$ and In were detected by X-ray diffraction. At this stage the reaction is no longer uniform.

INTRODUCTION

Metal/III-V semiconductor structures play an important role for devices based on III-V compounds. The electrical contact of the device is provided by the metal/semiconductor interface. The characteristics of such contacts are dependent on the morphology and the phases at the interface. Understanding of the interface metallurgy of the systems is essential for obtaining the desired electrical properties [1-5].

In recent years the use of InP in microwave and optoelectronic devices has led to an interest in the properties of metal/InP contacts. It is also important to study those contact systems as the first step toward understanding more complex metallization schemes on InP based alloys, e.g. metals on InGaAsP [6-7].

This work focuses on the interfacial reactions between Co and InP, studying the reaction mechanisms and phase formation during annealing.

EXPERIMENTAL DETAILS

(100) oriented n-type InP wafers were used as substrates. The InP wafers were chemically cleaned by dipping into 1% HF solution for two minutes prior to introduction into the electron beam evaporation chamber. Co films, 1000Å thick, were deposited at room temperature.

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Heat treatments were carried out in a quartz tube in Ar ambient in the temperature range of 150 to 600^{0}C for 30 minutes. Samples to be annealed at 400^{0}C and higher were capped first on both sides with SiO_2 layers by sputtering, or sealed in a small capsule with a few milligrams of elemental P.
The depth distribution of the elements as a function of the applied heat treatments was determined by Rutherford Backscattering Spectrometry (RBS) using a 1.8MeV He^+ beam, and Auger Electron Spectroscopy (AES) combined with Ar^+ ion sputtering. Phase identification and microstructural analyses were carried out by X-ray diffraction and by transmission electron microscopy (TEM).

RESULTS

A cross section TEM image of the as-deposited state is shown in fig.1a. A very thin (10nm) reacted layer is observed at the interface Co/InP. A TEM micrograph of the as-deposited Co film, shown in fig.1b, reveals very fine grains with the stable hexagonal structure of α-Co. A TEM micrograph of same reacted regions are given in fig.1c-d. Electron diffraction that was obtained from these areas reveals the formation of cubic CoP_4 and $CoIn_3$.

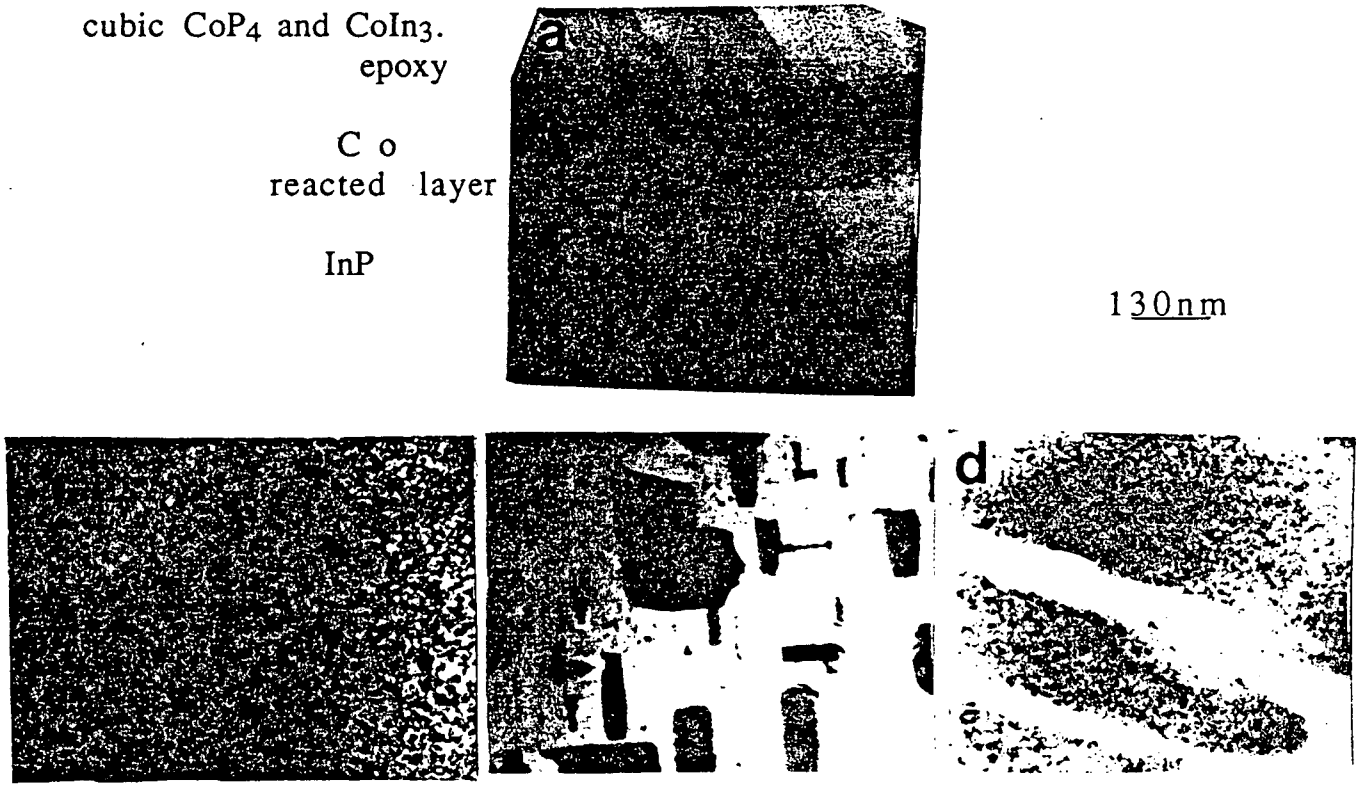

Figure 1: Co on InP in the as deposited state : (a) Cross-section TEM image. (b) Plan-view TEM micrograph of the Co film. (c) Plan-view TEM micrograph of the CoP_4 film. (d) Plan-view TEM micrograph of the $CoIn_3$ film.

After annealing at 250^{0}C for 30 min. phase separation had taken place. The cross section TEM image of the sample at this annealing condition is given in fig. 2a. In addition to the Co layer, two more layers were observed. One layer with thickness of 50nm in contact to the Co film and a second, polycrystalline layer with thickness 10nm in contact to the substrate. Big voids (about 70nm in diameter) were observed at the interface between these two layers. Plan-view TEM of this sample, shown in fig. 2b, reveals the formation of grains with a diameter of 20nm. Electron diffraction taken from these grains indicates the formation of Co_2P.

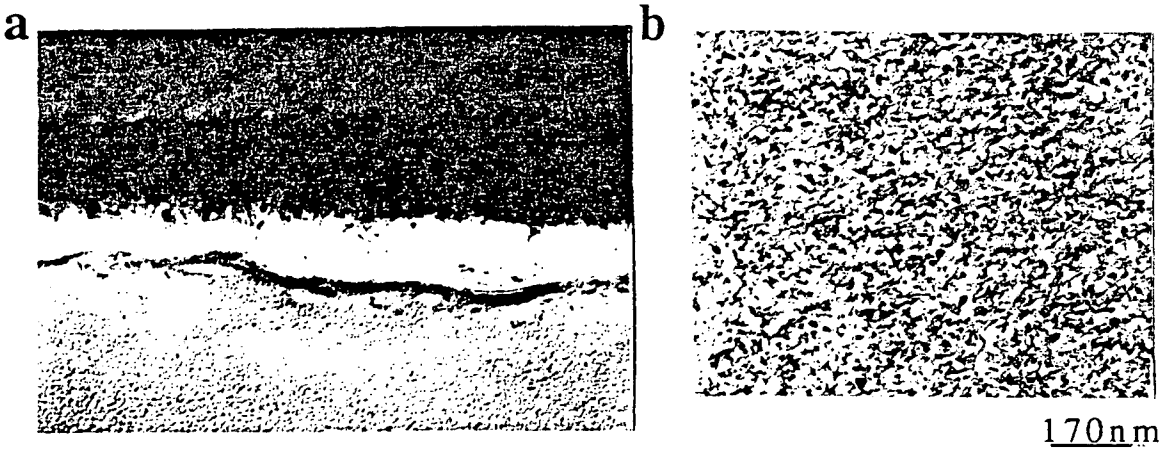

Figure 2 : Co on InP following a 250^{0}C 30 min., anneal :
(a) Cross-sectional TEM image.
(b) Plan-view TEM micrograph of the Co_2P film.

Rutherford backscattering spectra and Auger electron spectroscopy depth profiles, given in fig. 3 a&b, indicate that vertical phase separation is maintained up to 400^{0}C. In contact with the substrate is a Co-P compound, while the layer close to the surface was rich in In. X-ray diffraction taken from the sample shown in fig 3 indicates the presence of CoP_4, Co_2P and In. There was no evidence for the presence of unreacted Co for this sample.
At higher temperatures, 500-600^{0}C, P is released from the substrate in spite of annealing under P over-pressure or SiO_2 capping. The RBS spectrum shown in fig. 4a reveals non-uniform reactions. From the Auger electron spectroscopy depth profile, shown in fig 4b , we conclude that a Co-P was compound in contact with the substrate, similar to the sample annealed at 400^{0}C. On the outer surface we find an accumulation of In. In addition, a new layer is formed. This layer is composed of Co, In and P. X-ray diffraction from this sample indicates the coexistence of CoP_4, Co_2P, $CoIn_2$ and In. There is no evidence of ternary phases.

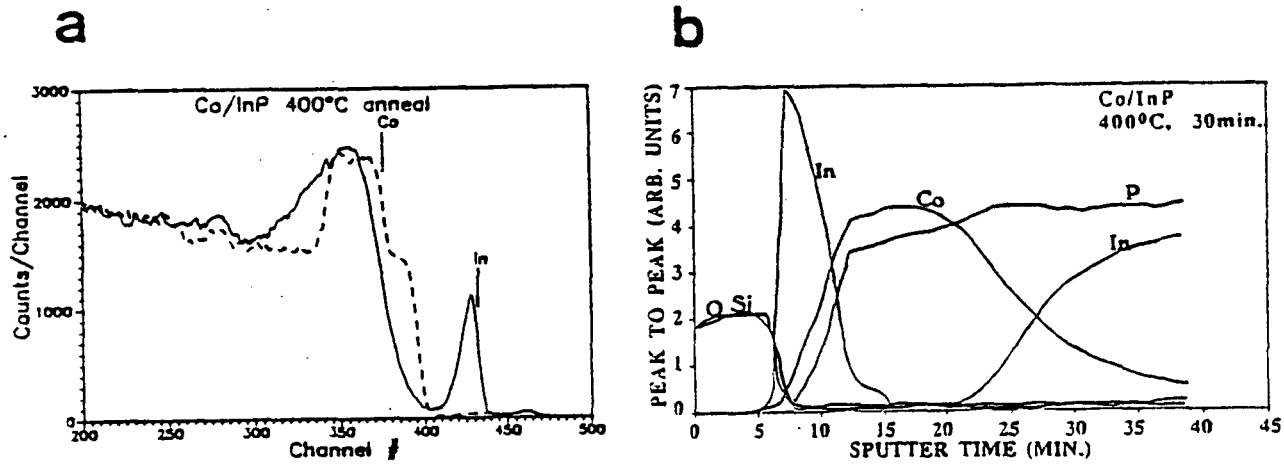

Figure 3 : Co on InP following a 400^{0}C 30 min., anneal : (a) Rutherford backscattering spectrum. (b) Auger electron spectroscopy depth profiles.

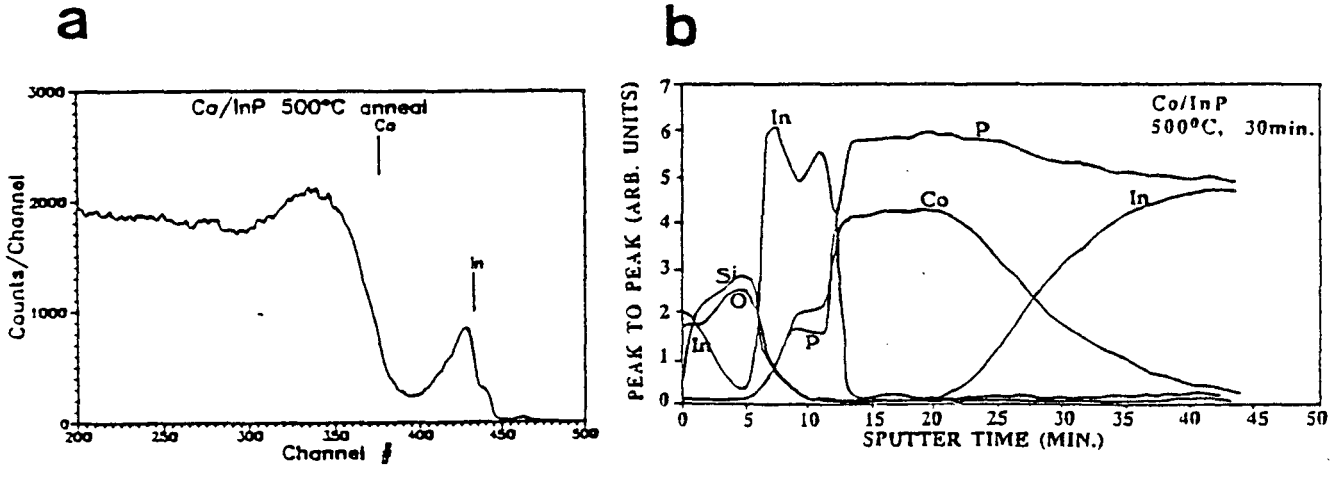

Figure 4 : Co on InP following 500^{0}C 30 min., anneal : (a) Rutherford backscattering spectrum. (b) Auger electron spectroscopy depth profiles.

DISCUSSION

The phase formation sequence of the metallization scheme Co/InP upon annealing can be divided into three main stages. The first stage involves room temperature reactions, i. e. in the as deposited state. The second stage, takes place in the temperature range 250-400^{0}C. The third stage, the high temperatures reactions, occur between 500-600^{0}C.

As Deposited State

From our TEM analysis we conclude that in the as deposited state Co diffuses into the substrate forming binary phases, $CoIn_3$ and CoP_4,phases rich In and P respectively. These phases are polycrystalline. It is important to note that this process occur at very low temperatures, less than 100^{0}C, during deposition or sample preparation for the TEM analysis. The same behavior has been observed in the case of Pd/InP [8] and Au/Ni/InP [9]. For these two systems, however, the reactions start through diffusion of the metal into the semiconductor, and amorphous ternary phases were detected.

Low Temperature Reactions (250-400^{0}C)

At 250^{0}C the diffusion of the Co into the substrate is enhanced and a compound richer in Co is formed, Co_2P. In this stage TEM cross-section analysis reveals vertical phase separation. The Co_2P is in contact with the substrate, unreacted Co is found at the outer surface, and an intermediate layer between them.
At 400^{0}C all the Co is consumed by the reactions forming Co_2P and CoP_4. These compounds remain in contact with the substrate. Simultaneously, diffusion of In from the substrate to the outer surface occurs.
The same vertical phase separation was observed for the case Au/Ni/InP [9] with the P compounds in contact to the substrate and the In compounds at the outer surface.

High Temperature Reactions (500-600^{0}C)

At this stage, the reaction region is divided into three main layers: P-Co compounds with contact to the InP substrate, In at the outer surface (just as at lower temperatures), and an interfacial layer between these two layers. This layer is composed of binary phases of In, P and Co. From the X-ray diffraction there is no evidence for ternary phases.

CONCLUSIONS

The solid state reactions between Co and InP are governed by Co diffusion to the substrate and In from the substrate to the outer surface. Vertical phase separation is maintained even at high temperatures. At all stages, no preferred crystal orientations are observed and no ternary phases are formed.

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LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720