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INTERFACIAL REACTIONS BETWEEN THIN FILMS OF ZINC AND (100) InP*

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The effects of interaction between thin films of Zn and (100)InP were studied with secondary ion mass spectrometry, X-ray diffraction and transmission electron microscopy. Zn was found to penetrate the native oxide on InP surface during deposition and to form an ohmic contact when deposited on highly doped *n*-type InP. Heat treatment causes the formation of Zn₃P₂ phase lattice matched to InP.

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Zinc is currently being used as a dopant element in ohmic contact metallizations to *p*-type III-V compound semiconductors. A low contact resistivity of Zn-containing contacts is attributed to a diffusion of Zn atoms, resulting in a highly doped interface layer. The results of our recent study on Zn-based metallizations to *p*-GaAs, however, strongly suggest that Zn plays a more fundamental role in the formation of an ohmic contact. When deposited directly onto GaAs, Zn penetrates the native oxide [1]. Added to Au metallization lowers the temperature of reaction between Au and GaAs. Furthermore, Zn stabilizes the size of metallization grains [2, 3].

In this work we focus on the reactivity of thin Zn films deposited on InP in order to determine to what extent the interaction of zinc with native oxides can be generalized to other compound semiconductors. We study structural and electrical properties of the contacts using XRD (X-ray diffraction), TEM (transmission electron microscopy), SIMS (secondary ion mass spectrometry), and specific contact resistance measurements.

Conventional TEM and high resolution electron microscopy (HREM) investigations were made on cross-sectional specimens, with [110] InP normal to the surface, prepared by a standard technique with the final iodine ion milling. SIMS profiling was carried out using Cs⁺ as a primary beam with detection of CsM_i⁺ secondary cluster ions, enabling thus determination of the relative concentration

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of the sample constituents M_i with reduced matrix effects. Such configuration, together with the pressure in the analysis chamber of the order of 10^{-10} Tr makes it possible to simultaneously monitor different species e.g. oxygen and indium.

Zn films, 200 to 1100 nm thick, were vacuum deposited on (100) oriented InP. The single crystal substrates were either *p*-type doped with Zn ($p = 4 \times 10^{18} \text{ cm}^{-3}$) or *n*-type undoped and doped with S ($n = 5 \times 10^{15} - 1 \times 10^{18} \text{ cm}^{-3}$). Prior to metal deposition the surface of InP was processed in hot organic solvents, etched in $\text{HCl}:\text{CH}_3\text{COOH}:\text{H}_2\text{O}_2$ (1:2:1), rinsed in H_2O DI, and dipped for 15 s in $\text{NH}_4\text{OH}:\text{H}_2\text{O}$ (1:10). The samples were annealed under flowing hydrogen for 3 to 10 min at temperatures in the range from 200 to 400°C.

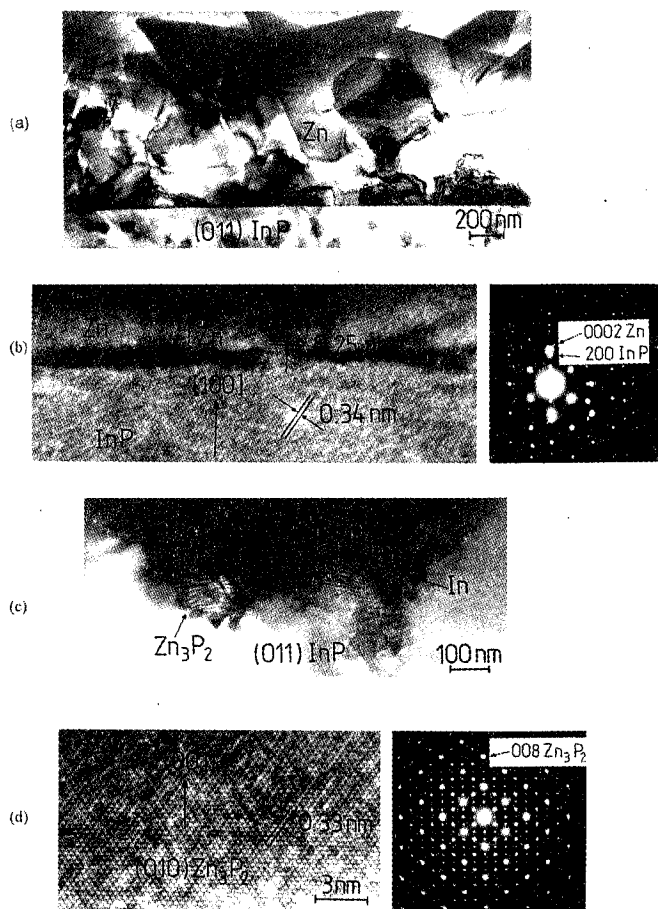


Fig. 1. (011) transmission electron micrograph of Zn/InP contact: (a) as deposited contact, (b) HREM lattice image and corresponding SAD (selected area diffraction) pattern of the as deposited contact, (c) contact annealed at 320°C for 3 min, (d) HREM lattice image of Zn_3P_2 phase.

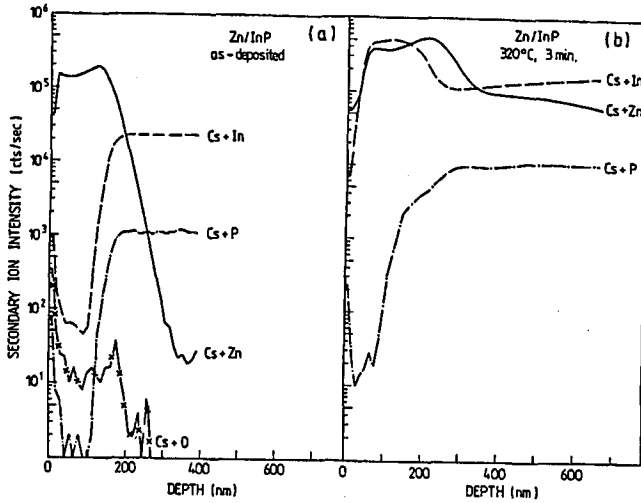


Fig. 2. SIMS in-depth profiles from Zn/InP contact: (a) as deposited, (b) annealed at 320°C for 3 min.

Upon deposition Zn forms large, irregularly shaped grains (200 × 600 nm). Figure 1a shows the Zn/InP interface at low magnification demonstrating the polycrystalline nature and distinct grains of the metallization. Most of these grains are epitaxial with their $(01\bar{1}0)_{\text{Zn}}$ or $(2\bar{1}\bar{1}0)_{\text{Zn}}$ orientation parallel to the $(011)_{\text{InP}}$ orientation, and $[0001]_{\text{Zn}} \parallel [100]_{\text{InP}}$. The interface is abrupt, smooth and displays no evidence of an interfacial oxide. Zinc is in intimate contact with the substrate, which is clearly seen in the high resolution image (Fig. 1b). SIMS profiles for the as-deposited Zn/InP contacts, displayed in Fig. 2a, clearly demonstrate the ability of Zn to permeate the oxide layers.

As a result of annealing at around 200°C, the interface roughens. Triangular protrusions, with sides delineated by InP $\{111\}$ planes form (Fig. 1c). A tetragonal Zn_3P_2 phase with $a = 0.8113$ nm and $c = 1.147$ nm was identified by electron and X-ray diffraction. Zn_3P_2 is lattice matched to InP with the orientation relationships: $(010)_{\text{Zn}_3\text{P}_2} \parallel (011)_{\text{InP}}$ and $[001]_{\text{Zn}_3\text{P}_2} \parallel [100]_{\text{InP}}$ (Fig. 1d). At higher temperatures and longer annealing times, this phase penetrates deeply into the substrate.

The formation of a binary compound which contains Zn and P results in an excess number of In atoms. In fact, an important intermixing between Zn and InP accompanied by outdiffusion of In into the metallic layer is evidenced by SIMS depth profiling of the heat treated contact (Fig. 2b). Also TEM analysis shows the formation of crystalline In inclusions in the Zn layer in the vicinity of the Zn_3P_2 phase protrusions (Fig. 1c).

Electrical measurements show that Zn/*p*-InP contacts, in contrast to Zn/*p*-GaAs ones, are not ohmic. Instead, Zn deposited on *n*-type doped ($n = 7 \times 10^{17} \text{ cm}^{-3}$) InP does exhibit linear I - V characteristics. Even if the resistivity of such a system is relatively high ($4.4 \times 10^{-4} \Omega \text{ cm}^2$), this observation seems to contradict the generally accepted opinion according to which ohmic behaviour of

Zn-containing contacts is ascribed to the formation of a p^+ layer.

We postulate that assuring appropriate penetration of the metal through the native oxide together with a close matching to the semiconductor surface may play a fundamental role in the formation of an ohmic contact.

References

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