A Study on AuZn Ohmic Contacts to p-Type Indium Phosphide

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Abstract

We investigated the electrical and metallurgical behaviors of AuZn ohmic contacts formed on p-type InP. We also evaluated the effect the Zn content in the AuZn/p-type InP metallization system had on the specific contact resistance and the role of Au and Zn in achieving low-resistance ohmic contact.

We found that the specific contact resistance was as low as 8 x 10^{-5} $\Omega \cdot \text{cm}^2$ when the Zn content was as small as 0.4 wt.% and that the concentration of Zn at the metal/InP interface was as small as the detection limit during Auger electron spectroscopic measurement. We presumed that the thermionic emission current governed the current-voltage characteristics of the AuZn / p-type InP ohmic contact.

Introduction

Ohmic contacts on p-type indium phosphide (InP) are necessary in the fabrication of electronic and optoelectronic devices. Although it scarcely needs saying that low-resistance, highly stable and highly reliable contacts are essential to obtain maximum performance in these devices, it is unexpectedly difficult because of the high Schottky-barrier height and the large hole-effective mass of p-type InP.

Conventional metallization schemes to p-type InP involve the use of Au-group II element alloys such as Au:Be¹⁻³, Au:Mg⁴, Au:Zn⁵⁻¹⁰, Au:Zn(Sb)¹¹, and Au(Pd):Zn^{12,13}. Previous studies have shown that these alloyed contacts formed on p-type InP with carrier concentrations of $1\sim2\times10^{18}$ cm⁻³ produce ohmic contacts with a specific contact resistance (r_c) of 5×10^{-5} $\Omega \cdot \text{cm}^2$ for Au:Be, 1×10^{-4} $\Omega \cdot \text{cm}^2$ for Au:Mg, 4.5×10^{-5} $\Omega \cdot \text{cm}^2$ for Au:Zn, 4×10^{-5} $\Omega \cdot \text{cm}^2$ for Au:Zn(Sb), and 4×10^{-5} $\Omega \cdot \text{cm}^2$ for Au(Pd):Zn. Although Au:Zn alloys with a zinc content of $2\sim10$ wt % have widely been used^{6,10}, this content of Zn has to be reduced, wherever possible, because higher Zn content

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occasionally causes poor contact resistance and poor reproducibility. These problems are caused by our limited knowledge of the mechanisms underlying the electrical and the metallurgical behaviors at the metal-semiconductor interface.

In particular, three mechanisms have been proposed⁹⁾ that govern current flow in ohmic contacts: (1) thermionic emission, (2) thermionic-field emission, and (3) field emission. It is generally believed that group II elements such as Be, Mg, and Zn behave as acceptors and form a p⁺ layer at the metal-semiconductor interface and that thermionic-field emission and/or field emission are dominant for metal/p-type InP contacts. However, this point of view is unacceptable because the carrier concentrations of the p⁺ layer formed at the interface during the alloying process are supposed to be less than the middle value of 10¹⁸ cm⁻³ as we will discuss below. This tells us that field-emission and themionic-field-emission mechanisms are improbable.

In this study, we investigated the effect of zinc content in Au:Zn alloys had on the electrical and the metallurgical properties of ohmic contacts formed on p-type InP, the mechanism responsible for current flow through the metal-semiconductor junction and the role of zinc played in ohmic contacts.

Experimental

The material used in this study was a Zn-doped bulk (100) - oriented Czochralski-grown InP wafer with a carrier concentration of 2×10^{18} cm⁻³. The wafer was etched in a solution of H_2SO_4 : H_2O_2 : H_2O (5:1:1) for 2 minutes at 50 °C to remove surface damage and native oxide. Then the wafer was rinsed with deionized water and blown dry with N_2 gas.

Thin films of Au, Zn, and Au were deposited sequentially onto the substrate surface by thermal evaporation in a vacuum of $1-2 \times 10^{-6}$ Torr through a metal mask. The thickness of the first Au layer was fixed on 200 Å. The Zn content in the Au/Zn/Au metallizations was varied from 0.4 to 14.5 by wt.% by controlling the film thicknesses of the intermediate Zn layer and the outermost surface layer of the Au film. Alloying was subsequently carried out at a temperature of 400 $^{\circ}$ C for 30 seconds, in which the wafer was put onto a heated plate. The heated plate was placed in a globe box where there was a flow of nitrogen gas.

The transmission line method^{11·13)} has primarily been used to measure specific contact resistance, whereas the Cox and Strack method¹⁴⁾ has also been used at times to compare the results. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) combined with argon ion beam etching have also been used to obtain elemental composition profiles and information on the electronic interactions between In, P, Au, and Zn.

Results and Discussion

The minimum specific contact resistance is plotted in Fig. 1 against the Zn content in Au/Zn/Au/p InP metallization systems. It can be seen that the contact has ohmic behavior with a Zn content as low as 0.4 wt % and the specific contact resistance does not greatly depend on the content. The lowest specific contact resistance is obtained at an alloying temperature of 400 °C, and this is $0.8 \sim 1 \times 10^{-4} \Omega \cdot \text{cm}^2$. The temperature for producing minimum specific contact resistance has little dependence on the Zn content of metallizations. The Zn content of 0.4 wt.% employed in this experiment is extremely small compared to that used in conventional Au/Zn metallizations to p-type InP, where more than 2~10 wt.% 6,7,9,10 is almost always used. Fatemi and Weizer8) only reported that the minimum rc values appear to be independent of Zn content above about 0.1 at.% to 35 at.% and ohmic behavior can be achieved by adding as little as 0.05 at.% Zn even though the specific contact resistance is two orders of magnitude high. To investigate how can we reduce the amount of Zn to achieve ohmic behaviors, we deposited singlelayer Au films of various thicknesses on the p-type InP substrate surface and alloyed then in a temperature range from 300 to 550 °C for 30 seconds. We found all the contacts exhibited rectifying current voltage characteristics. This indicates that no matter how small the quantity, Zn is indispensable in producing ohmic behavior.

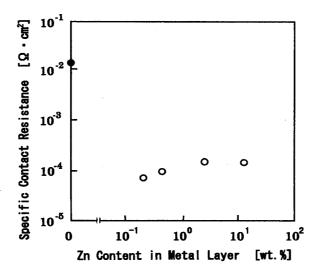


Fig. 1 Minimum specific contact resistances are plotted against Zn content in Au/Zn/Au/p·InP metallizations. Closed circle is represents Au/p·InP system.

To study the effect of the first Au layer on specific contact resistance, Zn and Au layers were sequentially deposited onto the substrate surface, where the Zn content was 13.5 wt.%. Although

the contact produced ohmic behavior, the specific contact resistance was $1 \times 10^{-3} \Omega \cdot \text{cm}^2$ which is one or two orders of magnitude higher than that in an Au/Zn/An metal system with a Zn content of 14.5 wt.%.

Figure 2 shows depth profiles of Au, Zn, In, P, and O obtained from AES for a sample with 0.4 wt.% Zn. We found that Au diffuses deeply into the substrate and In diffuses completely throughout the metal layers. The P diffusion is less extreme which is in striking contrast to In. Zn diffusion has only been observed on the surface of the metal, and hardly none has been detected at the metal- semiconductor interface.

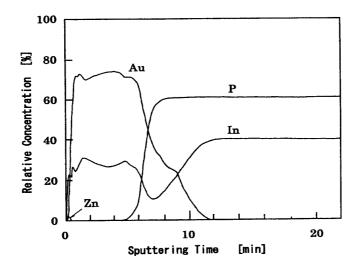


Fig. 2 Depth profiles of In, P, Au, and Zn obtained from AES for sample with Zn content of 0.4 wt.%.

In Fig. 3, the XPS spectra of an Au-4f related signal for a sample with a Zn content of 0.4 wt.% are plotted against sputtering time. It can clearly be observed that the peak energy of the spectra shifts from 83.8 eV to 85.0 eV in the vicinity of the metal/p-type InP interface and the full width half minimum increases with increasing peak energy shift. In XPS measurement, no chemical shift was observed in the spectra of In-, P-, and Zn-related signals.

The results obtained in this study can be summarized as follows;

- (1) Metal (Au/Zn/Au) / semiconductor (p-type InP) contacts exhibited ohmic behavior even when the Zn content was as small as 0.4 wt. %.
- (2) The specific contact resistance has little dependence on the Zn content in a range from 0.4 wt. % to 14.5 wt. %. We achieved a specific contact resistance of $0.8 \sim 2 \times 10^{-4} \Omega \cdot \text{cm}^2$.
- (3) In Au/p-type InP metallization systems, the contacts exhibited rectifying current-voltage characteristics even though the sample was heated to a temperature of 550 °C.

- (4) We observed from Auger electron spectroscopic measurement that Zn was only detected at the surface, but not at the metal-semiconductor interface, where all the samples exhibited ohmic behavior.
- (5) We observed chemical shift in the Au-4f related signal in the vicinity of the metal-semiconductor interface.

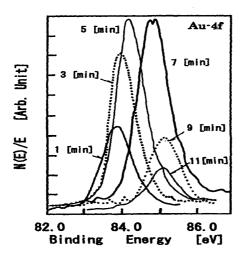


Fig. 3 Au-4f related XPS spectra for sample with Zn content of 0.4 wt.% plotted as parameter of sputtering time.

These results suggest that an extremely small amount of Zn that is less than the detection limit of Auger electron spectroscopic measurement is essential to obtain excellent ohmic contacts. Ohmic contacts with a specific contact resistance of 8 x 10^{-5} $\Omega \cdot \text{cm}^2$ have been obtained with a Zn content as small as 0.4 wt.%, which corresponds to a 21.6-A-thick Zn layer in a 2000-A-thick Au layer. Since the lattice structure of a single zinc crystal is a closely packed hexagonal with a lattice constant of a= 2.665 Å and c= 4.95 Å¹⁸, the atomic density of this single crystal can be calculated to be 1.06 x 10²³ cm⁻³. Thus, the number of zinc atoms in an area of 1 cm² and a thickness of 21.6Å is about 2.29 x 1016. Since the distribution coefficient for Zn-doped liquid phase epitaxial InP grown at 650 °C is 0.9819, most of the atoms that have diffused into the InP substrate act as a carrier. If half the Zn atoms in the evaporated film diffuse outside and the remaining half is assumed to diffuse from the substrate surface to a depth of 500 Å, this results in a layer with a Zn concentration of 2.24 x 10²¹ cm⁻³. This is less than the detection limit for Zn using Auger electron spectroscopic measurement. This coincides with the experimental results previously described. Fatemi and Weizer® also reported that ohmic behavior could be achieved by using AuZn films with a Zn content as small as 0.05 at.% and that this could be accomplished by incorporating a layer of Zn only 1A thick in a 2000-A-thick Au layer. This leads to acceptor doping concentrations of 1.04 x 10^{20} cm⁻³. We concluded that an extremely low Zn concentration of 2.24×10^{21} cm⁻³ is essential in producing ohmic contacts with a low specific contact resistance of $1 \times 10^{-4} \Omega \cdot \text{cm}^2$.

Chemical shift in Au-4f related XPS spectra has only been observed in the vicinity of the metal-semiconductor interface and has not been observed in the surface region where large amounts of In have been detected, as well as Au, but not P. This indicates that chemical shift is caused by the formation of an Au-P compound. This is very likely to be Au₂P₃. Piotrowska et al²⁰, Valois et al², Clausen et al.^{6, 9}, and Fatemi et al.⁸ reported on the formation of Au₂P₃ from their studies on Au:Zn/p-type InP metallization systems.

We presumed that the mechanism for the ohmic contact formation operated as follows. In the initial stage of alloying, indium atoms out-diffuse into the first Au layer deposited on the substrate surface but hardly no phosphorus atoms out-diffuse. At that time, gold atoms diffuse into InP and form compounds with P. Since the solubility of the zinc in InP is about $4 \times 10^{18} \, \text{cm}^{-3}$ at 650 °C, the depletion layer width is calculated to be 161 Å and 94 Å for bias voltages of V=0 V and V=0.5 V, respectively. We used a barrier height Φ_B of 0.76 V this calculation for the Au Schottky barrier diode formed on p-type InP²¹⁾. The tunneling provability T_t was calculated from the following equation²¹⁾;

$$T_t = \exp \left\{-4(2m_p)^{1/2}E_g^{3/2}/3qh_{\varepsilon}\right\}$$

where m_p , E_g , q, and h stand for hole effective mass, energy band gap, magnitude of electronic charge, and Plank constant, respectively and the values of these constants are $m_p/m_e=0.56,\ 1.351$ eV, 1.6×10^{-19} C, and 6.626×10^{-34} J·s, respectively. The electric field strength ϵ is given by $\epsilon=-2\Phi_B/w_d$, where Φ_B and w_d are the barrier height and the depletion layer width, respectively, and w_d is calculated from the equation $w_d=\{2\ \epsilon\ _0\ \epsilon\ _s(\Phi_B-V_f)/q\ N_A\}$. Typical T_t 's are 1.4×10^{-6} for $V_f=0\ V$, 2.1×10^{-4} for $V_f=0.5\ V$, and 0.018 for $V_f=0.7\ V$.

Two mechanisms that control the current flow through the metal-semiconductor contact have been proposed to explain ohmic behavior in metal (Au/Zn)-semiconductor (InP) contacts: (1) The zinc atoms introduced into InP create the p⁺ layer at the interface and reduce the depletion layer width, resulting in an increase in the tunnel current through the contact. (2) The compounds formed during the sintering process reduce the barrier height, producing increased themionic emission current. The tunnel current can be calculated from the following equation²¹⁾ and is 1.46 x 10^{-6} pA/(μ m)² for $\Phi_B = 0.76$ V.

$$J_{\text{tunnel}} = \exp(-q \Phi_B/E_{00})$$

where $E_{00}=(qh/4\pi)(N_A/\epsilon_0\epsilon_s m_h)^{1/2}$, Φ_B is the barrier height of the metal for p-type InP ,and N_A is the acceptor density of the p⁺ layer formed by alloying. It can be calculated from the following equation for thermionic emission current.

$$J_{\text{thermionic emission}} = A * T^2 \exp(-q \Phi_B/kT) \{ \exp(qV/kT) - 1 \}$$

where $A^*=4 \pi q m_e k^2/h^3$ and V is the applied voltage.

A typical value at a bias voltage of 0.1 V is 3.27 pA/(μ m)². We used a barrier height Φ_B of 0.76 V²¹, an acceptor density NA of 4 x 10¹⁸ cm⁻³, a specific dielectric constant ϵ s of 12.35, and an effective mass of holes m_b/m_e of 0.56 in this calculation. Why we adopted this value as the acceptor density is based on results obtained by Abrams et al¹⁸ and Mihashi²² who reported that the acceptor density of Zn-doped InP layers grown at 650 °C by liquid phase and metal organic chemical vapor deposition is about 4 x 10¹⁸ cm⁻³. Gurp et al.²³ also reported that carrier concentrations of the p⁺ layer diffused at 550 °C are 5~6 x 10¹⁸ cm⁻³.

As the barrier height is decreased to half of 0.76 eV, the tunnel current and thermionic emission current are 1.21 x 10^{-3} pA/(μ m)² and 7.83 μ A/(μ m)². Even if the carrier concentration is assumed to be 1 x 10^{21} cm⁻³, the tunnel current increases to 4.6 x 10^{-1} pA/(μ m)² for $\Phi_B = 0.76$ V and is still incredibly small. This implies that the contribution of tunneling current to total current is negligible compared with thermionic emission current even if the barrier height is reduced to half. The calculations indicate that the tunneling current is minuscule and thermionic emission current governs current flow in Au/Zn/Au/p-type InP ohmic contacts.

To obtain reasonable thermionic emission current density of several microamperes/(μ m)², it is obvious from calculation that the barrier height Φ_B has to be halved. Clausen and Leistiko⁹ reported that the effective barrier height can be reduced almost to zero volt by alloying AuZn(Ni) metallizations at 440 °C and they also suggested that lowered barrier height and compound formation during the sintering process are closely related. They also speculated in another research paper that very low specific contact resistance can be obtained by growing a certain binary compound such as Au₃In which enhances metal-phosphide formation, resulting in lower barrier height. The results we obtained indicate that Au/p-type InP contacts do not exhibit ohmic behaviors even if they are alloyed up to 550 °C and a small amount of Zn is essential to obtain linear current-voltage curves. This suggests that ohmic contacts are not only caused by the formation of compounds such as Au₂P₃ and Au₃In, but zinc contributes to lowering the Au and/or Au₂P₃ and/or Au₃In Schottky barrier heights to p-type InP. Yousuf et al.²⁴⁾ reported that the barrier height of a Pd-InP Schottky diode decreases dramatically by exposing the diode to some gases. Huber reported that the work function of gold dramatically decreased to 0.5 eV with the presence of a trace of Hg²⁵⁾. Similar barrier lowering has been obtained in Au²Zn/p-type GaP by

introducing 0.5 wt% Sb²⁶. Fatemi and Weizer⁸ also pointed out the importance of introducing traces of foreign species into the metal/p·type InP interface, resulting in substantial changes in the metal work function.

Summary

We studied the electronic and metallurgical behaviors of ohmic contacts of Au/Zn/Au to p-type InP and obtained the following results:

- (1) Contacts with an extremely small amount of Zn which could not be detected at or inside the metal-semiconductor interface by Auger electron spectroscopic measurement exhibited ohmic behaviors where the specific contact resistance was as small as $2 \times 10^{-4} [\Omega \cdot \text{cm}^2]$.
- (2) Depth profiles of constituent atoms obtained by Auger electron spectroscopic measurement show that indium diffuses into gold film, but hardly no phosphorous is out-diffused during the alloying process.
- (3) We observed chemical shift in the Au-4f related XPS signal around the metal-semiconductor interface, indicating the formation of a compound with P such as Au₂P₃
- (4) Thermionic emission current governs the current flow through ohmic contacts because tunneling current is negligibly small.
- (5) To produce reasonable thermionic emission current, the Schottky barrier height of Au to p-type InP has to be reduced to less than half the original barrier height of 0.76 eV.
- (6) We concluded that a small amount of Zn which cannot be detected by Auger electron spectroscopic measurement causes the barrier height to lower.

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