

PtIn₂ ohmic contacts to *n*-GaAs via an In-Ga exchange mechanism

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(Received 21 August 1995; accepted for publication 24 October 1995)

Using sputter-deposited PtIn₂ films as metallizations, it is demonstrated that the recently identified exchange mechanism may be utilized to form ohmic contacts to *n*-GaAs. Specific contact resistances as low as $3.0 \times 10^{-6} \Omega \text{ cm}^2$ are obtained upon annealing in the temperature range of 800–850 °C. Contacts processed under optimum conditions show little degradation in electrical properties after 100 h of thermal aging at 400 or 500 °C. Auger depth profiles of as-deposited and annealed samples are consistent with the hypothesis of an exchange of In and Ga atoms at the contact interface.
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Over the past decade, the application of metallurgical principles and characterization techniques to the study of metal-GaAs interfaces has led to significant advances in GaAs contact technology (see, for example, Refs. 1–3). Early investigations focused on rationalizing the evolution of metal-GaAs chemical reactions and identifying and fabricating thermodynamically stable, epitaxial contact materials. More recently, the knowledge base acquired during this early work has allowed for the development of proactive metallization schemes, in which multielemental metallizations are actually designed to react with GaAs in a predictable, reproducible manner, forming contacts with the desired electrical properties.

Two reaction mechanisms have been identified which may be utilized to tailor the electrical properties of contacts to GaAs. The first, which has been termed the solid phase regrowth mechanism, has been developed by Sands *et al.*⁴ In the solid phase regrowth mechanism, a two-step chemical reaction occurs in which a shallow layer of GaAs is first consumed by reaction with a transition metal. The consumed layer is then regrown epitaxially on the remaining GaAs substrate when the transition metal participates in a second chemical reaction with an additional element, such as Si, Ge, In, or Al.

During the regrowth process, some of the additional element is incorporated into the regrown GaAs layer. The subsequent electrical properties of the contact depend upon the nature of the incorporated element. For example, the incorporation of Si, Ge, or In into the regrown GaAs layer leads to ohmic behavior, whereas the incorporation of Al into the regrown GaAs layer leads to Schottky barrier enhancement. The incorporation of each of these elements into GaAs via the solid phase regrowth mechanism, and the resulting change in electrical behavior of the contact, have been demonstrated experimentally.^{4–7}

The second reaction mechanism for controlling the electrical properties of contacts to GaAs is the exchange mechanism. As its name implies, the exchange mechanism is a simple solid-state exchange of one element from a single

phase metallization layer with a second element from the compound semiconductor. In the strict thermodynamic sense, no new phases are formed at the metal-compound semiconductor interface; only the compositions of the original phases are changed.

While conceptually the exchange mechanism is rather straightforward, a metallization must meet rather stringent criteria to be capable of participating in an exchange reaction with GaAs. Jan⁸ has identified these criteria, and has developed a thermodynamic/kinetic framework to rationalize the exchange mechanism. A summary of his analysis has recently been presented by Chang.⁹ The reader is referred to this latter reference for a quantitative description of the mechanism.

The exchange mechanism was first hypothesized by Sands *et al.*,¹⁰ who noted Schottky barrier enhancement of Ni/Al/Ni/*n*-GaAs contacts after high temperature heat treatment. They attributed this change in electrical properties to the formation of Al_xGa_{1-x}As at the contact interface through the exchange of Al and Ga atoms between the NiAl metallization and the GaAs substrate. Chen *et al.*¹¹ have recently corroborated the exchange mechanism by directly sputter-depositing the intermetallic compound NiAl on *n*-GaAs. Like Sands *et al.*, they found Schottky barrier enhancement to occur upon heat treatment of the contact. Moreover, they confirmed the formation of Al_xGa_{1-x}As at the contact interface using cross-sectional transmission electron microscopy.

While it has been established experimentally that the exchange mechanism may be employed to obtain Schottky barrier enhancement of contacts to *n*-GaAs, it should also be possible to form ohmic contacts to *n*-GaAs through the application of this mechanism. If one were to employ an appropriate metal indide as a contact metallization, one would anticipate the formation of In_xGa_{1-x}As at the contact interface, which in turn would lead to ohmic electrical behavior. However, such a possibility has not yet been demonstrated.

A recent study of the Ga-In-Pt-As system¹² has identified the fluorite-structured intermetallic compound PtIn₂ as an indide which meets all of the criteria outlined by Jan for par-

ticipating in an exchange reaction with GaAs. In the present investigation, PtIn₂/n-GaAs ohmic contacts have been fabricated, and it is demonstrated that the exchange mechanism may be used to obtain ohmic contacts to n-GaAs. The remainder of this work focuses on the electrical properties of PtIn₂/n-GaAs contacts as a function of annealing conditions. A detailed analysis of contact metallurgy and phase equilibria in the Ga-In-Pt-As system will be published at a later date.

To fabricate contacts, Si-doped ($n = 1.6 - 1.8 \times 10^{19} \text{ cm}^{-3}$), (100)-oriented GaAs wafers were ultrasonically degreased in hot trichloroethylene, acetone, and methanol for 5 min each. They were then rinsed in flowing deionized (DI) H₂O for 2 min, and etched in a 1:10 HF:DI H₂O solution for 2 min, followed by another rinsing in flowing DI H₂O for 3 min. Subsequently, an array of 65 μm diameter dots spaced 1500 μm apart was defined using a standard lift-off photolithographic technique. After photolithography, the substrates were again etched in a 1:10 HF:DI H₂O solution for 2 min, and rinsed in flowing DI H₂O for 3 min. They were blown dry with high-purity N₂, and were immediately loaded into a cryopumped vacuum chamber with a base pressure of better than 3×10^{-7} Torr.

Thin film deposition was accomplished by dc magnetron sputtering from a single 2 in. target, which was fabricated by vacuum hot-pressing a powdered master alloy. Metal films were deposited at a rate of 15 nm/min, under an Ar⁺ pressure of 4 mTorr. A thick film (1.2 μm) was sputtered on a glass slide and analyzed with a Cameca electron microprobe to verify the composition of the sputtered alloy. X-ray diffraction analysis of the thick film, using a Nicolet diffractometer with Cu K α radiation, confirmed that the film was single phase PtIn₂. All films deposited on GaAs were 200 nm in thickness.

After sputter deposition, the photoresist was removed from the substrates by soaking them in ultrasonically agitated acetone. Contacts were then processed using an AG Associates Heatpulse Minipulse rapid thermal annealing furnace under an atmosphere of purified Ar. During heat treatment, the substrates were placed within a graphite susceptor

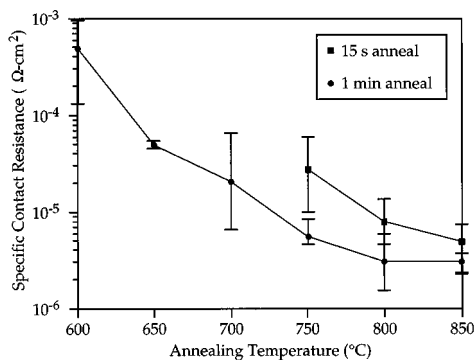


FIG. 1. Specific contact resistances of PtIn₂/n-GaAs contacts as a function of annealing temperature. The symbols denote average values, and the error bars indicate the highest and lowest specific contact resistances measured for each annealing condition. Squares represent data for contacts annealed for 15 s, whereas circles represent data for contacts annealed for 1 min.

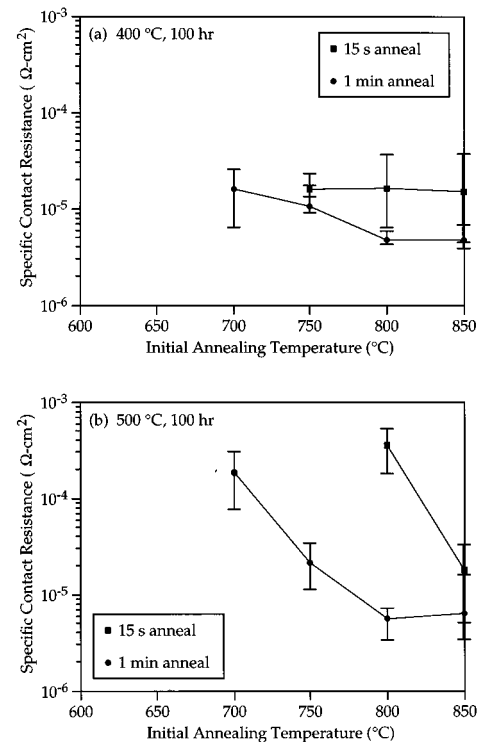


FIG. 2. Specific contact resistances of PtIn₂/n-GaAs contacts aged for 100 h at (a) 400 °C or (b) 500 °C as a function of initial annealing temperature. As was the case in Fig. 1, the symbols denote average values, and the error bars indicate the highest and lowest specific contact resistances measured for each annealing condition. Squares represent data for contacts annealed for 15 s, whereas circles represent data for contacts annealed for 1 min.

face-to-face with a sacrificial GaAs wafer. Contacts were annealed at temperatures between 600 and 850 °C for times of either 15 s or 1 min.

Specific contact resistances (ρ_c 's) were measured using a modified four-point probe method as outlined by Kuphal.¹³ A Keithley Model 236 electrometer was employed as a current source and voltage meter. At least five independent measurements of ρ_c were taken for each annealing condition.

Subsequent to the initial heat treatment and electrical characterization, the thermal stability of the contacts was assessed using long term annealing experiments. This was accomplished by encapsulating the substrates in quartz ampoules, which were evacuated in a turbopumped vacuum system to pressures in the high 10^{-7} Torr range, and furnace annealing at 400 or 500 °C for 100 h.

Finally, the chemical reactions at the metal-semiconductor interface were characterized by Auger depth profiling of as-deposited and annealed contacts, using a Perkin-Elmer scanning electron microprobe.

The ρ_c 's of the contacts as a function of annealing temperature are given in Fig. 1. As-deposited contacts were found to be rectifying. Contacts annealed for 15 s were also found to be rectifying if annealed below 750 °C, as were contacts annealed for 1 min at temperatures below 600 °C. The lowest ρ_c 's ($3.0 \times 10^{-6} \Omega \text{ cm}^{-2}$) were obtained upon annealing for 1 min in the temperature range of 800–850 °C.

The effects of thermal aging for 100 h at 400 and 500 °C

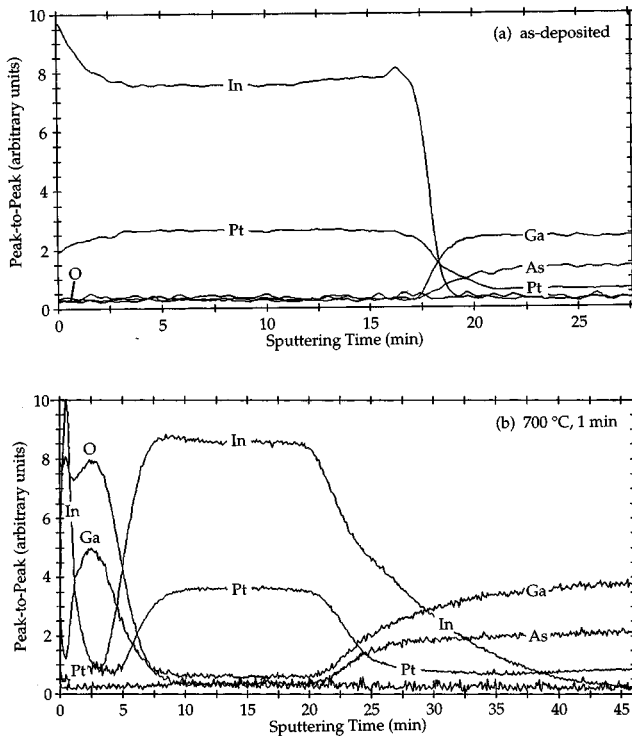


FIG. 3. Auger depth profiles of (a) as-deposited $\text{PtIn}_2/n\text{-GaAs}$ contacts, and (b) $\text{PtIn}_2/n\text{-GaAs}$ contacts annealed at $700\text{ }^\circ\text{C}$ for 1 min.

on the electrical properties of the contacts are summarized in Figs. 2(a) and 2(b), respectively, as a function of initial annealing temperature. All of the contacts exhibited a certain amount of electrical degradation upon thermal aging at either temperature. The most extreme cases of degradation involved contacts initially annealed at $600\text{ }^\circ\text{C}$ for 1 min, which became rectifying after thermal aging at both 400 and $500\text{ }^\circ\text{C}$, and contacts initially annealed at $750\text{ }^\circ\text{C}$ for 15 s, which became rectifying upon thermal aging at $500\text{ }^\circ\text{C}$. However, contacts initially annealed under optimum conditions exhibited good thermal stability. The ρ_c 's of contacts initially annealed for 1 min at $800\text{--}850\text{ }^\circ\text{C}$ increased to $4.5 \times 10^{-6}\ \Omega\ \text{cm}^2$ and approximately $6.0 \times 10^{-6}\ \Omega\ \text{cm}^2$ after 100 h of heat treatment at 400 and $500\text{ }^\circ\text{C}$, respectively. This level of thermal stability is similar to that exhibited by other In-based contacts to $n\text{-GaAs}$ ^{6,14} and is more than sufficient to withstand thermal device processing steps required subsequent to contact formation.

In Figs. 3(a) and 3(b), Auger depth profiles are presented of an as-deposited contact and a contact annealed at $700\text{ }^\circ\text{C}$ for 1 min, respectively. It may be seen that in the as-deposited contact, there are abrupt changes in composition of all elements at the $\text{PtIn}_2/\text{GaAs}$ interface. However, in the annealed contact, a long tail of In extends into the GaAs substrate, suggesting the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$. More-

over, some Ga appears to have completely penetrated the PtIn_2 layer and has accumulated at the contact surface, forming Ga_2O_3 , although it should be noted that a portion of this surface Ga may be attributable to the sacrificial GaAs wafer employed during thermal processing. Concomitantly, the concentration profiles of Pt and As in the annealed contact remain unchanged from those of the as-deposited contact; they are abrupt at the $\text{PtIn}_2/\text{GaAs}$ interface, and flat away from the interface. Overall, these Auger data strongly suggest that no new phases have formed in the contact upon annealing, but rather an exchange of In and Ga atoms has occurred between the PtIn_2 and the GaAs. This is exactly what one would expect to observe when the exchange mechanism is operative.

In summary, by employing the intermetallic compound PtIn_2 as a metallization, it has been demonstrated that the exchange mechanism may be utilized to form ohmic contacts to $n\text{-GaAs}$. Specific contact resistances as low as $3.0 \times 10^{-6}\ \Omega\ \text{cm}^2$ have been achieved upon annealing in the temperature range of $800\text{--}850\text{ }^\circ\text{C}$ for 1 min. Moreover, these contacts exhibit little degradation in electrical properties upon thermal aging under conditions as severe as $500\text{ }^\circ\text{C}$ for 100 h. The predicted exchange of In and Ga atoms at the contact interface is consistent with experimental Auger depth profiles of annealed samples.

The present investigation, in conjunction with those of previous workers, demonstrates the great utility of the exchange mechanism in terms of GaAs contact technology. By selecting the appropriate metallization, this single mechanism may be used to produce both enhanced Schottky barriers and ohmic contacts to $n\text{-GaAs}$.

The authors gratefully acknowledge the National Science Foundation for its support of this project through grant number DMR-94-24478. They also wish to thank S. E. Mohney and D. B. Ingerly for reviewing this manuscript.

¹T. Sands, *Mater. Sci. Eng. B* **1**, 289 (1989).

²M. Murakami, *Mater. Sci. Rep.* **5**, 273 (1990).

³C. J. Palmström and T. D. Sands, in *Contacts to Semiconductors: Fundamentals and Technology*, edited by L. J. Brillson (Noyes, Park Ridge, NJ, 1993), p. 67.

⁴T. Sands, E. D. Marshall, and L. C. Wang, *J. Mater. Res.* **3**, 914 (1988).

⁵E. D. Marshall, B. Zhang, L. C. Wang, P. F. Jiao, W. X. Chen, T. Sawada, S. S. Lau, K. L. Kavanagh, and T. F. Kuech, *J. Appl. Phys.* **62**, 942 (1987).

⁶L. C. Wang, X. Z. Wang, S. S. Lau, T. Sands, W. K. Chan, and T. F. Kuech, *Appl. Phys. Lett.* **56**, 2129 (1990).

⁷C.-P. Chen, Y. A. Chang, and T. F. Kuech, *J. Appl. Phys.* **77**, 4777 (1995).

⁸C.-H. Jan, Ph.D. Thesis, University of Wisconsin-Madison, 1991.

⁹Y. A. Chang, *Mater. Res. Soc. Symp. Proc.* **260**, 43 (1992).

¹⁰T. Sands, W. K. Chan, C. C. Chang, E. W. Chase, and V. G. Keramidis, *Appl. Phys. Lett.* **52**, 1338 (1988).

¹¹C.-P. Chen, Y. A. Chang, and T. F. Kuech, *Appl. Phys. Lett.* **64**, 3485 (1994).

¹²D. Swenson, Ph.D. Thesis, University of Wisconsin-Madison, 1994.

¹³E. Kuphal, *Solid-State Electron.* **24**, 69 (1981).

¹⁴M. Murakami and W. H. Price, *Appl. Phys. Lett.* **51**, 664 (1987).