Thermally stable PdIn ohmic contacts to *n*-GaAs via exchange mechanism

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Thermally stable, low-resistance ohmic contacts to GaAs (Si-doped, $n = 1.6\text{--}1.8 \times 10^{18} \text{ cm}^{-3}$) were formed using PdIn metallization sputter-deposited from an alloy target. Average specific contact resistances (ρ_c) in the $10^{-6} \Omega \text{ cm}^2$ range were reached upon annealing at 600 °C or higher. Contacts annealed under the optimum condition of 850 °C for 15 s exhibited an average ρ_c of $2.5 \times 10^{-6} \Omega \text{ cm}^2$. The 100 h of thermal aging at 400 or 500 °C increased their average ρ_c to 3.0×10^{-6} and $1.0 \times 10^{-5} \Omega \text{ cm}^2$, respectively. The ohmic behavior of the annealed contacts was ascribed to the exchange of In and Ga atoms between the metallization and the semiconductor and the concomitant formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$, whose presence at the contact interface was confirmed using cross-sectional transmission electron microscopy. © 1997 American Institute of Physics. [S0021-8979(97)04801-9]

INTRODUCTION

Contacts comprising Pd and In are among the most studied nonalloyed metallizations to *n*-GaAs to date.^{1–8} They exhibit very good electrical properties, generally yielding specific contact resistances ρ_c in the low to mid- $10^{-6} \Omega \text{ cm}^2$ range, and show excellent uniformity and thermal stability. It is well established that the ohmic behavior of these contacts may be attributed to the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ at the interface, which reduces the interfacial Schottky barrier height and thus facilitates electron transport between the metal and semiconductor. However, the exact chemical mechanism of $\text{In}_x\text{Ga}_{1-x}\text{As}$ formation in annealed Pd–In contacts is less well characterized. Early investigators, such as Allen *et al.*,¹ Stremisdoerfer *et al.*,² and Prasad and co-workers,⁴ concentrated on measuring electrical properties of annealed contacts and neither of them identified clearly the reaction products that ensued from thermal processing. Moreover, significant differences in metallization composition, deposition method, and annealing procedure employed by each of these investigators would have made a direct comparison of their studies difficult in any case.

Wang *et al.*^{3,5} were the first to identify a possible mechanism for the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ from the chemical interaction between Pd–In metallizations and *n*-GaAs. This mechanism is termed the solid-phase regrowth mechanism, and has been described in detail by Sands, Marshall, and Wang.⁹ Wang *et al.* postulated the regrowth mechanism to proceed as follows. Pd and In are deposited in layers, with the configuration of Pd/In/Pd/*n*-GaAs. The ratio of Pd to In is chosen to correspond to that of slightly In-rich PdIn, an intermetallic phase with the CsCl (*B2*) structure. The contacts are formed by a two-step annealing process. Upon annealing at low temperature (~ 100 °C), the bottom Pd layer reacts with the GaAs substrate to form a metastable ternary compound Pd_4GaAs . This reaction has been well characterized in the study of Pd/GaAs couples.¹⁰ Simultaneously, the PdIn_3 phase is produced from the reaction between In layer

and the outer Pd layer, resulting in the configuration of $\text{PdIn}_3/\text{Pd}_4\text{GaAs}/n\text{-GaAs}$. During the second stage of annealing (≥ 550 °C), PdIn_3 and Pd_4GaAs react with each other to form PdIn and regrown GaAs. During the regrowth process some In is incorporated into the GaAs layer, forming $\text{In}_x\text{Ga}_{1-x}\text{As}$, and the displaced Ga is incorporated into the metal layer.

Although this reaction mechanism is quite plausible, the specific means by which In is incorporated into the regrown GaAs layer is not clear. Indeed, transmission electron microscopy (TEM) by Wang *et al.*⁵ suggests that solid-phase regrowth occurs at low temperatures (e.g., 325 °C), yet no In is incorporated into the regrown GaAs layer. This implies that the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ may not result from the regrowth process.

Recent work by Fu and Huang^{7,8} further indicates that solid-phase regrowth is not required for the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ in Pd–In contacts to *n*-GaAs. Fu and Huang compared the electrical properties of codeposited PdIn (*B2* structure) and layered Pd/In/Pd contacts to *n*-GaAs. They have found that for each initial configuration, the same ρ_c –*T* relationship and the same final phase configuration ($\text{PdIn}/\text{In}_x\text{Ga}_{1-x}\text{As}/n\text{-GaAs}$) are obtained upon heat treatment. Because codeposited PdIn cannot participate in the solid-phase regrowth process, a different mechanism must be responsible for the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ at the contact interface.

The work from Fu and Huang suggests that codeposited PdIn contacts to *n*-GaAs become ohmic due to the exchange mechanism, which was postulated by Sands *et al.*¹¹ and described theoretically by Jan¹² and Chang, Jan, and Chen.^{13,14} Because PdIn and Pd/In/Pd contacts share the same ρ_c –*T* relationship and final phase configuration, it is very likely that for Pd/In/Pd contacts, instead of the regrowth mechanism, it is the exchange mechanism between PdIn, which forms as a result of the regrowth process, and GaAs that gives rise to the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$. The operation of

the exchange mechanism has recently been demonstrated by the present investigators¹⁵ in the study of PtIn₂ ohmic contacts to *n*-GaAs. (In Ref. 15 a typographical error was made concerning the doping concentration of *n*-GaAs used. It should be $1.6\text{--}1.8\times 10^{18}\text{ cm}^{-3}$ instead of $1.6\text{--}1.8\times 10^{19}\text{ cm}^{-3}$. In fact, the doping concentration is the same as the one used in the present study.) In this article we report the formation of ohmic contacts via the exchange mechanism between alloy target deposited PdIn and *n*-GaAs.

Our thermodynamic/kinetic study of the Ga-In-Pd-As system¹⁶ reveals that the intermetallic compound PdIn satisfies the criteria for participating in an exchange reaction with GaAs. Two solid solution phases, Pd(In,Ga) (*B2* structure) and (In,Ga)As, are in thermodynamic equilibrium. However, the equilibrium does not exist between PdIn and GaAs, which are the specific compositions of the Pd(In,Ga) and (In,Ga)As phases, respectively. There would thus be an exchange of In and Ga atoms upon heat treatment in order for the phases to reach their equilibrium compositions at the interface. This exchange causes a composition shift of the original phases at the interface but does not lead to the formation of any new phases. The result is the formation of In_{*x*}Ga_{1-*x*}As at the interface, which gives rise to the contact's ohmic behavior. Accordingly, the reacted metal layer becomes PdIn_{*y*}Ga_{1-*y*}. The merit of this contact scheme is the simplicity and uniformity of the microstructure one may anticipate when no new phase forms at the contact interface. In this article the electrical behavior, as well as preliminary TEM characterization, is presented for PdIn/*n*-GaAs contacts. A detailed thermodynamic/kinetic analysis of PdIn/*n*-GaAs and interfacial reaction characterization will be published at a later date.

EXPERIMENT

The fabrication of contacts involves target fabrication, lithographic patterning, thin-film deposition, and thermal treatment. Contacts to be used for cross-sectional TEM characterization were prepared the same way as described below, except that the lithography was omitted. A PdIn compound target was fabricated by vacuum hot pressing a powdered PdIn master alloy. For lithographic patterning, Si-doped ($n=1.6\text{--}1.8\times 10^{18}\text{ cm}^{-3}$) (100)-oriented GaAs wafers were degreased in the sequence of trichloroethylene, acetone, and methanol under heat and ultrasonication for 5 min each. They were then rinsed in flowing de-ionized (DI) H₂O and etched in HF:DI-H₂O (1:10) solution for 2 min each, followed by another DI-H₂O rinsing for 3 min. Subsequently, the standard lift-off photolithographic technique defined the test pattern of an array of 65- μm -diam dots spaced 1500 μm apart. After lithography, the substrates were again etched in a HF:DI-H₂O (1:10) 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 the base pressure lower than 3×10^{-7} Torr.

Thin-film deposition was accomplished by dc magnetron sputtering from a disk-shaped PdIn compound target. Metal films were deposited at a rate of 15 nm/min, under 4.0 mTorr of high-purity Ar gas pressure. A thick film (2.0 μm) was

FIG. 1. Specific contact resistances of PdIn/*n*-GaAs contacts as a function of annealing temperature. The symbols denote average values of at least five independent measurements. The error bars indicate the highest and lowest specific contact resistances measured for each annealing condition.

sputtered on a glass slide and analyzed by a Cameca electron microprobe to verify the composition of the sputtered film. X-ray-diffraction analysis of this thick film, using a Nicolet diffractometer with Cu *Kα* radiation, confirmed that the film was single phase PdIn. All films deposited on GaAs were nominally 200 nm in thickness.

After sputter deposition the wafers were soaked in ultrasonically agitated acetone to remove the photoresist. The thermal treatment of the thin film contacts was then performed using an AG Associate Heatpulse Minipulse rapid thermal annealing furnace, which was ramped to the desired temperature at the rate of 50 °C/s. Sacrificial pieces of GaAs were laid face to face with the samples during annealing to reduce As outgassing. The furnace environment was the flowing high-purity Ar gas.

Specific contact resistances ρ_c were measured using a modified four-point-probe method outlined by Kuphal.¹⁷ A Keithley model 236 measurement unit was employed as a current source and voltage meter. At least five independent measurements of ρ_c were taken for each annealing condition.

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

RESULTS AND DISCUSSION

The ρ_c of the contacts as a function of annealing temperature are given in Fig. 1. Contacts were rectifying in the as-deposited state; they became ohmic after being annealed at 500 °C for 1 min. The ρ_c dropped to the $10^{-6}\text{ }\Omega\text{ cm}^2$ range after the contacts were annealed at 600 °C or higher. The lowest ρ_c ($2.5\times 10^{-6}\text{ }\Omega\text{ cm}^2$) were obtained after annealing at 850 °C for 15 s.

FIG. 2. Specific contact resistances of PdIn/n-GaAs contacts aged for 100 h at (a) 400 $^{\circ}\text{C}$ or (b) 500 $^{\circ}\text{C}$ as a function of initial annealing temperature. As was the case in Fig. 1, the symbols denote average values, and the error bar indicates the highest and lowest specific contact resistances measured for each annealing condition.

The ρ_c of the contacts after thermal aging for 100 h at 400 and 500 $^{\circ}\text{C}$ as a function of the initial annealing temperature are given in Figs. 2(a) and 2(b), respectively. As shown in Fig. 2(a), there was practically no degradation for the contacts thermally aged at 400 $^{\circ}\text{C}$ for 100 h; the values of ρ_c remain approximately the same compared with those shown in Fig. 1; however, this is not the case for contacts aged at 500 $^{\circ}\text{C}$ for 100 h. As shown in Fig. 2(b), the ρ_c for contacts annealed at 700, 750, 800, and 850 $^{\circ}\text{C}$ are higher than the corresponding values shown in Fig. 1. The contacts annealed at 600 $^{\circ}\text{C}$ or lower became rectifying and thus had no data point in Fig. 2(b). The average ρ_c of the contacts initially annealed at the optimum condition of 850 $^{\circ}\text{C}$ /15 s increased from $2.5 \times 10^{-6} \Omega \text{ cm}^2$ to 3.0×10^{-6} and $1.0 \times 10^{-5} \Omega \text{ cm}^2$ after 100 h treatment at 400 and 500 $^{\circ}\text{C}$, respectively. This level of thermal stability is more than sufficient to withstand the thermal processing steps for device fabrication after contact formation.

The contact interface was characterized by cross-sectional TEM using a JOEL 200CX transmission electron microscope equipped with an energy-dispersive spectrometer

FIG. 3. Bright-field transmission electron micrograph of a cross-sectional view of PdIn/n-GaAs contact after annealing at 600 $^{\circ}\text{C}$ for 1 min.

(EDS). Figure 3 is a cross-sectional TEM micrograph of a contact annealed at 600 $^{\circ}\text{C}$ for 1 min. The interface shows an aggregate structure. The light reacted region, denoted “ α ” in Fig. 3, has a contrast similar to that of the GaAs substrate. The EDS spectrum shown in Fig. 4(a) indicates that it contains In, Ga, and As, but no Pd; it suggests that this is the reacted $\text{In}_x\text{Ga}_{1-x}\text{As}$, which lowers the specific contact resistances. Conversely, the dark reacted region, denoted “ β ” in Fig. 3, has a contrast similar to that of the PdIn metal. This

(a)

(b)

FIG. 4. EDS spectra of (a) a light region and (b) a dark region corresponding to the α and β in Fig. 3, respectively.

region is shown to contain Pd, In, and Ga as shown in the EDS spectrum given in Fig. 4(b), suggesting that it is the reacted $\text{PdIn}_y\text{Ga}_{1-y}$. The presence of Cu peaks in both Figs. 4(a) and 4(b) was due to the ion milling of the Cu sample holding grid and needs no further discussion. The results of this interface characterization are consistent with the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ at the contact interface due to the exchange of In and Ga atoms between PdIn and GaAs substrate.

CONCLUSION

In summary, the intermetallic compound PdIn is used as a contact metallization to *n*-GaAs, as it fulfills the criteria for ohmic contact formation via the exchange mechanism. Average specific contact resistances reached $10^{-6} \Omega \text{ cm}^2$ range upon annealing at 600 °C or above. Specific contact resistances as low as $2.5 \times 10^{-6} \Omega \text{ cm}^2$ were obtained after annealing at 850 °C for 15 s. The contacts exhibited excellent thermal stability after being subjected to a heat treatment of 400 °C for 100 h, while their electrical properties degraded after a similar thermal aging at 500 °C for 100 h. Interfacial characterization by cross-sectional TEM suggests that the formation of $\text{In}_x\text{Ga}_{1-x}\text{As}$ is due to the exchange of In and Ga atoms at the contact interface, consistent with the exchange mechanism.

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