PdIn contacts to *n*-type and *p*-type GaP

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PdIn was used as a contact material to *n*-type and *p*-type GaP. On *n*-type GaP it forms a low resistance ohmic contact upon rapid thermal annealing. PdIn/*n*-GaP (S doped at 2–3 $\times 10^{18}$ cm^{-3}) contacts annealed at 600 °C for 1 min had specific contact resistance's lower than 1×10^{-4} Ω cm^2. Unlike the contacts to *n*-GaP, PdIn contacts to *p*-GaP (Zn doped $1-2\times 10^{18}$ cm^{-3}) show rectifying behavior at all annealing conditions. However, the effective Schottky barrier height seems to decrease significantly with thermal annealing. In addition to the electrical measurements, glancing angle x-ray diffraction was used to characterize the contacts. The glancing angle x-ray diffusion pattern of PdIn/*n*-GaP, annealed at 600 °C for 1 min, is consistent with the formation of an $(In_yGa_{1-y})P$ phase due to the thermal annealing. The ohmic behavior of the PdIn contacts to *n*-type GaP and the decrease in the contact's Schottky barrier height on *p*-type GaP is attributed to the formation of this $(In_yGa_{1-y})P$ phase at the contact's interface. © *1996 American Institute of Physics.* [S0003-6951(96)03749-7]

The semiconductor gallium phosphide (GaP), due to its large energy band gap (E_g=2.26 eV) and good thermal stability, is a potential material for optical and high-temperature devices. Light-emitting diodes,[1] betacells,[2] GaP/Si optoelectronic devices,[3] and bipolar junction transistors (BJTs) operating at temperatures higher than 350 °C have all been demonstrated using GaP.[4] Like other electronic devices, GaP-based devices require stable ohmic contacts with low resistance for current transportation on both *n*-type and *p*-type materials.[2,5] Since most elemental metals form Schottky contacts to *n*-type GaP,[6] possibly due to its high-energy gap, it is necessary to develop alternative metallization methods that utilize two or more elements.

The solid-state exchange reaction had been identified as a systematic approach for tailoring metal/semiconductor contact properties.[7,8] During the exchange reaction one element in the metal phase exchanges with a second element in the compound semiconductor. Therefore, at the contact interface, the composition of each phase is changed thus altering the contact properties. For example, in NiAl/*n*-GaAs contacts, the Al-Ga exchange reaction creates an (Al,Ga)As interfacial layer which enhances the Schottky barrier height of the contact.[9] In $PtIn_2$/*n*-GaAs contacts the In-Ga exchange reaction forms an (In,Ga)As interface layer producing an ohmic contact with low specific contact resistance.[10] In order to select suitable metals and metallic compounds for participating the exchange reaction, Jan[7] and Chang[8] have formulated criteria based on thermodynamic and kinetics considerations.

Based on the criteria for the In-Ga exchange reaction with *n*-type and *p*-type GaP, PdIn was selected as a contact material. PdIn is an intermetallic compound with CsCl (B2) structure, good electrical conductivity and a high melting point (congruent melting point at 1285 °C). Its high melting point makes it potentially more thermally stable than the commonly used Au-Ge-Ni alloyed contacts. Pd-In based metallizations have been used for ohmic contacts to *n*-GaAs,[11–13] *n*-InP,[14] and Si.[15] Fu and Huang[11] have shown that the ohmic behavior of Pd-In metallizations on *n*-GaAs can be attributed to the formation of an $(In_xGa_{1-x})As$ phase at the contact interface, which has a lower-energy band gap than GaAs. This $(In_xGa_{1-x})As$ interface layer increases the probability of electron tunneling and thereby decreasing the contact's resistance.[16] Similar to the $(In_xGa_{1-x})As$ layer in PdIn/*n*-GaAs contacts, if an $(In_yGa_{1-y})P$ phase forms at the metal/GaP contact interface it should decrease the contact resistance of metal/*n*-GaP contacts.

Moheny[14] studied PdIn/*n*-InP (doped $\sim 4\times 10^{18}$ cm^{-3}) contacts. These contacts showed ohmic behavior with specific contact resistance's in the mid 10^{-5} Ω cm^2 range over a large range of annealing conditions, including the as-deposited state. Provided a $(In_yGa_{1-y})P$ layer forms upon annealing and it is InP rich, the PdIn/*n*-GaP contacts should likewise form low resistance ohmic contacts. There are no such electrical studies done on PdIn/*p*-InP contacts. Additionally Moheny studied the PdIn-PdGa-InP-GaP reciprocal system. Her study showed that the formation of an InP-rich (In,Ga)P phase at the interface is likely. A detailed analysis of the contact metallurgy and phase equilibria in the Pd-In-Ga-P system will be published later.

In this study PdIn/GaP contacts were characterized by current-voltage ($I-V$) measurements on both *n*-type and *p*-type GaP substrates, as well as glancing angle x-ray diffraction (GAXRD). S-doped (100) *n*-type GaP (2–3 $\times 10^{18}$ cm^{-3}) and Zn-doped (100) *p*-type GaP ($1-2\times 10^{18}$ cm^{-3}) wafers polished on both sides were used as substrates. The following procedures were used to prepare all samples examined in this study, with the photolithography steps being omitted on substrates used for GAXRD. The substrates were first degreased with trichlorethylene, acetone, and methanol, followed by photolithography to the define equal-space circular patterns 150 μm in diameter and 750 μm apart used for the $I-V$ measurement. Additionally, for improved precision in the specific contact resistance measurement a second pattern was also used; it consisted of equal-spaced circular patterns 65 μm in diameter and 1500 μm apart. The patterned substrates were then etched in 5% NH_4OH solution for 1 min and immediately loaded into a vacuum chamber with background pressure less than 3×10^{-7} Torr.

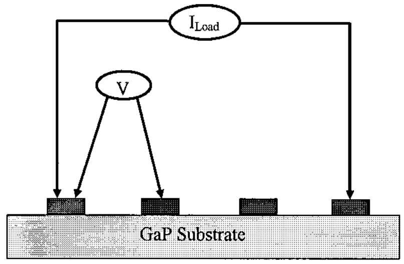

FIG. 1. Probe geometry used to measure the contact's current-voltage behavior.

Nominally 120 nm PdIn films were deposited onto the substrates by a dc magnetron sputtering from a single alloy target. The PdIn target was fabricated by vacuum hot pressing a powder master alloy of the appropriate composition. GAXRD was used to confirm that the sputtered film's crystal structure matched that of PdIn. After the sputtering step, the photoresist was lifted off in an acetone bath leaving circular PdIn pads on the wafers. Following liftoff, samples were annealed in a AG Associated MiniPulse rapid thermal anneal (RTA) system using a flowing high-purity Ar gas atmosphere. All samples were annealed for 1 min at temperatures ranging from 300 to 700 °C.

After annealing, $I-V$ data were measured with a Keithley Model 236 electrometer. Figure 1 shows the contact geometry used when measuring the $I-V$ behavior of the contacts. If a contact exhibited ohmic behavior, the specific contact resistance was calculated using Kuphal's four-point probe method.[17] It should be noted that Wang *et al.*[12] have shown that four-point probe method gives higher values of specific contact resistance than other methods such as transmission line and Kelvin's methods. Therefore the actual value of specific contact resistance of the contacts may be lower than the value obtained in this study. In addition to the electrical measurements, GAXRD was used to characterize the interface. GAXRD was carried out with Nicolet diffractometer using Cu$K\alpha$ radiation; the angle of incident x ray was carefully adjusted until all possible peaks were observed.

Figure 2 shows the $I-V$ characteristics of PdIn/n-GaP contacts annealed for 1 min at temperatures between 500 and 700 °C. It should be noted that contacts in their as-deposited state and those annealed at 300 and 400 °C show highly rectifying behavior. As Fig. 2 illustrates, the contact resistance decreases as the temperature is increased until at 600 °C a minimum contact resistance occurs. Additionally, the contact annealed at 600 °C for 1 min clearly demonstrates ohmic behavior. For this annealing condition, specific contact resistances lower than $1\times10^{-4}\ \Omega\ \mathrm{cm}^2$ were obtained for the PdIn/n-GaP contacts. This is lower than the reported values for the commonly used Au-Ge-Ni alloyed contacts, which had specific contact resistance as low as $7\times10^{-4}\ \Omega\ \mathrm{cm}^2$ on n-GaP (S doped $4\times10^{17}\ \mathrm{cm}^{-3}$).[18] However, the higher doping level of the n-GaP used in our study ($2-3\times10^{18}\ \mathrm{cm}^{-3}$) makes direct comparison of specific contact resistance between the two studies inappropriate since it is well established that the doping level of a semiconductor has

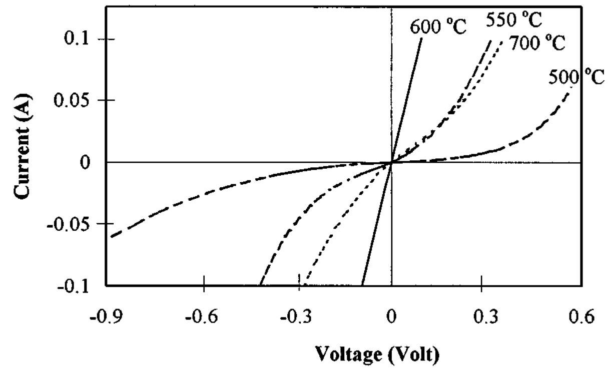

FIG. 2. $I-V$ characteristics of PdIn/n-GaP contacts with respect to annealing temperature. All contacts were annealed for 1 min.

a significant effect on the specific contact resistance. For the same metallization, the specific contact resistance will decrease as the doping level of the semiconductor is increased.[19] When this is taken into account, the specific contact resistance of PdIn/n-GaP contacts annealed at 600 °C for 1 min is comparable to that of Au-Ge-Ni contacts processed under optimized conditions.

The $I-V$ measurements on both n-type and p-type GaP are consistent with the proposed exchange reaction mechanism, where an In-Ga exchange at the semiconductor/metal interface leads to the formation of a $(\mathrm{In}_y\mathrm{Ga}_{1-y})$P phase. Since $(\mathrm{In}_y\mathrm{Ga}_{1-y})$P has lower-energy band gap than GaP, it can be expected that the barrier height of a metal contact on n-type and p-type $(\mathrm{In}_y\mathrm{Ga}_{1-y})$P will be lower than that of the same metal on n-type and p-type GaP. It should be noted that the composition and microstructure of the $(\mathrm{In}_y\mathrm{Ga}_{1-y})$P phase, and therefore the contact behavior, is controlled by the annealing temperature. This explains the significant change in the electrical properties of the PdIn/GaP contacts due to different annealing temperatures.

To confirm the existence of the $(\mathrm{In}_y\mathrm{Ga}_{1-y})$P phase GAXRD of annealed PdIn/n-GaP was used. Figure 4 shows the diffraction pattern of PdIn/n-GaP annealed at 600 °C for 1 min. Three phases were identified: PdIn, GaP, and $(\mathrm{In}_y\mathrm{Ga}_{1-y})$P. To identify the PdIn and GaP phases in this

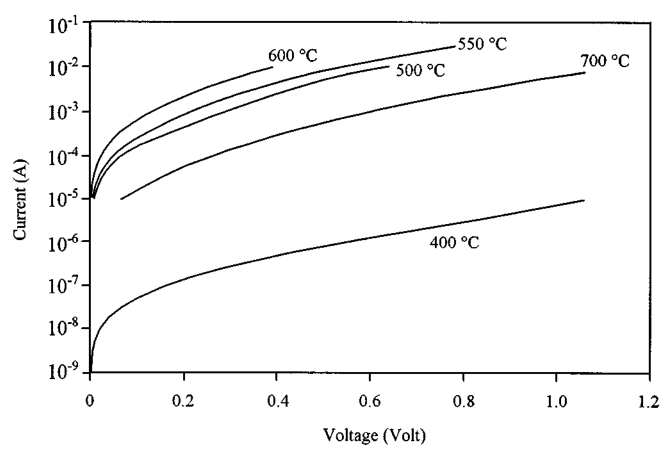

FIG. 3. $I-V$ characteristics of PdIn/p-GaP contacts with respect to annealing temperature. All contacts were annealed for 1 min.

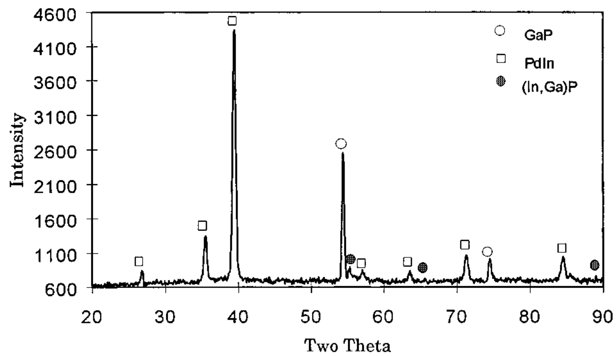

FIG. 4. Glancing angle x-ray diffraction pattern of PdIn/n-GaP annealed at 600 °C for 1 min.

pattern, it was compared to the pattern of PdIn deposited on a glass slide using the same sputtering conditions, as well as the pattern of the GaP substrate; with PdIn and GaP peaks matched to those of the control samples. Identification of $(In_yGa_{1-y})P$ was more complicated because many of the $(In_yGa_{1-y})P$ peaks are overlapped with PdIn peaks. However, the pattern was indexed based on nonoverlapped peaks and a lattice constant calculated. From the obtained lattice constant, assuming a linear relationship between the composition and lattice constant, the composition of $(In_yGa_{1-y})P$ was estimated to be $(In_{0.7}Ga_{0.3})P$. Due to the majority of the $(In_yGa_{1-y})P$ peaks overlapping PdIn peaks and the low intensities of the nonoverlapped peaks it is difficult to determine how accurate this estimation of the composition is. This uncertainty does not diminish the most important results, that the GAXRD pattern is consistent with the formation of a $(In_yGa_{1-y})P$ phase and no other phases were found.

In summary, using PdIn as the contact material we have fabricated low resistance ohmic contacts on n-type GaP and lowered the barrier height of contacts on p-type GaP. For PdIn/n-GaP contacts annealed at 600 °C for 1 min, specific contact resistances lower than $1\times10^{-4}\ \Omega\ cm^2$ were measured using a modified four-point probe method. This is comparable to the reported values for Au-Ge-Ni contacts to n-GaP. Annealed PdIn contacts on p-type GaP show a decrease in the effective Schottky barrier height with increasing annealing temperatures. A minimum effective barrier height occurs with contacts annealed at 600 °C for 1 min, but contacts always exhibit rectifying behavior. The $I-V$ characteristics of PdIn/n-GaP and PdIn/p-GaP contacts, as well as GAXRD all indicate the formation of an $(In_yGa_{1-y})P$ phase at PdIn/GaP contact interface as a result of thermal annealing. The authors believe it is the formation of this phase that is responsible for the ohmic behavior of the PdIn contacts on n-GaP and lower Schottky barrier height of contacts on p-GaP.

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