

Final Technical Report

Ohmic Contacts for Technology for Frequency Agile
Digitally Synthesized Transmitters (Phase III)

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ABSTRACT

Researchers at The Pennsylvania State University have investigated ohmic contacts to p-InGaAs and n-InGaAs, which are needed for heterojunction bipolar transistors. They have refined an electroless deposition process for ohmic contacts to p-InGaAs in which the metals selectively deposit on the semiconductor but not on dielectric layers such as silicon nitride. This process produces contacts with a low specific contact resistance and offers the potential for self-aligned contacts. The researchers have also investigated the factors that affect the resistance of contacts to InGaAs, including pre-metallization surface preparation and method of deposition, and have analyzed errors involved with extracting very low specific contact resistances. This work has resulted in the recognition of reproducible trends in contact resistance with processing conditions as well as insight into how to more accurately measure the specific contact resistance of very low-resistance contacts.

PROGRAM GOALS

The objective of this work was to develop contacts with very low specific contact resistances prepared using processes compatible with the fabrication of InP heterojunction bipolar transistors (HBTs). Special attention was devoted to the electroless deposition of ohmic contacts. The principal investigator was also available as a resource for information on contacts to compound semiconductors for companies participating in the DARPA Technology for Frequency Agile Digitally Synthesized Transmitters (TFAST) program.

RESULTS AND DISCUSSION

This program resulted in significant progress toward the development of ohmic contacts with very low resistance suitable for use in heterojunction bipolar transistors. The findings fall into three categories: (1) the optimization of a selective, electroless Pd/Ru/Au ohmic contact to p-type InGaAs, including examination of the influence of pre-metallization surface preparation on contact resistance; (2) an investigation of the influence of the deposition method on the resistance of contacts to n- and p-type InGaAs; and (3) an examination of the accuracy of the measurement of very low specific contact resistances using the transfer length method (TLM), which is based on the transmission line model.

Selective, electroless Pd/Ru/Au ohmic contacts to p-InGaAs

Placing ohmic contacts to the emitter and base in close proximity (<200 nm) on a heterojunction bipolar transistor (HBT) reduces the base resistance and base-collector junction capacitance and improves high frequency performance. Ohmic contacts to compound semiconductors are usually formed using electron beam evaporation and liftoff, but self-alignment of such contacts relies on very careful control of the resist profile and semiconductor undercut, which is difficult to reproducibly achieve for very small devices.

Selective metal deposition on the semiconductor surface simplifies the formation of self-aligned contacts, as shown previously for the base ohmic contacts of InP-based HBTs [1], where an electrical isolation between the base and emitter ohmic contacts was provided by a dielectric sidewall spacer and the base ohmic contact was electroplated. Conventional electroplating requires a power supply to provide current through the semiconductor, so there is a voltage drop across the semiconductor that can result in a non-uniform plating potential (and a non-uniform deposition rate) across the wafer. Alternatively, a selective *electroless* process can be used with no power supply needed, potentially providing uniform deposition across the wafer.

The contact developed in this work consisted of a very thin layer (~ 5 nm) of Pd to reduce the resistance at the metal/semiconductor interface. This layer reacts only a few nanometers into the semiconductor. Above this layer is a non-reactive Ru diffusion barrier and a top layer of Au to reduce the metal sheet resistance. Ohmic contacts to $p\text{-In}_{0.53}\text{Ga}_{0.47}\text{As}$ were prepared on a 40 nm thick Be-doped ($5 \times 10^{19}/\text{cm}^3$) InGaAs epilayer with a sheet resistance of $950 \Omega/\square$ on an undoped InAlAs buffer layer. Pieces were coated with 200 nm of silicon nitride, and prior to photolithography, all samples were degreased for 60s in turn in acetone, methanol and deionized (DI) water and blown dry with compressed N_2 . Openings were etched into the silicon nitride for a circular transfer length method (CTLM) test structure [2]. After removing the photoresist, the samples were again degreased. The semiconductor surface of different samples were also subjected to a variety of treatments prior to plating, and the effect of these treatments on the contact resistance was studied.

The procedure for depositing each of the layers in the Pd/Ru/Au contact has been published by Lysczek and Mohny [3] in the *Journal of the Electrochemical Society*. However, some improvements were made between the time of publication and the conclusion of this program.

Table I provides the components of the Pd plating bath adapted from the bath reported by Henry [4]. The step-by-step procedure for preparing the bath is provided in our paper [3]. A large range of dilutions and pH values were tested to arrive at the compositions in the table, and it was discovered that by increasing the pH of the bath to 13 using NaOH, the incubation time commonly required for electroless plating was essentially eliminated. The Pd layer plates selectively on p-InGaAs and not on silicon nitride, facilitating self-alignment of the contact.

Deposition of Ru is catalyzed by the Pd layer, and the Ru bath used in this work was adapted from the bath by Torikai *et al.* [5]. The Ru deposition is selective, depositing on Pd but not silicon nitride. A starter solution of ruthe-

nium nitrosylamine is first prepared from the reagents listed in Table II and combined to form the bath in Table III. The pH is again a critical parameter and must be maintained from 12.8–13.

Table I. Palladium bath adapted from Henry [4].

Palladium Bath	
Palladium (II) Chloride	10 g/L
Potassium Sodium Tartrate	19 g/L
Ethylenediamine	25.6 g/L
Sodium Hypophosphite	4.1 g/L
NaOH	As required
Alkalinity	pH = 13
Temperature	T = 70°C

Table II. Ruthenium nitrosylamine solution (one component of the Ru bath) [5].

Ruthenium Nitrosylamine Solution	
Ruthenium (III) Chloride	5.2 g/L
Sodium Nitrite (NaNO_2)	5 g/L
Hydroxylamine (NH_2OH)	2.0g/L
28-30% NH_4OH	40 ml/L
37% HCl	1 ml/L

Table III. Electroless Ru plating bath [5].

Ruthenium Plating Bath	
Ruthenium Nitrosylamine Solution	40 ml
DI H ₂ O	10 ml
28-30% NH ₄ OH	30 ml
NaOH	1.0 g
Hydrazine Hydrate	0.75 ml

In our published work, two plating baths for Au were used sequentially. The first Au bath [6], prepared using the reagents in Table IV, deposits on Ru but not on silicon nitride. However, it is not an “auto-catalytic” bath—Au will not necessarily deposit on top of a Au film. Therefore, a second bath that was catalytic [7] and listed in Table V, was used to deposit a thicker Au layer on the first Au film. This autocatalytic Au bath does not plate directly on Ru, only on Au. More details on preparing the baths are provided in our paper [3].

Low specific contact resistances were achieved with this bath when a UV ozone treatment was followed by a 30 s buffered oxide etch (BOE—buffered HF) or 30 s in undiluted NH₄OH. Specific contact resistances of $2 \pm 1 \times 10^{-7} \Omega\text{cm}^2$ were routinely achieved, and significantly lower values were measured on other epilayers with different doping. Figure 1 shows a cross-section of the contact from transmission electron microscopy (TEM).

The contacts show very good thermal stability after aging for 4 h at 250 °C; however, a few notes about reproducibly achieving low contact resistances are in order. Much higher specific contact resistances (on the order of $10^{-6} \Omega\text{cm}^2$) were routinely measured when 1:1 HCl:H₂O was used in place of BOE

or NH_4OH . It was also very important to use dry bottled air rather than room air (in which the humidity may vary) for the UV ozone treatment to reduce sample-to-sample variation. Finally, we found that we had to make a change to the Au plating bath to increase our yield. An investigation of this last factor, discovered after publication of our manuscript, led to a change in our final process for preparing electroless Pd/Ru/Au contacts.

Table IV. First electroless Au bath (catalyzed by Ru). [6]

Au Bath #1 (Catalyzed by Ru)	
Gold potassium cyanide	0.2 g/L
Hydrazine hydrate	4 ml/L
NaOH (pH adjustment)	As needed
pH	12.2
Temperature	70 - 80°C

Table V. Second electroless Au bath (auto-catalytic). [7]

Au Bath #2 (Auto-catalytic)	
Gold potassium cyanide	5.8 g/L
Potassium cyanide	6.5 g/L
KOH	11.2 g/L
KBH_4	10.8 g/L
Temperature	65 - 75°C

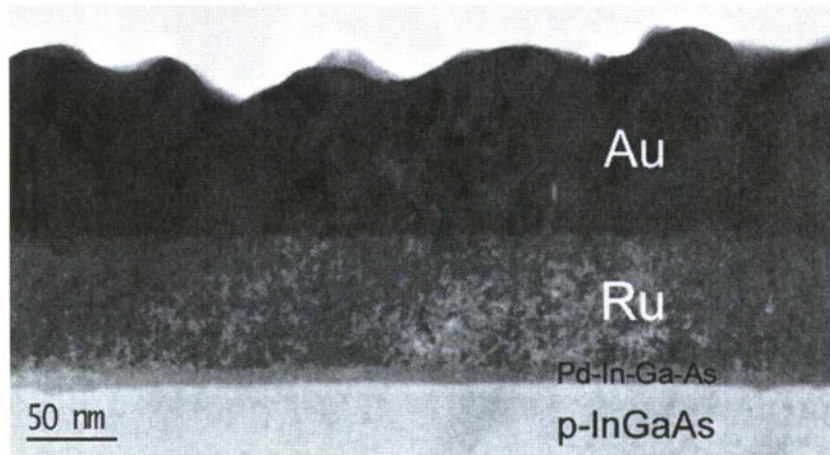


Figure 1. Cross-sectional TEM image of the selective, electroless Pd/Ru/Au contact to p-type InGaAs.

The second Au plating bath, particularly after it is stored for months, can etch InGaAs and attack semiconductor at the edge of the contact. Such etching is unacceptable when fabricating an HBT. Therefore, more samples were prepared using only the first Au plating bath and omitting the second. We discovered that given enough time (20 min), a sufficiently thick Au layer could be deposited using the first bath to allow accurate measurements of the specific contact resistance. It is speculated that a few small pores remain, even after the Au film thickens, allowing the underlying Ru film to catalyze the deposition of the Au film to a much greater thickness than originally expected.

Influence of deposition method on the resistance of contacts to InGaAs

Much of the work in this program focused on the electroless ohmic contacts to p-InGaAs. Little difference was ultimately observed between the resistance of Pd/Ru/Au ohmic contacts to p-InGaAs prepared by electroless deposition and e-beam evaporation. However, the use of sputter deposition can have a definite effect on the resistance of ohmic contacts to p-InGaAs. Bombardment by energetic particles during sputter deposition can make it difficult to form an ohmic contact to p-InGaAs at all. This problem was chosen for study be-

cause a combination of sputtering and etch back was reported by Crook *et al.* for contacts to n-InGaAs for high-frequency transistors [8], and the metallization used was TiW. In our study, TiW/Au (50/100 nm) ohmic contacts sputtered onto p-type InGaAs were either ohmic or non-ohmic depending on the conditions used to create the plasma for sputtering. As shown in Fig. 2, when a low Ar pressure of 2 mTorr was used, a non-ohmic contact was formed. Changing to a pressure of 10 mTorr yielded linear I-V curves (an ohmic contact). It is important to note here that a lower working pressure during sputtering leads to a longer mean free path between collisions of particles in the plasma; thus, species can arrive at the substrate surface with higher energy. Interestingly but not surprisingly, an opposite trend with respect to Ar pressure was observed for ohmic contacts to n-InGaAs, with more current transport when the lower 2 mTorr working pressure was used (Fig. 3).

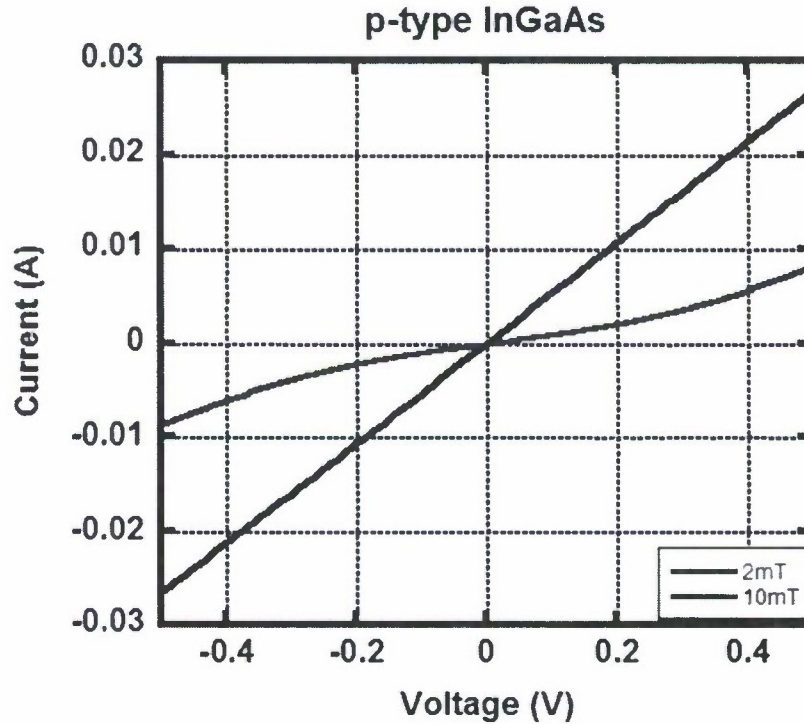


Figure 2. I-V curves of sputtered TiW/Au contacts to p-type InGaAs prepared using two different Ar pressures in the deposition chamber.

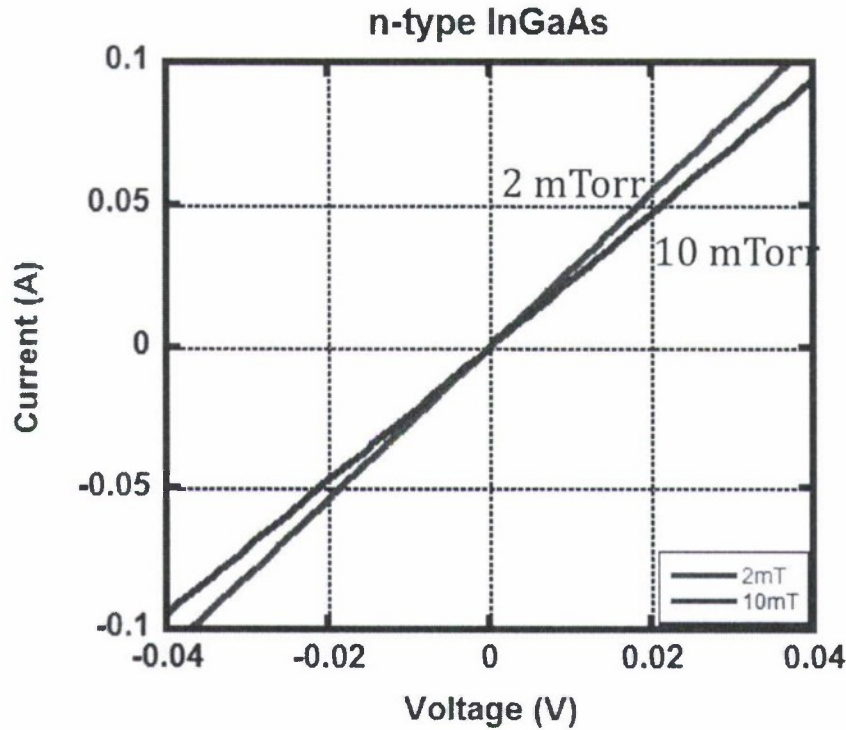


Figure 3. I-V curves of sputtered TiW/Au contacts to n-type InGaAs prepared using two different Ar pressures in the deposition chamber.

Bombardment by plasmas and ion beams has been reported to alter the electronic properties of compound semiconductors [9, 10]. In both cases, donor-like defects have been reported in the near-surface region of the semiconductor. However, the effect of sputter deposition on ohmic contacts to III-V semiconductors has not received much attention. We now conclude that the use of a low working pressure during sputtering can lead to the creation of such a high number of compensating donors in p-InGaAs such that an ohmic contact cannot necessarily be formed, while donor creation under energetic bombardment may result in greater doping, leading to higher currents in contacts to n-InGaAs. This finding potentially provides important insight into how to minimize the specific contact resistance of contacts to InGaAs.

Eric Lysczek prepared a draft of a manuscript on this work, comparing the specific contact resistances of ohmic contacts to n-type InGaAs prepared us-

ing different conditions to generate a plasma for sputter deposition. However, the manuscript was never submitted to a journal because we realized that our measurements of specific contact resistance contained unacceptably large errors and that a different test structure would be required to complete the study. This source of error was not present in our prior work on contacts to p-InGaAs because we worked with samples with much higher semiconductor sheet resistances. The problem led us to more closely evaluate the errors in the measurement of specific contact resistances, a topic that was pursued by Robert Dormaier III.

Measuring very low specific contact resistances

The measurement of specific contact resistance can be affected by the sheet resistance of the metal film used to make the contact. Though usually unimportant, this contribution matters when the specific contact resistance (resistance at the metal/semiconductor interface) and semiconductor sheet resistance are low. It has long been understood that the resistance of the metal itself can be responsible for the extraction of an artificially high specific contact resistance. [11,12] In fact, we encountered this problem when extracting the specific contact resistance of sputtered contacts to n-InGaAs when we used the circular transfer length method (CTLM) test structure for our contacts to epilayers with a very low semiconductor sheet resistance ($\sim 10 \Omega/\text{Sq}$).

Interestingly, we realized as we contemplated a new test structure for our next measurements that a heretofore unrecognized artifact was also possible: the contribution from the metal sheet resistance could lead to an artificially *low* value of the specific contact resistance when using particular test structures. To understand how this effect is possible, consider a transfer length method (TLM) test structure with rectangular pads through which current is sourced at opposite corners diagonal to those where the voltage it is measured, as shown in Fig. 4. This approach is somewhat similar to the test

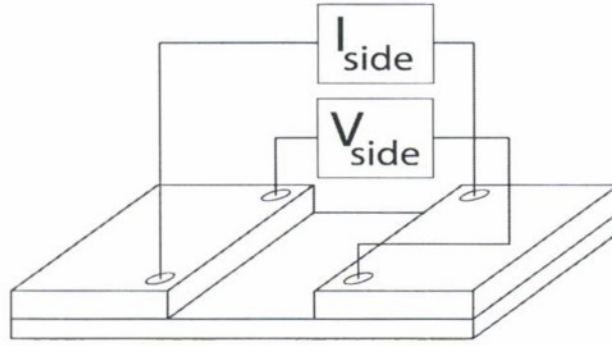


Figure 4. Probe configuration for the first set of simulations.

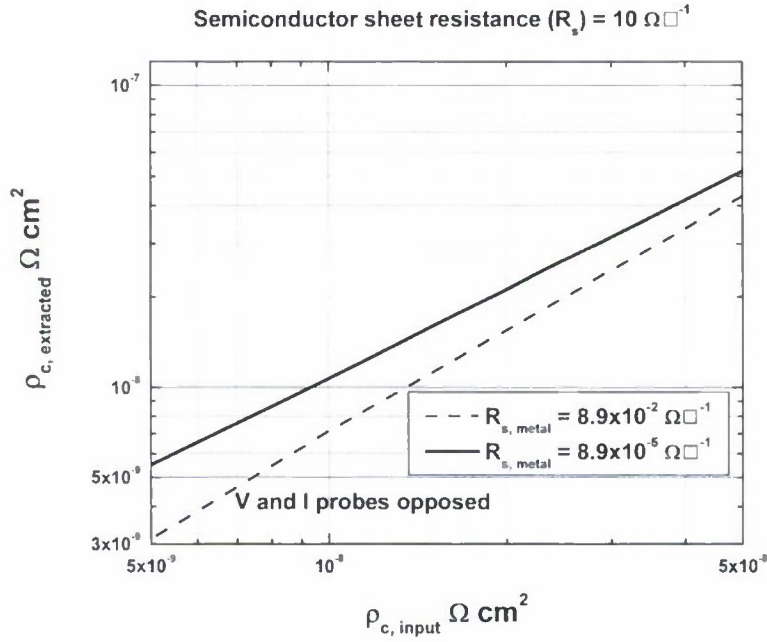


Figure 5. Extracted vs. input specific contact resistance for diagonal probes (Fig. 4).

structure used in the first of the recent reports of specific contact resistances $< 10^{-8} \, \Omega \text{ cm}^2$ on n-InGaAs [13]. The test structure in Fig. 4 was simulated using COMSOL Multiphysics. Values of $\Delta V/I$ were obtained from the simulation for contact pairs with different gap spacings, as well as for pairs with different specific contact resistances and metal sheet resistances. The semiconductor sheet resistance was set to $10 \, \Omega/\text{Sq}$. The data collected from the simulations were then treated as we would normally fit experimental data and on a

plot of Resistance vs. Gap Spacing, allowing us to extract the specific contact resistance. We see that the metal sheet resistance—even when it is less than $0.09 \text{ } \Omega/\text{Sq}$ —alters the extracted specific contact resistance, making it appear lower than the input values by nearly a factor of 2 for the lowest specific contact resistances plotted on Fig. 5.

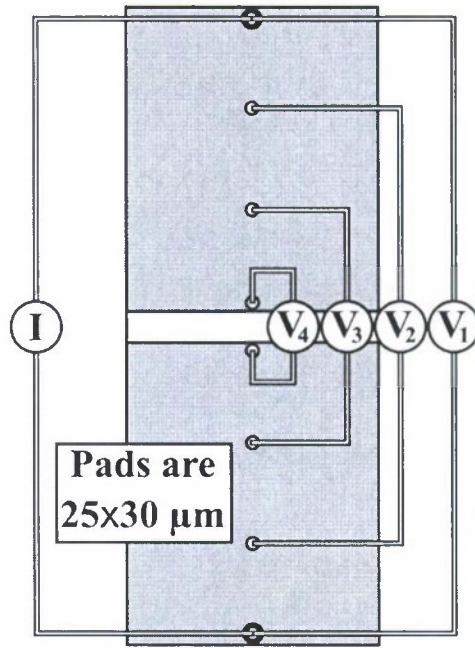


Figure 6. Configuration of probes for second set of simulations.

A preferable approach is to source the current from the back of the contacts and probe the potential at the front, as shown in Fig. 6, which illustrates the influence of the position of the probes on the extracted specific contact resistance, again for a semiconductor sheet resistance of $10 \text{ } \Omega/\text{Sq}$. The simulations reveal that there is little effect from the metal sheet resistance when the probes are placed at the front of the contacts (probe 1). As the probes are moved farther toward the back of the contacts (probes 2-4), an artificially high specific contact resistance value emerges, and the extracted specific contact resistance can be as much as a factor of 6 too high for the conditions

and probe positions shown on Figs. 7 and 6, respectively. Artificially low values are not extracted since the current is sourced from the back of the contacts instead of the sides. Lateral variations in potential across the contacts are also minimized by the contact geometry. The simulations have not been published to date due to the lack of a sufficiently complete data set. However, they provide valuable insight to guide further measurements of very low values of specific contact resistances.

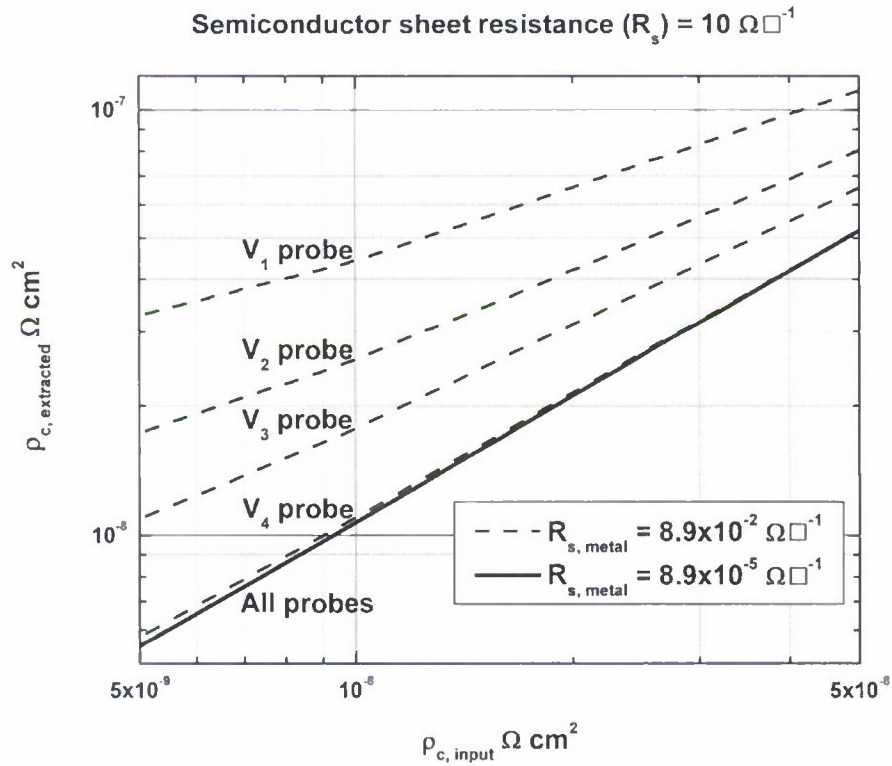


Figure 7. Extracted specific contact resistance for probe placements in Fig. 6.

In addition to the scientific contributions of the program, the principal investigator was available for questions on contacts to InGaAs and responded to Teledyne and Northrop Grumman on multiple occasions during the course of this program.

GRADUATE STUDENTS

Eric Lysczek was supported by a research assistantship in late 2007 and 2008 and has completed all the experiments needed for his doctoral thesis. He accepted full-time employment in early 2009 and has not yet finished writing his doctoral thesis. His results have already been reported to ONR, and there are no remaining experiments needed to complete the thesis. Eric worked on pre-metallization surface preparation, as well as plated and sputtered contacts.

Robert Dormaier III joined the project on a research assistantship in 2008. He also tested sputtered contacts, and the simulations on the errors involved in measuring very low specific contact resistances are his contribution. He is continuing doctoral work at Penn State and is expected to graduate in 2011.

PUBLICATIONS

E. M. Lysczek and S. E. Mohnney, "Selective Deposition of Ohmic Contacts to p-InGaAs by Electroless Plating," *J. Electrochem. Soc.* **155**, H699 (2008).

REFERENCES

1. M. Urteaga, P. Rowell, R. Pierson, B. Brar, M. Dahlstrom, Z. Griffith, M. Rodwell, S. Lee, N. Nguyen and C. Nguyen, *2004 Device Research Conference* (IEEE, Piscataway, NJ) 239 (2004).
2. G. S. Marlowe and M. B. Das, *Solid-State Electron.* **25**, 91 (1982).
3. E. M. Lysczek and S. E. Mohnney, *J. Electrochem. Soc.* **155**, H699 (2008).
4. James Henry, *Metal Finishing*, **101**, 345 (2001).
5. E. Torikai, Y. Kawami, and K. Takenaka, Japanese patent 59-080766 (1984).
6. L. G. Bhatgadde, S. Joseph, and S. C. Kulkarni, *Met. Finish.* **94**, 45 (1996).

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7. G. O. Mallory and J. B. Hajdu, *Electroless Plating: Fundamentals and Applications*, (American Electroplaters and Surface Finishers Society, Orlando, FL) 402 (1990).
 8. A.M. Crook, E.Lind, Z. Griffith, and M.J. Rodwell, *Appl. Phys. Lett.*, **91**, p. 192114 (2007).
 9. S. Ashok, *7th ICSICT International Conference on Solid-State and Integrated Circuits Technology* (IEEE, Piscataway, NJ), pp. 532-537 (2004).
 10. L. Joulaud, J. Mangeney, N. Chimot, P. Crozat, G. Fishman, and J.C. Bourgoin, *J. Appl. Phys.*, **97**, 063515 (2005).
 11. G. S. Marlowe and M. B. Das, *Solid-State Electron.* **25**, 91 (1982).
 12. S. H. Wang, S. E. Mohny, B. A. Hull, and B. R. Bennett, *J. Vac. Sci. Technol. B* **21**, 633 (2003).
 13. U. Singisetti, A. M. Crook, E. Lind, J. D. Zimmerman, M. A. Wistey, A. C. Gosard, and M. J. W. Rodwell, *2007 Device Research Conference* (IEEE, Piscataway, NJ), pp. 149-150 (2007).