

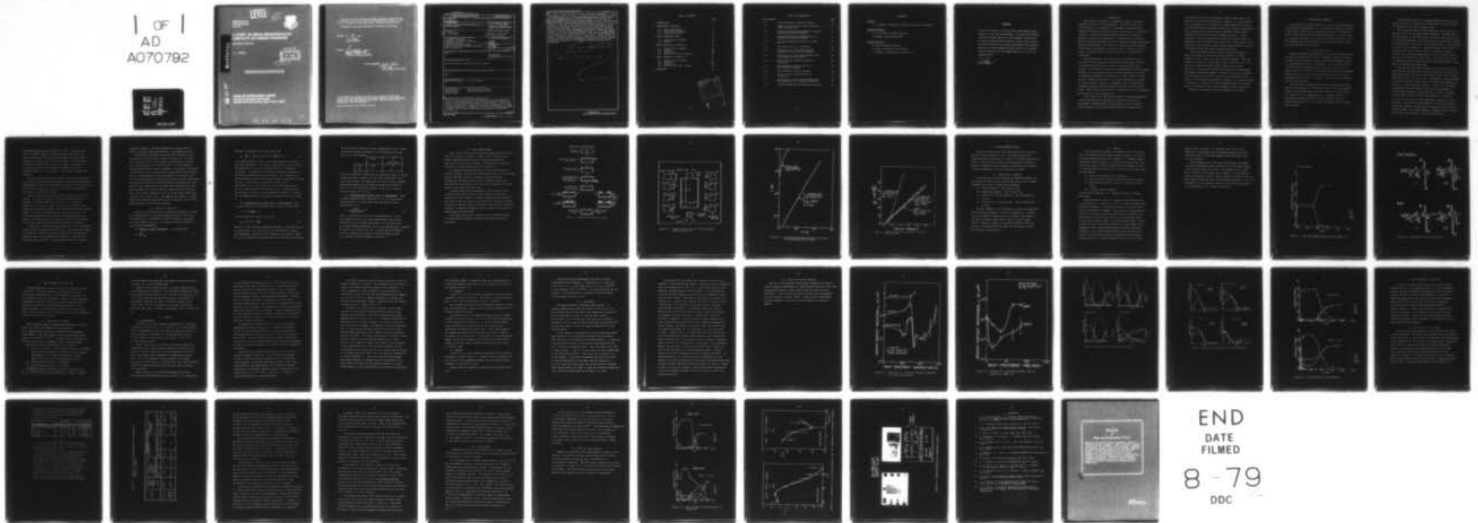
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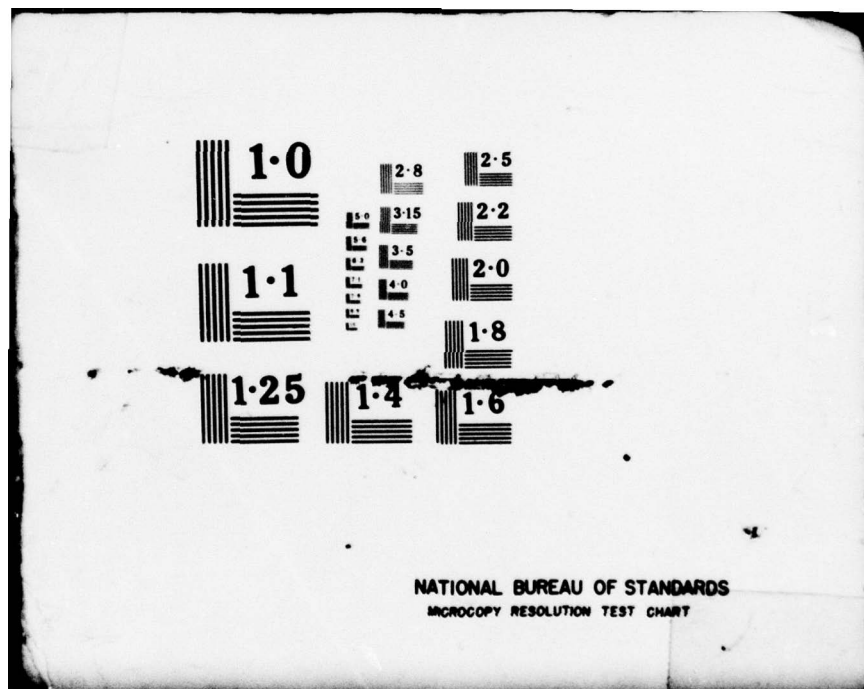
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Final Technical Report
May 1979

A STUDY OF METAL-SEMICONDUCTOR CONTACTS ON INDIUM PHOSPHIDE

University of Minnesota

G. Y. ROBINSON

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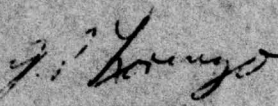
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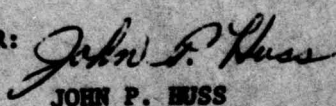
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes the research accomplished during a 14-month program of research on metal-semiconductor contacts on indium phosphide. Emphasis was placed on fabrication and characterization of ohmic contacts to p- and n-type InP using the deposition of thin metallic layers and subsequent heat treatment at elevated temperatures. Extensive use of Auger electron spectroscopy (AES) was made in order to obtain depth-composition profiles of the thin-film structures.			

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For contact to n-type InP, three thin-film systems were investigated: Au, Ni, and a composite layer of Ni/Au/Ge. The specific contact resistance (r_c) of the Ni/Au/Ge/In system varied in a systematic manner with heat-treatment temperature, and a minimum value of r_c of $3 \times 10^{-5} \Omega\text{-cm}^2$ at 325°C was found for $N_D = 3 \times 10^{16} \text{cm}^{-3}$. Several nickel germanide phases, detected by AES and X-ray diffraction, were formed during heat treatment and were found to affect r_c . For contact to p-type InP, a film consisting of Au/Mg was investigated. For heat treatment of the Au/Mg/InP system above 350°C , r_c decreased with increasing heat-treatment temperature and the surface morphology exhibited increasing signs of alloying at higher temperatures. The smoothest surface was obtained at 446°C for 50 minutes with $r_c \sim 10^{-4} \Omega\text{-cm}^2$ for $N_A = 6 \times 10^{17} \text{cm}^{-3}$. Extensive lateral melting of the Au/Mg film occurred at 500°C due to the rapid transport of In resulting from dissociation of the InP surface. For the as-deposited samples, the Schottky-barrier energy was always found to be higher on p-type than on n-type InP, unlike Schottky barriers on GaAs and Si. Data was obtained on impurity concentration and uniformity of InP wafers grown in Air Force laboratories.

n sub c
 n sub c approx. 0.0001 ohm/sg.cm
 0.0003 ohm-sg.cm

$N(D) = 3 \times 10^{16}$ to the 16th power/cc

$N(A) = 6 \times 10^{17}$ to the 17th power/cc

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Evaluation

The object of this work is to provide a basic understanding of ohmic contacts to n and p-type Indium Phosphide. The detailed and systematic study done using Auger analysis has given remarkable insight toward the electrical and metalurgical properties of ohmic contact formation. This work has provided a more complete understanding of the technology required to use Indium Phosphide and alloys grown on it as efficient source and detector devices for communications in the 1.2 to 1.3 μm wavelength region.


J. P. LORENZO
Project Engineer

1. INTRODUCTION

This research program is a fundamental study of metal/semiconductor contacts on indium phosphide. The primary objective of the program is to determine the fundamental parameters which control the electrical and metallurgical properties of the metal/InP interface. The principal experimental tools of this research program are electrical measurement of contact barrier energy and specific contact resistance and surface chemical analysis using Auger electron spectroscopy. The results of the program should provide guidelines for development of practical ohmic contacts for use in future InP devices, such as infrared detectors or field-effect transistors.

Metal-semiconductor structures play an important role in the field of microelectronics by providing either ohmic contacts or Schottky-barrier diodes in discrete and integrated circuit devices. The fundamental theoretical understanding of the electrical properties of a rectifying Schottky metal-semiconductor interface is essentially complete; the theory for an ohmic contact is less so but a complete understanding is rapidly developing as a result of recent advances. However, a comparable level of experimental knowledge regarding metal-semiconductor contacts does not as yet exist. This is particularly true for contacts to the III-V compound semiconductors, such as GaAs and InP.

In the case of InP, the limited amount of metal-semiconductor research that has been reported has concentrated primarily on preliminary investigations of various types of ohmic contacts. Ohmic contacts to any lightly doped semiconductor material can

be achieved by use of an intermediate, heavily doped layer (e.g., metal/n⁺/n or metal/p⁺/p structures). However, in InP the fabrication of selected n⁺ or p⁺ regions with high temperature diffusion or other conventional techniques have not yet proven to be practical. Thus, research data has been largely confined to ohmic contact formation on InP using the alloy regrowth technique. In this technique, a thin film containing a metal and suitable dopant is deposited on the InP surface and heated until a thin layer of InP is dissolved. Upon cooling, a heavily doped regrowth layer is formed in intimate contact with the overlaying metal film.

It was the purpose of this research program to examine in detail the electrical and metallurgical properties of ohmic contacts to InP by using the alloy regrowth technique. For ohmic contact to n-type InP, a multilayer contact consisting of Ni, Au, and Ge was chosen for study, and the results are given in Section 4. To provide the necessary background for understanding the complex Ni/Au/Ge/InP system, a series of tests were conducted on films consisting of only Ni and Ge on inert substrates; the results of this study are presented in Section 3. For ohmic contact to p-type InP, a multilayer thin-film system using Au and Mg was chosen; the results of the Au/Mg/InP study is given in Section 5.

Plans for future work are also discussed in the report.

2. EXPERIMENTAL PROCEDURE

The properties of ohmic contacts to InP are strongly dependent on the method of preparation; thus, the contact fabrication process is described in detail below. Furthermore, proper interpretation of the electrical and metallurgical data depends to a large extent on a thorough knowledge of the contact evaluation techniques. Hence the techniques for characterization of metal-semiconductor diodes are also described in this section.

2.1. Device Fabrication

After considerable experimentation, the process steps outlined in Figure 2.1 were found to yield a reasonable compromise between the conflicting requirements of metal etching, photoresist stability, and protection of the InP substrate. The InP wafers were of $\langle 100 \rangle$ and $\langle 111 \rangle$ orientation, both n and p type, and varied in doping from 10^{16} to 10^{18} cm^{-3} . The wafers were purchased from Metal Specialities, Inc. or were obtained from Hanscom Air Force base where they were grown by J. K. Kennedy. All wafers were received with one face polished.

The first step in fabricating metal/InP diodes was to clean each wafer by degreasing in successive rinses in trichlorethylene, acetone, and deionized water, and then etching for five minutes in a solution of 3:1:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$. It was found that this solution etched $\langle 100 \rangle$ InP at about $200 \text{ \AA}/\text{min}$ leaving a smooth surface and $\langle 111 \rangle$ InP at about $150 \text{ \AA}/\text{min}$ leaving a slightly pitted surface.

The breakdown voltage of a tungsten probe placed on the InP surface was used to indicate the cleanliness of the surface and as a measure of the impurity doping level.

Next pyrolytic chemical vapour deposition (CVD) was used to deposit a SiO_2 layer of about 3000 \AA thickness. The deposition was performed in an AMT Silox reactor using the gases O_2 and SiH_4 . It was established that a high quality SiO_2 layer could be obtained by deposition at 300°C using a rapid start-up cycle. The resulting SiO_2 film could be etched in a controlled manner, was uniform in thickness, and was free of pin holes. Evidence was found to indicate that excessive dissociation of the InP surface occurred during CVD at temperatures above 300°C . The SiO_2 film was used as a mask during photolithography and for accurate control of the edge of the metal/InP contact area.

Some SiO_2 was unavoidably deposited on the back of the InP wafer and the next step was to remove this SiO_2 in an HF solution while masking the oxide on the front surface with either a thick photoresist layer or a film of wax. The masking film was removed; the wafer was briefly etched in the InP etchant and immediately placed in a vacuum deposition system. A metal film was vacuum deposited onto the back surface; the thin film consisted of several layers chosen to produce an ohmic contact. The wafer was next heat treated in an open-tube furnace in flowing N_2 gas with careful control of the temperature and period of heat treatment. The current-voltage behavior of the large area back contact was checked to ensure that low resistance ohmic contact has been formed. For n-type samples, a composite layer of first 250 \AA of Ge, then 520 \AA of Au, and then 150 \AA of Ni

was deposited and alloyed at 500°C for 2 min. For p-type InP with $6 \times 10^{17} \text{cm}^{-3}$ doping, it was found that a 1500 Å film of pure In alloyed at 350°C for 30 min produced an adequate ohmic contact to the back. This metal film, however, did not produce the desired ohmic behavior on the lower doped p-type material. A Au/Mg layer (400 Å of Mg followed by 1600 Å of Au) heat treated at 446°C for 5 min, however, did produce an ohmic back contact.

The next major processing step was to selectively etch holes in the SiO_2 layer using photolithography. Shipley AZ-1350B positive photoresist was used since the Shipley developer is a mild solution which shows no evidence of etching the InP and the photoresist can be easily removed with acetone.

The next step was to form the metal/InP diodes in the oxide windows. As shown in Figure 2.1, two different methods were employed. For metals that could be etched in a controlled fashion (Ni, Au, Ge), the metal film was first deposited, then etched into the desired pattern using a protective layer of resist. However, for the films containing the highly reactive Mg, the resist was applied first and the metal film deposited over the resist. The diodes were then formed by lifting the excess metal off the wafer surface when dissolving the resist in acetone.

In all cases, the metal films were deposited in an ion-pumped vacuum system at pressures below 10^{-6} Torr. The wafers were below 50°C during film deposition and each metal layer was sequentially deposited from a multi-hearth source heated by an electron gun during the same pump down. Low back ground pressures, titanium

sublimation pumping, and high evaporation rates were used in order to minimize oxygen contamination of the composite films.

The wafers were scribed and cleaved into individual cells. The layout of each cell used is shown in Figure 2.2. Each unit cell contains a total of nine diodes, each differing in active area. The diodes of $10 \times 10 \mu\text{m}^2$ to $100 \times 100 \mu\text{m}^2$ are used to determine the specific contact resistance. The largest area contact in the center of the cell was used for capacitance-voltage measurements of Schottky barrier energy and impurity concentration and for thin film composition profiling using Auger electron spectroscopy. The samples were optically examined through a metallurgical microscope for any visible defects and then characterized electrically. Heat treatments for various times and temperatures were carried out in the constant temperature zone of an open tube furnace with a N_2 gas flow of 1000 cc/min. The samples were placed on a quartz paddle and the paddle was inserted into the furnace, left for the desired length of time and then removed.

2.2 Electrical Evaluation

Electrical Characterization of the metal/InP diodes consisted of the determination of metal-semiconductor barrier energy ϕ_B , the diode factor n , the specific contact resistance r_c , and the net doping density N_A or N_D . The electrical tests consisted of the following measurements:

- (a) Specific contact resistance. r_c is defined as¹

$$r_c = \left. \frac{dV}{dJ} \right|_{V \rightarrow 0} \quad (1)$$

The total resistance, R_T , of the contact is²

$$R_T = \frac{r_c}{a^2} + \sqrt{\left(\frac{\pi}{4}\right)} \frac{\rho}{\pi a} \arctan \left(4 \sqrt{\left(\frac{\pi}{4}\right)} \frac{h}{a} \right) + R_O, \quad (2)$$

for a square contact of side a , with semiconductor resistivity ρ , and wafer thickness h . R_O is the resistance of the back contact. The second term of Eq. (2) represents the contact spreading resistance. To determine r_c , the diode current was measured for diode bias voltages from -10 mV to +10 mV. The resistance R_T was determined by taking the reciprocal slope of the diode I-V plot near $V=0$. A plot of R_T vs. $\frac{1}{a^2}$ will be linear with a slope equal to r_c if the first term on the right-hand side of Eq. (2) is much greater than the second term. Where this was not the case, the second term was computed (knowing a , ρ , and h) and then subtracted from R_T to yield a corrected plot with slope r_c .

(b) Schottky-barrier height from I-V measurements. The J-V characteristic of a Schottky-barrier diode is of the form³

$$J = J_S \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \quad (3)$$

with the saturation current J_S given by

$$J_S = A^{**} T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \quad (4)$$

where A^{**} is the effective Richardson constant. By fitting Eq. (3) to plots of $\log J$ vs. V (see Fig. 2.3), the values of n and ϕ_B were determined. The value of A^{**} depends on the effective mass m^* , and the values of the electron effective mass and, particularly,

the hole effective mass are not yet established for InP. Based on the best available information, the following values were used in our calculations:

	m^*/m_0	A^{**} ($A/cm^2 \cdot ^\circ K^2$)
n type	0.082	9.8
p type	0.5	60

Since the Richardson constant was not accurately known, a limited attempt was made to measure A^{**} for p-type InP diodes. For a fixed forward bias, the temperature was varied, using a heated-wafer-chuck system, and the measured current was plotted as J/T^2 vs. $1/T$ and fitted to Equations (3) and (4) in order to extract values of A^{**} and ϕ_B .

(c) Schottky-barrier height from C-V measurements. Using an abrupt depletion layer approximation for a reverse-biased Schottky barrier it can be shown that the depletion layer capacitance, C , is³:

$$C = \left[\frac{q\epsilon_s N_A^2}{2(V_{bi} - V - kT/q)} \right]^{1/2} \quad (5)$$

where ϵ_s is the permittivity of the semiconductor, N is the hole concentration N_A for p-type substrates and the electron concentration N_D for n-type substrates, A is the diode area, V_{bi} is the diffusion potential, and V is the applied bias. Equation (5) was fit to a plot of $1/C^2$ vs. V for the metal/InP diodes in order to obtain N_D or N_A and the barrier energy ϕ_B from V_{bi} . Typical results are shown in Figure 2.4.

2.3. Auger Spectroscopy

Auger electron spectroscopy (AES) and in-situ sputter etching with Ar^+ ions were utilized to examine contact surfaces and to obtain depth-composition profiles of selected samples for qualitative metallurgical analysis. The purpose was to obtain correlation to the observed electrical properties.

All samples were analyzed using a 5-kv electron beam to produce the Auger electrons and were sputtered with a 2-kv ion beam. Special attention was paid to chemical identification of elements and compounds present by noting chemical shifts and characteristic peak shapes in the Auger energy spectra at various depths in the metal/InP structures.

The Auger peak-to-peak amplitude of each element was converted to atomic percent using standard Auger electron sensitivities of the elements. This data reduction method does not take into account the simultaneous presence of different elements or different chemical states of the same element in the film being analyzed. A computer program was used to convert the raw data to depth-composition profiles¹⁴.

Additional metallurgical analysis of the samples utilized x-ray diffraction, scanning electron microscopy, and optical microscopy.

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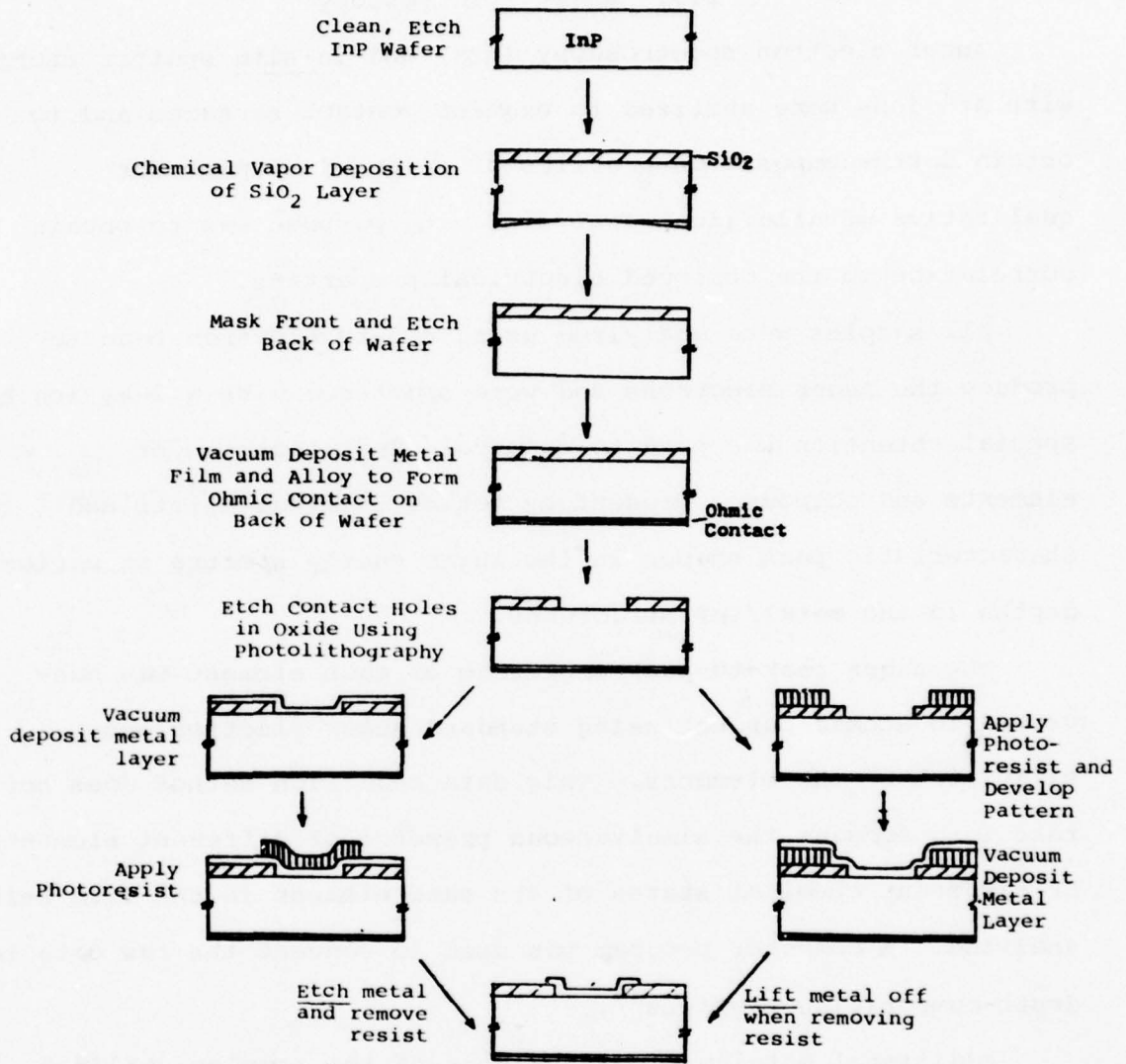


Figure 2.1. Process Scheme for metal/InP contacts.

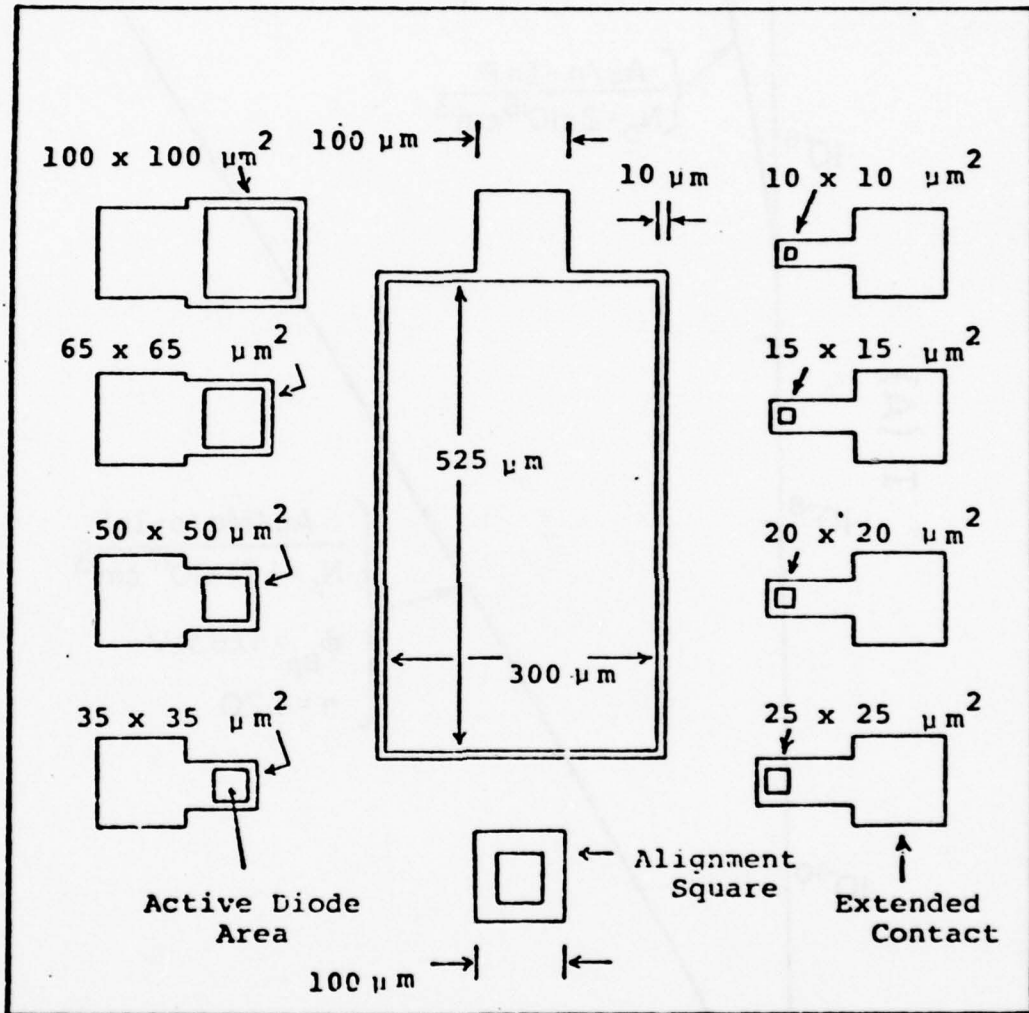


Figure 2.2. Layout of unit cell for diode evaluation (from reference 15).

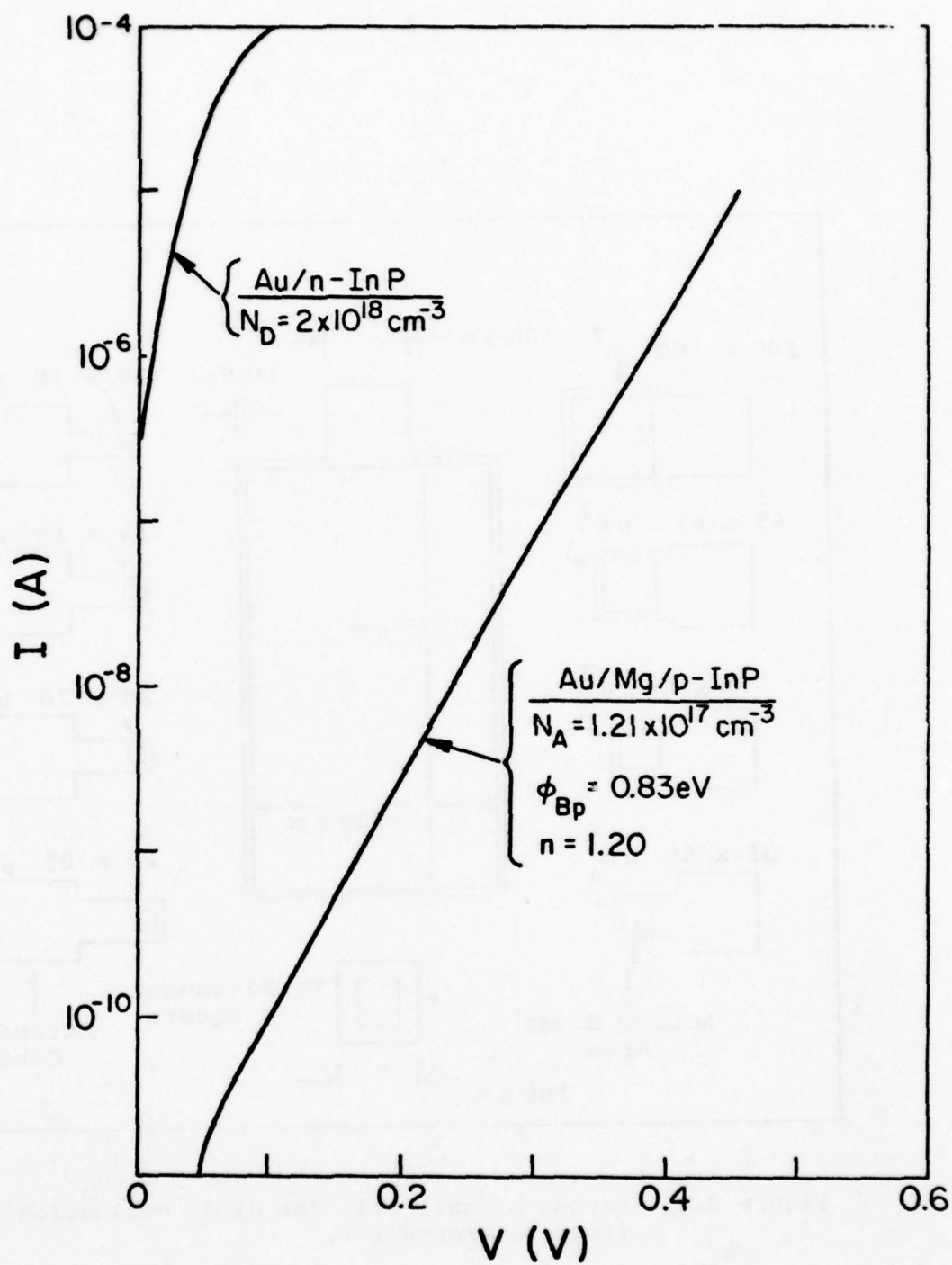


Figure 2.3. Current-voltage characteristics of typical as-deposited metal/InP diodes.

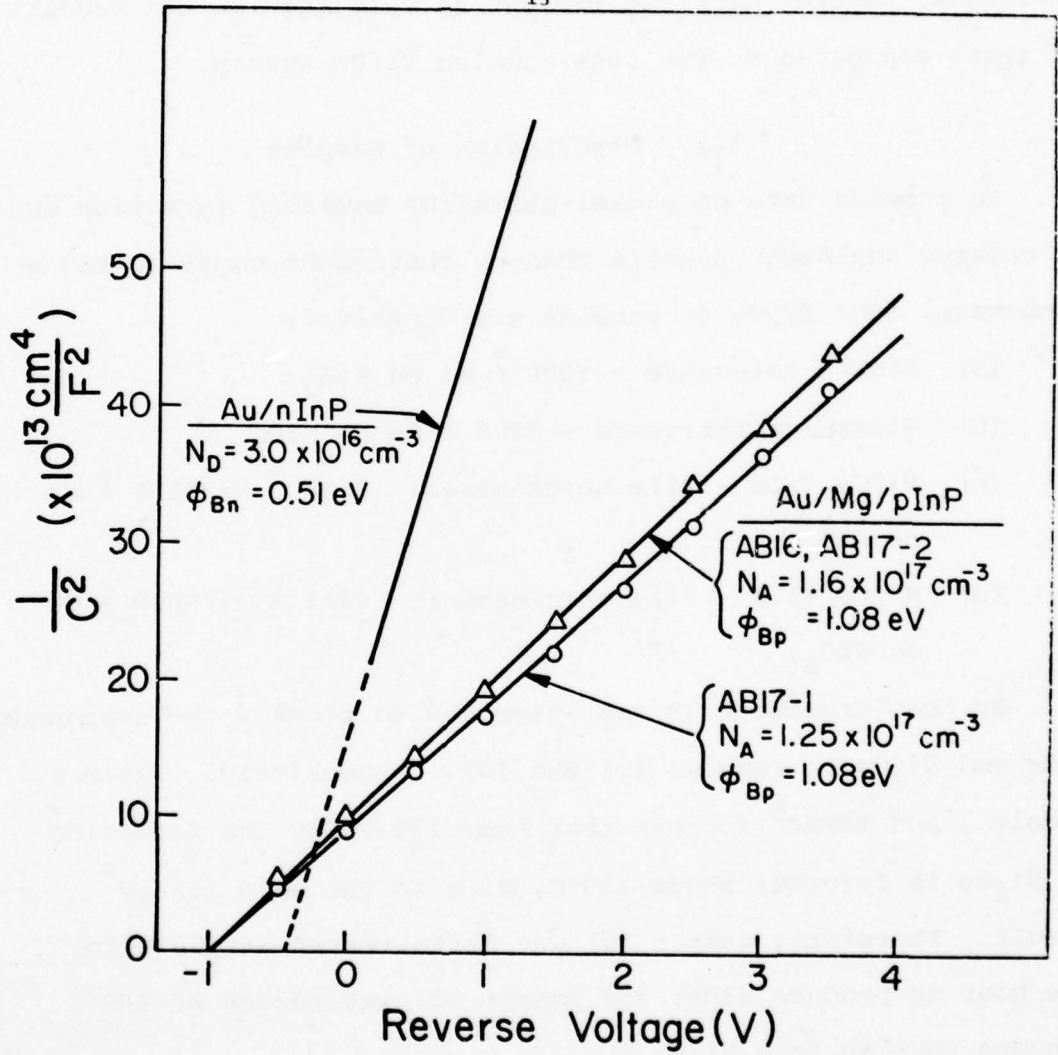


Figure 2.4. capacitance-voltage characteristics of as-deposited metal/InP diodes.

3. NICKEL-GERMANIUM FILMS

Several different metal films were examined for their suitability as ohmic contacts to InP. One system studied was a composite system consisting of a layer of Ni covering layers of Ge and Au. This thin-film system will be discussed in detail in Section 4; however we first present in this section the results of tests conducted on the less complex Ni/Ge system.

3.1. Description of Samples

To provide data on nickel-germanium compound formation and to observe any Auger spectra changes that might occur in these compounds, four types of samples were prepared:

- (a) Nickel reference - 5000 Å Ni on SiO₂
- (b) Germanium reference - 5000 Å Ge on SiO₂
- (c) Ni/Ge film - film thicknesses: 3290 Å Ni/6800 Å Ge on SiO₂.
- (d) Ni/Ge film - film thicknesses: 4824 Å Ni/5000 Å Ge on SiO₂.

By heat treatment it was attempted to produce the compounds NiGe and Ni₂Ge on samples (c) and (d), respectively. Wittmer, Nicolet, and Mayer⁵ suggest that from 150-250°C the formation of Ni₂Ge is favored; above 250°C, NiGe is the more likely result. Therefore, sample (c) was heat-treated at 350°C for one hour to produce NiGe, and sample (d) was heated at 200°C for one hour to form Ni₂Ge.

3.2. Results

X-ray diffraction analysis was conducted, and it was found that the compound NiGe had indeed formed on sample (c), while no detectable compounds were seen on sample (d). Compound identification was done by comparing the measured angles of the x-ray diffraction peaks with those computed from the d-spacings given in the ASTM Powder Diffraction File, and the following was found for each sample:

- (a) only Ni with strong (111) orientation.
- (b) only Ge with indication of polycrystalline structure.
- (c) mostly NiGe with some Ni and Ge. One weak line for Ni₂Ge.
- (d) no Ni₂Ge, only Ni observed.

No other Ni-Ge compounds (i.e., Ni₁₉Ge₁₂, Ni₅Ge₂, or Ni₅Ge₃) were found.

Auger analysis on sample (c) supported the results of the x-ray diffraction. The profile in Fig. 3.1 shows a uniform layer of NiGe on germanium. The horizontal scale is ion dose and is directly proportional to depth. The sensitivity factors used to reduce the raw Auger signal data would yield the expected 1:1 Ni:Ge levels if either the Ni sensitivity was slightly lower or that of Ge slightly higher. The sensitivities used, 3.85 for Ni and 7.69 for Ge, were the reciprocals of those found in the Handbook of Auger Electron Spectroscopy, Physical Electronics Industries, Inc. Arbitrarily adjusting the Ge sensitivity to yield a 1:1 Ni:Ge atomic percent concentration, we now have a Ge sensitivity of 8.74 which should be valid for the Ge signal

whenever NiGe is present. In addition, Auger tests in our laboratory on elemental Ni and Ge produced sensitivity factors whose ratio was in very close agreement with those taken from the above Handbook.

Careful examination of the Auger peak energies and shapes revealed no measurable energy shifts but did reveal some changes in peak shapes for both Ni and Ge. The changes in the Ni LMM Auger peaks were rather subtle while changes in the Ge LMM peak shapes were somewhat clearer; typical spectra are shown in Fig. 3.2. The Ge spectra were both taken from the sample profiled in Fig. 3.1, the spectra of Ge as NiGe at a dose of 150 units and the spectra of Ge as elemental Ge at a dose of 2000 units.

NI-GE PLOT:

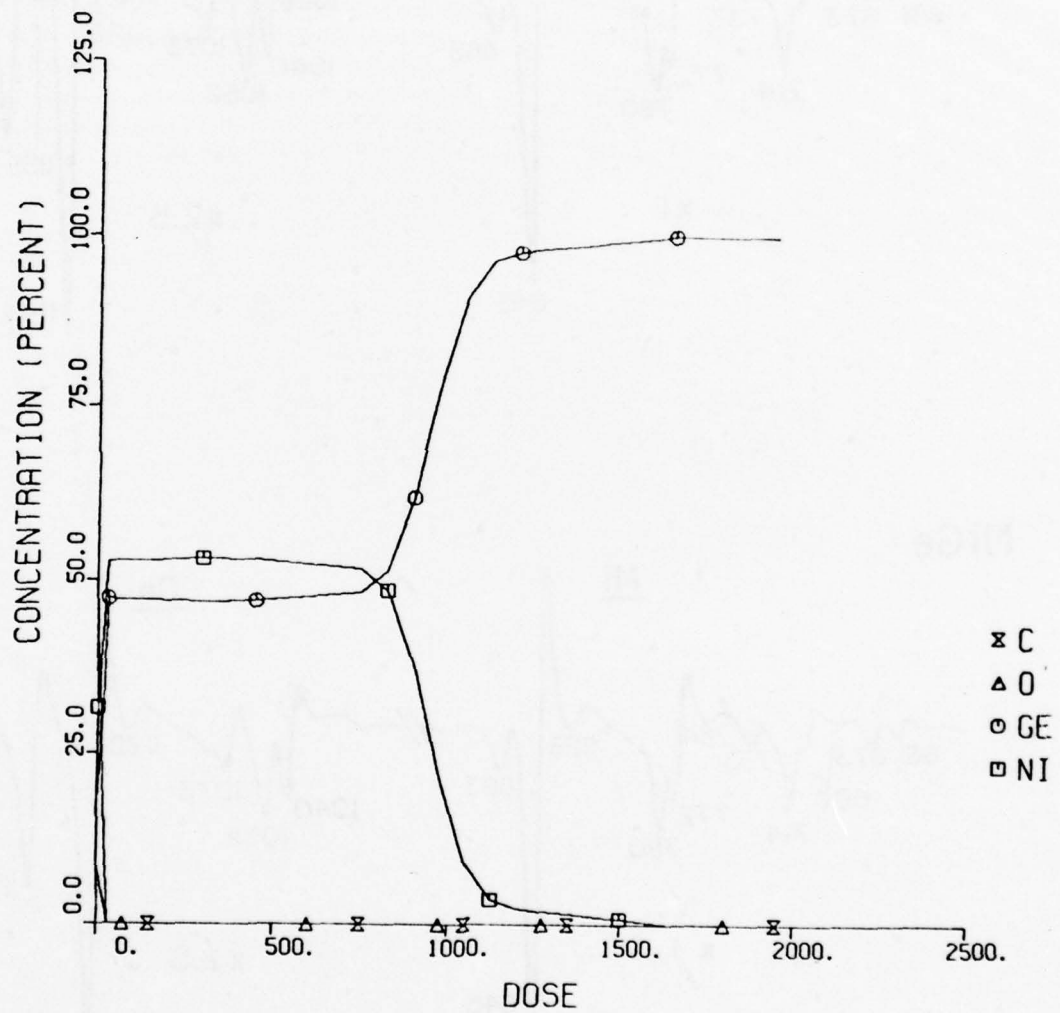
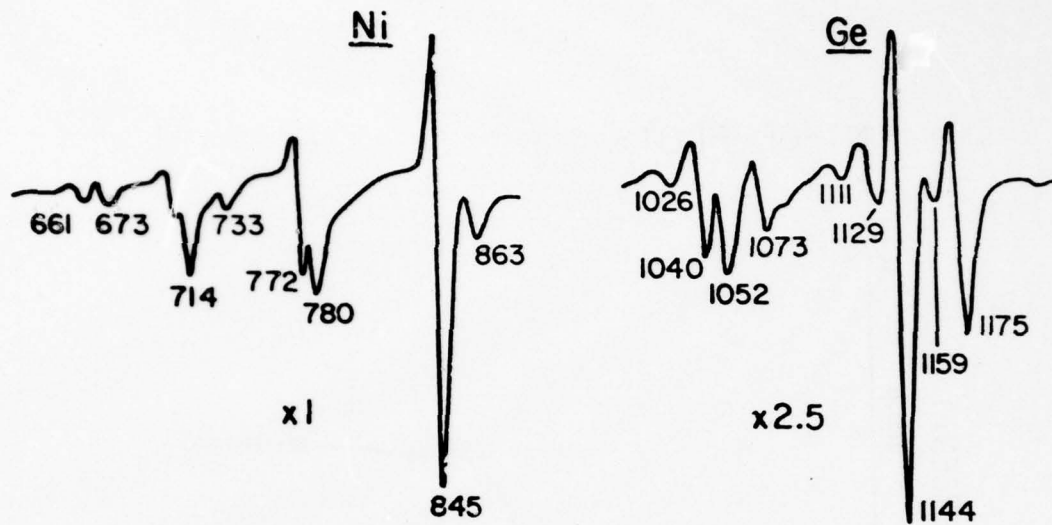


Figure 3.1. AES depth-composition profile of sample (c).

Pure Elements:



NiGe:

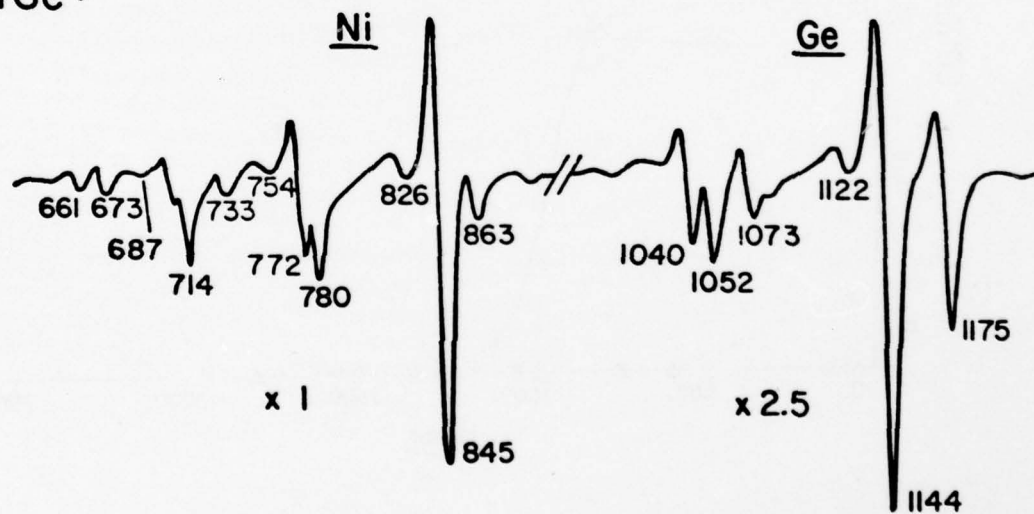


Figure 3.2. AES spectra of Ni, Ge, and NiGe.

4. OHMIC CONTACTS TO n-TYPE InP

The principal ohmic contact to n-type InP studied was that of Ni/Au/Ge. Additional supporting work has been done on Ni/nInP and Au/nInP contacts. Heat-treatments of varying time and temperature have been conducted. Specific contact resistance measurements and Auger electron spectroscopy have been used to correlate the electrical and metallurgical behavior of the contact systems. The X-ray diffraction data of Section 3 was used to determine the role of any Ni-Ge reactions in the electrical behavior of the Ni/Au/Ge system.

4.1. Description of Samples

Three different types of samples were fabricated as listed below. All wafers were etched for five minutes in 3:1:1 H₂SO₄:H₂O₂:H₂O just prior to loading in the ion-pumped vacuum system. Films were deposited using electron-beam evaporation in a vacuum of 2×10^{-7} T. Multiple layer films were done one layer at a time in one pumpdown, using a multiple source.

The types of samples fabricated were as follows:

- (a) 150 Å Ni + 420 Å Au + 250 Å Ge/nInP with $N_D = 3 \times 10^{16} \text{ cm}^{-3}$.

The Au and Ge thicknesses in these first three samples corresponded to the eutectic combination of Au-Ge (88% - 12% by wt.) with a melting point at 356°C.

- (b) 1000 Å Ni/nInP with $N_D = 3 \times 10^{16} \text{ cm}^{-3}$.

- (c) 2000 Å Au/nInP with $N_D = 3 \times 10^{16} \text{ cm}^{-3}$.

An additional sample consisting of 600 Å Au on nInP with $N_D = 2 \times 10^{18} \text{ cm}^{-3}$ was previously fabricated. However, results

from this sample were unreliable and, except for one of the plots in Figure 2.3, are not reported here.

Removal of the Ni/Au/Ge layers in a manner compatible with photolithography was difficult. The following procedure was found to be adequate and was used to etch, not lift, the metal film off the INP using Shipley AZ-1350B photo resist: dip the wafer in $\text{HNO}_3:\text{HF}:\text{H}_2\text{O}$ (100:1:10) for about 3 seconds to remove the Ni, rinse in H_2O , dip for 10 seconds in $\text{KI}:\text{I}_2:\text{H}_2\text{O}$ to etch the Au, and follow with about 3 seconds in $\text{HNO}_3:\text{HF}:\text{H}_2\text{O}$ again to remove the Ge.

4.2. Results

(a) Ni/Au/Ge/nINP

A plot of r_c vs. heat-treatment temperature for five minute treatments is given in Fig. 4.1. Plots of r_c vs. heat-treatment time at temperatures of 225°C and 400°C are shown in Figure 4.2. Specific contact resistances for this system were as low as $2 \times 10^{-5} \Omega\text{-cm}^2$ for five minutes at 325°C and $7 \times 10^{-5} \Omega\text{-cm}^2$ for two minutes at 400°C.

Surface condition of the treated contacts was observed at 400X magnification. Metal contacts appeared very smooth with little or no color change for all heat treatments at 300°C and below. Five-minute heat treatments for temperatures between 300°C and 450°C produced a slight wrinkling of the metal surface and a color change to a lighter gold color, while contacts treated at temperatures above 450°C had very rough, brownish-colored surfaces.

Auger profiles for an as-deposited sample and various heat-treated Ni/Au/Ge samples are given in Fig. 4.3. The profile

for the as-deposited sample indicates that the sample may not be considered to be truly "as-deposited". It appears that much of the Ge, originally all deposited directly on the InP surface, has moved through the Au film and is now associated largely with the Ni, possibly forming a nickel-germanium compound. It may be that the 5-minute post-bake of photoresist at 145°C used in the photolithography after metallization of the sample, effectively acted as a heat treatment. The composition of this "as-deposited" sample may, therefore, be as follows: a layer of elemental Ni on a nickel-germanium compound or mixture, followed by a relatively pure and immobile Au layer, on a thin layer of Ge, all of which covers the n-type InP substrate.

The sample heat treated at 225°C for five minutes had a depth-composition profile, Figure 4.3, that was very similar to that for the "as-deposited" case. Less Ge appears at the metal-semiconductor interface and more of it is now associated with the Ni. This profile provides more evidence that Ge has affinity for the Ni and readily moves away from the InP substrate to react with the Ni overlayer in the early stages of alloying of the contact.

The profile for a sample heat-treated at 275°C for five minutes is shown in Figure 4.3. All of the Ge has diffused to near the surface and now Ni appears at the InP interface. Nickel produces a relatively high barrier height on InP, when heat-treated at this temperature, and is therefore probably responsible for the higher specific contact resistance of this sample (about $7.5 \times 10^{-3} \Omega\text{-cm}^2$ in Figure 4.1). Details of the Ni/nInP system will be presented later.

The depth-composition profiles show considerable change for samples treated at over 400°C. The components of the contact no longer form distinct layers but appear to be intermixed. At higher temperatures In_2O_3 is found on the free surface, as verified by the ratio of In:O and the indium Auger peak shapes⁶. Au, Ni, Ge, In, and P all appear throughout the system, with Au usually the predominant element, especially near the surface. A typical profile is shown in Fig. 4.3.

To observe the Ni-Ge reaction in greater detail, Auger profiles of the Ni and Ge concentrations for four Ni/Au/Ge samples, heat-treated for 5 minutes at progressively higher temperatures, are given in Fig. 4.4. In these profiles the Ge sensitivity for Ge in NiGe is used. For clarity, the Au, In, and P profiles are omitted. The sequence of profiles indicates that a Ni-Ge reaction proceeds through the film with rising heat-treatment temperature until complete reaction is reached at about 275-300°C. The atomic percentages of Ni and Ge in the profiles indicate that the compound being formed is NiGe. Further, the Ge LMM Auger spectra were found to be very similar to that characteristic of Ge as NiGe and the spectra for Ni corresponded to Ni as NiGe (see Fig. 3.2) except near the surface of the sample treated at 200°C, Fig. 4.4, where the composition is largely elemental Ni. From the Ni-Ge profiles and Auger peak shapes observed, it appears that the end product of the Ni/Ge reaction is NiGe with the possible formation of intermediate phases in those regions where the reaction is incomplete.

Such reactions appear to consume all the Ge, leaving excess Ni, as would be expected since the ratio of Ni atoms to Ge atoms for this system is about 1.24.

(b) Ni/nInP

A plot of r_c vs. heat-treatment temperature for five minute treatments is given in Fig. 4.1. The lowest r_c observed thus far was $4 \times 10^{-5} \Omega\text{-cm}^2$, heat-treated at 325°C , 5 minutes.

The as-deposited surface was very slightly wrinkled, becoming more non-uniform with increasing heat-treatment temperature, but remaining unbroken at 325°C .

Auger profiles for an as-deposited sample and for a sample treated at 325°C are given in Fig. 4.5. Both profiles exhibit an In deficiency near the interface. In the heat-treated sample, In_2O_3 was seen on the surface, and In and P appear to be distributed throughout the nickel layer. The Ni peak shapes in the as-deposited sample are unchanged from those of elemental Ni, except near the interface. At this point in the as-deposited sample, as well as throughout the Ni-layer in the heat-treated sample, the Ni peak shapes resemble closely those seen in the Ni found as NiGe.

(c) Au/nInP

A plot of r_c vs. heat-treatment temperature for five-minute treatments is given in Fig. 4.1. Specific contact resistance is $0.47 \Omega\text{-cm}^2$ for the as-deposited sample and increases with heat-treatment to $1.64 \Omega\text{-cm}^2$ at 325°C .

Surface condition appeared to change little with heat treatment.

Capacitance-voltage measurements were done on several as-deposited Au/nInP samples. A representative C-V curve was given in Fig. 2.4. N_D was found to be $(3.0 \pm 0.1) \times 10^{16} \text{ cm}^{-3}$, in good agreement with $4 \times 10^{16} \text{ cm}^{-3}$, the value quoted by the InP supplier. The Schottky-barrier energy for a Au/nInP contact by this method was $0.50 \pm .01 \text{ eV}$.

4.3. Conclusions

The Ni/Au/Ge system on nGaAs has been studied². A eutectic combination of Au-Ge will melt at 356°C, and it is believed that upon alloying above that temperature, the Ge will dope the GaAs heavily n-type to form an ohmic contact⁷. A thin layer of Ni, covering the Au-Ge layer was originally believed to act as a cap, preventing the Au-Ge from balling up⁸, but was later shown to alter the wetting properties of molten Au-Ge on GaAs².

On InP, however, the process may not be as described above. Ohmic behavior of the Ni/Au/Ge/nInP system occurred between 300°C and 325°C, well below the 356°C Au-Ge eutectic. In addition, the Ni and Ge were found to react easily and extensively even with a layer of Au separating them. Also, just before the onset of ohmic behavior, a layer of Ni was found to be well established at the metal/nInP interface. Thus the Ni has an active role in this system. It may even be possible that the nickel alone is largely responsible for the ohmic behavior observed at 300-325°C since both the Ni/nInP and the Ni/Au/Ge/nInP systems (same doping) become very ohmic in that heat-treatment temperature range, and both systems approach the same r_c at 325°C.

The results thus far suggest the following tentative understanding of the Ni/Au/Ge/nInP system. Referring to the r_c -temperature plot for Ni/Au/Ge/nInP in Fig. 4.1, it can be seen that the curve exhibits a minimum between 150°C and 250°C. In this temperature range, Ge has been diffusing away from the InP interface to react with the top Ni layer. The contact is probably not assuming the character of a simple Au/nInP system, since such a system exhibits a much higher r_c for material of the same doping at the same heat-treatment conditions. It seems more likely that some Ge doping of the InP has taken place, creating a Ge/n⁺InP interface, or possibly an Au/n⁺InP interface. Around 275°C the Ni-Ge reaction is complete. Since the reaction product appears to be NiGe, there would be excess Ni left after complete consumption of the Ge present. The excess Ni diffuses to the InP interface and is probably responsible for the increase in r_c , seen from 250°C to 300°C. Indeed, both r_c vs. temperature plots for the Ni/nInP and the Ni/Au/Ge/nInP systems exhibit maxima on this temperature range, although the r_c for Ni/nInP is about an order of magnitude higher than that for Ni/Au/Ge/nInP at this point. This difference, however, points again to the possibility that some n⁺ doping of the InP has taken place in the Ni/Au/Ge/nInP system. Between 300°C and 325°C the Ni/Au/Ge/nInP contact becomes very ohmic. As suggested earlier, the nickel may also be responsible for this behavior since both the Ni/nInP and Ni/Au/Ge/nInP system become ohmic at about the same temperature and drop to about the same r_c . Auger analysis at this point, however, reveals considerable intermixing of all five elements involved, and it is difficult to draw firm conclusions as yet.

4.4. Plans for the Next Interval

Work yet to be completed includes heat treatments and specific contact resistance measurements on Au/Ni/Ge/nINP diodes and additional Ni/Au/Ge/nINP diodes of higher doping which have been recently fabricated. On the Au/nINP and Ni/nINP contacts such measurements will be continued in greater detail. Auger electron spectroscopy and depth composition profiling will be conducted on selected samples.

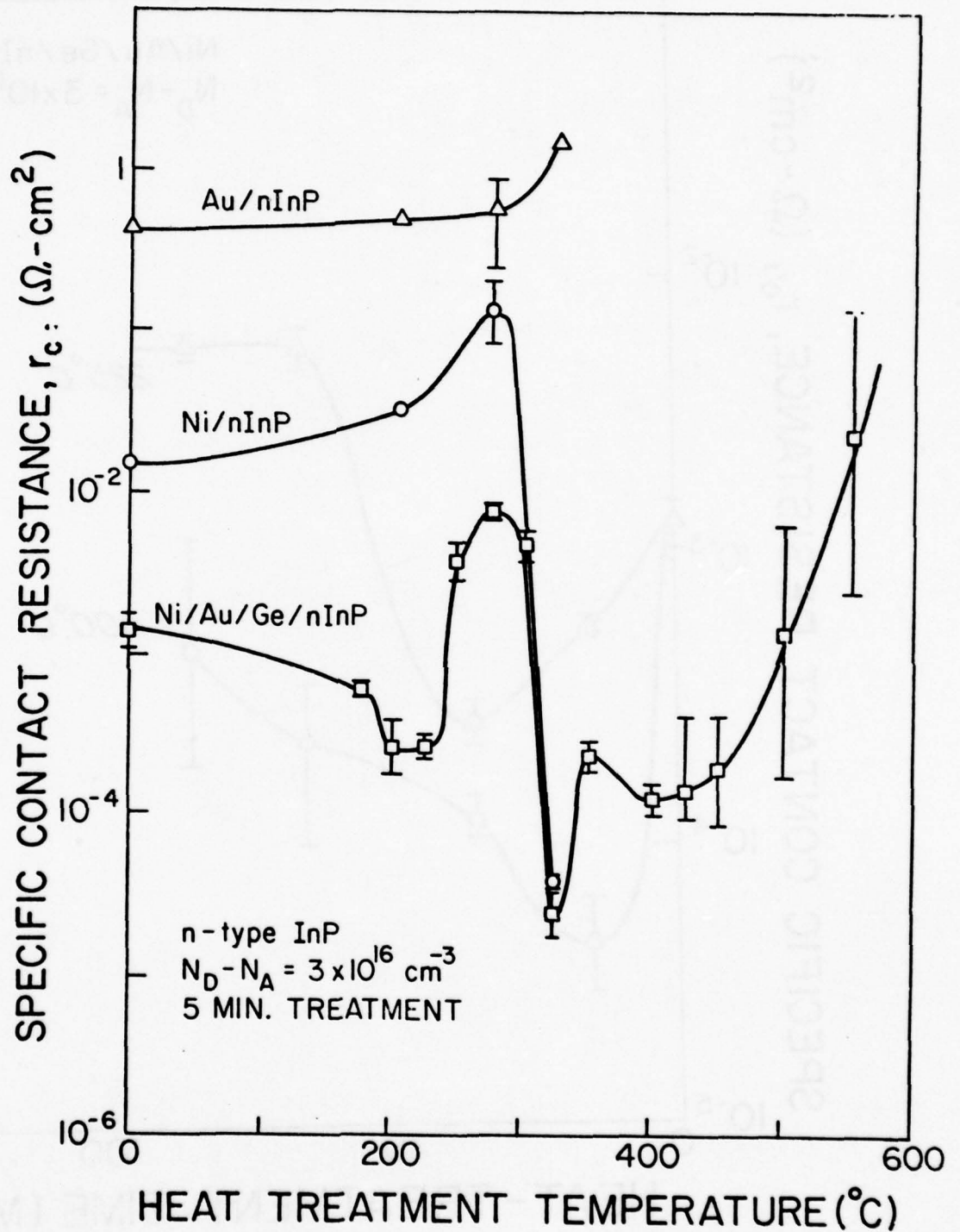


Figure 4.1. Variation of r_c with heat-treatment temperature for n-type InP contacts.

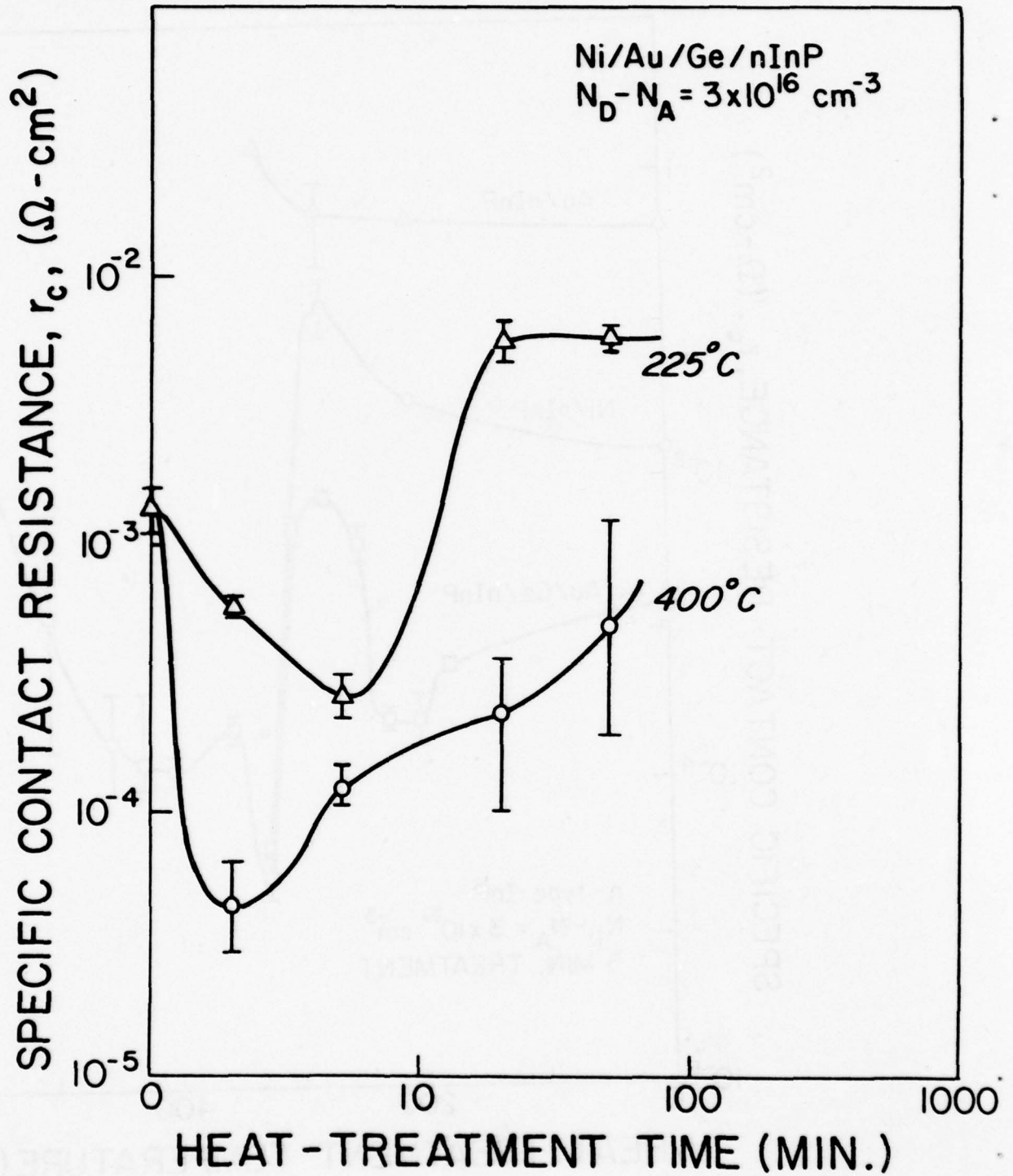


Figure 4.2. Variation of r_c with heat-treatment time for contacts to n-type InP.

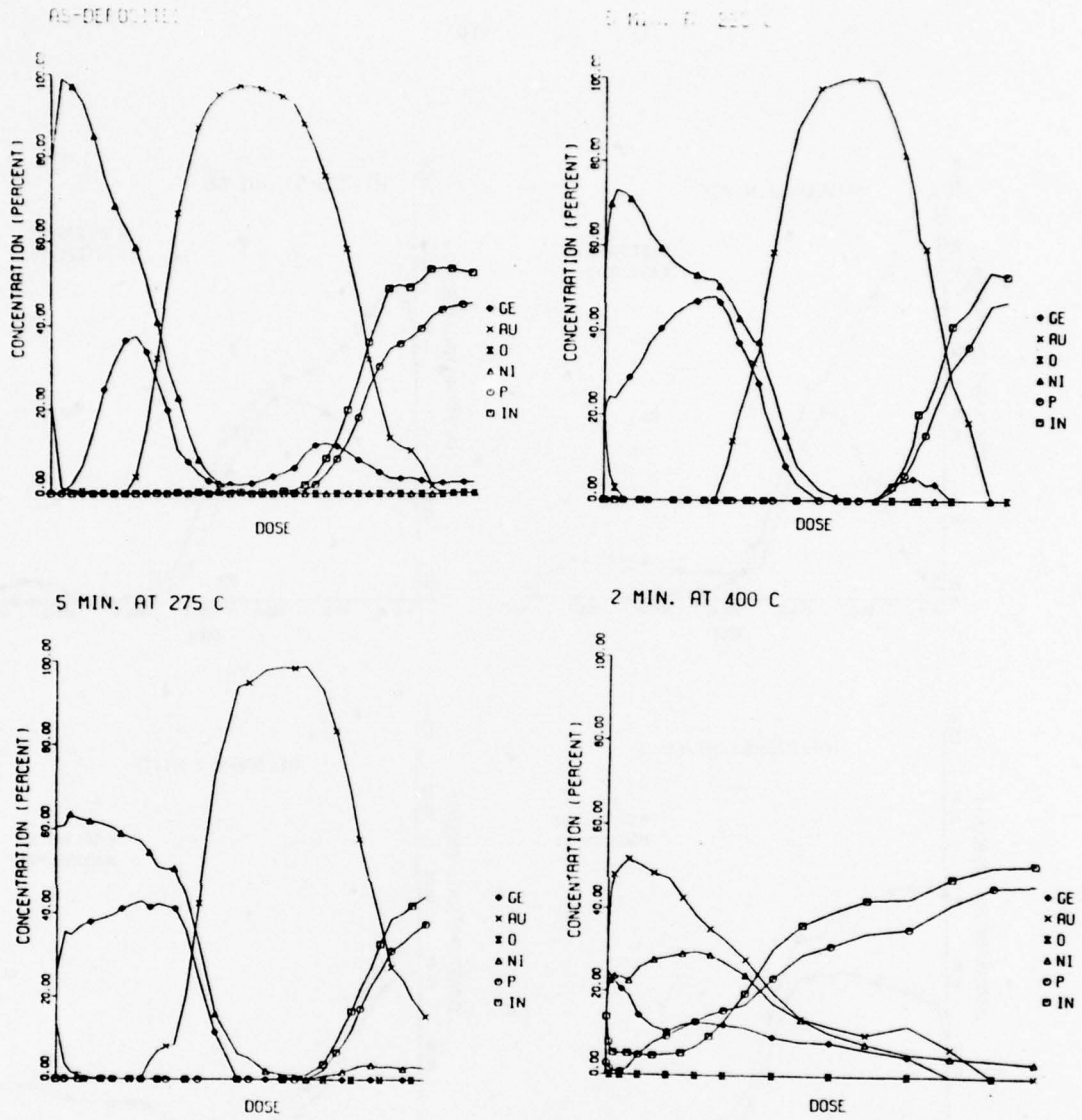


Figure 4.3. AES profiles of Ni/Au/Ge contacts on n-type InP.

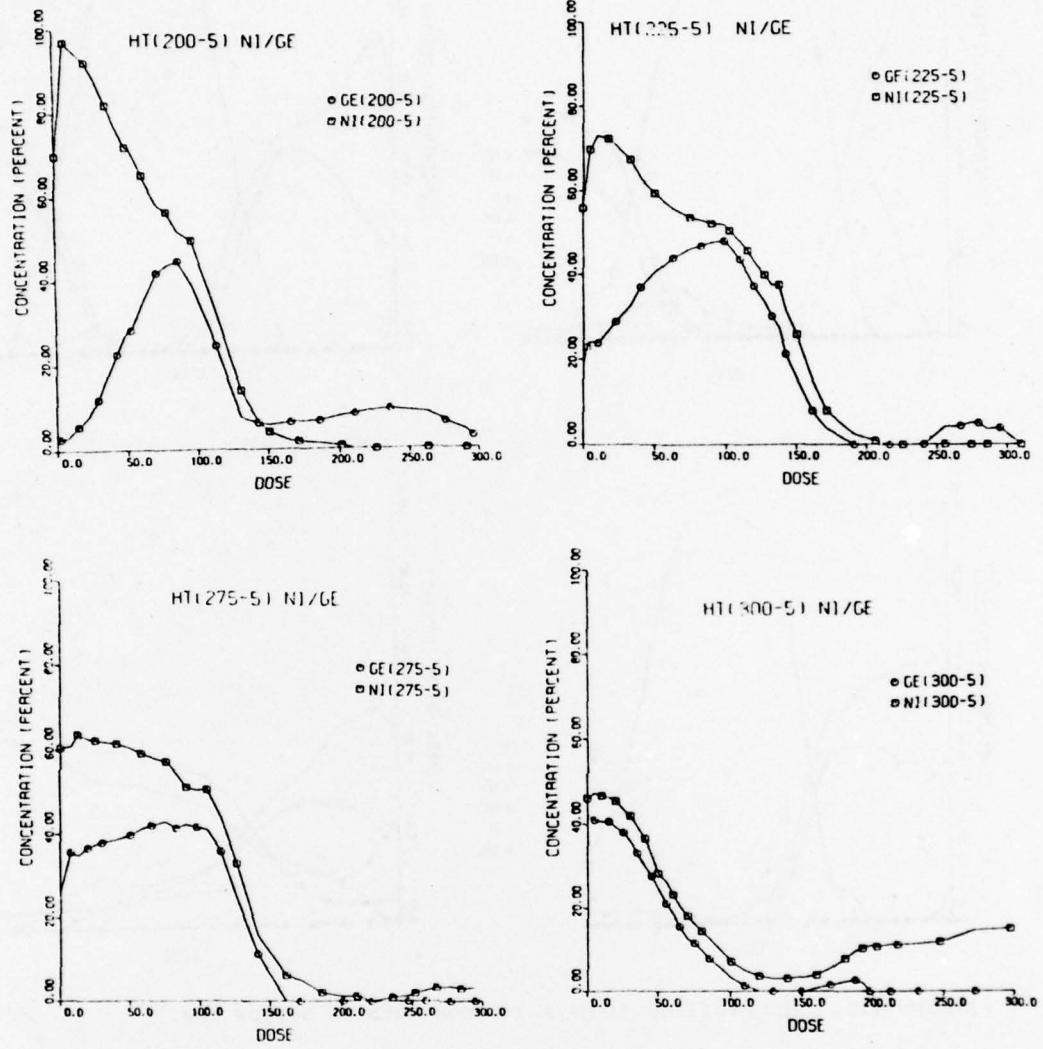


Figure 4.4. AES profiles of only Ni and Ge in Ni/Au/Ge/nInp contacts.

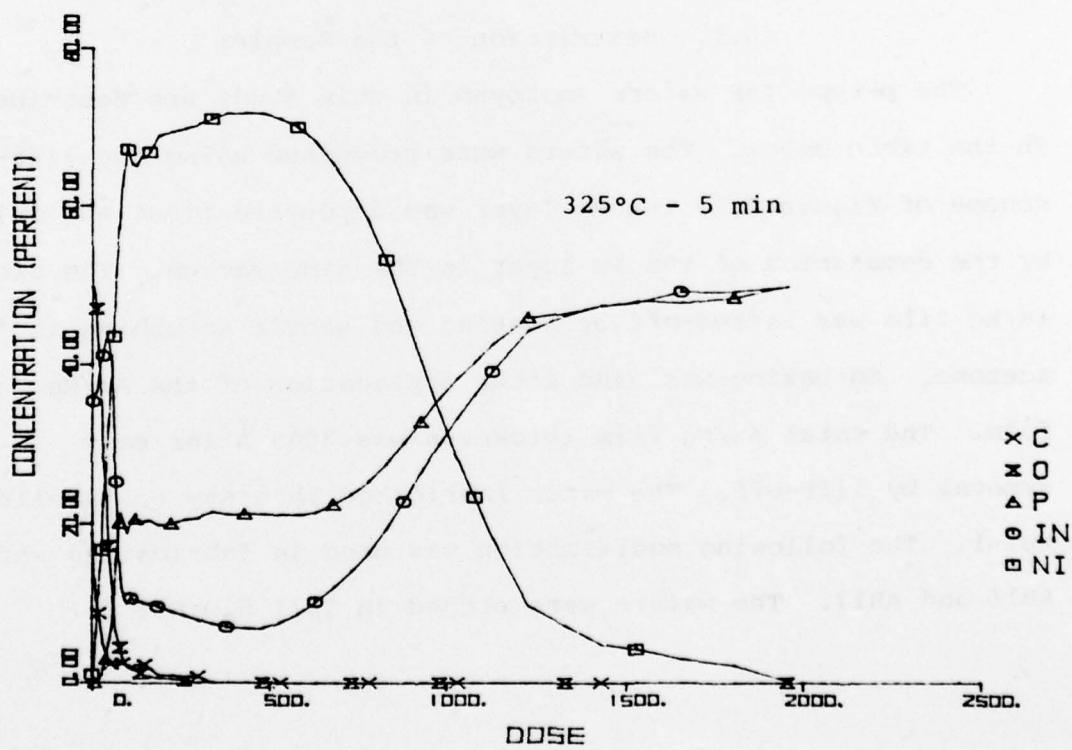
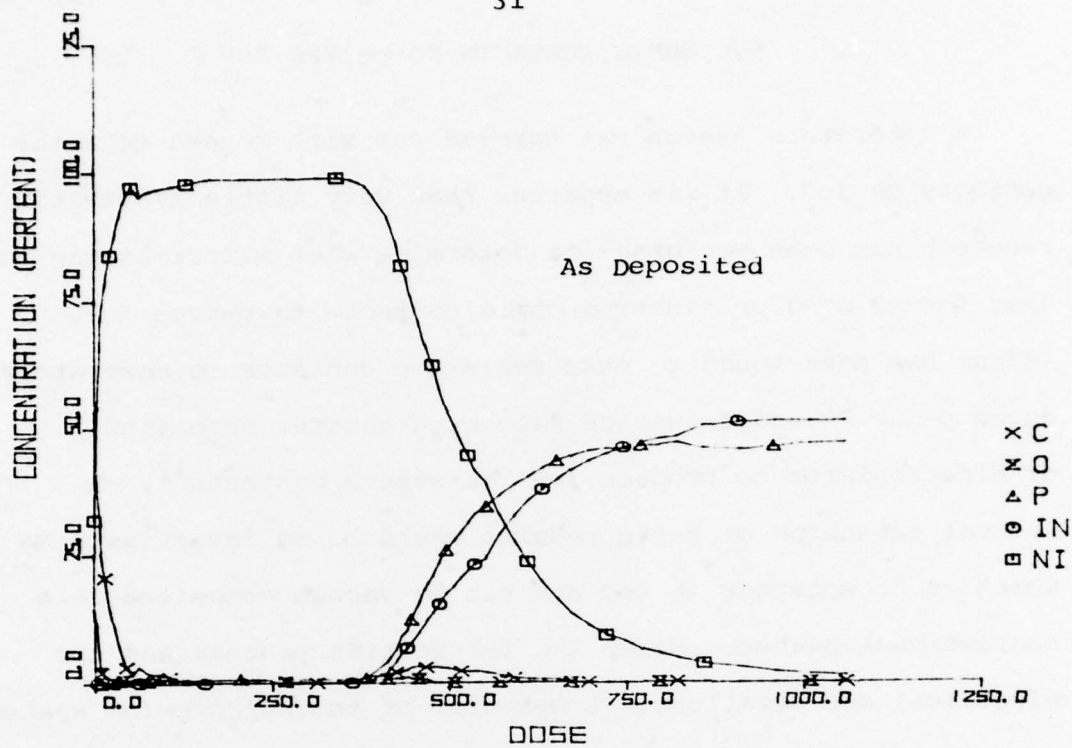


Figure 4.5. AES profiles of Ni/nInP samples.

5. OHMIC CONTACTS TO p-TYPE InP

A literature search was carried out with regard to metal contacts on InP. It was apparent that very little systematic research has been performed to determine what materials can be used for alloyed or sintered ohmic contacts to p-type InP. Indium has been found to make resistive contacts to moderately doped p-InP,¹¹ and Zn and Cd have been sputter deposited or electroplated to produce low resistance contacts¹². A natural extension of these results would be to investigate Mg which is an acceptor in InP and can be vacuum deposited in a conventional manner. Hence the fabrication process and the electrical and metallurgical behavior of the Au/Mg/p-InP system are presented in this section.

5.1. Description of the Samples

The p-type InP wafers employed in this study are described in the table below. The wafers were processed using the lift-off scheme of Figure 2.1; the Mg layer was deposited first and followed by the deposition of the Au layer in the same vacuum. The excess Au/Mg film was lifted-off by soaking and gently scrubbing in acetone. No baking was used after application of the Au/Mg film. The total Au/Mg film thickness was 2000 Å for easy removal by lift-off. The wafer fabricated this way is labelled MBl-1. The following modification was used in fabricating wafers AB16 and AB17. The wafers were etched in 10:1 H₂O:HCl for

30 seconds just prior to placement in the vacuum system for Au/Mg metallization. This extra step was used in an attempt to remove any native oxide present on the InP surface and thus produce a cleaner metal/p-InP interface.

Wafer	Supplier	Dopant	Doping (cm^{-3})	Orientation	Au/Mg Film Thickness (\AA)
MB1-1	Metal Specialities	Zn	6×10^{17}	$\langle 111 \rangle$	1600/400
AB16	Air Force	Zn	1×10^{17}	$\langle 100 \rangle$	1600/400
AB17-1				3° -OFF	1800/200
AB17-2				to $\langle 111 \rangle$	1200/800

5.2. Results

The Au/Mg/InP diodes were characterized electrically before the heat treatments were begun. Table 5.1 summarizes the electrical properties of the as-deposited contacts.

All of the wafers exhibited rectifying Schottky diode behavior in the as-deposited condition. The following Schottky parameters were measured: the barrier energy ϕ_{BP} and the diode factor n using forward-biased I-V measurement at room temperature (a typical curve is shown in Fig. 2.3), ϕ_{BP} and the Richardson constant A^{**} using the variation of saturation current I_s with temperature T , and ϕ_{BP} and the net hole concentration N_A using reverse-biased C-V measurements. As is observed from Table 5.1, wafer MB1-1 showed the greatest disparity for the three values of ϕ_{BP} obtained. The high value of n and the large value of ϕ_{BP} (C-V) indicate that wafer MB1-1 probably had a thin oxide layer between

Table 5.1. Summary of Electrical Measurements on As-Deposited Au/Mg/p-InP Diodes.

Wafers	N_A as given by the manufacturer (cm^{-3})	MEASUREMENT TECHNIQUE				Capacitance-Voltage	
		I-vs-V at $T=300^\circ\text{K}$ (Assume $A^{**} = 60\text{A}/\text{cm}^2\text{-}^\circ\text{K}^2$)	I_s/T^2 -vs- $1/T$	I_s/T^2 -vs- $1/T$	Capacitance-Voltage		
		ϕ_{Bp} (ev)	n	ϕ_{Bp} (ev)	A ($\text{A}/\text{cm}^2\text{-}^\circ\text{K}^2$)	ϕ_{Bp} (ev)	N_A (cm^{-3})
MB 1-1	6×10^{17}	0.68	1.42	~ 0.18	~ 0.3	1.67	6.24×10^{17}
AB16 } AB17 }	1×10^{17}	0.87 ± 0.04	1.19 ± 0.06	~ 0.54	~ 30	1.08 ± 0.02	$(1.21 \pm 0.05) \times 10^{17}$

the deposited Au/Mg and the InP substrate. This is verified by the AES depth profile for the as-deposited MB-1 wafer shown in Figure 5.1, where oxygen is detected at the metal/InP interface. We are unable at present to explain all of the as-deposited electrical data of Table 5.1 for MB-1 in terms of a single model of carrier transport (i.e. conduction by diffusion, thermionic emission, recombination, or field emission).

The as-deposited MB-1 wafer also exhibited considerable separation of the Mg during deposition of the Au layer (Fig. 5.1). The heat of condensation of Au may have supplied the energy for diffusion of the Mg to the free surface. Furthermore, part of the Mg on the surface was in the form of MgO, as determined by chemical shifts in the Auger peaks, and illustrates the high affinity of Mg for oxygen.

With reference to Table 5.1, many of the diodes on wafers AB16 and AB17 exhibited characteristics much closer to that of an ideal Schottky diode. The oxide-etch step performed on these wafers and not on MB-1 may be responsible for this difference. However, considerable variation in the I-V characteristics from diode to diode was observed for wafers AB16 and AB17. Thus improvement in the processing procedure is still needed.

It should be noted that the experimentally determined value of A^{**} differs considerably from the assumed value of $A^{**} = 60 \text{ A/cm}^2 \cdot \text{K}^2$ used to calculate ϕ_{Bp} from I-V measurements. However the scatter, although small, in the I_s -vs- $1/T$ data is such that A^{**} can be determined only within several orders of magnitude. In addition, a difference of 0.2 eV between ϕ_{Bp} (I-V) and ϕ_{Bp} (C-V) is not unusual for Schottky diodes fabricated in our laboratory and elsewhere.

As shown in Table 5.1, the value of N_A for all wafers was found to agree with the doping level given by the supplier. The Air Force wafers proved to be very uniformly doped, both across a given wafer and from wafer to wafer. This is best demonstrated by an examination of the slope of the $\frac{1}{C^2}$ -vs- V curves shown in Fig. 2.4.

The specific contact resistance for the wafer MB1-1 was measured as a function of both heat-treatment time and temperature. The results are shown in Fig. 5.2. As can be seen the contact resistance has a wide range of values, but a heat treatment of 446°C for 50 min. produced both the lowest r_c and the smoothest surface. The depth composition profile for a Au/Mg sample heat treated under these conditions is shown in Fig. 5.1. MgO is again found on the surface, followed by a region which is mixed in composition, all covering the InP substrate.

It was found for the Au/Mg/InP system that the surface morphology is very strongly dependent on heat-treatment temperature and moderately dependent on heat-treatment time. The surface roughness increases for heat-treatment temperatures above 400°C with extensive melting of the metal film on top of the SiO₂ as well in the InP contact windows at 500°C and above. Although the surface of the InP in the contact window was far from perfectly smooth at 446°C for 50 min, the contact resistance was less than $10^{-4} \Omega\text{-cm}^2$ for $6 \times 10^{17} \text{ cm}^{-3}$ doping.

To determine the nature of the lateral melting of the Au/Mg film on top of the oxide, the scanning Auger microprobe (SAM) was used and the results are shown in Figure 5.3. The region labeled A appears to be unreacted metal with a top surface of Mg and MgO. Region B shows evidence of extensive reaction with

melt formation during heat-treatment at 500°C. A high concentration of Au and In were found on the unspattered surface between Regions A and B. It was apparent that the extent of Region B is proportional to the area of the exposed InP, Region C. It was also found that for a given heat-treatment cycle, the specific contact resistance r_c depended on the extent to which the metal film on top of the oxide has melted. For example, the value of r_c for the sample of Figure 5.3 increased in proportion to the ratio of the area of Region B to the area of Region C.

5.3. Conclusions

Although our study of alloyed Au/Mg films as ohmic contacts to p-type InP is far from complete, some preliminary interpretations of the results to date can be made.

It is expected that if during heat-treatment a loss of In from the InP substrate occurs, a high concentration of In vacancies would exist near the metal/InP interface. Furthermore, if Mg is present as a substitutional defect at In sites, then Mg should behave as an acceptor impurity. The depth profiles of Fig. 5.1 as well as the SAM data all indicate increasing loss of In with increasing heat-treatment temperature, probably as a result of the high solubility of In in Au. For example, the concentrations of 90% Au and 10% In between 500 to 800 dose in the heat-treatment sample of Fig. 5.1 agree with the reported solubility of In in Au at this temperature¹³. Also Mg is found at depths where the In/P ratio is less than unity. Thus the substitution of Mg for In and the resulting p+ layer could explain the decreasing value of r_c with increasing heat-treatment temperature of Fig. 5.2.

If this description of the Au/Mg/InP alloying process is correct, then the Au layer plays a conflicting role. The Au is indirectly responsible for the low value of r_c but also produces poor surface uniformity when heated above the Au-In eutectic temperature of about 450°C ¹³. By maintaining the temperature below 450°C and allowing sufficient time for In to diffuse out of the substrate, then a low value of r_c can be obtained without evidence of surface melting. More research is needed to further clarify the roles of Au and Mg during ohmic contact formation.

5.4. plans for Next Interval

Research on controlling the Au/Mg system on p-type InP will continue. The new set of diodes (wafers AB16, AB17-1, AB17-2) will be evaluated for both ϕ_{Bp} and r_c as functions of heat-treatment conditions. Extensive Auger analysis will be used to determine the composition of Au/Mg/pInP structure both laterally and in depth. The lateral melting which occurs in the Au/Mg system at high temperatures will be further investigated.

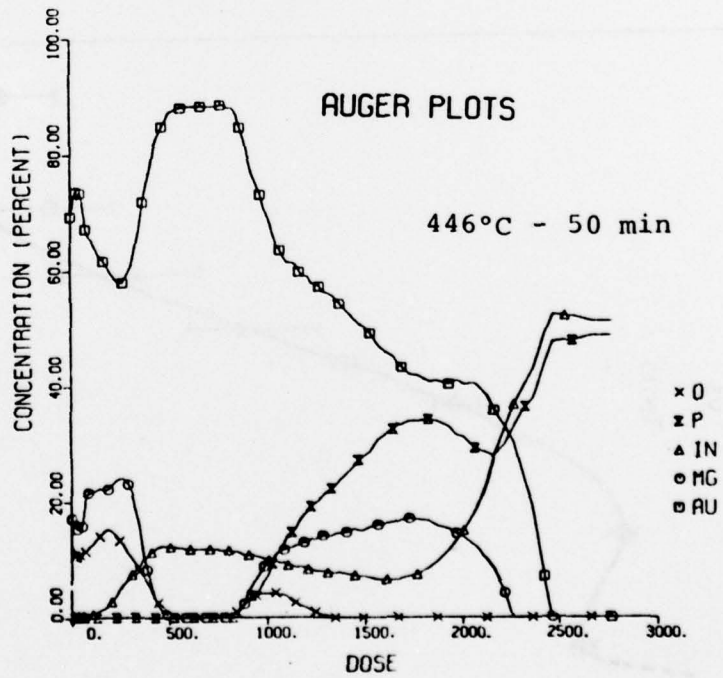
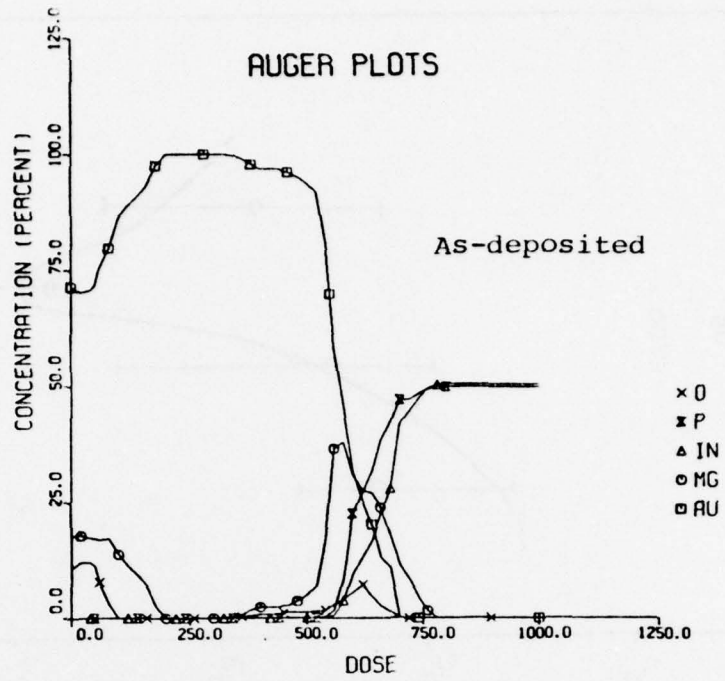


Figure 5.1. AES profiles of Au/Mg contacts on p-type InP.

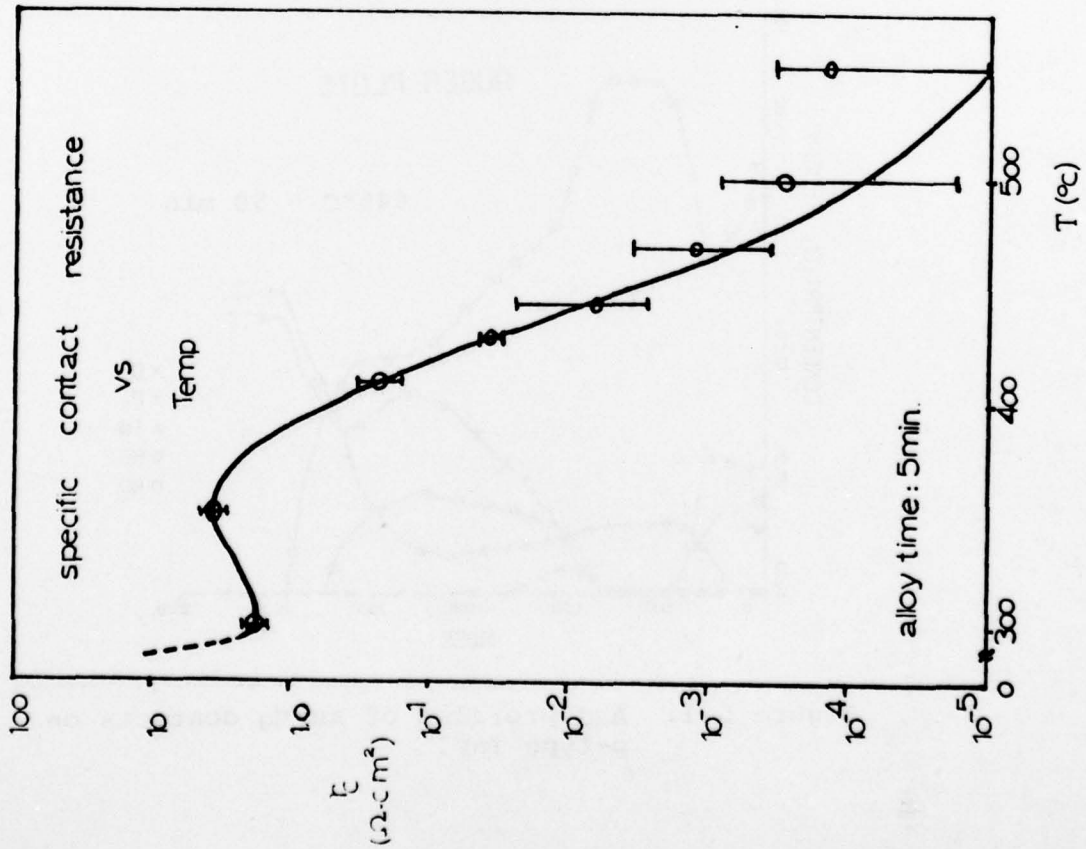
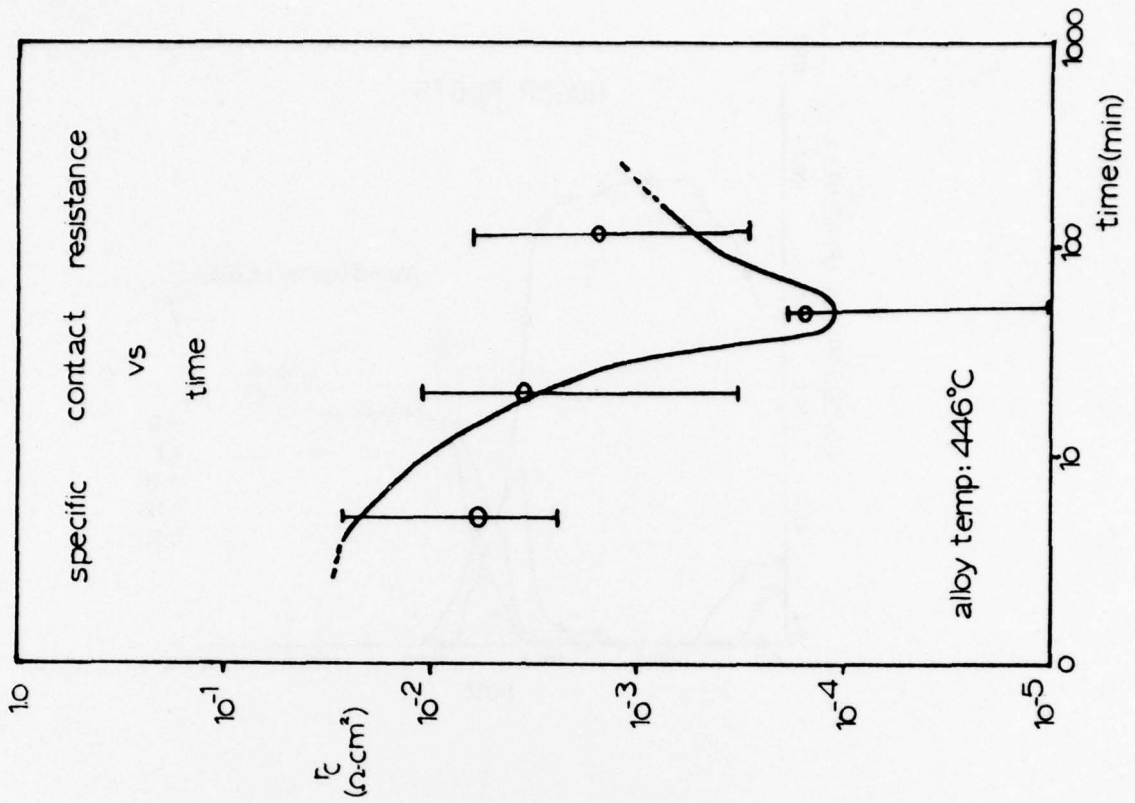


Figure 5.2. Variation of r_c with heat-treatment time and temperature for Au/Mg/pInp contacts.

Au / Mg / pInP
500°C - 5 min.

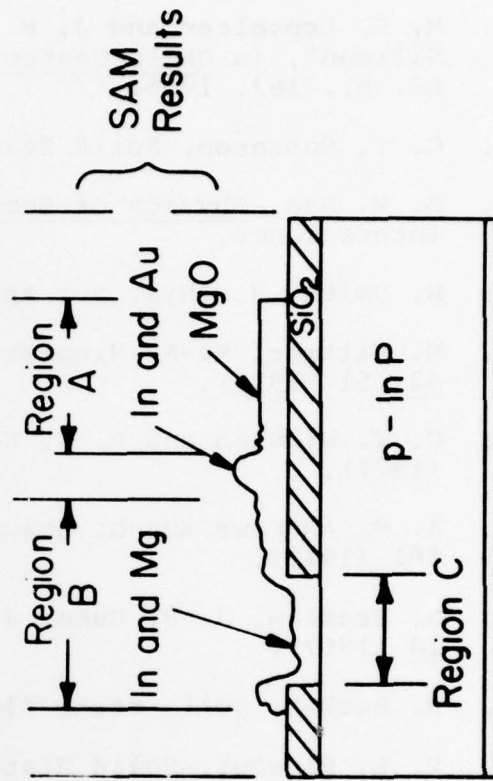
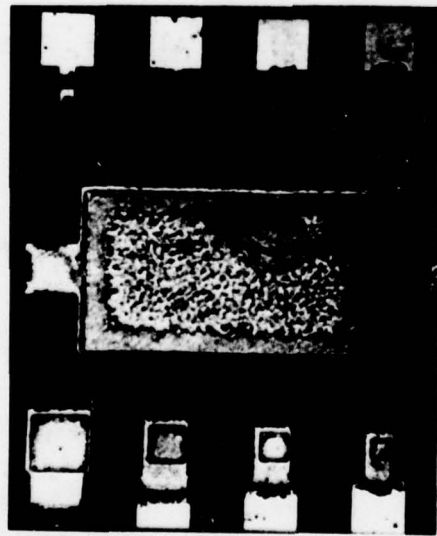


Figure 5.3. Surface morphology for Au/Mg/pInP contacts.

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