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Aging Behavior of Au-based Ohmic Contacts to GaAs

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Summary

Gold based alloys, commonly used as ohmic contacts for solar cells, are known to react readily with GaAs. It is shown that the contact interaction with the underlying GaAs can continue even at room temperature upon aging, altering both the electrical characteristics of the contacts and the nearby pn junction. Au-Ge-Ni as-deposited (no heat-treatment) contacts made to thin emitter (0.15μm) GaAs diodes have shown severe shunting of the pn junction upon aging for several months at room temperature. The heat-treated contacts, despite showing degradation in contact resistance, did not affect the underlying pn junction. Au-Zn-Au contacts to p-GaAs emitter (0.2μm) diodes, however, showed slight improvement in contact resistance upon 200°C isothermal annealing for several months, without degrading the pn junction. The effect of aging on electrical characteristics of the as-deposited and heat-treated contacts and the nearby pn junction, as well as on the surface morphology of the contacts are presented.

Introduction

Gold-based alloys are the most commonly used metallization materials for both the front grid and the back ohmic contacts of GaAs solar cells. Au-Zn and Au-Ge-Ni have been the most popular systems for making ohmic contacts to p- and n-GaAs respectively, mainly due to very low values of specific contact resistivity (ρ_c) achievable with these systems upon a post deposition heat-treatment. ρ_c values in the low 10^{-6} Ω-cm^2 range have been reported by many workers for these contact systems to variously doped GaAs substrates [refs. 1,2,3]. These low values are necessary to keep the contact resistance contribution to the series resistance of a solar cell negligible if these cells are to be operated under >100× sunlight concentrations [ref. 4].

It is highly desirable that the ohmic contacts remain stable during the life of the solar cell regardless of its operating temperature. Space concentrator solar cells e.g., are expected to operate in the 80-100°C range. They may also be annealed periodically at 200 to 400°C for a few hours at a time in order to reverse the radiation damage effects caused by electron and proton bombardment in the space environment [refs. 5,6]. Several months of cumulative periodic high-temperature annealing may therefore be necessary during the life of the solar cell. High temperature aging studies of Au-Ge-Ni contacts at 330 to 390°C for several days, for example, have revealed increased interactions between GaAs and the contacts and also a general increase in contact resistance [refs. 7,8], pointing to possible instability of these contacts with high temperature aging.

In this work, the high temperature (200 and 400°C) aging stability of Au-Zn contacts to p-GaAs, as well as the room temperature aging stability of Au-Ge-Ni contacts to n-GaAs for several months were investigated. The effects of aging on specific contact resistivity, metal-GaAs interaction, and surface morphology of the contacts are presented.

Au-Zn Contacts

Au-Zn contacts were made to highly doped ($2 \times 10^{18} cm^{-3}$) thin emitter ($0.2 \mu m$ quasi-neutral region thickness) p-type epi-layer GaAs (obtained from Spire), whose structure is shown in figure 1b. The 200-300Å thin Au layer interposed between GaAs and Zn helps the uniformity and adhesion of the contact at the interface. Six samples were heat-treated immediately after E-Beam deposition of the contacts to a maximum temperature of 434°C for 90 seconds. The ρ_c values for these contacts varied from 4.7×10^{-6} to $3.4 \times 10^{-5} \Omega - cm^2$. The samples were then annealed at 200°C in flowing N_2 for a period of slightly more than 3 months. Subsequently, they were also subjected to a 400°C anneal for a period of 64 hr in air. Contact resistance values, measured via the Transmission Line Method [ref. 9], and current-voltage characteristics of the p/n diodes underneath the contacts were monitored periodically for all samples. The effect of 200 and 400°C isothermal annealing of these contacts, as well as 13 months of subsequent aging of the contacts at room temperature on ρ_c is given in Table 1. Figure 2 compares a typical p/n diode I-V curve with a Au-Zn emitter contact at various stages of aging.

As shown in Table 1, the 200°C isothermal annealing actually slightly improved ρ_c for all samples, indicating the stability of these contacts with high temperature aging, although the Au-Zn/GaAs interaction must have continued to some degree as to bring about the change in ρ_c . However, this continued interaction between the contact and GaAs does not appear to have a significant effect on the nearby p/n junction as evident from figures 2a and 2b. At 400°C however Au-Zn/GaAs interactions were more severe, as shown in figure 2c, resulting in much degradation in the I-V characteristics of the underlying junction. The contact resistance, on the other hand, showed little degradation for most samples and a slight improvement for one sample. Also, the subsequent room temperature aging of the contacts for 13 months did not appear to affect ρ_c or p/n diode I-V characteristics of these samples significantly (fig. 2d).

Despite the minimal changes occurring in ρ_c for Au-Zn contacts after 13 months, the interaction in the Au-Zn/GaAs system continues at room temperature. This room temperature aging is portrayed in figure 3, where the surface morphologies of the contacts for both as-deposited and heat-treated contacts are compared for new and aged contacts. As shown in figures 3a and 3c, the 450°C heat-treatment for 1 min did not appear to change the surface morphology of the contact, whereas the 13 months room temperature aging of both as-deposited (fig. 3b) and heat-treated (fig. 3d) contacts altered the surface morphology dramatically.

Au-Ge-Ni Contacts

Au-Ge-Ni contacts were made to variously doped n-GaAs epi-layers (MOCVD grown, in-house). The n/p current-voltage characteristic measurements however, were done on moderately doped ($6 \times 10^{17} cm^{-3}$) thin emitter ($0.15 \mu m$) n-GaAs samples (obtained from Spire Co.), as shown in fig. 1a. For these samples, the as-deposited contacts showed rectifying characteristics. Upon heat-treatment in the 353 to 490°C temperature range for short periods (15 to 60 sec.), however, most samples exhibited $10^{-6} \Omega - cm^2$ ρ_c values. In Table 2 the ρ_c values for many samples heat-treated at different temperatures and aged at room temperature for 9 to 31 months are given. As shown, the change in ρ_c upon aging for most samples was slight regardless of the heat-treatment temperature or the period of aging. In some cases, ρ_c values for identically treated samples took different directions upon aging for the same time period. This points to the complex mechanism involved in the low resistance contact formation at the metal-GaAs interface. The relative stability of the heat-treated contacts, however, is attributed to the formation of the low resistance ternary Ni_2GaAs phase at the interface [ref. 10]. It is apparent, therefore that the room temperature aging of these contacts should not cause any dramatic increases in the contact resistance in solar cells.

The main concern for using Au-Ge-Ni as the front grid metallization in shallow junction solar cells is that penetration of the contact species into GaAs can damage the nearby n/p junction. As shown in figures 5a and 5b, heat-treating the contacts at 360 and 395°C for 20 sec can severely short out the junction. One solution to this problem is not to heat-treat the contacts. In case of low to moderately doped emitters, the contacts will be rectifying, but in case of highly doped ($> 1 \times 10^{18} cm^{-3}$) emitters, ρ_c will be in the high $10^{-4}\Omega-cm^2$ range which is acceptable for one sun operation of solar cells. However, if the contacts are not heat-treated, the Au-Ge-Ni/GaAs interactions can continue at room temperature to a greater degree than for the heat-treated contacts. This can be due to the absence of stable binary and ternary phases which are created at the metal-semiconductor interface upon heat-treatment. Figure 4 shows typical n/p diode I-V characteristics for several diodes with as-deposited Au-Ge-Ni contacts aged at room temperature for 14 months. As shown in figure 4a, the newly deposited contact to $6 \times 10^{17} cm^{-3}$ doped emitter is rectifying. Upon aging, most contacts became non-rectifying (i.e. showing linear metal-semiconductor I-V behavior over a given current range), but most of them also severely degrade the nearby (0.15 μm) n/p junction (figs. 4c and 4d). In rare cases, the contacts can become non-rectifying and at the same time do not shunt the junction (fig. 4b).

Consequently, contacts must be heat-treated to remain stable with room temperature aging. But as mentioned earlier, heat-treatment of the contacts can severely shunt the n/p junction under a thin emitter. One method to circumvent this problem is by encapsulating the contacts with SiO_2 or Ta_2O_5, and/or by the use of a diffusion barrier such as TiN incorporated into the contact system prior to heat-treatment (ref. 12). The diffusion barrier in the case of Au-Ge-Ni contacts can be interposed between the top Au(1550Å) layer and the underlying Ni-Ge-Au thin active layer, replacing the 100Å Ni layer. The ρ_c values for the contacts made with and without TiN barriers were measured to be comparable.

Figures 5c and 5d show the I-V characteristics of two n/p diodes with Au-Ge-Ni contacts heat-treated to 396 and 400°C for 20 sec, respectively. The contacts of the diodes in fig. 5c contained TiN (600Å) layers and those in figure 5d were encapsulated with Ta_2O_5 (600Å), and they were aged for 8 and 21 months at room temperature, respectively. As shown, no sign of shunting can be detected in these I-V curves even after long periods of room temperature aging. Therefore, the use of diffusion barriers and/or dielectric encapsulants with Au-Ge-Ni contacts made to thin emitter diodes seems to be a necessity.

Additional evidence for the continued interactions between Au-Ge-Ni and GaAs is the change that occurs in the surface morphology of the contacts upon room temperature aging. Figure 6 compares the surface morphology of the as-deposited new (fig. 6a), as-deposited and aged for 11 months (fig. 6b), heat-treated new (400°C) (fig. 6c), and heat-treated and aged for 9 months (fig. 6d) contacts. Upon aging, both the as-deposited and heat-treated contacts seem to approach an end form with a more definite grain structure not evident prior to the aging process. High temperature aging of these contacts indicates the continued out diffusion of Ga through the metallization and

Ga_2O_3 oxide formation at the surface of the contact [ref. 7]. Again, an effective diffusion barrier incorporated into the contact system should limit the dissolution of Ga into the metallization system greatly.

It is known that GaAs reacts readily with pure Au at room temperature [ref. 11]. The effect of this room temperature interaction of Au with GaAs upon aging on ρ_c was also studied. Au contacts were made to highly doped ($5 \times 10^{18} cm^{-3}$) thick (1 to 1.2 μm) n-type GaAs epi-layers. As shown in Table 3, hardly any degradation in ρ_c is observed for any of the contacts after room temperature aging of the contacts for 32 months. This indicates that the Au-GaAs interaction does not appear to affect the resistance at the metal-semiconductor interface.

Conclusions

Isothermal annealing of Au-Zn contacts on p-GaAs at 200 and 400°C for 3 months and 64 hrs, respectively have shown that the specific contact resistivity of these contacts are relatively stable with high temperature aging. No p/n junction degradation was observed in the 200°C aging study, but for the case of annealing at 400°C, the p/n diodes underneath the contacts degraded severely. The emitter thickness in both cases was 0.2μm.

Room temperature aging of Au-Ge-Ni contacts on n-GaAs for several months indicates that ρ_c values for these contacts do not increase significantly compared to their as-fabricated values, and for many cases they remain very stable. It was also shown that the as-deposited contacts continue to interact with the underlying GaAs at room temperature, usually resulting in n/p junction degradation underneath the 0.15μm emitter. The heat-treated contacts on the other hand can severely short out the n/p junction underneath after 360°C heat-treatment for a few seconds. The use of a TiN diffusion barrier and a SiO_2 or Ta_2O_5 dielectric encapsulant can prevent degradation, even with these shallow emitters (0.15 μm), even after heat-treating the contacts to 400°C. Their use will also inhibit the metal-GaAs interactions that would otherwise occur during room-temperature aging.

In addition, the contact resistances for pure Au contacts were found to be very stable after 32 months of room temperature aging. It was also shown that the surface morphology of Au-Zn and Au-Ge-Ni contacts alter after several months of room temperature aging for both as-deposited and heat-treated contacts, which is another indication that the interaction between GaAs and its metallization continues at room temperature, whether or not the contact is heat-treated. The I-V characteristics of the junction underneath the contacts, however, indicate that this interaction is negligible for the heat-treated contacts compared to the as-deposited contacts.

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Table 1. Effect of Isothermal Annealing at 200°C for 3 Months, at 400°C for 64 Hours, and Room Temperature Aging for 13 Months on the Specific Contact Resistivity of Au-Zn Ohmic Contacts to p-GaAs

Sample	ρ_c(ohm-cm^2)	ρ_c,200°C	ρ_c, 400 °C	ρ_c, Room Temp.
SR004-1	4.7E-6	3.8E-6	5.3E-6	5.1E-6
SRO05-2	3.4E-5	2.5E-5	1.7E-5	1.6E-5
SR008-1	9.6E-6	8.8E-6	2.9E-5	2.8E-5
SR008-2	5.9E-6	5.3E-6	9.OE-6	7.7E-6
SR010-1	8.8E-6	7.7E-6	*	*
SROIO-2	1.3E-5	1.IE-5	3.6E-5	3.2E-5

* TLM data line fit not good enough for meaningful extraction of ρ_c due to unequal contact resistance of TLM contact electrodes

Table 2 Effect of Aging on Specific Contact Resistivity of Au-Ge-Ni Ohmic Contacts to n-GaAs

Sample	ρ_c(ohm-cm^2)	ρ_c(ohm-cm^2)/aged (months)	Heat-treatment (sec., °C)
050-2A	7.8E-6	6.8E-6 / 31	30, 353
050-2B	7.2E-6	1.6E-5 / 31	30, 353
053-2	1.IE-4	1.9E-4 / 31	240,600
056-4	1.BE-6	8.5E-7 / 30	60, 371
057-1	3.1E-5	4.7E-5 / 26	60, 490
057-2	1.1E-5	1.IE-5 / 26	60, 490
058-5	9.2E-6	6.2E-6 / 23	600,450
128-4A	4.OE-6	3.9E-6 / 12	20, 490
SPO14-F	1.5E-6	9.7E-6 / 12	35, 385
2SP025-1	7.2E-6	8.5E-6 / 10	20, 370
2SP026-1	1.OE-5	* / 10	20, 503
2SP027-1	3.4E-6	* / 9	15, 400
2SP031-A	1.OE-5	1.OE-5 / 9	15, 400
2SP033-A	5.OE-6	3.4E-5 / 9	15, 400

* TLM data line fit not good enough for meaningful extraction of ρ_c due to unequal contact resistance of TLM contact electrodes

Table 3 Effect of 32 Months of Aging on Specific Contact Resistivity of Au Ohmic Contacts to n-GaAs

Sample	ρ_c(ohm-cm^2)	ρ_c(ohm-cm^2)	Heat-treatment (min., °C)
058-1	1.6E-5	1.5E-5	2.0, 371
058-2	1.9E-5	2.IE-5	4.0, 409
059-1	7.7E-5	8.6E-5	1.0, 350
059-2L	7.9E-5	7.7E-5	1.0, 350
059-2R	5.3E-5	5.3E-5	1.0, 350
059-3L	6.OE-5	6.2E-5	1.0, 350
059-3R	7.1E-5	7.4E-5	1.0, 350

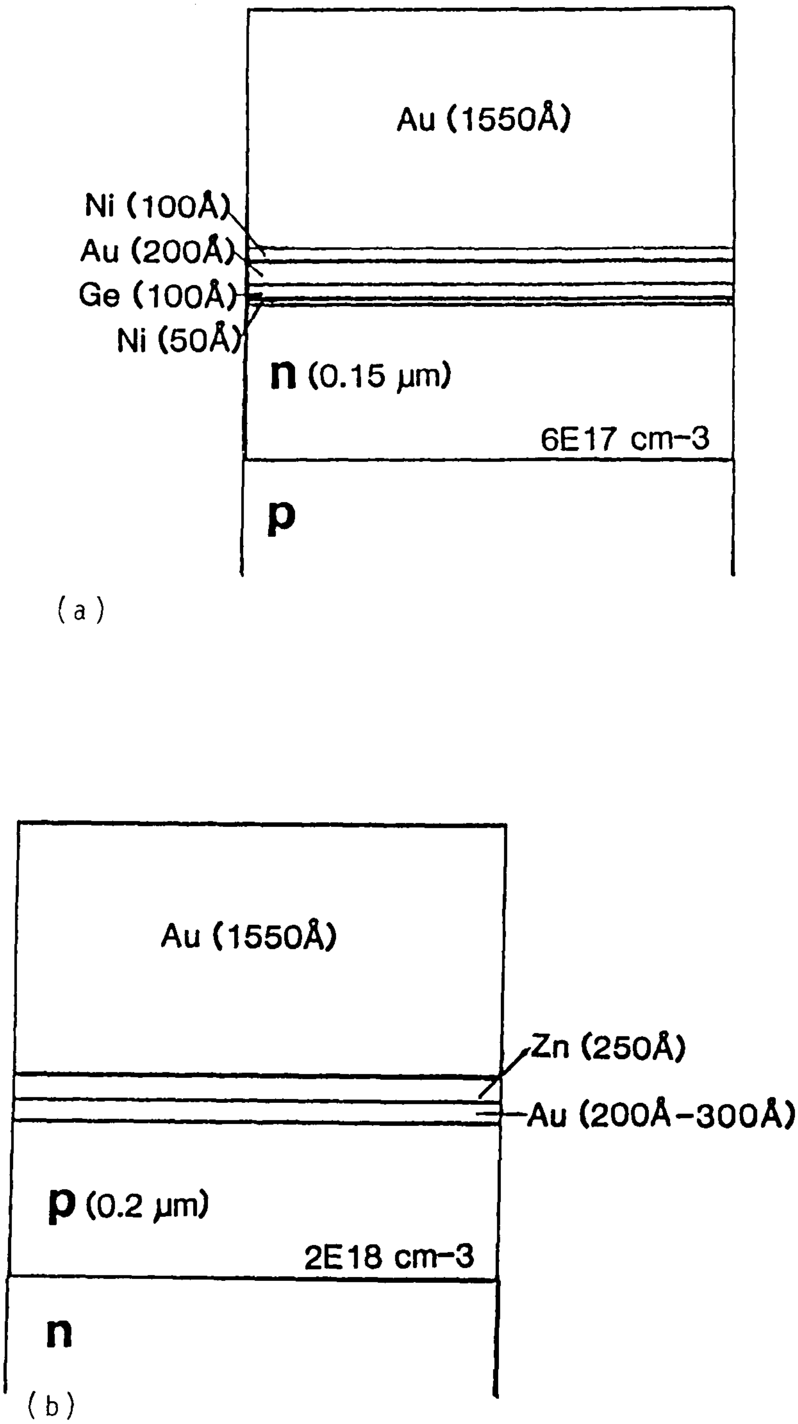

Figure 1.
(a) Au-Ge-Ni contact structure,
(b) Au-Zn contact structure.

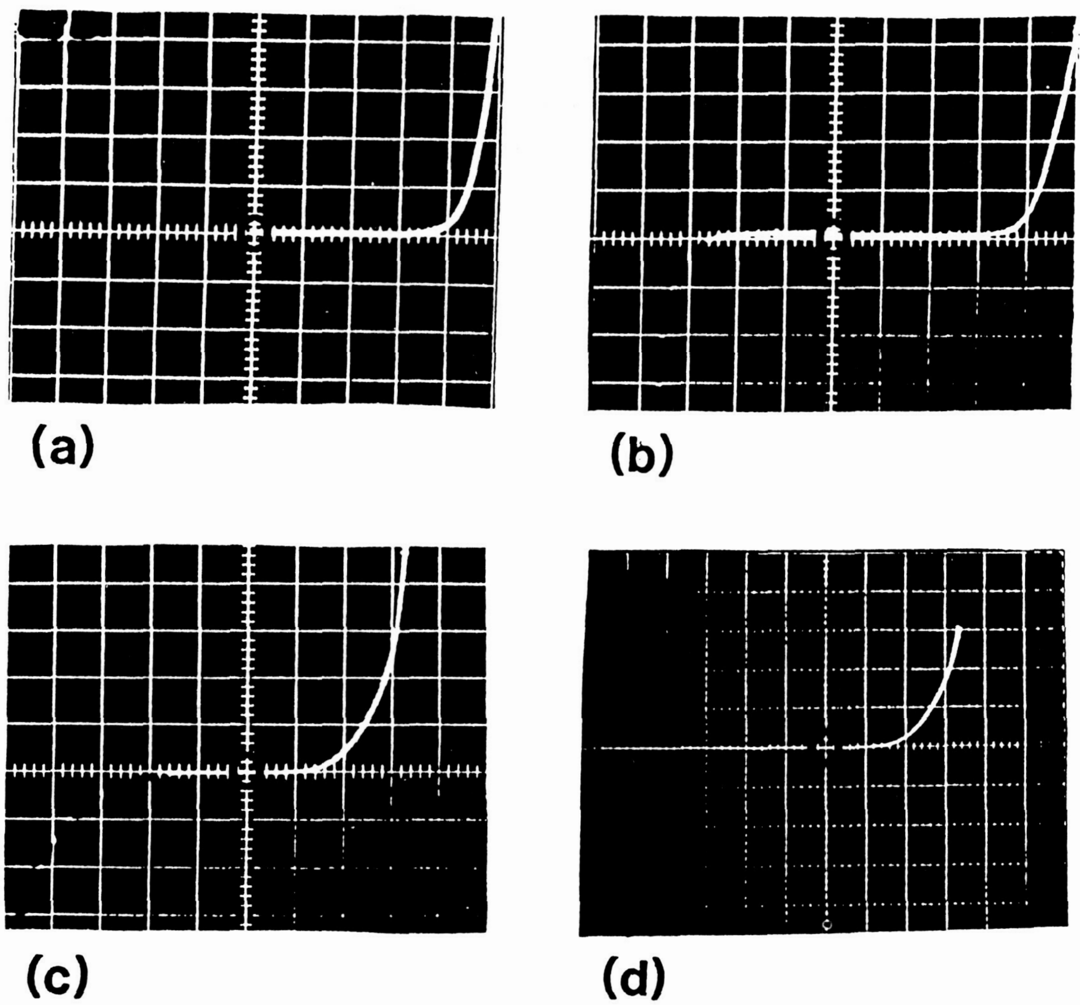

Figure 2. p/n diode I-V curves (0.2V, 1mA/div.) with Au-Zn contacts aged for,
(a) 432 hours at 200 °C,
(b) 3 months at 200°C,
(c) 64 hours at 400 °C,
(d) 13 months at room temperature.

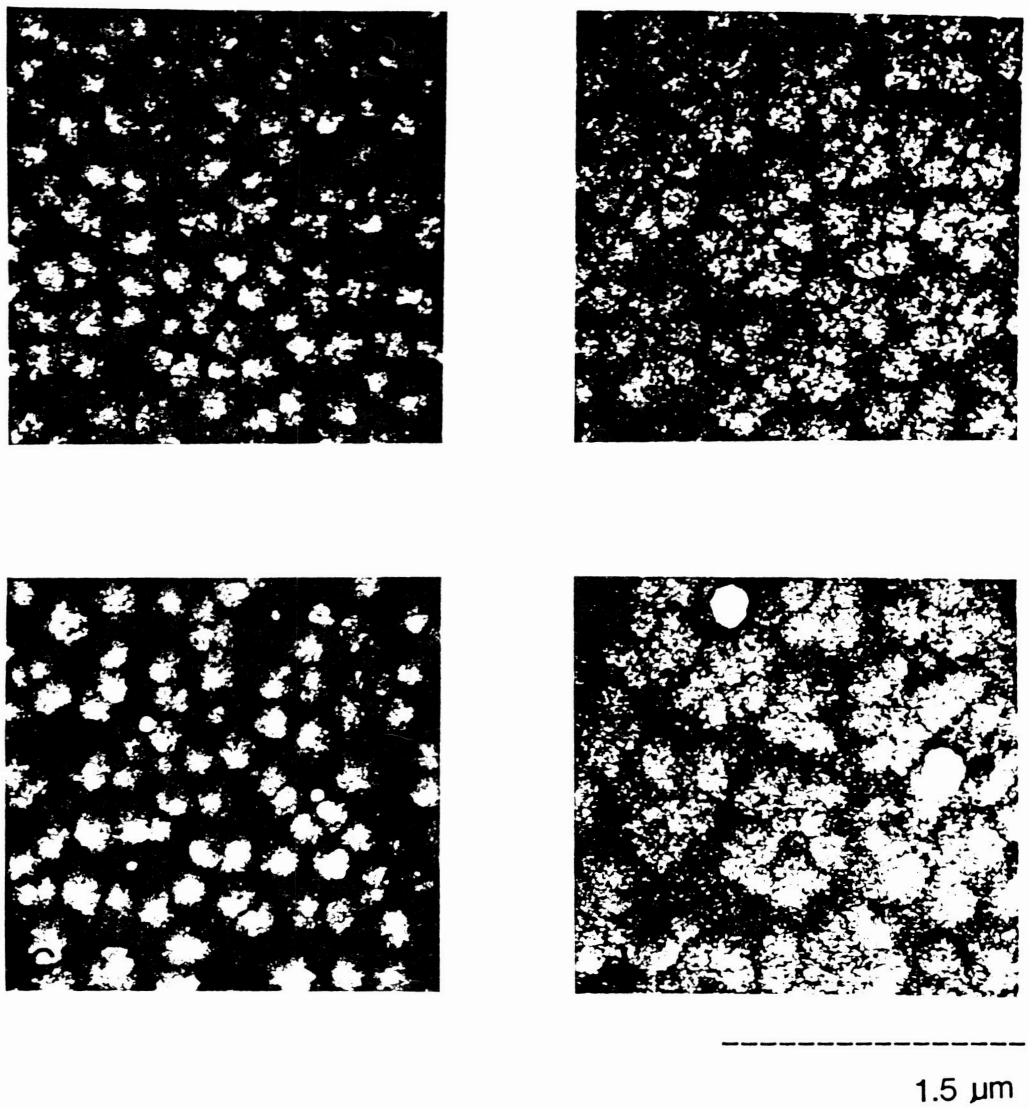

Figure 3. Surface morphology of Au-Zn contacts,
(a) as-deposited new,
(b) as-deposited aged for 13 months,
(c) heat-treated at 450 °C new,
(d) heat-treated at 450 °C aged for 13 months.

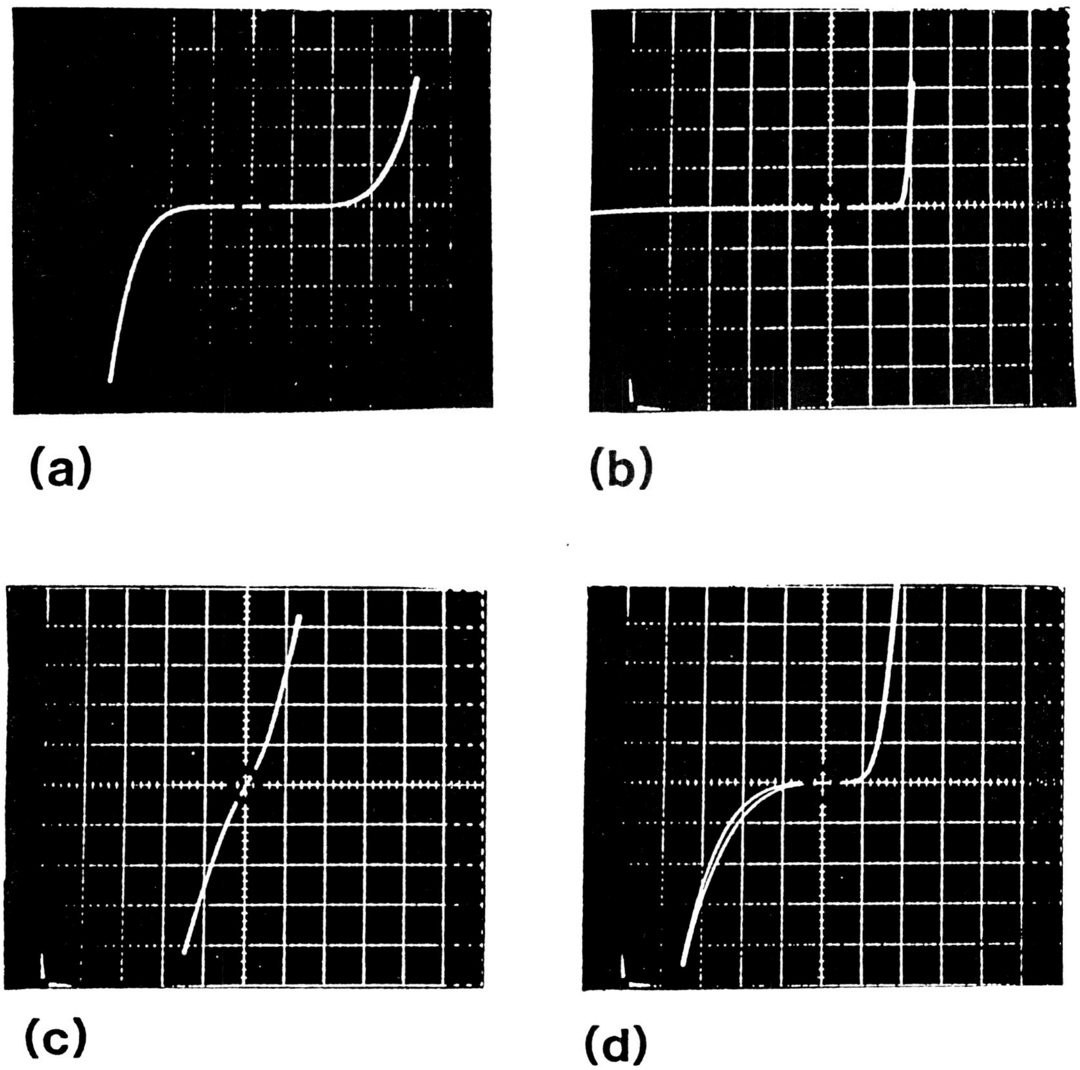

Figure 4. n/p diode I-V curves with as-deposited Au-Ge-Ni contacts aged for 14 months,

(a) new contacts are rectifying (1.0V, 1mA/div.),
(b) non-rectifying and non-shunting (0.5V, 1mA/div.),
(c) severely shorted (0.5V, 1mA/div.),
(d) most typical with as-deposited aged contacts 0.5V, 1mA/div.).

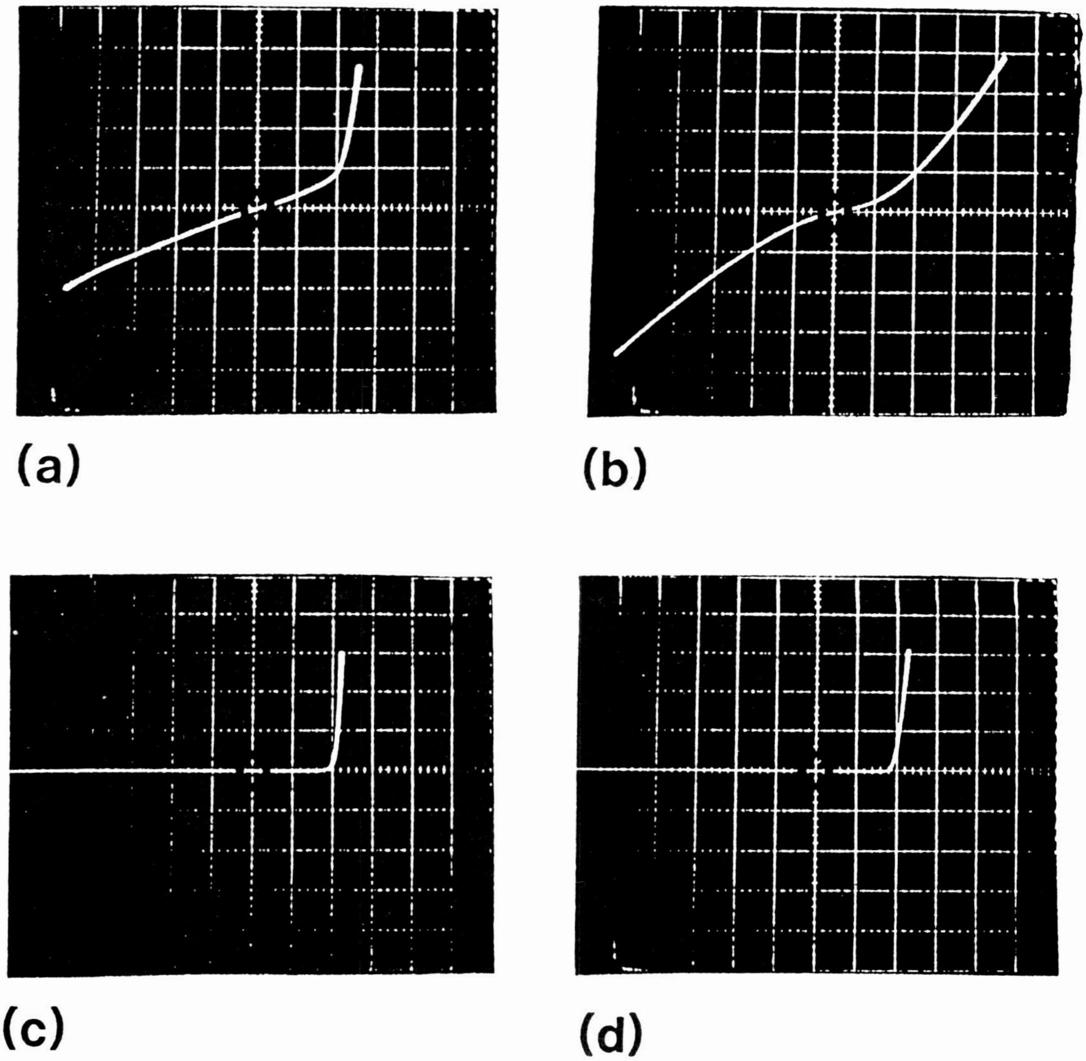

Figure 5. n/p diode I-V curves with heat-treated Au-Ge-Ni contacts (0.5V, 1mA/div.),
(a) 360 °C for 20 sec. new,
(b) 395 °C for 20 sec. new,
(c) 396 °C for 20 sec. with TiN aged for 8 months,
(d) 400 °C for 20 sec. with Ta_2O_5 encapsulation aged for 21 months.

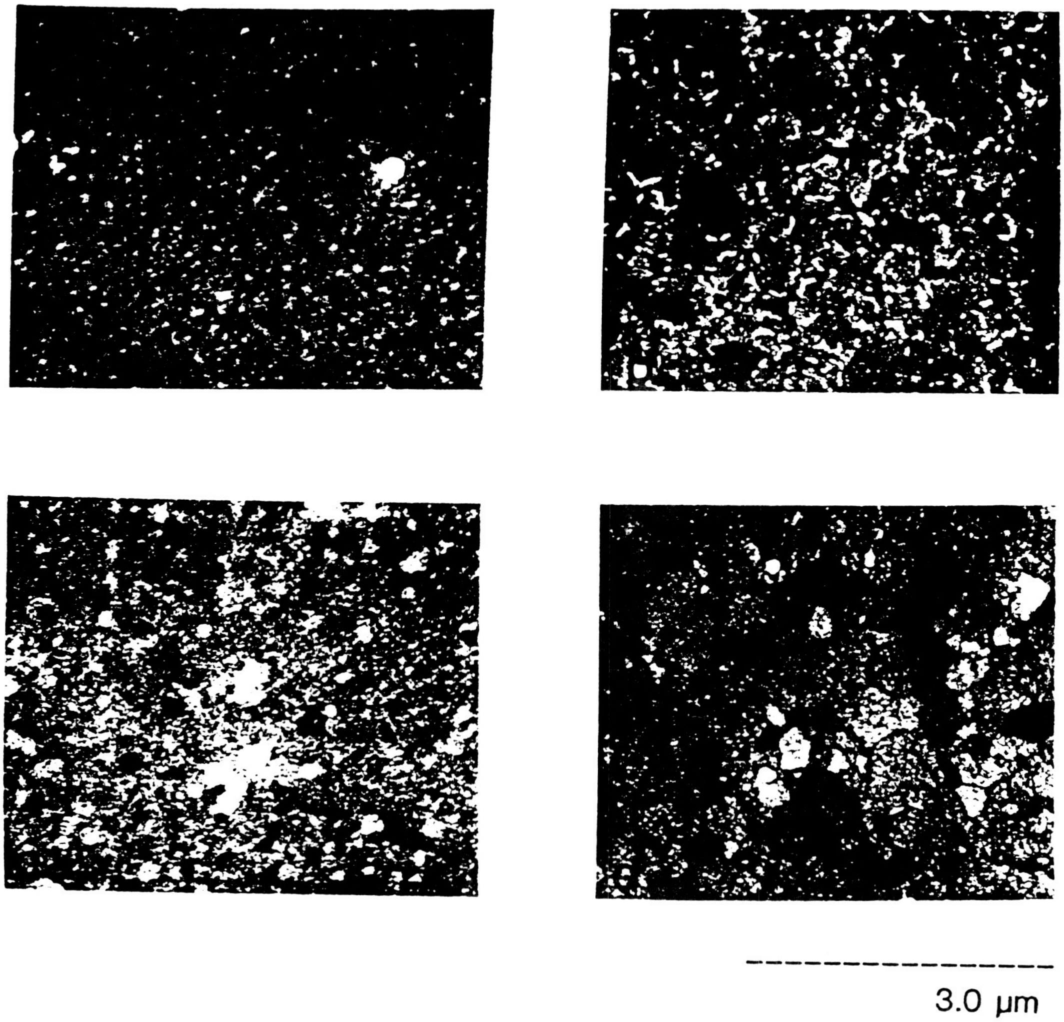

Figure 6. Surface morphology of Au-Ge-Ni contacts,
(a) as-deposited new,
(b) as-deposited aged for 11 months,
(c) heat-treated at 400 °C new,
(d) heat-treated at 400 °C aged for 9 months.