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N91-19203

Semiconductor Structural Damage Attendant to Contact Formation in III-V Solar Cells

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In order to keep the resistive losses in solar cells to a minimum, it is often necessary for the ohmic contacts to be heat treated to lower the metal- semiconductor contact resistivity to acceptable values. Sintering of the contacts, however can result in extensive mechanical damage of the semiconductor surface under the metallization. An investigation of the detailed mechanisms involved in the process of contact formation during heat treatment may enable us to control the structural damage incurred by the semiconductor surface to acceptable levels, while achieving the desired values of contact resistivity for the ohmic contacts. In this work, we have determined the reaction kinetics of sintered gold contacts to InP. We have found that the Au-InP interaction involves three consecutive stages marked by distinct color changes observed on the surface of the Au, and that each stage is governed by a different mechanism. A detailed description of these mechanisms and options to control them are presented.

Introduction

Gold and gold-based contact systems are extensively used as metallization materials for III-V solar cells. In some cases, acceptably low metal-semiconductor contact resistivity is achieved to highly doped emitters by as-deposited contacts. For instance, as-deposited Au contacts on InP and Au-Zn contacts on GaAs heavily doped substrates can produce specific contact resistivity (R_c) values in the 10^{-4} ohm-cm^2 range [refs. 1-2]. Although this contact resistivity range may be adequate for one sun operation of solar cells, it falls short of the 10^{-6} ohm-cm^2 values often required for concentrator applications. There are also concerns about the stability of these contacts with aging, for no stable compounds are present at the metal-semiconductor interface. The most prominent advantage of the as-deposited contacts is that virtually no structural damage is suffered by the semiconductor under the metallization.

On the other hand, much lower R_c values are readily obtained by heat treating Au-based contacts to variously doped III-V semiconductors. R_c values in the 10^{-6} and 10^{-7} ohm-cm^2 range have been measured by Au-based systems to InP and GaAs substrates [refs. 2-6]. Heat treated contacts also tend to be more stable with aging [ref. 6]. The greatest disadvantage of the heat treating process is the appearance of severe pitting at the metal-semiconductor interface during contact formation. The electrical and mechanical changes which occur during the heat treatment process

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however, may not necessarily be related. For example, encapsulation of Au-Ge-Ni and Au-Zn contacts with SiO_2 prior to heat treatment can not only slightly reduce the metal-GaAs interaction rate but at the same time produce lower R_c values [refs. 7-9].

The purpose of our research program is to understand contact formation in III-V semiconductor materials, and use that knowledge, to devise a contact system and/or a processing scheme by which desired R_c values are achieved with minimal structural damage to the semiconductor. In this paper, our focus has been on the investigation of the mechanisms involved in contact formation in the Au-InP system.

The Kinetics of the Au-InP Interaction

The Au-InP interaction consists of three consecutive stages of reaction, each governed by a different rate limiting mechanism. The three stages are: 1. Au-to-Au(In) (saturated solid solution), 2. Au(In)-to-Au_3In, and 3. Au_3In-to-$AuIn_2$ transitions. In addition, spreading of Au contacts occurs concurrent with the third stage of the reaction. In what follows, a discussion of the mechanisms operating in each stage, as well as in the Au spreading phenomenon, and means to control them are presented.

STAGE I. At this early stage of the reaction In is dissolved into the Au lattice via a dissociative diffusion mechanism until the saturation limit of 10% atomic is reached. Rapid interstitial diffusion of In from the InP lattice toward the surface of the Au is controlled by the rate of vacancy generation at the free surface of the metallization. Consequently, the condition of the Au surface can dictate the reaction rate at the Au-InP interface. The reaction suppressing effect of the capping of the contacts with SiO_2 before heat treatment is due to the suppression of vacancy generation rate at that surface. Conversely, surface abrasion of the Au tends to enhance the reaction rate at the metal-semiconductor interface due to the fact that regions of lattice disorder in the metallization are a greater source of vacancies than the undisturbed regions. We have previously demonstrated the effect of surface damage and capping of the contacts on the metal-semiconductor reaction rates in both the Au-GaAs and Au-InP systems [refs. 10-11].

STAGE II. The conversion of Au(In) into Au_3In occurs via nucleation and grain growth. The reaction proceeds via an exchange or kickout mechanism by which the substitutional Au atoms are displaced by interstitial In atoms, forcing the Au atoms to become interstitial. These interstitial Au atoms, in turn diffuse to the Au-InP interface, filling the vacancies left there by the out-diffusing In atoms. There they form the compound Au_2P_3 with the unbound P. Au_2P_3 and Au_3In are formed simultaneously with the phosphide located directly underneath the Au_3In nucleation sites.

Since stage II is governed by the kickout mechanism, it was expected that capping of the contacts would have no effect on the reaction rate. To verify this, we deposited a

saturated solid solution of In in Au (10% atomic) on a number of (100) oriented p-type InP substrates doped to about 2.5×10^{16} cm^{-3} and capped half of each sample with 600 Å layer of SiO_2. Indeed after heat treating these samples at various temperatures, no difference in the reaction rates of capped vs. uncapped areas could be detected. It should be noted that much structural damage is done to the InP surface during this stage of the interaction.

Since the compound Au_3In is pink in color, its nucleation and grain growth is easily distinguished in the gold colored Au(In) matrix. Upon isothermal annealing of the Au contacts, after an initial incubation period, the growth (i.e., the area) of the Au_3In grains increases linearly with time. Repeating such isothermal annealing experiments at different temperatures and measuring the time required (in the linear region) for the metallization to convert to 100% Au_3In, allows us to measure the activation energy (E_a) for stage II. The results, shown in figure 1, indicate an activation energy of about 2.6 eV.

It should be mentioned that because the Au_3In grain growth is linear with time all the way to completion, and not proportional to the circumference of the grains as they grow in size, the rate limiting mechanism with an E_a of 2.6 eV is not the activation energy for the localized kickout mechanism. In fact, the rate limiting mechanism in this case is the rate of In release from the InP substrate, which also would have to have a slower rate than the kickout mechanism.

Although for the data points of figure 1, we had used Au(In) contacts, repeating the same experiment for samples with pure Au as the contacting metal, we essentially obtained the same activation energy (2.8 eV) for stage II. Also since the capping of the pure Au contacts suppresses the reaction rate for stage I, and therefore delays the emergence of stage II, repeating the same isothermal annealing experiments with half-capped Au samples enabled us to extract the activation energy for stage I. Using the delay times caused by capping of the contacts in the growth of Au_3In grains and plotting them as a function of temperature, we obtained the data points in figure 2. Although there is much scatter in the data points, the least square fit to the points renders an E_a value of about 1.1 eV. This is slightly lower than the gold self-diffusion activation energy of 1.8 eV expected for the reaction rate for Stage I. But our calculations based on the In concentration profiles at and near the Au surface obtained by Auger electron Spectroscopy (AES) show that surface effects can lower this activation energy to the vicinity of 1 eV. A thorough discussion of the kinetics of stage I and stage II is presented in an upcoming publication [ref. 12].

STAGE III. Much like the reaction in stage II, the conversion of Au_3In to $AuIn_2$ occurs via nucleation and grain growth. We believe that similar to stage II, the reaction rate in this stage is also governed by the kickout mechanism, given the localized nature of the interaction. One marked difference here is that the compound Au_2P_3 which was created at the Au-InP interface in stage II, does not form in stage III. In other words, no Au_2P_3 was observed to grow under the $AuIn_2$ nucleation sites when

a layer of Au-In alloy with slightly lower In concentration than the Au_3In compound was deposited on InP and heat treated to stage III nucleation. However, if the Au_2P_3 compound is already present at the metal-InP interface (leftover from stage II), it is observed to grow further under the $AuIn_2$ nucleation sites at temperatures below approximately 431°C . At temperatures above 431°C, the phosphide layer seems to remain unchanged from its original form when created during stage II.

As with the marked color change from gold to pink occurring during stage II, the $AuIn_2$ grains are silver in color and are easily distinguished from the pink Au_3In background matrix. Using the same procedure described for measuring the activation energy for stage II, we find that there are two distinct activation energies present for stage III with their intersection point at about 431°C.

As shown in figure 3, for temperatures above 431°C , E_a has a value of 12.1 eV, and for temperatures below 431°C, E_a increases to 28.5 eV. The measurement of such abnormally high activation energies is perhaps the result of a multi-step reaction process, with each step having a much lower activation energy. Similarly a high activation energy of 8.6 ± 3 eV has been reported by Elias, et al [ref. 13] while investigating a phenomenon known as gold spreading in the Au-InP system. The results of our findings on this spreading phenomenon and its relationship with stage III are presented in the following section.

Lateral Spreading of Au Contacts

The lateral spreading of Au dots beyond the metallization boundaries on the surface of InP upon heat treatment was first observed by Keramidas, et al [ref. 14]. Silver colored spread regions were observed to grow faster in certain crystallographic directions. Later, Elias, et al [ref. 13], reported on the characteristics of the spreading phenomenon and determined the activation energy of the process. In our investigations, we have observed that the lateral spreading of the contacts occurs concurrent with stage III of the Au-InP interaction. In other words, the region on the Au dot adjacent to the spread area has to be transformed to $AuIn_2$ before the spreading can start.

Lateral spreading of a Au dot (2000 Å) heat treated at 434°C for 2.5 hours is shown in figure 4a. An analysis of the rate of the growth front indicates that the rapid rate of spreading is about four orders of magnitude faster than what would be expected for a common vacancy dependent diffusion process. The only diffusion mechanism capable of reconciling such a high growth rate is the interstitial transport of Au to, and In from, the spread front. EDAX analysis has revealed the presence of significant amounts of both In and Au in the spread region.

The activation energy that Elias, et al [ref. 13], measured for the spreading of the Au contacts (8.6 ± 3 eV) is close to the E_a of 12.1 eV that we measured for stage

III for temperatures greater than 431°C . This is an indication that perhaps similar mechanisms operate in both processes.

The Au dot of figure 4a is shown in figure 4b after removing the metallization by a thiourea based chemical etchant. As shown in the figure, the gold phosphide (Au_2P_3) is present only in the dot region and not in the spread area. Also apparent from the enlarged view of figure 4b in figure 4c is the large amount of InP which has disappeared from the growth area. This volume loss along with the absence of the phosphide layer in the spread area suggest that the P atoms made available after In interstitial transport toward the Au dot, had to volitalize before having an opportunity to form the compound Au_2P_3 with the interstitial Au atoms.

From the above argument, it becomes clear that in order to prevent the spreading process, the loss of P should be inhibited. To test this, we capped a few Au dots and their adjacent InP surface with a 600Å layer of SiO_2 and heat treated them along with a few uncapped samples. Indeed, capping prevented the spreading of the contacts. It was observed that the spread front is able to move under the cap for a distance of about one micron before stopping. This one micron represents the P escape length. The effect of capping on suppressing the spreading process is shown in figure 5.

Another method to prevent spreading is to deposit, instead of pure Au, Au-In alloys having In concentrations in excess of 25% (i.e., Au_3In) on InP. Such alloys will not only inhibit the spreading process, but they will also suppress the interaction rate of the metal-InP to a large degree. As mentioned earlier, no Au_2P_3 compound is formed during the interaction of these alloys with InP, for the formation of the phosphide is strictly a stage II phenomenon. The presence of Au_2P_3 at the Au-InP interface slows down the reaction to such an extent that it is easier for the reaction to proceed to a phosphide free location (i.e., outside of the Au dot on the InP surface) where the reaction rate is much faster. But in the absence of the phosphide layer the reaction can continue underneath the Au dot, and there is no need for the reaction to move outside of the metallization region.

Figures 6a and 6b are comparisons of the structural damage incurred by the semiconductor by heat treating a pure Au and a Au-In alloy with nearly 25% In concentration samples on InP at 434°C for 2.5 hours with all the reaction products removed. As shown in these figures, the Au-In alloy sample has reduced the pitting of the InP surface to a great extent compared to the pure Au sample.

Summary and Conclusions

The purpose of our research program has been to identify the mechanisms involved in the process of contact formation in metal-semiconductor interactions. Fundamental understanding of these mechanisms should enable us to manipulate them in such a way as to satisfy our requirements of a nearly ideal metal-semiconductor contact system (i.e., low R_c values plus minimum structural damage to the semiconductor).

In this paper, we have presented the results of an investigation of the mechanisms involved in the contact formation process in the Au-InP system.

We have shown that the Au-InP interaction entails three consecutive stages of reactions. Stage I of this interaction operates via a dissociative diffusion mechanism, and the vacancy generation rate on the surface of the metallization is rate limiting with an activation energy of about 1 eV. Capping of the metal surface or deposition of a Au(In) layer instead of pure Au suppresses the reaction rate at this stage.

Stage II operates via an exchange or kickout mechanism. The reaction is localized, and it is controlled by the rate of In release from the InP substrate with an activation energy of about 2.6 eV. Extensive pitting of the semiconductor surface is observed after this stage goes to completion. Deposition of the alloy Au_3In in place of pure Au inhibits the reaction at this stage.

Stage III reaction is also localized in nature and is likely to operate via the kickout mechanism. There are two activation energies observed for this stage: 12.1 eV for temperatures greater than 431°C, and 28.5 eV for temperatures below 431°C. It is likely that such high activation energy values are the result of many steps involved for the reaction to go to completion, with each step having much lower activation energy. The resultant activation energy would then be a complicated sum of these smaller activation energies.

Also concurrent with stage III, a phenomenon known as spreading of Au is observed. Fast interstitial movements of Au and In control the rate of reaction for this process. We have shown that capping of the InP surface near the spread region inhibits the process by preventing the escape of P from the InP surface. In addition, in contrast to pure Au, it was demonstrated that Au-In alloys (In concentration $\geq 25\%$) show no sign of spreading.

We have shown that the mechanical damage to the semiconductor incurred by heat treatment can be reduced considerably through deposition of Au-In alloys ($\geq 25\%$ In) on InP in place of pure Au. We have also shown that capping of the contacts suppresses the reaction rate. Our future thrust is to compare the electrical characteristics of Au-In alloys with that of pure Au, and also to correlate the electrical behavior of heat treated contacts (unary, binary, and ternary systems) with their metallurgical behavior.

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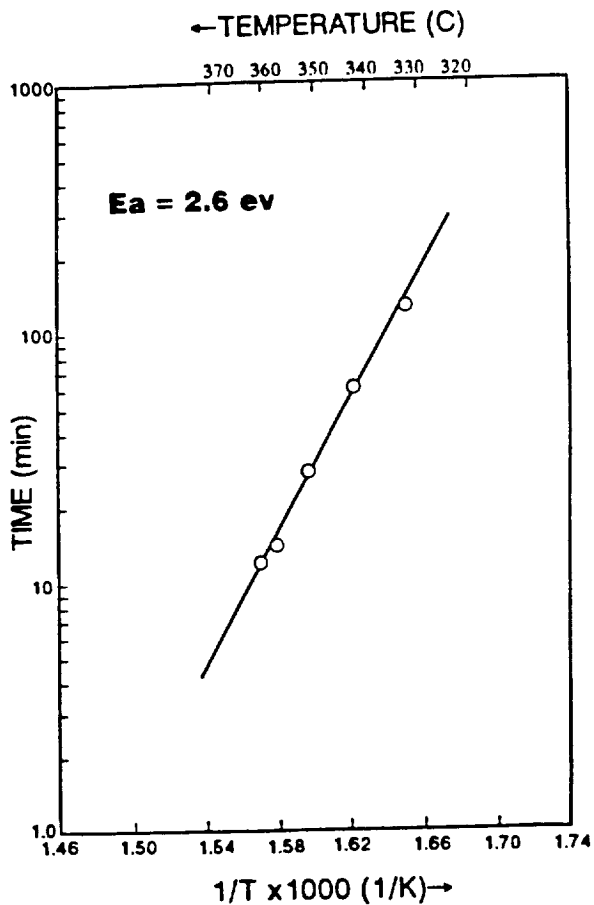[14.] V. G. Keramidas, H. Temkin, S. Mahajan, Inst. Phys. Conf. Ser. No. 56: Chapter 5, 293.
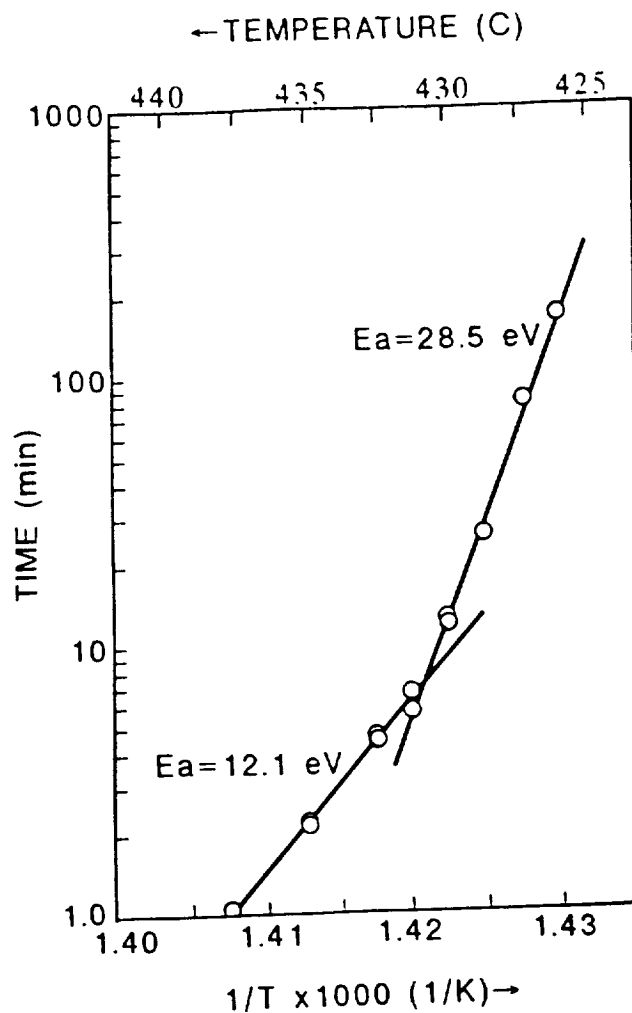
Fig. 1 Activation energy plot for stage II.
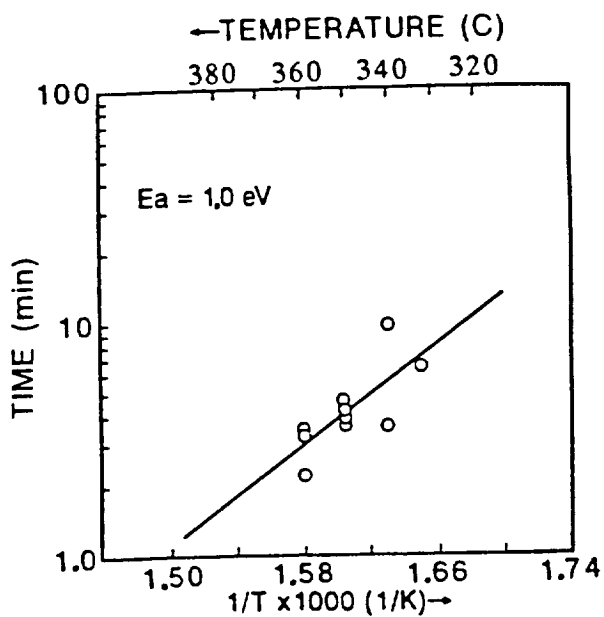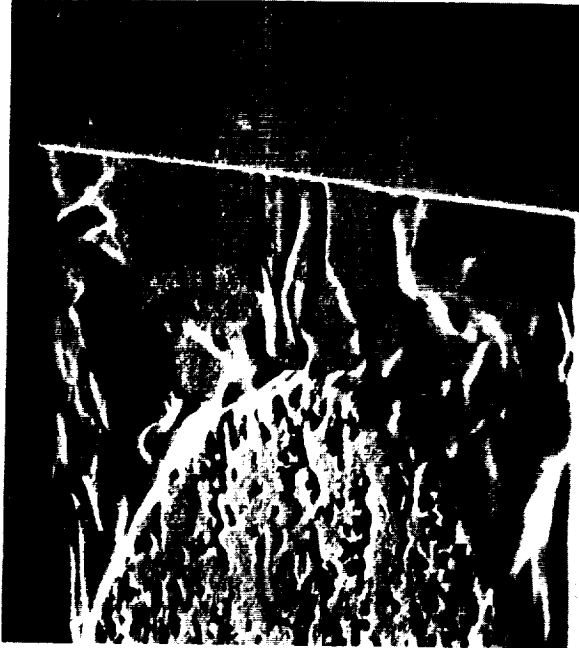

Fig. 3 Activation energy plot for stage III.

Fig. 2 Activation energy plot for stage I.
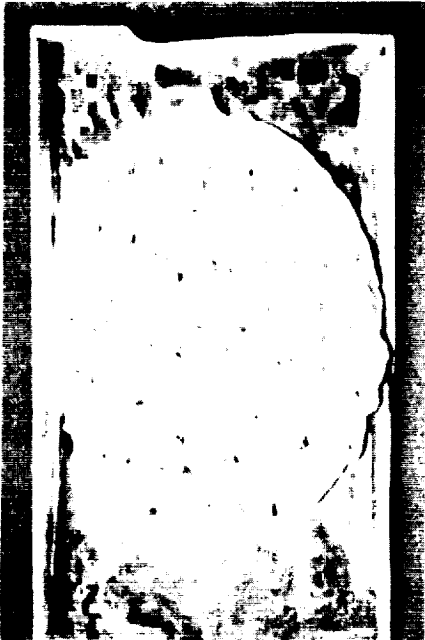
Fig. 4 Spreading of Au on InP heat treated at 434 °C for 2.5 hrs. a) Spreading of a Au dot, b) with the Au removed, and c) enlarged view of b.
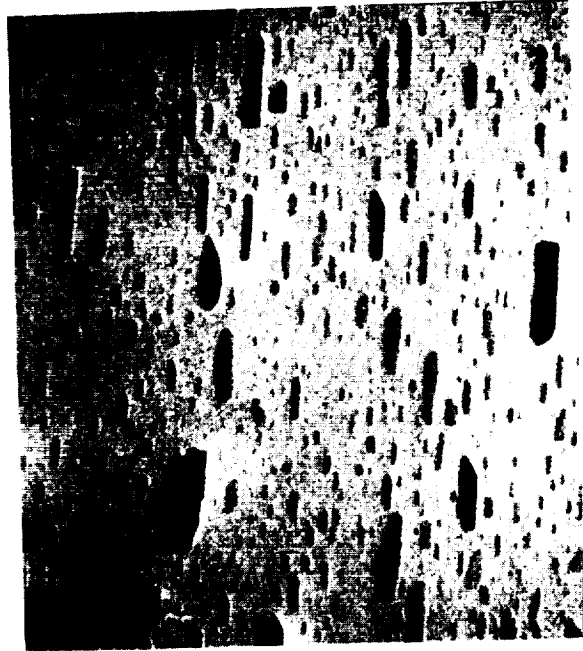
←— 3.8 μm —→

a

b

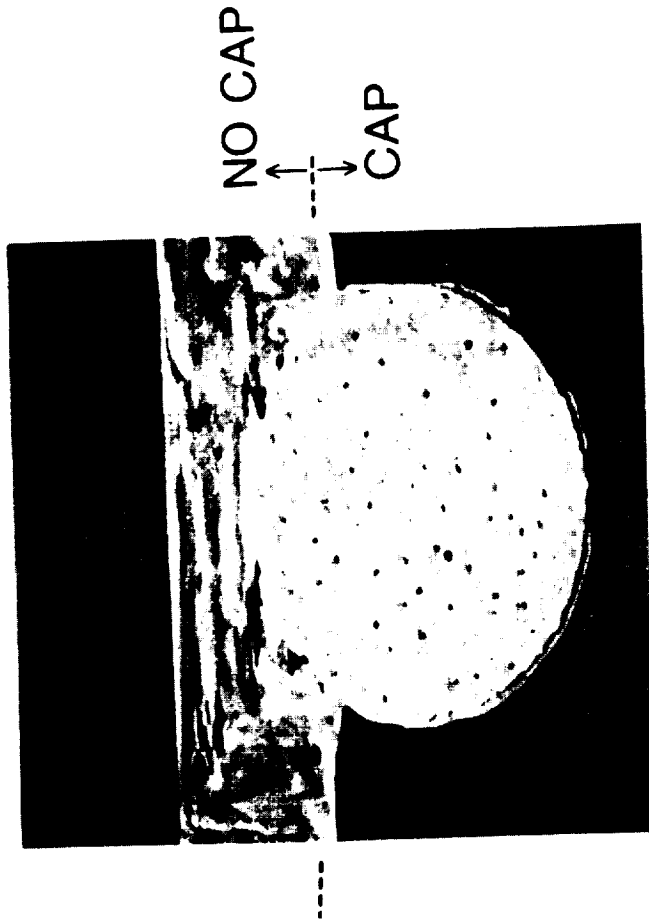←— 25 μm —→

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Fig. 5   The effect of SiO₂ capping on the spreading of Au heat-treated at 434 °C for 2.5 hrs.

Fig. 6   Pitting on the InP surface under the metallization heat-treated at 434 °C for 2.5 hrs. a) Au removed, b) Au₃In removed.

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