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An Analysis of the Contact Sintering Process in III–V Solar Cells

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ABSTRACT

The purpose of this work is to investigate the possibility of eliminating the gross mechanical changes that take place during sintering while retaining the processes that reduce contact resistivity. Before considering the electrical aspects, however, it is necessary to understand the relevant metallurgy. As the sintering process proceeds in the InP-Au system, dramatic color changes occur that enable a precise measurement of the kinetics of each step. A detailed insight into the processes that control each stage in the InP-Au interaction has resulted. We show that contact sintering in the InP-Au system consists of three consecutive stages, each of which is controlled by a separate mechanism.

INTRODUCTION

While unsintered contacts can be effectively employed in III-V solar cells intended for one sun use, the high current densities achieved in concentrator cells make sintering mandatory if unacceptably high internal voltage drops are to be avoided. The sintering process, however, has two effects. It causes both electrical and mechanical changes to occur in the cell, changes that are not necessarily related. The intended improvement in electrical characteristics is often accompanied by unwanted and sometimes catastrophic mechanical damage to the cell. The pitting that occurs in the semiconductor as a result of the sintering process is especially destructive to shallow junction devices.

Contact formation to III-V materials is, at present, a difficult and inexact art. This state of affairs is due, in great part, to the fact that so little is known about the mechanisms involved in the relevant metal-semiconductor interactions. In an attempt to remedy this situation a program was initiated at this laboratory to study the interaction of various III-V semiconductors with their contact metallization. The purpose was to see if it is possible to eliminate the gross

mechanical changes that take place during sintering while retaining the processes that lower the contact resistivity. To do this we must first understand the processes that control the mechanical or metallurgical interactions. With this knowledge in hand we can then explore the electrical aspects of the problem.

We chose to start by studying the interaction of gold-based alloys with GaAs, InP, GaSb, and GaP. Preliminary investigations indicate that these materials are similar in their reaction with gold-based contacts. One of these materials, however, stands out from the rest with respect to the insight it provides into the details of the interaction of the III-V semiconductors with Au-based contacts. We have found that the contact sintering process in the InP-Au system is accompanied by dramatic color changes in the metallization that enable a precise measurement of the kinetics of each step in the process. We have thus been able to obtain a detailed insight into the processes that control each stage in the InP-Au interaction. We have found that the sintering process on the InP-Au system consists of three consecutive stages, each controlled by a separate mechanism. In all of the stages there is vigorous dissolution of InP into the metallization.

In a recent publication these color changes have been used to identify the initial two stages in the Au-InP interaction.[1] As the reaction proceeds, both In and P leave the semiconductor and enter the metallization. The first stage, which continues until the In content in the Au lattice reaches the solid solubility limit, has been shown to be controlled by the vacancy generation rate at the free surface of the metallization.[1] During this stage the P atoms either take non-lattice sites in the metal or they leave the system unreacted. Stage I proceeds very rapidly, dissolution being quite detectable even at room temperature.[1,2]

If stage I is allowed to go to completion, a second InP dissolution mechanism becomes active.[1] This stage proceeds rapidly in the temperature range used for contact sintering. The rate

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limiting step in this stage has been determined to be the release of In from the InP and its insertion interstitially into the Au lattice.[1] In entry continues until the metallization is converted from the saturated Au(In) solid solution to the pink colored compound Au_3In. Whereas in stage I the P atoms released with the In leave the system without reacting, in stage II they react to form the compound Au_2P_3 at the metal-semiconductor interface.

The purpose of this paper is to describe the results of an investigation into the processes occurring as the sintering process proceeds further. At the completion of stage II, additional dissolution of In into the metallization causes the nucleation and growth of a silver colored alloy. At the same time a rapid lateral spreading of the metallization (observable in small area contacts) sets in.[3,4] In what follows we will describe these two phenomena and give evidence that they are manifestations of the same basic mechanism.

THE PINK TO SILVER TRANSITION - STAGE III

The end of stage II, i.e. the formation of the pink compound Au_3In, is followed, upon further heat treatment, by the nucleation and growth of a silver colored compound in the contact metallization. In order to study the events occurring during this third stage without interference from stages I and II, we deposited Au_3In on a number of InP substrates, and then observed the behavior of this system at elevated temperatures. We found that while stage II had been observed to proceed to completion in tens of minutes at temperatures in the 340 to 360 C range, similar rates for the third stage required temperatures in the vicinity of 450 C. It was observed that conversion from pink to silver starts as a continuous band around the periphery of the sample which then proceeds to grow radially inward toward the center of the sample.

The Stage III Alloy. Since there are a number of stable Au-In compounds with higher In content than Au_3In[5], our first task was to identify the silver colored product of stage III. To do this we employed an XPS system that we had calibrated for use with the Au-In binary alloys. The results of our investigation indicate that the In content of the stage III alloy is close to 30 a%. The end point of stage III was therefore identified as Au_9In_4.[5] These results are in agreement with those of Vandenberg, et al., who also observed Au_9In_4 to form in this temperature range.[6]

The Role of Phosphorus. We have found that there is a major difference in the behavior of the phosphorus atoms released into the metallization during stage III as compared to stage II. In Au-contacted and annealed samples where stage II has gone to completion, one observes the presence of the compound Au_2P_3 at the InP-metal interface when the Au-In alloys are chemically removed.[7] However, after the above experiments where stage II is bypassed by depositing and annealing Au_3In, no sign of Au_2P_3 is
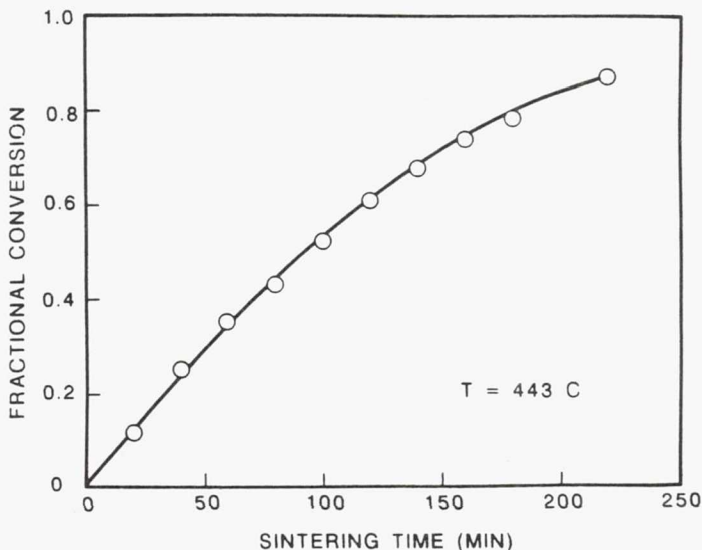

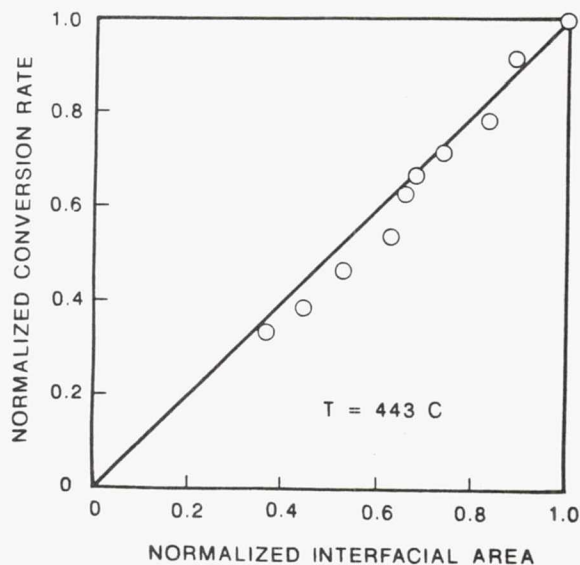Figure 1. Fractional Au_3In-to-Au_9In_4 conversion with sintering time.

Figure 2. The Au_3In-to-Au_9In_4 conversion rate versus interfacial area.

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found. Thus in stage III as in stage I[1] the P atoms released into the contact metallization either take non-lattice sites or they leave the system.

Stage III Kinetics. Our next task was to determine the activation energy for the rate controlling step in the stage III transition. Accomplishing this required the measurement of the isothermal conversion rate at various annealing temperatures. Figure 1 is a plot of the measured fractional conversion (pink to silver) as a function of sintering time at 443 C.

As can be seen, the reaction rate (slope) appears to decrease monotonically with time. This is in contrast with similar plots from stage II where the reaction rate remained constant after an initial incubation period.[1]

Upon further consideration of the data we have found that the reaction rate is proportional to the area of the interface between the pink Au_3In phase and the silver colored Au_9In_4 phase. Figure 2, for example, illustrates the proportionality between the reaction rates taken graphically from figure 1 and the measured interfacial area. It is apparent from figure 2 that the stage III reaction rate is indeed being controlled by the magnitude of the interfacial area.
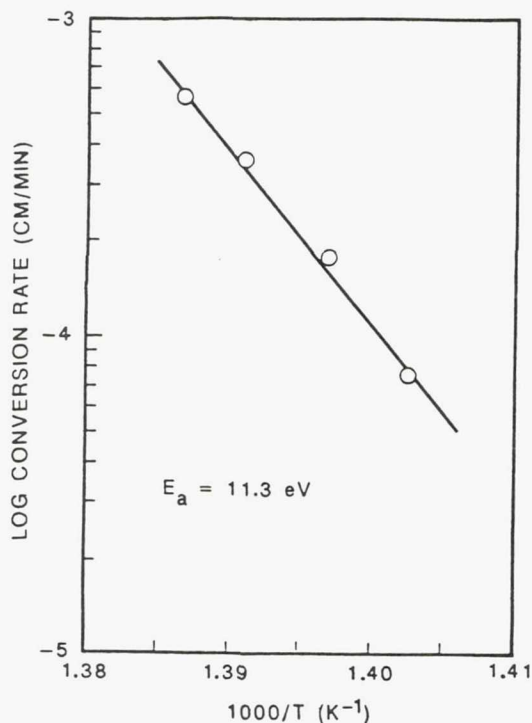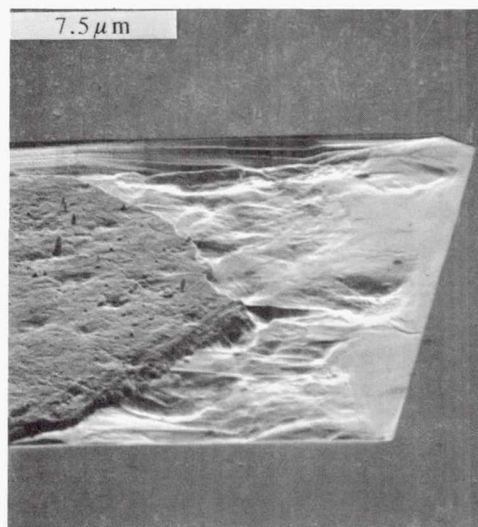
From the data used to construct

FIGURE 4. Contact spreading after 2.5 hours at 435 C.

figure 2 one can determine the volume of material converted per unit time per unit interfacial area (which is invariant with sintering time). A plot of the logarithm of this rate versus the reciprocal temperature (figure 3) yields an activation energy of 11.3 eV.

It should be noted that although an 11.3 eV activation energy is large compared to most other processes in common experience, it is within the range of values determined by Elias, et al.[4], for the closely related (as we will attempt to show) lateral spreading phenomenon.

In summary, we have found that: 1) The stage III reaction product is Au_9In_4, 2) The activation energy for the transition is about 11 eV, 3) An interfacial Au_2P_3 layer does not form, and 4) The reaction rate is proportional to the Au_3In-Au_9In_4 interfacial area.

CONTACT SPREADING

Geometrical Considerations. When small area Au-based contacts on InP are sintered at temperatures above 400 C, a rapid lateral growth along the semiconductor surface can be observed.[3,4] This is illustrated in figure 4 where we show the results of heating a 2000 A thick, 30 micrometer diameter circular gold pad deposited on a polished, (100) oriented InP surface for 2.5 hours at 435 C. As can be seen, the metal-semiconductor contact area has been increased by more than a factor of two. It can also be seen that a significant amount of InP surrounding the circular

Figure 3. The effect of temperature on the Au_3In-to-Au_9In_4 conversion rate per unit interfacial area.

pad has been replaced by the silver-colored metallization. The metallization, which has been identified as Au_9In_4 by Keramidas, et al.[3], can be seen to be more or less flush with the unreacted InP along the reaction front. Closer to the original disc, however, the surface of the metallization drops considerably below the surrounding InP. Since the disc itself is not observed to increase in size, the drop in the level of the metal indicates that spreading is accompanied by a significant mass loss.

The amount of InP dissolved in the reaction can be determined by chemically removing the metallization in the spread regions. The resulting topography (for an identically processed sample) is shown in figure 5. What we find when we remove the metallization is that the InP has been eroded to an undulating, but on the average constant, depth. The metallization in the spread region is therefore much thicker near the reaction front than it is closer to the disc. Most importantly, the spread regions were found to contain no trace of an interfacial Au_2P_3 layer, even though it was found to form under the original Au disc.

Growth Dynamics. As we followed the progress of the spreading process we noted that the spreading regions were always silver in color, and that when spreading starts at a given point on the periphery of a disc, the adjacent regions of the disc are also silver in color. As spreading proceeds, the entire disc is seen to change (from pink) to silver.

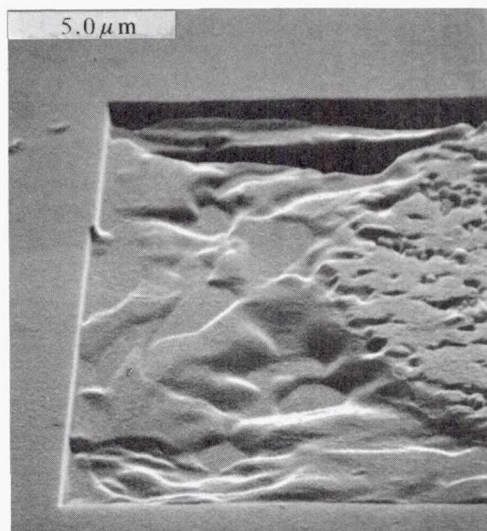It is evident that during the

FIGURE 5. InP topography after removal of metallization from spread region.

spreading process Au is being transported from the disc to the reaction front in the spread region. If the only mass flow during spreading were the diffusion of Au from the disc to the reaction front, however, then at the front

$$9Au + 4InP \rightarrow Au_9In_4 + 4P.$$

This reaction would result in a 28% increase in the volume of the spread regions even if the P atoms dissipated. Since we actually see a substantial decrease in the volume of the metal in the spread regions, we must conclude that In is being transported from the reaction front to the disc.

We can get a rough estimate of the speed of this transport by considering the magnitude of the diffusion coefficient determined by Elias, et al.[4], from spreading rate measurements. The values they found are not in conflict with those expected in an intermetallic alloy with a solidus temperature T_m in the 460 C range where, according to the empirical rule[8],

$$D = 0.3 \exp[-18T_m/T]. \qquad (3)$$

However, the 8.6 ± 3 eV activation energy they determined is much higher than would be expected for a normal diffusion process (i.e., $Q = 18kT_m$[8]). It appears, therefore, that a process other than diffusion is limiting the rate of spreading, the actual diffusion of Au and In during spreading being faster than Elias' measurements indicate.

Summarizing, the major characteristics of the spreading process appear to be: 1) The spread regions are composed of the compound Au_9In_4[3], 2) The activation energy lies between 5.6 and 11.6 eV[4], 3) No interfacial Au_2P_3 is observed in the spread regions, 4) Transport of both Au and In takes place in the spread regions during growth, and 5) The rate limiting process is not the diffusion of Au or In.

DISCUSSION

The Equivalence of Stage III and Lateral Spreading. From the preceding analysis it is quite apparent that stage III and the spreading phenomenon are closely related, possibly manifestations of the same basic process. The arguments for the latter are as follows:

1) In both cases the reaction product has been shown to be the compound Au_9In_4.

2) The activation energies for the two processes agree within the published limits of uncertainty.

3) In neither case does the interfacial Au_2P_3 layer form.

4) Stage III (pink to silver) conversion in the deposited Au disc is observed to take place concurrently with the nucleation and growth of the spread

regions in the adjacent InP.

On the basis of the above similarities, it seems reasonable to conclude that the processes occurring during spreading are the same as those taking place during the stage III reaction, that is, that spreading is but another manifestation of the stage III phase transition.

The Stage III/Spreading Mechanism. We have presented evidence that stage III and the spreading process are manifestations of the same phase transformation mechanism. In the following we will attempt to show that the same basic mechanism proposed to be active in stage II (i.e., the kickout mechanism) is also operating during stage III/spreading.

A unique characteristic of the kickout process is the fact that both species (Au and In) diffuse interstitially (and therefore very rapidly). The extremely rapid diffusion of both Au and In that has been observed in a wide variety of Au-In alloys[9-11] is thus consistent with a suggestion that the kickout process is active in the stage III/spreading reaction.

Although it has been shown that In diffuses substitutionally in pure Au[12], there is evidence that it enters and diffuses interstitially when sufficient In is present in the Au lattice. For example, Powell and Braun[9] have shown that In diffusion in all of the intermediate Au-In compounds proceeds at a rate that is 3 to 4 orders of magnitude faster than one would expect (according to equation 3) for substitutional diffusion.

Au also has been shown to diffuse interstitially in the Au-In lattice. Anthony and Turnbull[10], for instance, have shown that Au diffuses interstitially in pure In. While there are no data available concerning the rate of diffusion of Au in Au-In alloys, Au has been shown to diffuse very rapidly in the closely related Au-Sn system. . The diffusivity of Au in both $AuSn_2$[13] and $AuSn$[14], as well as in pure Sn[15] is 3 to 4 orders of magnitude greater than would be expected (equation 3) if substitutional diffusion were taking place. On the basis of the behavior of Au in this closely related system it appears likely that Au diffusion is interstitial in nature in the intermediate Au-In compounds as it is in pure In.

A second characteristic of the stage III/spreading process that is indicative of a kickout mechanism is the fact that the Au_3In-to-Au_9In_4 conversion rate is proportional to the area of the interface between the two phases. If the kickout step were rate controlling, the reaction rate should be proportional to the number of potential kickout sites. Since these sites are restricted to the boundary between the two phases, the kickout rate should be proportional to the Au_3In-Au_9In_4 interfacial area, which is what is observed.

Therefore, with the reasonable assumption that atomic transport in the Au-In system takes place via interstitial diffusion of Au as well as In, we propose that the stage III/spreading mechanism consists of the interstitial entry and diffusion of In in the metal lattice, and its exchange with a substitutional Au atom (kickout) at the Au_3In-Au_9In_4 interphase boundary where Au_3In is transformed to Au_9In_4. The reaction is proposed to proceed as

$$13 \; Au_3In + 3 \; In_i \rightarrow 4 \; Au_9In_4 + 3 \; Au_i$$

where the subscript indicates interstitial siting.

The Spreading Mechanism. The spreading process is envisioned to proceed in essentially the same manner as described above for stage III, the major difference being the large distances that the interstitial species have to travel. In, entering the metallization at the InP-metal reaction front must travel to an Au_3In-Au_9In_4 interphase boundary in the distant Au-rich disc where it becomes part of the growing Au_9In_4 lattice by displacing a substitutional Au atom. The Au interstitial so formed must then be transported back through the Au_9In_4 lattice in the spread region to the source of In at the InP-metal reaction front. At the reaction front the Au interstitials react with interstitial In and lattice vacancies to form additional Au_9In_4, which we observe as lateral spreading.

Phosphide Formation. Although we have proposed that stage II and stage III are similar in that they both involve the kickout process, there is a major difference in that in stage II the compound Au_2P_3 is formed at the metal-semiconductor interface, whereas in stage III (and stage I) it is not. The explanation presented previously to explain phosphide growth in stage II but not in stage I centered around the presence or absence of the Au interstitial.[1] It was postulated that if interstitial Au atoms are present in the metallization, they can, because of their high mobility, seek out and react with newly released P atoms before they get a chance to dissipate. Since the kickout process in stage II produces interstitial Au whereas the dissociative diffusion process of stage I does not, phosphide formation would be expected to take place in stage II but not in stage I.

A problem arises here, however, in

that we have postulated that the kickout mechanism is active in stage III as well as in stage II, and yet we do not observe phosphide formation in stage III even though interstitial Au is present. An explanation for this can be found in the fact that while stages II and III involve the same basic series of events, they are both controlled by different steps in that series.

In stage II where the In insertion step is controlling[1], we see that as soon as an In atom is released into the metallization, it readily displaces a Au atom which in turn diffuses to and reacts with a recently released P atom to form Au_2P_3. Since In release is the rate limiting process, the concentrations of interstitial In and Au remain very low.

In stage III, on the other hand, the In-Au exchange step is limiting so that there is a delay between the release of In (and P) into the metallization and the arrival of the displaced Au atom at the site of phosphorus release. It is suggested that the time delay is sufficient to allow the unbound P atoms to dissipate without reacting, with the result that no phosphide is formed. Also, because the In release rate is much faster than the In-Au exchange rate, the In interstitial concentration should approach saturation. The displaced Au interstitials, rather than reacting with phosphorus (which has already dissipated), could react instead with In from the saturated interstitial pool and vacant lattice sites (created at the

InP-metal interface when the substitutional In atoms enter the metal as interstitials) to form Au_9In_4 there.

The Effect of SiO_2 Capping. While an SiO_2 cap layer does not affect the ability of a disc to spread when it is deposited on the disc itself, it is very effective in preventing spreading when deposited on the InP surface adjacent to the disc. Figure 6, for instance, shows the spreading that emanated from three partially capped (600 A SiO_2) Au discs (2000 A thick) after 1 hour at 442 C in forming gas. As can be seen, spreading took place only into uncapped InP. We have also demonstrated that spreading from an uncapped sample is terminated upon encountering an SiO_2 cap on the InP surface.

While a cap layer is effective in stopping the advance of spreading, it does not do so abruptly. A close look at the intersection of the spread region with capped InP reveals that the spread region tunnels under the cap for about 1 micrometer before stopping. An interesting feature of this tunnelling is that the metallization under the cap does not show the volume change that the uncapped metallization shows. While it is not completely clear, at the present time, what the details of the reaction suppressing mechanism are, it is possible that it is associated with the escape of phosphorus and/or the vacancies left behind by the out-diffusing P atoms.
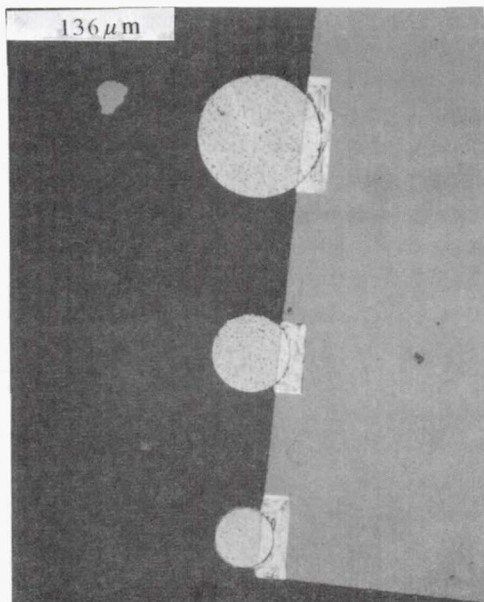

FIGURE 6. Spreading from partially capped contacts.

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16. Abstract

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