Effect of contact alloying behaviour on the electrical characteristic of GaxIn1-xSb diodes with gold coating

J.M. Peransin, J.F. Bresse, J. Michel, Alexandre Boyer, E. Groubert

MICROWAVE DEVICES.

EFFECT OF CONTACT ALLOYING BEHAVIOUR ON THE ELECTRICAL CHARACTERISTIC OF $Ga_xIn_{1-x}Sb$ DIODES WITH GOLD COATING

J. M. PERANSIN, J. F. BRESSE, J. MICHEL, A. BOYER and E. GROUBERT

Centre d'Etudes d'Electroniques des Solides associé au C.N.R.S., U.S.T.L., 34060 Montpellier, France

Résumé. — Nous étudions les changements de caractéristiques qui interviennent dans des diodes $Au/Ga_xIn_{1-x}Sb$ montées par thermocompression durant une série de recuits. Nous examinons les effets du temps de recuit et de la hauteur de la température. Par des profiles de concentration en profondeur nous avons mis en évidence un effet de diffusion externe et deux régions distinctes dans le semi-conducteur. La région intermédiaire correspond à une diffusion rapide de l'or, nous pensons qu'elle est due à une zone endommagée par la thermocompression. La qualité des contacts, déterminée par des mesures de l'émission microonde et des courbes courant-tension, a été associée aux mesures métallurgiques pour déterminer des performances optimums.

Abstract. — This paper reports on the characteristic changes of $Au/Ga_xIn_{1-x}Sb$ thermocompressed Gunn diodes after undergoing heating cycles. The effects of annealing time and temperature on metallurgical interdiffusion have been studied. By measuring the relative concentration depth profiles, both out-diffusion and two distinct depth regions inside the semiconductor were found. A rapid indiffusion of gold was associated to an intermediate region, we believe this may be due to a damaged zone by the thermocompression. The contact quality, characterised by current-voltage and microwave emission measurements, has been correlated to metallurgical transformations of contact layer in order to achieve optimum device performances.

1. **Introduction.** — The very high electron mobility and convenient band structure of $Ga_xIn_{1-x}Sb$ compound indicate that it appears as one of the most promising microwave materials [1]. Thus to realize transferred electron devices with low dissipation power [2], the threshold field of $Ga_xIn_{1-x}Sb$ is reported to be in the range of 400 to 900 V/cm against a value as high as 3.4 kV/cm in GaAs [3]. However optimum conditions for the contact technology in $Ga_xIn_{1-x}Sb$ are not yet well known as compared to many studies which are achieved for GaAs [4] or InP [5]. The purpose of this paper is to explore the metallurgical contact aspect in connexion with electrical measurements. Layered structures are formed by solid-solid reactions in the range of 200 to 280 °C, at temperatures substantially below the eutectic temperatures. The relative concentration profiles of contact layers have been analysed for composition as function of depth by using a SEM -X-ray analysis along metal-semiconductor junction.

Experimental procedure : The contacts were manufactured by evaporating a 1 000 Å thick dot of gold. Then the diode is mounted by thermocompression under a pressure of 1 000 kg/cm^2 at 180 °C. Considerable metallic interdiffusion occurs in the ternary compounds. Microprobe analysis shows that whereas the diffusion coefficients of Ga and In in Au are large, that of Sb is negligibly small [6]. The contact process causes complexed solid solutions forming multilayer structures on both sides of the initial gold-semiconductor plane. We have studied the influence of the heat-treatment on the intermetallic phases in the following two ways. In hydrogen atmosphere the samples were first subjected to heat cycles for 6 min fixed annealing time in the 200-280 °C range. Then for 200 °C fixed temperature the annealing time was increased by steps. After the above experiment a side wall of the diode was lapped and etched for SEM observation along the ⟨ 111 ⟩ crystal orientation. It is clear that the relative thickness of Au present during the annealing process has an important effect on the penetration depth and concentration of Au, and on the out-migration. We have investigated only the restricted cases where the gold coat (constituted not only by the evaporated film but mainly by the thermocompressed layer) is thick enough to maintain a pure gold out-layer.

2. **Results and discussion.** — Figure 1 illustrates a set of relative concentration profiles for Au, GaIn and Sb showing a typical interdiffusion behaviour between 200 and 240 °C. A double layered structure appears quite significantly on each side of the original interface. A stable intermetallic phase forms a top-layer, corresponding to an out-diffusion of only Ga and In. Another layer in intermediate position in front of the bulk semiconductor is due to a large Au diffusion. Note that no Sb out-diffusion was detected in the top-layer and that Ga and In concentration levels in this out-layer exceeds the levels in the intermediate layer. The depth profiles of the various elements are

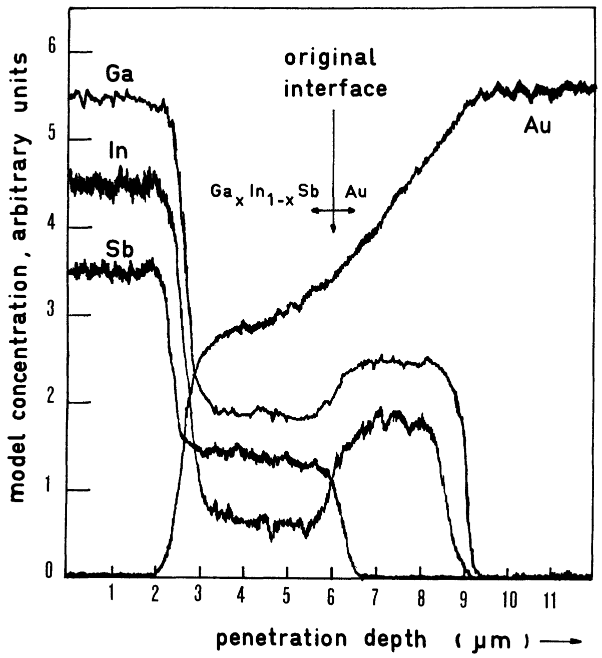

FIG. 1. — SEM X-ray elemental concentration profiles of Au, Ga, In and Sb along metal-semiconductor junction showing In and Ga out-diffusion and Au in-diffusion for 6 min. at 220 °C heat-treatment.

again displayed in figure 2 in three-dimensional form to describe the effects of heat treatment temperature. In most tested samples at 280 °C limit temperature, the Au surface layer is completely consumed and penetrates into the $Ga_xIn_{1-x}Sb$, inducing diode destruction after 6 min. At 240 °C a significant transformation of Ga profiles is observed close to the single crystal. A higher level of Ga concentration shows that a third in-layer appears between the preceding intermediate layer and the active bulk semiconductor.

This result is similar to the observations during investigations by heating cycles of various times. Figure 3 gives a detailled SEM X-ray distribution profiles of elemental concentrations for a long term operation at 200 °C. The relative levels show a well behaved case of a three layered structure. The region forming this in-layer in contact to the bulk-semiconductor has also stable metallurgical caracteristics. The profile levels indicate that only a very small amont of In is incorporated in this region. Three-dimensional composite of SEM Au, Ga, In and Sb depth profiles against time treatment is presented in figure 4 for a fixed temperature at 200 °C. At first both Ga and In out-migrations occur rapidly from $Ga_xIn_{1-x}Sb$ sur-

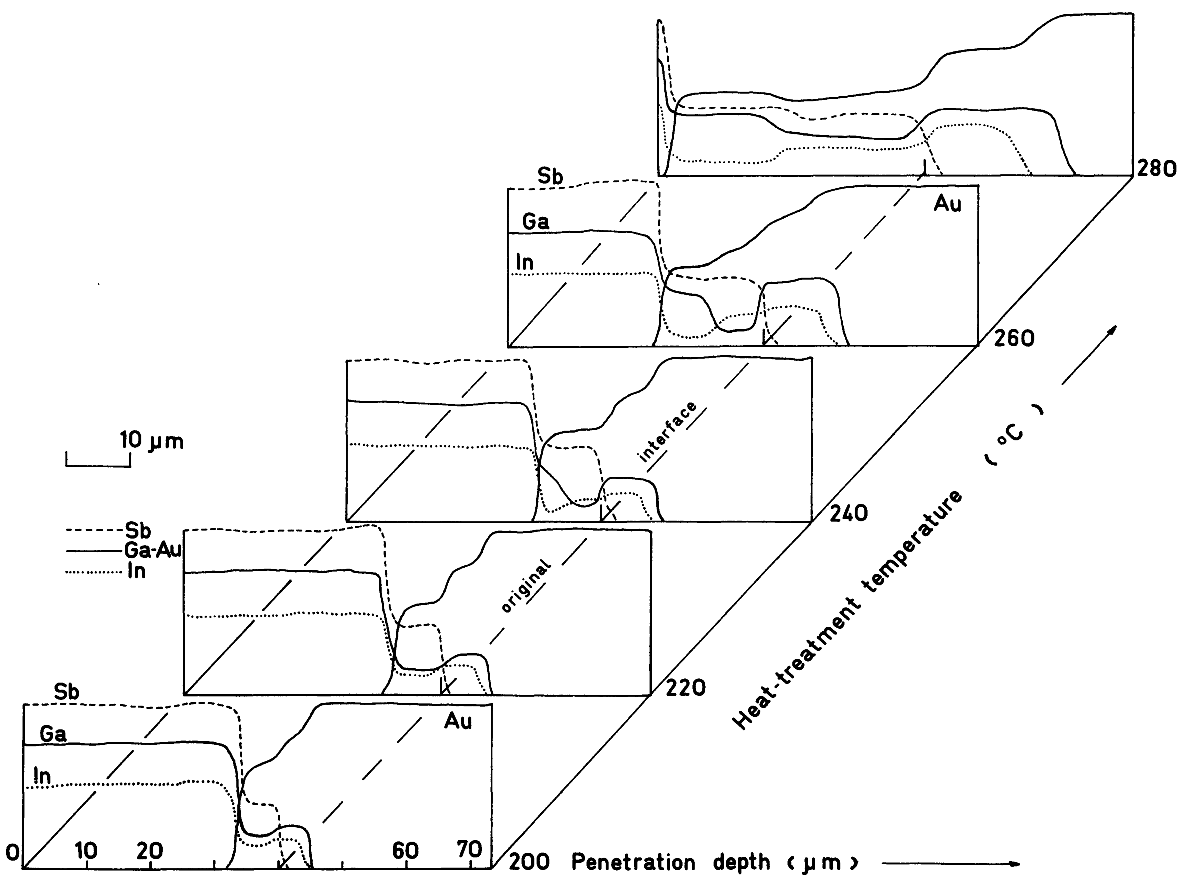

FIG. 2. — Three-dimensional composite of depth relative concentration profiles against heat-treatment temperature for 6 min. duration.

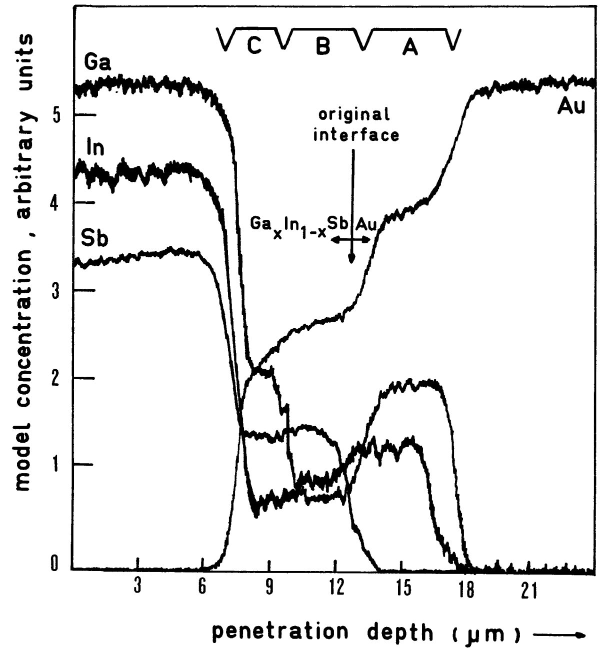

FIG. 3. — The various elemental profiles, analysed along the contact junction showing : A) the top-layer, B) the intermediate-layer and C) the in-layer after 8 min. heat-treatment.

face into the gold until the solid solubility limit is reached, after one or two minutes. These two out-diffusions are very noticeable but in long time experiments the migration depth of Ga into the gold film is more important. The Sb-Au interface still remains abrupt up to 30 min. annealing time. During gold migration, a first rapid diffusion of Au accross the intermediate-layer is observed. It is followed by a comparatively slow progression during the in-layer formation. In general the third layer is started at a depth of 6 to 8 µm from the initial surface. Therefore this limit appears as a second metallurgical interface in the contact process. The Sb concentration is stable when it is combined with Au. In contrast the steps in Ga and In distribution give straight borders for each different layer. The formation of this third in-layer is an important factor in the processing of devices. From these results, we expect the existence of a damaged region under the initial contact plane with a high dislocation density. Therefore the Au penetrates into this region with a very rapid diffusion velocity depending on temperature conditions. Anomalous high Sb concentrations were often found immediately underneath the gold front. Sb appears as turned out

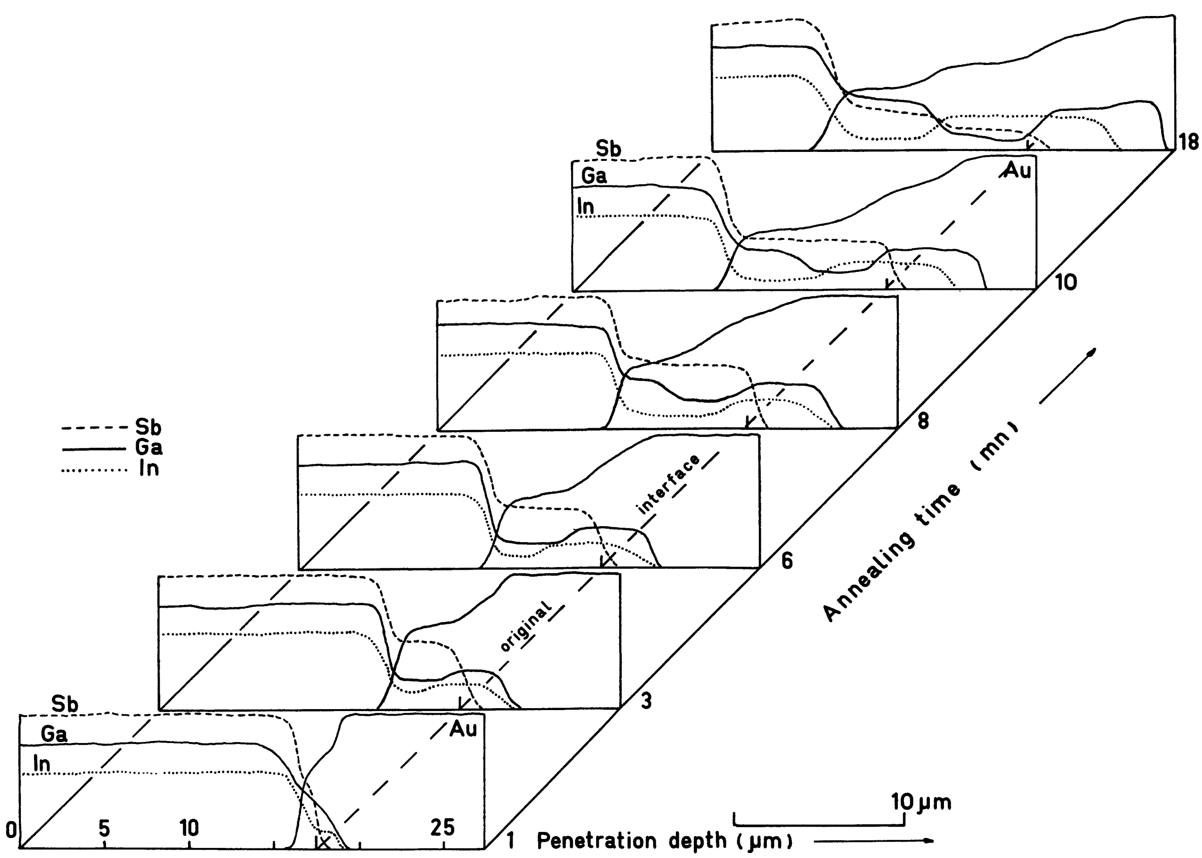

FIG. 4. — Three-dimensionnal composite of depth relative concentration profiles against various annealing time at 200 °C.

by Au and accumulates in the left degraded part. In some cases the Sb level increased up to 10 % resulting apparently in a different stoichiometric compound. When the Au in-diffusion overruns the limit of the damaged zone, the migration slackens speed. This is accompanied by a striking variation in the Ga and In alloyed concentration forming the third in-layer.

Electrical measurements have been correlated with the interdiffusion effects in the $Ga_xIn_{1-x}Sb$ gold coated diodes. Current-voltage characteristics are examined under pulsed DC conditions (*I-V* curves were drawn using very short pulses by time domain reflectometry or using pulses of 20 ns length in a resistive circuit). Figure 5 shows one of the results obtained for a diode of 70 μm length, exhibiting typical current changes. After thermocompression bonding the device is subjected to successive 2 min. annealing cycles. After each cycle the *I-V* curve is recorded; the traces show only the average current. The threshold voltage slowly increases from 3 to 4 V but it is apparent that the current of saturation is highly increasing with annealing time. Just after encapsulation the current does not reach saturation limit but rises gradually with the applied voltage increase. After 14 min. of heat-treatment the diode exhibits a negative differential characteristic with a current drop. This drop is accompanied by emission of microwave energy indicating the onset of Gunn effect. The current instabilities appear during the heating process between 6 and 8 min. of annealing time. Spectral analysis shows that this microwave emission is centered about 4 GHz

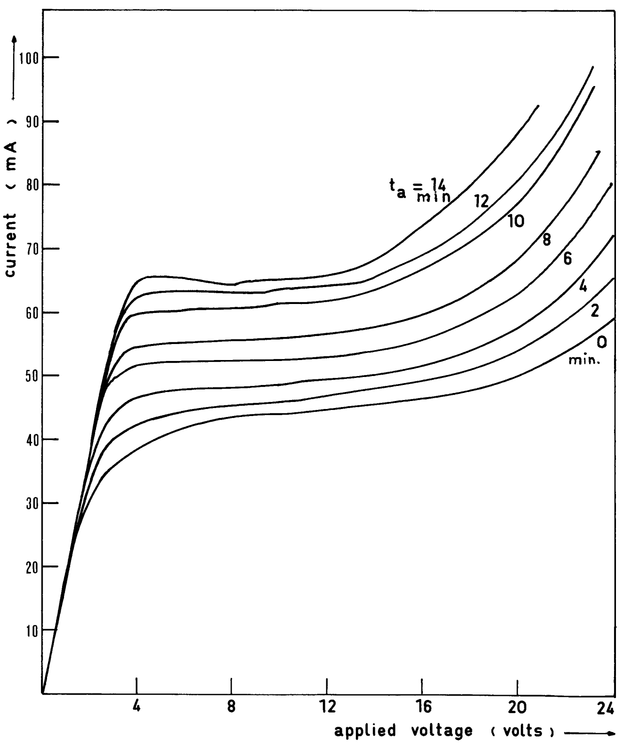

FIG. 5. — Annealing time dependence of current-voltage relations with 2 min. heating-time between each curve (t_a is the complete heat-treatment time after each cycle).

frequency and is related to the bias voltage. Further samples have shown that the frequency has no simple relationship with the device length as that expected for transit-time operation at a fixed space-charge velocity. As suggested by W. Gurney [7] in order to characterise contact imperfections, we have used a parameter β which offers the possibility of systematic investigations at intermediate stages in the manufacture of the diode. β is a quality factor depending on the degree to which the velocity/field curve is degraded in the contact region. This quality factor is defined as the ratio of peak device current I_p to the expected peak current in a perfect device :

$$\beta = I_p/n_0 . e . V_p . A ;$$

where $n_0 = 10^{15}$ cm^{-3} is the carrier concentration, e the electronic charge, A is the device cross-sectional area. The velocity V_p at the peak of the velocity-field curve is 2.7×10^7 cm.S^{-1} from T. Ikoma *and al.* models [8]. The experimental measurements of microwave power generated during the heating cycles are given in figure 6, in which it is shown that microwave emission is correlate with the parameter β. The onset of power output occurs for $\beta > 0.45$. So it is seen that as for other semiconductors, a minimum contact perfection must be necessary in the $Ga_xIn_{1-x}Sb$ diodes. Because of important dislocation region induced during thermocompression bonding, a direct pressure is to be avoided if we want obtain a good device reliability. These facts suggest at least that a large buffer layer is needed to protect against both plastic deformation and thermomigration.

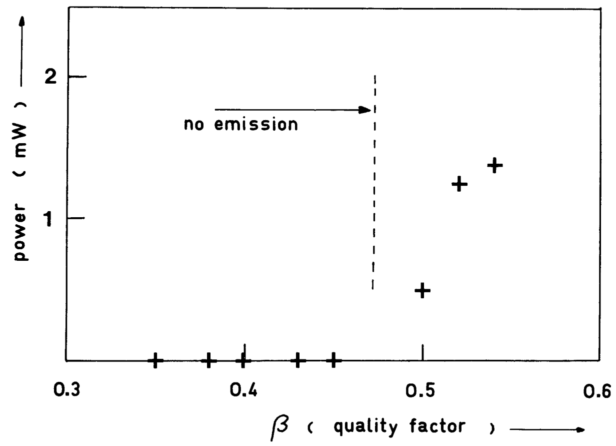

FIG. 6. — Microwave emission against contact quality during seven successive annealing cycles of 2 min.

From previous experiments on GaAs [9] and InP [10] samples it was shown that Gunn diodes exhibit similar effects on the characteristics, depending upon the doping profile in the active part of the diode. In particular a *notch* doping can be introduced by localised crystal alteration. These conductivity or donor notchs affect considerably the microwave behaviour of transferred electron devices and can provide better efficiency than ohmic contact. The physical origin of notchs may be due to various causes, to the strain induced by the high Au concentration or possibily to out-diffusion effect [11]. In the GaInSb diodes the out-diffusion results in an excess of antimony and/or In and Ga losses in the semiconductor causing an increase in the doping density near to the interface. These effects cannot take place in the heavy damaged zone and must only appear when the Au penetration reaches the $Ga_xIn_{1-x}Sb$ unaltered part. The complete crossing of damaged region in the thermocompression process is pointed out by current instabilities which appear on current pulses.

3. **Conclusion.** — The Au/$Ga_xIn_{1-x}Sb$ thermocompressed contact system has been analysed as a function of processing temperature and times with SEM microprobe measurements. A diffusion process results in the inward migration of gold into the $Ga_xIn_{1-x}Sb$ and corresponding outward movement of Gallium and Indium through the gold. A three layer structure appears with stable solid solubilities. The intermediate-layer can be explained by a high dislocation region damaged by stress thermocompression. A clear correlation was found between the electrical characteristics and contact layers. The entire changes in the *I-V* characteristics and microwave emissions of the thermocompressed $Ga_xIn_{1-x}Sb$ diode can be attributed to the formation of this damaged region under the contact resulting from bonding pressure.

Acknowledgment. — The authors would like to thank R. Lorival for the thermocompression bonding and Dr. A. Joullie for supplying the $Ga_xIn_{1-x}Sb$ compound used in this investigation and supported by DRME agreement nº 72642.

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