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PALLADIUM BASED CONTACTS TO GaAs AND InP[1]

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Abstract

Au(85nm)/Pd(55nm) and Pd(55nm) metallizations were deposited on GaAs(100) and InP(100) substrates. The samples were heat treated in a scanning electron microscope (SEM) equipped with a quadrupole mass spectrometer. The simultaneous observation of the volatile component loss (*in situ*) by Evolved Gas Analysis (EGA) and the change in surface morphology by SEM during the heart treatment using a heating rate of 30°C/min were carried out. The interaction of the metallization with compound semiconductor substrates was observed after the heat treatment by transmission electron microscopy (TEM) using samples prepared by cross-sectional technique.

In the course of the present work a large volatile component (arsenic and phosphorus) loss was observed for the samples coated by single layer metallization (at 410°C for Pd/GaAs and at 580°C for Pd/InP) and two peaks were registered in the case of Au/Pd metallization. In the latter case the cause of the second evaporation peak is the interaction between diffused gold and compound semiconductor. The SEM images of the surfaces demonstrate a significant change of the surface morphology at the singularities of the EGA curves.

The grains grown into the semiconductors are shown by the cross-sectional images of the heat treated samples.

Keywords: contacts, compound semiconductors, mass spectrometer, evolved gas analysis.

1. Introduction

Gold and gold based contacts to compound semiconductor structures are sufficient parts of these devices. The parameters of these contacts influence the device quality such as reliability, stability, noise. The behaviour of these contacts is determined by the microstructure of these functions and this latter is the product of the metal – compound semiconductor interaction during the heat treatment following the deposition of the thin multilayer metallization.

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Different analytical techniques can be applied for the investigation of the metallurgical reactions and their end products. No single technique can provide a complete description of the processes and the microstructure, that is why the characterization strategy should be based on a combination of different methods. In situ methods should be preferred in the course of these investigations.

In the present work a combination of the evolved gas analysis technique (EGA) and the scanning electron microscopy (SEM) was realized. In this way the heat treatment of the metallized samples was carried out in the chamber of the SEM equipped with a quadrupole mass spectrometer.

2. Experimental

2.1. Experimental Techniques

Evolved Gas Analysis is a mass spectrometric method [1]. The sample situated in vacuum is heated applying a constant heating rate, and the volatile component loss is monitored using a quadrupole mass spectrometer.

Our previous results [2,3] showed that the surface morphology of the samples had a drastic transformation reaching some characteristic temperatures corresponding to the intensity peaks of volatile component loss vs. temperature curve. To study *in situ* the volatile component loss and the actual surface morphology, a combined SEM and quadrupole mass spectrometer system was developed (*Fig. 1*). The investigated specimen is placed into a micro-oven (*Fig. 2*). Applying this micro-oven the sample can be heated up to 630°C. The heating rate is adjustable between 20°C/min and 150°C/min. To improve the quality of the SEM micrograph, a special care should be taken when applying the heat and electric shields in the oven and the quadrupole head should be placed in that position from where the electrons emitted by the cathode of the mass spectrometer cannot destroy the SEM image. This problem was solved inserting a vacuum knee between the vacuum column of the SEM system and the head of quadrupole mass spectrometer.

To study the cross-sectional structure of the samples, the XTEM technique was applied using ion beam thinning equipment [4].

2.2. Sample Preparation

GaAs wafers were prepared from n-type (Sn doped) GaAs single crystals of (100) orientation with carrier concentration of 2 to 3×10^{23} m^{-3}. InP

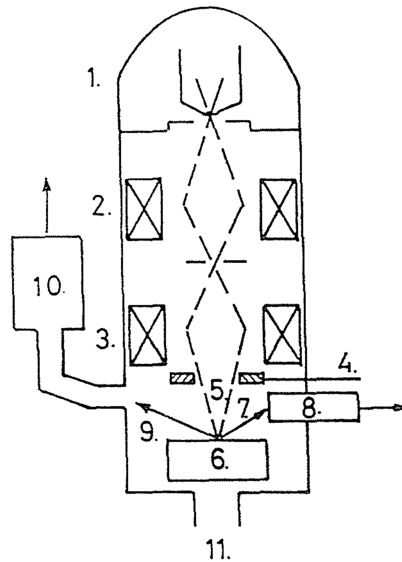

Fig. 1. Experimental arrangement for the in situ simultaneous observation of the volatile component loss (EGA) and the surface morphology system by the scanning electron microscope (SEM). (1) Electron gun (2) Condenser lens (3) Objective lens (4) Deflecting coil (5) electron probe (6) Specimen, mounted into the micro-oven (7) Secondary electron (8) Detector (9) Volatile component of the specimen material (10) Quadrupole mass spectrometer (11) Pumping unit.

wafers were prepared from n-type (Sn doped) InP single crystals of (100) orientation with carrier concentration of 1×10^{24} m^{-3}. After the mechanical and chemical polishing to a mirror-like surface the wafers were chemically cleaned and etched. The applied cleaning and etching procedure was as follows:

- 5 minutes boiling in toluene, 3 minutes boiling in methanol,
- 15 seconds etching in CH_3COOH : H_2O_2 (3:1) , 3× washing in distilled H_2O,
- 15 seconds etching in HF : H_2O (1:20), rinsing in methanol,
- 5 minutes boiling in methanol, drying by stream of N_2.

This procedure was carried out immediately prior to deposition.

The metal layers deposition was performed in an ultra-high vacuum evaporator type Balzers BA 350 U equipped with oil-diffusion pumps and LN_2 cooled trap. Before the deposition the wafers were outgased at 175°C and during the deposition the substrates were held at 75°C. The vacuum was lower than 10^{-4} Pa during the evaporation. In the case of the Au/Pd metallization both of the metal layers were evaporated in the same vacuum

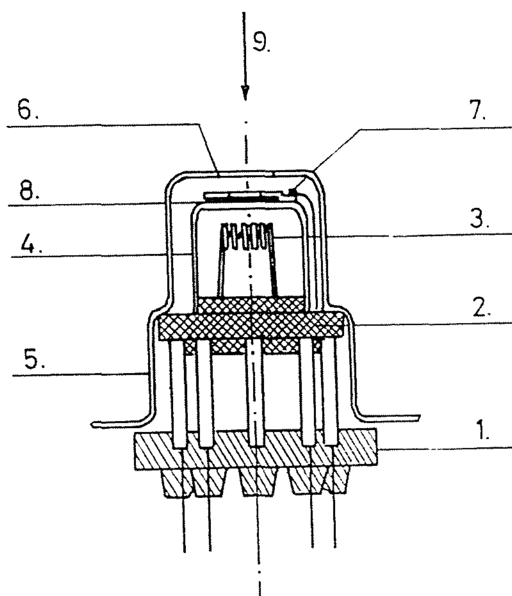

Fig. 2. The micro-oven for in situ EGA measurement. (1) Glass stage (2) Ceramic plate (3) Tungsten heating coil (4) Fe – Ni – Co alloy house of the heating coil (5) Fe – Ni – Co alloy heat shield (6) Ta plate, to fix the specimen (7) NiCr–Ni thermopair (8) Specimen (9) Electron beam.

cycle. After the deposition the samples were cooled down to room temperature in a high vacuum.

The samples were annealed in a JEOL JSM-T20 type scanning electron microscope applying the developed micro-oven (*Fig. 2*) using a heating rate of 30°C/min. The volatile component loss was monitored by an ATOMKI Q100PC type quadrupole mass spectrometer and the SEM pictures of characteristic surface morphologies were taken during the heat treatments.

To prepare samples for TEM investigations, two small chips from each sample were bonded face to face and embedded into a small aluminium ring with a diameter of 3 mm. The samples were thinned by mechanical grinding to approximately 50 μm and finally they were thinned by ion milling. We used Ar^+ ions accelerated by a potential of 10 kV. The samples were milled at a beam angle of $3^\circ - 5^\circ$ to the specimen surface with a gun current of 2-3 mA per gun. Details of the sample preparation are given in [4].

The thinned samples were examined using a Phillips CM 20 transmission electron microscope.

3. Results

Even in the case of as-deposited Au/Pd/GaAs sample (*Fig. 3*) some reaction products were observed on the cross-section. (In the case of samples investigated using TEM the thickness of Au layer was 125 nm while the Pd layer was 35 nm thick.) We observed that the palladium reacted with GaAs forming intermetallic grains. It is known that these reaction products are the phase I/$Pd_5(GaAS)_2$/ as it was identified by SANDS et al. [5]. In *Fig. 3* the Moire fringes (marked by arrow) indicate the presence of the ternary phase at the palladium GaAs interface.

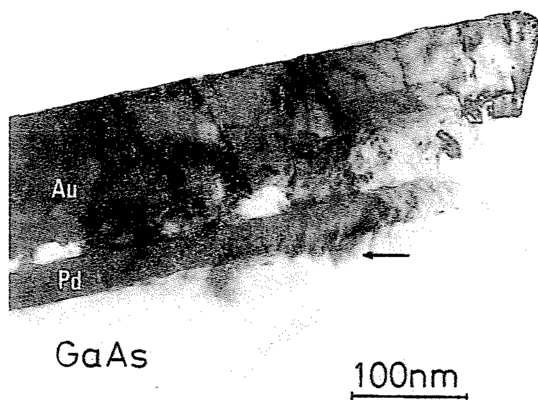

Fig. 3. Cross-sectional electron micrograph of the as-deposited Au/Pd/GaAs sample. The arrow shows Moire-fringes at the palladium GaAs interface.

The volatile loss of arsenic vs. temperature curves of the Pd/GaAs and Au/Pd/GaAs samples are shown in *Fig. 4*.

Already SANDS et al. [5] assumed that at about 400°C a certain amount of arsenic evaporated from the sample due to the:

$$Pd_4GaAs + 3GaAs = 4PdGa + 4As \uparrow$$

reaction.

Applying the EGA method we have shown that at about this temperature arsenic evaporates from the sample (see *Fig. 4a*). In the EGA curve of the Au/Pd/GaAs sample (*Fig. 4b*) two characteristic peaks of arsenic evaporation were observed. The first one is due to the above mentioned reaction between palladium and GaAs while the second one is due to the interaction of gold with gallium. The temperature of that evaporation peak is by 50–60°C lower in the case of Au/GaAs [2], but here there

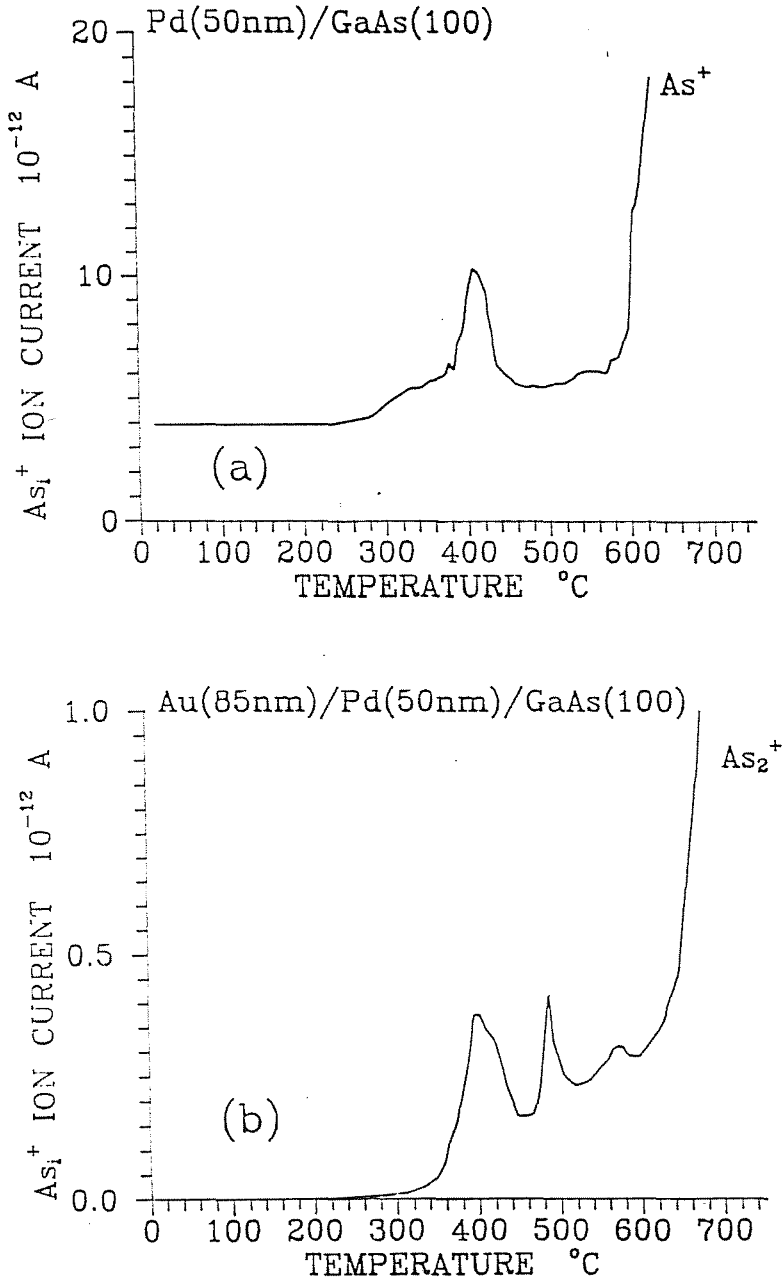

Fig. 4. EGA curves of the samples, volatile loss of arsenic vs. temperature cur Pd/GaAs (a) and Au/Pd/GaAs (b).

is the intermediate palladium layer and the diffusion of gold and gallium species through that layer needs a higher temperature.

LAMOUCHE et al. found [6] that the specific contact resistance of this system tended toward ohmic above 360°C. They reached the optimum of specific contact resistance at about 500°C.

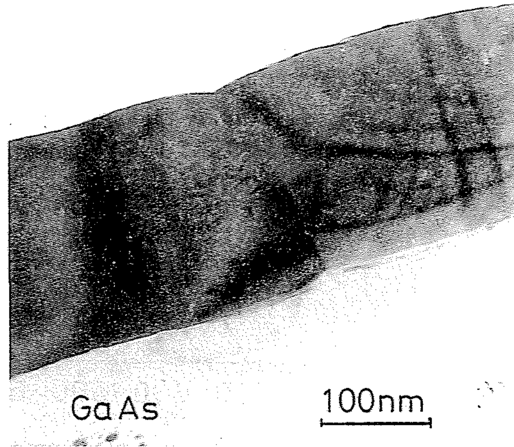

Fig. 5. Cross-section of the Au/Pd/GaAs sample annealed up to 480°C.

The cross-section of an alloyed contact is shown in *Fig. 5.* The sample was heat treated up to the temperature of 480°C that corresponds to the temperature of the second evaporation peak in *Fig. 4b.* The grain size of the alloyed layer is in the range of a few hundred nanometers. Based on the results of earlier electrical investigation [6] the contact is supposed to be ohmic.

The same experimental procedure was carried out with the InP samples. *Fig. 6a* shows the EGA curve for single layer metallization and *Fig. 6b* for Au/Pd system. For the two layer metallization two peaks can be observed. The peak for the Pd layer is a giant one while the gold peak is smaller. Observing the surface morphology below the peak small protrusions can be detected.

Fig. 7a illustrates a typical surface morphology in the vicinity of the peak, while *Fig. 7b* shows the melting of the metallization and the 'balling up' of contact material.

In *Fig. 8* the surface morphology of the Au/Pd/InP sample reaching the temperature characteristic to the P^+ peak due to the gold InP interaction can be seen.

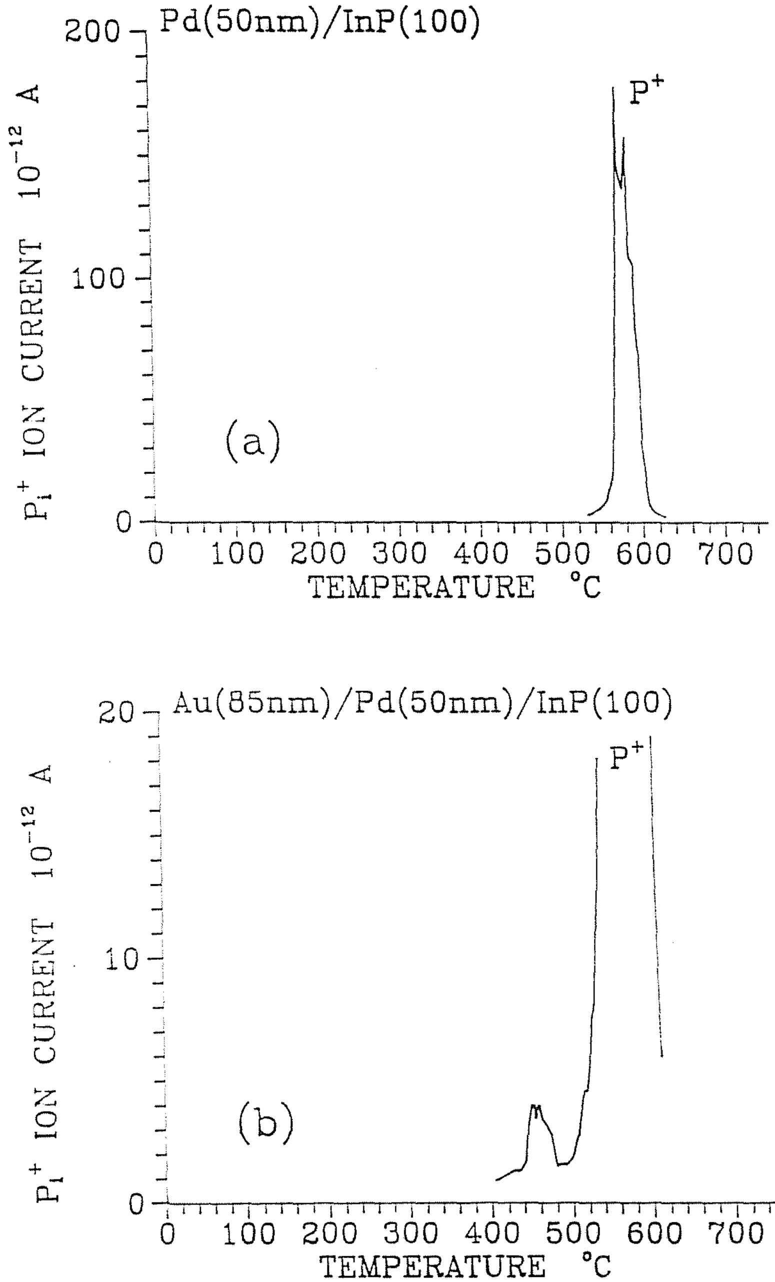

Fig. 6. EGA curves of the samples, volatile loss of phosphorous vs. temperature of Pd/InP (a) and Au/Pd/InP (b).

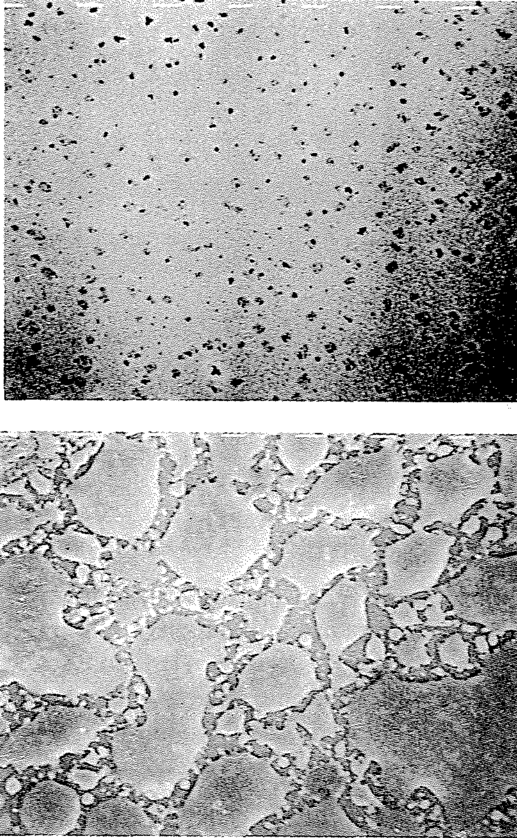

Fig. 7. SEM micrographs of Pd/InP samples annealed by the joined EGA-SEM system up to 530°C (a) up to 580°C (b) .

4. Discussion

Analysing our results we conclude that the simultaneous application of the EGA and SEM can lead to a valuable contribution to the investigation of the interaction of metallic layers with compound semiconductor materials. in our previous works the surface morphology was only investigated after the heat treatment 'freezing' the sample at a given temperature. Combining the two above mentioned techniques allowed to take a picture from the surface and to continue the heat treatment at the same vacuum cycle and to repeat it many times.

The EGA results for the investigated systems are comparable to those of investigated earlier [1-3]. Gold metallization causes an intensive interaction with the compound semiconductor leading to the formation of differ-

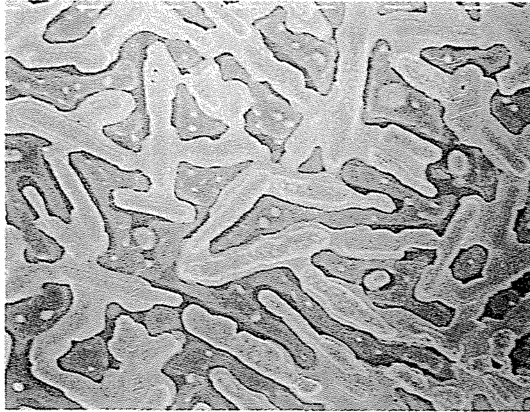

Fig. 8. SEM micrograph of Au/Pd/InP sample annealed by the joined EGA-SEM system up to 480°C.

ent intermetallic compounds. The characteristic forming temperatures of these intermetallic compounds are only slightly influenced by the presence of any intermediate metal layer if this is permeable for gold.

In this work we obtained the characteristic temperatures for Pd/GaAs and Pd/InP structures. It showed that Pd begins to destroy the InP surface at a much higher temperature than in the case of Pd/GaAs system.

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