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THERMAL DECOMPOSITION OF COMPOUND SEMICONDUCTORS COVERED WITH THIN METALLIC LAYERS

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Abstract

The aim of these investigations was to study the processes taking place during the heat treatment of compound semiconductor structures covered with thin metallic layers. This situation models the heat treatment of metallized wafer in the device technology. To investigate these samples a liquid nitrogen cooled UHV system was constructed, and the volatile component loss during the heat treatment was measured with a quadrupole mass spectrometer. The output signals are collected and evaluated by microcomputers. Special care was taken for the precise measurement of the sample to ensure the exact determination of the large peaks in volatile component loss. This method is suitable not only to measure the evaporation of the volatile component during annealing as a function of temperature, but to provide samples annealed in well- controlled circumstances for later investigations. As an example the measurement of the resistance of selected alloyed samples will also be shown.

Keywords: compound semiconductors, thin layers.

Introduction

The metal–semiconductor junction is one of the most important parts of semiconductor devices. The basic type of this structure is a thin film metallization on the top of a bulk semiconductor material. In the more sophisticated semiconductor devices an active semiconductor layer is grown onto the bulk substrate and the thickness of the metallization is in the same order of magnitude. It means that the problem of analysis of the system contact–semiconductor in many cases can be regarded as a 'pure' thin film problem and in some cases as thin film on the surface of a bulk material.

In the compound semiconductor device technology heat treatment plays an important role. The deposition of the contact layer is carried out on a pre-heated substrate and for obtaining good quality contacts it is necessary to include a heat treatment into the technology. This is the reason that the understanding of the processes taking place during the heat treatment is a key for making reliable compound semiconductor devices of high quality. For analysis of these metal–semiconductor systems various analytical methods can be applied, but *in situ* methods should be preferred.

Evolved Gas Analysis

One of the *in situ* methods is the mass spectroscopic evolved gas analysis (EGA), or evolved gas spectroscopy (EGS) method, which is based on the analysis of the ambient over the sample covered by metallization. The samples are annealed in vacuum and the evaluation of volatile component is monitored as a function of temperature with a mass spectrometer. The application of this method for the investigation of metal–compound semiconductor contacts (MCSCs) was firstly proposed by co-workers of our laboratory [1] and since it has been further applied to study these phenomena in our laboratory [2–23] and in other laboratories, as well [24–25].

Gold and gold-based alloys were found to enhance very much the thermal decomposition of GaAs [5, 9, 12, 24, 25], InP [6, 15, 16, 17] and other $A^{III}B^{V}$ semiconductors [10, 13, 14] at moderate temperatures (well below the temperature where the semiconductors, considerably decompose without a contact metallization). The evolution of volatile component is a process characterized by high increase of entropy, so at high enough temperatures even endothermic reactions may take place, as the change of Gibbs free energy of the system for a given reaction can be less than zero [26]. The two main driving forces of the reactions are the formation of $Au{-}A^{III}$ alloys and the entropy of vaporization of B^{V} component.

The EGA method is applied mostly to obtain an evaporation vs temperature curve of a given system. Comparing the EGA curve of an as–deposited contact with measurement of a similar contact after ion-beam modification or pre-alloying can provide us with information about the effects of these processes.

During an EGA measurement electrical parameters of MCSCs can be measured simultaneously [5, 7]. This way, the transformation of a Schottky-barrier contact into an ohmic contact can be directly observed.

Strong evaporation of the volatile component can be disastrous in device technology. EGA is in fact the best method to test the ability of a diffusion barrier layer (refractory metal, silicide, etc.) or a capping layer (SiO_2, Si_3N_4, etc.) to hinder the disadvantageous processes.

To study the metallurgical changes in MCSCs, samples are usually annealed at atmospheric pressure in oxygen-free atmosphere, and are investigated with other techniques (e.g. Auger Electron Spectroscopy) later. However, it is very difficult to find the best annealing temperatures. Controlled annealing in an EGA apparatus is a very good solution to this problem. The samples can be cooled down from characteristic points of the evaporation vs temperature curve for later investigations [21].

Experimental Set-up

Our apparatus is based on an ATOMKI (Hungary) Q 300 C quadrupole mass spectrometer which is attached to a microcomputer through an interface unit (*Fig. 1*). The interface unit contains A/D and D/A converters and digital I/O ports. One D/A converter serves as a programmable peak selector which allows the selection of the different species in the vacuum chamber. The computer controls the linear temperature controller unit, as well. Useful heating rates are between 10°C/min and 150°C/min, but the whole range is 2÷1000°C/min. The heating is performed by using a tungsten filament from the back side. The temperature is measured with NiCr–Ni thermocouples connected to the tantalum plates which hold the sample. Usually the temperature is measured on the top of tantalum plate, but in the case of one sample holder it can be measured on the bottom one, as well. Based on experiments with this sample holder, it was estimated that the surface temperatures of the samples are about 30°C higher than the measured temperature on the covering plate at around 600°C and this systematic error is proportional to the temperature. A simple correction was therefore applied to the temperature axis in the figures. The vacuum chamber is cooled with liquid nitrogen to reduce the noise (or background) level. The softwares for measurements and evaluation of data were written in Basic and Pascal. During rising the temperature the measurement of temperature and several species are performed as frequently as possible. However, having developed a special subroutine, the storage of data bearing no important information is avoided while the quickly proceeding processes are successfully recorded.

Application Examples

The Effect of Different Metals on the Thermal Decomposition of Compound Semiconductors

The thermal decomposition of semiconductors is greatly enhanced by gold. The total amount of evaporated phosphorus is roughly proportional to the thickness of gold. On the evaporation *vs* temperature curve of Au(55 nm)/n– InP samples two smaller peaks appeared at around 370°C

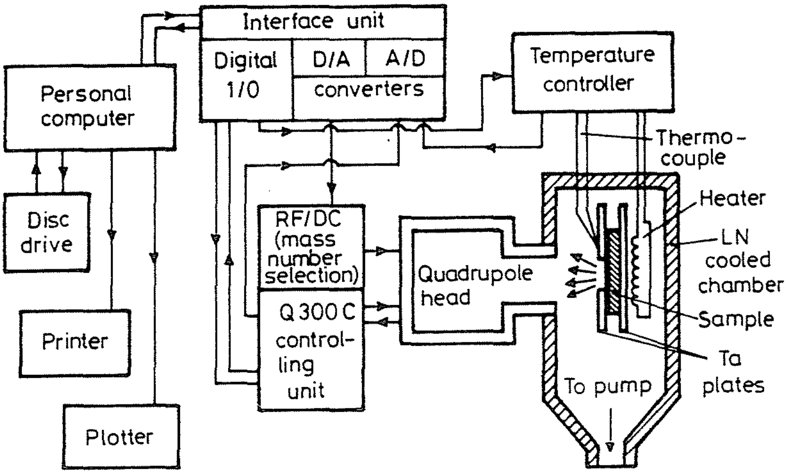

Fig. 1. The experimental set-up of EGA apparatus

and 420°C as a result of reactions proceeding in the solid phase. At around 440°C a large, sharp peak appeared and the metallization melted. The thickness of metallization inevitably affects the shape of the EGA curve (*Fig. 2*).

Our recent measurement revealed that Pd — beside gold and silver — enhances the decomposition of compound semiconductors and the evolution of volatile components very much (*Fig. 3*). Pd(50 nm)/n–InP samples were annealed in the EGA apparatus using 30°C/min heating rate. The decomposition of InP starts slightly below 400°C because of the reaction with Pd. Silver is less reactive from the point of view of volatile component loss, though at around 400°C the reaction between Ag and InP is accompanied with minor evaporation of phosphorus.

The Use of Barrier Metal Layers

Gold is the basic component of many metallizations in device technology, either as an important constituent or as a covering metal to allow easy bonding. However, the diffusion of gold to the semiconductor interface can be disadvantageous because it greatly enhances the decomposition of InP (and GaAs, as well). One way to prevent the strong evolution of volatile component is to hinder the interdiffusion and interaction of Au with the semiconductor using barrier metals. Several metals were tested. Cr and Ti

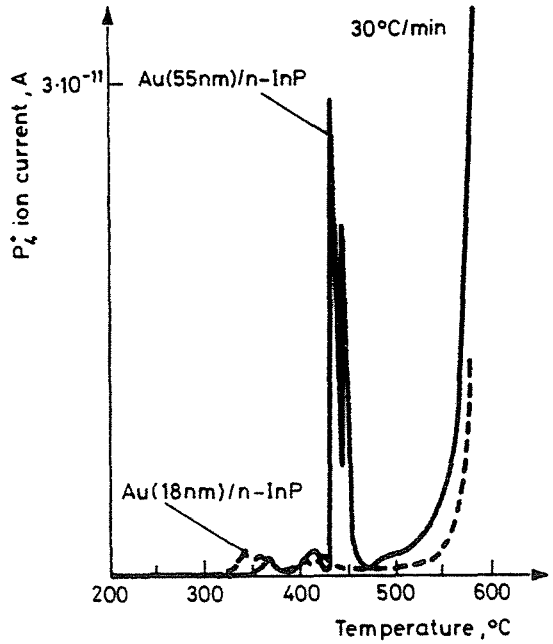

Fig. 2. The evaporation of phosphorus from Au(55 nm)–InP (solid line) and Au(18 nm)–InP samples (dashed line)

were found to be the most effective ones, Pt was less effective barrier metal, while the performance of Ni was very poor, as it can be seen in *Fig. 4*.

The Use of Insulating Capping Layers

AuGeNi is still the most popular ohmic metallization to n type III–IV semiconductors. Being gold one of its components, the phosphorus loss is high in this system, as well. Its consequence is the melting and 'balling up' of the metallization at temperatures close to the usual annealing temperatures. Using a capping insulating — e. g. SiO_2 layer — the evaporation of phosphorus can be largely suppressed (*Fig. 5*). However, it should be mentioned that small amount of phosphorus evolves at lower temperatures than in the case of non-capped sample. It suggests that the reactions are not simply suppressed, but the interaction takes place differently. An explanation of the reduced volatile component loss is that the evolution of volatile component depends on the ambient phosphorus (or arsenic) pressure, as well. High volatile component pressure in the ambient hinders

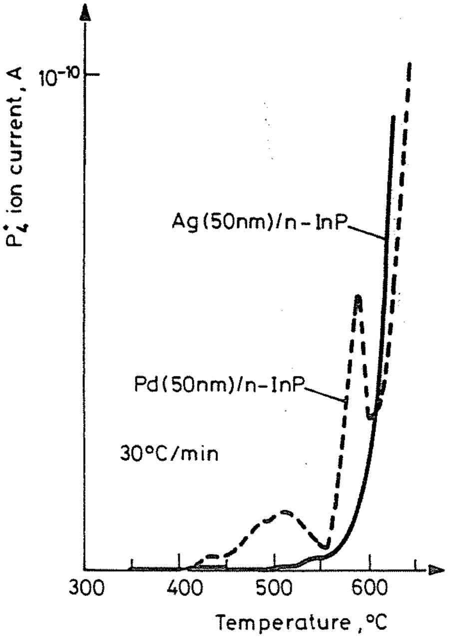

Fig. 3. Phosphorus evolution from Ag(50 nm)–InP (solid line) and Pd(50 nm)–InP samples (dashed line)

the reactions. Using capping layers on the top of the metallization, local over-pressure of P or As can be achieved.

Microstructural Characterization

It is not surprising that the combination of gold and palladium is highly reactive with compound semiconductors. The EGA curve (*Fig. 6*) shows a small peak at about 290°C and two large volatile component loss peaks. A shoulder can also be seen after these two peaks, so we can suppose at least five reaction steps below 600°C.

The microstructure of this contact system was also studied. The samples were heat treated in flowing forming gas (95% N_2 + 5% H_2) for 10 min in the 325–425°C temperature range.

Cross sections were cut off from the samples and were thinned by ion milling using Ar^+ ions [27]. These samples were investigated by TEM using a JEOL 100U transmission electron microscope.

Even in the case of as-deposited sample some reaction products can be seen on the cross section (*Fig. 7*). We observed that the palladium reacted

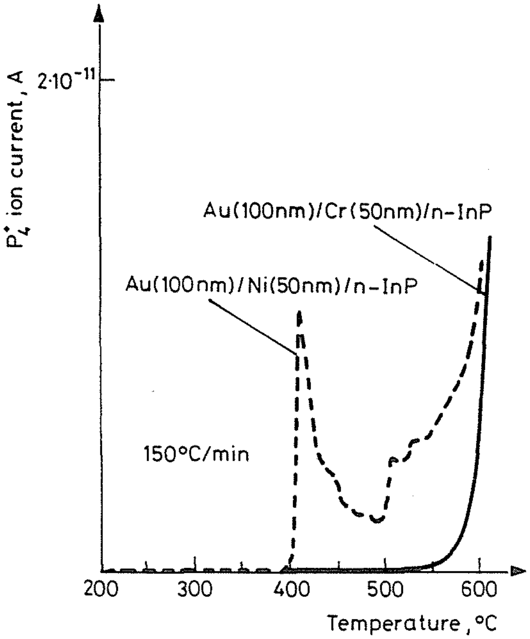

Fig. 4. The evaporation of phosphorus from Au(100 nm)/Cr(50 nm)–InP (solid line) and Au(100 nm)/Ni(50 nm)–InP samples (dashed line)

with GaAs forming intermetallic grains. They are about 25 nm thick and 100 nm wide. A very thin layer of native oxide was also observable. Our earlier RBS investigations show [19] that the gold layer, which is the top layer of the sample, remained mainly unreacted up to 300°C. Significant Pd indiffusion is evident already in the case of sample annealed at 325°C and a slight Au diffusion is also noticeable. Only a little change can be seen on the spectrum of sample annealed at 350°C. The average Au content of the upper 50 nm thick layer is about 93%, as it was estimated from the lowering of the gold peak of the RBS spectrum. A strong reaction took place between the GaAs and the metallization in the case of sample heat treated at 375°C (*Fig. 8*). Very large grains appeared in samples heat treated at higher temperatures. For example, in the case of sample annealed at 425°C they were about 250 nm large.

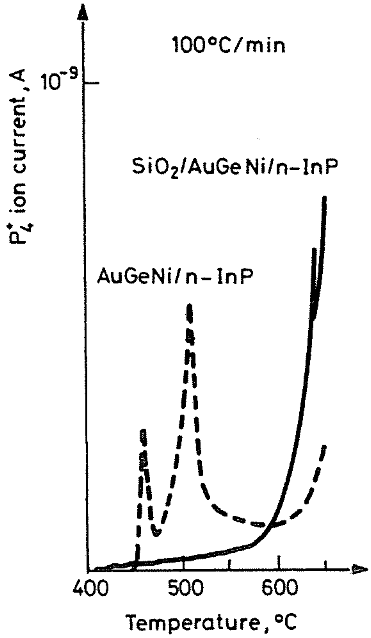

Fig. 5. The decreased evaporation of phosphorus from SiO_2/AuGeNi–InP contact (solid line) compared to the AuGeNi–InP system (dashed line)

Correlation between the Volatile Component Loss and the Ohmic Contact Parameters

To study the correlation between the results of EGA technique and the electrical parameters of the ohmic contacts, a set of samples were heat treated in the EGA apparatus and later their ohmic parameters were evaluated.

The metallization was prepared by the sequential evaporation of 5 nm Ni, 75 nm AuGe (eutectic), 30 nm Ni, and finally 400 nm Au onto GaAs. The GaAs wafer was Cr–doped semiinsulating substrate with a 0.35 μm thick n–type epitaxial layer on it (the carrier concentration of the epitaxial layer was $1.65 \cdot 10^{17}\,\mathrm{cm}^{-3}$).

The alloying was carried out in a vacuum chamber, where the evolved volatile products were monitored by a quadrupole mass spectrometer. Several samples were heated up to different temperatures, and after the heat treatment the ohmic contact parameters were obtained using a computer controlled measuring system. *Fig. 9* shows the volatile component loss during the heat treatment. Letter 'A' through 'G' marked the temperature values where the annealing of the samples was stopped.

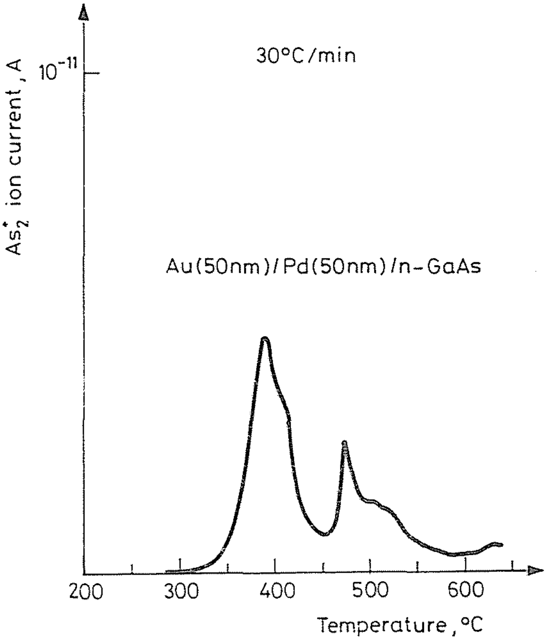

Fig. 6. The evolution of arsenic from Au(50 nm)/Pd(50 nm)–GaAs sample

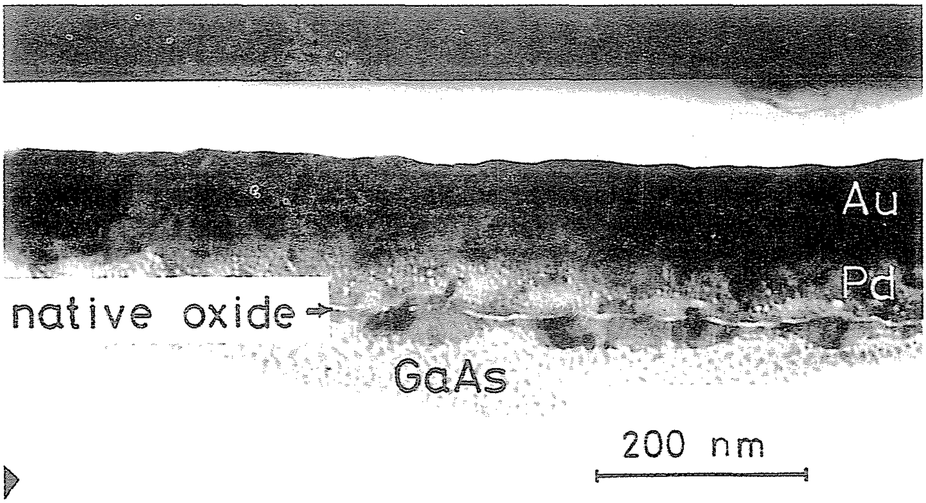

Fig. 7. Cross sectional view of as-deposited Au(50 nm)/Pd(50 nm)–GaAs sample

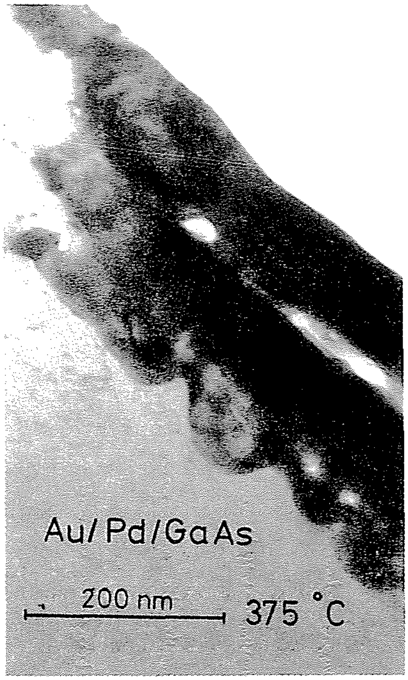

Fig. 8. Cross-sectional view of Au(50 nm)/Pd(50 nm)–GaAs sample heat treated at 375°C.

To determine the parameters of ohmic contacts a lot of measuring routine are known. The application of the so-called TLM method [28] (Transmission Line Model) and the 'six terminal Kelvin resistor' method [29] is a very promising way in the case of very thin epitaxial layer structures. However, these methods are acceptable only in that case, when the contact metal has very low sheet resistance or the contact sizes are only a few microns long [30, 31].

To measure the contact parameters a specially designed Process Control Monitor was applied using a computer controlled measuring system [32].

To obtain the sheet resistance of the epitaxial layer and the specific contact resistance, two separate 'van der Pauw' crosses were used. The evaluation error of these crosses was less than 1%. The specific contact resistance was measured by four terminal Kelvin resistor. As the metal-compound semiconductor interface became inhomogeneous during the heat treatment, it is advisable to consider the obtained specific contact resistance as an average parameter.

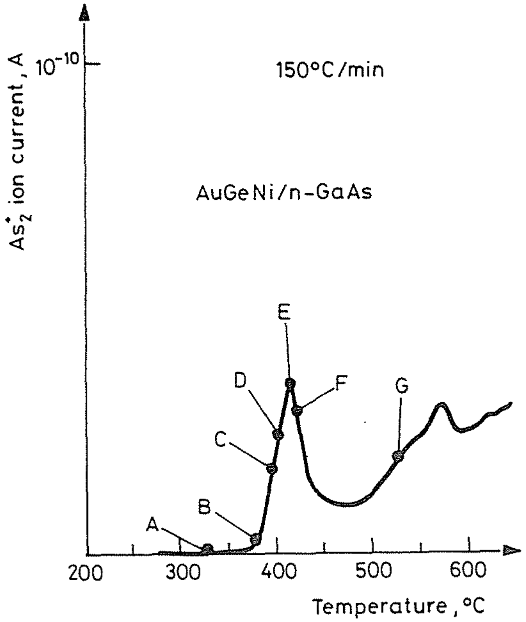

Fig. 9. The arsenic loss versus heat treatment temperature of Au/Ni/AuGe/Ni/GaAs samples

Evaluating the contact parameters, the sheet resistance between the contacts was 500±30 ohm/sqr for the samples. Since the applied material was made by VPE, this scattering is in the range of original deviation of epitaxial layer parameters. This result supports that the surface of uncoated GaAs does not dissociate in the temperature range used.

The metal sheet resistance increased by raising alloying peak temperature (*Fig. 9*, *Table 1*). We suppose that this is due to the increasing Ga extent in the metallization, which is caused by the formation of NiAs at the interface, and then the increased decomposition of GaAs, caused by gold. This behaviour of the metal sheet resistance is general in any type of annealing process. (*Fig. 10*).

The lowest value of specific contact resistance was obtained at the point E (*Fig. 9*, *Table 1*), where the first peak evolution of arsenic appeared. As gold is known to be a good 'sink' for Ga, a contact with low contact resistivity is supposed to form at temperatures, when outdiffusion of Ga atoms is high, because the otherwise amphoteric Ge will be donor when occupying their sites. We suppose that these processes accelerate at temperatures corresponding to points *B*, *C*, *D*. Though the evolution

Table 1
The measured contact electrical parameters (after annealing of Au/Ni/AuGe/Ni/GaAs samples in the EGA apparatus, in vacuum)

Peak temperature point	Specific contact resistance Ωcm^2	Metal sheet resistance Ω/sqr
A	$3.2 \cdot 10^{-6}$	0.2
B	$1.0 \cdot 10^{-6}$	0.2
C	$1.6 \cdot 10^{-6}$	0.4
D	$7.0 \cdot 10^{-7}$	0.4
E	$8.0 \cdot 10^{-7}$	0.4
F	$1.3 \cdot 10^{-6}$	0.4
G	$1.8 \cdot 10^{-6}$	0.6

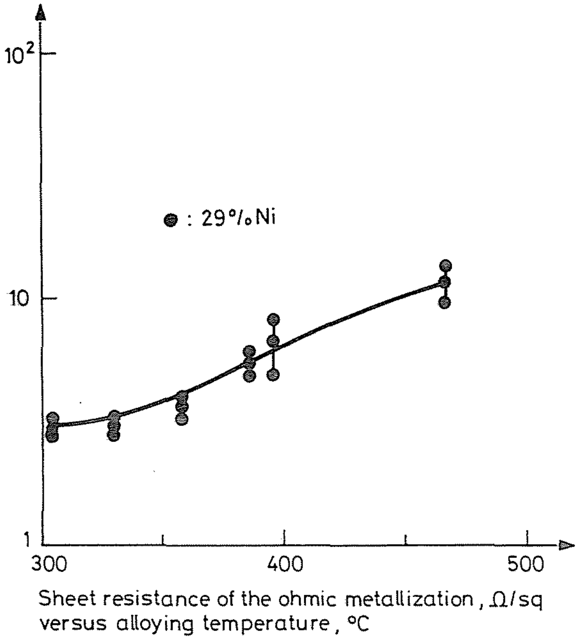

Fig. 10. The metal sheet resistance versus annealing temperature (the heat treatment was carried out in an open tube furnace, using flowing forming gas atmosphere)

of arsenic is increasing at these temperatures, the total quantity of evaporated arsenic is still low. Further increasing the temperature, rise of specific contact resistance can be observed (point *F*), because more arsenic than Ga vacancies will be available for the Ge to occupy. However, alternative explanations are possible, and further experiments are in progress in our laboratory to correlate the electrical parameters with volatile component loss and metallurgical transformation of contacts.

Summary

The mass spectroscopic evolved gas analysis was proved to be a useful — yet not expensive — method for the investigation of metal/compound semiconductor contacts. It was successfully applied to study novel contact systems and contacts already in use in the device technology. Other useful applications are the controlled annealing of samples in the EGA apparatus and combination with other methods.

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