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MASS SPECTROMETRIC STUDY OF SEMICONDUCTOR LAYER STRUCTURES

By

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The mass spectrometric study of the evaporation of As and P, respectively, during contacting of GaAs and GaP diodes was reported at the 7th International Vacuum Congress (Vienna 1977). Now new results obtained on various contact-crystal systems are presented.

A laboratory SIMS system was built using a Riber QML 51 quadrupole mass spectrometer. The study of contacting processes was followed by SIMS in depth profiling of the contact-GaAs layer structures. Some SIMS studies of SiO_2 layers prepared by various methods are described.

I. Introduction

This paper is devoted to mass spectrometric studies on some semiconductor $A^{III}B^{V}$ layer structures and Si-SiO_2 systems, using the methods and equipment developed in our laboratory. The mass spectrometric study of the evaporation of volatile components during heat treatment of metallized $A^{III}B^{V}$ semiconductor layer structures was performed and described by SEBESTYÉN and coworkers [1, 2]. KINSBRON gave new data on the dissociation of GaAs and GaAlAs covered with gold contact films [3]. Now some new results are presented on systems containing gold and silver.

II. Experimental results and discussion

The decomposition, outdiffusion and evaporation of components from metallized semiconductor surfaces were studied by a Riber QML 51 quadrupole mass spectrometer.

The contacting processes of diodes prepared from $A^{III}B^{V}$ (GaAs or GaP) crystals using various contact structures were studied in detail. Thin (100—400 nm) film of Au, AuGe, AuGeNi, AuNi, AuCr, Ag, AgSn, AgNi and InGeAg have been deposited on both faces on GaAs (100) wafers (3×3 mm^2) or on GaP (111) surfaces.

During the alloying process in the range of 300—600 °C As_2 or P_2 losses were detected by the mass spectrometer. The loss of the volatile component (Y) originates from the decomposition of the contact-crystal interface layers [1, 2]. A steep rise characteristic of the contact composition and substrate occurs at the onset of alloying.

The temperature variation of the resistance of the metal — semiconductor structure was recorded during the annealing simultaneously with the arsenic evaporation rates. According to the method described in [4] a low measuring current was applied to the specimen and the potential drop was recorded during the annealing. This voltage is proportional to the momentary resistance of the sample in the 20—200 °C temperature range as it was shown in [5]. Some characteristic $R(T)$ and $Y(T)$ curves are presented in the Figures. The study of contact system AuGeNi — GaAs has already been described in [2, 4]. The $Y(T)$ and $R(T)$ characteristics are strongly affected by the composition of the layer structures. Fig. 1 represents the R-Y-T curves for the Au—GaAs—Au system during the alloying cycle.

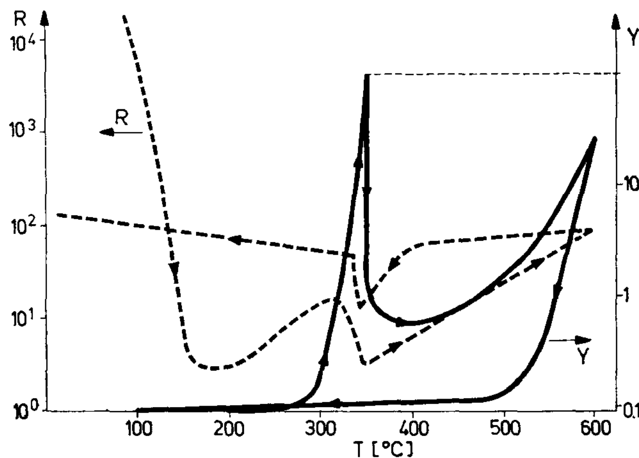

Fig. 1. Variation of R and Y (arbitrary units) with T for Au-GaAs-Au during the first annealing cycle. Heating and cooling rate 150 °C/min

Applying a second heat treatment a drastic change occurs in the R-Y-T curves due to further As_2 losses as shown in Fig. 2.

Fig. 3. represents the case of Ag—GaAs—Ag layer structures.

An interaction of an As_2 molecular beam with GaAs — metal system and same metal structures deposited on molybdenum plates was described in our recent paper [6].

Recently, mass spectrometric studies of semiconductor layer structures have been completed by SIMS studies [7, 8]. A laboratory SIMS system has been built using a Riber QML 51 mass spectrometer mounted on an UHV

system built with Tungsram components, working at 10^{-7} Pa pressure range. The system operated with a PHI 04—191 ion gun, at 10^{-3}—10^{-5} Pa Ar pressure using 3—300 $\mu A/cm^2$ ion current and 0,5—5 keV. More details of the SIMS system are given in [9].

The interference microscope picture after in-depth profiling with a scanning ion beam and a copper diaphragm of 2,5 mm diameter hole, producing a steep and uniform crater is shown in Fig. 4.

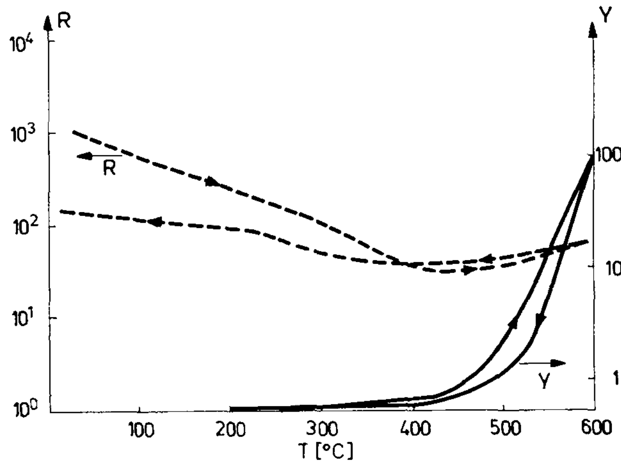

Fig. 2. Variation of R and Y (arbitrary units) with T for Au-GaAs-Au during the second annealing cycle. Heating and cooling rate 150 °C/min

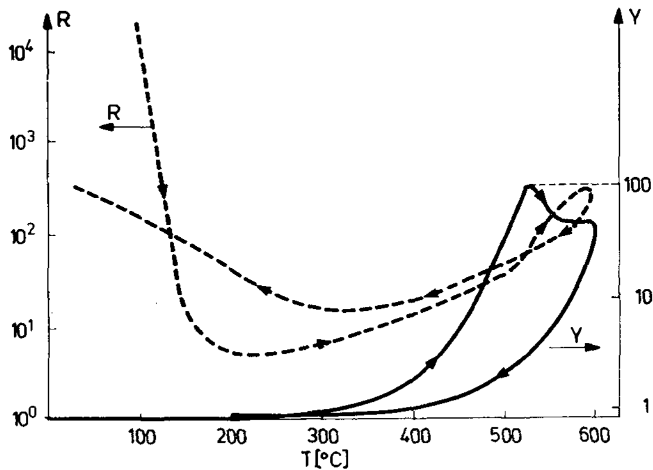

Fig. 3. Variation of R and Y (arbitrary units) with T for Ag-GaAs-Ag. Heating and cooling rate 150 °C/min. Alloying cycle

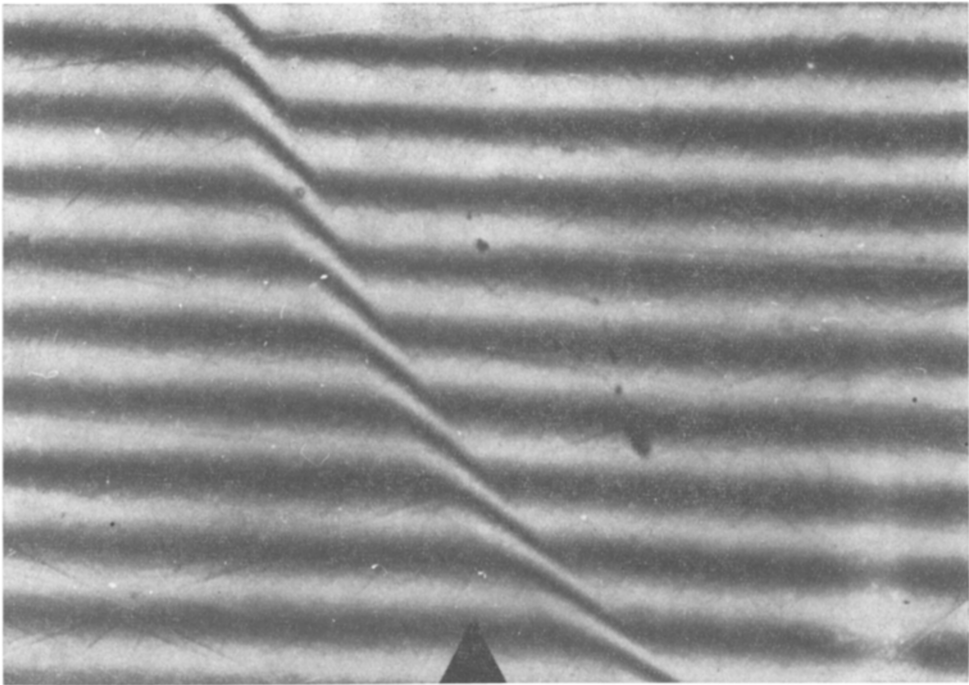

Fig. 4. Interference microscopic picture of a sputtered crater

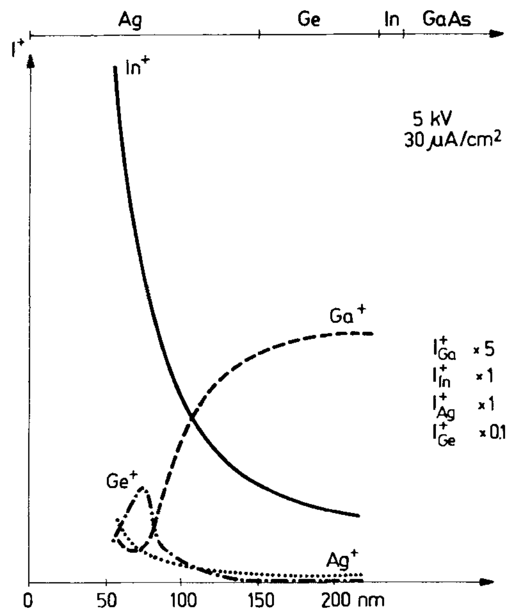

Fig. 5. In-depth profile of an Ag-Ge-In contact system evaporated on GaAs, exhibiting diffusion of the components. I_{Ge} etc. SIMS peaks in arbitrary units

Analyzing the fringes the depth of sputtering in Fig. 4 was determined as 270 nm. Sputtering rates can be determined using this method.

Some preliminary results obtained on contacted GaAs and $Si-SiO_2$ layer structures are presented in Figs. 5—7 and Tables I—III.

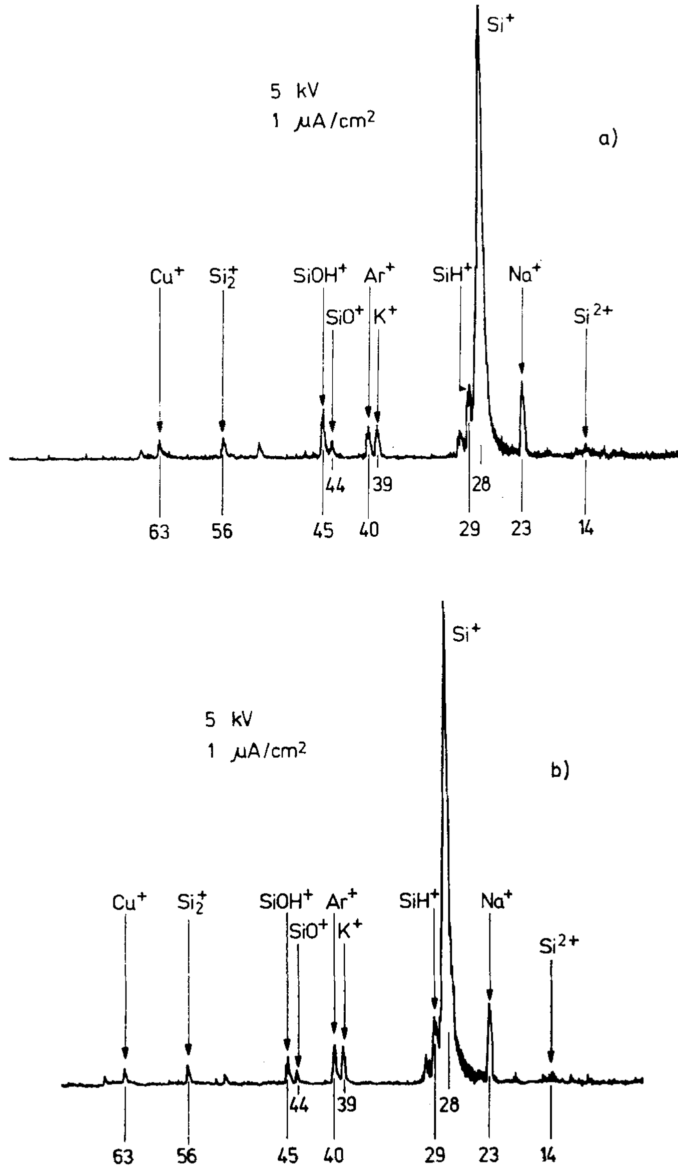

Fig. 6. SIMS spectra of two SiO_2 layer structures, prepared by different technological processes by M. NÉMETH-SALLAY. Sample a) oxidized in dry O_2; b) the same ether-treated [8]

Table I

Relative SIMS intensities of the most commonly used elements

Al^+	Si^+	Ga^+	Ge^+	In^+	Ag^+
1000	10—240	1000	10—30	100—500	5

Table II

Characteristic peaks referred to Si^+

Mass number	ion	oxidized in			
		dry O_2	wet O_2	dry O_2	wet O_2
		—	—	ether-treated	
14	Si^{2+}	0.0068	0.0079	0.0093	0.013
29	SiH^+	0.14	0.12	0.11	0.122
44	SiO^+	0.030	0.020	0.047	0.023
45	$SiOH^+$	0.093	0.038	0.049	0.040
56	Si_2^+	0.036	0.038	0.038	0.055

Table III

Characteristic peaks referred to Cu^+

Mass number	ion	oxidized in			
		dry O_2	wet O_2	dry O_2	wet O_2
		—	—	ether-treated	
14	Si^{2+}	0.20	0.19	0.39	0.30
28	Si^+	29.6	24.5	36.7	22.9
29	SiH^+	4.0	2.9	4.2	2.9
44	SiO^+	0.88	0.5	1.7	0.53
45	$SiOH^+$	2.74	0.92	1.8	0.93
56	Si_2^+	1.1	0.7	1.4	1.3

Fig. 5 represents the in-depth profile of an AgGeIn contact system evaporated on GaAs exhibiting diffusion of the components [10]. I_{Ge} etc SIMS peaks are presented in arbitrary units. As is well known, the sputtering and ion yield in SIMS studies are strongly affected by the composition of the target, conditions of sputtering on the mass spectrometer system and matching. The recorded intensities in Fig. 5 are not corrected for sputtering yield and sensitivity

factors of the secondary ionization. To make a rough estimation of relative concentrations, relative secondary ion yield data taken from the literature and averaged from several authors' results [7] are given in Table I.

The $Si-SiO_2$ system was investigated by several authors. Here MAUL [10] and BÁRSONY [11] are quoted, reporting on the variation of SIMS spectra with methods of preparation of the oxide layer. In a recent paper BARNA and coworkers [12] have dealt with ether-treated SiO_2 layers. In our paper, some additional results are presented. In Figs. 6A and B SIMS spectra of two SiO_2 layer structures prepared by different technological processes, described in [12] are presented.

As found by BARNA and coworkers [12] the main effects manifest themselves in the variation of hydroxil content (observed as $SiOH^+$ ions) on SiO layers prepared by different methods. Ether-treating appreciably reduces the hydroxil content.

The copper diaphragm used for in-depth profiling supplies some kind of reference standard for the SIMS spectra, obtained on various samples.

This paper is confined to some mass spectrometric studies, illustrating their applications on semiconductor problems, associated with technology, but omitting the technological aspects. More details are given in the references quoted and will be published in other papers.

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