PHYSICOCHEMICAL INTERACTIONS IN THIN FILM Pb—GaAs STRUCTURES UPON THERMAL ANNEALING

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Morphology and elemental and phase composition of Pb—GaAs contacts prepared by electroprecipitation of the metal and annealed in a hydrogen atmosphere are studied. It is shown that the interaction of the lead with the gallium arsenide occurs with participation of a liquid phase which appears at 100-300°C due to dissociation of the semiconductor and gallium diffusion into the metallic coating. The absence of complex ions of the $Pb_nGa_m(As_m)^+$ type in the secondary ion mass spectra of the contacts analyzed indicates that chemical interaction of the lead with gallium and arsenic does not occur.

This study will offer results of an investigation of the effect of thermal annealing on elemental and phase composition of Pb—GaAs contacts. These structures require study because of the use of lead in creating active superconductor components [1], ohmic contacts, and solders for gallium arsenide [2, 3].

Specimens were prepared from plates of electronic type gallium arsenide ($n_0 = 3 \cdot 10^{16} cm^{-3}$) oriented along planes (111)A, (111)B, and (110). Lead films ~0.3 μm thick were deposited at a temperature of 20°C from an electrolyte with composition (g/liter): $(PbCO_3) \cdot Pb(OH)_2$, 122; H_3BO_3, 106.5; gelatine, 3; HBF_4, 215 ml, pH < 6. Current density during film deposition was $5 \cdot 10^{-3}$ A/cm². Each specimen was thermally annealed once for 10 min in a hydrogen atmosphere in the temperature range 100-600°C. Elemental and phase compositions were studied with an MKh1303 mass spectrometer provided with an attachment for atomization of the material being studied [4]. The atomization was performed by a beam of Ar^+ ions with energy of 3.5 keV, current density of 2.5·10.6 A/cm², and beam diameter of 2 mm. The positive component of the secondary ion emission was recorded, containing mass lines corresponding to the basic components of the contacts (Ga^+, $Ga_2{}^+$, $GaAs^+$, Pb^+), together with ion complexes including oxygen (GaO^+, Ga_2O^+, PbO^+, $PbO_2{}^+$). That portion of the mass spectrum in which $Pb_nGa_m(As_m)^+$ cluster ions would appear was also analyzed. The mass spectra were recorded continuously over the entire target bombardment period. Crater depth was measured to an accuracy of 10% with a model B-26 profilometer-profilograph. Contact surface morphology was studied with an RÉM-200 scanning electron microscope.

The microphotographs shown in Fig. 1 indicate that for the electroprecipitation conditions chosen solid large crystal coatings are formed (Fig. 1a). Contact morphology changes significantly upon thermal processing. Beginning at 100°C the lead interacts with the gallium arsenide with participation of a liquid phase. This is evident from the formation of protuberances, the form and number of which depend on the crystallographic orientation of the gallium arsenide and the annealing temperature. The coating becomes inhomogeneous over its thickness, but remains continuous. The latter was confirmed by analysis of secondary ion mass spectroscopy data.

A unique feature of the secondary ion emission of Pb—GaAs structures thermally processed at low (100-300°C) temperatures is the anomalously high intensities of the Pb^+ and Ga^+ ion currents with Ga^+ ions being recorded from the very beginning of the atomization process (Fig. 2). The intensity of the Pb^+ current for specimens annealed at 100°C is 18 times that of pure cast lead under identical experimental conditions. As the annealing temperature increases ($T_{ann} \cong 400°C$) the intensity of the ion current decreases, reaching values corresponding to pure lead. For specimens thermally processed at 500-600°C there

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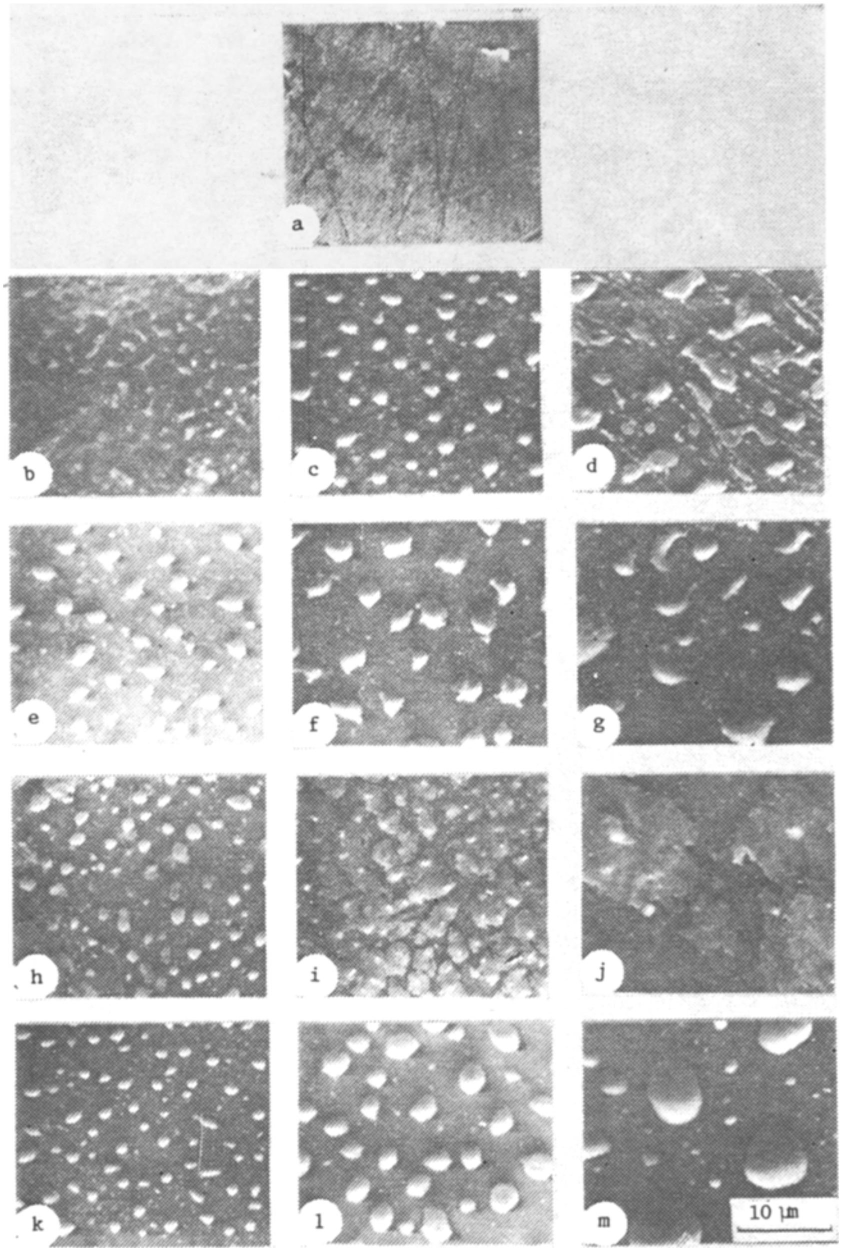

Fig. 1. Microphotographs of Pb–GaAs contact surfaces for various annealing tempratures, °C: a) unannealed; b, c, d) 100; e, f, g) 300; h, i, j) 400; k, l, m) 500. Crystallographic orientation of gallium arsenide surface in contact with lead: b, e, h, k) (111) A; a, c, f, i, l) (110); d, g, j, m) (111) B.

is a further reduction in I^+_{Pb}, while contact atomization time decreases also. The intensity of the Ga^+ ion current in the region of the Pb film increases with increase in T_{ann} from 100 to 300°C, decreases at 400°C, and increases again at 500-600°C, comprising 50% of I^+_{Ga} for atomization of gallium arsenide.

The mass spectra of freshly prepared structures contain PbO_2^+ ions, with the intensity of current from such ions decreasing as the annealing temperature is raised. Apparently upon cathode precipitation there occurs a partial passivation of the lead by oxygen dissolved in the electrolyte [5] and a precipitate containing oxides is formed. Thermal processing in a hydrogen atmosphere encourages change in the stoichiometric composition of the oxides, or at 550-600°C, their reduction to free lead. This process is revealed well by the change in intensity of PbO_2^+ and PbO^+ ion currents. At 100°C the ratio $I^+_{PbO_2}/I^+_{PbO} \cong 10^2$, decreasing to unity at 300°C. Further increase in annealing temperature leads to disappearance of PbO_2^+, while PbO^+ falls to the noise level at 600°C.

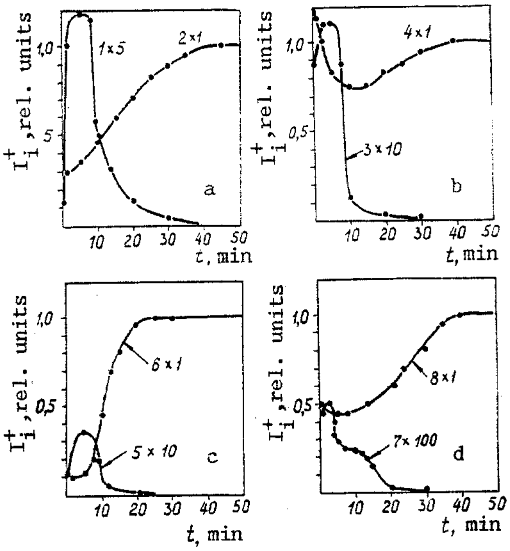

Fig. 2. Intensity of Pb^+ (1, 3, 5, 7) and Ga^+ (2, 4, 6, 8) secondary ion currents vs Pb–GaAs contact atomization time. Annealing temperature, °C: a) 1, 2 – 100; b) 3, 4 – 300; c) 5, 6 – 400; d) 7, 8 – 500.

The principles established permit certain conclusions regarding the physicochemical reactions which occur during preparation and thermal processing of contacts between gallium arsenide and an electrically precipitated lead layer. The presence of Ga^+ ions in the mass spectra of unannealed films indicates the presence therein of some quantity of Ga atoms. Dissociation of gallium arsenide and penetration of gallium and arsenic into the metallic coating have been observed for vacuum and galvanic deposition of a large number of metals [6]. It has been proposed that at low temperature diffusion occurs along grain boundaries in polycrystalline coatings. This is also the most probable mechanism in lead layers with a coarse crystalline structure. The interaction of lead with gallium arsenide with participtation of a liquid phase at T_{ann} = 100-300°C can only be explained by presence of free gallium. In fact, analysis of the Pb–GaAs state diagram [7] shows that the solubility of gallium arsenide in lead does not exceed 10^{-4} at.% up to temperatures of 400°C, while in the Pb–Ga state diagram [8] there is a eutectic at 29.7°C and a monotectic at 313°C, with the solubility of gallium in lead reaching 0.47 at.%. Addition of arsenic reduces the fusion point of lead [9].

The secondary ion mass spectroscopy method does not permit acquisition of reliable data on the behavior of the arsenic, since the As^+ mass lines are difficult to distinguish from the background of the similar mass Ga^+ signal which has a relative output approximately three orders of magnitude greater than the As^+ ion output. Nevertheless, it can be proposed that together with gallium, the arsenic also diffuses into the Pb layer, as has been observed in metal–GaAs contacts studied previously [6].

The anomalously high output of Pb^+ and Ga^+ from specimens thermally processed at low temperatures is caused by the known effect of increase in the secondary ion emission coefficient of elements in the presence of oxygen in oxides [10]. As the oxygen content decreases with reduction of the oxides upon thermal processing in a hydrogen atmosphere the Pb^+ output decreases. The complex dependence of I_{Ga}^+ on annealing temperature indicates that two competing processes occur: with increase in T_{ann} the quantity of gallium in the lead film increases, while the effect of secondary ion emission intensification due to oxygen is attenuated. The effect of oxygen becomes insignificant at $T_{ann} \geq 400$°C. Therefore beginning at some temperature the results of layer-by-layer secondary ion mass spectroscopy analysis correspond to a greater degree to the true distribution of elements over contact depth. Despite the anomalously high output of secondary ions upon atomization of the lead film containing oxygen, the intensity of the Ga^+ ion current increases significantly with movement of the atomization front through the phase boundary into the gallium arsenide region (Fig. 2). This fact permits the proposal that the microfusion phenomenon is not accompanied by exposure of a significant portion of the gallium arsenide surface, i.e., the coating remains basically continuous.

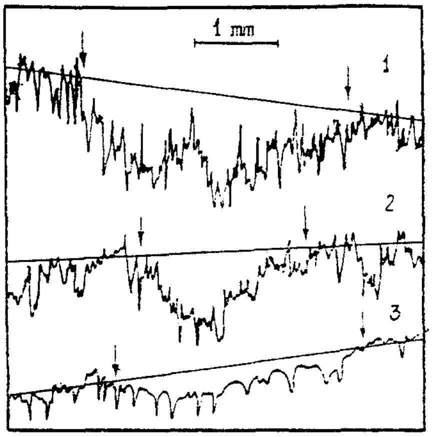

Fig. 3. Surface and atomization crater profilograms for (111)A Pb–GaAs contacts. Arrows delimit atomization crater. Annealing temperature, °C: 1, 100; 2, 400; 3, 600. Magnification along ordinate 4000×.

The decrease in Pb^+ ion intensity and Pb film atomization time at 500-600°C is related to lead desorption and decrease in coating thickness. At these temperatures Pb evaporation has also been observed in experiments on deposition of submonolayer coatings in a superhigh vacuum [11]. The effect of decrease in Pb film thickness as well as formation of complex contact relief during the reaction with liquid phase participation are illustrated well by the surface and atomization crater bottom profilograms shown in Fig. 3. The surface structure is especially well developed at low annealing temperatures, where the interactions apparently occur in local regions with an accumulation of free gallium.

The authors have demonstrated previously [12] that the presence in secondary ion emission spectra of metal–GaAs structures of $Me_nGa_m(As_m)^+$ cluster ions indicates formation of intermetallic compounds, while the stoichiometry of the ions having the highest intensity often corresponds to the stoichiometry of the phases that actually exist. In the secondary ion mass spectra of the Pb–GaAs contacts ions containing Pb in combination with Ga or As are absent at all annealing temperatures. Consequently, in this system during thermal processing formation of chemical compounds of lead with gallium and arsenic does not occur. Veen et al. [11] arrived at a similar conclusion on the basis of a study of electron structure of submonolayer lead coatings deposited on a (100) GaAs surface in superhigh vacuum. The results obtained correspond to the Pb–Ga, Pb–As, and Pb–GaAs state diagrams [7-9].

Within the limits of device sensitivity the secondary ion mass spectra and the principles of their change with thermal processing do not vary for specimens prepared on the (111)A, (111)B, and (110) faces of gallium arsenide. Apparently crystallographic orientation does not have a principal effect on the course of physicochemical reactions, but does determine the wettability of GaAs [13] and the morphology of contacts formed with these reactions.

Thus, the distinguishing feature of the interaction of thin lead films with gallium arsenide is the presence of a liquid phase at temperatures below the melting point of lead, which is related to dissociation of the semiconductor and diffusion of gallium into the metallic coating.

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TRANSIENT PHOTOCURRENTS ACCOMPANYING IRRADIATION OF CHARGED FILMS OF POLYTETRAFLUOROETHYLENE

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It was established experimentally that the transient photocurrents arising when PTFE films charged in a corona discharge are illuminated are reversible. It is shown that the transient current is of a thermal origin and is formed by the superposition of two oppositely directed components. The characteristics of the photocurrents are explained by the existence of internal polarization (heterocharge), arising in a strong field generated by the homocharge trapped on the surface, in the films. The existence of heterocharge in nonpolar films indicates that it is in principle possible to make stable electrets, in which the potential is maintained constant owing to slow self-consistent relaxation of the homo- and heterocharge.

The investigation of transient photocurrents is widely employed for studying the electret state of dielectrics as well as for diagnostics of the volume charge in them [1, 2]. In the standard technique electrodes are deposited on both sides of a flat charged dielectric; the electrodes are short-circuited and the current produced when one of the electrodes is illuminated is recorded. The transient current usually results from the motion of a heat pulse through the volume of the dielectric with a nonuniform charge distribution.

To study electrified films of polytetrafluoroethylene (PTFE) this technique is unsuitable, since the excess charge located in this polymer on the surface of the film or near it (homocharge) will be completely compensated by the induced charge of the nearest electrode [1]. As a result of this there is no electric response to irradiation of short-circuited charged PTFE films.

In this work the heat-pulse method [2] is substantially modified. The free (nonmetallized) surface of the dielectric is irradiated through a metallic, reticular electrode, located at a distance of 2-3 mm from this surface. Thus, unlike the classical scheme of Collins with short-circuited electrodes and zero mean field [2], the electric circuit was opened with an air gap, and the dielectric was located in a strong field generated by charges trapped during charging. The purpose of this work was to determine from an analysis of the transient photocurrents the relation between the homo- and heterocharge in PTFE films charged by means of a corona discharge.

An aluminum electrode was deposited on one side of the 10-μm-thick PTFE films by evaporation in a vacuum. The free surface was exposed to a corona discharge with negative polarity, excited by a sharpened tungsten electrode. The magnitude of the potential to

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