VERSITA DOI: 10.2478/eces-2013-0042 ECOL CHEM ENG S. 2013;20(3):579-599

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STUDY ON PROPERTIES OF ALLOYS WITH GALLIUM, ANTIMONY AND ZINC FROM RECYCLING

OCENA WŁAŚCIWOŚCI POCHODZĄCYCH Z ODZYSKU STOPÓW GALU, ANTYMONU I CYNKU

Abstract: Alloys with gallium, antimony and zinc, whose elements, metal constituent WEEE (they are specified for mobile phones) are particularly important for developing photoelectron devices, simple reproductive methods of producing p-n structures GaSb, also for production and construction of photo-wave cells in solar panels and they are also processes which develop ceramic semiconductors. In addition, these alloys represent possible substitute for standard lead-tin seam. For the complete definition of the properties of the ternary Ga-Sb-Zn system there were performed many researches of the alloys. The microstructures of the alloys were investigated by usage of SEM with EDS and optic microscopy. By usage of CALPHAD method there was detected the isothermal cross-section at 25ºC. The GaSb has similarities in the properties and behaviour with GaAs, and it is a potential material for the construction of the p-n diode, the photo-wave and thermo-photo-wave cells in solar panels and LCDs. Newly developed materials have been recommended as an adequate replacement for lead and arsenic, which are very dangerous and harmful metals.

Keywords: Ga-Sb-Zn alloys, characteristics and behavior, usage of new materials in LCDs, replacement of lead and arsenic

Introduction

Very rapid technological development creates the need for constant upgrading of information and technical systems, in order to achieve the appropriate technology requirements, while outdated systems are being been rejected. A wide range of obsolete electrical and electronic equipment global growth rate of 3 to 5% per year is making e-waste the fastest growing waste on the planet. According to UN estimates, the worldwide annual production is 20 to 50 million Mg of WEEE (*Waste Electrical and Electronic Equipment*), or 4,000 Mg per hour [1]. The problem is not only in quantity but also the toxicity of constituents of this waste that pose a grave danger to the environment and human health [2, 3].

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The concentration of metals in discarded WEEE or materials intended for recycling is much higher than the minimum of these metals in profitable ores [4]. The recycling of the metal parts of mobile phones and other WEEE (*Waste Electrical and Electronic Equipment*) can imply significant amounts of metals, which at the same time achieve the following strategic goals: saving natural resources, reduction of toxic materials emissions, removal of heavy metals from the natural environment, environmental protection and job creation.

In recent years, the subject of interest and study for many researchers is definition and characterization of alloys in the systems perspective which are multicomponent alloys. Achieved results represent basic, fundamental knowledge of new materials. Significant place in this research belongs to the ecological, lead-free solder materials [5, 6], materials for the development of photoelectron [7] and photo-wave devices [8] in the solar panels, as well as the development of ceramic materials for semiconductor [9]. In effort to use appropriate evaluation methods in the process of recycling metal, it is necessary to know the thermodynamic system characteristics, formed by combining the constituent elements of recyclable materials [10].

Some of the substances that are found in WEEE can be very useful; others may pose a potential threat to the environment [11, 12].

There is a significant importance of the ternary Ga-Sb-Zn system, as one of the GaSb-based systems, considering the development of optoelectronic devices. In order to develop a simple and reproducible method to fabricate p-n type of GaSb for opt electric devices, zinc diffusion into *n*-doped GaSb substrates was studied by Luo et al [13]. The Zn diffusion process was found to be a very suitable process for producing GaSb (Thermo) photovoltaic cells. In comparison to the other methods, the Zn diffusion process is much simpler from a technological point of view. Different Zn doping levels and post-growth annealing parameters were investigated [14]. Bracht et al [15] investigated self-diffusion of Ga and Sb in undoped GaSb and revealed that Ga diffuses faster than Sb by several orders of magnitude. The diffusion behaviour of Zn in n-type GaSb was investigated by Ye et al [16, 17] and Nicols [18]. Zheng et al [19] investigated zinc diffusion in tellurium doped GaSb, with the aim of constructing booster cell, while others have studied the possibility of fabrication and passivation of GaSb photodiodes [20]. Also, the topic of many researchers is a different ternary systems, as a possible lead-free solder materials [21], as well as usage of different methods to assess the durability of electrical solders [22]. The negative impact of heavy and toxic metals from lead-free solder joints has long been known [23], but recently many researchers got involved in LCA (*Life Cycle Assessment*) impact assessment of products for people and the environment [24]. Dervisevic et al [25] defines several quasi binary sections for the system, comparing obtained and predicted experimental values by using *Differential Thermal Analysis* (DTA). All these studies pointed out the importance of definition of ternary Ga-Sb-Zn system. The calculated isothermal section at 25ºC of ternary Ga-Sb-Zn system were done by applying CALPHAD method, using optimized thermodynamic parameters for constitutive binary systems which were included in database COST 531 [26].

Reducing pollution, global warming, impact on environment, natural resources and the use of cleaner technologies and sustainable development planning are only, some of a set of priorities that are crucial for the future of all humanity. People have become aware that they

can reduce production costs and reduce pollution from industrial waste, or discarded, old products, such as the discarded materials become raw material for the production of others.

A recycling is a dynamic process in which materials are normally intended to be used for disposal in landfills, aside from the general waste stream, which reduces the amount of material that is otherwise intended to be used for disposal, and the need for the original materials and natural resources.

Definition of phase diagrams and characterization of alloys that can be obtained in the recycling process as the final products, give us the ability to link two very promising and important processes, such as: recycling in the field of waste management and development of new environmentally friendly materials. Cognition of the behaviour and properties of new materials has the potential to rule out the use of toxic, hazardous and harmful materials and find adequate replacements by the same non-toxic or less hazardous materials, which is in accordance with the regulations and standards of the European Union.

Significant quantities of metals in the WEEE

In the close future, humanity will likely be forced to use recycled materials as a raw materials, due to the limited amount of natural resources. Using material obtained by recycling, multiple benefits can be achieved: it reduces the amount of waste for disposal, preserves natural resources and protects the environment. Concept consists of the appliance of cleaner technologies, energy efficiency and economy, which explores potential new ideas for sustainable development in the future.

Analyzing melted metal parts, whose parts in process of melting as one of the stages of recycling, make alloys, *ie* multicomponent systems, whose phase diagrams are crucial to define, in order to learn more about the properties and future application of these metallic materials, based on their characteristics.

Defining the phase diagram, multicomponent systems, whose elements are constituent of the WEEE, (specifically for mobile phones), knowledge physics, chemical, mechanical, electrical characteristics of multicomponent alloys is a step forward in understanding the characteristics and behaviour of new materials.

Experiment

The proposed, newly developed alloys for substitution of hazardous and harmful metals such as lead and arsenic were obtained by the used metal purity 99.999% gallium, antimony and zinc produced by Alfa Aesar (Germany). Alloys were experimentally investigated with different mole fractions of the constituent elements, in order to see which alloys that were tested show the best features, reliability and stability at elevated temperatures.

The samples mass weight of 4 g was prepared and cooled on air, in inductive furnace, in argon atmosphere. The samples of alloy are examined, prepared and homogenised on SEM-EDS analysis. Grinding and polishing samples were done by using traditional metallographic methods. Electron microscopy has been done on SEM (*scanning electron microscopy*), type JEOL (JSM-6610LV), which has a resolution of 10 nm at 25 kV and magnification to 300,000x, equipped with EDS (*energy dispersive spectrometer*) analyzer, type X-Max Large Area Analytical Silcon Drift by Oxford Instruments, served during the study to determine the total chemical composition of samples and the equilibrium phase.

The samples used for optic microscopy, electric conductivity measurements and hardness tests were prepared by classic metallographic procedure without penetration. Optic microscopy has been done by using Optic microscope OLYMPUS GX4, whose possible magnification is up to 10,000 times. Hardness was measured by Duroscope method using HL-400DL instrument, with a striking mechanism IMPAKT-D and microhardness was measured with Buehler Micro Met 5101 Vickers floor device 1600-5101VD (manufacturer Buehler, Germany). Electrical conductivity measurements were carried out with the apparatus Fisher SIGMASCOPE SMP 10 (Raises Electrical Conductivity Measurement to New Levels).

Results and discussion

Phase names used in this paper with phase names included in thermodynamic data [26] with their Pearson's symbols are listed in Table 1.

Table 1

Considered phases, phase's name in the thermodynamic data base and Pearson's symbols [27]

Phase common names	Thermodynamic database name	Pearson's symbol
L	LIQUID	*n/a*
(Ga)	ORT	*oC8*
(Sb)	RHOMBOHEDRAL_A7	*hR2*
GaSb	FCC_B3	*cF8*
(Zn)	HCP_ZN	*hP2*
β	BETA_SBZN	*oP16*
γ	GAMMA_SBZN	…
ε	EPSILON_SBZN	…
δ	DELTA_SBZN	…
ξ	ZETA_SBZN	*oI*[*]
η	ETA_SBZN	*oP30*

[*] - unknown number of atoms in elemental cell

(...) - marks that in listed ε and δ phases Pearson's symbols were not completely determined in literature and it can be either *hR22* or *oP28* (Bravais' lattice is either rhombohedral (*hR*) with 22 atoms in elemental cell or orthorhombic (*oP*) with 28 atoms in elemental cell).

Microstructure analysis

In order to determine microstructure of the alloys of the ternary Ga-Sb-Zn system the microstructures for numerous alloys were determined (twelve to be precise) and the compositions of the considered alloys were given with isothermal section at 25ºC on Figure 1.

Considered alloys compositions given in molar proportion are shown in Table 2.

The obtained microstructures samples were presented in Figure 2.

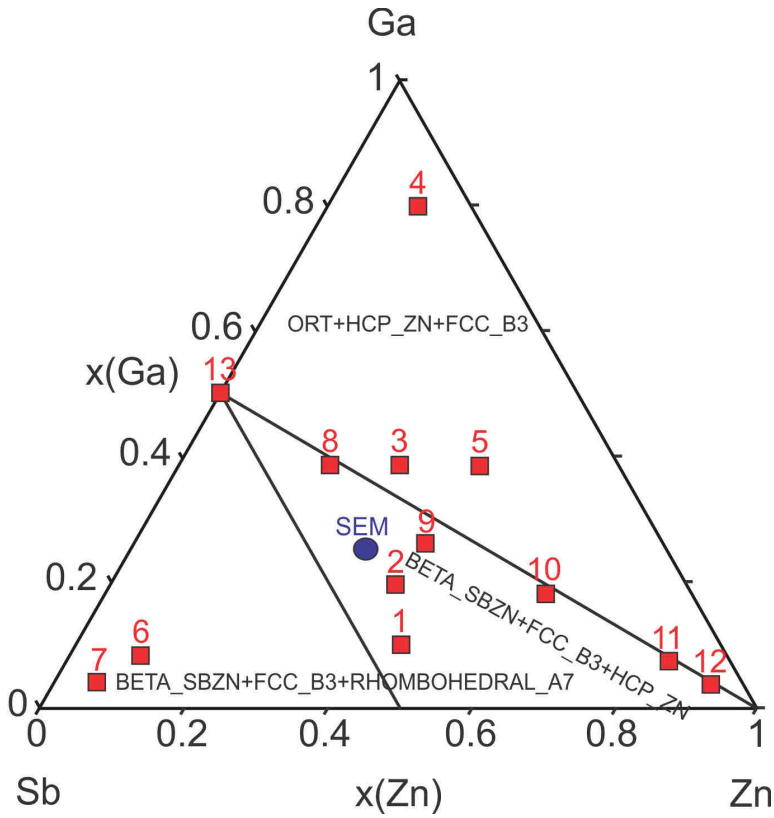


Fig. 1. Isothermal section at 25ºC

Table 2

Alloys compositions of ternary Ga-Sb-Zn system

Samples	x(Ga)	x(Sb)	x(Zn)
1.	0.1	0.45	0.45
2.	0.2	0.4	0.4
3.	0.4	0.3	0.3
4.	0.8	0.1	0.1
5.	0.4	0.2	0.4
6.	0.1	0.8	0.1
7.	0.05	0.9	0.05
8.	0.4	0.4	0.2
9.	0.3	0.3	0.4
10.	0.2	0.2	0.6
11.	0.1	0.1	0.8
12.	0.05	0.05	0.9
13.	0.5	0.5	0.0

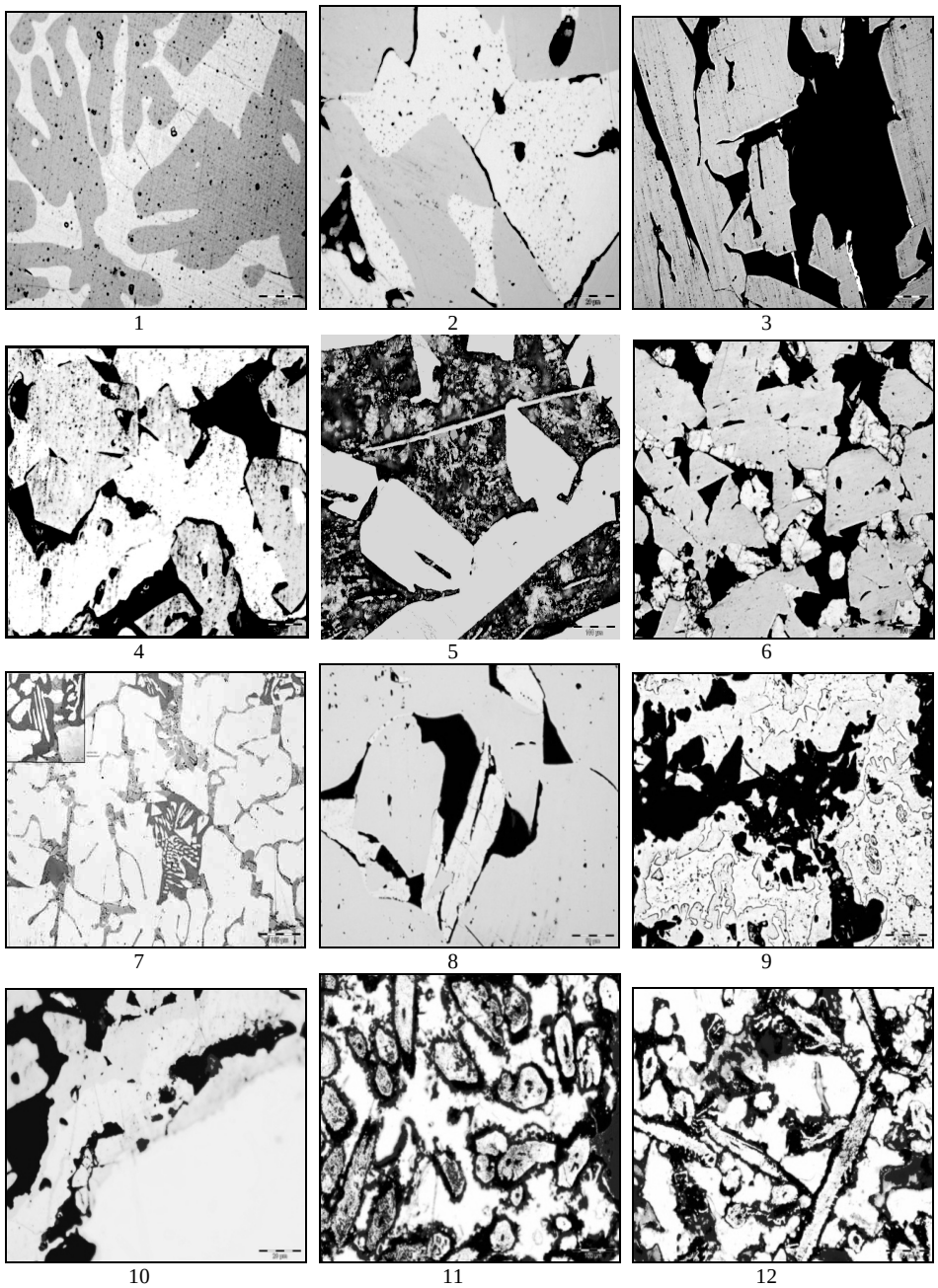


Fig. 2. Microstructures of alloys

Almost in every microstructure shown in Figure 2, existence of all three phases is evident. The brightest, lightest phase is rich in antimony, the darker phase is rich in gallium

and the darkest is rich in zinc. Estimated isothermal cross-section in 25ºC shows three bigger areas. All three areas shown in Figure 1 have three phases. Microstructures of relevant alloys, shown in Figure 2, are highlighted in Figure 1 and clearly show the presence of three phases.

In the next part, the alloy with molar ratio x(Ga) = 0.3, x(Sb) = 0.4 and with x(Zn) = 0.3 and the alloy with molar ratio x(Ga) = 0.8, x(Sb) = 0.1 and with x(Zn) = 0.1 were analyzed on SEM with EDS, and microstructure obtained was presented in Figure 3. There were three phases on the microstructure, and three compositions for each phase were analyzed. Based on the obtained results, the phases on the microstructure were marked in Figure 1.

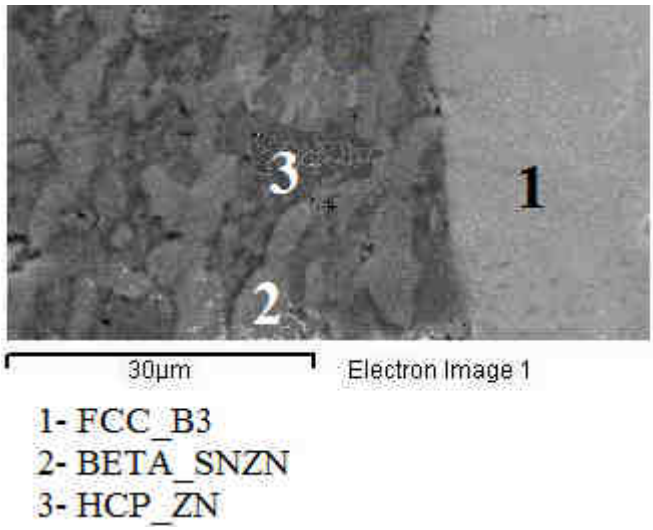


Fig. 3. Results of SEM-EDS analysis of the sample SEM

Table 3

Spectrum analysis of the investigated sample

Phase in the microstructure	Composition phase		
	Ga [%]	**Sb** [%]	**Zn** [%]
1-FCC_B3	44.79	45.21	0.00
2-BETA_SBZN	0.00	32.87	67.13
3-HCP_ZN	2.02	0.00	97.98

Electric conductivity of alloys

As the alloy's components in the ternary Ga-Sb-Zn system were not properly studied until now, the electric conductivity has been examined here. The electric conductivity consists of three vertical sections SbZn-Ga, GaZn-Sb and GaSb-Zn was examined. The compositions of the referring alloys and their electric conductivities were presented in Table 2. Three measurements were performed and then the mean value was calculated, the values obtained are shown in Table 4. Graphic dependence of mean values, electric conductivity depending on the molar share, is shown in Figures from 4 to 6.

Table 4

Alloys compositions and electric conductivity of the ternary Ga-Sb-Zn system

	Measurement 1 [MS/m]	**Measurement 2 [MS/m]**	**Measurement 3 [MS/m]**	**Average value**
x(Ga) *Vertical section Ga-SbZn*				
0	0.175	0.195	0.225	0.198
0.2	0.244	0.224	0.245	0.238
0.4	0.363	0.349	0.343	0.352
0.6	1.223	1.109	1.249	1.194
0.7	1.498	1.467	1.451	1.472
0.8	1.754	1.806	1.633	1.731
1	6.780	6.780	6.780	6.780
x(Sb) *Vertical section Sb-GaZn*				
0	2.328	2.375	2.269	2.324
0.2	1.499	1.379	1.553	1.477
0.4	0.754	0.694	0.782	0.743
0.6	0.625	0.590	0.626	0.614
0.8	0.427	0.422	0.402	0.417
0.9	0.340	0.360	0.377	0.359
1	2.880	2.880	2.880	2.880
x(Zn) *Vertical section Zn-GaSb*				
0	0.187	0.246	0.239	0.224
0.2	0.368	0.379	0.353	0.367
0.4	0.580	0.677	0.554	0.604
0.6	2.110	2.084	1.987	2.060
0.8	3.896	4.050	4.185	4.044
0.9	6.567	7.384	6.786	6.912
1	16.600	16.600	16.600	16.600

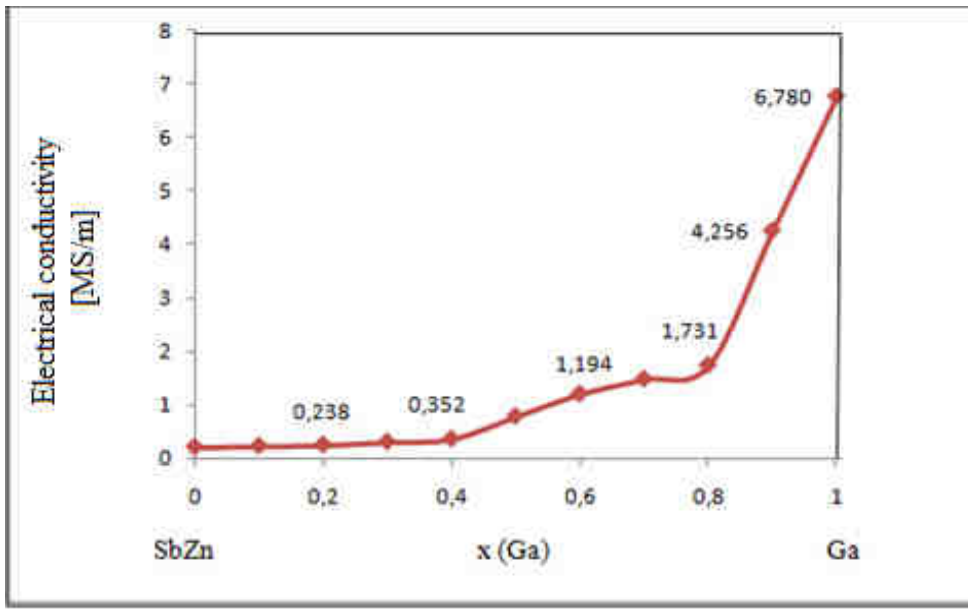


Fig. 4. The mean value of electrical conductivity alloys vertical section Ga-SbZn

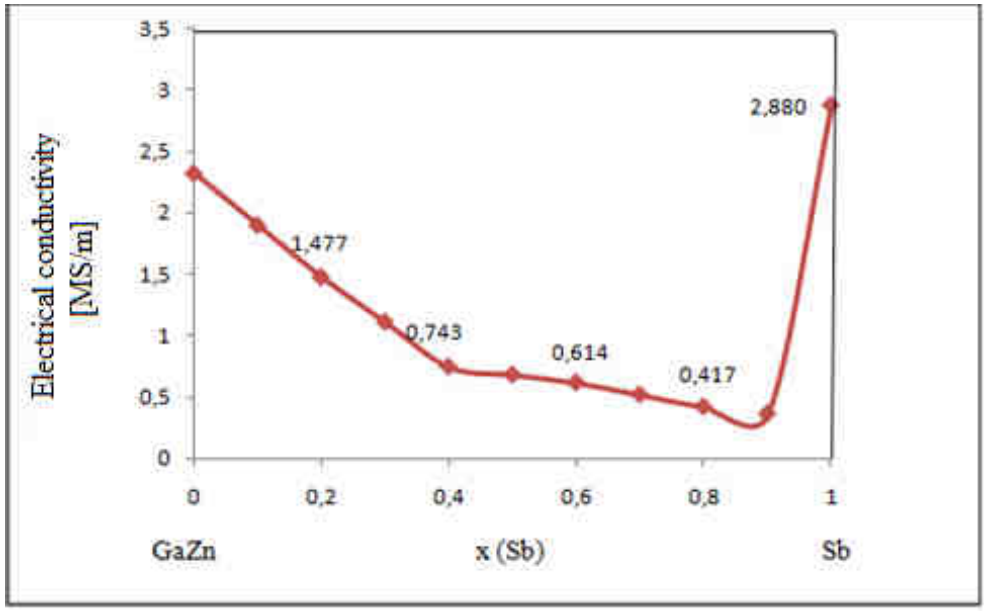


Fig. 5. The mean value of electrical conductivity alloys vertical section Sb-GaZn

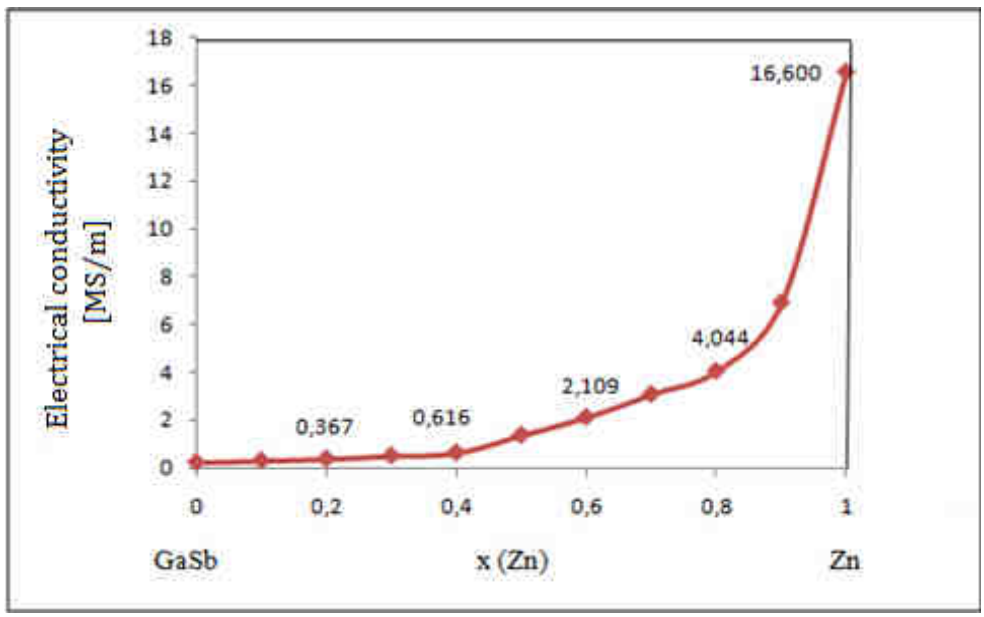


Fig. 6. The mean value of electrical conductivity alloys vertical section Zn-GaSb

Analyzing the diagram shown in Figure 4, which demonstrates electric conductivity for vertical section Ga-SbZn is presenting dependency of electric conductivity from molar concentration of gallium. It can be observed in a way that by increasing molar concentration of gallium the conductivity will increase too. Significant increase of electric conductivity is clearly obvious when molar concentration of gallium is more than 0.4 moles, while alloys with molar concentration of gallium are below 0.8 moles, electric conductivity increases linearly when increasing the molar concentration of gallium.

In contrast to previous situation, diagram shown in Figure 5 demonstrates electric conductivity for vertical section Sb-GaZn, which represents dependency of electric conductivity from molar concentration of antimony; we can see that when increasing molar concentration of Sb, the conductivity reduces. Significant decrease of electric conductivity is clearly obvious even with lower molar concentration of antimony; therefore with molar concentration of 0.5 Sb, electric conductivity decreases below 0.5 MS/m.

Results of electric conductivity of alloys obtained by vertical section Zn-GaSb in diagram shown in Figure 6 are the same as in previous two cases; the dependency of electric conductivity form molar concentration as shown, we can see that when increasing molar concentration of Zn in this case, conductivity also increases. Significant increase of electric conductivity which shows linear dependency from molar concentration of Zn is clearly obvious then molar concentration of zinc is higher than 0.4 mole and electric conductivity is the highest in a case of this vertical section. Based on experimentally determined electric conductivities of alloys for three vertical sections, the electric conductivity for all ternary Ga-Sb-Zn system was determined by usage of regression model [28]. Theoretic regression model can be presented in a form of multiplied quadratic regression:

$$\hat{Y} = b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \tag{1}$$

Unknown values of the coefficients of multiplied regression were determined by the least square method, *ie* from the condition that sum of the quadrates of errors:

$$S = S(b_1, b_2, b_3, b_{12}, b_{13}, b_{23}) = \sum_{i=1}^{N} \varepsilon_i^2 = \sum_{i=1}^{N} (Y_i - \hat{Y}_i)^2$$

$$S = \sum_{i=1}^{N} \varepsilon_i^2 = \sum_{i=1}^{N} \left[Y_i - (b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3)_i \right]^2 \tag{2}$$

is minimum. The coefficients of regression were determined and mathematic model is presented by the equation (1) and it could be written as:

$$\begin{aligned} \sigma(\text{MS/m}) = {} & 5.98\text{x(Ga)} + 2.36\text{x(Sb)} + 13.01\text{x(Zn)} - 9.99\text{x(Ga)x(Sb)} - \\ & 28.36\text{x(Ga)x(Zn)} - 27.78\text{x(Sb)x(Zn)} \end{aligned} \tag{3}$$

The marking of selected parameters from the regression mathematic model, and a confidence interval of individual regression coefficients is presented in Table 5.

In the diagram, the electrical conductivity Ga-Sb-Zn system is shown in Figure 7, we can see that the electrical conductivity of alloys depends directly on the alloy composition.

So for a selected conductivity values that need to be accomplished use the appropriate composition of the alloy.

Table 5

Estimation of the parameters for multiplied quadratic regression model of electric conductivity of the ternary Ga-Sb-Zn system and confidence intervals on the individual regression coefficients

Component	Coefficient Estimate	Standard Error	95% CI Low	95% CI High	t for H0	*p*	VIF
x1 (Zn)	13.01	1.18	10.50	15.53	11.04	0.0041	2.32
x2 (Ga)	5.98	1.35	3.1	8.87	4.42	0.0238	2.80
x3 (Sb)	2.36	1.18	–0.15	4.88	2.00	0.0915	2.32
x1x2	–28.36	6.26	–41.71	–15.02	–4.53	0.0227	3.07
x1x3	–27.78	6.14	–40.86	–14.70	–4.53	0.0227	2.82
x2x3	–9.99	6.26	–23.33	3.35	–1.60	0.1258	3.07

The mathematic model defined by equation (3) is presented as a graph in Figure 7.

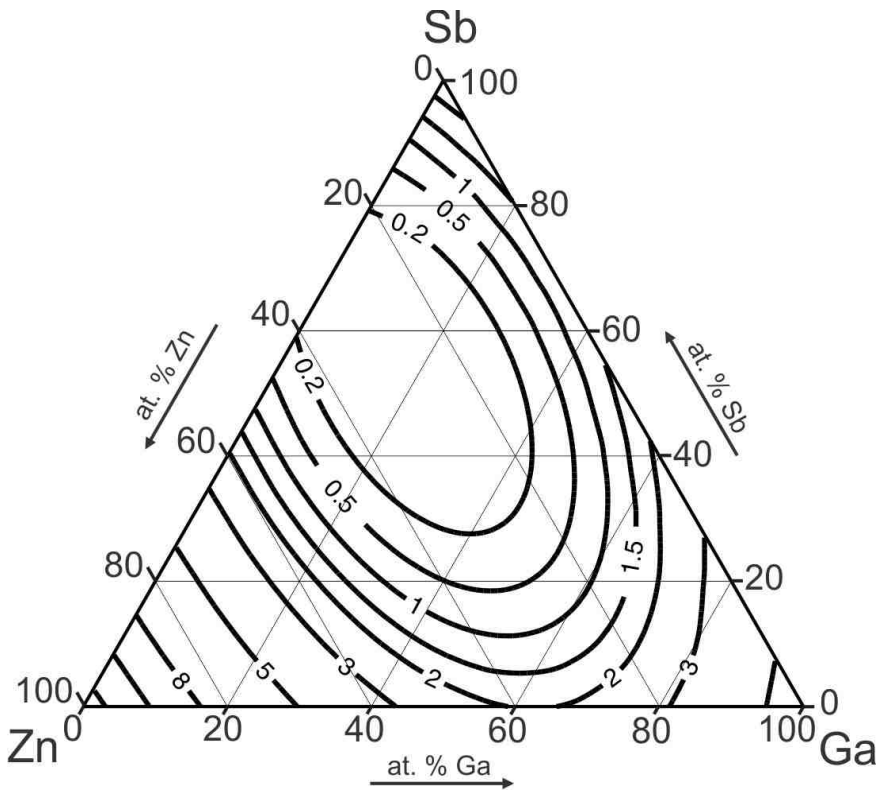


Fig. 7. Electric conductivity of the ternary Ga-Sb-Zn system: two-dimensional contour plot of Iso-lines

For quadratic model of multiplied regression given by equation (1), the quadrates of discrepancies of empiric values from regression equation; and sum of quadrates of

discrepancies were obtained SK = 37.20. As the absolute value of the highest discrepancies was ε_{max} = 3.586 and less than 3**E* = 3.90 so based on the three σ rule, the assumed functional dependence was considered accurate.

Mechanical properties

The hardness of alloys was determined by Brinell hardness. The hardness of alloys in three vertical sections of ternary Ga-Sb-Zn system: SbZn-Ga, GaZn-Sb and GaSb-Zn were examined. Each section starts from angle of one of the relevant elements - from ternary system, towards half of the opposite-binary, constructive system. Hardness is measured from three different points on the surface of the analyzed sample, and then the mean value of a found hardness is determined. Dependency of the measured hardness's and determined mean value in function of molar ratio is shown in the Table 6. Graphic dependencies of the hardness of vertical sections in function of molar ratio are shown in the Figures 8, 9 and 10.

Table 6

Hardness alloys of the ternary Ga-Sb-Zn system determined by Brinell method

	HB-measurement 1 [MN/m^2]	**HB-measurement 2 [MN/m^2]**	**HB-measurement 3 [MN/m^2]**	**Average value**
x(Ga) *Vertical section Ga-SbZn*				
0	245	252	267	255
0.1	237	231	232	233
0.2	97	95	99	97
0.4	61	62	59	61
0.6	59	57	60	59
0.8	56	59	55	57
1	60	60	60	60
x(Sb) *Vertical section Sb-GaZn*				
0	289	275	269	278
0.2	79	59	65	67
0.4	119	98	125	114
0.6	159	181	163	167
0.8	165	153	158	159
0.9	186	192	147	175
1	294	294	294	294
x(Zn) *Vertical section Zn-GaSb*				
0	145	165	143	151
0.2	51	55	45	50
0.4	52	44	56	54
0.6	68	65	73	69
0.8	67	73	86	75
0.9	298	312	300	303
1	412	412	412	412

Hardness by Brinell method is different for all three binary vertical sections depending on molar concentration of constructive elements. Alloys in which concentration of gallium is increasing have proportionally decreasing hardness which is considerably equalized after molar concentration of the 0.5 gallium. In the case of binary vertical alloys, with section in antimony angle, hardness is increasing with the increase of molar concentration of Sb from 0.2 to 0.6, while with higher molar concentration of antimony hardness is considerably equalized within the value 160 MN/m^2, a bit higher or lower in that range. In case of

vertical binary alloy samples, with section in zinc angle, hardness significantly decreases after 0.2 x(Zn), with a tendency of slight increase; although zinc is quite hard, after melting with other zinc components it loses its own hardness.

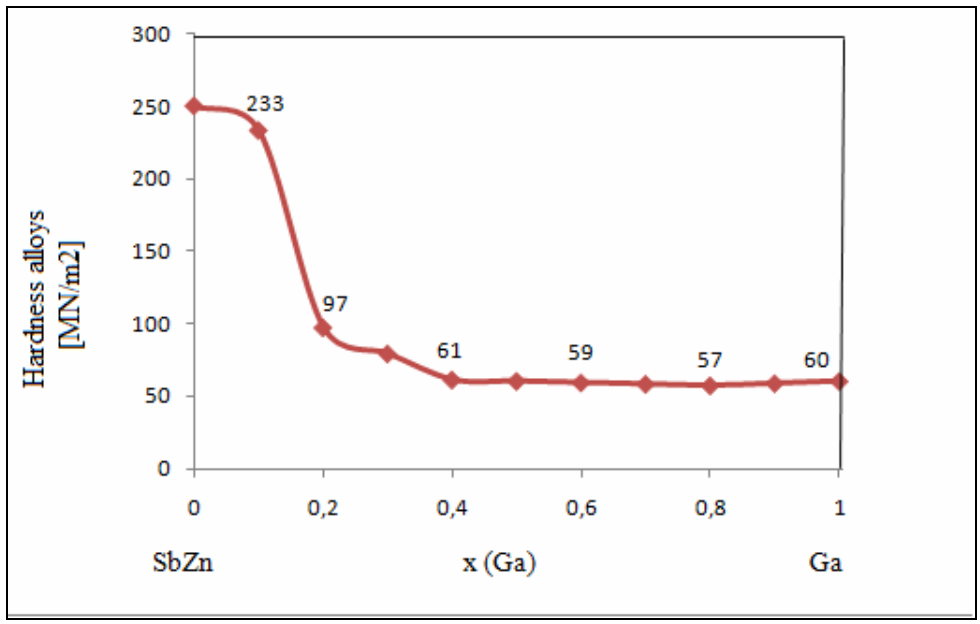


Fig. 8. The mean value of hardness alloys vertical section Ga-SbZn

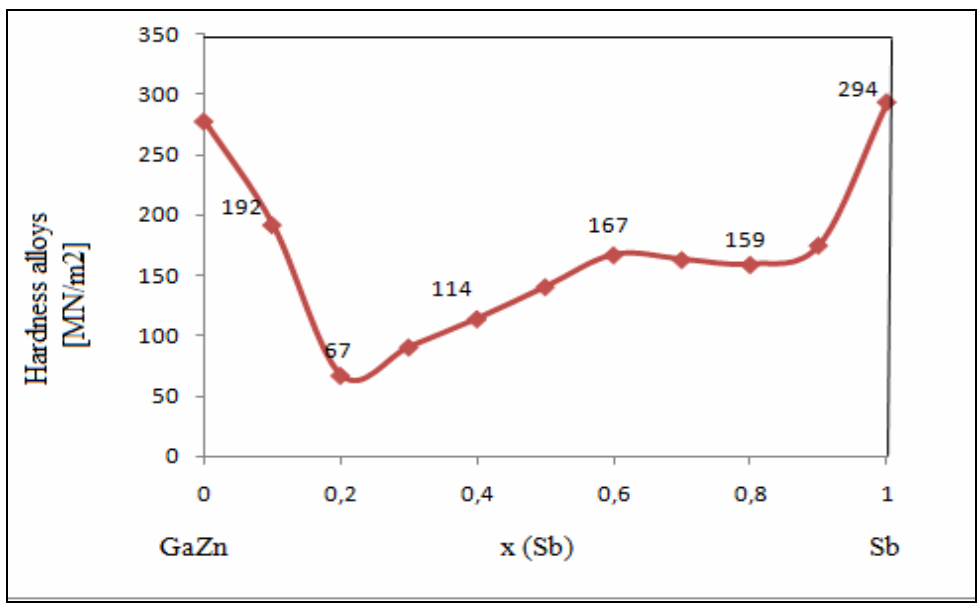


Fig. 9. The mean value of hardness alloys vertical section Sb-GaZn

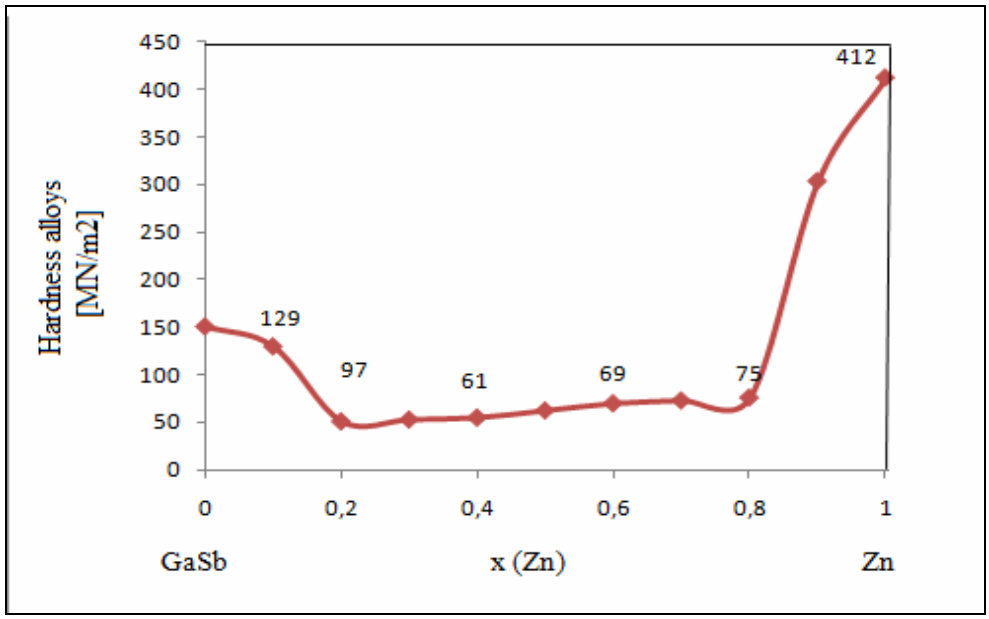


Fig. 10. The mean value of hardness alloys vertical section Zn-GaSb

For alloy's hardness by Brinell in the ternary Ga-Sb-Zn system is select Special cubic mixture regression Model:

$$HB(MN/m^2) = 321.68x(Zn) + 62.16x(Ga) + 258.1x(Sb) + 57.16x(Zn)x(Ga) - 189.07x(Zn)x(Sb) - 18.23x(Ga)x(Sb) - 3800.93x(Zn)\,x(Ga)\,x(Sb) \quad (4)$$

Estimation of the parameters for special cubic mixture regression model for alloy's hardness by Brinell in ternary Ga-Sb-Zn system and confidence intervals on the individual regression coefficients was presented in Table 7.

Table 7
Estimation of the parameters for special cubic mixture regression model for alloy's hardness by Brinell in ternary Ga-Sb-Zn system and confidence intervals on the individual regression coefficients

Component	Coefficient Estimate	Standard Error	95% CI Low	95% CI High	t for H0	p	VIF
x1 (Zn)	321.68	53.60	206.71	436.65	6.00	0.01	2.52
x2 (Ga)	62.16	62.66	–72.23	196.55	0.99	0.21	2.64
x3 (Sb)	258.09	53.60	143.13	373.06	4.81	0.02	2.52
x1x2	57.16	330.20	–651.05	765.38	0.17	0.44	4.10
x1x3	–189.07	304.07	–841.22	463.09	–0.62	0.30	4.24
x2x3	–18.23	330.20	–726.44	689.98	–0.05	0.48	4.10
x1x2x3	–3800.93	1760.27	–7576.34	–25.52	–2.16	0.08	5.85

Mathematical model defined by equation (4) was presented as graph in Figure 11.

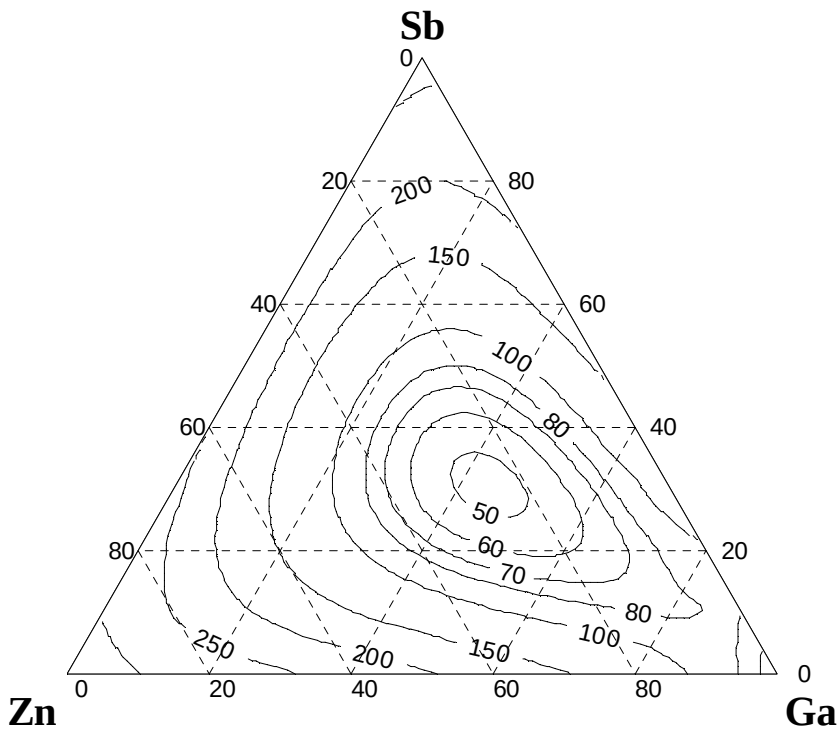


Fig. 11. Hardness by Brinell of the ternary Ga-Sb-Zn system: two-dimensional contour plot of Iso-lines

In the diagram, the hardness GaSbZn system is shown in Figure 11, we see that it is directly proportional to the hardness of alloy composition of the alloy. So the hardness values for the selected alloys that you need to make use appropriate alloy composition.

Combining the results of the diagram in Figure 7 and Figure 11, we can make some variations in selected alloys depending on their future application and the necessary electrical conductivity and hardness.

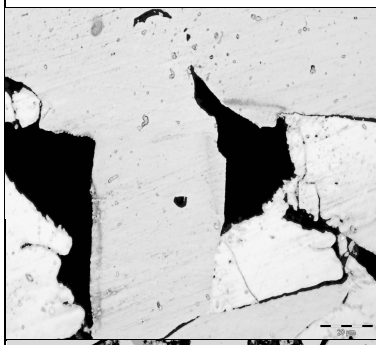
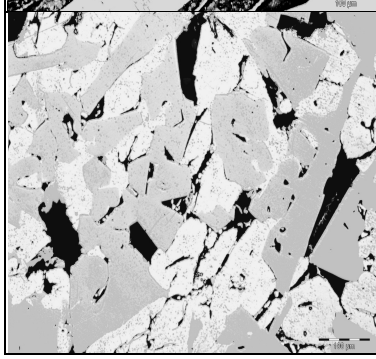
Table 8 shows the microhardness values for each phase. The tested samples were from different three-phase fields:

- sample 2 belongs to the phase field: FCC_B3 + HCP_ZN + BETA_SBZN;
- sample 5 belongs to the phase field: ORT + HCP_ZN + FCC_B3;
- sample 6 belongs to the phase field: BETA_SBZN + FCC_B3 + RHOMBO_A7.

Based on these results, we may conclude that the maximum hardness occurs that generally the darkest, black phase of the samples, corresponds to phases in which zinc occurs, in the form: HCP_ZN and BETA_SBZN, while the lowest hardness occurs ORT phase, which is characteristic of gallium. We concluded that the phases in which antimony appear in combination with other elements: FCC_B3 (GaSb) and BETA_SBZN (SbZn) are characterized by solid hardness.

Table 8

Measurement of microhardness ($HV_{0.025}$); Load: 25 gf (245.2 mN); Injection time: 10 s

Photos of microstructure	Samples	Nr. meas.	d_1 [μm]	d_2 [μm]	$HV_{0.025}$ [MPa]	$HV_{0.025\ av}$ [MPa]	Conversion [HB]
	Sample 2 brightest gray phase	1	10.4	10.6	420.5	**412.67**	**393**
		2	10.8	10.6	404.9		
		3	10.4	10.8	412.6		
	Sample 2 dark gray phase	1	14.3	14.3	226.7	**222.6**	**211**
		2	14.3	14.5	223.6		
		3	14.5	14.7	217.5		
	Sample 2 black phase	1	12.7	12.9	283.0	**275.8**	**261.5**
		2	13.2	12.8	274.3		
		3	13.5	12.7	270.1		
	Sample 5 brightest gray phase	1	10.3	10.7	420.5	**423.2**	**402**
		2	10.2	10.6	428.6		
		3	10.5	10.5	420.5		
	Sample 5 base-light gray phase	1	11.3	12.1	338.7	**318.9**	**304**
		2	11.9	12.9	301.5		
		3	12.3	11.9	316.6		
	Sample 5 base-dark gray phase	1	12.7	14.5	250.6	**251.9**	**240**
		2	13.5	13.7	250.6		
		3	14.3	12.7	254.4		
	Sample 5 base-black phase	1	9.1	9.9	513.7	**514.1**	**486**
		2	9.7	9.7	492.7		
		3	9.5	9.1	536.0		
	Sample 6 base-dark gray phase	1	10.5	10.5	420.5	**425.9**	**405**
		2	10.0	10.8	428.6		
		3	10.5	10.3	428.6		
	Sample 6 brightest gray phase	1	14.1	14.7	223.6	**234.5**	**223**
		2	14.0	14.0	236.5		
		3	13.8	13.8	243.4		
	Sample 6 black phase	1	8.7	7.9	672.9	**701.7**	**656**
		2	8.0	7.8	742.8		
		3	8.5	7.9	689.5		

Application of new alloys in LED technology and the development of new ceramic materials

Particular type of LED semiconductor diode is composed of the following components:

- LED chips with a hint of the structure of doped p-n junction;
- cathode and anode;
- reflectors.

The diode LED consists of a cathode luminescence of electron, or electron group that directs movement towards the electrodes of different voltages transferred from higher to lower energy levels and thereby emit light waves. The wavelength of the emitted light, and therefore the colour of light can be ultraviolet, visible or infrared and depends on the nature of the electron group formed p-n junction. The development of LED lighting begins with the appearance of infrared and red LEDs with gallium arsenide.

New materials have enabled the conquest of LEDs that produce light in colour. These are the LED light sources constructed from p-n chip covered with sediment emission of metal alloy IIIa and group Va of the periodic table: Ga, Al, In, As, P, Sb and Zn. Compounds and alloys of these elements have a direct energy gap, which is necessary in this case, because otherwise large no radiation recombination.

Ternary Ga-Sb-Zn system belongs to the group of systems that can be used for development of photoelectron devices. It has been thoroughly experimentally tested and analyzed [25] temperatures of phase transformations and all phases of the system have been determined and the whole system has been completely defined. GaSb based systems are of particular importance. They have been extensively studied in order to develop simple reproductive methods for production of p-n GaSb structures, for application in solar panels and for production and construction of photo-wave and thermo-photo-wave cells. The great similarity of GaAs with GaSb and Zn-diffused in n-doped GaSb substrates at a temperature of 300ºC, qualify these systems as an adequate substitute for a GaAs material in LCDs. Application of GaSb in LCDs instead of GaAs would exclude As from use and eliminate its negative effects on the environment and human health. The thin films of GaSb from the discarded LCDs, in the future could be used in production of photo-wave and thermo-photo-wave cells for solar panels, which is consistent with the concept of recovery and reuse of the individual components, in order to reduce the amount of materials intended for recycling or final disposal. The Ga-Sb-Zn system has also recently been investigated in connection with development of ceramic semiconductor.

The diagrams in this paper (Figs. 7 and 11) represent characteristic electrical conductivities and hardness of alloys of the ternary Ga-Sb-Zn system, whose constituent elements can be found in metal parts of mobile phones and other WEEE. The results of investigation of thermal, structural, mechanical and electrical properties, reliability and durability of these alloys suggest that they might represent an adequate material for the development and construction of p-n junction. GaSb is a potential material for the production of thin films for LCDs and also is adequate material for construction of the p-n diode as well as photo-wave and thermo-photo-wave cells in solar panels.

Properties, behavior, and thus application of Ga-Sb-Zn alloys just depend on the chemical composition and the molar fraction of the individual components in the alloy. Alloys with a higher content of Sb, possess properties of ceramic materials and are hard and brittle.

Therefore by changing the contents of individual constituent elements, we can influence the properties of alloys. Changing the behavior of alloys depending on the mole fractions of the constituent elements is shown in Figure 7 and Figure 11, which connects the properties of alloys, in this case the electrical conductivity and hardness with the alloy composition.

On the basis of known and already mentioned, obtained results confirm that:

- A very good agreement between predicted (thermodynamic calculation) and experimental values defined triple phase diagrams of the system Ga-Sb-Zn.
- Certain liquidus surface and the composition of equilibrium and intermetallic phases.
- Isothermal section.
- As well as on the characterization of properties and behaviour of the examined Ga-Sb-Zn alloys.
- Then, the similarities GaAs with GaSb not only behavioural traits and characteristics, but also in the thermodynamic state diagrams; imposes the idea of a possible application of Ga-Sb-Zn alloys to produce LEDs and injection laser diodes (Fig. 12).

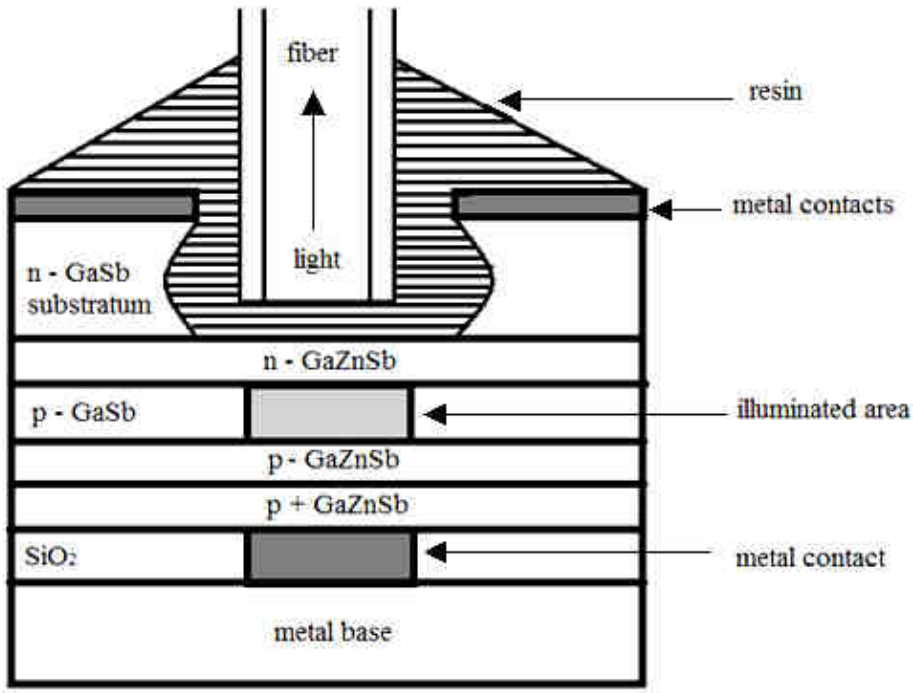


Fig. 12. LED structure with surface radiation

With both sides set the active layer by one layer of semiconductor with larger energy gap, a lower index of refraction. In this way, the potential barriers in places of heterojunction fully localize injected carriers within the active layer. At the same time, it was formed as an active waveguide region and has a higher refractive index than the surrounding layers, and the realized localization of photons in the active region. This multilayer structure is called heterostructures (Fig. 13 a, b). In addition to thickness and widths of the active region should be as small as possible to the current threshold to a minimum, and to deliver better focus radiation.

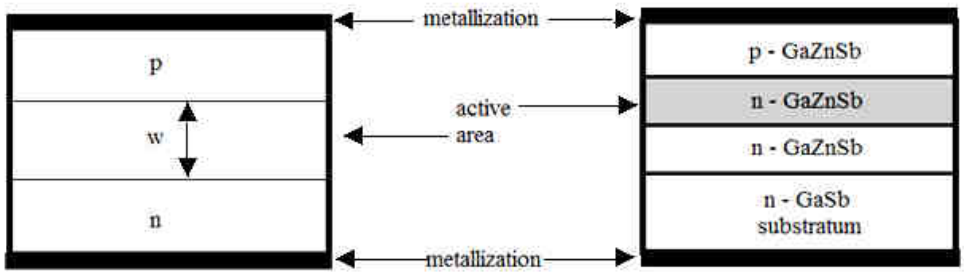


Fig. 13. Structural views of laser diodes: a) as simple pn junction and b) as heterostructures

Good diffusion of zinc in the doped layer GaSb, also recommends Ga-Sb-Zn alloys as very good ceramic materials.

These elements are part of recycled mobile phones and can be used in LED technology and the new ceramic materials. The aim of this study was the use of waste materials and developing new materials that have significant potential applications.

Zn-diffused n doped GaSb layer (substrate) and similar materials [29] are recommended as a replacement material for GaAs devices in the LCD. This substitution is very significant, because of possible discharge of hazardous materials from LCDs into the environment and for their future recycling [30].

Suggested and newly developed alloys for substitution of hazardous and harmful metals such as arsenic, were obtained from the metals of 99.99% purity. Alloys were tested with different mole fractions of the constituent elements, in order to see in which composition of components tested alloys exhibit the best properties, reliability and stability at elevated temperatures.

Conclusion

Environmental protection is a priority and complex problem, implemented in all areas of human activity that should complement one another and build on. Therefore, the definition and study of the behaviour of multicomponent systems that may arise in the process of recycling of WEEE is very important, not only in terms of utilization of waste materials and reduce emissions of pollutants, but also the possible substitution of some hazardous and harmful, non-toxic or less hazardous.

Alloys characterization in perspective systems represents the first necessary step towards development of new lead-free solder materials, ecological materials, which might have a broader application. Analyzing characteristics, behaviour, application and reliability of new materials are permanent subject of examination for many researchers.

The microstructures of the alloys of ternary Ga-Sb-Zn system are presented in this paper. Phases in microstructures show good agreement with calculated phases at 25ºC. That was confirmed by SEM - microstructure, for which the analysis was done in single point for all existing phases. Based on previous research and results we conclude that the alloy Ga-Sb-Zn could be an adequate replacement, not only with lead solder materials, but also possible adequate replacement for gallium arsenide in the LCD screens of mobile phones,

computers and other modern devices using TFT-LCD (*thin film liquid crystal display*) technology in order to improve image quality (*eg* addressability, contrast).

Acknowledgements

This research is conducted a part of the Project N^0 III 43007 Global Climate Change Impact the Environment: Adaptation, Mitigation; and N^0 TR 37016 Lead and zinc production impact the Environment; supported by the Ministry of Education and Science of the Republic of Serbia.

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OCENA WŁAŚCIWOŚCI POCHODZĄCYCH Z ODZYSKU STOPÓW GALU, ANTYMONU I CYNKU

Abstrakt: Stopy zawierające gal, antymon i cynk, będące metalicznymi składnikami e-odpadów (są wykorzystywane zwłaszcza w telefonach komórkowych), są szczególnie ważne w budowie urządzeń fotoelektrycznych, w wytwarzaniu struktur p-n GaSb, także w produkcji ogniw fotowoltaicznych i w wytwarzaniu półprzewodników ceramicznych. Ponadto stopy te mogą zastąpić standardowe stopy ołowiowo-cynowe. Dla pełnego określenia właściwości trójskładnikowego układu Ga-Sb-Zn badania stopów przeprowadzono w wielu powtórzeniach. Mikrostruktury stopów badano z wykorzystaniem SEM z EDS i mikroskopii optycznej. Dzięki wykorzystaniu metody CALPHAD stworzono diagram fazowy dla temperatury 25ºC. GaSb wykazuje podobne właściwości i zachowanie do GaAs, a to stwarza możliwość wykorzystania tego stopu do budowy diod p-n, elementów fotoelektrycznych i termofotoelektrycznych, wykorzystywanych w panelach słonecznych i LCD. Nowo opracowane materiały są zalecane jako odpowiednie zamienniki ołowiu i arsenu, które są metalami bardzo niebezpiecznymi i szkodliwymi.

Słowa kluczowe: Ga-Sb-Zn, właściwości i zachowanie, wykorzystanie nowych materiałów w technologii LCD, zastąpienie ołowiu i arsenu