DETERMINATION OF GALLIUM IN SEMICONDUCTING ALLOYS BY OSCILLOGRAPHIC POLAROGRAPHY

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There are a number of difficulties connected with the polarographic determination of gallium. In particular, slight variations in acidity lead to changes in or to suppression of the gallium wave. The waves obtained at normal temperature in a potassium thiocyanate solution [1] are not very suitable for analytical purposes.

We have developed a method for the analysis of semiconducting alloys containing tenths of a percent of gallium. For analysis we used spectrographic standard pellets, 50-200 μ in diameter. These standards were produced by Sotnikov and his collaborators [2] by passing alloy of the required composition through a capillary in heated silicone grease. By chemical analysis it is possible to ascertain whether the same uniform distribution of the components in the molten alloy is retained in the pellets, i.e., whether they can be used as standards for microspectrographic analysis.

The work was carried out on an OP-1 oscillographic polarograph where the voltage supply was synchronized with the removal of the drop. A slowly dropping mercury electrode was used as cathode, with m = 0.326 mg/sec and t = 25 sec. The anode was the mercury at the bottom of the cell. When a solution of 0.1 N sodium salicylate + 0.1 M sodium chloride was used as supporting electrolyte [3] the peak obtained was indistinct, it was displaced by pH variations of ± 0.1, and the reproducibility was low.

We used a 0.2-M solution of tetraethylammonium iodide as supporting electrolyte. For its preparation 1.53 g tetraethylammonium iodide was dissolved in 30 ml alcohol (1:4). With this electrolyte gallium forms a distinct, easily reproducible wave with a peak at E = -1.70 V (relative to a normal calomel electrode). Figure 1 shows the polarographic wave for gallium obtained by cathodic polarization of the electrode-electrolyte system using 3.2 × 10^{-4} g/liter gallium in a 0.2-M alcoholic solution of tetraethylammonium iodide. The oscillopolarogram was recorded with a voltage variation rate of 0.5 V/sec, a sensitivity of 1 μA/cm, and a delay of 6 sec.

The line of the supporting electrolyte was readily reproducible at pH values of four or greater. The residual acidity of the analyzed solutions gave pH values of 5-6.

A standard gallium solution was prepared by dissolving a 2-mg sample in 5-10 ml hydrochloric acid (1.19), and the solution was evaporated to dryness. The dry residue was dissolved in the supporting electrolyte and transferred to a 250-ml measuring flask.

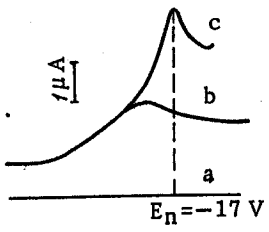

Fig. 1

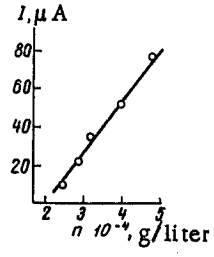

Fig. 2

Fig. 1. Oscillographic polarograms for gallium: a) zero line; b) supporting electrolyte line; c) oscillopolarogram for gallium.

Fig. 2. Calibration curve for gallium determination.

TABLE 1. Results of Analysis of the Investigated Mixtures

i for pure soln., μA	Amount added, g/liter × 10^{-3}		i av after additions, μA	n	S^2	S	Variation coeff., %
In	Sb	Ga	In				
3,3	2—6	—	3,0	3	0,045	0,21	7,0
3,3	2—6	0,16—8	3,2	4	0,040	0,20	6,2
Sb	In	Ga	Sb				
3,1	20—80	—	3,1	3	0,010	0,10	3,2
	80	0,16	3,0	3	0,070	0,26	8,6
Ga	In	Sb	Ga				
5,0	20	—	4,9	3	0,010	0,1	2,1
5,0	20	40—80	5,0	4	0,060	0,24	4,8

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TABLE 2. Results of Analysis of Semiconducting Alloys

System	Pellet diam., μ	No. of pellets	Found, % In	Found, % Sb	Found, % Ga	n	S^2	S	Variation coeff., %
In–Ga	200–300	1	99,4	—	0,45	9	0,0041	0,064	14,2
	200–300	10	99,2	—	0,44	3	0,0007	0,027	6,1
In–Ga	140–160	1	99,0	—	0,49	3	0,0021	0,046	9,4
	140–160	10	99,2	—	0,48	3	0,0001	0,010	2,1
In–Sb–Ga	180–240	1	97,6	1,0	0,95	3	0,0175	0,132	13,8
	180–240	10	97,3	1,1	1,2	3	0,010	0,1	8,3
In–Sb–Au–Ga	Ingot	—	31,1	—	0,54	5	0,0067	0,082	15,2
In–Pb–Bi–Sb–Au–Ga	»	—	40,0	—	0,31	3	0,0004	0,020	6,4

Note. The statistical method was only used to calculate the results for gallium.

Aliquot portions of the solution—0.2, 0.3 ml., etc.—were taken for construction of a calibration curve and diluted to 5 ml with the supporting electrolyte; polarograms were then taken.

The calibration curve was constructed for the concentration range 2×10^{-4} to 1×10^{3} g/liter (Fig. 2). It did not pass through the origin, possibly due to the adsorption nature of the gallium reduction.

To determine the reduction mechanism, besides setting up a whole series of additional experiments, it is necessary to investigate a wider range of concentrations. However for our purposes the concentration range examined was sufficient.

The effects of indium and antimony on the oscillopolarographic determination of gallium were determined. Analysis of artificial mixtures showed that they do not interfere. The oscillopolarograms for indium and antimony were recorded by a method we developed earlier [4] against a supporting electrolyte of 1 N hydrochloric acid. The gallium wave does not appear in this electrolyte. The results from the analysis of artificial mixtures are given in Table 1.

The gallium content of the samples was not greater than 1%, and the pellets weighed 0.1-0.05 mg.

Each pellet was dissolved by heating in 2-5 ml hydrochloric acid (1.19), and the solution was transferred to the polarographic microcell and made up to 7 ml.

To determine the indium and antimony contents of the alloys a separate sample was taken, fused with $KHSO_4$, and leached with a mixture of acids. Oscillopolarograms for indium and antimony were taken against a supporting electrolyte of 1 M hydrochloric acid.

When gallium was determined in alloys containing gold, lead, and bismuth the pellet was dissolved in nitric acid (1.4), and the solution was evaporated to dryness. On dissolving in the supporting electrolyte, a precipitate was formed, which dissolved when the solution was acidified slightly.

The analytical results from semiconducting alloys are shown in Table 2. The results were calculated by a statistical method, and the variation coefficient was not greater than 15%.

LITERATURE CITED

1. V. A. Tsimmergakl and A. M. Vovnenko, Ukr. Khim. Zhurnal, 20, No. 5, 564 (1954).
2. V. S. Sotnikov et al., Proceedings of Conference on the Analytical Chemistry of Semiconductors [in Russian], Kishinev (1965), p. 71.
3. E N. Vinogradova and N. N. Chudinova, Zavod. Lab., 22, 1280 (1956).
4. Yu. S. Lyalikov and L. S. Kopanskaya, Ukr. Khim. Zhurnal, 30, No. 1, 91 (1964).