Determination of trace amounts of copper and lead in gallium arsenide crystals by anodic stripping voltammetry with mercury drop semimicroelectrode

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Trace amounts of Pb and Cu were determined in gallium arsenide crystals by anodic stripping voltammetry on mercury drop electrode. Two types of electrodes were used: electrode of conventional dimension ($r = 440$ μm) and semimicroelectrode ($r = 80$ μm). The GaAs samples were dissolved in the mixture HCl—HNO$_3$ ($\varphi_r = 2:1$) and analyzed. The detection limits of Cu and Pb for the macroelectrode were 13 ng cm^{-3} and 37 ng cm^{-3}, respectively, those for the semimicroelectrode were 6 ng cm^{-3} and 13 ng cm^{-3}, respectively. The reproducibility of the results was about 10 % for both types of electrodes. The accuracy of the results was checked by graphite furnace AAS.

Методом инверсионной вольтамперометрии на капельном ртутном электроде определены следы свинца и меди в кристалле арсенида галлия. Использовались два типа электродов: электрод обычных размеров радиуса 440 мкм и полумикроэлектрод радиуса 80 мкм. Пробу арсенида галлия растворяли в смеси хлористоводородной и азотной кислот ($\varphi_r = 2:1$) и анализировали. Предел обнаружения при электроде обычных размеров был 13 нг см$^{-3}$ (медь), 37 нг см$^{-3}$ (свинец) и для полумикроэлектрода 6 нг см$^{-3}$ (медь), 13 нг см$^{-3}$ (свинец). Относительное стандартное отклонение было не более 10 % для обоих типов электродов. Правильность результатов была подтверждена сравнением с методом ААС.

Gallium arsenide is considered to become the material of future in electronics since it exhibits excellent electronic and optoelectronic properties. The utility of gallium arsenide for microelectronics and optoelectronics arises from its suitable electrical behaviour, broad temperature working range, resistance against radiation.

Impurities in amount 1 ppm or even lower can deteriorate the suitable properties of GaAs crystals. Undoped GaAs crystals obtained by the liquid--encapsulated Czochralski technique could contain impurities of $w < 10^{-8}$ [1]. The use of analytical methods with high sensitivity and reliability is therefore demanded for the control of impurity levels in the GaAs crystals.

Various methods have been used for the bulk as well as for the local analysis of GaAs crystals. Fig. 1 depicts a block diagram of possible procedures in the analysis of GaAs.
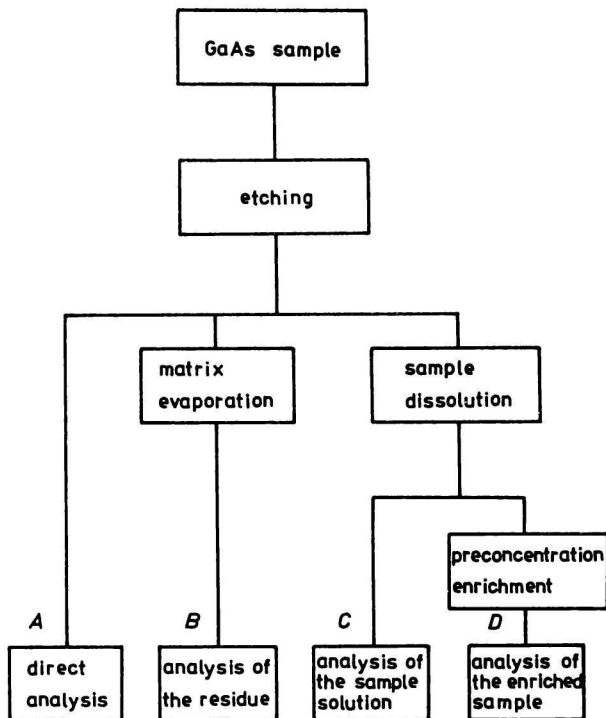

Fig. 1. Block diagram of the GaAs analysis.

The sample etching with mixtures of acids is inevitable to remove surface impurities like O, Ca, Na, Si, *etc.* which can easily be deposited by air contamination.

The most challenging way in the analysis of GaAs is the use of direct methods like SIMS [1], activation analysis [2—5], solid sampling thermoelectric graphite furnace atomic absorption spectroscopy (GF AAS) [6, 7]. The disadvantage of these methods is high costs and the need of reference materials.

Route *A* in Fig. 1 represents a direct way without influence of matrix and route *B* represents a simple way for matrix removal through matrix evaporation. *Beinrohr* [8] has described a method based on the evaporation of the matrix with bromine vapours. The matrix can also be evaporated with chlorine in argon [9].

In the bulk analysis of GaAs the most commonly used route is through sample dissolution in a mixture of acids or in a hydroxide. The dissolved sample

is then analyzed directly (route C) or after the separation of the matrix from the treated trace elements (route D). For the direct analysis of the sample solution, spectrophotometry [10—12], atomic emission spectrometry [13], flame or electrothermal AAS [7—9, 14—21], voltammetry [11, 13, 22—24] are commonly used. For the separation of the matrix liquid—liquid extraction, matrix evaporation, separation on ionexes, coprecipitation [1, 25—27] have been used.

This paper presents a procedure for the determination of Cu and Pb traces in GaAs crystals by anodic stripping voltammetry on hanging mercury drop electrode of conventional dimension and hanging mercury drop semimicroelectrode. Our objective was to elaborate a simple but reliable method for the routine analysis of high-purity GaAs materials.

Experimental

The voltammetric measurements were performed on the PA-3 polarographic analyzer (Laboratorní přístroje, Prague) equipped with the static mercury drop electrode SMDE-1 (Laboratorní přístroje, Prague). Two sizes of electrode were used: mercury drop electrode of conventional dimension with a radius $r = 440$ μm (macroelectrode) and mercury drop semimicroelectrode ($r = 80$ μm).

When using the macroelectrode as the working electrode the three-electrode system was used: platinum auxiliary electrode (Radelkis, Budapest) and the reference calomel electrode with 4 M-NaCl. In the measurements with the semimicroelectrode the two-electrode system with a calomel electrode (4 M-NaCl) as reference electrode was used.

The control measurements were carried out on a double-beam atomic absorption spectrometer AAS 3 operating in the single-beam regime with deuterium lamp background compensation. The spectrometer was equipped with the EA-3 graphite furnace and MPE autosampler (all Zeiss, Jena). Pyrolytically coated graphite tubes (Zeiss, Jena) were used. The operating conditions and the procedures were the same as in Ref. [16].

Anal. grade purity reagents and distilled deionized water (DDW) were used in the experiments. The hydrochloric acid was prepared by isothermal distillation in a PTFE vessel. The nitric acid was purified by subboiling distillation in a quartz apparatus. The laboratory ware was cleaned with acids and DDW and then steamed with HNO_3 in a cleaning device [28, 29] for 4 h. All the operations with the solution and samples were carried out in a box with laminar flow of filtered air (Služba, Žilina).

The GaAs samples were dissolved in a quartz beaker: To 1 g sample 10 cm³ of a mixture of concentrated HCl and HNO_3 ($\varphi_r = 2:1$) was added and on mild heating the sample was dissolved. The sample solution was transferred to a quartz volumetric flask and its volume was adjusted to 100 cm³ with DDW.

For the analysis 10 cm³ sample solution was pipetted to the electrochemical vessel. Oxygen in the solution was removed by bubbling oxygen-free nitrogen through the sample solution for 10 min.

Results and discussion

In the analysis of GaAs by anodic stripping voltammetry the following problems had to be cleared: i) sample dissolution, ii) adjustment of the sample solution pH, iii) deposition time and iv) the influence of dissolved oxygen on the determination of copper. For the analysis the static drop macroelectrode and semimicroelectrode were tested.

Various methods for the dissolution of GaAs are known. The simplest way is to dissolve it in a mixture of HCl and HNO_3. The high acidity of the resulting sample solution was decreased either by diluting the sample solution with DDW or by evaporating the acids under an IR lamp. No significant losses of the content of Cu and Pb during the evaporation were observed. The resulting sirupic solution was then diluted with DDW and analyzed.

The optimum deposition potentials were found by voltammetry with linear pulses on stationary mercury drop electrode. The analyte concentrations in these experiments were 1000-times higher than in anodic stripping voltammetry (ASV). The deposition potentials were chosen by 200—250 mV more negative than the potential $E_{1/2}$ [30]. For the simultaneous determination of Cu and Pb the optimum deposition potential was found to be $E_d = -0.75$ V.

The voltammograms for synthetic samples obtained with static mercury drop macroelectrode are composed of two stripping peaks and their heights are linearly dependent on the concentrations of Cu and Pb. For the real sample solutions no significant differences were observed. The analytical figures of merit for the macroelectrode (A) and for the semimicroelectrode (B) are collected in Table 1.

Static mercury drop electrode with the radius of about 0.5 mm is commonly used in stripping voltammetry. Electrochemical accumulation of analyte de-

Table 1

Analytical figures of merit for mercury drop macroelectrode (A) and semimicroelectrode (B)*

Element	Electrode	Deposition potential E_d/V	Peak potential E/V	Detection limit $c/(\text{mol dm}^{-3})$
Cu	A	-0.75 (-0.35)	-0.14	2.1×10^{-8}
	B	-0.75 (-0.35)	-0.15	1.8×10^{-8}
Pb	A	-0.75	-0.42	1.0×10^{-8}
	B	-0.75	-0.43	0.7×10^{-8}

*Potentials are given against calomel electrode with 4 M-NaCl.

mands enhanced mass transport due to stirring of the solution. Stirring also secures time independence of the transport. Insufficiently equable and reproducible intensity of stirring is a major source of error in stripping voltammetry [31].

With the decrease of radius of electrode the ration of time-independent spherical diffusion in the overall analyte flux increases. Since the linear diffusion component decreases with time, a steady-state analyte transport is achieved after certain electrolysis time. The smaller is the electrode the higher is the value of flux density (flux per electrode surface unit). Thus it is possible to carry out the accumulation on the microelectrodes without stirring the solution or rotating the electrode. As a result the stripping voltammograms at microelectrodes exhibit excellent reproducibility.

Semimicroelectrode applied in the present analytical problem keeps to a certain extent this property. Higher value of its radius (80 μm) causes relatively large values of currents well measurable with conventional electroanalytical instrumentation (see Experimental).

An additional advantage of the semimicroelectrode over the macroelectrode is the low polarization potential which arises from the low currents. That is why
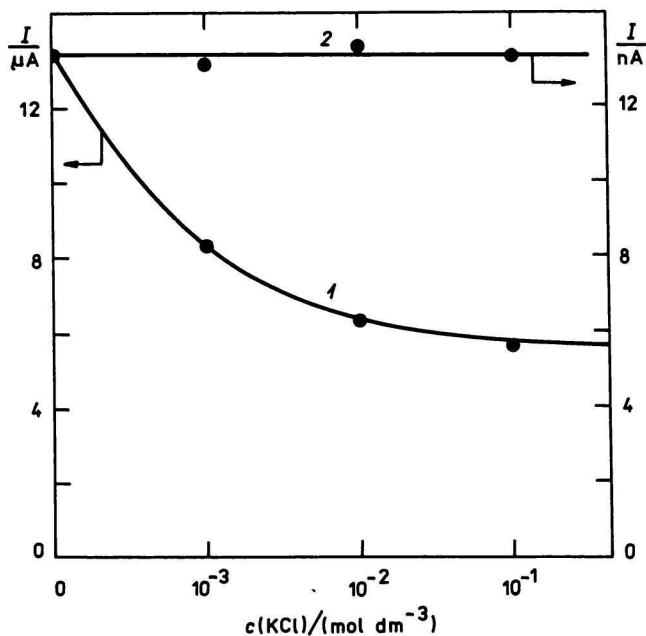

Fig. 2. Effect of the supporting electrolyte concentration on the measured current in the solution of 10^{-3} M-Pb^{2+}. *1.* DC polarography; *2.* DC voltammetry on hanging mercury drop semimicroelectrode.

the measured current is almost independent of the supporting electrolyte concentration, which is visualized in Fig. 2.

Stripping voltammograms obtained with the semimicroelectrode are of the same shape as for macroelectrode, but they should be recorded at higher current sensitivity. The optimum working parameters are quite similar to those obtained for the macroelectrode (Table 1).

At equal duration of electrochemical accumulation the detection limit is slightly lower in the case of semimicroelectrode.

When copper traces below 2×10^{-8} mol dm^{-3} are to be determined some negative interferences of the stripping peak with chlorides or oxygen were observed. The influence of oxygen caused lower reproducibility of the stripping peak. This could be only removed by a very long deaeration of the analyzed solution with purified nitrogen. Chlorides caused higher values of background current and some difficulties in evaluating stripping peak. In the case of samples with lower content of Cu medium exchange technique [32] has been applied. After the accumulation phase of experiment the original solution has been exchanged for 0.1 M-HClO$_4$.

Table 2 brings analytical data for the analysis of GaAs samples with both macroelectrode (A) and semimicroelectrode (B).

Table 2

Analyses of GaAs samples

Element	w(found)/ppm		
	ASV		GF AAS
	A	B	
Cu	0.18 ± 0.04	0.17 ± 0.02	0.20 ± 0.05
	0.20 ± 0.03	0.19 ± 0.02	0.20 ± 0.05
	0.30 ± 0.05	0.31 ± 0.04	0.33 ± 0.06
Pb	0.09 ± 0.02	0.11 ± 0.01	0.08 ± 0.03
	0.12 ± 0.03	0.10 ± 0.02	0.10 ± 0.04
	0.42 ± 0.05	0.40 ± 0.03	0.43 ± 0.10

The correctness of these results was checked by graphite furnace AAS utilizing the procedure from literature [16]. As Table 2 implies, both types of electrodes provide the same results, moreover, they are in good agreement with the reference data.

Anodic stripping voltammetry thus provides correct and reproducible results for the determination of Cu and Pb traces in GaAs materials. Both the mercury

drop electrode of conventional dimension and the mercury semimicroelectrode can be used, but the latter makes the experiments simpler.

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