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Voltammetric detection of metals and metal compounds on surfaces following a new sampling technique using alkali amalgam droplets

Gennady Mokrousov · Elena Knyazeva · Liubov Maliy

Abstract We propose a new method for the voltammetric detection of metals and metal compounds on surfaces of sold materials. The method is based on the reduction of oxidized metal compounds using an alkali amalgam droplet, the dissolution of the metals in the amalgam droplet, finally followed by recording the voltammetric anodic dissolution of the metal. The sample collection and all the following steps, including the voltammetric measurement, are performed at the same site of the sample and without any temporal interruption as one and the same electrode system is used for all steps. The proposed method is as an easy to handle, non-destructive express analysis for a wide range of samples.

Keywords Amalgam electrode · Surface analysis · Metals · Oxides · Voltammetry

Introduction

The identification of micro and nanoquantities of metals and metal oxides in different samples remains an important task. Various techniques of voltammetry are often used for the determination of impurities on the surface of solid materials. Examples are the application of carbon paste electrodes, hold-down cells (in local electrochemical analysis), and also abrasive stripping voltammetry [1–5]. However, so far it was impossible to use the same electrode system for the simultaneous determination of elemental and oxidized forms of metals. The solution of this problem described here in this paper facilitates the analysis procedure and widens the opportunities of the method, expanding it to the local determination of phase composition of surface layers, and even allowing studies of the formation of surface layers.

The local electrochemical analysis permits to study the surface phase composition of conductive materials. In this way, the sample itself is used as the working electrode [2, 6]. However, this method cannot be used for the identification of metal compounds [7] at a surface of poorly conductive semiconductors and dielectrics. Moreover, qualitative and quantitative composition changes of the analyzed sample may occur upon contacting them with the base electrolyte because of chemical and electrochemical reactions at the sample–base electrolyte interface. In this case, it is difficult to perform quantitative and semi-quantitative analyses.

In this paper, we propose a new approach to the voltammetric determination of the content of metals and metal compounds at the surface of solid materials. The method is based on the reduction of the oxidized metal compound, the dissolution of the metal in the low-melting conductive systems (e.g., mercury or alkali amalgam droplet), followed by recording the voltammogram of anodic oxidation of the metal. In this method, the sample collection from the solid surface, the reduction of the metal compound, the dissolution of the metal in the mercury (or amalgam) droplet, and the electrochemical oxidation (voltammetric scan) are

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combined in time and place due to the use of the same electrode system.

Experimental

Apparatus and chemicals

All chemicals were of analytical grade and used without further purification. All solutions were prepared using double-distilled water. All the electrochemical measurements were performed applying the polarographic analyzer PU-1 (Measuring Apparatus Factory of Gomel, Belarus) using a three-electrode cell. The working electrode was either a mercury droplet or an amalgam droplet. In case of contacting voltammetry, the semiconductor itself was the working electrode. An Ag/AgCl$_{(KCl\ sat)}$ electrode was used as a reference electrode and a platinum wire as auxiliary electrode. All potentials were measured against the Ag/AgCl$_{(KCl\ sat)}$. The first derivative of current with respect to potential (dI/dE) was recorded.

Procedure

The analysis procedure includes the following steps: First, a mercury droplet is deposited at the end of the silver wire by electroplating [8]. Then, a voltammogram is recorded using this mercury electrode and an appropriate base electrolyte. Following this, the mercury droplet is placed on the surface of a solid material to be analyzed for 1–2 min (the drop may "roll" on the sample surface) and finally, a new voltammogram is recorded using the mercury droplet after the collection procedure.

After the mercury droplet was allowed to have contact with the surface of the sample, the voltammograms exhibit anodic peaks due to the oxidation of the metals dissolved in the mercury droplet, providing these metals have been present on the surface of the studied sample. It is also possible to use a mercury film on the silver electrode instead of a mercury droplet. Further, it is possible to use a droplet of alkali metal amalgam in order to reduce metal compounds which are present on the surface of a sample. In that case, the alkali metal dissolved in the mercury acts as a chemical reductant.

Safety considerations: When properly performed, no contamination of samples or the environment with mercury will happen. The mercury droplets have to be carefully collected and disposed of.

Results and discussion

The proposed method allows the reliable identification of metals and metal compounds on the basis of stripping voltammetry. In order to detect not only elemental metals but also compounds in which the metal is in an oxidized state (e.g., metal oxides or salts), we propose the use of an alkali metal amalgam droplet instead of a pure mercury one. This can be obtained preliminarily by electrochemical reduction of alkali metal ions on the mercury droplet [8, 9]. When the amalgam droplet contacts the surface of the sample, the metal ions of the metal compounds are reduced by the active alkali metal and dissolved in the mercury. Following this, the voltammogram of the obtained amalgam is recorded.

The contact of sodium amalgam with the surface of solid material is carried out in air or under a protective liquid (e.g., isobutyl alcohol). The sodium metal, i.e., the active component of the amalgam, is partly oxidized on air, but this does not cause any problems for the analysis.

The proposed voltammetric technique provides an easy to handle semi-quantitative method to determine metals and metal compounds at the level of 10^{-6}–10^{-11} g with a relative standard deviation of 20–40%. The method can be applied for assays of large and small surface areas (down to 0.001 cm^2) and the procedure excludes contacting the sample surface with a base electrolyte and mechanical damage while sampling.

Thermodynamic background

The thermodynamic equilibrium describing the reduction and phase exchange process when being in contact with an alkali metal amalgam was calculated in order to corroborate the proposed approach. Calculations have been made for the oxide, hydroxide, sulfate, and chloride of copper and for the oxide, hydroxide, and arsenide of gallium. Compounds of copper and gallium were considered because of their different solubility in mercury. Additionally, gallium is the main component and a dopant of many semiconducting substances and copper which is adsorbed at a solid surface essentially affects the electrophysical parameters. The possibility of using mercury to remove the analyzed elements from a surface of solid materials was estimated by thermodynamic calculations. The standard Gibbs free energy changes $\Delta_r G^\ominus$ of some typical chemical reactions are presented in Table 1.

As Table 1 shows, the reduction of copper and gallium compounds is possible with the help of sodium amalgam, but not with pure mercury. There is one exception, the case of copper chloride reduction, which can be performed even using pure mercury, driven by the very low solubility of the formed calomel.

Examination of gallium arsenide plates

The theoretical calculations have been confirmed by the experimental results obtained using the model systems. In all cases, quantitative chemical (spectrophotometry using ammonium solution for copper and xylenol orange for gallium determination) and electrochemical analysis have

Table 1 Standard Gibbs energy changes of some reactions

No.	Reactions	$\Delta_r G^{\ominus}$, kJ mol^{-1}
1	$CuO + 2NaHg \rightarrow Cu(Hg) + Na_2O$	−164.50
2	$Cu(OH)_2 + 2NaHg \rightarrow Cu(Hg) + 2NaOH$	−317.87
3	$CuCl_2 + 2NaHg \rightarrow Cu(Hg) + 2NaCl$	−514.75
4	$CuSO_4 + 2NaHg \rightarrow Cu(Hg) + Na_2SO_4$	−527.33
5	$CuO + Hg \rightarrow Cu(Hg) + HgO$	69.66
6	$Cu(OH)_2 + Hg \rightarrow Cu(Hg) + Hg(OH)_2$	208.21
7	$CuCl_2 + 2Hg \rightarrow Cu(Hg) + Hg_2Cl_2$	−40.34
8	$CuSO_4 + 2Hg \rightarrow Cu(Hg) + Hg_2SO_4$	33.31
9	$Ga_2O_3 + 6NaHg \rightarrow 2\ Ga(Hg) + 3Na_2O$	115.71
10	$Ga_2O_3 + 2Na_3Hg \rightarrow 2\ Ga(Hg) + 3Na_2O$	−41.02
11	$Ga(OH)_3 + 3NaHg \rightarrow Ga(Hg) + 3NaOH$	−382.24
12	$Ga(OH)_3 + Na_3Hg \rightarrow Ga(Hg) + 3NaOH$	−460.60
13	$GaAs + 3NaHg \rightarrow Ga(Hg) + Na_3As$	−2.91
14	$Ga_2O_3 + 3Hg \rightarrow 2\ Ga(Hg) + 3HgO$	818.19
15	$2\ Ga(OH)_3 + 3Hg \rightarrow 2\ Ga(Hg) + 3Hg(OH)_2$	813.76
16	$Ga + Hg \rightarrow Ga(Hg)$	−1.67

Fig. 1 Anodic voltammograms of *1* the gallium arsenide plate after sulfuric acid etching and *2* gallium oxide (III) formed on the surface of the plate. Voltammograms were obtained using the hold-down cell with the scan rate of 30 mV s^{-1}; the solution of 0.005 M HCl was used as a base electrolyte. The first derivative of current with respect to potential (dI/dE) was recorded

confirmed the presence of reduced metal in the amalgam after contacting of copper and gallium compounds with sodium amalgam and the absence of reduced metal after contacting with pure mercury, except for copper chloride (Table 2).

We experimentally studied the interaction of sodium amalgam with gallium arsenide plates, which had been differently treated before.

The phase composition of a semiconductor surface was previously examined according to the procedure developed by Zakharchuk et al. [2] using the hold-down cell (Fig. 1).

Following the contact of sodium amalgam (prepared according to [10]) with the surface of a gallium arsenide plate, the voltammogram of anodic dissolution of the reduced metal was recorded (Fig. 2). As Figs. 1 and 2 (curves 1) show, gallium arsenide is not reduced by the sodium amalgam and no gallium is entering the amalgam droplet. However, after the formation of a gallium oxide layer on the surface by boiling in water for 10–30 min, the examination of the surface in a hold-down cell has confirmed the presence of gallium oxide phase (curve 2 in Fig. 1). The anodic oxidation peak of
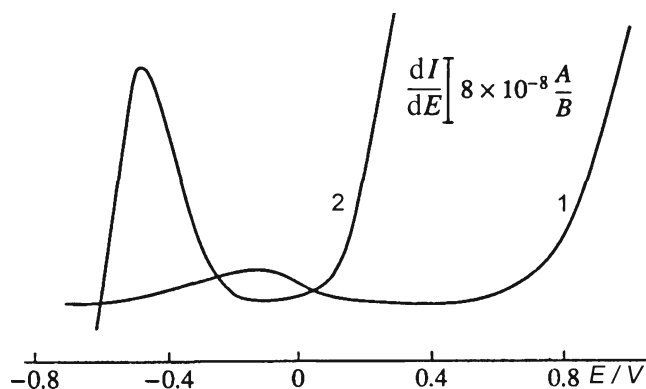
gallium also appeared on the voltammograms after contacting it with the sodium amalgam (curve 2 in Fig. 2). The obtained data prove that the sodium amalgam does not reduce the gallium arsenide semiconducting material, but it does reduce the gallium oxide phase at the gallium arsenide surface. The analysis of the surface of the semiconducting plate having a gallium oxide layer on its surface did not show the peak of gallium on the voltammetric curves when the surface was contacted by a pure mercury droplet. If the gallium oxide at the surface was chemically or electrochemically reduced, the anodic oxidation peak of gallium appeared on the voltammograms after contacting it with a pure mercury droplet.

The experiments show that the two variants of the proposed method allow the identification of metals on the surface of solid samples, be they in the elemental state (i. e., as metals) or in an oxidized state as metal compounds. The described method was successfully applied for the identification of phases of metals of the second and third groups at the surface of plates of gallium arsenide, indium arsenide, indium phosphide, and cadmium telluride, for the identification of dopant impurities (on germanium samples etched by gallium) and metal contaminants such as zinc, cadmium, copper, and lead adsorbed at the surface of these

Table 2 Analysis results of surface of semiconductive materials, which were previously differently treated, using mercury electrode

| Sample	Kind of surface treatment	Anodic peak potential, V	Corresponding metal [10]
Gallium arsenide doped with Te	Mechanical lapping	−0.58	Ga
Gallium arsenide doped with Sn	Mechanical lapping	−0.66	Sn
		−0.57	Ga
Gallium arsenide doped with Sn	Fracture	No signal	–
Indium phosphide doped with Ga	Mechanical lapping, treating with solution of 1 M Na$_2$SO$_3$	−0.68	Ga
Germanium doped with Ga	Mechanical lapping, external electrical field of $E = -1.8$ V applying	−0.72	Ga
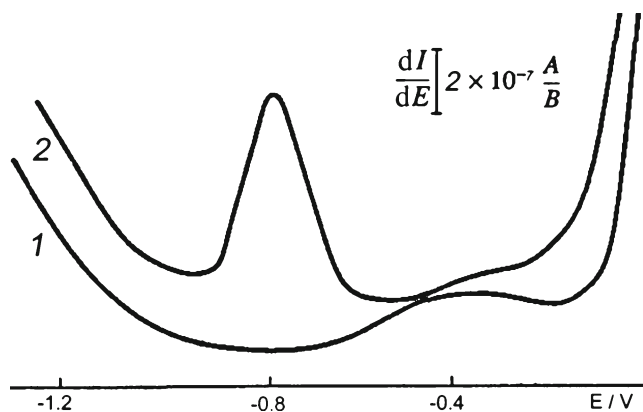
Fig. 2 Anodic voltammograms of the spherical mercury electrode in the base electrolyte of 0.1 M KCl after contact of the sodium amalgam with the gallium arsenide plate, which was *1* previously etched with sulfuric acid and which was *2* boiled in water for 10–30 min (to form gallium oxide (III)). The scan rate was 30 mV s^{-1}. The first derivative of current with respect to potential (dI/dE) was recorded

materials. It was shown that it is possible to examine very small (as little as 0.001 cm^2) surface areas with the relative standard deviations of 20–40%.

Environmental application

The described method can be used for different applications. The possibility of express environmental monitoring using a non-destructive voltammetric method is of great interest for ecologists. And the air chemical monitoring (e.g., atmosphere, working zone, and industrial emission) permits to evaluate the emission rate of the various metal pollutants into the environment.

The voltammetric analysis with sampling technique using alkali amalgam droplet was applied for the cartographic assays of the environmental pollution by heavy metals. Sampling was performed using silica glasses with 4 cm^2 area that were placed at specific sites of the city for a particular period of time (not less than 1 day). The evaluation of the deposited substances was performed by the sampling technique using a sodium amalgam electrode; the contact time was 2 min. Voltammograms of amalgam droplet were recorded in the solution of 0.02 M citric acid used as a base electrolyte. Model systems containing cadmium and lead salts were prepared for the semi-quantitative analysis. The model systems were analyzed in the same manner as the real samples. The metal content was evaluated according to calibration plots obtained using the model systems. As a result of analysis, the lead and cadmium emission into the environment per diem was assessed in different places of the city. The data presented in Table 3 show that the metal content on the analyzed glass varied in the ranges of 4.5·10^{-7}–34.0·10^{-7} g m^{-2} and 6.0·10^{-7}–16.0·10^{-7} g m^{-2}.

Table 3 Heavy metal pollution of different city sites

Sample	Anodic peak potential, V	Peak current, μA	Concentration, μg/m^2	Corresponding metal [10]
1	No signal	–	–	–
2	−0.45	0.12	0.9	Pb
3	No signal	–	–	–
4	−0.01	3.31	–	Cu
	−0.54	1.10	1.6	Cd
5	−0.37	0.14	0.9	Pb
	−0.01	3.00	–	Cu
6	−0.01	2.28	–`	Cu
7	−0.37	0.80	1.8	Pb
	−0.01	1.06	–	Cu
8	No signal	–	–	–
9	−0.40	1.76	2.9	Pb
10	−0.65	0.32	0.6	Cd
	−0.45	0.12	0.9	Pb
11	−0.45	0.06	0.45	Pb
12	−0.40	1.82	3.4	Pb
	−0.01	0.72	–	Cu

Using the model systems, we also studied the possibility of the proposed method to determine the heavy metals trapped by air filters, including filters for aerosol determination. The filters were previously placed in solutions with different quantities of cadmium and lead (10^{-6}–10^{-4} M) for 19 h and dried, and then they were voltammetrically analyzed using the sampling technique with alkali amalgam (Na) droplet. The contact time was 2 min. After that, the droplet was replaced in the electrochemical cell, kept for about 40 s for the removing extra amount of sodium, and then the anodic voltammogram was recorded in the range from −1.2 V till 0.0 V in the base electrolyte of 0.1 M KCl. The analytical responses appeared at $E=-0.64$ V and $E=-0.41$ V for cadmium and lead correspondently. The increase of concentration of salt solution, in which the filters were held, was accompanied by an increase of the analytical signals but the dependence was non-linear (Table 4). The results of voltammetric analysis of the model systems were in a good

Table 4 Analytical responses of lead and cadmium salts of different concentrations after filters contact with amalgam droplet

Solution	Concentration, μM	Peak current, μA
Cd(NO$_3$)$_2$	5	1.7
	50	11.7
	500	31.0
Pb(NO$_3$)$_2$	5	3.3
	50	15.2
	500	50.2

correlation with the data obtained using emission spectroscopic methods.

Conclusion

Our research demonstrated that the proposed approach of voltammetric analysis to assess the presence of metals and metal compounds on the surface of solid materials is applicable as a simple and reliable non-destructive sampling and detection technique for a wide range of samples. It was shown that the method can be applied to analyze the surfaces of semiconducting plates and can be used in the environmental and chemical monitoring as well.

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