

Applications of stripping voltammetry in investigations of electrodeposition and ionization of metals on semiconductors

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ABSTRACT

The presented brief review reveals that the application of the method of Anodic Stripping Voltammetry is very useful for investigation of many aspects of electrodeposition of metals on semiconductors such as peculiarities of slow deposition at small and very small cathodic overpotentials, precise determination of the onset potential of this process, exploring of the energy states of electrodeposited metals, and so on (if anodic ionization of the deposited metal is possible). Detailed description of these applications is presented.

KEYWORDS: electrodeposition, single-crystal semiconductor cathode, underpotential deposition (UPD), metal, ionization

ABBREVIATIONS

- EMSSC – Electrodeposition of metals on semiconductor single-crystal cathodes
ASV – Anodic Stripping Voltammetry
CVA – Cyclic Voltammetry
OPD – Overpotential Deposition
(electrodeposition at potentials which are more negative than the equilibrium Nernst potential of the red-ox pair *metal/cations of this metal in the electrolyte* designated as E_{eq})
UPD – Underpotential Deposition
(electrodeposition at potentials which are more positive than the E_{eq} value)
ES – Energy State (of electrodeposited metal)

INTRODUCTION

The method of anodic stripping voltammetry (ASV) was elaborated for analytical purposes in the 20th century [1-3]. Its characteristic feature is the cathodic electrodeposition of a metal from the solution onto an inert electrode at a definite constant potential value E_d . The duration of this cathodic stage (t_d) is not limited, it may be very long. Therefore, it enables us to accumulate noticeable amounts of the deposited metal on the electrode even if the concentration of its cations in the solution is as small as $10^{-9} - 10^{-10}$ M [1, 2]. Then the deposited metal is ionized anodically during the stripping step which produces anodic oxidation peak whose height provides the information about the amount of the metal accumulated on the electrode and, hence, about the concentration of its cations in the analyzed solution. Therefore, the ASV method is very useful for the purposes of analysis of very dilute solutions [1-4].

It had led the author to the idea that this method may be very helpful also in other field, namely, for investigations of such slowly proceeding cathodic processes as electrodeposition of metals on semiconductor electrodes at small and very small cathodic overpotentials and of UPD of adatoms on semiconductors. For example, we proposed to use it for investigations of thermodynamic properties (energy state, activity) of metals deposited on semiconductors at small cathodic overpotentials and kinetics of their deposition process in these conditions [5-7]. Now we propose to use the ASV method for the precise determination of the onset

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potential of electrodeposition of metals on semiconductor electrodes.

The author had a memorable chance to co-operate with one of the greatest specialists in the field of ASV method - Professor Dr. Kh. Z. Brainina - in the years 1987-1993*. Using and developing her ideas and methods, we had proposed the applications of the ASV method for the detailed and systematic scientific investigations of the peculiarities of the initial stages of electrodeposition of metals on semiconductors (such as Cd on CdSe) and of subsequent anodic ionization of the deposited metals on semiconductor electrodes [5-10]. This direction of investigations proved to be very useful and fruitful for gaining a lot of valuable and interesting scientific information in all cases where the process of anodic ionization of the deposited metal is possible {if the contact *metal/semiconductor* (forming during electrodeposition) does not restrict anodic current values substantially [10]}. It is the general condition of applicability of the ASV method on semiconductor electrodes and its only restriction [10]. Further, we shall consider only such systems *metal/semiconductor* which satisfy this general condition. The author wishes to show some of the possibilities which can be provided by the ASV method in this field.

Precise determination of the onset potential of EMSSC

Precise determination of the onset potential of electrodeposition of metals on each semiconductor electrode is very important both for the fundamental science and for the practical applications of EMSSC. However, the commonly used method of cyclic voltammetry does not ensure to do this with the necessary exactness because the cathodic currents corresponding to the reduction of metal cations are very small at low cathodic overpotentials and they are often masked by the currents caused by other parallel processes such as cathodic reduction of adsorbed oxygen [6] and hydrogen ions [9].

We propose the following method of precise determination of the onset potential of EMSSC.

*Unfortunately, our co-operation and our investigations had been interrupted later on by an extremely hard and prolonged crisis. But their results are still useful at the present time.

It requires performing of a series of ASV experiments with the durations of their cathodic stages (t_d) which are equal to 1000 seconds and with the following potentials of the cathodic stages:

- 1) $E_d = E_{eq}$ (the latter value should be calculated preliminarily by accurately using Nernst equation as described in the work [6]),
- 2) $E_d = E_{eq} - 0.01$ V,
- 3) $E_d = E_{eq} - 0.02$ V,

and so on (by changing the E_d values by 0.01 V in the negative direction in each of the subsequent experiments as compared to the previous one) until the anodic current peak appears during the anodic sweep. The corresponding potential value (E_d) will be the onset potential of the EMSSC process within the accuracy of 0.01 V (E_{onset}).

Further, another series of experiments can be performed in a similar way with stepwise changing of the E_d values by 0.001 V in the negative direction in each of the subsequent experiments as compared to the previous one for determination of the onset potential of the EMSSC within the accuracy of 0.001 V.

For example, our experiments performed on non-degenerated *n*-CdSe single-crystal electrodes immersed in the aqueous solution containing Na₂SO₄ (0.5 M) and CdSO₄ ($3.2 \cdot 10^{-4} \div 5.3 \cdot 10^{-4}$ M) [5, 11] revealed that the anodic peak is always absent on the stripping voltammograms when E_d value is equal to E_{eq} [11]. This is an evidence of the full absence of UPD of cadmium adatoms on these electrodes [10, 11]. The anodic peak appears on other stripping voltammograms only if the E_d values are more negative than $(E_{eq} - 0.02$ V) \div $(E_{eq} - 0.05$ V) (the value of the minimal cathodic overpotential depends on the microrelief of the electrode surface; obviously, it is necessary for the formation of three-dimensional metallic nuclei).

Investigations of energy states of deposited metals on semiconductor electrodes

Using the ASV method, we managed to confirm the idea of Prof. Kh. Z. Brainina concerning the possibility of the existence of three energy states (ES) of any electrodeposited metal [1] in its application to semiconductor electrodes, namely, cadmium on CdSe for example [5-11]. Our investigations also confirmed the idea of Prof. Kh. Z. Brainina that

the properties of each electrodeposited metal may depend both on its amount on the electrode and on the potential of deposition (E_d). Only the ASV method provides the possibility to investigate the effects of these two factors separately (independently), for example, by performing a series of experiments with various durations of deposition (t_d) (within wide ranges) at any constant E_d value and at constant values of other experimental parameters. It results in the series of anodic voltammograms with similar shapes but with different values of the maximal anodic current (I_m), the potential of the anodic peak (E_m), the potential of zero current ($E_{I=0}$), and in the area of the figures defined by them [which corresponds to the value of the electric charge (q) which is necessary for ionization of the deposited metal during the anodic sweep]. The analysis of the relationships between all these values may provide much information about the thermodynamic properties of the deposited metal such as its activity corresponding to various t_d values and to various q values if the anodic process is reversible*. This analysis is performed with the aid of the powerful theoretical apparatus of the ASV method which had been elaborated by the scientific school of Prof. Kh. Z. Brainina [1, 2, 12] and which had been developed by us further for applications on semiconductor electrodes [8]. Our investigations revealed that the energy state of the metal (cadmium) deposited slowly at small cathodic overpotentials (less than 0.1 V) on non-degenerated CdSe surface is close to the ES of the stable modification of this bulk metal. Energy state of this sort of a deposited metal is called the 2nd ES (or equilibrium energy state) according to the terminology which had been proposed by Prof. Kh. Z. Brainina [1]. Probably, the crystalline structure of this sort of deposited metal is similar to that of a stable bulk metal crystal. The potential of zero current ($E_{I=0}$) as determined by voltammograms registered on CdSe electrode is close to the equilibrium Nernst potential of bulk

cadmium electrode in the same solution. Moreover, these $E_{I=0}$ values are practically constant within a very wide range of q values [5], that is, the activity of this sort of metal is practically independent of its amount on the electrode which is the characteristic feature of a macrophase of the metal which is similar to the bulk metal phase [1-3].

All the above-mentioned features can be explained very well on the basis of the Volmer-Weber growth mechanism for this sort of the deposited metal (by formation of three-dimensional nuclei and subsequent island-like growth of the metal deposit) as it is characteristic for the great majority of metals deposited on single-crystal non-degenerated semiconductors [5, 10, 13].

If the metal (cadmium) is deposited at greater cathodic overpotentials (exceeding 0.15 – 0.2 V) on the same CdSe electrode, then its molar Gibbs energy becomes greater than that of the stable modification of the same bulk metal (it is proved by the fact that the $E_{I=0}$ values are more negative in this case than those which had been described above). Therefore, this energy state of the metal is called the 3rd (or rich in energy) ES [5]. The peaks of current of anodic ionization of this sort of deposited metal appear at more negative potential values than that corresponding to the ionization of the metal with the 2nd ES [5].

The differences between the 2nd and the 3rd energy states of a deposited metal are more pronounced on some semiconductor electrodes such as CdSe [5] and germanium [1] than on inert electrodes like glassy carbon or graphite. We explain this by the fact that solid-state reduction of the surface layers of CdSe substrate or of surface oxides on germanium electrode proceed at high cathodic overpotentials and the products of these processes (having disordered crystalline structure) influence the structure of the metal deposited from the solution due to epitaxial mechanism [10].

*Preliminary experiments are necessary for determining whether the process of anodic ionization of the concerned metal is reversible or irreversible on the electrode used. It can be done with the aid of chronoamperometry of this process performed at any constant potential value which is more positive than E_{eq} . If the shape of current vs. time graph is hyperbolic, it is the evidence of reversibility of this process [3].

Detailed investigations of UPD of adatom layers and submonolayers

The processes of underpotential deposition of adatom layers and submonolayers (when they are possible) proceed more slowly on semiconductor cathodes than those on metal electrodes because of relatively small values of exchange current

densities on the former. For example, the complete formation of cadmium adatom monolayer proceeds during approximately 100 seconds [5]. The ASV method ensures it readily. Further, it provides some additional important possibilities (as compared with the CVA method) for more detailed investigations of UPD processes because it provides us the possibility to perform a series of experiments at any constant potential value (E_d) with various durations of the cathodic stage (t_d) resulting in various amounts of adatoms deposited on the electrode and, hence, with various activity values of the metal in submonolayers [5]. Our experiments performed with the aid of the ASV method revealed that the increasing of t_d within the interval of 10 to 100 seconds always results in the increase of the amount of cadmium adatoms deposited on activated (degenerated) CdSe electrode, but at greater values of t_d this amount remains constant at each constant E_d value [5]. It is the characteristic feature of adatom layer formation process at any constant potential value which defines the limiting activity of the metal deposited on the electrode and, hence, the limiting amount of adatoms on its surface [12]. Further, our experiments revealed that the limiting amount of the adatoms existing on the electrode surface depends on the potential E_d value and that this amount is maximal at E_d value which is equal to the equilibrium Nernst potential of the red-ox pair *cadmium/Cd²⁺ ions* [5] in accordance with the theory [12].

Investigations of the effect of external factors on the kinetics of EMSSC processes

The ASV is the best method for detailed investigations of the influence of illumination, stirring of the electrolyte, its aeration and other external factors on the rate of electrodeposition of any metal on each semiconductor electrode because it provides us the possibility to perform such study at each constant potential value E_d and with equal duration of the cathodic stage (t_d) comparing the amounts of the metal electrodeposited with and without this factor (by means of comparison of the corresponding q values). It is very important to emphasize that the same external factor may result in different effects at different potential values of the EMSSC process. For example, we revealed with the aid of the ASV method that stirring of the solution accelerates

significantly the electrodeposition of cadmium from the sulphate electrolyte on *n*-CdSe only if overpotential exceeds ≈ 0.1 V (when it may result in increase of the q values by as much as $3 \div 4$ times or even more), but it does not influence the rate of this process at small overpotentials (≈ 0.09 V or less) [7]. It reveals that the diffusion of Cd^{2+} ions in the solution is the rate limiting step of this process only at high overpotential values, but some other stage (probably, nucleation) becomes the rate limiting step at minimal overpotentials [7].

Investigations of ionization of deposited metals by ASV method with various sweep rates

Pradhananga a. o. [14] investigated the process of cathodic reduction of CdS with the ASV method. They had registered four anodic voltammograms of ionization of the product of this process using four different anodic sweep rates (v); but they did not discuss these results and made no conclusions from them.

We performed more systematic theoretical investigations of the influence of v values on the height and potential of the anodic peaks appearing during ionization of the metal phase layer on the semiconductor electrode [8]. They revealed that the maximum anodic current density (I_m) is proportional to $d\Phi_H/dt$ value (where Φ_H is the potential drop in Helmholtz layer) and that changing of the anodic sweep rate from v_1 to v_2 value must lead to the following variation of Φ_H value corresponding to the anodic peak (if the ionization process is reversible):

$$\Delta(\Phi_H)_m = \frac{RT}{2zF} \ln \left[\frac{(I_m)_{v_2}}{(I_m)_{v_1}} \right], \quad (1)$$

where F is the Faraday constant,
 T - absolute temperature,
 R - the molar gas constant,
 z - the number of electrons involved in the elementary act of the process.

The corresponding variation of the registered peak potential is equal to

$$\Delta E_m = \Delta(\Phi_H)_m + \Delta(\Phi_{sc}^*)_m + \Delta(IR_{ohm})_m, \quad (2)$$

where $\Delta(\Phi_{sc}^*)_m$ is the corresponding variation of the potential drop in the space charge region of the semiconductor electrode, $\Delta(IR_{ohm})_m$ is the

corresponding variation of the sum of ohmic potential drops in the electrolyte and in the semiconductor electrode which are included in the real potential measurement circuits [8].

These relationships (1, 2) enable us to perform the detailed analysis of the experimental dependences of E_m and I_m values on the sweep rate registered in the anodic stages of ASV experiments. Applying this method to the CdSe electrode covered with cadmium, we revealed that the potential drop in the space charge region of the metallized semiconductor electrode is less dependent on the electrode potential than in bare semiconductor electrode [6]. This conclusion is in agreement with the results of other investigators obtained with the aid of other method on GaAs electrode [15].

CONCLUSION

It is evident from the above-mentioned results that the ASV can be a valuable method for investigations of EMSSC (both in the OPD and UPD regions) in all cases where the anodic ionization of the deposited metal is possible. It should be used together with all other well known methods.

ACKNOWLEDGEMENT

The author is grateful to Prof. Kh. Z. Brainina for her very helpful co-operation, attention, discussions, and all-round support.

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