

SHORT COMMUNICATION

Photoemission of electrons into electrolyte from cadmium oxide layers formed by anodic oxidation of undeformed and plastically deformed cadmium plates

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1. Introduction

Studies of electron emission (external photoeffect) at the electrode/solution interface are an important part of contemporary photoelectrochemistry. The results of systematic studies of this phenomenon led to the formulation of fundamental relationships and to new methods for investigation of the physicochemical processes occurring at the electrode–electrolyte interface [1–4]. In particular, photoemission measurements enabled a number of parameters relating to the structure of the semiconductor/electrolyte interface to be determined.

The photoemission current from semiconductors with many surface states to solutions with a sufficiently high electrolyte concentration is described by the well known ‘three halves power law’ [5]

$$j = C \left[h\nu - E_g - \left(1 + \frac{m_e}{m_v} \right) \times \{ \chi(0) + e\phi \} \right]^{3/2} \quad (1)$$

where C is a constant, ν is the frequency of the incident light, ϕ the emitter potential, m_e and m_v are the effective masses of the electron in the conduction band and the hole in the valence band, $\chi(0)$ is the value of the electron affinity at the semiconductor potential, regarded as zero, E_g is the energetic band gap width, h is Planck’s constant and e denotes the electronic charge.

From Equation 1, it follows that at a given frequency of incident light, the value of the photocurrent, j , may be controlled by applying an external voltage between the emitting and reference electrode. At a given value of the wavelength of the incident light there is a threshold value of ϕ above which photoemission occurs.

The effect of the physical state of the emitter on the measurable photoemission parameters has been little studied. Recently [6–8], we have started systematic studies of the effect of plastic deformation of the emitting electrode on photoemission into electrolyte. It has been found that both the intensity and the threshold voltage of photoemission into electrolyte from lead and cadmium are strongly affected by cold rolling of the emitter prior to measurements. Parallel investigations of the effect of the cold working of cadmium electrodes on the electroluminescence accompanying their anodic oxidation [9–11] revealed, that plastic deformation of the cadmium substrate causes an increase in the luminescence intensity. It has been

demonstrated that the observed enhancement of the electroluminescence of anodically formed oxide layer is governed by changes in the defect structure of the oxide layer which, in turn, is genetically related to the defect structure of the mother substrate which changes with change in the degree of plastic deformation. The purpose of the present study was to check if the plastic deformation of cadmium electrodes affects the parameters of the photoemission from cadmium oxide layers anodically grown on their surfaces. An attempt to determine the ratio of the effective mass of the electron in the conduction band to the mass of the hole in the valence band, m_e/m_v , for thin anodically formed cadmium oxide layers is also made.

2. Experimental procedure

The investigated layers of cadmium oxide CdO were prepared by anodic oxidation of cadmium plates cut from industrial cadmium sheet of purity 99.95 wt % containing trace amounts of Zn, Pb, Fe and Tl. The nominal surface area of all samples was the same (about 500 mm²). Before the experiments the plates were chemically cleaned in solution of composition: 22 wt % CrO₃, 2.5 wt % H₂SO₄, 1.5 wt % CH₃COOH and 74 wt % H₂O. The plates were rinsed in running and distilled water. Finally, the plates were immersed for 10 s in 10% aqueous KOH and again rinsed in water. Prior to oxidation some of the cadmium plates were plastically deformed by rolling at room temperature. The deformation degree was estimated as the relative reduction in thickness due to the cold-rolling procedure.

The electrolytic oxidation of cadmium plates was conducted in solution containing 0.1 M of KOH and 0.1 M of K₂CO₃ per litre. During the electrolytic oxidation the cadmium plates were used as anodes, the platinum plate being used as the cathode. The oxidation process was carried out at a constant voltage of 38 V.

The photoemission of electrons from anodically oxidized cadmium plates was measured in two different electrolyte solutions. The first, denoted by I, was an aqueous solution of composition: 0.5 M KCl, 2 × 10⁻³ M HCl and 1 × 10⁻⁴ M tetrabutylammonium (TBABr) (C₄H₉)₄NBr. In solution II the concentrations of KCl and HCl were doubled (1 M and 4 × 10⁻³ M, respectively), the TBABr content being unchanged.

The potential of the oxidized cadmium photocathode was measured relative to the silver chloride electrode (Cl^-/AgCl , Ag). The counterelectrode (anode) was a platinum plate. The photoemission cell, equipped with an optical quartz window, was made of organic glass. A modulation technique was employed to separate the photocurrent from the relatively intensive dark current. The light beam produced by a high-pressure mercury lamp HBO 200F, monochromatized ($\lambda = 365 \text{ nm}$) by passing through an absorptive filter UG1, was periodically modulated with the aid of an electromechanical chopper. The modulation frequency (30 Hz) also produced a reference signal for a lock-in voltmeter used for measuring the photocurrent. A more detailed description of the setup used for measurements of the photoemission of electrons into electrolyte is provided in [6] and [7].

3. Results and discussion

Figure 1 represents the experimentally determined dependencies $j^{2/3} = f(\phi)$ for thin cadmium oxide films anodically grown on the surface of undeformed and cold rolled cadmium substrates, determined from the measurements of the voltage dependence of the photoemission current in electrolyte. All the experimentally determined $j^{2/3} = f(\phi)$ dependencies are curved. This means that the 'three halves power law' is not fulfilled. At a given voltage, the intensity of photoemission is higher, the higher the deformation

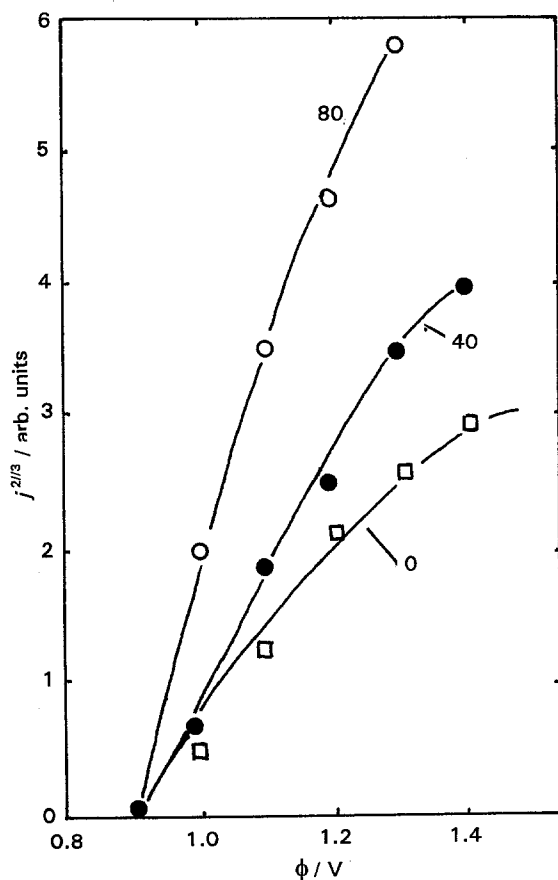


Fig. 1. Voltage dependencies of the photoemission current from anodically formed cadmium oxide layers as measured in electrolyte I. Parameter—deformation degree of the cadmium substrate (%).

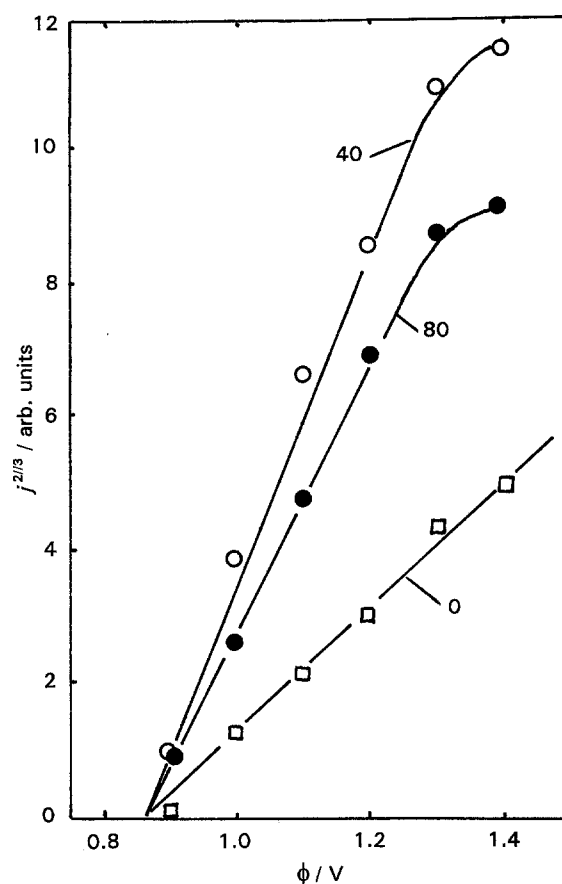


Fig. 2. Voltage dependencies of the photoemission current from anodically formed cadmium oxide layers as measured in electrolyte II. Parameter—deformation degree of the cadmium substrate (%).

degree, but the threshold potential (-0.9 V) for the photoemission does not depend on the deformation degree of the cadmium substrate.

The 'three halves power law' is based on the assumption that the electrolyte concentration is sufficiently high. This suggests that one of the probable reasons for the observed deviations of the results obtained for samples formed on the undeformed and extremely deformed cadmium substrates is insufficient concentration of electrolyte used. In this situation it was decided to repeat the measurements in more concentrated electrolyte solution (II) using the same samples. The results are presented in Fig. 2. In the range of voltages lower than -1.2 V the 'three halves power law' holds for the photoemission from all samples. The threshold voltage for photoemission is the same (for all samples), and, as in electrolyte I, equals -0.9 V .

A comparison of the results of photoemission measurements in electrolyte I and electrolyte II indicate that, at a given emitter potential in the case of electrolyte I, the intensity of photoemission monotonically increases with increasing deformation. In electrolyte II these changes are not monotonic, that is, current from the sample deformed to 40% is always larger than that from the sample formed on the substrate deformed to $D = 80\%$. The reasons for this irregularity are unclear. It is worth noting that the threshold voltage for photoemission into electrolyte from the pure metallic cadmium surface also displays

a nonmonotonic dependence on the degree of deformation of the emitting electrode with a minimum value at about $D = 50\%$ [8].

The determination of the threshold potential for photoemission opens the possibility of estimating the value of the ratio of the effective mass of the electron in the conduction band to the mass of the hole in the valence band, m_e/m_v , for thin anodically formed cadmium oxide layers. For $j = 0$ Equation 1 gives

$$h\nu - E_g - \left(1 + \frac{m_e}{m_v}\right) \times [\chi(0) + e\phi_0] = 0 \quad (2)$$

The experimentally determined value of the threshold potential, $\phi = -0.9$ V, was measured relative to the silver chloride electrode. By subtracting the potential of platinum relative to the silver chloride electrode, $\phi_{Pt} = -0.2$ V, the value of the threshold potential of the emitting CdO layer relative to Pt, is determined as $\phi_0 = -0.7$ V. Substituting this value into Equation 2 together with the energy of incident light quanta $h\nu = 3.4$ eV and literature data on the values of the band gap width $E_g = 2.5$ eV [12] and the electron affinity $\chi(0) = 3.3$ eV [1], the value of $m_e/m_v = 0.65$ is obtained, similar to that for III-V semiconductors.

Acknowledgements

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