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ELECTROLYTIC DEPOSITION OF BISMUTH ON CdS(0001) SINGLE-CRYSTAL SURFACES

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Abstract—The electrolytic deposition of Bi on CdS(0001) single-crystal surfaces has been studied in aqueous 0.5 M $NaClO_4 + x$ M $Bi(ClO_4)_3$ solutions (pH 2) using electrochemical *dc* and pulse polarization techniques under potentiostatic control. The initial steps of Bi deposition are interpreted in terms of a nucleation and growth model based on progressive nucleation with diffusion-controlled transfer of Bi^{3+} at three-dimensional growth centres. The number-density and mean size of the Bi crystallites are determined as a function of the amount of Bi deposited. The formation of a localized Schottky barrier at the interface between the Bi crystallites and the CdS surface was found to prevent the anodic dissolution of the Bi deposit even at high anodic polarization in the dark as well as under illumination of the electrode surface. The deposition of Bi inhibits the photoanodic dissolution owing to geometrical blocking of the CdS surface by Bi crystallites.

1. INTRODUCTION

Thin metal films on semiconductor surfaces are of considerable interest in view of their technical importance for Schottky barrier devices[1], optical energy conversion systems[2] and heterogeneous catalysis[3]. The properties of metal coatings on semiconductor surfaces have also been studied as a possible approach to circumvent the problem of photodegradation[2, 4–6]. The aim of these studies was to evaporate noble metals, *eg* Au, Ag and Pd, onto *n*-GaP, *n*-Si, *p*-GaP and *p*-Si semiconductor surfaces to obtain thin inert films which were semi-transparent or partially translucent to light but impermeable to the electrolyte.

The photo-activity and stability of the semiconductor electrodes modified in this way were found to be strongly dependent on the rate of evaporation and on the morphology of the film, indicating that the metallizing conditions are of major importance.

Another possible approach to modify the properties of semiconductor surfaces is the formation of thin metal deposits from aqueous solutions. In this case one may distinguish between electrodeposition under cathodic polarization and electrodeless immersion techniques. Under certain conditions metal ions can be deposited at open-circuit potential due to a displacement reaction between metal ions in the solution and metal ions at the semiconductor surface[7–13].

Underpotential deposition of submonolayer and monolayer metal films, which is a well-known phenomenon from studies on poly- and monocrystalline metal electrodes[14–16], has not been confirmed experimentally on semiconductor surfaces up to now [7, 13].

In contrast to the efforts made in thermodynamic and kinetic studies of bulk metal deposition on metal substrates, only a few systematic investigations where semiconductor surfaces have been used as substrates can be found in the literature.

Bindra *et al.* studied the deposition of Pb, Ag and Pd on ZnO, CdS, *n*-GaP, *n*-GaAs and SnO[7]. They found that the actual overvoltage, which is necessary for the metal deposition process to take place at an appreciable rate, is determined by the difference between the Me/Me^{z+} reversible potential and the flatband potential of the semiconductor. From the shape of potentiostatic current-density transients they concluded that the nucleation mechanism in particular is related to the work function difference of the semiconductor and the metal to be deposited[7]. Scharifker and Hills studied the nucleation and growth kinetics of Pb deposition on ZnO[8]. From potential step experiments they observed fast instantaneous nucleation taking place on a relatively small number of active sites which were exhausted at an early stage of the deposition process.

The present paper reports on the electrodeposition of bismuth on CdS single-crystal surfaces. Potentiostatic current density–time transients were analysed to obtain information about the nucleation and growth mechanism. The dependence of the photocurrent density on the degree of Bi coverage was also investigated.

2. EXPERIMENTAL

The experiments were carried out at room temperature using a conventional three-compartment electrochemical cell with a Pt counter-electrode of 2 cm^2 geometrical area and a Hg/Hg_2SO_4, Na_2SO_4 (saturated) reference electrode, both separated by glass diaphragms from the main cell compartment of the working electrode. All potentials are referred to a *nhe*.

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The CdS single crystals of specific resistivity $\rho = 27\ \Omega$ cm were prepared at the Crystal and Materials Laboratory of the University of Karlsruhe, using a modified Piper–Polich method with a leak ampoule[17]. Disks of 3 mm thickness and 0.65 cm^2 geometrical area were cut perpendicular to the c-axes of the CdS single crystals and mounted in a polyethylene holder using epoxy resin (Araldite, Ciba Geigy). Ohmic contact was made with In–Ga alloy. The electrodes could be used as rotating disks with the (0001) crystal face exposed to the solution. The surface preparation consisted of a mechanical diamond polishing (7 μm) and a final chemical etching in concentrated HCl for about 10 s.

The electrolyte solutions consisted of 0.5 M $NaClO_4 + x$ M $Bi(ClO_4)_3 + y$ M $HClO_4$ and were prepared from $HClO_4$, NaOH (Suprapure, Merck), Bi_2O_3 (Extrapure, Merck) and water which had been distilled four times. In all the experiments the solutions were purged with purified nitrogen and the acidity was adjusted to pH 2.

The quasi-steady-state cyclic voltammetric current density–potential curves and the current density–time transients were measured using a specially designed potentiostat (Wenking, PGS 77F) connected to a potential sweep generator and a multi-channel pulse galvanostat (MP-IM 400, Megaphysik Rastatt) which provided the application of both the linear sweep and the pulse polarization technique. The transients were recorded using an X–Y–t recorder (HP 7046 A) and a storage oscilloscope (Tectronix, 7623 A with plug in 7A13 and 7B50). *Ac*-impedance measurements were performed with a Solartron Frequency Response Analyzer 1172. Experimental details are described elsewhere[13].

For the photocurrent measurements, a defined illumination of the electrode surface through a plane parallel glass window at the bottom of the cell was provided by an optical system with a 100 W tungsten lamp[13]. The light intensity was adjusted to a constant reproducible photocurrent density of 120 $\mu\text{A cm}^{-2}$ on a freshly prepared CdS electrode.

3. RESULTS AND DISCUSSION

3.1. *Dc-polarization behaviour*

Typical current density–potential curves are shown in Fig. 1, which illustrates the effect of Bi deposition on the photo-anodic polarization behaviour of CdS electrodes. Polarization curve (1) in Fig. 1 is typical of the photo-anodic dissolution of CdS according to the reaction[18, 19]

$$CdS + 2h^+ \rightarrow Cd^{2+} + S. \qquad (1)$$

The defect electrons h^+ are generated by photons of energy $h\nu > E_g$ within the depletion layer at the semiconductor–electrolyte interface, where $E_g = 2.4$ eV is the band gap of CdS[20]. Restriction of the formation and transport of h^+ within the depletion layer leads to the potential-independent limiting current density at sufficient anodic polarization. At potentials positive to the flatband potential $E_{fb} = -0.65$ V [7, 13], the anodic current densities in the dark are negligibly small ($< 1\ \mu\text{A cm}^{-2}$).

In the presence of Bi^{3+} ions in the solution ($x = 2.4 \times 10^{-4}$), appreciable cathodic current densities arise at potentials $E_H \lesssim 100$ mV, as is indicated by curve (2) in Fig. 1. At these potentials the electrodeposition of Bi on the CdS surface takes place according to the reaction

$$Bi^{3+} + 3e^- \rightarrow Bi. \qquad (2)$$

The equilibrium potential of the bismuth electrode in the same solution was measured to be $E_{Bi/Bi^{3+}} = 190$ mV. According to the interpretation of Bindra *et al.*[7], the observed overvoltage of about 100 mV should be attributed to a relatively low surface concentration of electrons n_s near the equilibrium potential.

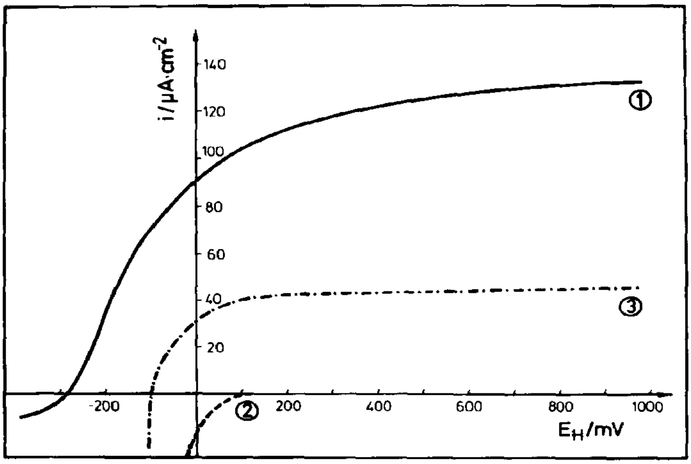

Fig. 1. Current density–potential curves $dE/dt = 10\ \text{mV s}^{-1}$. System: CdS/0.5 M $NaClO_4 + 2.5 \times 10^{-4}$ M $Bi(ClO_4)_3 + y$ M $HClO_4$ (pH 2); $T = 298$ K. (1) Freshly polished CdS in Bi^{3+}-free solution; (2) Bi deposition in the dark; (3) photocurrent after deposition of 3×10^{-7} mol of Bi.

An approximate value for n_s can be estimated from equation

$$n_s = N_D \exp[-(E - E_{fb})F/RT] \qquad (3)$$

where N_D denotes the bulk donor concentration of the semiconductor. From high-frequency *ac*-impedance measurements ($f \approx 10$ kHz) the space charge capacity C of the investigated material was determined as a function of the electrode potential. Extrapolation of the linear Mott–Schottky relation $1/C^2$ *vs* E_H in Fig. 2 yields the flatband potential E_{fb} as the intercept on the potential axis at about $E_H = -0.6$ V, which is close to the value of -0.65 V reported in the literature[13, 20]. The donor concentration N_D evaluated from the slope of the Mott–Schottky plot was found to be $N_D = 10^{15}\,\mathrm{cm}^{-3}$. If these values are used, Equation (3) predicts surface concentrations of electrons $n_s = 1\,\mathrm{cm}^{-3}$ at $E = E_{\mathrm{Bi/Bi^{3+}}}$ and $n_s = 10^4\,\mathrm{cm}^{-3}$ at a cathodic overvoltage of $E - E_{\mathrm{Bi/Bi^{3+}}} = 100$ mV for $T = 298$ K. Both values are much lower than the critical concentration $n_s \approx 10^{10}\,\mathrm{cm}^{-3}$, which is necessary for the metal deposition to occur at a measurable rate[7]. Similar to that found in the case of Ag deposition on CdS[7, 13], a strong chemical interaction between $\mathrm{Bi^{3+}}$ and the CdS substrate must be taken into consideration to account for the relatively low overvoltage for Bi deposition observed experimentally. Recent investigations have clearly shown that the composition of the CdS surface can be modified substantially owing to the formation of highly insoluble metal sulphides, $\mathrm{Me_2S_n}$, by the exchange of metal ions $\mathrm{Me^{n+}}$ in the solution and $\mathrm{Cd^{2+}}$ ions at the semiconductor surface[13] according to the following overall reaction:

$$n\mathrm{CdS} + 2\mathrm{Me}^{n+} \rightarrow \mathrm{Me_2S}_n + n\mathrm{Cd}^{2+}. \qquad (4)$$

For $\mathrm{Me^{n+}} = \mathrm{Bi^{3+}}$, a standard free enthalpy of $\Delta G° = -29\,\mathrm{kJ\,mol^{-1}}$ as the driving force for reaction (4) can be calculated from the solubility data of CdS and $\mathrm{Bi_2S_3}$[13]. Distinct changes of the *ac*-impedance data are observed after long time polarization of CdS in solutions containing $\mathrm{Bi^{3+}}$ ions, indicating considerable changes of the electronic properties of the interface. A Mott–Schottky plot obtained after 2 h polarization at $E_H = 1.5$ V in a solution containing 2.5×10^{-4} M $\mathrm{Bi^{3+}}$ exhibits significant deviations from that of the pure CdS system, as shown in Fig. 2. Details about the formation of the sulphides $\mathrm{Ag_2S}$, HgS and $\mathrm{Bi_2S_3}$ and their effect on the photo-dissolution of CdS will be published in a forthcoming paper[21].

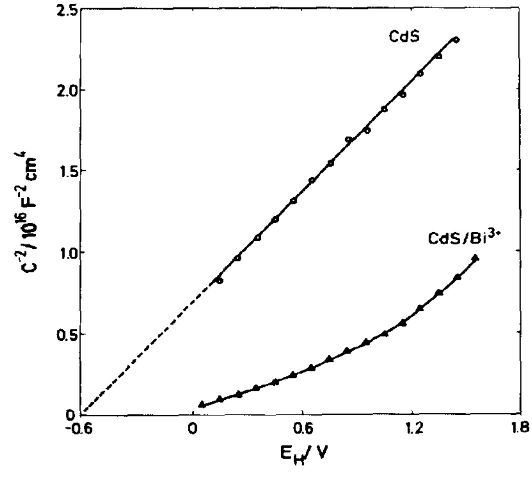

Fig. 2. Mott–Schottky plots of CdS in 0.5 M $\mathrm{NaClO_4}$ (pH 2) solution. o, Freshly polished CdS electrode; ▲ after 2 h polarization at $E_H = 1.5$ V in solution containing 2.5×10^{-4} M $\mathrm{Bi(ClO_4)_3}$.

At this point it is important to note that the electrolytically deposited bismuth [according to Equation (2)] could not be dissolved anodically from the CdS surface, even at high anodic overpotentials, either in the dark [anodic currents in the dark are not detectable in the anodic sweep of polarization curve (2) in Fig. 1] or under illumination (as will be discussed below). Passivation cannot account for this effect, as was proved by corresponding experiments using Au instead of CdS as the substrate. Obviously, the work function difference between the CdS semiconductor and the Bi metal provides the formation of a localized Schottky barrier at the CdS–Bi interface. Dissolution cannot take place because the metal deposit screens the barrier layer from the incident light, thus preventing the generation of defect electrons which are necessary for the anodic dissolution process. Consequently, the photo-dissolution of CdS, according to Equation (1), is expected to be inhibited too at those parts of the electrode surface which are covered by the deposited Bi. A decrease of the photocurrent density with increasing amount of deposited Bi was indeed observed. This is shown, for example, by polarization curve (3) in Fig. 1, which was obtained after the deposition of 3×10^{-7} mol of Bi. The dependence of the photocurrent density on the degree of Bi coverage will be discussed more quantitatively in Section 3.3.

3.2. *Nucleation and growth kinetics*

Electrodeposition of metals from solution on a foreign substrate is a first-order phase transition process associated with nucleation of the new metal phase. The number of nuclei and the rate of their formation are strongly dependent on the supersaturation (overvoltage) and on the metal–substrate interactions. The evaluation of nucleation and growth mechanisms is usually performed by analysing experimental current density–time transients in terms of theoretically derived models[8, 22–25].

Experimental *i–t* transients of Bi deposition on CdS, obtained from potential pulse experiments at different overvoltages, are shown in Fig. 3. Each transient was measured on a freshly prepared CdS surface. As can be seen from the inset of Fig. 3, the initial part of the transients follows a $i \propto t^{3/2}$ dependence, which is typical of a progressive nucleation mechanism with hemispherical or linear diffusion control[8, 22–25].

If overlapping effects are ignored during the initial period of the deposition process $\mathrm{Me^{n+}} + ne^- \rightarrow \mathrm{Me}$, the overall current density i for multiple nucleation with independently growing nuclei is given by the convolution of the nucleation rate $\mathrm{d}N/\mathrm{d}t$ and the flux J_1 of $\mathrm{Me^{n+}}$ into a single nucleus:

$$i = -nF(\mathrm{d}N/\mathrm{d}t * J_1). \qquad (5)$$

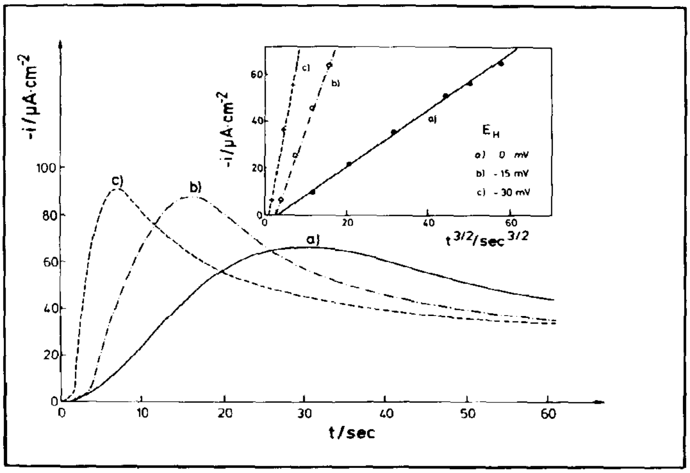

Fig. 3. Potentiostatic current-density transients of Bi deposition on CdS from a 0.5 M $NaClO_4 + 10^{-3}$ M $Bi(ClO_4)_3$ solution (pH 2). i *vs* $t^{3/2}$ plots and deposition potentials E_H are given in the inset.

The experimental i–t transients of Bi deposition on CdS (Fig. 3) can be well interpreted by assuming first-order nucleation kinetics, where the number density of nuclei $N(t)$ as a function of time is expressed by[24]

$$N(t) = N_s(1 - \exp(-kt)). \qquad (6)$$

In Equation (6), N_s denotes the density of potentially active nucleation sites on the substrate surface and k is the steady-state nucleation rate constant. In general both N_s and k are potential-dependent parameters. During the initial period of nucleation $[t \ll 1/k, N(t) = N_s kt]$ the nucleation rate can be considered as constant (progressive nucleation):

$$dN/dt = kN_s. \qquad (7)$$

After a certain time delay, further nucleation is arrested owing to the exhaustion of active sites, and "progressive" nucleation turns into "instantaneous" nucleation $[t \gg 1/k, N(t) = N_s]$.

Assuming hemispherical geometry of the growing 3-D crystallites, the flux J_1 in Equation (5) is related to the flux density j of Me^{n+} by

$$J_1 = 2\pi V_m^2 j(j * 1)^2 \qquad (8)$$

where V_m is the molar volume of the deposited metal Me. For hemispherical diffusion j is sufficiently well approximated by

$$j = (c_b D/2V_m t)^{1/2} \qquad (9)$$

where c_b is the bulk concentration and D is the diffusion coefficient of Me^{n+}. Combining Equations (5)–(9), we obtain the following expression for the overall deposition current density as a function of time:

$$i = -nF\, 2/3\pi k N_s (2Dc_b)^{3/2} V_m^{1/2} t^{3/2}. \qquad (10)$$

The initial part of the experimental i–t transients in Fig. 3 exhibits the time dependence predicted by Equation (10).

A further diagnostic criterion to prove the validity of the model proposed was only recently derived by Scharifker and Hills[8] taking into account overlap of the diffusion zones of the growing nuclei. For progressive nucleation with hemispherical diffusion the following relation should hold[8]:

$$i_{max}^2 t_{max} = 0.26\,(zFc_b)^2 D \qquad (11)$$

where i_{max} and t_{max} are the coordinates at the maximum of the i–t transient. Equation (11) does not contain the parameters k and N_s. Therefore, the product $i_{max}^2 t_{max}$ is expected to be constant, independent of the applied potential. This condition was fulfilled sufficiently well by the experimental transients described above, yielding an appropriate value of $D = 6 \times 10^{-6}\ cm^2\ s^{-1}$ for the diffusion coefficient of Bi^{3+}.

However, it is important to note that the $i \propto t^{3/2}$ dependence was observed only on a freshly prepared CdS surface. Transients obtained subsequent to a corresponding pulse experiment (even after anodic polarization at $E_H = 1$ V) exhibited an $i \propto t^{-1/2}$ dependence without any indication of a rising part in the response or an incubation period at very short times ($t \lesssim 10\ \mu s$) as was proved experimentally by oscillographic measurements. These findings confirm that the deposited Bi is not dissolved anodically. Obviously, without surface renewal further deposition of Bi occurs under pure transport control on the predeposited Bi crystallites without the need of further nuclei formation.

3.3. *Dependence of photocurrent on Bi coverage*

The fact that cathodically deposited Bi is not dissolved anodically, not even under illumination of the electrode surface, offers the possibility of studying the dependence of the photocurrent on the degree of Bi coverage by repeated deposition of Bi and subsequent photocurrent measurements. The polarization routine which was applied for this purpose is described schematically in Fig. 4 with the potential programme in Fig. 4(a) and the current response in Fig. 4(b). Bismuth was deposited during the periods τ_1 at potentials $E_- < E_{Bi/Bi^{3+}}$ in the dark (shaded area in

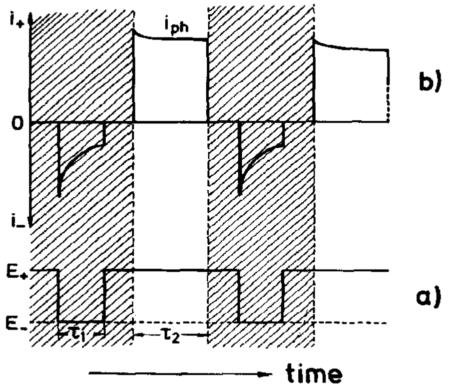

Fig. 4. Schematic representation of the polarization routine applied for evaluation of the dependence of the photocurrent density on the degree of Bi coverage in Fig. 5. (a) Potential–time programme: Bi deposition at $E_- = 0$ mV, -20 mV, -50 mV during time τ_1 and photocurrent measurement at $E_+ = 1$ V during τ_2; shaded area indicates dark periods; (b) current–time response.

Fig. 4) and the photocurrent i_{ph} was measured during the periods τ_2 of subsequent illumination after switching the potential from E_- to $E_+ = 1$ V.

The experimentally observed decrease of the photocurrent density i_{ph} with increasing amount of deposited Bi indicates that the photoanodic dissolution process, Equation (1), is restricted to that part of the CdS surface which is not covered by Bi. Assuming a simple geometrical blocking effect, the photocurrent density can be expressed as

$$i_{ph} = i^{\circ}_{ph}(1 - \theta_{\mathrm{Bi}}) \tag{12}$$

where θ_{Bi} denotes the fraction of the surface covered by Bi and i°_{ph} is the photocurrent density of the uncovered CdS surface at $\theta_{\mathrm{Bi}} = 0$.

A double logarithmic plot of the relative change of the photocurrent density $(i^{\circ}_{ph} - i_{ph})/i^{\circ}_{ph}$ *vs* the amount of Bi deposited is shown in Fig. 5 for three different deposition potentials E_-. The amount of deposited Bi, expressed by the volume V_{Bi} in Fig. 5, was obtained from integration of the cathodic Faradaic deposition current over time periods τ_1.

As long as overlapping of the growing Bi crystallites can be neglected, the results in Fig. 5 are well described by the relation

$$\theta_{\mathrm{Bi}} = K V^{m}_{\mathrm{Bi}} \tag{13}$$

with a constant K and an exponent close to $m = 2/3$. Considering the Bi deposit to consist of N_s hemispherical crystallites of mean radius r, Equation (13) is easily derived from the following simple geometric relations:

$$V_{\mathrm{Bi}} = N_s \cdot 2/3\pi r^3 \tag{14}$$

and

$$\theta_{\mathrm{Bi}} = N_s \cdot \pi r^2. \tag{15}$$

Accordingly, the constant K in Equation (13) is related to N_s by

$$K = N_s^{1/3}\pi^{1/3}(3/2)^{2/3}. \tag{16}$$

At $\theta_{\mathrm{Bi}} = 0.5$, a number density of about $N_s = 5 \times 10^9\ \mathrm{cm}^{-2}$ and a mean radius $r = 50$ nm are evaluated from the experimental results in Fig. 5. The slight parallel shift of the linear plots in Fig. 5 can be explained by an increase of the number density N_s of Bi nuclei with increasing cathodic overpotential E_-. At a higher degree of surface coverage ($\theta_{\mathrm{Bi}} \gtrsim 0.6$), the experimental points in Fig. 5 deviate from the linear dependence predicted by Equation (13). Such deviations are expected to occur owing to overlapping of the growing Bi crystallites.

The results described above are in accordance with the nucleation and growth model discussed in Section 3.2 and justify the basic assumption that the Bi crystallites are not dissolved anodically even under illumination of the surface.

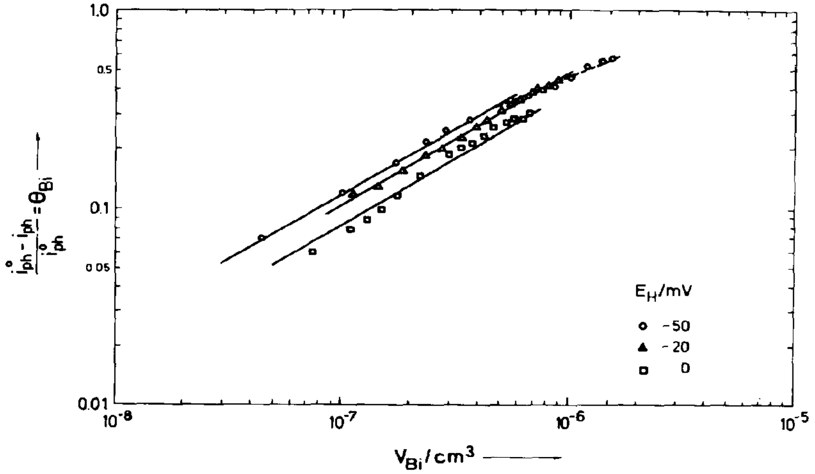

Fig. 5. Degree of Bi coverage θ_{Bi} expressed by the relative change of the photocurrent as a function of the volume of Bi deposited, V_{Bi}, determined at three different potentials, E_H, as indicated. System: CdS/0.5 M $NaClO_4 + 2.5 \times 10^{-4}$ M $Bi(ClO_4)_3$ (pH 2).

4. CONCLUSIONS

The electrolyte deposition of Bi on CdS semiconductor surfaces can be characterized by the following points:

(i) the initial stage of Bi deposition follows a progressive nucleation model with hemispherical or linear diffusion control of the Bi^{3+} transfer at three-dimensional growth centres.

(ii) The formation of a localized Schottky barrier at the interface between the Bi crystallites and the CdS surface prevents anodic dissolution of the deposit, even under illumination.

(iii) The decrease of the photoanodic dissolution of CdS with increasing Bi coverage can be referred to simple geometrical blocking of the CdS surface.

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