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Polarisation Phenomena Occurring at Cu/Semiconducting Te Layer/Electrolyte Interfaces Studied by Rapid Pulse Techniques

Nawal A. Darwish * and **Allam M. Allam**

Chemistry Department, Faculty of Science, University of Cairo, Giza, Egypt

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Tellurium films of different thickness are cathodically deposited on copper substrate using sodium tellurite solutions of *p*OH 3.95. The kinetics of the primary processes and modes of conduction occurring at the Cu/Te layer/electrolyte interfaces are studied using rapid galvanostatic rectangular pulses. Approximate values for the specific conductance of the surface layer are calculated from the experimental resistance overpotential. Activation overpotentials are explained in view of charge transfer reactions associated with reactions occurring at the electrode/solution interface.

(Keywords: Electrochemistry; Pulse polarisation technique; Tellurium layers)

Polarisationsphänomene an Cu/*halbleitende* Te-*Schicht/Elektrolyt-Phasengrenzen*

Tellur-Schichten verschiedener Dicke wurden aus Natriumtelluritlösungen von *p*OH 3,95 kathodisch auf Kupfer abgeschieden. Es wurden die Kinetik der Primärprozesse und die Art der Leitung an den Cu/Te-Schicht/Elektrolyt-Phasengrenzen mittels schneller galvanostatischer Rechtwinkel-Pulstechnik untersucht. Dabei wurden angenäherte Werte für die spezifische Leitfähigkeit der Oberflächenschicht aus den experimentellen Widerstands-Überpotentialen errechnet. Die Aktivierungsüberpotentiale werden im Hinblick auf Ladungsübertragungsreaktionen in Verbindung mit Reaktionen an der Phasengrenze Elektrode/Lösung erklärt.

Introduction

In a previous work[1] the electrochemical properties of cathodically deposited thin Te[1] and Se[2] films on Sn substrate were investigated. Several studies have been reported[3] on the electrochemical properties of massive Te, however, very little work is as yet carried out on the behaviour of thin Te films electrodeposited on metal substrates in

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contact with different electrolytes. *De Becdelievre*[4] studied the electrochemical properties of cathodically polarised Te and Se in H_2SO_4 solutions and reported that for Te no limitation of the kinetics of hydrogen ion discharge was noticeable and the surface was covered with an oxide film which screened the semiconducting properties.

The electrical properties of fine-grained films of Te prepared by vapour deposition in vacue were investigated by *Pokrovskii*[5]. The results showed the existence of electron-acceptor surface levels immediately below the filled zone of the semiconductor. *Cermak*[6] showed that the direct current electrical resistance of thin tellurium films decreased irreversibly with time at a constant temperature due to disappearance of lattice defects.

Most of the previous investigations[7] were concerned with the electrical properties of Te films deposited by condensation in vacue on different substrates especially on glass and mica. *Mumtaz* et al.[8], *Oancha* et al.[9] and *Capers* and *White*[10] measured the electrical conductivity of deposited Te films on glass. They reported that the films possessed polycrystalline structures with a grain size dependent on deposition parameters. The specific electrical conductivity of such films increased with increasing thickness, rate of deposition and the transition from the non-annealed state.

The semiconducting properties of vacuum-deposited Te films on glass have been studied as a function of film thickness and of the rate of deposition by *Goswami* and *Jog*[11]. They found that the activation energy varied from 0.14 to 0.20 eV depending upon the thickness and the rate of evaporation of films, higher thickness favouring lower values. They and other investigators[12] found that the magnitude of temperature coefficient of resistance was generally decreased with rise of temperature. The non-ohmic behaviour of tellurium films with intrinsic, or near-intrinsic carrier concentration was studied by *Liederer* and *Kuzmany*[13].

It is of interest to investigate the kinetics of the primary processes and modes of conduction occurring at the Cu/Te layer/electrolyte system. The present work includes galvanostatic anodic polarisation of the above system using rectangular pulses along a wide current density range.

Experimental

Electrodeposition of Te *Layer on* Cu *Substrate*

Mathers and *Turner*[14] were able to deposit firm smooth films of Te upon lead cathodes from solutions of TeO_2 in mixtures of HF and H_2SO_4. *Khairy* and *Darwish*[15] obtained fairly good adherent selenium films on a copper substrate cathode from a sodium selenite bath buffered at about *pH* 9.6.

In the present study, Te thin films were cathodically electrodeposited on spec-pure copper electrodes from a 0.1 *M* sodium tellurite bath ($p\text{OH} = 3.95$). The cathodic deposition of tellurium was studied at current densities ranging from 0.1 to 5.0 mA/cm^2. Homogeneous adherent layers have been obtained at 3.0 mA/cm^2, which conditions was chosen to prepare the electrodes used in the

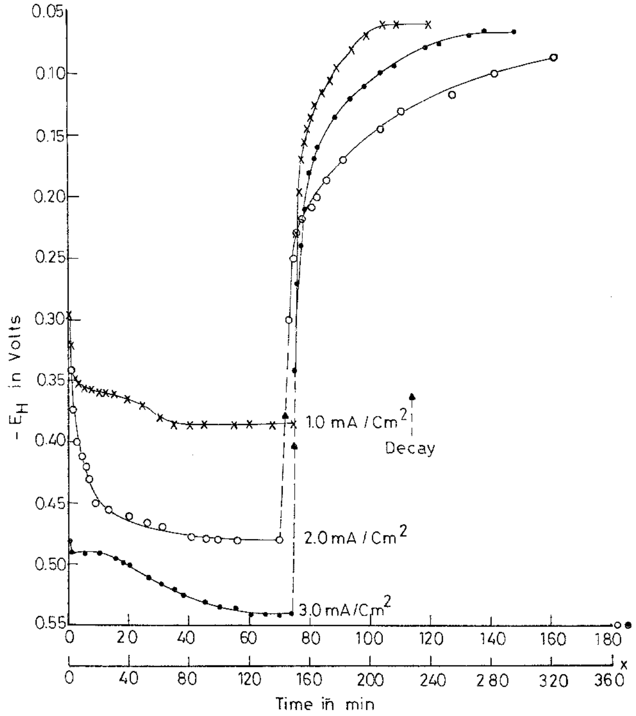

Fig. 1. Charging and decay E_H—time curves during the cathodic deposition of Te on Cu electrodes in 0.1 M Na_2TeO_3

succeeding anodic polarisation experiments. Representative curves are shown in Fig. 1. On switching on the polarising current, the potential falls gradually until it acquires a steady state which lasts till the end of the polarising period. The decay potentials shift with time towards more or less steady state values.

The cathodic process involves the reduction of tellurite yielding elemental tellurium:

$$TeO_3^{2-} + 3\,H_2O + 4e = Te + 6\,OH^-$$

$$E_H = —0.569 + 0.089\,pOH + 0.015 \log a_{TeO_3^{2-}} \qquad (1)$$

This process is presumably subjected to overpotential effects including chiefly charge transfer and concentration polarisation. Whence a protecting layer is established on the electrode surface, the cathode potential falls down due to increase of layer resistance with increase of thickness. This proceeds untill a layer of appropriate thickness is formed with a suitable population of space charges so that the electronic current would be conducted under the prevailing field strength at a more or less steady potential.

Rapid Anodic Polarisation Using Rectangular Pulses

The copper/tellurium electrode system was anodically polarised in 0.1 M Na_2TeO_3 ($pOH = 3.95$), $2.5 \cdot 10^{-2}\,M$ NaOH, 0.22 and 0.022 M HCl, 0.2 and

0.02 M NaCl and 0.1 M $CuSO_4$ solutions. In all experiments 1.0 M KNO_3 was used as a supporting electrolyte. A saturated calomel half-cell was used as a reference electrode and bright platinum as an auxiliary electrode.

Rapid galvanostatic pulses of duration ranging from 0.1 to 20.0 ms can be supplied by means of a Tektronix wave-form generator, type 162, in conjunction with a power supply, type 160 A. These pulses are suitable for direct use at relatively low current strengths up to 1 mA. In order to obtain pulses at higher current strengths up to about 40 mA, an auxiliary circuit[2] was utilised.

In the present study, galvanostatic pulses of 2.0 ms duration are passed through the copper/tellurium/electrolyte system over a wide range of current density, at ambient temperature (25 °C). The potential-time traces are recorded on the screen of a Tektronix oscillograph type 531 A provided with polaroid-film camera type C-27.

Results and Discussion

The curves obtained on galvanostatic anodic polarisation of the Cu/Te system at different current densities using pulses of 2 ms duration are characterised by a rapid and sharp initial potential jump which is chiefly due to drop of potential, η_r, across the ohmic resistance of the surface layer, presumably associated with adsorbed solvent and anions. It has to be pointed out that the electrodeposited tellurium consists mainly of crystallites, very likely inclused with amorphous particles, such a structure would expectedly possess considerably more resistance than the vacum deposited films obtained thermally, which exhibit semiconductivity[5,6]. The anode potential then exhibits a more gradual rise with time which comprises activation overpotential, η_a, associated with the charging of the double layer and/or charge-transfer processes including reactions operative at the metal/surface layer/solution interfaces. Steady values are approached which increase with increase of C.d. The decay transients exhibit an initial rapid fall, equivalent to resistance overpotential, followed by the gradual decay of activation overpotential.

Specific Conductance of the Tellurium Surface Layer

Approximate values for the apparent specific conductance, σ, of the Te layer can be calculated from the corresponding η_r values, using the relation:

$$\sigma = \frac{i\,\Delta}{\eta_r} \tag{2}$$

where i is the current density and Δ is the layer thickness. Table 1 comprises representative values of the observed overpotentials and the calculated σ values. It is obvious that at all investigated current

Table 1. *Overpotentials, η, and specific conductance, σ, of tellurium layers in* $0.1\,M\,Na_2TeO_3 + 1.0\,M\,KNO_3$ (*pH* 10.44); *pulse duration 2 ms*

Layer Thickness μm	C_d i (mA cm^{-2})	η mV	η_r mV	η_a mV	$10^6\,\sigma$/ Ohm^{-1} · cm^{-1}
1.0	0.050	5.5	4.9	0.6	1.0
	0.087	9.7	8.5	1.2	1.0
	0.170	18.5	16.5	2.0	1.0
	0.467	45.1	39.0	6.1	1.2
	0.904	94.6	82.4	12.2	1.1
	4.779	463.6	402.6	61.0	1.2
	5.325	524.6	451.4	73.2	1.2
	6.000	591.7	512.4	79.3	1.2
	6.961	683.2	597.8	85.4	1.2
	8.413	793.0	701.5	91.5	1.2
	10.310	994.5	884.5	110.0	1.2
	13.430	1296.3	1159.0	137.3	1.2
	19.480	1860.5	1708.0	152.5	1.1
					Average 1.1 ± 0.1
5.0	0.467	43.9	39.0	4.9	6.0
	0.909	88.3	79.3	9.0	5.7
	2.545	244.0	201.3	42.7	6.3
	3.714	368.1	311.1	57.0	6.0
	5.039	512.4	427.0	85.4	5.9
	5.636	533.8	442.3	91.5	6.4
	6.571	625.3	518.5	106.8	6.3
	7.740	732.0	610.0	122.0	6.3
	12.700	1098.0	945.5	152.5	6.7
					Average 6.15 ± 0.55

densities, the apparent specific conductance of the layer assumes more or less constant values in the same electrolyte and at the same layer thickness; σ is almost independent of the pulse duration. The average calculated σ values (Table 2) are invariably smaller than those reported for vacuum-deposited films[5]. This may be ascribed to less defected structure of the electrodeposited film, together with the presence of amorphous inclusions of tellurium in the otherwise crystalline deposit. This results in a subsequent decrease of space charge carrier density.

σ values obtained at a layer thickness of 5 μm are considerably greater than those at the thinner film, 1 μm thick. This reveals increased population of space charges and hole concentrations[6, 16]. Besides, the film may also be rendered more porous with increase of layer thickness. One may also argue that under the considerably high field strength at the layer/metal interface, diffusion of Cu^{2+} ions and

Table 2. *Average specific conductance*, σ, *of* Te *surface layer on* Cu

Electrolyte	$0.1\,M$ Na_2TeO_3 ($pH = 10.44$)	$0.025\,M$ NaOH ($pH = 12.60$)	$0.1\,M$ $CuSO_4$ ($pH = 4.18$)	$0.22\,M$ HCl ($pH = 0.43$)	$0.022\,M$ HCl ($pH = 1.44$)	$0.2\,M$ NaCl ($pH = 6.29$)	$0.02\,M$ NaCl ($pH = 6.79$)
$10^6\,\sigma$ (average)/ $Ohm^{-1}\,cm^{-1}$	1.1 ± 0.1 [a]	1.0 ± 0.1	2.1 ± 0.1	2.5 ± 0.2	2.35 ± 0.25	1.3 ± 0.1	1.05 ± 0.05
	6.15 ± 0.55[b]	9.3 ± 1.0	10.5 ± 0.5	13.0 ± 1.0	10.0 ± 1.0	8.8 ± 0.5	5.6 ± 0.5

[a] Values obtained at a layer thickness of 1 μm; [b] 5 μm.

electrons through the layer may occur with subsequent formation of dendrites of CuTe, especially concentrated nearer to the Te/substrate interface.

The electrolyte concentration, respectively the population and persistence of adsorbed anions, seems to affect layer specific conductance. Thus, the values of σ are closely comparable in slightly acid to alkaline media and are considerably smaller than the values accomplished in hydrochloric acid media. This may plausibly be ascribed to different adsorbed anion effects. Adsorbed Cl^- ions may act as a negatively charged surface film that replaces the inhibiting initially adsorbed water film. It is apparent that Cl^- ions are more preferentially adsorbed in acid than in neutral to alkaline media. The above state of affairs pertains at the electrode/solution interface on open-circuit, as well as in the initial stages of the anodic process under the prevailing nonstationary pulse polarisation conditions.

Activation Overpotential—Current Density Relations

The values of η_a comprise the observed overpotentials associated with processes at the electrode/solution interface, including charging of the double layer and charge transfer polarisation associated with rate-determining reactions occurring under the applied field. The total current, i_t, which is caused to jump to a constant value under galvanostatic conditions, comprises the faradic current, i_f, and the coulombic current, i_c. The former is associated with the charging of the double layer and the latter with the electrochemical reaction at the electrode/solution interface. The faradic current is given by[17]:

$$i_f = nFD_0\,(\partial C_0/\partial X)_{x=0} \tag{3}$$

Boundary condition for solving *Fick*'s diffusion law is given by equation (4)

$$i = C_d\frac{d_\eta}{dt} + nFD_0\left(\frac{\partial C_0}{\partial X}\right)_{x=0} = constant \tag{4}$$

where C_d is the double layer capacity. At $\eta_a \ll \frac{RT}{nF}$, the current is chiefly faradic. The small overpotentials, $\leq 5\,\text{mV}$, encountered at relatively low C_d are chiefly due to the passage of faradic rather than coulombic current. At higher C_d, considerably higher overpotentials are observed which are caused by charge transfer processes, the faradic contribution of current being relatively very small. One should recall that the prevailing experimental conditions involve rapid perturbation of equilibrium at the interface through the galvanostatic rectangular current pulses, followed by relatively slower relaxation. Under such circumstance and in the presence of a considerable excess of supporting electrolyte in the medium, the anodic rate-determining reactions are principally diffusion-controlled. The following kinetic relation holds:

$$i = i_0 \left[\exp\left\{ \alpha \varphi \eta_a \right\} - \exp\left\{ -(1-\alpha) \varphi \eta_a \right\} \right] \quad (5)$$

where i is the net anodic current density, i_0 is the exchange C_d, α is the charge transfer coefficient and $\varphi = \frac{zF}{RT}$, where z is the number of electrons involved in the reaction determining the electrode kinetics. At very low values of η_a, viz., at low C_d, the above exponent (5) may be expanded into a series. Taking the first term of the series, one gets:

$$i \approx i_0 \cdot \varphi \eta_a \quad (6)$$

from which the value of i_0 is evaluated. At relatively higher overpotentials, equation (5) can be put in the form:

$$\log \frac{i}{1 - 10^{-\varphi \eta_a / 2.303}} = \log i_0 + \alpha \varphi \eta_a / 2.303 \quad (7)$$

In the rate-determining reaction governing the electrode process, the plot of the left-hand side of equation (7) against η_a, one gets a straight line whose slope equals $\alpha\varphi/2.303$ and intercept at $\eta_a = 0$ yields i_0.

The anodic dissolution of tellurium proceeds according to[18]:

$Te + OH^- = TeO^{2+} + H^+ + 4e$ (highly acidic solutions) (8)
$Te + 2\,OH^-_{(ad)} = TeO_2 + 2\,H^+ + 4e$(moderate and weak acid solutions)(9)
$Te + 3\,OH^-_{(ad)} = TeO_3^{2-} + 3\,H^+ + 4e$ (neutral and alkaline media) (10)

In all cases, the rate of reaction is more likely determined by the diffusion of OH^- ions from the bulk of solution to the inner *Helmholtz* plane in the electrode vicinity.

Under appropriate conditions, viz., relatively high effective C_d, appropriate pulse duration and considerable layer porosity, dissolution of copper may occur within the pores of the tellurium yielding Cu^{2+} ions:

$$Cu = Cu^{2+} + 2e \quad (11)$$

In presence of Cl^- ions, CuCl may be formed according to:

$$Cu + Cu^{2+} + 2\,Cl^-_{(ad)} = 2\,CuCl \quad (12)$$

The insoluble salt would clog the pores of the surface film thus stopping further attack. Deviation from the purely diffusion-controlled process takes place and the electrode kinetics would be governed by surface conditions, mainly the porosity of the tellurium surface and availability of copper specks within the pores.

Based on the above arguments and using $z = 4$ in the above relations, the value of i_0 associated with the charging of the double layer can be calculated from equation (6), whereby a straight line i vs. η_a holds (see representative Fig. 2). The values thus obtained are shown in Table 3. It is clear that at the same layer thickness, i_0 assumes fairly comparable values in neutral and alkaline media. At the higher thickness, 5 μm, i_0 is considerably greater than at the lower thickness, 1 μm, which is due to the more porous surface film rendering it more active. The anodic dissolution of tellurium and/or of copper within its pores proceeds more rapidly at the thicker than the thinner surface layer. The appreciably higher i_0 values obtained in the HCl solutions, even at the 1 μm-thick layer, is a criterion of more active surface conditions caused by adsorbed corrosive Cl^- ions.

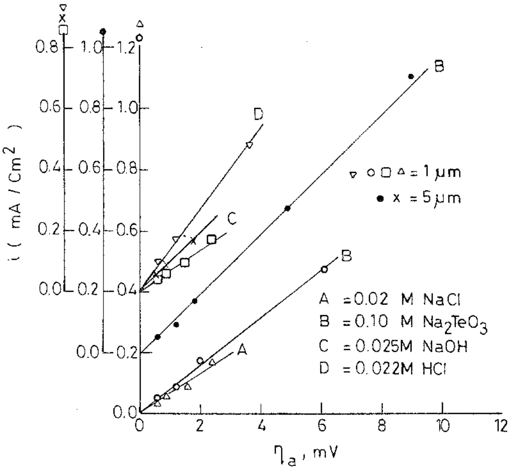

Fig. 2. i vs. η_a for anodic polarisation of Te layer in different media at low current densities

The kinetic parameters, i_0 and α, calculated for the diffusion-controlled process at relatively high overpotentials, from the half logarithmic relation[7], c.f. representative Figs. 3 and 4, are summarised in Table 3. It is noticeable that in all investigated electrolytes the values of the transfer coefficient are relatively small and fairly of the same order of magnitude, indicating an invariably slow anodic dissolu-

Table 3. *Exchange currents and transfer coefficients*

Electrolyte	Layer Thickness (μm)	Kinetic Parameters Low C_d Range i_0 (mA cm^{-2})	 High C_d Range i_0 (mA cm^{-2})	 α
0.1 M Na_2TeO_3	1	0.48	1.82	0.11
($pH = 10.44$)	5	0.61	1.35	0.11
0.025 M NaOH	1	0.42	2.40	0.14
($pH = 12.60$)	5	0.61	2.69	0.15
0.2 M NaCl	1	—	2.75	0.12
($pH = 6.29$)	5	—	3.02	0.12
0.02 M NaCl	1	0.42	—	—
($pH = 6.79$)				
0.1 M $CuSO_4$	1	—	2.95	0.15
($pH = 4.18$)	5	0.64	2.69	0.15
0.22 M HCl	1	0.70	4.27	0.09
($pH = 0.43$)				
0.022 M HCl	1	0.83	3.02	0.11
($pH = 1.44$)	5	—	3.39	0.09

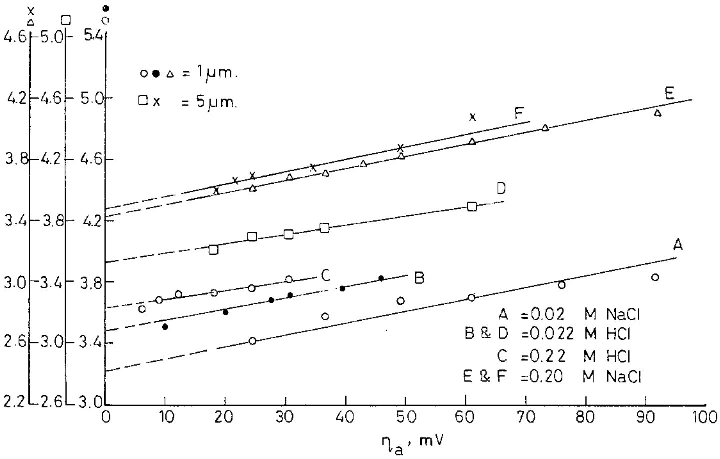

Fig. 3. η_a vs. log $i/(1-10^{-\varphi\eta_a/2.303})$ curves for Cu/Te electrodes in acidic and neutral media

tion process. The values of the exchange C_d are closely comparable with each other in all electrolytes except in the 0.1 M sodium tellurite, where considerably small i_0 is obtained, and in the 0.22 M HCl solution, where i_0 is appreciably high. The behaviour in the tellurite solution is more

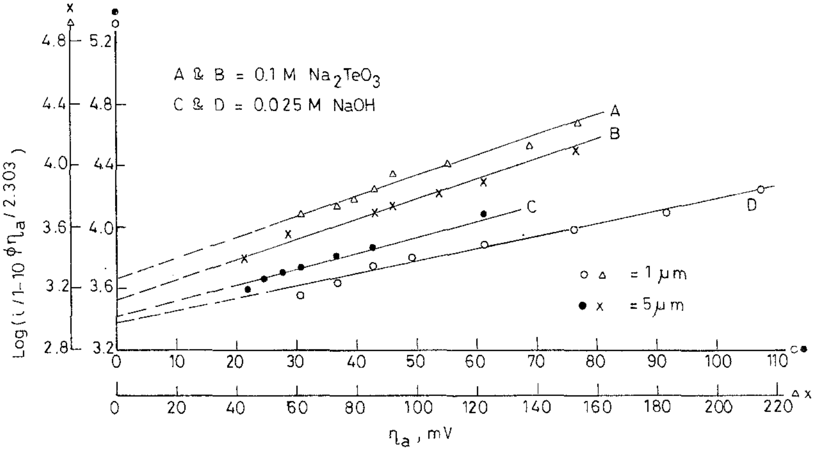

Fig. 4. η_a—$\log i/(1-10^{-\varphi\eta_a/2.303})$ curves for Cu/Te electrodes in alkaline media

likely due to hampered dissolution of tellurium in presence of a relative preponderence of TeO_3^{2-} ions in the double layer. On the other hand the dissolution of Te in the strong acid medium is more enhanced yielding TeO^{2+} ions, hence the higher i_0.

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