ACID BASE PHENOMENA AT THE n-TiO$_2$/ROOM TEMPERATURE MOLTEN SALT INTERPHASE

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Interphasial properties of the n-TiO$_2$/room temperature AlCl$_3$:1-butylpyridinium chloride melt system have been studied by cyclic voltammetry and ac impedance methods. Surface faradaic reactions, dependent on the Lewis acidity of the melt and the semiconductor dopant concentration, are thought to be due to ionizable surface complexes. Theoretical models for flat-band shifts with bulk electrolyte acidity may be complex if the surface coverage is variable or if multiple ligand ionization can occur.

Interactions between electrolytes and semiconductor surfaces are of interest because they are able to influence the efficacy of photoelectrochemical cells. In aqueous systems, it is well known that bulk solvent acid–base variations may lead to flat-band potential shifts and this effect generally has been ascribed to dissociative ionization of surface molecular constituents. For example, the flat-band dependence on pH of TiO$_2$ has been investigated thoroughly and found to shift $-(2\cdot3RT/nF)$ V per pH unit[1,2]. The amphoteric surface equilibria which give rise to the flat-band shift have been expressed in various ways, *e.g.*,

$$\text{TiOH}^- \;\rightleftarrows\; \text{TiO}^{2-} + \text{H}^+$$

or,

$$\text{TiOH}_2^+ - \text{H}^+ \;\rightleftarrows\; \text{TiOH} \;\rightleftarrows\; \text{TiO}^- + \text{H}^+$$

but the actual identity of surface species responsible has not been definitely established for any semiconductor substrate.

Similar behaviour occurs too in non-aqueous media. Uchida and coworkers[3,4] have studied the electrode behavior of Sb-doped polycrystalline tin oxide and n-TiO$_2$ in the high temperature AlCl$_3$:NaCl molten electrolytes and, in each case, the flat-band potentials determined from conventional Mott–Schottky analyses were found to shift 2 $(2\cdot3RT/F)$ V per pCl$^-$ unit change in the melt Lewis acidity. It was proposed that this behavior was due to specific adsorption of Cl$^-$ ions rather than originating from an acid–base interaction. Gale and coworkers[5] have found that the flat-band shifts at n-GaAs depend on the crystal orientation. The $\Delta V f_b$/pCl$^-$ slope of approximately $(2\cdot3RT/F)$ V for the (100) orientation was about one-half of that obtained with (111) n-GaAs crystals in room temperature AlCl$_3$:1-butylpyridinium

chloride melts[6]. This result strongly suggests that the crystal surface atom density and type may be in certain instances a significant factor in the interactions between substrate and electrolyte. Solely electrostatic forces should not be dependent on local crystal structure. By utilization of bulk acidity adjustments it has been possible to optimize the overlap of the substrate band edges with redox couple energy levels, thereby maximizing cell efficiency[5]. In view of the quantitative understanding of the solvent acid–base chemistry of the $AlCl_3$:1-butylpyridinium chloride (1-BPC) melts[7,8] this system was chosen for further studies of the surface interactions at an oxide semiconductor.

EXPERIMENTAL

Preparations of $AlCl_3$ and 1-BPC have been described in earlier publications[7,8]. Handling of the melt and electrochemical experiments were made in a drybox under purified Ar atmosphere, or in sealed cells. Capacitance measurements were made using a newly developed automated admittance technique[5]. TiO_2 electrode discs were clamped to a Teflon plug insert in a Pyrex glass cell to expose a known area. After prolonged immersion (5 days) in the molten salts, the exposed surfaces were not etched visibly but they had become temporarily hydrophilic, retaining a water drop. Geometrical areas are used for calculations. In-Ga ($\sim 1 : 3$) alloy was used for ohmic contact to a small Pt disc and spring. The counter electrode comprised a large area Pt foil and the reference electrode, isolated in a Fisher reference junction compartment, was an Al wire immersed in 2 : 1 molar ratio $AlCl_3$: 1-BPC ($\sim +0.39$ V, N.H.E.). The TiO_2 discs were of the rutile structure with their C axes perpendicular to the faces. Different doping levels were achieved by hydrogen reduction. First, the discs were etched in c.H_2SO_4 at 160° for 5 minutes, then immersed in boiling distilled water for 30 minutes, and finally dried and treated in a stream of either pure H_2 (high doped sample A) or Ar/H_2 (10%) mixture (lower doped sample B) at $700-750°$ for 10 minutes.

N_D values were determined for both samples by conventional Mott-Schottky analyses. For sample B values were also obtained by direct conductivity methods. Values obtained were 1.7 . 10^{19} cm^{-3} (0.1M-H_3PO_4/1M-KNO_3), 1.9 . 10^{19} cm^{-3} ($1.1 : 1$ melt, $\sim 30°$), 2.2 . 10^{19} cm^{-3} (4-point probe), and 2.4 . 10^{19} cm^{-3} (Van der Pauw), using a mobility $\mu = 0.1$ cm^2 V^{-1} s^{-1} (ref.[10]).

RESULTS

Typical cyclic voltammograms are illustrated in figure 1 for a TiO_2 sample in a basic ($0.8 : 1$) and acidic ($1.84 : 1$) melt composition, molar ratios $AlCl_3$:1-BPC, respectively. In the acidic melts, the deposition of Al metal was possible at ~ -0.43 V on sample B, at an overpotential, and the deposit could be stripped in a sharp peak on the reverse scan at ~ 0.0 V. In the basic solvent, the appearance of Cl$^-$ ion oxidation is at $\sim +2.0$ V, or about 1.3 V positive to the chlorine evolution potential on an inert metal electrode. Melt reduction of alkylpyridinium ion occurred at ~ -1.1 V, as on vitreous C electrodes, but scanning negative to -1.5 V revealed no oxidation currents on the reverse scan due to dimerized pyridinyl radical product. With sample A, the oxidation background of an acidic melt was $\sim +3.2$ V and Al

deposition commenced at ~ -0.6 V. Dissimilar to the lower doped sample, however, scanning to -1.4 V in a basic melt did reveal a dimer oxidation wave at ~ -0.5 V on reverse scan. Apparently, and Al film can be oxidized from either electrode but electron transfer to an organic species is only possible with the quasi-metallic sample A. Chloride ion oxidation exhibits a large overvoltage at each electrode compared to the behavior at vitreous C.

Cyclic voltammograms of all TiO_2 samples in the acidic melts show the occurrence of reduction and oxidation charge-transfer processes (Fig. 1 and 2). These processes did not vary in ambient room light to darkness. Scanning in the negative direction
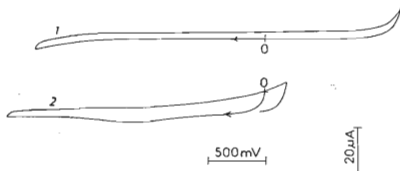

Fig. 1

Cyclic voltammograms of TiO_2. ($N_D = 1.9 . 10^{19}$ cm^{-3}) in 1 $0.8:1$ melt and 2 $1.84:1$ melt: $= 200$ mV s^{-1}, $30°$
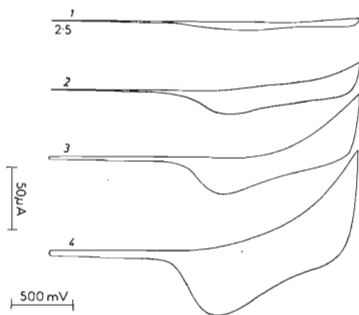
FIG. 2

Cyclic voltammograms of TiO_2 ($N_D = 4.5 . 10^{20}$ cm^{-3}) at v: 1 10 mV s^{-1}; 2 50 mV s^{-1}; 3 100 mV s^{-1}; 4 200 mV s^{-1}; $30°$

from 2·5 V, a cathodic current peak appears at $\sim +1\cdot2$ V and a shallow peak can be discerned sometimes at $\sim 0\cdot8$ V, followed by a gradual increase in current until Al deposition is reached. Forward and reverse charges are equal within the experimental reproducibility and approximately constant for $v > 100$ m V s^{-1}. These surface charge variations are given in Tables I and II. Background charging currents

TABLE I

Variation of charge (μC cm^{-2}) with scan rate for TiO$_2$ in 1·75 : 1 melt (30°C), $N_D = 4\cdot5 \cdot 10^{20}$ cm^{-3}

v, mV s^{-1}	q_{cath}	q_{an}
10	870	950
50	690	630
100	510	590
200	500	480
500	480	500

TABLE II

Variation of charge (μC cm^{-2}) with acidity and scan rate for a TiO$_2$ sample, $N_D = 1\cdot9 \cdot 10^{19}$ cm^{-3}, 0·0 to 2·0 V, 30°C

v, mV s^{-1}	Molar ratio AlCl$_3$: 1-BPC			
	2 : 1	1·75 : 1	1·5 : 1	1·25 : 1
	q_{cath}			
10	—	—	—	—
20	394	319	—	—
50	291	232	186	143
100	253	195	167	—
200	223	177	150	111
500	198	157	122	102
	q_{an}			
10	—	—	—	140
20	264	121	—	—
50	251	157	123	115
100	228	165	133	—
200	223	151	128	97
500	206	163	120	103

were subtracted by graphical extrapolation which is liable to greater uncertainty at the lower scan rates. Rotating disc experiments in which a TiO_2 disc was rotated to rates of 2 000 rpm did not affect the magnitudes of the surface faradaic processes compared to values obtained under convection-free conditions. Reproducibility was not especially good because the surface condition varied slowly over a 24 hour contact period with the melt. Nevertheless, the average charge $((q_{an} + q_{cath})/2)$ for the 0·0 to 2·0 V range was considerably larger for the higher doped sample at a particular acidity and the charges increased for both samples with increase in melt acidity. The anodic peak in the voltammograms for the pCl-range 11·5 to 15, shifted ~110 mV/pCl$^-$ unit and although the significance of this is not clear, it could imply a dependence of the charge transfer reaction on the melt acidity by ligand coordination changes. There is also a shift to positive potentials with increasing scan rate of $\sim(RT/F)$ V per decade.

Fig. 3 contains the frequency dispersion data for the frequencies 10 Hz to 10 KHz obtained using a classical bridge arrangement. The admittance plane plot for the lower doped sample in a slightly acidic melt fits a flattened semicircle, in reasonable agreement to the theoretical form for a simple series RC combination, i.e., the space charge capacitance and series resistance dominates the equivalent circuit for the interphase. Dispersion worsens with increase in melt acidity and highly distorted Cole-Cole plots were obtained with the higher doped sample, even at high positive
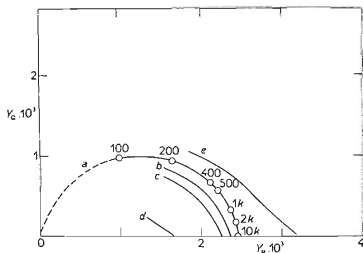

FIG. 3

Admittance plane plots for the frequency range 100 Hz-10 KHz; low-doped sample ($N_D = 1·9 . 10^{19}$ cm^{-3}). a 1·1 : 1, 2 V bias; b 1·5 : 1, 2V bias; c 2 : 1, 2 V bias; high-doped ($N_D = 4·5 . 10^{20}$ cm^{-3}) d 0·8 : 1, 0·0 V bias; sample e 1·5 : 1, 2 V bias

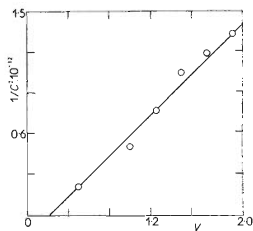FIG. 4

Mott–Schottky curve for TiO_2 in 1·1 : 1 melt from admittance data, $N_D = 1·9 . 10^{19}$ cm^{-3}

bias. Increased chemical modification of the surface, it would seem, is accompanied by deviations from the series RC model. It is not known whether these distortions arise from a faradaic impedance contribution to disruption of the classical model for the space charge distribution. Fig. 4 examplifies a Mott–Schottky plot from automated admittance measurements. Again, the conductance data reveal distortion from the simple model at frequencies below 1 KHz and little qualitative difference for data at 1·75 or 0·0 V bias (data are collected at a fixed bias and the surface faradaic process presumably is equilibrated).

DISCUSSION

Exhaustive surface faradaic processes were not obtained with Sb-doped SnO_2 electrodes[3], nor reported for n-TiO_2 in the high temperature $AlCl_3$:NaCl molten salt system[4]. Laitinen and coworkers[11] have described similar phenomena to those found in this study at the tin oxide semiconductor electrode in aqueous HCl. Unfortunately, reactions between semiconductor substrates and electrolytes can lead to complex behaviour of interphases and it is extremely difficult experimentally to identify the nature of the chemical composition changes that have occurred. Chlorination of both TiO_2 and SnO_2 by aluminum chloride is known[12,13] and Schafer and coworkers[14] have reported a free energy value for $\Delta G^0_{573} = -7$ Kcal for TiO_2 chlorination per mol AlOCl formed. It is to be expected that a surface chlorination reaction can ensue according to

$$\text{—Ti=O} + Al_2Cl_7^- \rightleftarrows \text{—TiCl}_2 + AlCl_4^- + AlOCl. \qquad (1)$$
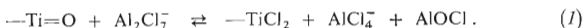
Such equilibria demonstrate that the extent of conversion can be dependent on the melt pCl^-, though its major acid–base equilibrium,

$$Al_2Cl_7 + Cl^- \rightleftarrows 2\ AlCl_4^- \qquad (2)$$

and can explain the experimental observations above, if the converted (chlorinated) surface becomes electroactive. Assuming a surface species reducible by 2e/molecule, a charge 500 μC cm^{-2} corresponds to $2\cdot6 \cdot 10^{-9}$ mol cm^{-2}, or an inclusive occupational area of 6·4 A^2/molecule in an ideal, 2-dimensional plane. Charge values of 1 100 μC cm^{-2} were obtained in highly acidic melts, but of course there is no reason to assume that the species distribution is only 2-dimensional as 3-dimensional nuclei or layers of discrete electroactive species might be present at the surface. Note that this situation could be different to the case in which the whole surface is considered to be converted, as is generally assumed for aqueous semiconductor systems. Assuming that the surface may become partially chlorinated, ionization of the surface complexes may be induced by further acid–base reactions, e.g.,

$$-TiCl_2 + Al_2Cl_7^- \rightleftarrows -TiCl^+ + 2\, AlCl_4^- , \qquad (3)$$
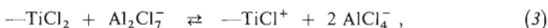
where the increase in acidity tends to create positively charged surface ions and the heptachloroaluminate ion is a stronger acid than $-TiCl_2$. Depending on the coordination of the titanium oxychloride species, one or several ionizations steps are possible,

$$-TiCl^+ + Al_2Cl_7^- \rightleftarrows -Ti^{2+} + 2\, AlCl_4^- . \qquad (4)$$
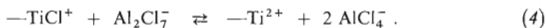
The possibility of Cl^- ion adsorption from acidic melts should be considered remote because the free Cl^- ion concentration in a $1{\cdot}75 : 1$ melt, for example, is only of the order $3 . 10^{-13}$M. Chloride ion adsorption isotherms would abruptly change their form at the neutral region and the flat-band/voltage dependency would be related to the particular adsorption isotherm. In the above model, negative surface charge could accumulate in the basic regions by $AlCl_4^-$ or Cl^- ion adsorption, or by complex equilibria, *e.g.*,

$$-TiCl_2 + 4\, AlCl_4^- \rightleftarrows -TiCl_4^{2-} + 2\, Al_2Cl_7^- . \qquad (5)$$
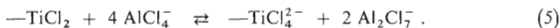
No thermodynamical data is available at present to confirm the relative significances of reactions of type $(3)-(5)$, and even if homogeneous data were available, its application to surface is questionable. The following conclusions result from this study:

(i) Surfaces processes are direct evidence that chemical modification of a surface can result from Lewis acidity changes in the bulk electrolyte. Although the charge may provide an estimate of the extent of reaction, spectroscopic techniques will be required to identify the structures of electroactive molecules (sites),

(ii) Flat-band potential shifts due to surface charge variations have been ascribed in the past to both ionizable complexes and/or ion adsorption (charge-transfer complexes). It is difficult to distinguish these, however, any model should be consistent over both the acidic and basic ranges of the bulk electrolyte composition,

(iii) Chemical changes to the surfaces of semiconductors are crucial to the understanding of the behavior of the non-polarized interphase as well as charge-transfer processes to both surface sites (states) and solvent species. Analogous phenomena to those found in aqueous electrolytes at semiconductor surfaces also occur in molten salt media.

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