Methylviologen Redox Reactions at Semiconductor Single Crystal Electrodes

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The mechanism of the two-step reduction of the methylviologen cation radical (MV^{2+}) was studied at CdS, GaAs and InP single crystal electrodes. In aqueous solution the second step $(MV^{+\bullet} \rightarrow MV^{0})$ gives rise to layer formation which is not observed in mixed ethanol/water solutions. This layer has interesting electrical properties. The reoxidation of MV^{0} occurs by electron injection into the conduction band of all three semiconductors. The reoxidation of $MV^{+\bullet}$ at InP is also a conduction band reaction and electroluminescence is observed with the p-type semiconductor. Electron injection from $MV^{+\bullet}$ into the conduction band of GaAs is not observed while the kinetics of the reaction at CdS depend critically on the state of the electrode surface and on the nature of the electrolyte solution.

Introduction

The methylviologen (1,1'-dimethyl-4,4' bipyridinium) dication (MV^{2+}) has been widely used as electron scavenger in studies of semiconductor colloidal aqueous suspensions including studies of Q-particles [1-14]. Despite this extensive work, relatively little attention has been devoted to the mechanism and kinetics of the redox reactions of the $MV^{2+}/MV^{+\bullet}$ and $MV^{+\bullet}/MV^{0}$ systems at single crystal semiconductor electrodes [15-18]. An interesting aspect of these redox couples is the strongly negative standard redox potential (-0.69 V (SCE) for) $MV^{2+}/MV^{+\bullet}$ and -1.12 V (SCE) for $MV^{+\bullet}/MV^{0}$ [19]) making them candidates for studies involving electron injection into the conduction band of the semiconductors. Recently, there has been a revival of interest in processes involving electron injection into the conduction band from redox systems in solution. The Grätzel solar cell concept [20] is based on this reaction: an electron is transferred from the excited state of an adsorbed dye molecule into the conduction band of a polycrystalline TiO₂ anode. There have been few systematic studies of majority carrier injection into the conduction band of n-type semiconductors in aqueous solutions, partly because reducing agents capable of injecting electrons into the conduction band, generally located at higher energy, are unstable in the solution (decomposing H_2O to give hydrogen). The $MV^{+\bullet}$ radical cation, while thermodynamically unstable in water, is kinetically stable thus making electron injection studies possible. Various viologens have been considered for applications in displays. The products of the reduction reactions can form strongly coloured layers on the electrode [21, 22].

The aim of the present work was to study the electrochemistry of the $MV^{2+}/MV^{+\bullet}$ and $MV^{+\bullet}/MV^{0}$ systems at semiconductor single crystal electrodes, with special emphasis on CdS. Both reduction and oxidation reactions including layer formation were investigated using rotating ring-disc voltammetry. Electron injection into the conduction band can give rise to electroluminescence in a p-type semiconductor. Since CdS is only available as n-type material, InP and GaAs were included in the study. To our

knowledge there have been only two previous reports of such anodic luminescence due to simple electron transfer reactions at p-type electrodes [23, 24]. Kooij et al. [23] have shown that electron injection from $MV^{+\bullet}$ into the conduction band of porous Si gives rise to emission of visible light. They showed that layer formation can be prevented by the use of a mixed ethanol/water electrolyte solution.

The position of the conduction band edge of the semiconductor is important, especially for electron injection. In Fig. 1 the location of the band edges of GaAs [25], InP [26] and CdS [27, 28] (based on literature data) are shown in relation to the redox potentials of the $MV^{2+}/MV^{+\bullet}$, $MV^{+\bullet}/MV^{0}$ and H^{+}/H_{2} couples at pH 2. On the basis of this figure, $MV^{+\bullet}$ is expected to inject electrons into InP but not into GaAs, whose conduction band edge is located at considerably higher energy. One should note the significant spread in the data for CdS, indicated by the bands in Fig. 1. Since the location of the conduction band edge is



Fig. 1

Location of the band edges of CdS, GaAs and InP based on literature values, compared with the standard redox potentials of the MV^{2+}/MV^{+*} , MV^{+*}/MV_0 and H^+/H_2 couples at pH 2. The bands shown for CdS represent the spread in the literature values

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critical in this case, we studied the influence of pretreatment on the flat band potential, as determined by impedance measurements.

Experimental

Single crystal CdS wafers with a donor density of 10^{16} cm⁻³ were obtained from the Eagle Picher Research Laboratory (USA). Both (0001)Cd and (0001)S surfaces were used. Before each measurement the electrodes were polished with diamond paste down to 1 µm grain size and were successively etched for 1 min in 1% Br₂/chloroform solution and in 0.1% Br₂/chloroform solutions before rinsing with chloroform [29]. The measurements reported here refer to the $(000\overline{1})$ face. Results for the (0001) face were similar. Single crystal InP and GaAs wafers, all (100)oriented, were obtained from MCP Electronic Materials Ltd. (United Kingdom). The doping levels were; p - InP $(5 \cdot 10^{16} \text{ cm}^{-3})$, n-InP $(5 \cdot 10^{15} \text{ cm}^{-3})$ and both n-GaAs and p-GaAs $(2 \cdot 10^{17} \text{ cm}^{-3})$. The polished InP were given a standard dip in concentrated HCl solution and the polished GaAs in 1% Br₂ in methanol.

Current-potential measurements were performed in a conventional cell with a salt bridge separating the working and the counter electrode compartments. A saturated calomel electrode (SCE) was used as a reference and potentials are given with respect to SCE. The DC measurements were carried out with a Bank POS 73 potentiostat. To determine flat band potentials (U_{fb}) electrical impedance measurements were performed with a Solartron FRA 1255 frequency response analyzer in combination with a PAR 273 A potentiostat. The CdS pretreatment, described above, gave very reproducible results with almost no dispersion in the Mott-Schottky plots in the frequency range 0.1 - 200 kHz. A silicon BPW 34 photodiode was used for measuring electroluminescence with a set-up as described elsewhere [30].

For the electrochemical measurements with CdS a rotating semiconductor disc electrode or a ring/disc electrode (with a Au ring) was used. At the Au-ring it was possible to analyze directly the products formed during the potential scan of the CdS disc. When necessary, $MV^{+\bullet}$ was generated in the bulk solution using an auxiliary gold electrode; the concentration of the electroactive species could be determined at the gold ring. For the luminescence measurements with InP a rotating gold disc/p-InP ring electrode was used [24]. In this case the $MV^{+\bullet}$, required for electron injection at the semiconductor ring, was generated at the Au disc by reduction of MV^{2+} .

The electrolyte solutions contained reagent grade chemicals dissolved in doubly distilled water. Because of the reactivity of $MV^{+\bullet}$ with oxygen, special care was taken to remove all traces of oxygen from the solution.

Results

The redox electrochemistry of the methylviologen system in aqueous and in mixed ethanol/water solutions is first described for stationary and rotating CdS electrodes. Special attention is paid to the kinetics of the oxidation of the $MV^{+\bullet}$ radical cation. The bandedge positions, as deduced from impedance measurements on CdS, are then considered. Finally results for GaAs and InP are given. The oxidation of $MV^{+\bullet}$ at p-InP and the resulting electro-luminescence are described.

Stationary CdS Electrodes

Fig. 2 shows the current density-potential (j-U) curve for a stationary CdS disc electrode in a 2 mM MVCl₂, 0.5 M K₂SO₄ aqueous solution. Two waves are clear in the forward scan (i.e. to more negative potentials). They can be ascribed to the first and second reduction steps of MV^{2+} : to $MV^{+\bullet}$ and to MV^0 , respectively. In the return scan two waves are also observed due to the oxidation of MV^0 to $MV^{+\bullet}$ and of $MV^{+\bullet}$ to MV^{2+} . Since the measurements were performed in the dark, anodic processes at an n-type semiconductor must involve injection of majority charge carriers. This leads to the conclusion that oxidation occurs via reactions (1) and (2):

$$MV^{0} \approx MV^{+\bullet} + e_{CB}^{-} \tag{1}$$

$$MV^{+\bullet} \rightleftharpoons MV^0 + e_{CB}^- \tag{2}$$

The reduction of the methylviologen dication on n-CdS could, in principle, involve two reactions:

$$MV^{2+} + e_{CB}^{-} \neq MV^{+\bullet}$$
(3)

$$MV^{2+} \neq MV^{+\bullet} + h_{VB}^{+}$$
⁽⁴⁾

The position of the band edges of n-CdS with respect to the redox potential (see Fig. 1) suggest, however, that reaction (4) is very unlikely. The fact that CdS is not etched in MV^{2+} solutions at the open circuit potential confirms this suggestion. Obviously, holes are not injected into the valence band. The empty levels of the $MV^{+\bullet}/MV^{0}$ system should show an even better overlap with the conduction

Fig. 2

j-U curve of a stationary n-CdS electrode in 2 mM MVCl_2, 0.5 M $\rm K_2SO_4$ aqueous solution; scan rate 20 mV/s



band states (see Fig. 1); it is clear that $MV^{+\bullet}$ is also reduced via the conduction band.

$$MV^{+\bullet} + e_{CB}^{-} \neq MV^{0}$$
⁽⁵⁾

It can therefore be concluded that both oxidation and reduction reactions occur via the conduction band of CdS.

Fig. 3 shows the current density-potential curve for a stationary CdS disc electrode in a mixed ethanol water (1:1) solvent. In the forward scan two reduction waves are again clear, while in the reverse scan only the oxidation of MV^0 to $MV^{+\bullet}$ leads to an anodic current. From this we conclude that the second oxidation ($MV^{+\bullet}$ to MV^{2+}) step does not occur in this electrolyte solution.

Rotating CdS Disc and CdS Disc-Au Ring Electrodes

In Fig. 4 the current density-potential curve for a rotating CdS disc electrode in a mixed water ethanol (1:1) electrolyte solution is given. In the forward scan the cathodic current due to the reduction of MV^{2+} to $MV^{+\bullet}$ starts at -0.6 V and reaches a limiting value at -0.8 V. The onset of the reduction of $MV^{+\bullet}$ to MV^{0} at -1.0 V is followed by a second plateau. A Levich plot of the limiting current in both plateaus confirms that mass transport of MV^{2+} to the electrode surface determines the rates of the two reactions. The scan in the negative direction coincides with the scan in the positive direction, as can be expected when soluble products are formed at a rotating electrode; the products are swept away from the surface before they can be reoxidized.



 $j \cdot U$ curve of a stationary n-CdS electrode in 2 mM MVCl₂, 1 M KCl ethanol/water (1:1) solution, scan rate 20 mV/s



Fig. 4

j-U curve of a rotating (1600 rpm) n-CdS electrode in 2 mM MVCl₂, 1 M KCl ethanol water (1:1) solution, scan rate 10 mV/s

In Fig. 5a a cyclic voltammogram is shown for the CdS disc of a ring-disc electrode scanned at 20 mV/s. In the forward direction current onset is observed at -0.6 V. At -0.8 V this current reaches a limiting value which, from a Levich analysis, proves to be diffusion limited. The cathodic disc current increases again at -1.05 V reaching a current density twice that of the diffusion limit for a single electron step. Up to this point the current-potential curve is similar to that measured in water/ethanol electrolytes (Fig. 4). In aqueous solutions, however, a current peak is observed instead of a plateau for the second reduction step; the current decreases after a certain cathodic charge has been passed. At more negative potentials the current dips below the plateau for the first reduction step but then returns to the plateau. Finally, hydrogen evolution is observed. The onset of this reaction is at a potential 300 mV more negative than the onset potential in an electrolyte solution without MV^{2+} . In the reverse scan an anodic peak, superimposed on the cathodic diffusion limited plateau, is observed at -0.9 V. This corresponds to the oxidation of MV^0 to $MV^{+\bullet}$. In contrast to the result in water/ethanol solutions, the MV⁰ product remains on the electrode surface in the aqueous solution. This is due to a considerably lower solubility of MV⁰ in water. The charge involved in the reoxidation corresponds to more than $10 \,\mathrm{MV}^0$ monolayers; a thick product layer is obviously formed. This layer blocks the surface and inhibits both the reduction of MV^{+•} to MV^0 and of H_2O to H_2 . It is however, surprising that, after the cathodic peak, the cathodic current does not decrease to a low value; it dips below the plateau for the first reduction step but then returns to the plateau. The absence of a second oxidation peak at more positive potentials shows that MV^{+•} is not retained at the electrode surface but dissolves in the solution.



Rotating n-CdS disc/Au ring electrode (1600 rpm) in 2 mM MVCl₂, 1 M KCl aqueous solution. a. *j*-U curve of n-CdS disc, scan rate 20 mV/s. b. The corresponding Au ring current at -0.3 V vs. the n-CdS disc potential

In Fig. 5 b the Au-ring result corresponding to the experiment with the CdS disc in Fig. 5 a is shown; the ring current at -0.3 V is plotted as a function of the disc potential. At -0.3 V current can be due to the reoxidation of MV^{+•} or MV⁰; the latter is unlikely since MV⁰ is adsorbed at the disc while MV⁰ in solution should conproportionate [31]:

$$MV^0 + MV^{2+} \Rightarrow 2MV^{+\bullet}$$
(6)

At the current onset of the CdS disc, the Au-ring gives an anodic current; MV^{+•} formed at the disc is oxidized at the ring. The ring current in the plateau corresponding to the diffusion limited reduction of MV^{+•} at the disc is that expected from the calculated collection efficiency of the ringdisc configuration (about 30%). During the cathodic peak due to the second reduction step, the ring current decreases. This supports the conclusion that MV^0 is adsorbed at the CdS surface. When the disc current again returns to the diffusion limited plateau during the forward scan, the ring also shows a plateau; MV^{+•} continues to be formed. The reduction of water to hydrogen at the CdS electrode has no effect on the ring current. In the reverse scan the oxidation of adsorbed MV⁰ at the CdS electrode is accompanied by an anodic ring peak. The dip below the diffusion limited current at -1.25 V in the forward disc scan disappears at lower scan rate. Surprisingly this dip at -1.25 V does not correspond to a drop in the ring current but rather to a maximum; clearly more MV^{+•} is being detected at the ring.

The influence of the rotation rate of the electrode at constant scan rate is illustrated by the current potential curves in Fig. 5 and 6a and b. Two effects can be seen: at lower rotation rates the cathodic peak is broader and the anodic MV^0 oxidation peak in the reverse scan is higher. Since the anodic ring current also indicates that more MV^0 is released at lower scan rate we conclude that the amount of MV^0 adsorbed on the electrode depends on the rotation rate. Both the width of the cathodic peak and the height of the anodic oxidation peak in the return scan depend on the scan rate for a fixed rotation rate. As the scan rate is increased the reduction peak becomes broader and the oxidation peak higher. The charge under the anodic peak is roughly independent of the scan rate.

When the CdS electrode was scanned to very negative potentials, an extra anodic peak showed up at -0.8 V in the return scan. It is known that CdS can be decomposed cathodically to give metallic Cd. The extra peak can be attributed to the oxidation of Cd.

Oxidation of MV^{+•} at CdS Electrodes

To study the kinetics of electron injection, a constant bulk concentration of $MV^{+\bullet}$ was generated by reduction of MV^{2+} at the auxiliary electrode. The ring electrode of the ring disc set-up was used to determine the concentration of both $MV^{+\bullet}$ and MV^{2+} in solution. Fig. 7 shows results for an n-type CdS electrode in a phosphate buffered solution of pH 7 containing 0.07 mM $MV^{+\bullet}$, 1.94 mM MV^{2+} and 0.1 M KCl. The potential of zero current agrees with the





 $j \cdot \overline{U}$ curves for an n-CdS disc/Au ring electrode in 2 mM MVCl₂, 1 M KCl solution, (scan rate 20 mV/s) rotated at: a. 400 rpm; b. 2500 rpm. (The Au ring current at -0.3 V vs. the n-CdS disc potential.)





j-U curve of an n-CdS electrode rotated at 1600 rpm in 0.07 mM $MV^{+\bullet}$, 1.91 mM MV^{2+} , 0.1 M KCl solution buffered at pH 7

calculated Nernst potential of the $MV^{2+}/MV^{+\bullet}$ couple. The anodic current due to electron injection from $MV^{+\bullet}$ is essentially independent of applied potential in a wide range. This is expected since the rate constant for electron transfer depends only on the overlap between filled states in the redox system and empty states in the conduction band. This overlap is not affected by changes in the applied potential, if the band edges remained pinned.

At low pH (3.5) the limiting anodic current (j_{lim}) depends on the square root of the electrode rotation rate; this means that electron injection from MV^{+•} is very fast and its rate is diffusion controlled. At higher pH (7 and 11) the reaction is slower and is under mixed diffusion/kinetic control. Koutecky-Levich plots of the results are shown in Fig. 8: the reciprocal limiting current density is plotted

against the square root of the reciprocal electrode rotation rate for three values of the pH for a solution containing 0.35 mM MV^{+•}. In Fig. 9 the kinetically limited current density j_{kin} , obtained from this analysis, is shown as a function of the MV^{+•} concentration for the experiment at pH 7. A linear dependence is observed, indicating simple first order kinetics. A first order rate constant k_a , defined by:

$$k_{\rm a} = j_{\rm kin} / F[\rm MV^{+\bullet}] \tag{7}$$

of 10^{-3} cm s⁻¹ was calculated for the results of Fig. 9 (*F* is the Faraday constant and [MV^{+•}] the bulk concentration in mol cm⁻³). A similar rate constant was found for electron injection at pH 11.

Mott-Schottky Plots of CdS Electrodes

Since the flat band potential of CdS in aqueous electrolyte solutions depends strongly on the pretreatment of the electrode, one must be careful when using literature



Fig. 8 Koutecky Levich plots for the oxidation of $MV^{+\bullet}$ at n-CdS at different pH values



Fig. 9

Kinetically limited current density of an n-CdS electrode vs. [MV^{+•}] in 1 M KCl, pH 7 unbuffered solution



 $1/C_{\rm S}^2$ plotted as a function of potential for an n-CdS electrode at different frequencies at pH 6.7

values. We have confirmed results of de Wit [29] who showed that, unlike various other methods, the Br₂/chloroform pretreatment gives completely reproducible initial values for the flat band potential of CdS. In Fig. 10 a typical Mott-Schottky plot for a CdS electrode at pH7 is given. In these measurements no dispersion was observed in a broad frequency range. The flat band potential was determined for the two crystallographic orientations at different pH values. The results of several measurements are summarized in Table 1. In contrast to reports by Feiner et al. [28], no difference was found between flat band potentials of the two crystallographic orientations. The flat band potential was however, not constant; there was a relatively fast shift from the initial value by about 100 mV in the positive direction, followed by a further slow change of about 200 mV over a period of hours to days. The flat band potential corresponding to the kinetic measurements in aqueous solution were, in all cases, approximately 100 mV more positive than the initial values shown in Table 1. The presence of MV^{2+} and $MV^{+\bullet}$ in solution did not affect the impedance results. Surprisingly, the flat band potential in the mixed ethanol/water solvent (-0.9 V) showed absolutely no drift. We should mention that the flat band potential of CdS is very sensitive to illumination even at extremely low light intensities.

InP and GaAs Results

The redox electrochemistry of methylviologen at n-type InP was similar to that at n-type CdS at low pH (see Fig. 2). The j - U curve for a stationary n-InP electrode also showed two anodic peaks during the reverse scan, which means that both MV^0 and $MV^{+\bullet}$ inject electrons into the conduction band. On the other hand, the second oxidation step was not

Table 1

Initial Flat band potential of n-CdS electrodes in aqueous electrolyte after Br_2 /chloroform pretreatment

pН	0001 face	0001 face
4	-0.8	-0.8
7	-0.9	-0.9
11	-0.9	-0.9

observed at n-GaAs. These results are expected on the basis of the energy diagram shown in Fig. 1.

We used the p-InP ring/Au disc electrode to investigate electron injection into the semiconductor. During generation of $MV^{+\bullet}$ at the Au-disc a j-U curve as shown in Fig. 11 (dashed curve) was observed. The anodic current at the p-InP ring electrode, due to the injection of electrons by oxidation of $MV^{+\bullet}$, starts at about -0.6V (not shown) and reaches a limiting value. At a potential close to the flat band value (0.65 V [26]) the current rises sharply; this is due ot anodic oxidation and dissolution of the semiconductor and is also observed in indifferent electrolyte solution. That MV^{+•} injects electrons into the conduction band is clear from the observation of light emission from the electrode (solid-line, Fig. 11). The electroluminescence starts at 0 V and reaches a maximum at about 0.2 V. At 0.4 V a second electroluminescence maximum is observed. During the reverse scan only one emission maximum is found at 0.25 V.



Electroluminescence and anodic current density vs. potential of a rotating Au disc/p-InP ring electrode in 2 mM MVCl₂, 0.1 M KCl solution at pH 2, (scan rate 20 mV/s; 1600 rpm) MV⁺⁺ production at the gold disc. Dashed line: p-InP ring current density, solid line: electroluminescence intensity

Discussion

It is clear from literature and from the present work that the flat band potential of CdS as determined by impedance measurements is very sensitive to the method of electrode pretreatment. While the pretreatment used here ($Br_2/$ chloroform) gave completely reproducible Mott Schottky plots with almost no frequency dispersion, the flat band potential measured in aqueous solution drifted as a function of time. In contrast, the measurements in mixed ethanol/water solutions did not show any drift. The pH dependence of $U_{\rm fb}$ in the range 4-11 was slight (Table 1) and no difference was observed between the two crystallographic faces studied. The dotted lines in the band of Fig. 1 represent the position of the bandedges of CdS as deduced from $U_{\rm fb}$ value, corresponding to the kinetic measurements at pH 4. At pH 7 and 11 the bandedges are about 100 mV higher in energy.

The general trends in the kinetic results obtained with the methylviologen redox system at n-type CdS are in agreement with what one would expect on the basis of the bandedge positions. Although the rearrangement energies and distribution functions of the redox couples are not known, an excellent overlap between the empty states of the two couples and the conduction band is expected (see Fig. 1). Such overlap favours electron transfer to both MV^{2+} and $MV^{+\bullet}$; in the limiting case, the reduction rates depend on mass transport of MV^{2+} to the surface. It is clear that in the aqueous solution MV^0 production leads to layer formation on the electrode (Fig. 5 and 6). The MV^0 product is soluble in the mixed water/ethanol electrolyte, as is clear from the RDE results (Fig. 4).

Oxidation of MV^0 to $MV^{+\bullet}$ is observed in both electrolyte solutions as one would expect since the MV⁰ occupied states correspond well with the empty conduction band states. The oxidation rate of $MV^{+\bullet}$ (to MV^{2+}) however depends critically on the location of the conduction band edge. In the most favourable case (aqueous electrolyte at low pH 4) electron injection into the conduction band is fast and is controlled by mass transport of MV^{+•} to the electrode (Fig. 8). At higher pH the position of the conduction band edge is at slightly higher energy and the oxidation reaction is under mixed kinetic/diffusion control (the rate constant k_a is the same for pH 7 and 11, as is the flat band potential). In all cases a potential independent anodic current is observed, typical of a reaction based on majority carrier injection. The position of the conduction band edge is unfavourable in the case of the water/ethanol solution and no oxidation of MV^{+•} is observed (Fig. 3). This can again be explained by the apparently poor overlap of the occupied $MV^{+\bullet}$ levels with the conduction band.

As a result of the second oxidation step a layer is formed on the CdS surface in aqueous solutions. Although the layer is relatively thick a diffusion limited one-electron reduction is observed at negative potentials. Using the SNIFTIRS technique Christensen and Hamnett [21] found that the layer formed on edge carbon electrodes consists of species of different valencies. Like Jansson et al. [32] they conclude that both MV^{+*} (as MVCl) and MV^0 are present. Very schematically, layer formation can be represented as follows:

$$(\xi + 1)MV_{(\text{soln})}^{+\bullet} + e^{-} \approx \xi MV^{+\bullet}/MV^{0}$$
(8)

in which $\xi MV^{+\bullet}/MV^0$ represents the ratio of the two valencies in the layer. Conduction can be attributed to an electron hopping mechanism of the type:

$$MV^{+\bullet} + MV^{0} \Rightarrow MV^{0} + MV^{+\bullet}$$
(9)

This should be an activated process depending on the electric field across the layer, which is determined by the potential drop and the layer thickness. From our results we must conclude that there is also a mechanism for layer removal. This is very likely a conproportionation reaction of the type:

$$\xi MV^{+\bullet}/MV^{0}(s) + MV^{2+} \approx (2+\xi)MV^{+\bullet}_{(soln)}$$
(10)

In the steady-state, the rate of growth of the layer (reaction (8)) is equal to the rate of its dissolution (reaction (10)).

As the layer is being formed in the second reduction peak, MV^0 and $MV^{+\bullet}$ species are trapped at the surface and are not available for oxidation at the ring. The ring current drops markedly. When the steady-state is reached, the reduction current passing through the CdS electrode via reaction (9) is in fact controlled by the rate of reaction (10), i.e. supply of MV^{2+} from solution; the combination of these two reactions is equivalent to a diffusion limited one-electron step. Consequently, when the rotation rate is increased, the rate of film dissolution increases and, as a result the steady-state current increases.

The "overshoot" in the cathodic current below the level of the diffusion-limited plateau during the scan in the negative direction may be due to an induction effect in film formation. Some time may be required to form a well-defined conducting $MV^0/MV^{+\bullet}$ layer from the initial randomly deposited layer at the electrode surface.

The injection of electrons by MV^{+•} ions into p-type InP electrodes leads to light emission as shown in Fig. 11. The form of the electroluminescence intensity-potential curve is similar to that found by Meulenkamp and Kelly for p-InP in $Cr(CN)_6^{4-}$ solution at high pH [24]. Athough electron injection begins at relatively negative potential (-0.6 V, not)shown), the onset of emission is only observed at 0V (see Fig. 11). This is probably due to effective surface recombination caused by the very strong band bending, which holds the electrons at the surface. This luminescence is quenched at more positive potentials as anodic discussion sets in. The second peak in the anodic scan direction is also observed without MV^{+•} [30, 33] and can be attributed to electron injection from a surface state intermediate of the anodic dissolution reaction. This has also been observed in electrolytes containing hydrogen peroxide [33]. That this peak is absent in the return scan can be attributed to surface oxide which can form on InP at pH 2. We have shown that at lower pH light emission is also observed in both scan directions with only slight hysteresis [30]. In contrast to InP, we observed no electroluminescence from p-type GaAs in the presence of MV^{+•}. The conduction band edge of GaAs is located at considerably higher energy [25] making electron injection impossible. Recent work has shown that the MV^{+•} radical cation can inject electrons into the conduction band of Si and can induce visible electroluminescence in p-type porous Si [23].

Conclusions

It was shown that both reduction steps of MV^{2+} occur via the conduction band of CdS. Although the second step causes film formation, the first reduction step is not inhibited by this solid film. The kinetics of the oxidation of MV^{++} at CdS electrodes can be explained on basis of the position of the bandedges. The oxidation of $MV^{+\bullet}$ at p-InP electrodes leads to electroluminescence; $MV^{+\bullet}$ is not capable of injecting electrons into the conduction band of GaAs.

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