Probing charge transfer processes at p-GaAs electrodes under weak optical excitation

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ABSTRACT

The p-GaAs photocathode/acetonitrile interface was characterised in the dark and with tens of μW/cm² laser powers at 830 nm wavelength, using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Two redox mediators were used that present completely different behaviours under low optical excitation: one (Tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate) is sensitive to the surface states of the photocathode and the other (benzoquinone) is not. The combined electrochemical methods allow us to characterize the energetics of the electrode-electrolyte interface as well as the dominant electron transfer process.

1. Introduction

GaAs semiconductors are technologically important materials, finding electrochemical utility in photovoltaics and solar to chemical energy conversion [1–7]. The GaAs surface can be modified with metal nanoparticles or organic monolayers, allowing the fine-tuning of the interface for various catalytic and electrochemical sensor purposes [8–14].

Fundamental studies of p- and n-GaAs electrochemistry, both in aqueous and organic media have been performed, and the results often highlight the instability of p-GaAs, especially in aqueous medium. The results suggest that the solvent, redox mediator, dopant concentration, as well as the quality of the GaAs material and the method of surface treatment all have intricate effects on the properties of the p-GaAs/electrolyte interface [15–20].

GaAs may also be an electrode material suitable to detect spin effects in electrochemistry. There is presently a growing interest for exploring spin-dependent charge transfer processes at electrodes [21–24]. The required spin polarisation can be achieved either by functionalizing a surface with chiral molecules [25–27], or in the case of direct band gap III-V semiconductors such as p-GaAs, by exciting electrons to the conduction band (CB) with circularly polarized light. The pioneering work of Chazalviel and Modestov & Kazarinov showed that the spin effects on bare p-GaAs were elusive, and were detected for a few redox mediators only [28,29].

Evidently, the charge transfer rate is a key consideration since the electron spins might relax faster than the electrons are transferred to the redox species. Furthermore, charge transfers may occur through surface states that are likely to mask spin effects. In this paper, we use cyclic voltammetry (CV) combined with electrochemical impedance spectroscopy (EIS) to provide information on the charge transfer mechanisms and rates at the p-GaAs/acetonitrile interface during photo-reduction. This study presents a characterization at very low laser powers and at a wavelength which is specific with respect to the band structure. This regime hasn’t typically been addressed in semiconductor electrochemistry but is of interest to us, especially in the field of spin dependent electrochemistry, as it represents the conditions for which spin dependent electrochemical kinetics have already been observed [28].

1,4-benzoquinone (BQ) was used as a redox mediator, and its behaviour was contrasted with Tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate (Ru(bpy)_3²⁺), which is known to display a strong interaction with the p-GaAs surface [15]. The results obtained through EIS and CV were compared to the properties derived from semiconductor electrode models in order to validate the quantitative results of our study. We also show the extent to which EIS data can discriminate among the most-used equivalent circuits.

2. Experimental methods

Epitaxially grown p-type GaAs (UniversityWafer Inc, Item 2178), Zn-doped to 2.9 × 10¹⁷ cm⁻³ was used as a working electrode with the
polished [111B] surface exposed to the sample solution. As-received p-GaAs wafers were oxygen-plasma etched from both sides to obtain a clean surface, after which Au was evaporated on the backside to establish an electrical contact. This contact preparation has been found to be adequate in previous work for electrochemical and impedance measurements on p-GaAs [16,30,31]. A connection with a Cu wire was established using silver paste. This contact was then insulated from the sample solution with a silicon sealant.

Kapton tape was used to define the active surface area, typically 0.01-0.025 cm². The p-GaAs surface was rinsed with acetone, etched for 1 min in 6 M HCl, rinsed with Milli-Q water (18.2 MΩ cm) and immediately placed into a glove box to prevent the surface from re-oxidising. The electrode was placed into a square 3 × 3 mm borosilicate tube together with a Pt wire tip as pseudo-reference electrode and a Pt wire coil as counter electrode.

All sample solutions were prepared from dry acetonitrile (Acros Organics 364315000, 99.9%, extra dry) with 0.2 M tetrafluorophosphate (Ru(bpy)₃²⁺), Aldrich 448974, 98 atom % D, 1.6 mM) and Tris(2,2’-bipyridine)ruthenium(II) hexafluorophosphate (Ru(bpy)₃²⁺), Aldrich 754730, 97%, 2 mM) served as redox mediators.¹

All samples were prepared and stored in a glove box, and taken out only in a sealed sample tube prior to experiments.

The electrochemical cell was protected from ambient light. A 830 nm laser diode, matching the band gap of the GaAs (1.42 eV), was used as an illumination source. The light beam was brought to the electrode surface through a 5 mm light guide.

A Gamry potentiostat (Interface 1000E) was used to record the CV and EIS, typically between 0.5–1 Hz to 10 kHz for BQ and 0.2 Hz to 10 kHz for Ru(bpy)₃²⁺ both for dark and illuminated conditions. 6 data points per decade were recorded with 10 mV modulation of the electrode potential. All of the EIS data were recorded in a steady state, which was readily achieved because of the low laser powers, implying that the reductive current was limited to a steady value determined by the availability of the conduction band (CB) electrons at the interface, and not by the diffusion of the redox mediator in the solution. When fitting the impedance spectra to equivalent circuits, non-linear least squares fitting (NLLS) was used to estimate the quality of the results, and had a typical residual value of 5e-4 or below in order for us to consider the fits acceptable.

After preparing the electrochemical cell, the p-GaAs/acetonitrile interface was allowed to stabilise, typically tens of minutes for BQ and a couple of hours for Ru(bpy)₃²⁺. Furthermore, it was important to allow the cell to re-equilibrate between experiments, sometimes for tens of minutes, in order to ensure a good reproducibility of the measurements.

3. Theory

The electronic structure of the interface for a p-type semiconductor electrode in contact with an electrolyte is shown schematically in Fig. 1 (32), where surface states (SS) are to be expected because of the discontinuity of the crystal lattice at the semiconductor surface (33). For a p-type semiconductor, incident light (G) generates minority charge carriers (electrons) in the CB, which are transferred to the electrode surface due to the electric field induced by the band bending across the space charge (SC) layer. The electrons are then either transferred to the redox mediator (in the solution) at a rate kₚ or they relax to the SS at a rate kₙ.

The presence of SS at the interface can facilitate the recombination of the electrons excited to the CB with the holes in the valence band

ⁱ BQ was deuterated because this leads to a simpler electron paramagnetic resonance (EPR) spectrum. In the future this will help us to manipulate the spins of the electrons and to detect the EDMR signals.

![Fig. 1. Schematic structure of the p-GaAs interface with processes related to the photo-generation of charge carriers (G) and the possible reaction pathways, showing the energy of the conduction band (E_CB), valence band (E_VB), the surface states (SS) and the Fermi level (E_F). The different rate constants (k) for the possible electron processes are also depicted.](Image 342x575 to 522x737)

(VB), as described by the pathway kₙ → kₚ (Fig. 1), a process that competes with the electron transfer (ET) across the interface. According to the Gärtner model of ET on a p-type semiconductor, the reduction current is assumed to start immediately at potentials more negative than the flat-band potential (E_{FB}), since the emerging electric field across the SC layer tends to bring electrons to the electrode surface while moving holes to the bulk of the semiconductor. In this case, the electrons are transferred to the electrolyte at a rate kₚ or kₙ, [34].

The question of whether the redox process occurs directly from the semiconductor bands or if it is mediated by the SS has been widely discussed in the literature [35-40]. Below, we will show that the measurement and analysis of the Open Circuit Potential (OCP) as a function of the laser power can help clarify this point.

The Gärtner model can break down because of recombination via SS. This process has been reported to be very fast at III-V semiconductor surfaces [41-45], and can be accounted for by the Wilson model. When recombination via SS dominates, potentials considerably more negative than E_{FB} must be applied in order to induce the reduction of the redox mediator [16,46-49]. Additional complications arise for redox mediators with a formal potential (E_p') outside of the band gap, as discussed in Section 5.2 for Ru(bpy)₃²⁺. In this case both Gärtner and Wilson models can become inadequate to describe the details of the ET.

In the discussion below, we assume that the Gerischer hypothesis concerning the ET holds, i.e. it occurs only between states of nearly the same energy [50,51]. For a photo-induced reduction process, this implies that the efficiency of the ET depends on the overlap of the density of states of the oxidized species (D_{Ox}) in the solution with the energy of the SS or the CB edge at the semiconductor surface.

It is assumed that the Helmholtz capacitance at the p-GaAs/solution interface, which is in series with the space charge capacitance (C_{SC}), remains constant when the potential is changed, and is much larger than the C_{GC}. Therefore, during the experiments the applied potential (E_{app}) affects only E_{F} while the VB and CB edges at the surface remain fixed [31,51,52].

4. Results

4.1. Cyclic voltammetry

Both BQ and Ru(bpy)₃²⁺ can be reduced at p-GaAs photocathode. Ru(bpy)₃²⁺ has been observed to go through three reduction processes, whereas for BQ only the first reduction process has previously been reported [18]. The redox processes for both mediators at metal electrodes are shown in S1, (Supplementary information).
Another striking difference between BQ and Ru(bpy)$_3^{2+}$ is the behaviour of the OCP when the laser powers varies. Fig. 3 shows that for BQ, the $E_p$ was shifted to more positive potentials at each stepwise increase of the laser power, starting at 28 $\mu$W/cm$^2$ (arrow). For each consecutive laser power increase, a steady value was reached within seconds. When the laser was turned off, the $E_p$ relaxed back to a value close to the original OCP (-0.26 V).

This behaviour can be accounted for when considering that at OCP there’s no net current flowing across the interface. Therefore, as the laser is turned on and the CB electrons generated, they are transferred to the surface of the electrode due to the voltage across the SC layer, and thus the band bending must decrease to reduce this driving force. For BQ an overlap between $E_{ox}$ and SS at the interface is not expected (Fig. 7a), and thus the OCP stabilises to a steady value as a function of the laser power.

For Ru(bpy)$_3^{2+}$, although the $E_p$ was initially shifted to a more positive potentials (Fig. 3b), it then spontaneously relaxed towards the original value even while the laser was still turned on. This indicates that any electrons generated by the laser light, after being transferred to the electrode surface, are removed by either recombination with the VB holes ($k_h \rightarrow k_p$, Fig. 1), or are transferred from the SS to the solution species ($k_e \rightarrow k_f$) [32]. Also, it is worth noticing that the magnitude of the OCP shift for Ru(bpy)$_3^{2+}$ was only a fraction of what it was for BQ.

### 4.3. Benzoquinone EIS

The recorded EIS spectra can be explained with electric circuits composed of resistors and capacitors. Often the capacitors are replaced by constant phase elements (CPE) to account for the non-ideality of the semiconductor/solution interface, an approach used also in this work [38,53,54].

Fig. 4a shows the circuit used to fit the EIS data for BQ. Here the SS capacitance ($C_{SS}$) was placed in series with the SS resistance ($R_{SS}$) as the interface appears to block the flow of the DC from the SS, thus explaining why the OCP in Fig. 3a does not relax spontaneously. Therefore the SS contribute to the interfacial impedance but do not participate to the ET, which occurs from the CB and is represented by the charge transfer resistance ($R_{CT}$) (related to $k_c$ in Fig. 1) [55]. This circuit has been applied to solid state devices [56,57], but also to characterise different minority and majority carrier processes at semiconductor/solution interface [58-63]. In systems where the SS are absent, or do not contribute to the interfacial impedance, this circuit simplifies to the Randles circuit [54].

Fig. 4b shows examples of Nyquist plots and the corresponding fits (solid lines) using the circuit in Fig. 4a with 28 $\mu$W/cm$^2$ laser power and $E_{app}$ values of $-0.2$, $-0.5$ and $-0.8$ V, i.e. at the onset, close to the middle and at the plateau current with respect to the CV in Fig. 2a. The fitted data allowed the numerical characterisation of the circuit components, and the complete results are shown in S4. Here we focus on the $C_{SC}$ as the interfacial parameters such as $E_{FB}$, the positions of the VB, the CB and the magnitude of band bending ($\phi_{ss}$) across the SC layer (discussed in S3) can be determined by using Mott-Schottky (M-S) equation: 

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_0 \varepsilon e N_A e^2} \left( -E_{app} + E_{FB} - \frac{kT}{e} \right)$$

(1)

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon$ the dielectric constant of p-GaAs (12.9), $e$ the electron charge, $N_A$ the doping density of the p-GaAs, $A$ the electrode area, $k$ the Boltzmann constant and $T$ the temperature.

In Fig. 4c the $C_{SC}$ values obtained through equivalent circuit fitting are plotted in M-S format (1/$C_{SC}^2$ vs $E_{app}$), for all the laser powers and potentials employed, where the black squares represent the theoretical values based on Eq. (1). The $E_{FB}$ values are also indicated by extrapolating the M-S plots to 1/$C_{SC}^2 = 0$ [31,64].
For the dark experiment, despite the significant scatter in the data points, the regression analysis shows almost an exact match with the theory for the slope, placing the $E_{FB}$ at $-12$ mV vs. Pt wire. For laser powers of 28 and 84 $\mu$W/cm$^2$, the extrapolation shows a slight light dependency of $E_{FB}$ which shifts to more negative values, as expected for p-type semiconductor [32]. The doping concentration can also be determined from the slope of the M–S plot, and the results match perfectly with the value reported by the manufacturer (see Experimental).

Here we have departed from the common practice which consists of measuring a Mott-Schottky plot at fixed frequency. This simpler method and its shortcomings for p-GaAs/BQ interface are discussed in S5.

Fig. 5 shows the measured steady state current densities during the EIS experiments (black connected markers, left y-axis) for 28 (triangles) and 84 $\mu$W/cm$^2$ (stars) laser powers and varying potentials. Also the $R_{CT}$ values obtained through EIS fitting (red markers, right y-axis) are included. In the dark the $R_{CT}$ values were of the order of 900 k$\Omega$ cm$^2$, irrespective of the potential (data not shown), whereas under laser illumination the minimum $R_{CT}$ dropped to 59 and 18 k$\Omega$ cm$^2$ for 28 and 84 $\mu$W/cm$^2$ respectively. This minimum is located at the middle of the current/voltage slope (-0.4 and -0.5 V). Calculating the resistance as $\Delta V/\Delta J$ [58] gives values of 56 and 20 k$\Omega$ cm$^2$ for the two laser power at voltages between $-0.4$ and $-0.5$ V, thus confirming the close agreement between the current/voltage and EIS data.

Interestingly, for BQ the $C_{SS}$ values were almost independent of $E_{appl}$ or laser power, further suggesting that their presence at the interface does not influence the ET mechanism. The comparison of the $C_{SC}$ and $C_{SS}$ values against each other and the theoretical values expected for the p-GaAs used in this study are given in S4.

4.4. Ru(bpy)$_3^{2+}$ EIS

If the ET is mediated by SS, the circuit in Fig. 4a must be modified to account for this process [65–67]. As shown in Fig. 6a, this can be achieved by adding an electron trapping resistance ($R_{trap}$) representing $k_n$ (Fig. 1), which is in series with the parallel combination of $C_{SS}$ and a SS mediated charge transfer ($R_{SS,CT}$) representing $k_s$. This equivalent circuit also explains why the OCP for Ru(bpy)$_3^{2+}$ in Fig. 3b can relax even while the laser light is on, as there’s no series capacitance at the interface to block the DC flow, indicating different ET path than for BQ.

The existence of an oxidative peak in the return scan around $-0.7$ V
(Fig. 2a) can be explained by a VB process, where holes from the VB are transferred to the reduced species \( \text{Ru(bpy)}_3^{2+} \) in the solution via SS at the interface. The effect of this process on the EIS spectrum has been proposed by Bertoluzzi & Bisquert (B&B). Thus an RC loop is added to the circuit (red circle in Fig. 6a) [68] where \( R_{VB} \) is the resistance associated with the hole transfer from the VB to the SS and the parallel combination \( C_{WB}/R_{VB,CT} \) is responsible for the hole transfer from the SS to the \( \text{Ru(bpy)}_3^{2+} \) in the solution. This circuit element gives rise to an additional half-circle in the Nyquist plot in Fig. 6b (blue dashed line), that indeed was detected at potentials of -0.7 and -0.8 V and a laser power of 28 \( \mu \)W/cm\(^2\). In addition to the experimental data, the equivalent circuit fits with and without the additional VB process are also shown in Fig. 6b. The improvement in the quality of the fit with the VB process is evident.

The Mott-Schottky plots in Fig. 6c were constructed by fitting the EIS spectra with the circuit of Fig. 6a and extracting the \( C_{SC} \) values. For all laser powers used, the extrapolation to \( 1/C_{SC}^2 = 0 \) yielded a value around -0.10 V. For most of the data the fitting was not improved by including the VB process, and thus only the ET from the SS via \( R_{SS,CT} \) was considered.

As discussed above, an exception was made for potentials of \(-0.7\) and \(-0.8\) V at 28 \( \mu \)W/cm\(^2\), for which the full circuit including the VB process had to be implemented to obtain a satisfactory fit (Fig. 6b). The effect of the improved linear fit towards \( C_{SC} \) values can be observed in Fig. 6c between the solid (without VB process) and hollow triangles (with VB process) at \(-0.7\) and \(-0.8\) V, giving much better linearity for the latter method. The detailed EIS results can be found in S6.

It is interesting to note that although the oxidative peak in Fig. 2a, which is related to the VB process, was observed only with the 84 \( \mu \)W/cm\(^2\) laser power, its \( E_{VB} \) which is related to the VB process, was observed only with the 84 \( \mu \)W/cm\(^2\) laser power. Indeed, all the EIS spectra at 84 \( \mu \)W/cm\(^2\) were successfully fitted without the inclusion of the VB process. This indicates that some fine details of the ET processes observed via EIS are lost when too much light excitation is used.

### 4.5. The energetics of p-GaAs/acetonitrile interface

We can summarize the results of CV and EIS measurements by sketching an energy level diagram for the p-GaAs/acetonitrile interface (Fig. 7). In order to estimate the position of the redox states of BQ and \( \text{Ru(bpy)}_3^{2+} \), we have calculated the solvation energies (\( \lambda \)) of both redox couples (S7) [69]. In Fig. 7 the left y-axis represents electron energy (eV) in absolute scale, and the right y-axis a potential scale vs Pt wire. The potential of the Pt wire was measured to be \(-0.34\) V vs the Standard Hydrogen Electrode (SHE), the absolute 0 V in electrochemistry. The SHE is equivalent to \(-4.5\) eV on the electron energy scale, and thus the 0 V vs Pt wire on the right y-axis is \(-4.16\) eV on the left y-axis.

Fig. 7a shows the p-GaAs/acetonitrile interface for BQ (1.6 mM) in the dark, where the CB, VB, \( E_F \) and the densities of states \( D_{CB} \) and \( D_{VB} \) have been drawn on potential and energy scales. The VB edge at the p-GaAs surface has been derived from the M-S plot depicted in Fig. 4c [36,49]. The value of \(-12\) mV corresponds to the p-GaAs \( E_F \) whereas the potential of the VB edge at the electrode surface (\( E_{VB,SD} \)) can be calculated from: [31]

\[
E_{VB,SD} = -eV_{FB} + kT\ln\left(\frac{N_a}{N_c}\right)
\]  

where \( V_{FB} \) is the flat-band potential of the p-type semiconductor and \( N_c \) the density of states in the valence band \((9.5 \times 10^{18} \text{ cm}^{-3})\) [70]. Thus the \( E_{VB,SD} \) is situated 90 mV positive from the \( E_F \) at flat band, i.e. 0.078 V vs Pt wire. Considering the band gap of 1.42 eV for p-GaAs, this places the CB edge at the electrode surface at ca. \(-1.34\) V.

When the interface is at equilibrium in the dark, the p-GaAs \( E_F \) matches the energy of the 1.6 mM BQ sample solution, giving an OCP of ca. \(-0.27\) V (Fig. 3a) with typically a \pm 10 mV variation depending on

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**Fig. 4.** a) equivalent circuit diagram used to analyse EIS data in b). b) Nyquist plots at -0.2 (red), -0.5 (green) and -0.8 V (blue) for 28 \( \mu \)W/cm\(^2\) laser power. Solid lines are best fits using the circuit in a). c) Mott-Schottky plots for \( C_{SC} \) as a function of potential, for 0, 28 and 84 \( \mu \)W/cm\(^2\) laser powers.

**Fig. 5.** Current (black connected markers, left y-axis) during EIS measurements and \( R_{CT} \) values (red markers, right y-axis) obtained through EIS fitting as a function of laser power and potential. Triangles and stars for 28 and 84 \( \mu \)W/cm\(^2\) laser powers, respectively.
the history of the electrode. Assigning a value of 0.9 eV to $\lambda$ (in agreement with a typical semiconductor/solution interface [48]) and $-0.63$ V to $E'_0$ (S1) for the p-GaAs/BQ interface, the maximum of $D_{Ox}$ can be assigned to be at $-1.53$ V, overlapping the CB edge at the electrode surface. With similar assumptions concerning the reduced species (red dashed line, Fig. 7a), the maximum of $D_{Red}$ is at 0.33 V.

In Fig. 7a we have placed the SS at ca. -0.4 V. The rationale for this placement is explained in S5 where the M–S results obtained by using fixed frequency are discussed. Clearly they are not expected to be situated energetically at negative enough values to interact with $D_{Ox}$ of the BQ, as their contribution towards the interfacial ET would become apparent in the EIS measurements.

Fig. 7b shows the energy levels for the p-GaAs/Ru(bpy)$_3^{2+}$ interface in the dark. The placement of $E_F$, VB and CB was carried out as for BQ above. The half-wave potential for the first reduction couple of Ru (bpy)$_3^{2+}$/Ru(bpy)$_3^{+}$ is rather negative; $-1.73$ V vs Fe/Fe$^+$ couple and...
– 1.31 V vs SSCE in acetonitrile [71,72]. When measured against Pt wire a $E^{0}$ of -1.83 V was obtained (S1), placing the first reduction potential of Ru(bpy)$_2^{2+}$ (and all the consecutive ones) outside of the p-GaAs band gap. According to the model used to estimate the reorganisation energies (S7), the larger diameter of Ru(bpy)$_2^{2+}$ compared to BQ gives a significantly smaller $\lambda$ (0.38 eV), although due to the activity of the SS at the interface the estimation of the energies of the solution species according to our simplified approach might not be completely accurate.

5. Discussion

5.1. Benzoquinone

For BQ the results were consistent between the different techniques used. The photoreduction is initiated as the potential is swept more negative from around $E_{FB}$, and shows a current plateau due to the limiting number of electrons at the CB edge (Fig. 2a). The OCP reached a stable value as a function of laser power, as the band bending across the SC layer adjusted to the generation of the photolelectrons at the interface (Fig. 3a). This behaviour could be accounted for with the equivalent circuit in Fig. 4a, where the $C_{SS}$ is in series with $R_{SS}$, thus blocking the flow of the DC.

The determination of the $E^{0}$ (S1) and the calculation of the $\lambda$ (S7) show that there is a significant overlap between the CB edge and $D_{OX}$ of BQ, once the energy diagram of the interface was constructed (Fig. 7). The placement of the SS at potential of -0.4 V (SS) shows that they are not expected to interact with the $D_{OX}$ of BQ, explaining their indifference towards laser power and potential (S4).

5.2. Ru(bpy)$_2^{2+}$

The results for Ru(bpy)$_2^{2+}$ do not merit such a definitive characterisation of the interface, mainly due to the strong interaction between the p-GaAs surface and the Ru(bpy)$_2^{2+}$. The relaxation of the OCP under illumination is a clear indication that compared to BQ there is an additional pathway for the electrons to relax from the CB edge, mainly due to the active SS at the interface.

The strong interaction between the electrode surface and the Ru (bpy)$_2^{2+}$ could lead to an adsorbed ruthenium species (Ru(bpy)$_2^{2+}$ads) with different reduction potential than suggested by the $E^{0}$ measured in the solution phase (S1). Thus, this adsorbed species could be available in the band gap to accept an electron from the SS. Also, the activity coefficients for the adsorbed species could vary significantly from the free solution species. This model would help to explain the SS mediated VB oxidation in the CV data (Fig. 2a) and the EIS results (Fig. 6b), where the impedance spectra were well fitted with the circuit in Fig. 6a, which is commonly used for SS mediated ET [35,38].

Another way to explain the reduction current observed in the CVs (Fig. 2a), despite the $D_{OX}$ being situated above the VB edge, is to use the concept of the Fermi level pinning [15]. In this model, due to the large density of SS, the sweeping of the E$_{FB}$ causes the potential drop to occur across the Helmholtz layer rather than the SC layer. This effectively leads to the unpinning of the VB and CB edges and their movement to more negative potentials with the sweep, facilitating the overlap between the CB edge and $D_{OX}$ around a potential of -0.7 V vs Pt wire.

For Ru(bpy)$_2^{2+}$ we have assigned the most significant SS energy to around -0.1 and -0.2 V due to the indifference of the OCP (Fig. 3b) and the $E_{FB}$ (Fig. 6c) from the laser power. This behaviour is known for situations where there is a large density of surface states at a relatively well-defined energy at the interface, although the SS are likely to be present across the entire band gap and beyond. Thus, although the CB edge can move with the potential sweep, the electron transfer could still be facilitated by the SS, especially as the detailed EIS analysis showed a significant change in $C_{SS}$, $R_{trap}$ and $R_{SS,CV}$ parameters as a function of the applied potential (S6). The fact that the $R_{SS,CV}$ follows the current/voltage curves at least qualitatively, having the minimum around -0.8 V (i.e. the maximum slope) further suggests that the charge transfer across the interface is facilitated by the SS, even under the conditions of Fermi level pinning.

6. Conclusions

We have combined CV and EIS techniques to determine flat band potentials, band bending, the position of the redox states of mediators relative to p-GaAs VB and CB, and the voltage at which the charge transfer kinetics were the fastest. In studies of spin effects, this method can be applied to test different mediators with appropriate redox potentials relative to the p-GaAs band edges, and to determine the potential region where the reduction kinetics is most sensitive to the ET rate and laser power.

For BQ, the presence of SS has been confirmed, but our results indicate that they do not participate in the electron transfer across the interface, most likely because of their location at potentials more positive to the $D_{OX}$ of the BQ. The reduction behaviour is typical of the Gärtner model, where the photocurrent initiates immediately at potentials more negative than the $E_{FB}$. A completely different behaviour was observed for the Ru(bpy)$_2^{2+}$, where relatively large negative potentials must be applied due to the strong SS effect and the fact that the $E^{0}$ is situated outside of the band gap.

The stability of p-GaAs is of concern, since the photo-cathodic behaviour can change over time, narrowing the time window for successful high precision measurements. The problem is known and has been dealt with by functionalising the p-GaAs surfaces [73–75]. It is possible that the molecules grafted on an electrode in the framework of spinference [21–24], or CISS studies [25–27], might have a stabilizing effect and block electron-transfer through surface states.

Declaration of interest

The authors declare no competing financial or personal interests.

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Appendix A. Supplementary data

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