The scanning microscope for semiconductor characterization (SMSC): electrolyte electroreflectance and photovoltage imaging study of the electrochemical activation of RuS\(_2\) photoelectrodes for oxygen evolution

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Abstract

The photoelectrochemical behaviour of the oxygen evolving n-RuS\(_2\) | H\(_2\)SO\(_4\) interface was investigated with the help of the scanning microscope for semiconductor characterization. Electrolyte electroreflectance and photovoltage digital images were obtained as a function of the pretreatment of the RuS\(_2\) surface (polishing and electrochemical etching). Polishing gives rise to an inhomogeneous, scarcely photoactive surface, while electrochemical etching destroys the damaged overlayer generated by polishing, leaving an inhomogeneous, highly photoactive surface in contact with the electrolyte. In general, more photoactive zones are characterized by a higher electrolyte electroreflectance signal (EER-s) generated at the interfacial hydroxide layer, and a smaller signal coming from the space charge layer. According to the observed influence of the donor concentration on the EER-s signal amplitude, the contrast observed in the EER-s image was attributed to lateral heterogeneities in the donor concentration. The difficulty of modulating the electric field in the hydroxide layer at relatively high frequencies was attributed to the low relaxation time constant of surface states involved in the EER-s signal. The fact that at low light modulation frequencies those zones with the highest EER-s amplitude also show the highest photovoltage indicates that the photovoltage intensity depends on the time constant. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

RuS\(_2\) is the first discovered photostable, low-energy gap semiconductor (SC) (\(E_g \approx 1.3\) eV), with energy bands derived from Ru-d states, able to photooxidize water under infrared illumination and supporting bias potential [1]. Under illumination, photogenerated valence-band holes are trapped at bandgap surface states (SS) associated with lattice Ru atoms, producing surface oxidation and inducing interfacial, coordination chemical reactions with water molecules, which finally leads to molecular oxygen evolution [2]. The presence of an interfacial hydroxide layer (IHL) when RuS\(_2\) is in contact with 0.5 M H\(_2\)SO\(_4\), explains the complex electrochemical [3] and photoelectrochemical [4,5] behaviour of this semiconducting compound. The role of this interfacial phase and the nature of the complexes involved in the reaction of oxygen evolution has been a subject of recent investigations [5,6], although there is no entirely clear explanation up to now.

Freshly mounted RuS\(_2\) electrodes show high dark currents and few photoeffects. Dark currents are partially due to the oxidation of interfacial states associated with the lattice Ru atoms coordinated to water molecules [5]. A dark current decrease and the simulta-
neous onset of an anodic photocurrent is observed during the surface oxidation process. The electrode soon stabilizes, then presenting the typical behaviour of an n-type SC able to photooxidize water with visible and infrared light [7]. This indicates that the photoelectrochemical quality of the electrode improves during the oxidative process.

It is known that dark currents in SC electrodes flow preferably through channels with a high density of defects which can act as efficient recombination centers. The corrosion process occurring during electrochemical etching in the dark, under positive bias at \( V_{dc} > E^\circ (O_2/H_2O) \) [5], is probably responsible for removing preferentially electrode material of poor electronic quality, which gives rise to the dark current decrease and photocurrent increase. When the stabilized RuS\(_2\) electrode is mechanically polished its behaviour becomes similar to that of the freshly mounted sample (absence of photoeffects), due to the introduction of lattice (electronic) defects in the space charge layer (SCL). Photoeffects reappear after renewed electrochemical etching, which removes the defective top layer generated by polishing. Additional evidence that the quality of the RuS\(_2\)-electrolyte junction depends strongly on the SC surface pretreatment is given by the fact that the polished electrode presents a continuous distribution of bandgap SS, while the electrochemically etched electrode has a Gaussian-like distribution of SS located in the middle of the gap. These different electronic surface structures give rise to a different potential distribution at the SC-electrolyte interface, which modifies drastically the photoelectrochemical behaviour of the RuS\(_2\) electrode [4].

The aim of this work is to investigate the influence of surface pretreatments (polishing and electrochemical etching) on the photoelectrochemical activity of n-RuS\(_2\) electrodes. With this purpose, electrolyte electroreflectance (EER) and photovoltage (PV) images were obtained with the help of the ‘scanning microscope for semiconductor characterization’ (SMSC).

The effect of pretreatments on the contrast of EER and PV images allows important information to be obtained about the influence of doping heterogeneities on the electric field distribution at the oxygen evolving the RuS\(_2\) | H\(_2\)SO\(_4\) interface.

2. Experimental

A synthetic n-RuS\(_2\) sample \( (N_d \approx 10^{18} \text{ cm}^{-3}) \) grown from bismuth melts [8] was used as the photoelectrode in a photoelectrochemical cell (PEC), with a Pt wire and a Hg | HgSO\(_4\) | 0.5 M H\(_2\)SO\(_4\) electrode (MSE) as counter and reference-electrode, respectively, and 0.5 M H\(_2\)SO\(_4\) as the electrolyte. The ohmic back contact was made with silver paste (Eliedit) on a platinum wire and insulated with Scotchcast 3 M resin. The RuS\(_2\) electrode whose exposed area is shown in Fig. 1 ( \( \approx 0.05 \text{ cm}^2 \) ) was polished to a mirror finish with Vinter diamond paste (down to 0.25 \( \mu \text{m} \) ) and etched with aqua regia. After this treatment the electrode showed very little photoresponse. Photoactivity was obtained only after electrochemical etching in 0.5 M H\(_2\)SO\(_4\), under polarization at 1.2 V. (MSE) (MSE = 0.65 V vs the standard hydrogen electrode). The electrolyte was prepared with reagent grade chemicals and ultrapure Millipore-Q water. EER and PV images were obtained under modulated light with the help of the SMSC, a light spot technique recently developed at the CSIC (Spain) for imaging different physical effects photoinduced at the SC-electrolyte interface with lateral resolution [9–14]. The SMSC experimental set up has been described elsewhere [12], the best image resolution (a few micrometers) being determined by optical resolution of SMSC 40 \( \times \) objective. PV images were acquired at 14 Hz with a 780 nm 5 mW diode laser (Lasermax) under open circuit and low injection conditions, which allows signals lower than a few mV to be obtained [14]. Localized EER spectra were obtained by using the chopped (100 Hz), unpolarized light from an Oriel monochromator illuminated with a 100 W Osram tungsten–halogen lamp. EER images were obtained under illumination with light of 780 and 415 nm from a diode-laser and an Ar-laser, respectively. Both wavelengths correspond to well defined signals of the EER spectra originating in the RuS\(_2\) surface and at the SCL (bulk), respectively (see next section).

3. Results

3.1. Photovoltage images

Fig. 1 shows the optical image of the n-RuS\(_2\) sample. The crystal surface shows different facets and dislocations. Special note should be taken at the relatively

![Fig. 1. Optical image of the as grown cubic n-RuS\(_2\) crystal used as the photoelectrode. Zones 1 and 2 are relatively smooth while zone 3 is a quite rough region of many microcrystalline defects.](image-url)
Fig. 2. Light intensity modulated photovoltage images of the n-RuS$_2$ crystal shown in Fig. 1. Image (A) corresponds to a highly oxidized surface before polishing; image (B) was obtained after mechanical polishing down to 0.25 μm and images (C) to (F) after further electrochemical etching in 0.5 M H$_2$SO$_4$, under polarization at 1.2 V (MSE) for 1, 2, 3 and 5 min, respectively. These images were obtained under open circuit conditions (Illumination source: 5 mW, 780 nm diode laser; spot radius (r) = 10 μm; modulation frequency (ν) = 70 Hz; electrolyte: 0.5 M H$_2$SO$_4$).

smooth zones 1 and 2 and the very rough region 3, where accumulation of impurities behaving as donor centers, in microcrystalline defects, is expected. As shown in the modulated photovoltage images of Fig. 2, before polishing, the highly oxidized surface shows little photoactivity (Fig. 2A). After polishing the photoresponse still decreases due to the generation of a huge number of recombination centers (Fig. 2B). The electrode becomes activated during the subsequent electrochemical etching treatment, as the perturbed top surface recombination layer produced by polishing is destroyed progressively; consequently, the photovoltage increases by a factor of 35 (Fig. 2C–F). However, electrode activation is not produced homogeneously, since the photovoltage appears to be clearly higher in zone 1 than in zone 2. The electroactivation process is apparently inhibited after 1–2 min of electrochemical etching in zone 1, where the photovoltage starts to decrease. For more than 3 min treatment, zone 1 become passivated and the photovoltage remains invariant. Such a surface passivation process is clearly retarded in zone 2 and 3, where the photoresponse increases during the first 3–4 min of electrochemical etching and then remains stable (Fig. 2 E–F).

3.2. EER-spectra

The effect of polishing and electrochemical etching can also be followed by monitoring the EER spectra. Fig. 3 A and B shows the EER-spectra corresponding to different times of electrochemical etching, under SCL electric field modulation at 15 and 300 Hz, respectively. The spectra (A) were obtained after polishing and before electrode electroactivation. All the spectra were obtained under external polarization at 0.3 V(MSE), a potential at which the electrode surface is not modified [15]. Just after polishing (0 min) the EER spectrum is not sensitive to the modulation frequency, and shows two broad peaks centered at 1.65–2.80 eV, respectively. These spectra correspond to the damaged surface which, due to the high concentration of surface states (recombination centers), completely absorbs V$_{ac}$ modulation. After electroactivation for 0.5 min, the spectra appear drastically modified. A fine structure of excitonic character can be observed in the 2.7–3.1 eV range, together with broader signals between 2.4 and 2.7 eV which correspond to optical direct transitions generated at the SCL [16,17], and are referred to in the following as the EER-b signal, while the stronger, broad signal appearing in the low energy range (1.5–2.0 eV) is
attributed to the surface hydroxide layer (EER-s signal) [15]. Electrochemical etching of the electrode for times up to 1.5 min produces a clear increase of the EER-b signal under modulation at 300 Hz (Fig. 3B), while it remains practically unchanged at 15 Hz (Fig. 3A). Electroactivation for times longer than 1.5 min apparently does not affect the EER spectra. In order to separate the low from the high-frequency distribution of the EER spectra, B spectra were subtracted from A spectra multiplied by a compensating factor \( f \), which corrects for the difference in height of the EER-b signal. This factor was obtained from the ratio of the peak-to-peak intensities corresponding to the signal at 2.9 eV. The resulting spectra, which therefore corresponds to the expression \( C = (f \times A) - B \), are shown in Fig. 3C. The similarity of the EER signal just after electrode polishing (0 min) to the EER-s spectrum seems to indicate that this signal come from the electrode surface and not from the SCL. It is important to note that, in general, the EER-s signal is more intense than the EER-b one at 15 Hz. The opposite behaviour is observed at 300 Hz for electroactivation times higher than 1 min. The potential dependence of the EER-b spectra is typical for a signal produced at the SCL of an n-type semiconductor [18]. This is not the case for the EER-s signal, which passes through a minimum of intensity at about 0.2 V (MSE), without changing shape, under external bias [15]. Moreover, due to the efficient modulation of the electric field at the electrode surface, EER-s was the only signal detected in highly doped (degenerated) n-RuS\(_2\) electrodes. By contrast, in the low doped samples, EER-b predominates over the EER-s signal due to an efficient electric field modulation at the SCL [15].

3.3. EER-images: wavelength and \( V_{ac} \) modulation frequency dependence

Fig. 4 shows the EER images of the n-RuS\(_2\) crystal of Fig. 1 after polishing and further electrochemical etching.
etching for about 5 min. Images (A) and (B) were obtained under modulation ($V_{ac}$) at 15 Hz and illumination with light of 750–415 nm, which correspond to the wavelengths of the EER-s and EER-b signal, respectively. In those areas where the modulation potential is mainly dropped at the SC surface the EER-s signal should be higher than the EER-b one; the opposite happens in regions where modulation is mainly dropped in the bulk. This is the behavior observed when images (A) and (B) are compared. The corresponding EER images at 385 Hz are shown in Fig. 4C, D. The small image contrast observed in this case in comparison to that of the images obtained at low 15 Hz (Fig. 4A, B) is a consequence of the decreasing fraction of $V_{ac}$ dropping in the Helmholtz layer as the modulation frequency increases.

4. Discussion

4.1. Electroactivation and corrosion mechanisms of the RuS$_2$ surface

The main factor defining the catalytic activity of RuS$_2$ electrodes for water oxidation, both in the dark and under illumination, is the existence of a low overpotential ($\eta \approx 0.3$ V for a current density of about 0.1 mA cm$^{-2}$), comparable to that of RuO$_2$, which is the best catalyst for oxygen evolution known to date. In a previous paper [5], we gave evidence that $\eta$ is controlled by the redox potential of the (OH$^+$ / OH$^-$)$_{ad}$ couple in the absorbed state, which depends strongly on the bonding energy of surface Ru atoms to OH$^-$ electrolyte species. S – Ru$^{|IV/0|\text{OH}}$ – represents the initial state of the RuS$_2$ surface groups active for oxygen evolution [6]. Electron transfer from S–Ru$_2$(OH$^-$)$_2$ surface groups, either to the CB in the dark or to the VB under illumination, takes place during the electrochemical activation of the electrode. The energy of the Ru–OH$^-$ bond increases as the Ru atoms become progressively oxidized, the maximum oxidation degree being reached at the potential of the S–Ru(IV)/S–Ru(VIII) transition [5].

The strong positive electric field generated at the Helmholtz layer during the surface oxidative process (Ru$^{IV}(\text{OH})_2$ + 4e$^-$ → Ru$^{IV}(\text{OH})_2$) is a key factor for the generation of stable, surface peroxo-type complexes according to the reaction sequence [5]:

$$\text{S} \rightarrow \text{Ru}^{IV(\text{OH})_2} + 2\text{H}^+ \rightarrow \text{S} \rightarrow \text{Ru}^{IV(\text{OH})_2} \rightarrow \text{S} \rightarrow \text{Ru}^{IV(\text{OH})_2} + 2\text{H}^+ \quad (1)$$

Oxygen is finally evolved via further oxidation of Ru(O$_2^{\cdot-}$) peroxo species (in the presence of water), according to:

$$\text{S} \rightarrow \text{Ru}^{IV(\text{O}_2^{\cdot-})} + 2\text{H}^+ \rightarrow \text{S} \rightarrow \text{Ru}_n \cdots \text{O}_2 \quad (2)$$

$$\text{Ru}_n \cdots \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ru}_n \cdots \text{O}_2 - 2\text{H}^+ + \text{O}_2^+ \quad (3)$$

The experimental observation of strong Fermi level pinning, as an important fraction of the applied potential drops at the Helmholtz layer, is in fact consistent with the idea that oxidation of surface Ru-states (surface accumulation of positive charge) from oxidation state II–VI is a necessary condition for oxygen to be evolved [5].

Another experimental indicator of the photocatalytic activity for oxygen evolution of RuS$_2$ is the photocurrent saturation reached at high enough illumination intensity, which indicates that oxygen evolution becomes limited by the generation rate of surface Ru–peroxo type complexes. When the surface oxidation rate (electron transfer rate from surface Ru atoms to the CB in the dark or to the VB under illumination) is higher than the oxygen evolution rate, an excess of positive charge is still accumulated at the SC surface (S–Ru(VI) → S–Ru(VIII)). Such an excess concentration of holes at the SC surface definitely contributes to RuS$_2$ dissolution, which is a reaction assisted by water (acidic medium), in which H$_2$O molecules interact with Ru(VIII) surface species forming unstable intermediate complexes that lead to the breaking of Ru–S surface bonds [5]. This complex dissolution process, in which 20 electrons participate, gives rise to RuO$_4$ and SO$_4^{2-}$ ions as the main corrosion products. Tentatively, this can be written [5]:

$$\text{RuS}_2 + 12\text{H}_2\text{O} \rightarrow \text{RuO}_4 + 2\text{SO}_4^{2-} + 24\text{H}^+ + 20\text{e}^- \quad (4)$$

Indirect experimental evidence for the corrosion of the RuS$_2$ crystal during the electroactivation treatment under polarization in the dark at 1.2 V (MSE) is given in Fig. 2. In fact, the removal of the damaged overlayer generated by polishing leaves a highly photoactive surface (free of defects) in contact with the electrolyte, as inferred from the observed dramatic increase of photocurrent. Oxygen evolution in the dark at the RuS$_2$/H$_2$SO$_4$ interface starts at $\approx 0.8$ V (MSE). At 1.2 V (MSE) the anodic dark current is of the order of $10^{-2}$ A cm$^{-2}$ [5], which is a high enough value to sustain appreciable electrocorrosion.

On the other hand, it is well known that the photoelectrochemical behaviour of semiconductor electrodes can be seen to be modified drastically due to the development of interfacial compounds generated from chemical reactions taking place at the SC|electrolyte interface. These interfacial compounds frequently act as intermediates for transfer of charge between the SC and the electrolyte. This is obviously the case for RuS$_2$ electrodes, where the formation of an interfacial hydroxide layer has to be invoked in order to explain their photochemical behaviour [19]. We have seen in Fig. 3 that two EER signals come from different phases.
compete for the $V_{ac}$ modulation potential: the EER-s signal generated at the interfacial hydroxide layer (Ru(OH)$_x$ layer) and the EER-b spectrum produced at the SCL. After polishing and before electroactivation of the electrode, EER-s is the only signal observed; the great lattice disorder generated by polishing prevents the EER-b signal from appearing. This behavior seems to indicate that the top layer Ru(OH)$_x$ was already present at the polished surface, before the electroactivation treatment was performed. Modulation of the electric field at the SCL, which is a necessary condition for the EER-b signal to be present, is evident after electroactivation of the polished electrode for 60 s, indicating that the damaged overlayer responsible for the Fermi level pinning is partially removed. Electroactivation for longer time induces a better SCL modulation at the expense of the interfacial hydroxide layer, although this effect is apparent only at 300 Hz. By contrast, at 15 Hz the EER spectrum is practically insensitive to the electroactivation process, which points out to the presence of fast interface states as responsible for the Fermi level pinning at 300 Hz. Obviously, such interface states must be removed progressively during the electroactivation treatment. Fast interfacial states can be identified with recombination centers which are apparently eliminated during the corrosion process (electrochemical etching). By contrast, the slow interfacial states responsible for Fermi level pinning at 15 Hz are apparently unaffected by the electroactivation treatment. The difficulty of modulating the electric field in the interfacial hydroxide layer as the frequency increases must be a consequence of the low relaxation time constant ($\tau$) of the interfacial states involved in the EER-s signal. Besides, $\tau$, which represents the time necessary for interface states to be charged and discharged, should be expected to decrease as the electrical conductivity of the electrode rises ($N_D$ increases). The fact that EER-s was the only signal detected in degenerated RuS$_2$ and that it was observed to collapse in low doped samples [10], is a confirmation of the expected dependence of $\tau$ on the doping level (donor concentration, $N_D$). It seems reasonable to assume, therefore, that the contrast observed in the EER-s image of Fig. 4 A is, at least, partially due to lateral heterogeneities of $N_D$ (i.e. white areas correspond to zones with a high $N_D$ while low doped zones appear black in the EER-s image).

The photovoltage is also sensitive to lateral heterogeneities of $N_D$, as can be seen in PV images of Fig. 2. In fact, the PV intensity strongly depends on the surface recombination rate, which is controlled by $\tau$ (the time necessary for interfacial states to be filled with conduction band electrons during the time $t$) of permanence of the electrode at darkness under light modulation ($t = 1/2\nu$, $\nu$ being the light modulation frequency expressed in s$^{-1}$). This is consistent with the observation that PV intensity decreases as $\nu$ rises, reaching its maximum value for $\tau > 1$.

On the other hand, it must be emphasized that at the initial stages of the electroactivation process, the highest PV intensity (Fig. 2C) corresponds to the lowest doped areas (e.g. zone 1, according to EER-s image of Fig. 4 A), where the hole flux towards the SC|electrolyte interface reaches maximum values. According to Gartner’s model the flux of photogenerated holes reaching the SC|electrolyte interface is given by the expression [20]:

$$\Phi(h^+) = \Phi_0 \left[ 1 - \frac{\exp(-zW)}{1 + zL_p} \right]$$

(5)

where $\Phi_0$ is the fraction of incident photon flux absorbed by the SC; $z$, is the absorption coefficient; $L_p$, the hole diffusion length and $W$, the depletion layer width, $(W = (2\omega_{0}/qN_D)^{1/2} \phi_s^{1/2}$, $\phi_s$, being the band bending and $\omega_0$ the SC dielectric constant and the vacuum permittivity, respectively). In our case, $zL_p \ll 1$, and can be neglected in [5]. As far as $z$ is constant through the crystal, $\Phi(h^+)$ is controlled by $W$, in such a way that the decrease of $N_D$ induces an increase of $W$ and, therefore, of $\Phi(h^+)$. As discussed previously, the electroactivation process produces two simultaneous effects: (a) oxidation of Ru surface ions and (b) electrode dissolution according to [4]. In addition, the growth of a RuO$_4$ top layer during the first minutes of the electroactivation process apparently leads to a temporal passivation of the electrode. As expected, the passivation rate under illumination is higher in zones with low $N_D$ where participation of photogenerated holes to the dissolution process increases. At the steady state, which is apparently reached after electroactivation for 5 min, the maximum photovoltage corresponds to the highest doped areas, like zone 2. Specially interesting in this respect is the resemblance between the PV image of Fig. 2F and the EER-s image of Fig. 4 A. The low $\tau$ in zones with high $N_D$ is the cause of this similarity.

5. Conclusions

The results here presented seem to confirm a previous model according to which the catalytic properties for O$_2$ evolution of RuS$_2$ electrodes can be attributed to the presence of an interfacial hydroxide layer generated in aqueous, acidic medium. RuS$_2$ becomes photoelectrochemically active after an electroactivation process under anodic polarization in the dark at a potential near the S–Ru(IV)/S–Ru(VIII) transition. The electrode surface becomes catalytically active for water oxidation when surface Ru atoms reach the oxidation state (VI). Then oxygen starts to be evolved at low current densities. Further surface oxidation from oxidation state...
(VI)–(VIII) leads to the break up of Ru–S surface bonds and electrode dissolution, volatile RuO₄ being the main corrosion product. Simultaneously O₂ is evolved at high current densities.

Electrolyte electroreflectance and photovoltage images obtained at the oxygen evolving RuS₂│H₂SO₄ interface give direct evidence for the first time for the influence of doping on the electric field distribution of the liquid junction. The electroactivation process as a function of time can be followed by mean of electroreflectance and photovoltage images obtained with the help of the scanning microscope for semiconductor characterization.

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