Semiconductor Electrodes

LVII. Differential Photocurrent and Second Harmonic Techniques for in situ Monitoring of Surface States on n-MoSe₂ in Aqueous Solutions

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ABSTRACT

Second harmonic ac impedance and differential photocurrent techniques are employed to monitor, in situ, the surface states on n-MoSe₂ electrodes in aqueous solutions containing the Fe(CN)₄⁻/³⁻ couple. These two techniques are qualitatively more sensitive to the presence of surface states on single-crystal n-MoSe₂ than first harmonic ac techniques. Surface states on this semiconductor electrode were passivated by a thin layer of RuO₂. This film also increased the PEC efficiency of both single-crystal and polycrystalline n-MoSe₂.

Surface states, either intrinsic or extrinsic, are known to affect the performance of photoelectrochemical (PEC) cells and behavior of semiconductor electrodes by promoting Fermi level pinning, acting as recombination centers, and abetting dark current flow. Several techniques for the study of surface states at electrode surfaces contacting electrolyte solutions are available; these include (i) current-potential methods, (ii) photocapacitance spectroscopy, (iii) electromluminescence spectroscopy, (iv) photoluminescence spectroscopy, (v) measurements of the subbandgap photoresponse, (vi) interfacial capacitance, and (vii) surface photovoltage. Recently, we reported that the ac impedance technique can provide information about both the energy distribution and density of surface states. This method could detect the presence of surface states even when their density was too small to cause Fermi level pinning on n-MoTe₂. We report here ac impedance studies of n-MoSe₂ and demonstrate the use of this method as a means of in situ monitoring of the semiconductor surface and the effects of surface treatments. In addition, two techniques are described which are qualitatively more sensitive to the presence of surface states: the second harmonic ac impedance and the differential photocurrent techniques. Deposition of a thin layer of RuO₂ on the surface of n-MoSe₂ was shown by all three techniques to passivate the surface states present. Concurrently, the photocurrent-voltage behavior showed a dramatic improvement. This provides strong evidence that all three techniques monitor the semiconductor surface, in situ, and that the surface states were responsible for the poor photocurrent-voltage behavior with the untreated surface. The improvement of the single-crystal behavior encouraged us to attempt to improve polycrystalline MoSe₂ films by the same method.

Experimental

Electrodes.—Single crystals of n-MoSe₂,¹ were used. The van der Waals surface (perpendicular to the C axis) was the face exposed to the solution. Ohmic contacts were made to the back surfaces with Ga/In eutectic. A copper wire lead for electrical contacting electrolyte solutions are available; these include (i) current-potential methods, (ii) photocapacitance spectroscopy, (iii) electromluminescence spectroscopy, (iv) photoluminescence spectroscopy, (v) measurements of the subbandgap photoresponse, (vi) interfacial capacitance, and (vii) surface photovoltage. Recently, we reported that the ac impedance technique can provide information about both the energy distribution and density of surface states. This method could detect the presence of surface states even when their density was too small to cause Fermi level pinning on n-MoTe₂. We report here ac impedance studies of n-MoSe₂ and demonstrate the use of this method as a means of in situ monitoring of the semiconductor surface and the effects of surface treatments. In addition, two techniques are described which are qualitatively more sensitive to the presence of surface states: the second harmonic ac impedance and the differential photocurrent techniques. Deposition of a thin layer of RuO₂ on the surface of n-MoSe₂ was shown by all three techniques to passivate the surface states present. Concurrently, the photocurrent-voltage behavior showed a dramatic improvement. This provides strong evidence that all three techniques monitor the semiconductor surface, in situ, and that the surface states were responsible for the poor photocurrent-voltage behavior with the untreated surface. The improvement of the single-crystal behavior encouraged us to attempt to improve polycrystalline MoSe₂ films by the same method.

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A conventional three-electrode single-compartment cell with a flat Pyrex window for illumination of the semiconductor electrode was used. The cell, which had a volume of about 30 ml, also contained a Pt gauze electrode (area > 40 cm²) which was used as the counterelectrode. The reference electrode was a saturated calomel electrode (SCE) separated from the cell by a KCl-saturated agar bridge. All potentials are reported vs. SCE.

Current-potential behavior was obtained with a PAR Model 173 potentiostat with Model 179 digital coulometer plug-in and Model 175 programmer (Princeton Applied Research, Princeton, New Jersey) and recorded with a Model 2000 X-Y recorder (Houston Instruments, Austin, Texas). Polychromatic illumination was obtained from a system.
Photodeposition of RuO$_x$ ($x = 2$) on the MoSe$_2$ electrodes was accomplished by a modification of the procedure reported by Anderson and Warren (15). To a solution of 1.7g of RuCl$_3$·3H$_2$O in 100 ml of 98% aqueous EtOH, 6 ml of 1,3-cyclohexadiene was added (16). The solution was refluxed in a boiling flask fitted with a reflux condenser and heated to 48°C for 3h. The reflux condenser was then removed, and the solution volume was reduced to 30 ml. The red precipitate of [Ru($\eta^6$-C$_6$H$_6$)Cl$_2$]$_2$ was collected by filtration, washed with EtOH, and allowed to dry in air. This species was dissolved in a minimum amount of water, and 4 mol AgBF$_4$ were added per mole of Ru dimer to obtain Ru($\eta^6$-C$_6$H$_6$)(OH)$_2$]$^{2+}$ and a precipitate of AgCl. The solution was filtered, and the filtrate was diluted to give 0.04M Ru. The pH was adjusted to 5 and NaClO$_4$ was used as supporting electrolyte at a concentration of 0.1M. The quated species can be oxidized on Pt at +0.9V vs. SCE to give a film of RuO$_x$ (15). On illuminated n-MoSe$_2$, photo-oxidation starts at +0.2V vs. SCE. The films were produced by illuminating the n-MoSe$_2$ with white light and biasing at +0.5V while monitoring the charge passed with a coulometer.

AC impedance.—The lock-in technique (13, 14) was used to measure the ac impedance behavior as a function of applied potential. In this technique, a small amplitude sine wave, 12 mV peak-to-peak, from a wide-range oscillator (Model 200 CD, Hewlett-Packard, Palo Alto, California) is superimposed on a slow (≤ 5 mV/s) dc ramp from the PAR universal programmer by the PAR potentiostat and applied to the cell. The output of the current follower of the potentiostat is input to a lock-in amplifier (PAR Model 5204 or 5206) which separates the signal into the components in and out of phase (90°) with the ac signal of the oscillator. These signals were calibrated using an RC circuit composed of a resistance substitution box checked with a digital multimeter and a precision decade capacitor (Hewlett-Packard Model 4440 B). The in and out of phase signals as a function of dc potential were plotted on an X-Y-Y recorder (Soltec, Sun Valley, California, Model 6432).

The second harmonic measurements were made by applying the same ac signal at a fundamental frequency (f) and setting the lock-in on the external 2f mode. The HP200 CD oscillator was found to have negligible harmonic distortion detectable at the sensitivities used, and, therefore, this oscillator was used for all ac measurements. All other instrumentation was the same as that used in the measurements at the fundamental frequency.

Differential photocurrent.—In this technique, the photocurrent is electronically differentiated with respect to potential as a function of potential (17). The method used the intermodulation frequency of chopped light and ac modulation of the electrode. This method has been described in detail elsewhere (18) and the results are plots of the photocurrent vs. voltage, as well as the differential photocurrent vs. voltage. Instrumentation is identical to that described previously (18).

Results and Discussion

Capacitance-voltage behavior of single-crystal n-MoSe$_2$.—Mott-Schottky (M-S) plots over the frequency range (f) 0.5-5 kHz are given in Fig. 1 for n-MoSe$_2$ in aqueous solution containing Fe(CN)$_6^{3-}$ as the redox couple. In this frequency regime, the capacitance values (C) were generally free from the deleterious effects of surface states and yielded values of C which were only slightly dependent on f. The value of flatband potential (V$_fb$) and the density of states within the gap ($N_v$) obtained from the M-S plots are around +0.1V vs. SCE and 2×10^{19} cm$^{-2}$. Taking the bandgap as 1.4 eV (19), we estimate that the valence band (VB) and conduction band (CB) edges are located, respectively, at +1.16 and -0.24V.

3. Photocurrent and differential photocurrent behavior of n-MoSe$_2$.—In Fig. 4 are given the photocurrent (j) and the differential photocurrent (Δj) vs. V for two n-MoSe$_2$ electrodes with monochromatic illumination at 500 nm in aqueous solution containing K$_4$Fe(CN)$_6$, as redox couple. The plots in Fig. 4a are for the same electrode as Fig. 2a. Note that the current axis for Δj is given in a logarithmic scale. The log Δj vs. V plots exhibit a large hump in the potential regime in which j vs. V curves exhibit a dip. Similar results were obtained when the two modulating frequencies were varied by ±20% while maintaining the intermodulation frequency constant at 400 Hz for ease of
filtering. Since $\Delta j$ is the differential photocurrent at any potential, information concerning inflections in the photocurrent attributable, for example, to surface recombination and surface states, are amplified in $\Delta j$. Even a very small dip or hump in $j$ vs. $V$ will be apparent in $\Delta j$ vs. $V$ plots. Recall that the in-phase component (Fig. 2) exhibits a peak in the same potential regime in which the $j$ and $\Delta j$ vs. $V$ plots exhibit a hump. This observation suggests that the differential photocurrent technique can be used as a diagnostic tool to probe the electrode surface for surface states.

The ac impedance and current-voltage behavior of $n$-MoSe$_2$ after surface modification with RuO$_x$.—These techniques, in conjunction with the ac impedance and current-voltage measurements, have been extended to regimes where surface states can be passivated by a thin layer of RuO$_x$. The thermodynamic potential for RuO$_x$ deposition from Ru($\eta^5$-C$_5$H$_5$OH)$_3$ complex is about +0.9 V vs. SCE. The VB edge of $n$-MoSe$_2$ is located at

![Fig. 2. AC impedance of n-MoSe$_2$ in 0.2M K$_4$Fe(CN)$_6$. (a) and (b) denote different electrodes. The upper plots are for 100 Hz, and the lower for 500 Hz. $G_p$, in-phase or equivalent parallel conductance, $C_p$, quadrature or equivalent parallel capacitance.](image)

![Fig. 3. Second harmonic ac impedance for n-MoSe$_2$ in aqueous 0.2M K$_4$Fe(CN)$_6$. Fundamental modulation frequency = 500 Hz. Sensitivity for $dG_p$ (second harmonic of $G_p$) and $dC_p$ (second harmonic of $C_p$) are 100x and 20x, respectively, $G_p$ and $C_p$ in Fig. 2b. Negative values are plotted upward.](image)

![Fig. 4. Photocurrent ($j$) and log differential photocurrent ($\Delta j$) vs. potential for n-MoSe$_2$ in 0.2M K$_4$Fe(CN)$_6$. Monochromatic illumination at 500 nm, $j$ obtained with light modulation at ~1.1 kHz, and $\Delta j$ at the difference frequency (~1.5 kHz) between the potential modulation (~1.5 kHz) and the light modulation. (a) and (b) denote different electrodes. The plots for (a) are for the electrode of Fig. 2a.](image)
Fig. 5. AC impedance of n-MoSe₂/RuOₓ in 0.2M K₄Fe(CN)₆. $G_p = \text{equivalent parallel conductance, } C_p = \text{equivalent parallel capacitance, } dG_p = \text{second harmonic of } G_p \text{ (sensitivity = } 5 \times G_p)$. Modulation frequency is 25 Hz (left) and 100 Hz (right). Negative values of $dG_p$ are plotted upward.

1.16V vs. SCE. We have photoelectrochemically deposited a thin layer of RuOₓ on the surface of the n-MoSe₂ electrode of Fig. 2a held at +0.5V under white light illumination from a 450W Xe lamp. The film appeared golden yellow, and the amount of charge passed was equal to 1.9 mC (~30 mC/cm²). In Fig. 5 are given plots of the impedance and the second harmonic ac impedance for two modulation frequencies in K₄Fe(CN)₆ solution. Both the ac impedance at the fundamental frequency and the more sensitive second harmonic exhibit smooth plots that are indicative of an improved surface. In Fig. 6 is shown the $j$ and $\Delta j$ vs. $V$ for n-MoSe₂ after depositing RuOₓ. Note the significant improvement in the shape of the current-voltage behavior. The photocurrent rises to saturation much more quickly than its counterpart in Fig. 4. This type of steep rise to saturation has been attributed to the absence of surface states and recombination effects (28, 29). At 0.3V, corresponding to the $V_{\text{redox}}$ of Fe(CN)₆⁴⁻⁻⁻, the photocurrent (roughly corresponding to the short-circuit photocurrent in a two-electrode PEC cell configuration) of the RuOₓ-modified electrode is approximately double that of the untreated electrode. Consider the behavior of the differential photocurrent. $\Delta j$ decreases more sharply with $V$ than its counterpart in Fig. 4. Further, the hump attributable to the presence of surface states is absent, suggesting the passivation of the surface states. The RuOₓ films were found to be stable in the presence of all mineral acids, but could be dissolved by sulfochromic acid. Short treatments in this acid of bare n-MoSe₂ electrodes were found not to affect the ac impedance behavior. In Fig. 7 is given the plot of $j$ and $\Delta j$ vs. $V$ after partially removing the RuOₓ layer by briefly dipping the electrode in chromic acid. Compare Fig. 6 and 7. In both cases, the $j$ vs. $V$ behavior is the same. The lower photocurrent in Fig. 6 is probably due to larger attenuation of the impinging light intensity by a thicker RuOₓ.
film. However, the $\Delta j$ vs. $V$ behavior is not the same. This plot exhibits a hump in the same potential regime in which both the ac impedance and differential photocurrent (before RuO$_x$ deposition) exhibit a hump. This observation indicates that the differential photocurrent method can be used to monitor the presence of surface states even at low levels, where the photocurrent behavior appears normal. In addition, even those states which cannot be charged in the dark but can be charged under illumination (30) are detectable by the differential photocurrent technique. In this respect it is even superior to the second harmonic impedance method for detecting surface states.

In a previous paper (14), we reported that the surface states existing on n-MoS$_2$ were not present in sufficient density to cause pinning of the Fermi level in acetonitrile solutions. The possibility that a Schottky barrier exists between the n-MoS$_2$ and the RuO$_x$ is ruled out by the constant onset potential of photocurrent in solutions of iodide, bromide, and ferrocyanide. Formation of insulating layers such as oxides could cause the measured impedance to be no longer equivalent to the combination of space charge layer and surface states illustrated by Fig. A-1 of Ref. (14). The fact that RuO$_x$ is a conducting layer, as well as the values of the capacitance away from the potential regime of the surface states before and after RuO$_x$ deposition (compare Fig. 2a and Fig. 5), strongly suggests that the space charge layer capacitance is being measured. Additional support for this contention lies in the fact that even at frequencies as low as 100 Hz, the Mott-Schottky plots are linear; this would not be the case if the space charge capacitance were not approximately equivalent to the measured capacitance.

PEC behavior of polycrystalline n-MoS$_2$.—Recent studies on polycrystalline films of p-WSe$_2$ (31) and n-WSe$_2$ (32) have been described. In the latter work, results of a modification procedure with silver and lanthanum ions were discussed. We report here work done on similar polycrystalline films of n-MoS$_2$ and results of surface modification with photodeposited RuO$_x$ films. In Fig. 8 is shown the $j$-$V$ behavior for the smooth side of polycrystalline n-MoS$_2$ in aqueous solution containing 1.0 M KBr as the redox couple before and after depositing...
a thin layer of RuO$_2$. The conditions are the same as used for the single-crystal n-MoSe$_2$ except the number of coulombs passed in RuO$_2$ deposition (~420 mC/cm$^2$ of projected surface area). (However, the actual surface area could be as much as an order of magnitude greater than the projected area.) The photoperformance is improved after RuO$_2$ deposition; not only is the photocurrent increased, but the onset of photocurrent is located at least 0.3V more negative. Although the i-V performance appears to be improved after modifying the electrode surface with RuO$_2$, the photocurrent and efficiency of the polycrystalline material is still much smaller than that of treated single-crystal MoSe$_2$. Under similar conditions, the untreated rough side of the polycrystalline MoSe$_2$ gave better photocurrent than the RuO$_2$-coated smooth side (Fig. 9). However, deposition of the RuO$_2$ on the rough side did not improve the behavior. Thus, the RuO$_2$ treatment appears to help a poor surface more than a good one.

**Conclusions**

Both the second harmonic and the differential photocurrent methods can be used as diagnostic tools for monitoring the presence of surface states. Even under conditions where the presence of surface states cannot be detected by the photocurrent, the differential photocurrent can be used to detect them. Further, even those states which are not charged in the dark but can be charged under illumination can be detected by the differential photocurrent. In this respect, it is even superior to the second harmonic impedance method. The second harmonic is more sensitive than the ac impedance of the fundamental frequency.

Photoelectrodeposition of a thin film of RuO$_2$ significantly improves both the potential for photocurrent onset as well as the short-circuit photocurrent for single-crystal n-MoSe$_2$ and the smooth side of polycrystalline MoSe$_2$. Attempts to study the behavior of similar n-MoTe$_2$ with RuO$_2$ films were not successful. The Ru($n^+\cdot\cdot\cdot$C$_6$H$_{12}$OH$_2$)$_2^+$ redox potential is more positive than the valence band-edge of this material (13) and, therefore, RuO$_2$ films could not be formed by this method.

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**REFERENCES**


