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## Semiconductor Electrodes

### LX. Photoelectrochemistry of p-ReS<sub>2</sub> and p-ReSe<sub>2</sub> in Aqueous Solutions

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Since the first work of Tributsch on layer-type semiconductors (1), this class of compounds has received considerable attention. Some of the more extensively studied compounds, MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub>, are quite stable under illumination in a photoelectrochemical (PEC) cell (2). Interest in these compounds is based on several factors. As originally discussed by Tributsch, both the conduction and valence bands have mainly metal d orbital character. Hence, absorbed light produces an electron-hole pair but does not result in the breaking of a bond (3). In principle, this should promote stability of the semiconductor lattice against decomposition, although photocorrosion of n-type layer materials still occurs when reactions that take place at very positive potentials (*e.g.*, oxygen evolution) are attempted. A second advantage of layer-type compounds is that fresh surfaces, often with a low density of surface states, can be prepared by peeling a layer of material from the surface ( $\perp$ C-axis). When edge planes are exposed, they can sometimes be passivated. The adsorption of I<sub>3</sub><sup>-</sup> is sometimes beneficial in the operation of PEC cells (4, 5). Finally, small single crystals of many of the layer compounds are readily prepared by vapor transport methods (6). The transport agents employed are an important factor in determining the type of majority carrier in the crystal produced (n or p). For example, transport of WSe<sub>2</sub> with Br<sub>2</sub> produces n-type crystals, while I<sub>2</sub> transport produces p-type crystals (7).

Marzik *et al.* recently reported the growth and PEC properties of ReS<sub>2</sub> and ReSe<sub>2</sub> (8). The compounds were produced with Br<sub>2</sub> as the transport agent, and n-type single crystals were described; this is the only report of the use of ReS<sub>2</sub> and ReSe<sub>2</sub> in PEC cells. While earlier reports of the semiconducting nature of ReS<sub>2</sub> and ReSe<sub>2</sub> can be found (9, 10), to our knowledge, p-type crystals of these compounds have not been described. Our interest in p-type crystals of these compounds derives from their possible application in PEC photovoltaic (or regenerative) cells. Moreover, p-type materials can be useful in photosynthetic applications, *e.g.*, for the reduction of CO<sub>2</sub> (11). Generally, a catalyst is required on the surface of a semiconductor to carry out a kinetically complex photoreduction. Since rhenium and its compounds have been used as catalysts (12, 13), p-ReS<sub>2</sub> and p-ReSe<sub>2</sub> might find application in photoelectrosynthesis. While a change in the majority carrier can be accomplished by choice of dopant in most semiconductors, by analogy to WSe<sub>2</sub>, we grew p-type crystals by using I<sub>2</sub> as the transport agent. This paper describes our first studies of the growth and PEC behavior in aqueous solutions of p-ReS<sub>2</sub> and p-ReSe<sub>2</sub>.

#### Experimental

*Crystal growth and electrode preparation*—Crystals of ReS<sub>2</sub> and ReSe<sub>2</sub> were prepared from rhenium (4N7 purity,

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Johnson Matthey, Incorporated, Seabrook, New Hampshire), sulfur (precipitated, Alfa, Danvers, Massachusetts), and selenium (3N purity, Johnson Matthey). The quartz ampuls used for growing the single crystals were rinsed successively with HF, HCl-HNO<sub>3</sub> (50%-50% by volume), HF, and finally, distilled water. The tubes were dried and then evacuated to *ca.* 10<sup>-5</sup> torr. The procedure of Marzik *et al.* (8) for preparation of the compounds was followed with minor changes. The Re was heated at 950°C in a stream of H<sub>2</sub> to remove any oxides and then heated at 350°C in a dynamic vacuum to remove adsorbed H<sub>2</sub>. The chalcogens were freshly sublimed in vacuum. Stoichiometric amounts of the elements, enough to make *ca.* 3g of compound, were ground together with an agate mortar and pestle and placed in a quartz tube that measured 15 cm long by 1.5 cm diameter. The tube was evacuated for 15 min and then filled with He. Triply sublimed I<sub>2</sub> (5 mg/cm<sup>2</sup>) was quickly added and the tube was cooled in liquid N<sub>2</sub>, evacuated, and then sealed. The temperatures and times used for growing the crystals were the same as those reported previously (8). A three-zone furnace (Lindberg, Watertown, Wisconsin) was used. At the conclusion of the experiment, the ampul was opened and the products rinsed several times with CCl<sub>4</sub>. There were many small (4 × 5 mm) crystals, many of which were twinned, and much polycrystalline powder. X-ray powder diffraction patterns of the products matched those of ReS<sub>2</sub> and ReSe<sub>2</sub> (ASTM card no. 27-502 for ReS<sub>2</sub>, no. 18-1086 for ReSe<sub>2</sub>). The single crystals were quite thin (*ca.* 100 μm) and easily bent; great care was needed to prepare a flat, edge-free, surface for an electrode. After a crystal had been selected, the back of the crystal was attached to a copper wire with a drop of silver paint (Acme Chemicals and Insulation, New Haven, Connecticut) and this connection was covered with 5 min epoxy cement (Devcon, Danvers, Massachusetts). The copper wire was placed through a 6 mm diameter glass tube and held in place with epoxy cement. All surfaces except the front surface of the crystal were then covered with silicone sealant (Dow-Corning Corporation, Midland, Michigan).

*Photoelectrochemical experiments*.—A standard one-compartment electrochemical cell, with optically flat windows for illumination of the semiconductor electrodes, was used. The counterelectrode was a large (>40 cm<sup>2</sup>) Pt gauze and the reference electrode was a saturated calomel electrode (SCE). A potentiostat [Princeton Applied Research (PAR) Model 173, Princeton, New Jersey] and programmer (PAR Model 175) were used for current-voltage measurements, recorded on an XYY recorder (Soltec Model 6432, Sun Valley, California). Capacitance measurements were performed with the preceding plus a PAR 5204 lock-in amplifier and HP200CD wide range oscillator (Hewlett-Packard, Palo Alto, California) by previously reported procedures (14).

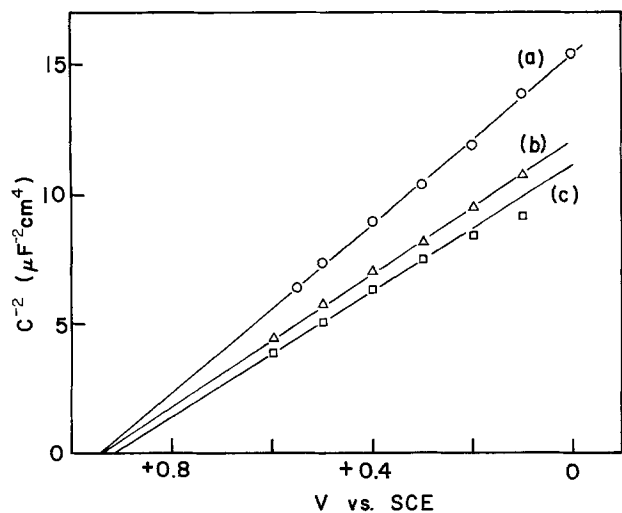


Fig. 1. Mott-Schottky plot of p-ReSe<sub>2</sub> in 0.1M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.1M Na<sub>2</sub>SO<sub>4</sub>, 50 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> (pH #5) at frequencies of (a) 2000, (b) 1000, (c) 500 Hz.

White light illumination of the electrode was by a 450W Xe arc lamp (Oriol Corporation, Stamford, Connecticut). Monochromatic illumination was provided by a 2500W Xe arc lamp (Schoeffel Instrument Company, Westwood, New Jersey) and monochromator (Oriol Model 7240).

### Results

**Capacitance measurements.**—Mott-Schottky (M-S) plots ( $1/C^2$  vs.  $V$ ), where  $C$  is capacitance and  $V$  is potential vs. SCE, for ReSe<sub>2</sub> in 0.1M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.1M Na<sub>2</sub>SO<sub>4</sub>, 50 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> are shown in Fig. 1. Although there was some frequency dispersion in the plots, estimates of the flat-band potential ( $V_{FB}$ ) and doping level can be obtained. The intercept with the potential axis gives a value of  $V_{FB} = 0.9 \pm 0.1V$  vs. SCE. With the assumption that the dielectric constant for ReSe<sub>2</sub> is close to that of ReS<sub>2</sub> ( $\epsilon = 7.8$ ) (9), the slope of the Mott-Schottky plot gives a value for the doping density of  $N_A = 1.3 \pm 0.3 \times 10^{18} \text{ cm}^{-3}$  (15). A value of the effective density of states in the valence conduction band,  $N_v$ , of  $2.5 \times 10^{19} \text{ cm}^{-3}$  can be calculated by taking the effective mass of holes in ReSe<sub>2</sub> to be the same as that in WSe<sub>2</sub> ( $m_h^* = m_e$ ) (16). With these values,  $\Delta E_F$ , the difference in energy between the valence band energy and the Fermi level is calculated to be 0.08 eV.

The ReS<sub>2</sub> crystals showed quite different  $1/C^2$  vs.  $V$  behavior. The resistance of these crystals was quite high and the capacitance varied little with bias. Mott-Schottky plots did not intercept the potential axis until quite positive potentials. In addition, the frequency dependence of these plots was such that values for  $V_{FB}$  and the doping density could not be obtained from those measurements.

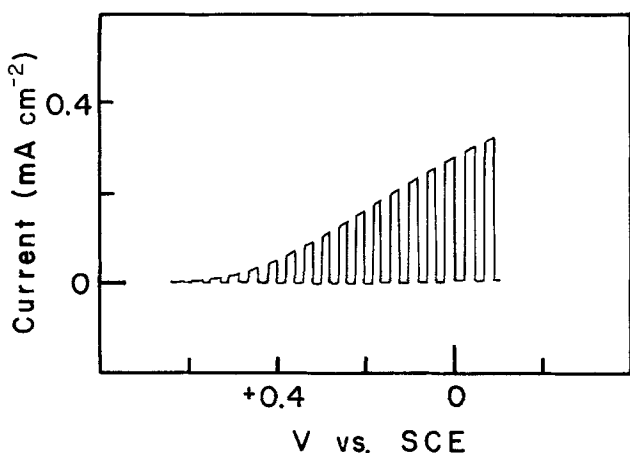


Fig. 2. Photocurrent-potential curve for p-ReSe<sub>2</sub> with chopped white light (ca. 50 mW/cm<sup>2</sup>). Solution was 50 mM Fe(II)EDTA, 50 mM Fe(III)EDTA, 0.2M Na<sub>2</sub>SO<sub>4</sub> adjusted to pH 5.

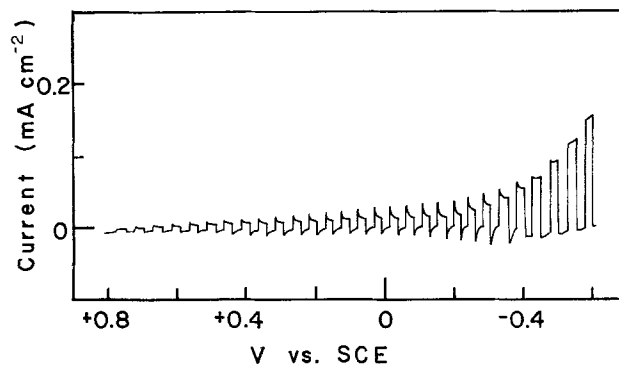


Fig. 3. Photocurrent-voltage curve for p-ReSe<sub>2</sub> with chopped white light (ca. 50 mW/cm<sup>2</sup>) in 0.1M MV<sup>2+</sup> in 1M KCl.

**PEC behavior.**—The photocurrent ( $i_{ph}$ )-potential behavior of a p-ReSe<sub>2</sub> electrode is shown in Fig. 2 for Fe(II)EDTA/Fe(III)EDTA, and in Fig. 3, for methyl viologen (MV<sup>2+</sup>) solutions. The behavior in the iron solution was clearly that of a p-type semiconductor and no photo-oxidation of Fe(II)EDTA or dark reduction of Fe(III)EDTA was observed. The onset of the photocurrent was just positive of +0.6V vs. SCE, but the current rose slowly and saturated only near the reversible potential for the couple,  $V_{redox} (-0.12V$  vs. SCE). In MV<sup>2+</sup> solutions (Fig. 3), only small photoeffects were seen as far positive as +0.8V vs. SCE, but net reduction current was seen only at potentials negative of +0.6V vs. SCE. Notice that the  $i_{ph}$ - $V$  curve, obtained with chopped irradiation, consisted of a series of current spikes, both cathodic as the light was turned on, and anodic as the light was turned off, unlike the Fe(II/III)EDTA solution. Moreover,  $i_{ph}$  did not attain a saturation value. A two-electrode cell (p-ReSe<sub>2</sub> and Pt) in the Fe(II/III)EDTA solution, illuminated with 50 mW/cm<sup>2</sup> white light, gave an open-circuit photovoltage ( $V_{oc}$ ) of about 400 mV. Plots of  $(\phi h\nu)^{1/2}$  vs.  $h\nu$  (Fig. 4), where  $\phi$  = quantum efficiency of photocurrent and  $h\nu$  is photon energy, gave a value of  $1.31 \pm 0.01$  eV for the indirect gap. This value agrees with that of Marzik *et al.* (8), who used the absorption coefficient to obtain a value of 1.32 eV for the indirect gap for n-ReS<sub>2</sub>. Short-circuit quantum efficiencies of > 10% at 600 nm were obtained (without correction of reflective losses from the mirror-like surfaces of the crystal).

The  $i_{ph}$ - $V$  behavior of p-ReSe<sub>2</sub> in the Fe(II/III)EDTA solution was similar to that for p-ReS<sub>2</sub> (Fig. 5). No oxidation current in the dark, or under irradiation over the potential region +0.6 to -0.2V was observed. The onset for  $i_{ph}$  was +0.4V vs. SCE, about 0.2V more negative than for p-ReS<sub>2</sub>. The photocurrent rose much more sharply and saturated close to 0 V vs. SCE. A two-electrode cell with this solution gave a  $V_{oc}$  of ca. 430 mV. A plot of  $(\phi h\nu)^{1/2}$  vs.  $h\nu$

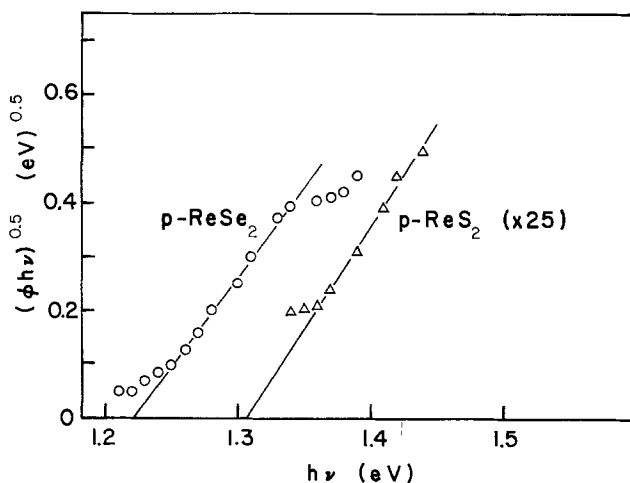


Fig. 4. Photocurrent vs. frequency (as  $(\phi h\nu)^{1/2}$  vs.  $h\nu$ ) for (a) p-ReSe<sub>2</sub> and (b) p-ReSe<sub>2</sub>; solution as in Fig. 2.

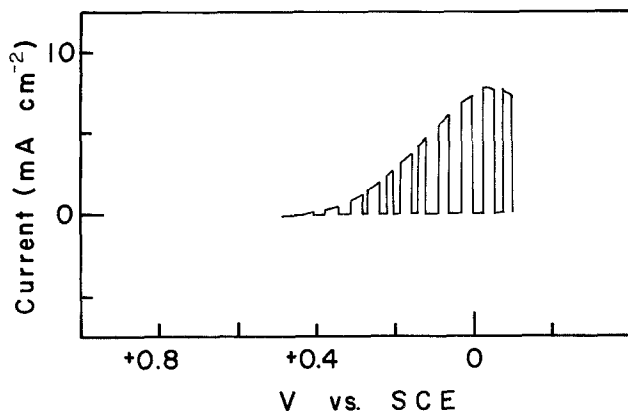


Fig. 5. Photocurrent-potential curve for p-ReSe<sub>2</sub> with chopped white light (ca. 50 mW/cm<sup>2</sup>) with same solution as in Fig. 2.

(Fig. 4) gave a value of  $1.22 \pm 0.01$  eV for the indirect gap, compared with 1.17 eV reported by Marzik *et al.* (for n-ReSe<sub>2</sub>). Short-circuit quantum efficiencies of about 50% were obtained at 800 nm (without correction for electrode reflectance).

### Discussion

Knowledge of  $V_{FB}$ ,  $E_g$ , and  $\Delta E_F$  allows calculation of the energy levels of the conduction and valence bands. This information is useful in the determination of proper redox couples for solar-to-electrical or chemical energy conversion. For our p-ReSe<sub>2</sub> crystal,  $V_{FB} = 0.9$  V vs. SCE and the valence band edge,  $E_v$ , is about 1.0 V vs. SCE. Since  $E_g$  was 1.2 eV, the conduction band edge ( $E_c$ ) will be near -0.2 V vs. SCE. Marzik *et al.* (8) found  $V_{FB}$  for n-ReSe<sub>2</sub> to be -0.2 V vs. SCE in a solution of 0.05 M NaI, 2 mM I<sub>2</sub>, 0.05 M H<sub>2</sub>SO<sub>4</sub>. With their reported value of the donor density ( $N_D = 7 \times 10^{16}$  cm<sup>-3</sup>) and the same assumption we used, *i.e.*, that the effective mass of electrons is the same as that for holes,  $\Delta E_F$  for n-ReSe<sub>2</sub> is 0.15 eV. Thus, for Marzik *et al.*, the conduction band edge should be -0.35 V vs. SCE. Layer type compounds usually do not show shifts of the band edge energies with different redox couples or with solution pH (14), although adsorption of I<sub>3</sub><sup>-</sup>, with a resultant negative shift of the bands, has been noted (4, 6). Within the uncertainties of the measurements and assumptions, the values for band energies found for n- and p-type are essentially the same.

No shift was observed in the photocurrent onset potential for either p-ReS<sub>2</sub> or p-ReSe<sub>2</sub> after soaking the electrodes in a 1 M KI, 50 mM I<sub>2</sub> solution, rinsing, and replacing the electrodes in Fe(II/III)EDTA or MV<sup>2+</sup> solutions. The photocurrent onset for p-ReSe<sub>2</sub> occurs at potentials more negative than the  $V_{FB}$  determined from capacitance measurements and would be equivalent to  $E_v = 0.7$  V and  $E_c = -0.5$  V vs. SCE. However, photocurrent onsets may not be reliable for estimates of band-edge energies, *e.g.*, because of recombination effects or because filling of surface states by electrons while the electrode is under illumination can cause the band edges to shift to more negative values (3, 17). The estimated band-edge potentials for p-ReSe<sub>2</sub>, along with the potentials of several redox couples, are given in Fig. 6. Note that  $E_c$  is positive of the redox potential for MV<sup>2+</sup> (-0.68 V vs. SCE), and no photoeffect should be observed. The small spiked photocurrents that are seen with this couple might be explained by a shift of the bands in a negative direction under illumination through the formation of an inversion layer at the surface (17-19) until electrons can reduce the solution species. The back (anodic) spike can be explained as reoxidation of MV<sup>+</sup>, as the conduction band in the dark again becomes positive of the redox potential.

The much slower rise to saturation for p-ReS<sub>2</sub> in the  $i_{ph}$ -V curves, the small quantum efficiencies, and the deviation of the C-V curves from the M-S equation can probably be attributed to the high resistivity of these crystals, although other factors may also be important. If the photocurrent onset (0.45 V vs. SCE) is taken as  $V_{FB}$ , the

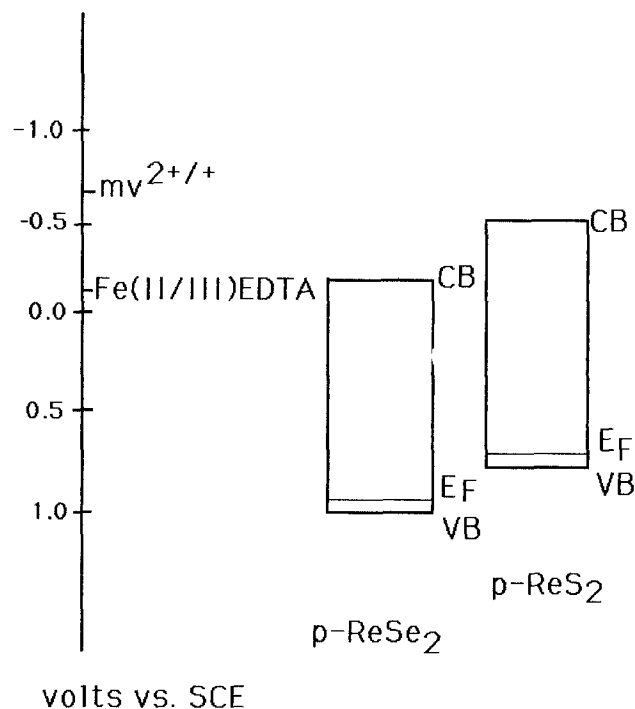


Fig. 6. Schematic diagram of the band positions of p-ReSe<sub>2</sub> and p-ReS<sub>2</sub>. Note that there is considerable uncertainty about the band positions of p-ReS<sub>2</sub>.

valence and conduction bands are located near 0.6 V vs. SCE and -0.7 V vs. SCE, respectively. Marzik *et al.* (8) report  $V_{FB}$  for n-ReS<sub>2</sub> as being positive of n-ReSe<sub>2</sub>. With the slightly larger bandgap energy, the valence band probably would be more positive for the sulfide than for the selenide, as evidenced by other sulfide and selenide compound semiconductors (20, 21). In this case,  $V_{redox}$  for MV<sup>2+</sup> is again negative of the conduction band minimum and poor photocurrent-voltage behavior is expected (as observed). The positions of the bands for p-ReS<sub>2</sub>, taking  $V_{FB} \approx 0.5$  V, are shown in Fig. 6. Note, however, that  $V_{FB}$  for p-ReS<sub>2</sub> is probably positive of the potential for the onset of photocurrent because of the high resistance in the semiconductor crystals.

### Conclusions

p-ReS<sub>2</sub> and p-ReSe<sub>2</sub> can be grown by following the procedure for growing n-ReS<sub>2</sub> and n-ReSe<sub>2</sub> by substituting I<sub>2</sub> for Br<sub>2</sub> as the transport agent. The reason for the change from donor to acceptor doping is unclear, but is also seen with other systems. The bandgaps of the compounds determined in this work agreed well with previously determined values for the n-type compounds. Open-circuit photovoltage values of ca. 400 mV were obtained from both crystals in Fe(II/III)EDTA solution. Unfortunately, the conduction band edges are too positive to photo-reduce CO<sub>2</sub>, but might be able to produce H<sub>2</sub> with a suitable catalyst. Work is currently under way in our laboratory to vary the conditions of crystal growth and add dopants to lower the resistivity of p-ReS<sub>2</sub>. Studies of the behavior of these compounds in nonaqueous solvents are also being undertaken.

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