

# Electrical Conductivity Measurements of Molten Alkaline-Earth Fluorides

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## ABSTRACT

The electrical conductivities of molten  $\text{BeF}_2$ ,  $\text{MgF}_2$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  were measured by electrochemical impedance spectroscopy. A new conductance cell was designed and constructed for the purpose of determining the electrical properties of highly conductive and very corrosive melts at temperatures as high as  $1600^\circ\text{C}$ . The cell is comprised of twin capillaries of pyrolytic boron nitride, 5 mm id  $\times$  10 cm long, two movable tungsten electrodes, and a molybdenum crucible. The ranking by specific electrical conductivity,  $\kappa$ , was  $\text{BeF}_2 < \text{MgF}_2 < \text{SrF}_2 < \text{BaF}_2 < \text{CaF}_2$ , and by molar electrical conductivity,  $\Lambda_m$ , was  $\text{BeF}_2 < \text{MgF}_2 < \text{CaF}_2 < \text{SrF}_2 < \text{BaF}_2$ .  $\Lambda_m$  was found to vary with the logarithm of the charge density of the metal cation over the entire series of alkaline-earth fluorides. With the exception of  $\text{BeF}_2$ ,  $\ln \Lambda_m$  was found to vary with  $\ln \{V_m^{2/3} \exp(E_c/RT)\}$ , where  $V_m$  is the molar volume and  $E_c$  is the coulombic energy between nearest neighbor ions in the melt.

The electrical conductivity of a molten salt is of both theoretical interest and technological importance. Electrical conductivity data reveal mechanisms of transport phenomena and provide information about melt structure. In electrometallurgical technologies such as fused salt electrolysis and electroslag welding one of the functions of the molten salt is to act as an electrical resistance element in which Joule heat is generated. In these operations, maintaining the thermal balance is critical, and so the electrical conductivity of the molten salt is arguably the most important information one needs for process design and optimization. As part of a systematic investigation of the physical properties of fluxes for use in electroslag welding of titanium, the electrical conductivities of binary solutions containing  $\text{CaF}_2$  and other alkaline-earth fluorides were measured by electrochemical impedance spectroscopy. A new conductance cell was designed and constructed for the purpose of determining the electrical properties of highly conductive and very corrosive melts at temperatures as high as  $1600^\circ\text{C}$ . This paper describes the new cell and reports the results for pure one-component melts of  $\text{BeF}_2$ ,  $\text{MgF}_2$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ .

## Literature

The database for electrical properties of molten fluorides is poor. Not only are there wide gaps in information, but there are serious discrepancies in much of what has been reported. Of the pure alkaline-earth fluorides, only  $\text{CaF}_2$  has been studied to any great extent, and these data have been reviewed by Mills and Keene (1). Missing from that review was a study by Voronin *et al.* (2). The electrical conductivity of pure  $\text{BeF}_2$  has previously been the subject of only two investigations, one by Mackenzie (3) and one by Desyatnik and Koverda (4). Likewise, the electrical conductivity of pure  $\text{MgF}_2$  has been the subject of two investigations, one by Ogino *et al.* (5) and one by Voronin *et al.*, cited previously in connection with  $\text{CaF}_2$  (2). Also, this last article appears to be the only report in the literature on  $\text{SrF}_2$  and  $\text{BaF}_2$ .

## Experimental

To avoid many of the problems with previous attempts to measure the electrical conductivities of molten alkaline-earth fluorides a new experimental apparatus was designed and constructed. Shown in Fig. 1, which is not drawn to scale, the heart of the apparatus is the conductance cell comprising twin capillaries, 5 mm id  $\times$  10 cm long, made of pyrolytic boron nitride tubing (Union Carbide Corporation, Cleveland, OH), movable tungsten electrodes, and a molybdenum crucible. Temperature was measured by a thermocouple, ASTM Type B, protected by a closed-one-end molybdenum tube (Rhenium Alloys Inc.,

East Elyria, OH) immersed in the melt. The capillaries were mounted in a fixture of hot-pressed boron nitride. Molybdenum bolts secured the capillaries to the fixture and the fixture to the molybdenum thermocouple sheath.

The components made of boron nitride were treated prior to use in the conductivity cell. The pyrolytic boron nitride capillaries were fired in air at  $700^\circ\text{C}$  for 10 h. The hot-pressed boron nitride fixture was heated at the rate of  $250 \text{ K h}^{-1}$  to  $1000^\circ\text{C}$ , held at this temperature for 10 h to remove moisture and binders, and then cooled to room temperature in flowing argon gas. Without this treatment, the boron nitride fixture would shatter as the conductivity cell was heated to the temperature of the experiment.

The electrodes were made of tungsten wire (Johnson Matthey-Alfa, Ward Hill, MA), 0.75 mm diam  $\times$  55 cm long. The part of the electrode immersed in the melt terminated in a tightly wound coil, 4 mm diam  $\times$  1 cm long. Comprising twelve turns, the coil would measure 15 cm fully extended. The upper ends of the electrodes were silver soldered to molybdenum rods, 3 mm diam  $\times$  20 cm long, which in turn were fed through O-ring compression fittings (ULTRA-TORR Fitting, Cajon Vacuum Products, Macedonia, OH) in the stainless steel cell cap from which the electrodes were electrically insulated with spacers

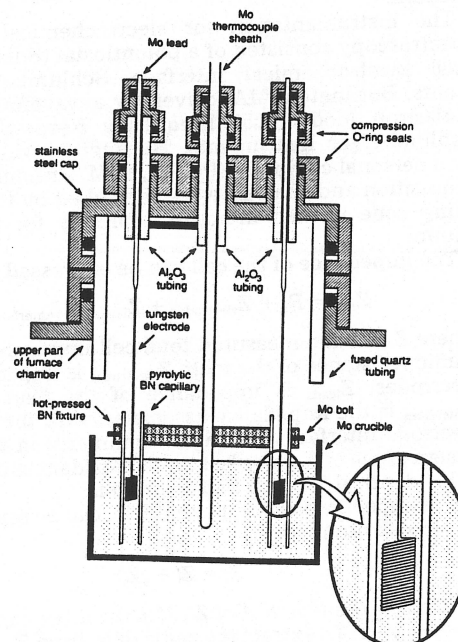


Fig. 1. Schematic of apparatus for electrical conductivity measurements.

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to change the interelectrode spacing. The instant position of the electrodes was measured to  $\pm 0.01$  mm by means of digital electronic calipers mounted on the cell cap. The range of electrode displacement was 2 cm which represents a variation in interelectrode spacing of 4 cm. The measured impedance data along with the electrical conductivity data of Emons and Brautigam (6) were used both in Eq. [5] in order to evaluate the cell constant,  $G$ , which ranged from 5 to 20  $\text{cm}^{-1}$  depending on the interelectrode separation and in Eq. [6] to evaluate the cell constant gradient,  $dG/d\ell$ . In repeated evaluations the cell constant varied by less than 0.05%. Furthermore,  $G$  was observed to be strictly linear in  $\ell$  over the entire range of interelectrode spacing. This finding was very significant as it relieved one of having to know the value of  $G$  or  $dG/d\ell$  at any specific  $\ell$  in order to calculate the value of  $\kappa$  directly from Eq. [6]. After the last measurement had been taken, the cell assembly was raised out of the melt and held above it to allow the salt to drain from the capillaries into the crucible. The electrodes were then withdrawn from the capillaries. Finally, power to the furnace was reduced in order to cool it to room temperature.

To complete the certification of the cell the electrical conductivity of pure molten KCl was measured, and the results were compared to those reported in the literature. To remove any NaCl remaining in the capillaries from the previous measurements the cell was heated to 1550°C at which temperature it was held for 5 h under vacuum. Following this, the cell was washed with the molten salt to be studied, namely, KCl. No water was used to clean the cell. Potassium chloride used for certifying the cell was 99.999% pure (CERAC, Milwaukee, WI) and was treated by the procedure described above for NaCl. Comparison with the results of Van Artsdalen and Yaffe (7) showed a maximum deviation between the two studies of less than 0.2%. This result reconfirmed the cell constant determination with molten NaCl and validated the technique of investigation. This entire procedure of cell constant determination with NaCl succeeded by measurement of the electrical conductivity of KCl was followed each time a new cell was commissioned for the study of alkaline-earth fluoride melts.

The electrical conductivities of molten alkaline-earth fluorides were measured by following the same experimental procedure used in certifying the conductance cell. Reagent grade salts, exceeding 99.9% purity with the exception of  $\text{BeF}_2$  which was 99.5% pure, were treated prior to melting by vacuum drying at 300°C for 12 h. Then dry argon gas, 99.995% pure and with a moisture content less than 10 ppm (Matheson Gas Products, Gloucester, MA), was admitted to the furnace chamber where it blanketed the specimen for the duration of the experiment. Before the first measurements were made, the specimen was held at 1600°C for 2 h to remove traces of volatile impurities. The melt depth was fixed at 4.5 cm, and the immersion depth of the pyrolytic boron nitride capillaries was 4 cm.

To determine the effect of prolonged exposure of the pyrolytic boron nitride to the corrosive alkaline-earth fluoride melts two of the capillary-type conductance cells were recalibrated after three experiments with molten  $\text{CaF}_2$ . Three experiments represent approximately 24 h of immersion. The cell was cleaned first by heating to 1600°C in vacuum and holding for 5 h before cooling. Next, the cell was immersed in molten NaCl at 900°C to dissolve any residual  $\text{CaF}_2$  in the capillaries. The cell was then taken out

of the crucible and cooled. Following this, the cell was heated to 1550°C, held at that temperature for 5 h under vacuum and then cooled to room temperature. Finally, the cell was dipped into and washed with molten NaCl at a temperature of approximately 850°C. At this point the cell constant was measured with pure NaCl and was found in the worst case to have decreased by only 1.4%.

## Results

The measured values of specific electrical conductivity for pure alkaline-earth fluorides have been fit by least squares regression to an Arrhenius type equation of the form

$$\ln \kappa = a - b/T \quad [7]$$

where  $\kappa$  is in  $\Omega^{-1} \text{cm}^{-1}$  and  $T$  is in Kelvins. Table I presents for each of the alkaline-earth fluorides the coefficients  $a$  and  $b$  as defined in Eq. [7], as well as the standard error of estimate of  $\ln \kappa$ ,  $s$ , the coefficient of correlation,  $r$ , the temperature range of investigation, and the number of data points,  $n$ .

$\text{BeF}_2$ .—The measured values of the specific electrical conductivity of  $\text{BeF}_2$  along with data from the literature are plotted in Fig. 2. The specific electrical conductivity of  $\text{BeF}_2$  is exceptional amongst the alkaline-earth fluorides in two respects. First,  $\kappa_{\text{BeF}_2}$  is several orders of magnitude lower than the specific electrical conductivities of the other alkaline-earth fluorides. Second, an Arrhenius plot of the temperature dependence of  $\kappa_{\text{BeF}_2}$  exhibits a change in slope at 1076°C. The activation energies in both temperature regimes are about an order of magnitude greater than those of the other alkaline-earth fluorides. The values of specific electrical conductivity measured in the present work lie between those of the two previously reported studies, about three to four times greater than the values obtained by Mackenzie (3) and about three times smaller than those obtained by Desyatnik and Koverda (4). As for activation energies, calculations performed on Mackenzie's data on the temperature interval spanning 850 to 950°C give a value of 190  $\text{kJ mol}^{-1}$  which agrees well with the value of 194  $\text{kJ mol}^{-1}$  found in this study to be valid at temperatures below 1076°C. Similar calculations performed on the data reported by Desyatnik and Koverda on the temperature interval spanning 800 to 900°C give a value of only 124  $\text{kJ mol}^{-1}$ .

The discrepancy in the values of  $\kappa_{\text{BeF}_2}$  may be due to the fact that the  $\text{BeF}_2$  Mackenzie used was only 99% pure and he took his measurements in a crucible-type conductance cell. In this study the  $\text{BeF}_2$  was 99.5% pure, and measurements were made in a capillary-type conductance cell. With its higher value of cell constant and well-defined current path the capillary-type conductance cell is superior to the crucible-type conductance cell, all other things being equal. Even though Desyatnik and Koverda used  $\text{BeF}_2$  that was 99.8% pure and took their measurements in a capillary-type conductance cell, the capillary was made of sintered polycrystalline  $\text{BeO}$  which, if chemically attacked, would be expected to dissolve in  $\text{BeF}_2$  and raise its electrical conductivity. Furthermore, Desyatnik and Koverda report that their data were taken at a fixed frequency of 50 kHz. In the present study which also employed a capillary-type conductance cell it was observed that simply taking measurements at high frequency did not eliminate all reactances. To assure that the data were comprised of

Table I. Least squares regression analysis of electrical conductivity data.

Composition	$a$ Coefficient of Eq. [7]	$b$ Coefficient of Eq. [7]	$s$ , Standard error of estimate of $\ln \kappa$	$r$ , Coefficient of correlation	Temperature range (°C)	$n$ , No. of data points
$\text{BeF}_2$	14.075	23,342	0.0268	0.9994	925-1,076	53
$\text{BeF}_2$	9.952	17,806	0.0281	0.9949	1,076-1,173	28
$\text{MgF}_2$	2.675	1,825	0.0039	0.9967	1,322-1,577	47
$\text{CaF}_2$	2.823	1,692	0.0011	0.9988	1,468-1,587	42
$\text{SrF}_2$	2.711	1,674	0.0011	0.9965	1,531-1,604	25
$\text{BaF}_2$	2.743	1,726	0.0017	0.9953	1,452-1,550	28



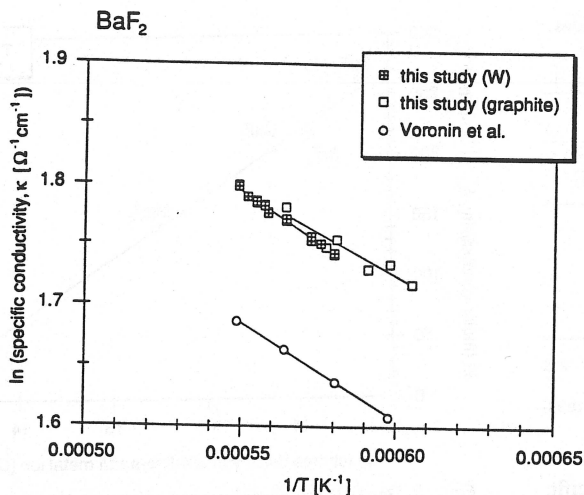


Fig. 6. Temperature dependence of the specific electrical conductivity of molten BaF<sub>2</sub>.

agreement in the results for CaF<sub>2</sub>, MgF<sub>2</sub>, and SrF<sub>2</sub>. Accordingly, a special effort was made to reconcile the difference in the BaF<sub>2</sub> results. Experiments were repeated with different specimens and with different electrodes. In all cases the values of κ<sub>BaF<sub>2</sub></sub> remained consistent within the limits of experimental error. Figure 6 shows that in the measurement of κ<sub>BaF<sub>2</sub></sub> tungsten electrodes and graphite electrodes performed identically. The graphite was spectroscopic grade and before use in the conductance cell was polished with emery paper, washed in liquid nitrogen, and chlorinated for 4 h at 800°C with thionyl chloride in an argon carrier gas. Perhaps the explanation for the difference between BaF<sub>2</sub> results of this work and those of Voronin *et al.* is that in the present investigation the salt was 99.9% pure, whereas Voronin *et al.* used CP grade material.

The comparison testing of tungsten and graphite electrodes was extended to include CaF<sub>2</sub> and SrF<sub>2</sub>. In the case of κ<sub>CaF<sub>2</sub></sub> the difference in the values of electrical conductivity was less than 1% which is imperceptible in Fig. 7 but evident in Fig. 4 with its finer scale. Also shown in Fig. 7 are the results of Ogino *et al.* (9) who reported that at 1500°C the value of κ<sub>CaF<sub>2</sub></sub> measured with molybdenum electrodes was 28.15% higher than that measured with graphite electrodes. In the present investigation the greatest effect of electrode material on the data was observed in the measurement of κ<sub>SrF<sub>2</sub></sub> where at 1550°C the values obtained with tungsten electrodes were 2.9% higher than those obtained with graphite electrodes. This is less than the difference between the results of this work and those of Voronin *et al.*

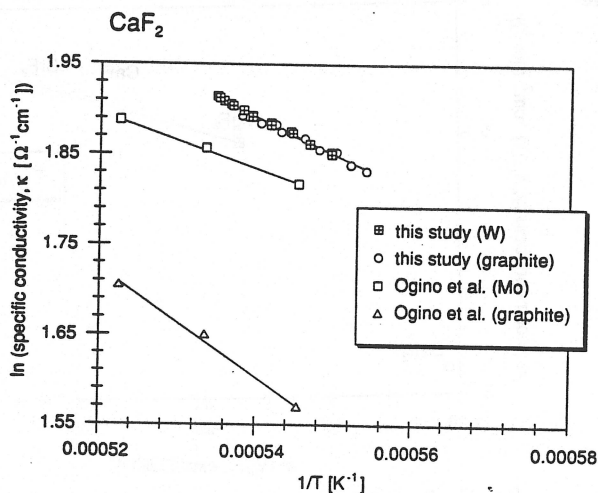


Fig. 7. Dependence of the specific electrical conductivity of molten CaF<sub>2</sub> on electrode composition.

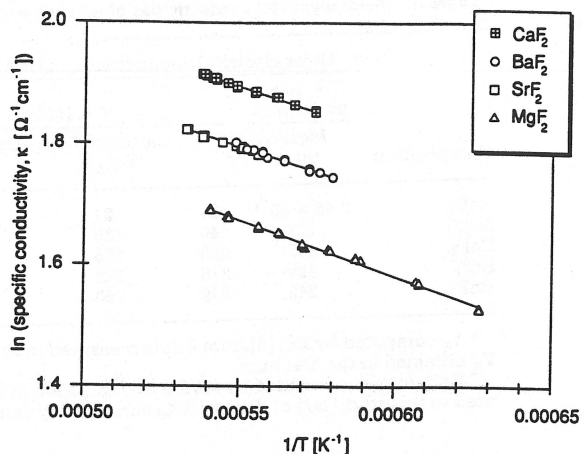


Fig. 8. Temperature dependence of the specific electrical conductivities of molten MgF<sub>2</sub>, CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>.

### Discussion

Figure 8 shows for all but BeF<sub>2</sub> the measured values of κ plotted on the same graph. Not surprisingly, the specific electrical conductivity of BeF<sub>2</sub> is by far the lowest of all the alkaline-earth fluorides and lies out of range of Fig. 8. Clearly, CaF<sub>2</sub> is the most conductive of the alkaline-earth fluorides. Curiously, SrF<sub>2</sub> and BaF<sub>2</sub> have almost identical values of specific electrical conductivity. However, κ<sub>MgF<sub>2</sub></sub> is low enough to set it apart from the other three heavier alkaline-earth fluorides. This last observation is important due to the fact that from a practical standpoint the specific electrical conductivity is the significant figure of merit. These data identify MgF<sub>2</sub> as a candidate solute with the potential to decrease the electrical conductivity of CaF<sub>2</sub>, the most common flux used in the electrometallurgy of reactive metals. In an alternative format the values of κ measured in the present study are summarized in Table II at two temperatures: 1525°C (column 2) and 100 K above the melting point of each salt (column 3).

The comparison of specific electrical conductivities suffers from the fact that κ is a practical unit representing the electrical current carrying capacity of a fixed volume of melt and thus is confounded by changes in density as well as changes in the electrical mobilities of the ions. More valuable from a theoretical standpoint is the molar conductivity, Λ<sub>m</sub>, which is compensated so as to represent a fixed number of chemical entities, if not a fixed number of charge carriers in the most ideal cases. In this work the molar electrical conductivity is defined as

$$\Lambda_m = \kappa V_m \quad [8]$$

where V<sub>m</sub> is the molar volume.

Figure 9 shows for all but BeF<sub>2</sub> the measured values of Λ<sub>m</sub> plotted on the same graph. Density measurements by Hara and Ogino (11) along with those compiled by Janz *et al.* (12) were used to calculate values of V<sub>m</sub>. Under the same conditions of temperature chosen for the entries in Table II, Table III shows two comparisons of the values of Λ<sub>m</sub> measured in the present study. There are differences in ranking between Fig. 8 and 9 as well as between Tables II and III. By measure of Λ<sub>m</sub>, BaF<sub>2</sub> is the most conductive of

Table II. Specific electrical conductivities of alkaline-earth fluorides.

	Specific electrical conductivity, κ (Ω <sup>-1</sup> cm <sup>-1</sup> )	
	T = 1525°C	T = 100 K above m.p.
BeF <sub>2</sub>	1.05	1.02 × 10 <sup>-5</sup>
MgF <sub>2</sub>	5.26	4.76
CaF <sub>2</sub>	6.57	6.54
SrF <sub>2</sub>	5.93	6.07
BaF <sub>2</sub>	5.95	5.72

\* BaF<sub>2</sub> entries computed by severe extrapolation of κ data in this study.

the interionic distance between the anion and cation in the melt. A relative permittivity value of 3 for molten fluorides (14) was used to calculate  $E_c$ . Studies of the structure of molten alkali halides by radial distribution function (15) show that the nearest neighbor distance in the liquid is slightly smaller than that of the crystal, yet molar volume increases upon melting. In view of this, the sum of the crystal radii of the alkaline-earth metal cation and the fluoride anion (14) was used for the value of the interionic distance,  $d$ .

Figure 11 displays the 1525°C isotherm of  $\ln \Lambda_m$  vs.  $\ln \{V_m^{2/3} \times \exp(E_c/k_B T)\}$ . For all but  $\text{BeF}_2$ , there is very good correlation. Least squares regression of the data for  $\text{MgF}_2$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  gave

$$\ln \Lambda_m = 7.064 + 0.07398 \ln \{V_m^{2/3} \exp(E_c/k_B T)\} \quad [15]$$

Table III shows values of  $\Lambda_m$  calculated by Eq. [15]. Deviations from measured values range from 0.4% for  $\text{BaF}_2$  to 3.4% for  $\text{CaF}_2$ . The lack of correlation on the part of  $\text{BeF}_2$  is attributed to its unique melt structure which sets it apart from the other alkaline-earth fluorides. This is supported by the exceptionally high value of the activation energy for electrical conduction in  $\text{BeF}_2$  as compared with that of other melts in this family of compounds.

### Summary

The electrical conductivities of molten  $\text{BeF}_2$ ,  $\text{MgF}_2$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  have been systematically measured by electrochemical impedance spectroscopy. The new conductance cell designed and constructed for this investigation has demonstrated itself to be capable of yielding data of high quality under severe conditions, namely, at temperatures as high as 1600°C with very corrosive and highly conductive melts. In principle, there is no reason why the cell cannot be used at temperatures approaching 2000°C.

$\text{BeF}_2$  was the least conductive of the alkaline-earth fluorides.  $\text{CaF}_2$  had the highest value of specific conductivity,  $\kappa$ , while  $\text{BaF}_2$  had the highest value of molar conductivity,  $\Lambda_m$ .  $\Lambda_m$  was found to vary with the logarithm of the charge density of the metal cation over the entire series of alkaline-earth fluorides. For all but  $\text{BeF}_2$ ,  $\ln \Lambda_m$  was found to vary with  $\ln \{V_m^{2/3} \exp(E_c/RT)\}$ , where  $V_m$  is the molar volume and  $E_c$  is the coulombic energy between nearest neighbor ions in the melt.

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## Photoelectrochemical Measurements of Thin Oxide Films: Multiple Internal Reflection Effects

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### ABSTRACT

Previous studies have shown that photoelectrochemical methods used to study the semiconducting properties of oxides may be extended to *in situ* investigations of thin oxide films. A new expression relating the photocurrent to the film thickness has been derived by combining a simplified Gärtner/Butler model and an optical model for multiple internal reflections. With this model it is shown that the observed dependence of the photocurrent on film thickness is caused by multiple internal reflections. There is a good fit to experimental data for  $\text{TiO}_2$  films illuminated at 350 nm and under moderate bias. The relevance of multiple internal reflections to the analysis of photoelectrochemical microscopy data is also discussed.

Photoelectrochemical studies are used to study the optical and electronic properties of semiconductor electrodes as bulk materials (1-7). By this means, processes at the various interfaces (electrolyte/semiconductor, semicon-

ductor/metal) may be separately observed. In addition, under appropriate conditions, high fields may be applied across a relatively narrow region just inside the surface of the semiconductor at the electrolyte junction, producing a depletion layer devoid of carriers of either sign. Optical excitation with light of energy larger than the bandgap leads

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