

band is likely related to those observed in the excited-state spectra. These results corroborate the suggestions of Petersen et al.²⁵ and Kalyanasundaram and Nazeeruddin,³⁵ and the second reduction of the binuclear complex may be unequivocally assigned as a dpp-based reduction. Only after the third reduction of the binuclear complex do the features of a reduced bpy ligand become apparent.^{39,53} These include a large increase in absorbance at 350 nm as well as resolved bands in the visible region at 495 and 525 nm. The spectrum of the triply reduced binuclear species may only be regarded as approximate because of the partial superposition of the third and fourth reduction waves. The essential point, however, is that bpy is not reduced until the third electron is added to the complex. With the third reduction of the mononuclear complex, the features of the reduced bpy moiety increase in intensity and dominate the spectrum, indicating that the third reduction of this complex is also a bpy-based reduction. Similar changes accompany the fourth reduction of the binuclear complex, and the conclusion that this reduction also occurs at a bpy ligand is obvious.

Conclusions

Ligand reduction, whether achieved via charge-transfer excitation or achieved via an outer-sphere process tends to give rise to single-ligand-localized species. The absorption spectra of the MLCT excited state and the singly reduced forms of $[(\text{bpy})_2\text{Ru}(\text{dpp})\text{Ru}(\text{bpy})_2]^{4+}$ and $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ can be readily understood in this context, with the transferred or added electron residing in a π^* orbital of the dpp ligand. On the basis of spectroelectrochemical measurements, the second reduction of the binuclear complex may also be unequivocally assigned as a dpp-based reduction, while the second reduction of the mononuclear complex is bpy based.

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Photochemistry of Semiconductor Surfaces: In Situ Photoreduction of SnS_2

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The in situ photoreduction of SnS_2 has been studied with X-ray photoelectron spectroscopy, residual gas analysis, photogravimetric analysis, and thermogravimetric analysis. Our results suggest that the photoreduction process is quite dependent on the amount of surface chloride ion that is left over during the commercial manufacture of SnS_2 from SnCl_4 . In the presence of Cl^- ions there is partial reduction of Sn^{4+} to Sn metal, which only occurs in the presence of light. Thermal treatment of impure SnS_2 does not lead to reduction to Sn. When highly pure SnS_2 is irradiated, there is no measurable reduction. The nature of the support for the SnS_2 pellet is also important since photoreduction was observed for chloride-contaminated SnS_2 mounted on Al but not when Mo was used as a holder. Surface hydroxyl groups on the Al are believed to be partially responsible for the observed photoreduction of SnS_2 . Finally, the photogravimetric analysis (PGA) method reported here is an excellent method for studies of light-sensitive materials. Our results suggest that impurity ions are responsible for the photoreduction of SnS_2 and that it may be possible to intentionally dope various semiconductors in order to initiate reduction.

Introduction

Photoprocesses in solids are important in many areas including absorption,¹ scattering,² electron-transfer,³ energy-transfer,⁴ and photocatalytic⁵ processes. Photolyses of zeolites,⁶ clays,⁷ alumina,⁸ coordination complexes,⁹ and organometallics¹⁰ have been done in order to understand and control absorption, scattering, the mode and type of electron and energy transfer, and rates of reactions. Partial or total decomposition of the solid being irradiated is of major importance in such studies. Stable solids are typically desired for such applications, although the search for systems with fast reversible absorptions or electron transfers has been intensified so that better optical storage devices may be produced. In most cases, a stable solid material would be desirable in order to achieve high efficiency or conversion.

On the other hand, the photoinstability of a solid surface is quite important in the photographic process,¹¹ in semiconductor photoresist processes,¹² and in the preparation of new materials.¹³ Photoreduction of solid surfaces or of adsorbed layers on surfaces may lead to the preparation of different isolated zerovalent clusters¹⁴ that may have properties different from those of bulk

metallic materials. Such materials might be useful in catalysis,¹⁵ semiconductor devices,¹⁶ ceramics,¹⁷ adhesion,¹⁸ and other fields.

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A series of intriguing papers concerning the photoreduction of semiconducting metal oxides was published by Fleisch and Mains¹⁹⁻²² in the early 1980s. Their surface science experiments showed that certain metal oxides could be photoreduced after prolonged irradiation under ultrahigh vacuum. It was proposed²³ by Fleisch and Mains that if the band gap of the irradiated semiconductor was greater in energy than the reverse of the heat of formation of the metal oxide, then the metal oxide could be reduced to the metallic state. This theory was quite interesting to us, and several experiments were designed in order to further test the theory. Other semiconducting materials, surface-deposited materials (rather than bulk powders¹⁹⁻²³), and materials used to prepare new catalysts and semiconductor devices are of interest.

Some of the questions that arise regarding this theory are as follows:

1. Is there a threshold energy for these photoreductions?
2. Are surface functional groups important in the photoreduction process?
3. Can this theory be applied to other semiconducting materials?
4. What is the extent of the photoreduction throughout the material?

We report here on the in situ photoreduction of SnS₂, although we have also reinvestigated several of the metal oxide systems reported by Fleisch and Mains.¹⁹⁻²³ Variable-wavelength irradiation experiments of SnS₂ and irradiation at ambient and low temperatures have been carried out. Several batches of SnS₂ of different levels of purity have been photolyzed in an ultrahigh-vacuum chamber, and the irradiated SnS₂ solids have been characterized with X-ray photoelectron spectroscopy and thermogravimetric analysis. Volatile gaseous species emitted during the photolysis procedure have been characterized in situ in an ultrahigh-vacuum chamber with a residual gas analyzer.

We have developed a photogravimetric analysis (PGA) procedure for measuring weight loss during irradiation. In addition to the weight loss, it is possible to measure the amount of increase in temperature during irradiation. This PGA method is a relatively simple method for studying the stability of solids during irradiation with ultraviolet or visible light.

The results of our studies suggest that semiconductors like CuO can be photoreduced if their band gaps are larger in energy than the reverse of the heat of formation of the metal complex. However, in the case of SnS₂ it is clear that surface impurities greatly enhance the extent of reduction.

Experimental Section

Surface Science Experiments. (1) **Sample Mounting Procedures.** Samples of SnS₂ were pelletized in a press to a pressure of about 19 000 psi. After being pelletized, samples were mounted on metal substrates such as Al, Mo, and Sn metal in order to cover the sample rod holder during analyses. Most experiments were done with Al or Mo holders to avoid any possible misidentification of Sn transitions from both the holder and the SnS₂ sample. In all cases the object was to totally cover the mount with the sample. Transitions for Mo and Al were not observed in these experiments, indicating that the sample rod was fully covered by the sample. For samples that were heated to remove water, these were loaded onto sample holders in a glovebox, which had <1 ppm water and <1 ppm air, transported in double-vial containers, and loaded into a

glovebag surrounding the surface analysis rod. All metal holders were machined to sizes of about 6 mm × 13 mm. All metals used for these holders were purchased from Alfa Ventron, Danvers, MA, as foils of 99.9% purity.

(2) **X-ray Photoelectron Spectroscopy Methods.** X-ray photoelectron spectroscopy (XPS) experiments were done with a Leybold Heraeus spectrometer with an EA-10 hemispherical energy analyzer and either Mg Kα or Al Kα X-rays, although Mg radiation was typically used. X-ray beam voltages of 13 kV and beam currents of 10 mA were used. A gold 4f_{7/2} binding energy of 83.8 eV and a copper 2p_{3/2} binding energy of 932.4 eV were used for calibration of the binding energy scale. In general, a survey (wide) scan was collected prior to narrow scans of specific elements. Survey scans were collected in the constant relative resolution mode with a retarding factor of 3. A constant absolute resolution mode was used for narrow (detailed) scans. All semiquantitative analyses and binding energy positions were determined from narrow scans. Specific transitions of importance in this work include the Sn M₅N₄₅N₄₅, Sn M₄N₄₅N₄₅, O 1s, Sn 3d_{5/2}, Sn 3d_{3/2}, C 1s, Cl 2p, and S 2p. Curve-fitting procedures used a damped nonlinear least-squares regression program based on Marquardt's algorithm. A base line sigmoid curve was used to correct for inelastically scattered photoelectron features. A stable minimum in the sum of the squares of the deviations between computed and experimental intensities was used as a criterion for best fits. Further details concerning curve-fitting procedures and analysis procedures can be found elsewhere.²⁴

(3) **Photolysis Experiments.** The in situ photolyses were done in a preparatory chamber of the surface spectrometer by irradiating the solid powder through a JENA glass window with a 1000-W Xe lamp manufactured by Oriol Corp. During photolyses, the pressure in this preparatory chamber did not exceed 1 × 10⁻⁶ mbar and usually was no lower than 1 × 10⁻⁷ mbar during photolysis. The light was focused into the spectrometer by a spherical section concave mirror. The distance of the mirror to the sample was about 36 in. Samples of SnS₂ were analyzed with XPS before and after irradiation. Typically 60-min photolyses were carried out.

(4) **Residual Gas Analyses.** An Inficon Model IQ200 residual gas analyzer (RGA) mounted on the preparatory chamber of the surface analysis instrument was used to analyze volatile gases evolved during the photolyses. Samples were introduced into the analytical chamber for XPS experiments before and after photolyses. The mass range of the RGA was calibrated with a mixture of inert gases including He, Ne, Xe, and Ar. Ion intensities of similar tin sulfide, selenide, and telluride complexes and tin halide complexes were used²⁵ to identify the residual gases. Relative intensities of different mass fragments were calculated from the known isotopic ratios of detected elements in order to check the assignments of each peak. Details of similar alternating RGA and XPS experiments done on thermally treated zeolite samples can be found elsewhere.³¹

(5) **Photogravimetric Analyses.** Photogravimetric analysis (PGA) experiments were done on a Du Pont 9900 thermogravimetric analyzer by irradiating the solid sample of SnS₂ with a 450-W Xe lamp made by Electronic Measurement, Inc. Samples were loaded into aluminum boats mounted on a quartz holder, and a thermocouple was used to measure the temperature of the sample during irradiation. No external temperature ramp was applied during these experiments. Sample size ranged from 10 to 200 mg. During these experiments the light was turned on and off in order to determine the direct effect of the irradiation. Experiments were carried out for as long as 180 min.

(6) **Thermogravimetric Analyses.** Thermogravimetric analyses (TGA) were done on the same instrument described above under photogravimetric analyses; however, an external temperature ramp was applied to the sample, and no irradiation was done. Further details can be found elsewhere.²⁶

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Table I. Binding Energies (eV) of Tin Sulfide Samples^a

sample	conditions	Sn M5	Sn M4	O	Sn3	Sn5	C	Cl	S
I, Al	initial	827.6	820.1	529.4	495.2	486.8	282.0	198.4	161.7
	+40 min, $h\nu$	828.5	821.8	530.8 <i>532.0</i>	495.4 492.3	487.0 483.8	281.8 284.6	195.3 <i>199.7</i> <i>196.8</i>	161.9
	+100 min, $h\nu$	828.6	822.1	530.8 <i>532.0</i>	495.5 492.4	487.1 483.9	281.8 284.6	195.4 <i>196.8</i> <i>199.3</i>	161.9
I, Al	initial	827.6	819.8	529.2	495.2	486.9	281.6 284.8	198.4	162.1
	+60 min, $h\nu$	828.0	820.6	529.8	495.5 493.0	487.1 484.8	281.6 284.6	196.6	162.1
I, Al	60 min, 250 °C	827.9	820.2	528.0	495.3	486.9	284.6	<i>b</i>	161.8
	+60 min, $h\nu$	828.1	820.7	531.3 530.8 528.2	495.5 491.8	487.1 483.4	281.1 284.7	<i>b</i> <i>b</i>	162.0 <i>163.0</i>
I, Sn	initial	828.3	820.2	531.6	495.2	486.8	284.6	198.4 <i>199.6</i>	161.5
	+60 min, $h\nu$	828.4	820.4	531.0	495.3	486.9	284.6	198.4 <i>199.7</i>	161.5
P, Mo	initial	827.0 <i>825.4</i>	818.8	531.5	494.5	486.1	284.6	198.7	161.4
	+60 min, $h\nu$	827.1 <i>825.4</i>	819.0	531.4	494.7	486.3	284.6	198.6	161.5
P, Al	initial	828.0 <i>830.4</i>	822.5 820.0	531.3	495.3	486.9	284.6 279.6	199.0	161.4
	+60 min, $h\nu$	827.0	818.7	531.0 526.1	494.7	486.3	284.6 279.3	<i>b</i>	161.4
P, Mo	initial	827.9	820.4	526.9 532.3	495.5	487.0	280.2 284.6	198.7 <i>200.0</i>	161.9 <i>162.8</i>
	+60 min, $h\nu$	827.6	820.3	526.0 530.9	495.3	486.9	280.1 284.6	198.6 <i>200.0</i> 194.0	161.7 <i>162.7</i>
P, Mo	HCl added	828.2	820.2	532.2	495.3	486.9	284.6	198.6	161.8
	+60 min, $h\nu$	828.2	820.2	530.8	495.3	486.9	284.6	198.6	161.8
I, Al	(500 °C)	828.8	820.6	532.2	495.5	487.1	284.6	198.6	161.9
	+60 min, $h\nu$	828.8	820.6	531.0	495.5	487.0	284.6	198.6	161.9

^a Italic values indicate weak peaks and shoulders. I = impure SnS₂; P = Purified SnS₂. Transitions in table: Sn M₅N₄₅N₄₅, Sn M₄N₄₅N₄₅, O 1s, Sn 3d_{3/2}, Sn 3d_{5/2}, C 1s, Cl 2p, S 2p. + means in addition to the above treatment. Al, Sn, Mo refer to the sample holders. ^b Not observed.

(7) **Purification of SnS₂.** Purification of SnS₂ was done by refluxing powders of impure SnS₂, obtained from Alfa Ventron Co., Danvers, MA, with distilled deionized water at about 100 °C. The major contaminant of this material was chloride ion. A Mohr titration was done to determine the relative amounts of chloride ion in the impure and the purified SnS₂ samples.

Results

A. X-ray Photoelectron Spectroscopy. The binding energies for the Sn M₅N₄₅N₄₅, Sn M₄N₄₅N₄₅, O 1s, Sn 3d_{3/2}, Sn 3d_{5/2}, C 1s, Cl 2p, and S 2p transitions for a variety of samples are given in Table I. There are two types of SnS₂ studied here which we refer to as impure and pure SnS₂. The impure SnS₂ was obtained from Alfa Ventron Co., was analyzed by a Mohr titration, and was found to contain 12 wt% chloride ion. The purified SnS₂ was found to be 0.5 wt% chloride by Mohr titration methods. The pure and impure SnS₂ pellets were mounted on Al, Mo, or Sn holders as shown in Table I. XPS data for the eight transitions listed above are given for the samples prior to irradiation and after irradiation. In certain cases, the samples were heated prior to irradiation in order to allow the evolution of water and other volatile surface species.

Note that for the impure SnS₂ sample on Al, two peaks in the Sn 3d_{3/2} and 3d_{5/2} regions are present after photolysis. The new Sn species has a considerably lower binding energy than that of the starting material. Thermal treatment of the sample to 250 °C also results in two Sn species on the surface after photolysis. On the other hand, purification of the SnS₂ or mounting the impure SnS₂ onto a holder of Sn or Mo (rather than Al) does not result in the observation of two types of tin species after photolysis.

The last two entries of Tables I and II are for photolyses done on HCl-treated Mo foil and Al foil heated to 500 °C for removal of hydroxyl groups. There are no significant changes in peak positions or relative intensities for Mo surfaces treated with HCl

Table II. Relative Elemental Ratios for Tin Sulfide Samples^a

sample	conditions	O	Sn	C	Cl	S
I, Al	initial	130	100	406	69	82
	+40 min, $h\nu$	105	100	202	46	96
	+100 min, $h\nu$	101	100	215	44	78
I, Al	initial	285	100	266	84	110
	+60 min, $h\nu$	215	100	239	48	116
I, Al	60 min, 250 °C	152	100	241	<i>b</i>	123
	+60 min, $h\nu$	91	100	74	<i>b</i>	108
I, Sn	initial	73	100	157	37	89
	+60 min, $h\nu$	76	100	143	46	90
P, Mo	initial	17	100	61	6	108
	+60 min, $h\nu$	23	100	67	4	95
P, Al	initial	140	100	79	2	61
	+60 min, $h\nu$	75	100	69	<i>b</i>	70
I, Mo	initial	219	100	355	48	148
	+60 min, $h\nu$	165	100	207	33	147
P, Mo	HCl added	93	100	142	40	153
	+60 min, $h\nu$	72	100	78	17	150
I, Al	500 °C	67	100	68	54	128
	+60 min, $h\nu$	62	100	42	37	122

^a I = impure SnS₂; P = purified SnS₂. ^b Not observed.

or for dehydroxylated Al substrates either before or after photolysis.

X-ray photoelectron spectra for the impure SnS₂ sample on an Al holder prior to irradiation and after 40 min of irradiation are given in Figure 1. A new peak at low binding energy having one-fourth of the total Sn signal is now observed. The different levels of chloride are shown in Figure 2a for the impure SnS₂ on Al before photolysis and in Figure 2b for the same material after photolysis.

The relative ratios of O, Sn, C, Cl, and S on the surfaces of these materials before and after photolysis are shown in Table

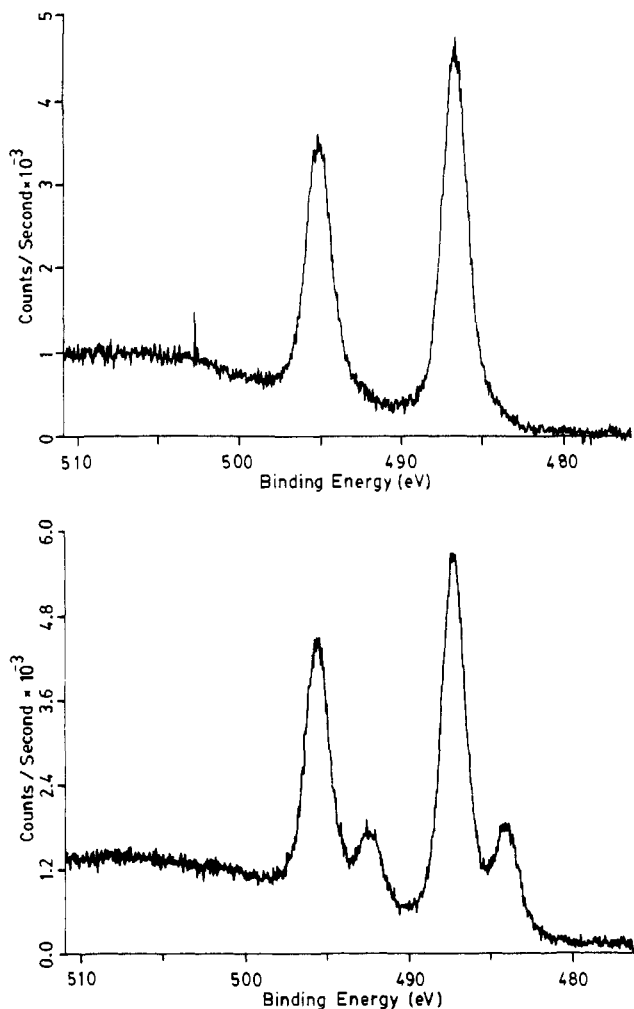


Figure 1. X-ray photoelectron Sn 3d_{3/2} spectra for impure SnS₂ on Al: (a, top) no irradiation; (b, bottom) irradiated with 1000-W Xe lamp for 40 min.

II. These data are all normalized to the Sn peak. After photolysis of the impure SnS₂ sample on Al, it is clear that the relative amounts of O, C, and Cl have decreased. The most substantial decrease is that of carbon. For the impure SnS₂ on Sn, there is only a slight loss in the C region after photolysis and very little change in the O and S regions. The chloride region has increased somewhat in intensity after photolysis. The purified SnS₂ on Mo shows a decrease in surface S and slight increases in O and C after photolysis whereas after photolysis the same material on Al shows a substantial decrease of O and Cl and a slight increase in S.

B. Photogravimetric Analyses. Data for photogravimetric analyses of impure SnS₂ are given in Figure 3. The initial weight of the sample is about 143.6 mg, which is shown by the curve at the upper left hand corner of Figure 3. The lower curve is the temperature of the sample during the photolysis and is a result of the irradiation. Notice that the temperature ranges from about 25 to 50 °C during the photolysis. These temperatures have been verified by direct irradiation of thermocouples and thermometers inserted into this apparatus. The photolysis process has been pulsed during this experiment and was started at the points marked by an asterisk (*) and stopped at the points marked by a prime ('). Note that as soon as the photolysis starts, the temperature starts to increase until the light is turned off. The small increase in mass at the end of each photolysis period is due to the characteristics of the Du Pont 9900 instrument. It uses an optical null balance detector for the mass measurement and is apparently slightly sensitive to extraneous light. Blank measurements with an empty Al boat indicated a reproducible change in mass of about ±20 μg in the presence and absence of a strong light flux. There has been a significant consecutive reduction in the weight of the sample after each pulse of irradiation.

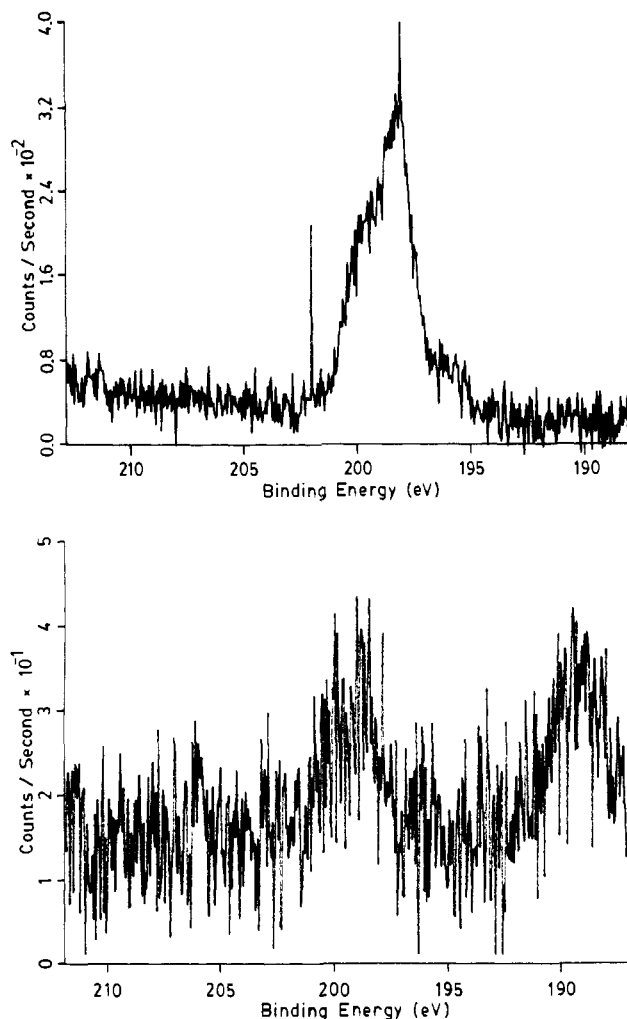


Figure 2. X-ray photoelectron spectra of the Cl 2p transitions for impure SnS₂ on Al: (a, top) no irradiation; (b, bottom) irradiated with 1000-W Xe lamp for 40 min.

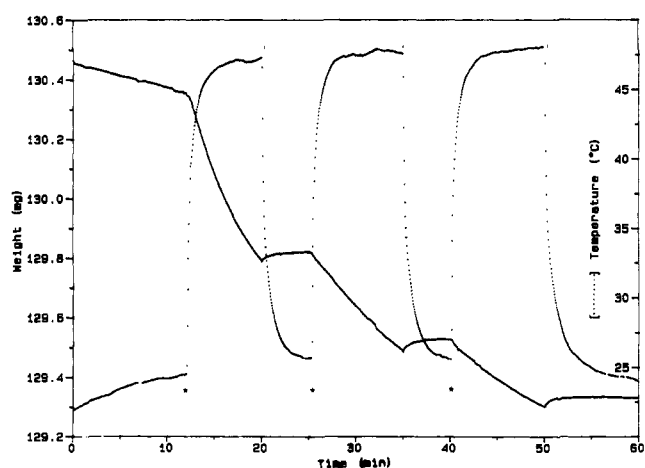


Figure 3. Photogravimetric analysis of impure SnS₂. The asterisk indicates the start of the photolysis, and the prime indicates the end.

Photogravimetric analysis data for the purified SnS₂ sample are given in Figure 4. The symbols used in Figure 4 are the same as those used in Figure 3. In this case it is clear that there is no significant permanent weight loss as that observed for the impure sample shown in Figure 3. The temperature rise is roughly the same for both the impure and pure SnS₂ samples. Results similar to those of Figure 4 were found for all impure SnS₂ samples on other supports.

C. Residual Gas Analyses. Table III includes peaks observed with a residual gas analyzer during the photolysis of impure SnS₂

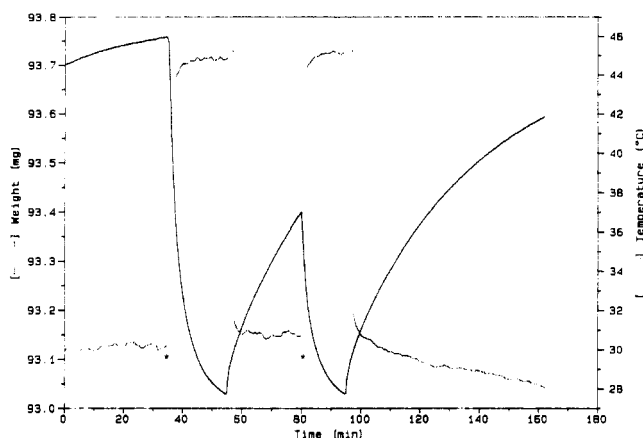


Figure 4. Photogravimetric analysis of purified SnS_2 . The asterisk indicates the start of the photolysis, and the prime indicates the end.

Table III. RGA Data

obsd m/e	assgnt	obsd m/e	assgnt
17.2	OH^+	38.9	H^{37}Cl
18	H_2O^+	72–82	Cl_2^+
32–35	S^+ , HS^+ , H_2S^+	111.7–119.4	Sn^+
35.9	^{35}Cl	142–155	SnS^+ , SnCl^+
36.9	H^{35}Cl	182–195	SnS_2^+ , SnCl_2^+
37.9	^{37}Cl		

on Al in the preparatory chamber of the surface instrument. Peaks at m/e 17.2, 18, 35.9, 36.9, 37.9, and 38.9 and between m/e 72 and 82, 111.7 and 119.4, 142 and 155, and 182 and 195 were observed. The most intense peaks were those near m/e 18 and 19. Similar RGA experiments were done on other samples. For the pure SnS_2 samples similar m/e peak positions were observed although the relative intensity of the m/e 18 and 19 peaks was much smaller than that of the peaks of the impure SnS_2 sample.

D. Thermogravimetric Analyses. Thermogravimetric analyses were done on samples at temperatures up to 50 °C to simulate the temperature increase observed in the photogravimetric analyses. The observed weight changes in these TGA experiments were much lower (1%) than those of the PGA experiments. TGA experiments were done up to temperatures of 250 °C to observe weight changes and possible effects of thermal treatment. While substantial weight loss was observed in these samples, RGA and XPS data indicated decomposition pathways different from those involving irradiation.

Discussion

A. In Situ Photoreduction of SnS_2 . The XPS data of Table I clearly show that the impure SnS_2 sample when photolyzed is reduced to the metallic state. However, only about one-fourth of the surface tin is reduced. These results are in accord with the suggestions of Fleisch and Mains^{19–23} concerning semiconductors with band gaps greater than the reverse of the heat of formation of the metal complex, since the reported²⁷ band gap of SnS_2 is 200 kJ/mol and the heat of formation of SnS_2 is –167.2 kJ/mol. Their reduction times^{19–23} were considerably longer than those used here, and this may be a reason for the relatively smaller amount of photoreduction observed in our experiments (25%) than in theirs (as high as 100% of the surface).

The threshold energy for photolysis does closely match the band gap of SnS_2 (2.22 eV) since photolyses at wavelengths less than 560 nm do lead to photoreduction whereas no photoreduction is observed for photolyses at wavelengths greater than 560 nm.

The XPS data of Table I also clearly show that once the SnS_2 is purified, there is no significant reduction via irradiative pathways. The substantial amount of chloride impurity is not altogether surprising, since quantitative analyses of the purity of such commercial samples are often commercially determined by methods like X-ray powder diffraction, which do not detect amorphous impurities and are not as quantitative as Mohr titrations, atomic absorption, and other methods. It is possible that chloride species provide defect donor sites in the band gap of the

impure SnS_2 that could aid the photoreduction process.

The narrow scans of the Sn 3d region of Figure 1 clearly show that some of the Sn^{4+} ions of the SnS_2 are being reduced as a result of photolysis. The different levels of chloride ion detected in the XPS experiments shown in Figure 2 show that there is a lower level of Cl^- on the surface of the purified SnS_2 than on the impure SnS_2 .

The full implications of the data of Table I have not yet been addressed. Comparative XPS data for the purified and impure SnS_2 samples mounted on different holders are obviously quite different. Only in the case of the Al holder for the impure sample of SnS_2 is photoreduction observed. This indicates that the surface of the Al is likely playing some role in the photoreduction process. It is possible that surface hydroxyl groups and water molecules are on the surface of the oxidized Al holder and that these hydroxyl groups are somehow involved in the photoreduction of Sn^{4+} to Sn. The Al holder might also act as a sacrificial anode. The true situation is difficult to know, since there are also chloride species on the surface of the SnS_2 which when removed yield a surface that cannot be photoreduced.

In order to distinguish the relative roles of surface hydroxyl, water, and chloride groups, experiments were carried out to reduce the amounts of water and hydroxyl groups. At temperatures above 250 °C, TGA data suggest that weight loss is minimal and that most changes in weight occur in these samples at temperatures lower than 250 °C. Samples of impure SnS_2 on Al heated to 250 °C followed by photolysis do show formation of Sn, but only one-ninth of the total Sn^{4+} on the surface is reduced rather than one-fourth reduced for unheated samples. Further reduction of the hydroxyl groups on the Al holder was achieved by heating the sample holder under vacuum to 500 °C, and corresponding XPS data showed no reduction of SnS_2 during photolysis. These data summarized in Table I suggest that the role of water and hydroxyl groups may be to reduce SnS_2 to Sn.

The semiquantitative data of Table II show that the level of chlorine markedly decreases during photolysis of the impure SnS_2 sample on Al where photoreduction is observed. This is possibly due to loss of Cl_2 or HCl from the surface of the material, which may be due to enhanced mobility of Cl^- via OH groups. Reduction potential data are in line with our suggestion that chloride ions are able to reduce Sn^{4+} (vide infra). The purified systems show considerably less chlorine on their surfaces. The intricate details of the loss or gain of O, C, or S in any of the systems shown in Table II are extremely complex and are not now interpretable. It would seem that a simple comparison of the band gap and the reverse of the heat of formation of the metal complex is not enough to predict whether photoreduction will or will not occur.

XPS data reported here suggest that less than 25% of the surface Sn^{4+} ions are reduced to metallic Sn during photolysis of impure SnS_2 . The extent of the photoreduction will clearly depend on the amount of surface Cl^- impurities, the depth of penetration of light into the pellet, the type of radiation (continuous vs pulsed, monochromatic vs broad band, etc.), photolysis time, and other factors.

B. Photogravimetric Analyses. The PGA data of Figure 3 clearly show that during photolysis there is a weight loss of the impure SnS_2 on Al along with an increase in the temperature of the surface. This weight loss is a permanent change and is an indication that the sample degrades in the presence of light. Thermal activation of the same samples at the temperatures measured during these PGA experiments do not lead to reduction of the SnS_2 , suggesting that light must be present and that excited-state species are responsible for the reduction of the SnS_2 under these conditions. PGA experiments on the pure SnS_2 of Figure 4 are clearly different from those of the impure material and suggest that impurities are involved in the photoreduction process.

We propose here that PGA methods can be used to study the photochemical stability of solids. In fact, the PGA methods are faster than in situ photolytic XPS or other spectroscopic experiments and can be used to screen the photochemical behavior of a variety of samples under vacuum or a variety of gaseous atmospheres.

C. Residual Gas Analyses and Mechanistic Photoreduction Pathways. The RGA data of Table III show that a variety of gas-phase species are present during photolysis of SnS₂. Assignments of the *m/e* peaks to specific gas-phase species have been made in Table III, and it appears that hydroxyl groups and water molecules are evolved during photolysis. Chlorine species are undoubtedly mobile and may be evolved either as chlorine atoms, as molecules, or in species bound to H⁺ or Sn⁺.

Earlier comments concerning surface data and these RGA data suggest that chlorine ions on the surface of the SnS₂ are involved in the photoreduction process. When samples are dried at elevated temperatures, the degree of photoreduction is minimized. These data taken together suggest that both water and chloride ions are involved in the photoreduction process.

D. Structural Effects. A reviewer has suggested that the surface potential may be observed by biasing the flat-band potential of SnS₂ and that this may influence the degree of photoreduction. In fact, the surface of SnS₂ has been sensitized with dyes and surface phase changes (intercalation) were observed during photolysis.²⁸ It is possible that intercalation of the SnS₂ occurs during our in situ photolyses; however, X-ray powder diffraction experiments of the photolyzed samples do not show any significant changes in the *d* spacings such as we have observed for MoS₂ intercalates.²⁹

E. Overview. The solids that Fleisch and Mains¹⁹⁻²³ observed to photoreduce are PdO, PtO, and CuO. There is considerable debate concerning the room-temperature stability of PdO and PtO. Such materials are no longer commercially available, so it is difficult to make an exact comparison to earlier work.¹⁹⁻²³ Studies in our laboratory of CuO indeed show that it is readily photoreduced to Cu. We have used these procedures to photoreduce CuO/polyimide surfaces that are important in semiconductor circuitry.³⁰

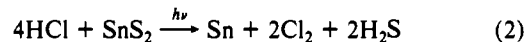
On the other hand, the theory of Fleisch and Mains¹⁹⁻²³ does not appear to hold for purified SnS₂ or other similar semiconductors like SnBr₂, SnCl₂, etc. It is clear that impurity ions and other species are needed to initiate photoreduction of these materials.

In the present study, an Al holder was used when photoreduction of SnS₂ was observed. This holder was oxidized and hydroxylated at the surface. RGA data suggest that HCl is evolved during the photoreduction and, therefore, that H⁺ from the holder is reacting with Cl⁻ from the SnS₂. The relative amount of HCl observed

for purified SnS₂ on Al holders is much less, and photoreduction is not observed. Careful dehydroxylation of the Al holders also leads to elimination of photoreduction of SnS₂.

SnS₂ can be decomposed by aqua regia. We believe that the photoreduction observed here is catalyzed by the migration of H⁺ off the Al (alumina on the surface) holder leading to formation of HCl, which also is mobile. The HCl then photoreduces the SnS₂. The corresponding oxidation of Cl⁻ to Cl₂ is also observed in the RGA experiments only during photolysis. RGA data also support mobility of OH groups.

These data suggest that the overall reaction scheme is as follows:



Both H₂S and Cl₂ are observed in the RGA data, and their relative amounts are roughly the same as that expected by the amount of SnS₂ photoreduced.

It could be possible that Cl⁻ donor ions lie at energy states within the band gap and that access to these sites aids in the photoreduction process. However, when impure SnS₂ is loaded onto Mo holders, there is no observed photoreduction. The surface of Mo is likely oxidized to MoO₃, which is known to be more basic than Al₂O₃. Acid-base interactions may indeed be important here, and it is also known that MoO₃ has fewer surface hydroxyl groups than alumina.³⁰

Conclusions

The data presented here concern the photoreduction of SnS₂. It appears that impurity chloride ions are important in the photoreduction of SnS₂. In this regard it may be possible to dope surfaces of various semiconductors with impurity levels of chloride (or other) ions in order to expedite photoreduction of semiconductors. In addition, we have developed a photogravimetric analysis method that may be used to study the photochemical stability of a variety of solid substances in the areas of catalysis, semiconductors, and photography.

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