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Preparation of Powder Precursors and Evaporation of Photoconductive Indium Sulfide Films

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Abstract

We have demonstrated significant photoconductance in indium sulfide thin films prepared by thermal vacuum evaporation of In_2S_3 powders synthesized in-house by chemical precipitation of InCl_3 or $\text{In}(\text{CH}_3\text{COO})_3$, and $(\text{NH}_4)_2\text{S}$ or Na_2S . The $\Delta G_\lambda/G_{\text{Dark}}$ values have been as high as 0.1 in the initial unoptimized films. Excess sulfur (via a mixture of polysulfide and sulfide ions in the synthesis bath) appears to be important in achieving reproducible and large photoconductivities. In_2S_3 is particularly attractive as a lower toxicity alternative to CdS in optoelectronic applications such as photovoltaic and photoconductive cells.

Introduction

In_2S_3 is an n-type semiconductor of yellow/orange color and bandgap near 2.0 eV (Bylander, 1971). Our group's recent emphasis (Siddiqui, et al., 1995; Johnson, et al., 1997) on development/identification of potentially lower hazard/toxicity photoconductors motivated us to investigate this previously little-studied semiconductor as a material that has (1) just recently received some attention as a low toxicity substitute for CdS in solar cells (Braunger et al., 1996), (2) would allow some transparency in the red/orange portion of the visible spectrum, and (3) still exhibit substantial photoconductivity in the yellow-to-violet part of the spectrum. Our initial work involved thermal vacuum evaporation of commercial In_2S_3 powders at 10^{-5} - 10^{-4} torr which yielded photoconductive films. However, later runs with supposedly identical material (99.999%) from a more recent lot/order from the same supplier as well as from material of comparable purities from several different suppliers led to radically variable results; some material yielded no photoconductance and some was as good as the initial runs. A serendipitous observation was made when one supplier who was out of "standard" In_2S_3 offered us some from an "experimental" lot that, based upon its analysis, did not meet the intended 99.999% purity (they estimated 99.99% purity), but was sulfur-rich. This material, when evaporated, produced films with the largest photoconductances (ΔG_λ) yet

($\Delta G_\lambda/G_{\text{Dark}} > 0.1$, where G_{Dark} is the ambient, unilluminated film conductance).

This led us to attempt in-house synthesis of our own material which would be made sulfur rich by dissolving elemental sulfur in $(\text{NH}_4)_2\text{S}$ or Na_2S solutions to yield up to 10% (relative to the S_1^{-2} concentration) polysulfide (primarily S_2^{-2}) in the primarily S^{2-} -bearing solution used to form In_2S_3 by mixing with a separate solution of In(III). The hypothesis was that some $\text{In}_2(\text{S}_x)_3$ ($x > 1$) (indium polysulfide) molecules would form in the In_2S_3 matrix which, when subsequently evaporated, would produce the sulfur richness in the film that appeared to enhance photoconductivity, as well as shifting the equilibrium away from possible formation of the other indium sulfide phases InS and In_2S and toward In_2S_3 . The hypothesis was verified in that such films were reproducibly photoconductive ($\Delta G_\lambda/G_{\text{Dark}}$ from 0.01-0.1) in contrast to those prepared from commercial material from different lots and/or different manufacturers.

Although evaporation onto low temperature substrates under these conditions might be expected to yield films with mixed phases (In_2S_3 , InS , In_2S , In , and S), higher substrate temperatures would be expected to activate (1) complete reaction between the plentiful sulfur and any In_2S , InS , or even In that might form upon dissociation of In_2S_3 upon evaporation to drive the film stoichiometry to "completion" (i.e., In_2S_3) and (2) completely revolatilize into the vapor phase any segregated elemental sulfur phases that might

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transiently form on the substrate due to either the excess sulfur or sulfur molecules formed by dissociation of the In_2S_3 upon evaporation (i.e., $\text{In}_2\text{S}_3 = \text{In}_2\text{S} + \text{S}_2$).

The decomposition of the In_2S_3 powder into other indium sulfide phases and sulfur upon resistive heating in the molybdenum boats was implied by (1) the darkening of the powder from bright orange to dark gray/brown, (2) occasional appearance of an initial white/yellow elemental sulfur "cloud" or film, and (3) occasional formation of indium-rich darker brown-orange (vs. the standard bright orange) films.

Materials and Methods

In_2S_3 powders were formed by mixing separate aqueous solutions of InCl_3 or $\text{In}(\text{CH}_3\text{COO})_3$, and $(\text{NH}_4)_2\text{S}$ or Na_2S . No large difference in the photoconductances of the subsequent films was found between the various reagents although those arising from the $\text{In}(\text{CH}_3\text{COO})_3$, and $(\text{NH}_4)_2\text{S}$ appear to be slightly more photoconductive (perhaps, due to an absence of trace Na^+ and/or Cl incorporation). HCl or CH_3COOH was slowly added to the $\text{In}(\text{III})$ bath until any cloudy color disappeared ($\text{pH} \leq 1.8$). The pH of the $\text{S}(-\text{II})$ baths was adjusted to between 7 and 8 (to avoid H_2S formation). Elemental sulfur (up to 10% by molarity relative to the $\text{S}(-\text{II})$) was then added to the $\text{S}(-\text{II})$ bath and mildly heated and stirred until it completely dissolved as polysulfides (S_x^{2-} and/or HS_x^{-1} , $x = 1-7$ with $x = 2$ probably dominant) due to association/reaction with the $\text{S}(-\text{II})$ (S^{2-} or HS^{-1}). Usually the molarity of the $\text{In}(\text{III})$ was of order 0.1 M with the combined $\text{S}^{2-}/\text{S}_x^{2-}$ molarity greater (up to three times), thereby minimizing any chance of In_2O_3 , $\text{In}(\text{OH})_3$, or other possible low solubility indium phases "contaminating" the resultant In_2S_3 (i.e., we wanted to make sure that there was "plenty" of $\text{S}^{2-}/\text{S}_x^{2-}$ to precipitate with the $\text{In}(\text{III})$). Usually, concentrations and volumes were calculated to yield 2-5g of In_2S_3 per run. Upon mixing, the combined solution was rapidly stirred and the pH quickly increased to 7-8 via NH_4OH addition (to avoid loss of $\text{S}(-\text{II})$ via H_2S). A yellow/orange $\text{In}_2\text{S}_3/\text{In}_2(\text{S}_x)_3$ precipitate rapidly formed upon mixing. After several minutes, the stirring was turned off and the precipitate isolated by filtering through a standard Hirsch filter/funnel with running water activated vacuum. Up to five followup washes/ rinses with distilled water while mixing the In_2S_3 "mud"/"paste" were made to flush out any residual soluble salts ($\text{Na}(\text{CH}_3\text{COO})$, NaCl , $\text{NH}_4(\text{CH}_3\text{COO})$, NH_4Cl , Na_2S , $(\text{NH}_4)_2\text{S}$, InCl_3 , or $\text{In}(\text{CH}_3\text{COO})_3$) from the indium sulfide. The powder was then dried under a heat lamp in air and then rebroken into a powder by manual stirring and/or mortar and pestle methods. Reagent purities ranged from 99.9% to 99.999% and were provided by Alfa/Johnson-Matthey, Aldrich, Fluka, and Cerac. Commercial distilled water was used for bath preparation.

The powder was subsequently placed in "V"-shaped molybdenum troughs/boats made in-house from Mo sheet metal and connected to the resistive heating power supply in our Kurt J. Lester Co. vacuum deposition unit with turbomolecular pump. Substrates were clamped roughly 15 cm. above the boat on a substrate stand/heater assembly controlled by an Omega temperature controller with platinum RTD temperature sensor. The unit was pumped down to between 10^{-5} and 10^{-4} torr, and the current of the boat slowly ramped manually until it began to glow orange and the In_2S_3 powder particles vibrated/"danced". At this point the In_2S_3 sublimed without melting and recondensed on the substrate surface as an orange film.

Substrates included both copper-clad printed circuit boards and Cu-on-Cr-on-glass pieces on which interdigitated, "comb-like" metal contacts had been defined by previous PC board processing methods and transparent/conductive Donnelly indium tin oxide-on-glass with alternating conductive ITO and insulating gaps, also delineated by PCB technology. Substrate temperatures during deposition ranged from room temperature to 280°C , and photoconductances were observed for films grown over the entire temperature range.

Deposition times typically ranged from 3-5 minutes or until all of the In_2S_3 powder was consumed (or vibrated out of the boat). Thickness/color was monitored visually via a glass microscope slide placed to the side of the primary substrates but still in the evaporation effluent "cone." Upon the films reaching adequate thickness, the boat and heater currents were set to zero and the substrates were allowed to cool for up to an hour while still in vacuum (to avoid reaction with O_2) prior to venting the bell jar to atmosphere. Then the bell jar and substrates were removed and the films inspected, labeled, and stored prior to subsequent characterization. The films were usually a bright orange color but were yellow when very thin, nearly red (and very flaky/non-adherent) when very thick ($\sim 1 \mu\text{m}$), and a darker orange-brown when substantially indium-rich.

Photoconductivity Measurements

The films were characterized by mounting in our custom photoconductivity apparatus (Fig. 1) containing an operational amplifier circuit producing an output voltage directly proportional to the conductance, G , of the sample: $v_o = -G R_F v_{in}$. A solid state laser diode ($\approx 2\text{mW}$) at the He-Ne laser wavelength (633 nm) was modulated by a computer controlled driver circuit to yield light pulses of variable duty cycle and intensity for measurement of the photoconductance. Typically, we ran at 95% of full power with a "train" of 50 μs -on and 100 μs -off light pulses separated by several ms between trains. This produced both high frequency and low frequency components in the pho-

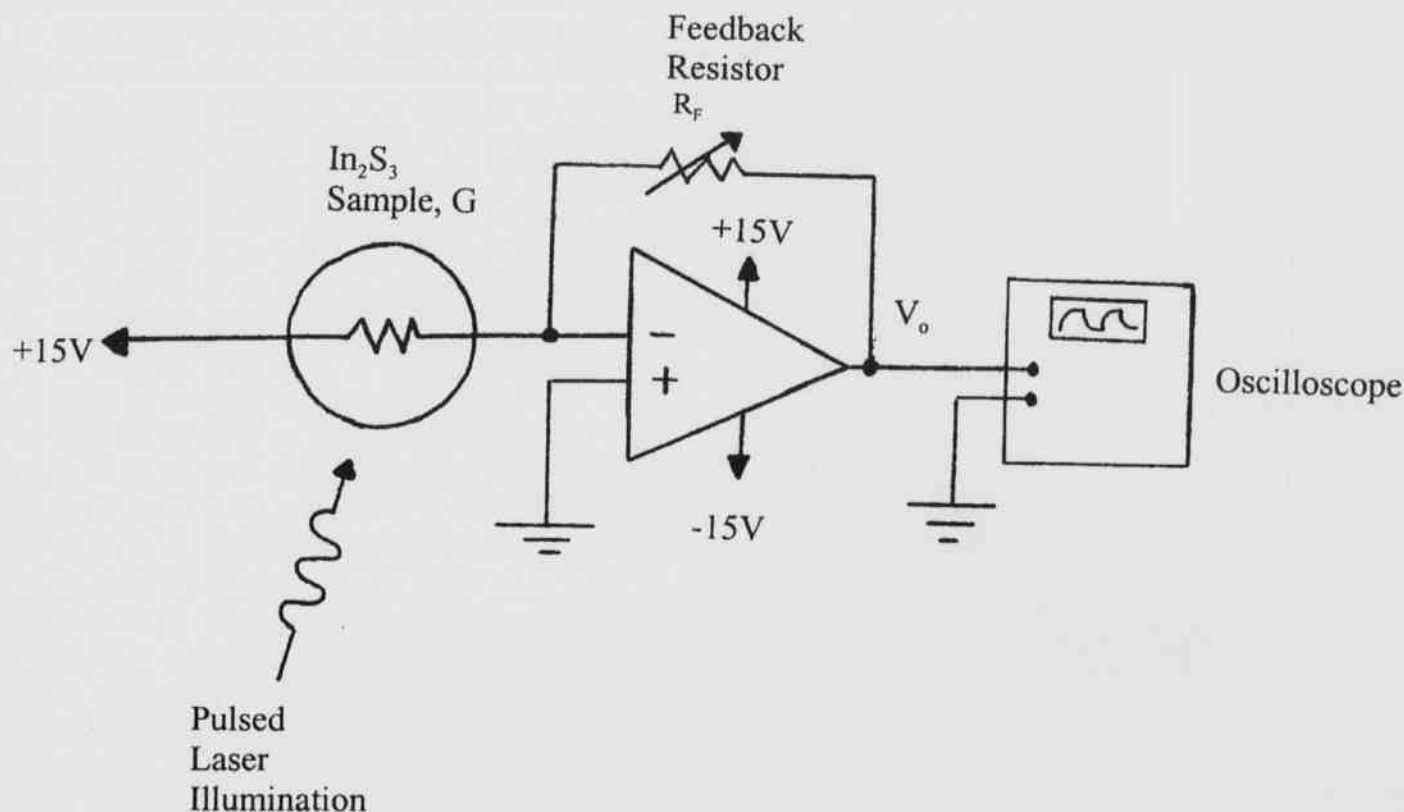


Fig. 1. Schematic diagram of photoconductive measurement apparatus: $v_o = -15 G R_F$ (V) and $\Delta v_o = -15 \Delta G R_F$ (V).

to voltage signal (Fig. 2). Typical DC bias voltages (v_{in}) between the two conductive contacts were 15 V with feedback resistances (R_F) from 10 k Ω to 10 M Ω . These allowed convenient measurement of photoconductive, ΔG_λ , and dark conductance, G_{Dark} , values in the 10^{-6} to 10^{10} range (depending upon sample thickness and area) by direct analysis of the photovoltage or dark voltage on an oscilloscope after an additional 1000 x amplification just before the oscilloscope. Typical $\Delta G_\lambda / G_{Dark}$ values ranged from 10^{-2} to 10^1 regardless of whether $InCl_3$ or $In(CH_3COO)_3$, or $(NH_4)_2S$ or Na_2S were used in the synthesis. Increasing excess sulfur (as polysulfide) in the synthesis bath improved photoconductive as long as small (< 10% of the S(-II) concentration). A greater excess led to initial evaporation of an elemental sulfur layer as the boat was slowly ramped up in temperature prior to In_2S_3 evaporation; a white-yellow sulfur "cloud" inside the bell jar resulted in a sulfur film on everything and increased cracking/ flaking of the film. The time constant of the quasi-exponential rise and decay of the photoconductive (measured on the low frequency component of the photovoltage waveform) was typically in the hundreds of microseconds range, indicating In_2S_3 as a potentially high bandwidth photoconductor.

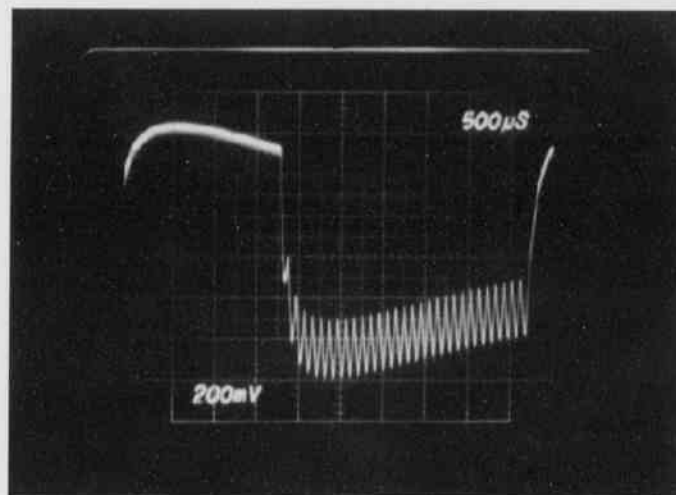


Fig. 2. Oscilloscope photograph of a typical photovoltage signal from an In_2S_3 film evaporated on/between interdigitated copper contacts on fiberglass printed circuit board.

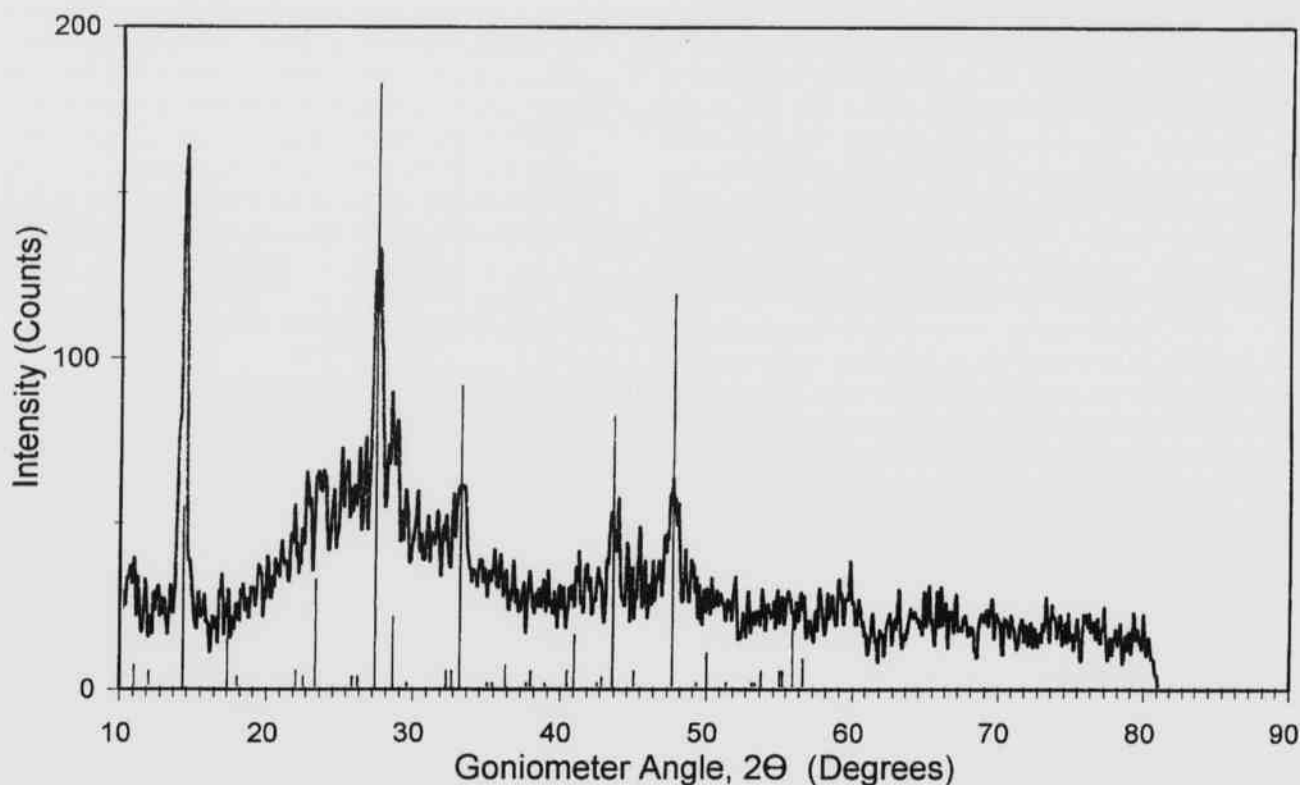


Fig. 3a. X-ray diffraction spectrum for an In_2S_3 film (bright orange) evaporated onto a glass microscope slide at 280°C . Note the excellent agreement between the dominant peaks and the vertical lines representing the In_2S_3 powder diffraction card standard (#25-390).

Other Characterization

Figures 3a and 3b exhibit typical x-ray diffraction spectra of bright orange In_2S_3 films grown at 280°C and 21°C , respectively, on glass microscope slides as measured on a Rigaku DMAX II X-ray diffractometer ($\text{Cu-K}\alpha$). The dominant peaks on Figure 3a match with the vertical lines for In_2S_3 Powder Diffraction File Card 25-390 whereas Figure 3b exhibits little or no peak structure consistent with a nearly amorphous material grown at room temperature. Figures 4a and 4b exhibit plots of optical absorbance vs. wavelength for the same films as with Figures 3a and 3b, as measured on a Perkin-Elmer Lambda 19 spectrophotometer. The rapid increases in absorbance near 600 nm are consistent with In_2S_3 's reported bandgap of 2.0 eV, albeit with some sub-bandgap absorbance "tailing" and "interference ripple."

Figure 5 exhibits energy dispersive x-ray analysis (EDAX) data for a film grown with a glass substrate temperature of 200°C and having a darker brown-orange color. This film was minimally photoconductive. Of particular interest is the fact that the gross film stoichiometry (46.91% In/53.09% S) is closer to InS (50% In/50% S) than In_2S_3

(40% In/60% S). Figure 6 exhibits an x-ray diffraction spectrum for this film. Surprisingly, in spite of indium richness, there is still and only a match with the In_2S_3 lines (just as with Figure 3a) rather than with those for InS, perhaps implying a mixture of In_2S_3 crystallites with an amorphous indium-rich In_xS ($x > 2/3$) matrix. Figure 7 exhibits an optical absorbance versus wavelength spectrum for this film. Note that the foot of the absorption edge has been shifted from near 600 nm to over 700 nm, consistent with either extensive band tailing and/or a reduction in bandgap due to the excess indium.

The data is consistent with the fact that In_xS and S_x (x predominately 2) vapors form upon evaporation of In_2S_3 . Evidently, there is a tendency for mixed stoichiometries between the equilibrium In_2S_3 and InS phases unless the excess elemental sulfur content of the starting powder is significant; that is, as both In_2S_3 and S_x condense on the substrate, they react to form subsequent InS, In_2S_3 and, perhaps, metastable intermediate phases. Only if "extra" S is present in the vapor stream will the stoichiometries be shifted completely to the highly photoconductive In_2S_3 (the bright orange phase vs. the darker brown-orange In-rich material).

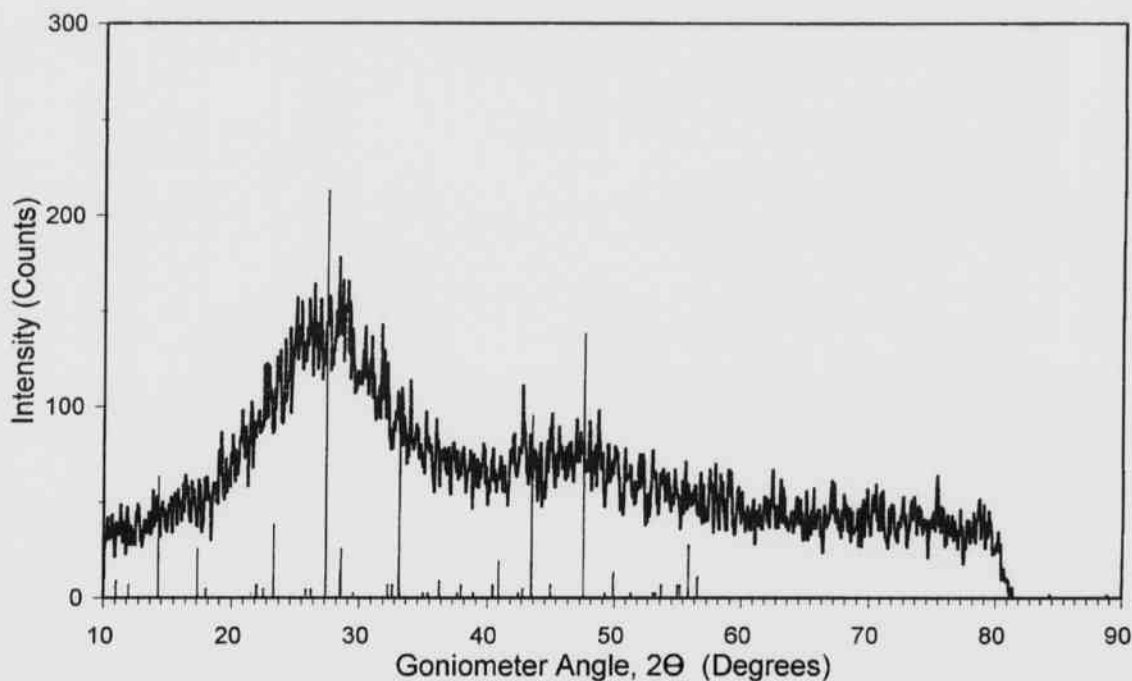


Fig. 3b. X-ray diffraction spectrum for an In_2S_3 film (bright orange) evaporated onto a glass microscope slide at room temperature. The large, broad peak centered near 26° is due to the glass substrate. The absence of the In_2S_3 peaks (denoted by the vertical lines) indicates nearly amorphous, probably sulfur-rich material.

Conclusions and Future Work

We have conducted "pioneering" research on synthesis of In_2S_3 powders and subsequent thermal vacuum evaporation of such as indium sulfide films on substrates with copper or indium tin oxide contacts to form photoconductive cells. Reproducible photoconductances were obtained over a broad range (21-280°C) of evaporation temperatures with a "figures-of-merit" $\Delta G_\lambda / G_{\text{Dark}}$ ratios in the 10^2 to 10^1 range and time constants in the hundreds of μs range when illuminated with pulsed 2 mW laser radiation at 633 nm. Excess sulfur significantly enhances the reproducibility and value of the photoconductance probably due the minimization of insoluble oxide, hydroxide, carbonate, chloride, or mixed phases of In and Na or other sulfur-deficient phases of indium sulfide (InS , In_2S) in the powder and/or film (as probably occur in some commercial material close to "perfect" 2:3 In:S stoichiometry) and, possibly, also due to minimization of sulfur vacancies in the n- In_2S_3 ; that is, excess chalcogen generally acts as an acceptor to make an n-type material less n-type, more intrinsic, and, hence, more photoconductive. X-ray diffraction and optical absorbance vs. wavelength measurements are consistent with semiconduct-

ing In_2S_3 with a bandgap near 2.0 eV. Without sufficient excess sulfur in the starting powder, the films tend to be slightly indium-rich, minimally photoconductive, and of a darker brown-orange color.

Future work will involve doping/sensitizing the In_2S_3 with copper, silver, and tellurium, detailed annealing and light soak studies, and optimization of the sulfur excess toward maximum photosensitivity. In_2S_3 appears to offer much potential as a photosensitive optoelectronic material "tuned" to the middle of the visible spectrum.

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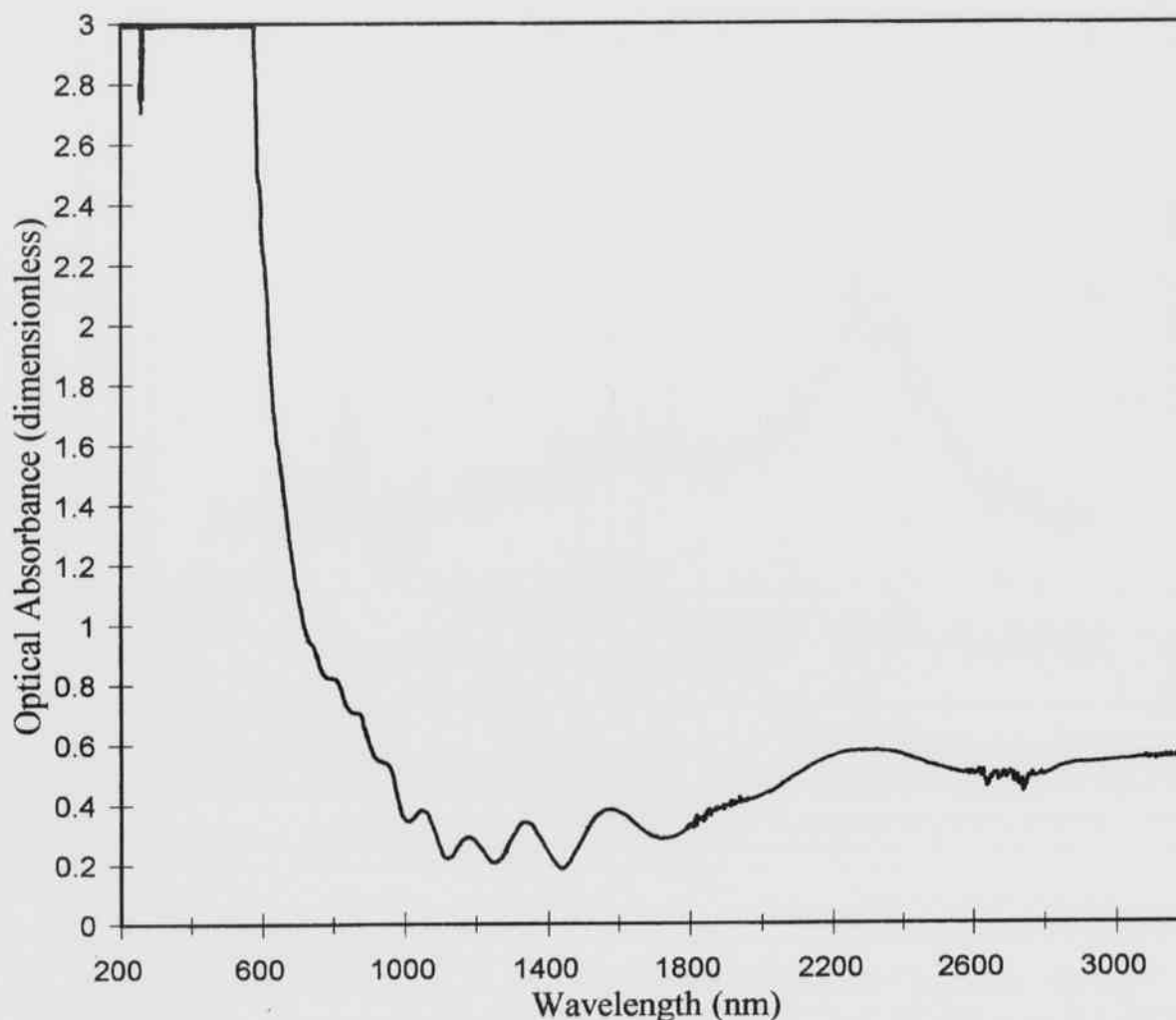


Fig. 4a. Optical absorbance versus wavelength spectrum for the same film as in Figure 3a. There is some "tailing" and "interference ripple" at wavelengths greater than 600 nm, near which the rapid rise in band-to-band absorbance begins.

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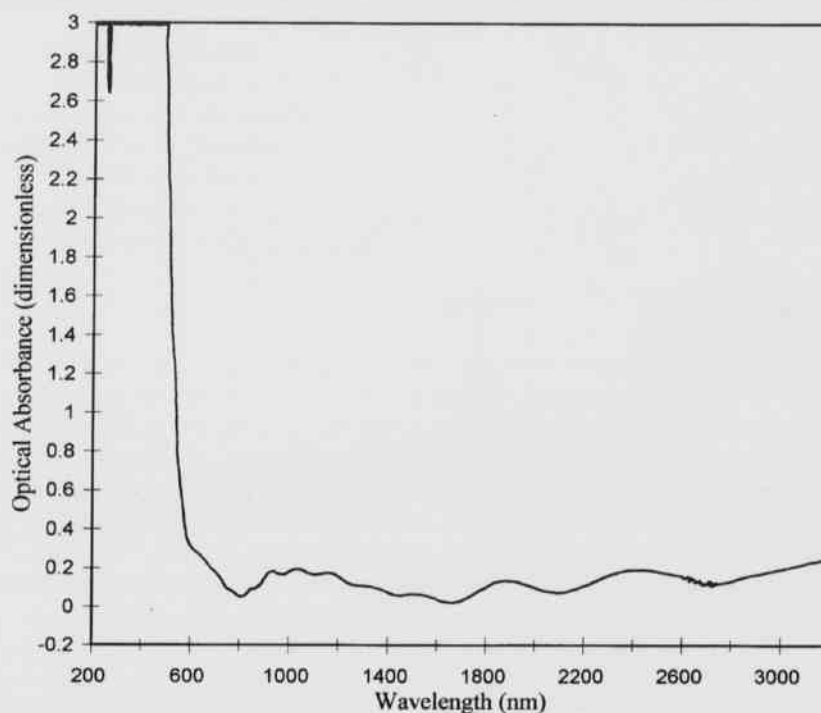


Fig. 4b. Optical absorbance versus wavelength spectrum for the same film as in Figure 3b. Again, note the rapid increase in absorbance near 600 nm consistent with the reported 2.0 eV.

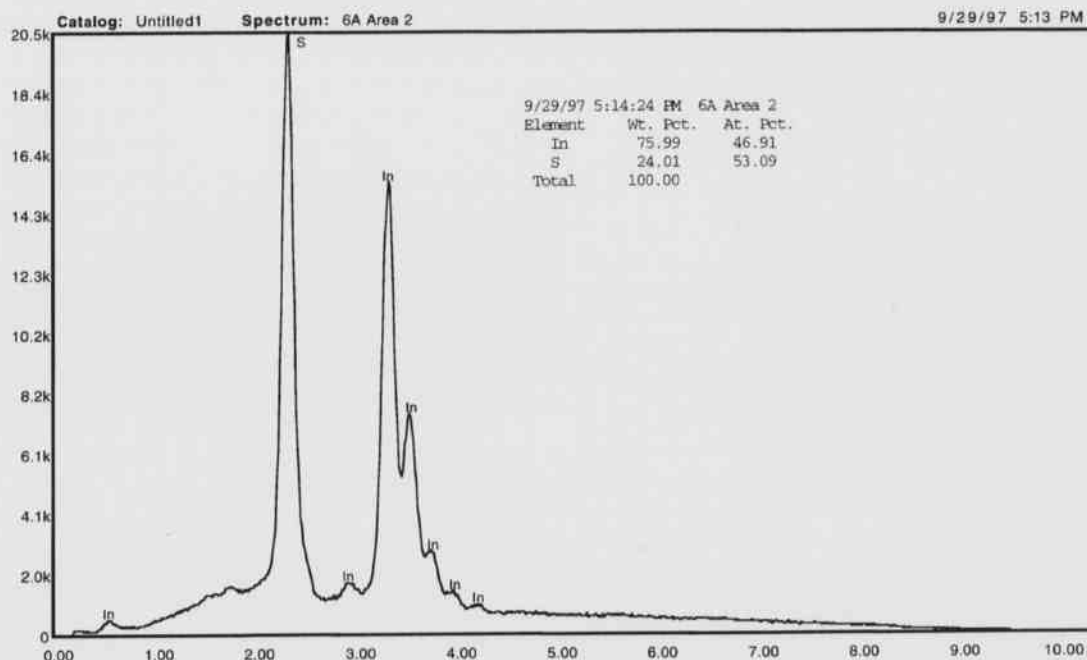


Fig. 5. Energy dispersive x-ray analysis (EDAX) data for a dark brown-orange (versus bright orange) indium sulfide film evaporated onto glass at 200°C. Note that the atomic percentages ($\approx 47\%$ In/ 53% S) indicate a film more indium rich than "pure" In_2S_3 .

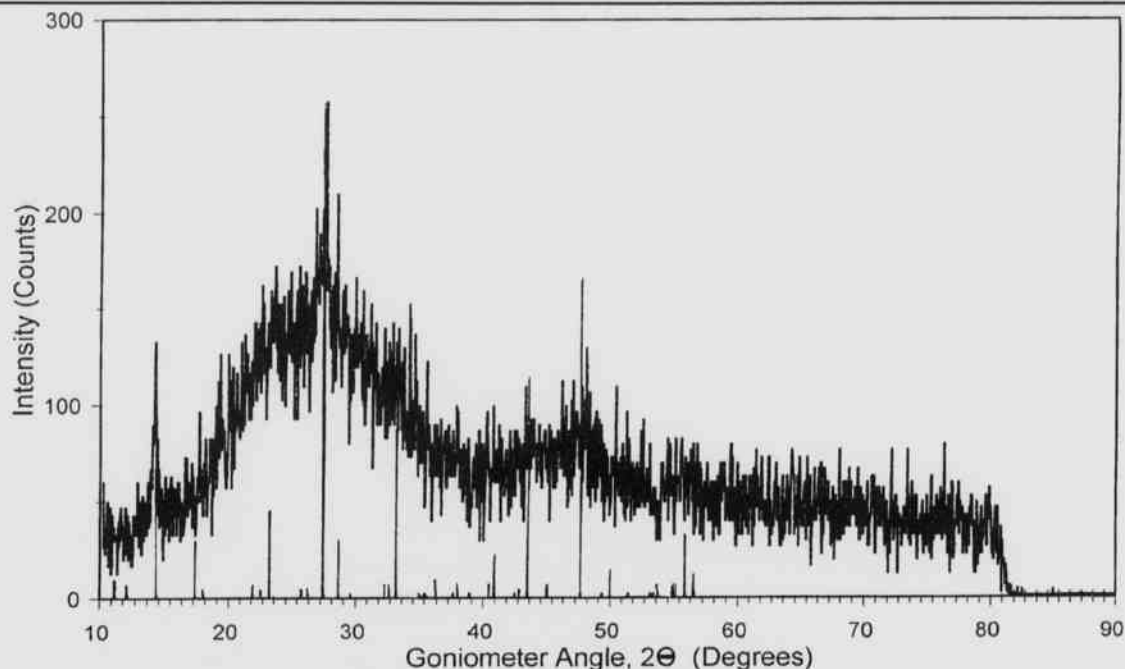


Fig. 6. X-ray diffraction spectrum for the film in Figure 5. Note that the only crystalline phase appearing is still In_2S_3 , thus, implying an amorphous, indium-rich background matrix.

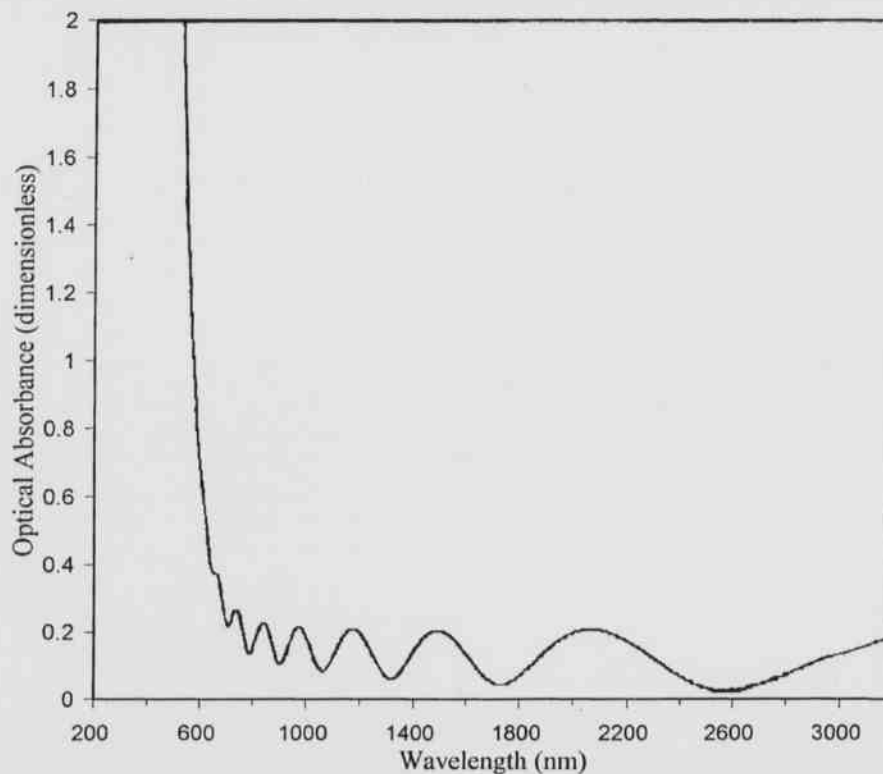


Fig. 7. Optical absorbance versus wavelength spectrum for the film in Figures 5 and 6. Note that the foot of the absorbance edge has been shifted from near 600 nm to over 700 nm, consistent with the darker color, and extensive bandtailing and/or a reduction in bandgap due to the excess indium.