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Abstract

Long term stability of photosensitivity versus time in indium (III) sulfide thin films thermally vacuum evaporated onto photocell-patterned printed circuit boards varies sensitively with several factors including contact metal type, contact metal diffusion and electromigration into the semiconductor, doping, and encapsulation method. Because of the significant photoconductivity and relative low toxicity and environmental impact of this compound semiconductor, it is important to better characterize these dependences toward commercial applications. We will report on measurements of photoconductivity vs. time as functions of such factors and evolving methods to stabilize this photoconductivity.

Introduction

Indium (III) sulfide, In_2S_3, is a photosensitive semiconductor with potential for various commercial applications because of its low toxicity and environmental impact, reasonable cost ($3.42/g – Cerac, Inc.), and ease of deposition as a thin film (Barber et al., 1997). It is an n-type semiconductor with 2.0 eV indirect bandgap and exhibits significant photoconductivity (Yu et al., 1999). There has been considerable recent interest in In_2S_3 and $In_2S_xO_{3-x}$ as possible safer alternatives to CdS for use as window materials in photovoltaic cells (Bayón et al., 1998). The Arkansas State University Optoelectronic Materials Research Laboratory is working on developing large area printed circuit boards (PCB's) containing a two-dimensional array of indium sulfide-based photocells for use in applications involving laser activation of computer or control commands.

The board consists of conductive photocell-patterned contacts, In_2S_3 as the photosensitive semiconductor film, and electronic interfacing components. The semiconductor film is deposited onto the photocell-patterned contacts by thermal vacuum evaporation. The semiconductor increases in electrical conductance in response to illumination with photon energies greater than the 2.0 eV bandgap of In_2S_3. Thus, when low power laser light strikes a photocell, it produces a proportional photovoltage, which can be amplified and used as an input signal for the computer or control interface.

Thermally vacuum evaporated thin films of this semiconductor on photocell-patterned contacts exhibit a photovoltage versus time stability that depends on several variables. These include contact material, doping, and encapsulation of the films.

The stability of the photovoltage was investigated using different contact materials such as bare copper, solder-coated copper, gold-on-nickel-coated copper, ITO-on-glass, and graphite. Underlying semiconductor films of bismuth (III) sulfide and tin (II) sulfide and polyurethane, indium (III) oxide, and molybdenum (VI) oxide encapsulant films were also investigated in an effort to enhance the photosensitivity and/or the stability of the In_2S_3 films on photocell patterns.

Materials and Methods

Copper, the standard material used in PCBs, was the first material to be tested. Solder (63% Sn / 37% Pb) and gold-on-nickel are common barrier coatings for underlying copper contacts and were also investigated. Indium tin oxide (ITO – 0.9 In_2O_3 / 0.1 SnO_2, 15 ohms/square) - coated glass was obtained commercially from Applied Films and patterned by photolithography and etching methods. Graphite ink (Aquadag®) was applied to glass sustrates in-house to produce graphite contact patterns. Indium (III) sulfide (In_2S_3 - 99.99%) was purchased from Cerac. Bismuth (III) sulfide (Bi_2S_3 - 99.999% - Cerac) and tin (II) sulfide (SnS - 99.9% - Alfa Aesar) were used in some instances as photoconductive barrier films between the PCB and upper In_2S_3 layer. Polyurethane, molybdenum (VI) oxide (MoO_3 - 99.95% - Alfa Aesar), and indium (III) oxide (In_2O_3 - 99.9% - Alfa Aesar) were investigated as encapsulants. The photocell patterns used on substrates with metal and ITO contacts were the basic interdigitated photocell layout shown in Fig. 1A, while two closely spaced parallel contact stripes were used with graphite (Fig. 1B).

Stability and Optimization of Photoconductivity in Thermally Vacuum Evaporated Indium (III) Sulfide Thin Films

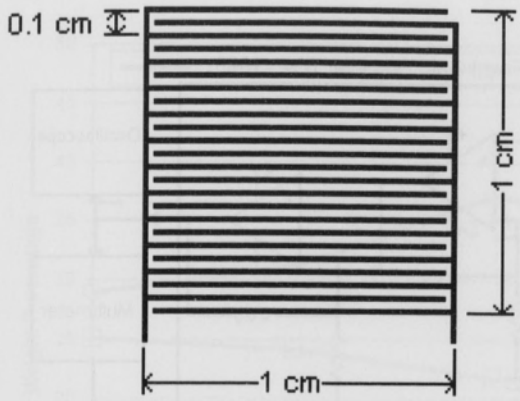

Fig. 1A. Photocell contact pattern used with bare copper, solder-coated copper, gold-on-nickel-coated copper, and ITO.

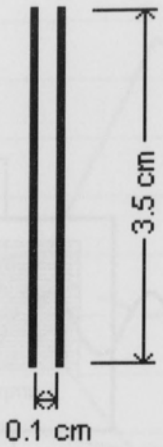

Fig. 1B. Photocell contact pattern used with graphite.

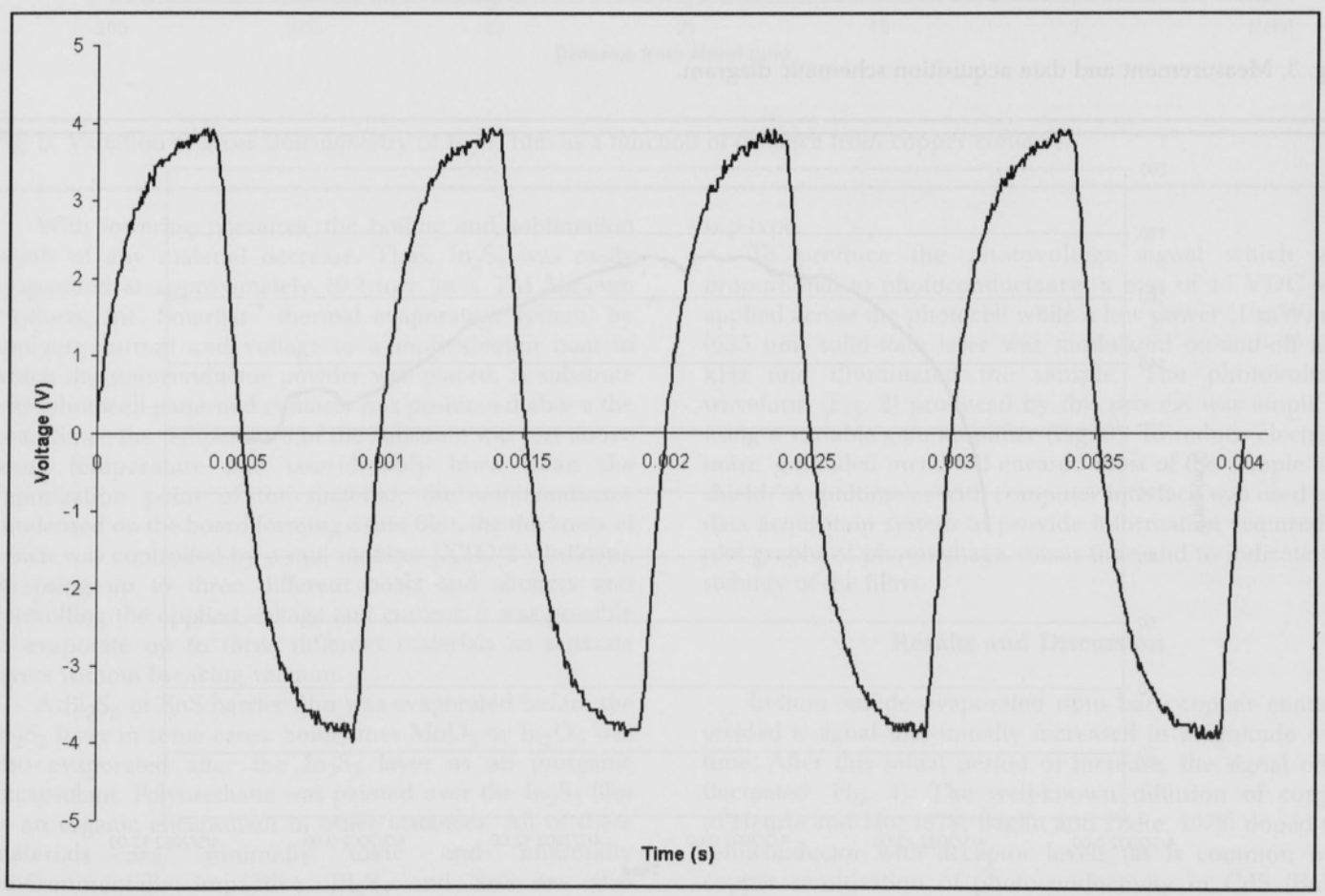

Fig. 2. Typical photovoltage vs. time waveform.

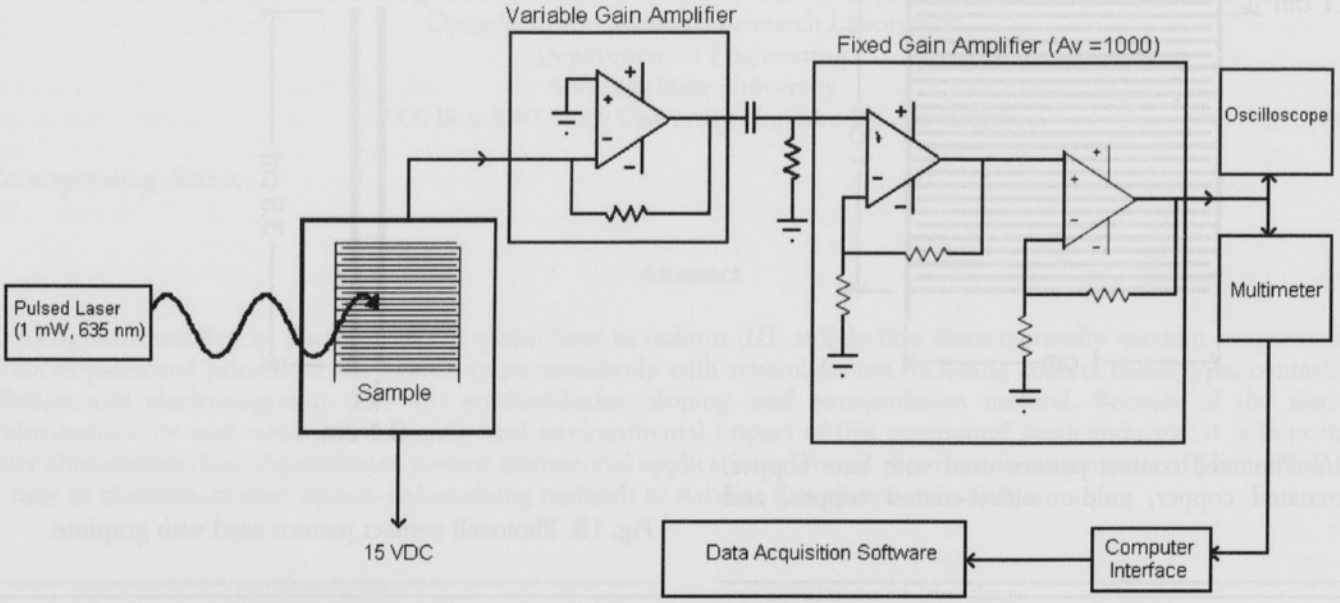

Fig. 3. Measurement and data acquisition schematic diagram.

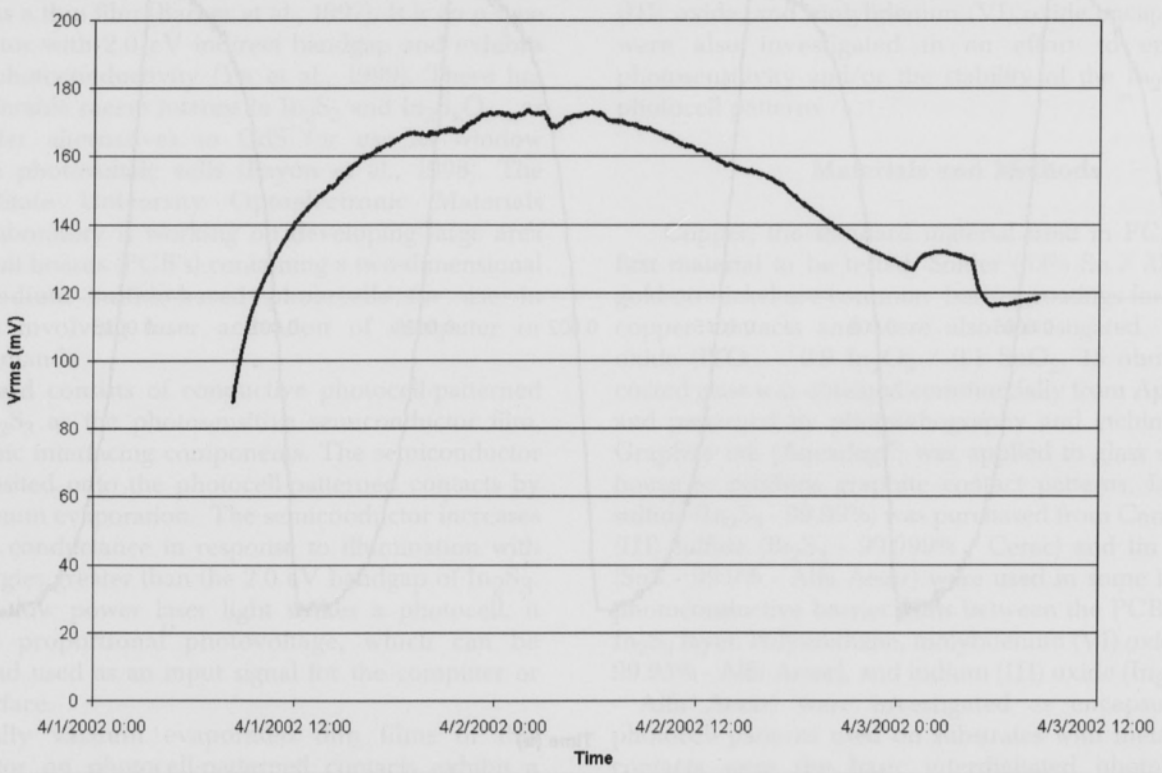

Fig. 4. Stability of photovoltage for In_2S_3 on bare copper contacts over time.

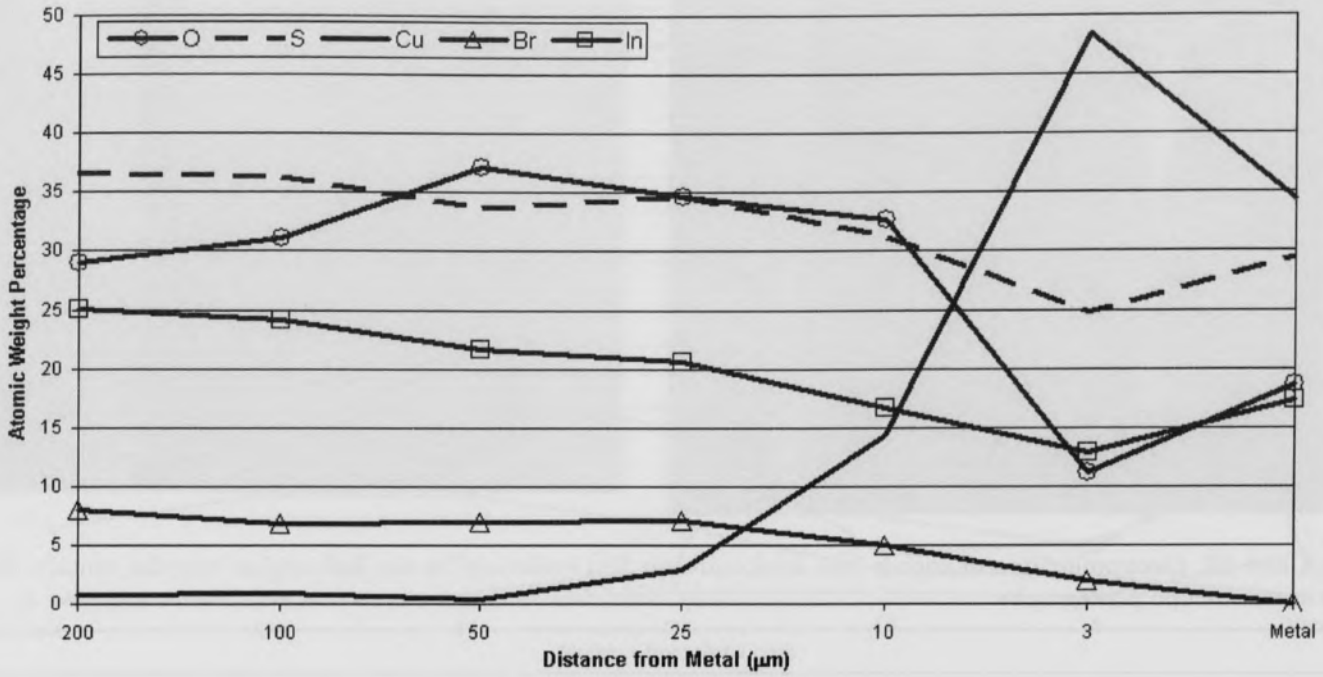

Fig. 5. Variation of gross stoichiometry of In_2S_3 film as a function of distance from copper contacts.

With lowering pressures, the boiling and sublimation points of any material decrease. Thus, In_2S_3 was easily evaporated at approximately 10^{-5} torr (in a TM Vacuum Products, Inc. Smartjar™ thermal evaporation system) by applying current and voltage to a molybdenum boat in which the semiconductor powder was placed. A substrate with photocell-patterned contacts was positioned above the boat. Since the temperature of the substrate was just above room temperature and considerably lower than the vaporization point of the material, the semiconductor condensed on the board forming a thin film, the thickness of which was controlled by a rate monitor (XTC/2 - Inficon). By using up to three different boats and shutters and controlling the applied voltage and current, it was possible to evaporate up to three different materials as separate layers without breaking vacuum.

A Bi_2S_3 or SnS barrier film was evaporated before the In_2S_3 layer in some cases. Sometimes MoO_3 or In_2O_3 was also evaporated after the In_2S_3 layer as an inorganic encapsulant. Polyurethane was painted over the In_2S_3 film as an organic encapsulant in other instances. All of these materials are minimally toxic and minimally environmentally impactive. Bi_2S_3 and SnS are also photoconductors (Johnson et al., 1999; Mishra et al., 1989) with nearly equal 1.3 eV bandgap; Bi_2S_3 is n-type and SnS is p-type.

To produce the photovoltage signal which was proportional to photoconductance, a bias of 15 VDC was applied across the photocell while a low power (1 mW) red (635 nm) solid-state laser was modulated on-and-off at 1 kHz and illuminated the sample. The photovoltage waveform (Fig. 2) produced by this process was amplified using a variable gain amplifier (Fig. 3). To reduce electrical noise, grounded metal foil encased most of the sample as a shield. A multimeter with computer interface was used as a data acquisition system to provide information required to plot graphs of photovoltage versus time and to indicate the stability of the films.

Results and Discussion

Indium sulfide evaporated onto bare copper contacts yielded a signal that initially increased in magnitude over time. After this initial period of increase, the signal often fluctuated (Fig. 4). The well-known diffusion of copper (d'Heurle and Ho, 1978; Baglin and Poate, 1978) doped the semiconductor with acceptor levels (as is common with copper sensitization of photoconductivity in CdS (Bube, 1960)) and increased the signal, as was seen initially. Eventually the diffusion could cause a conductive copper or

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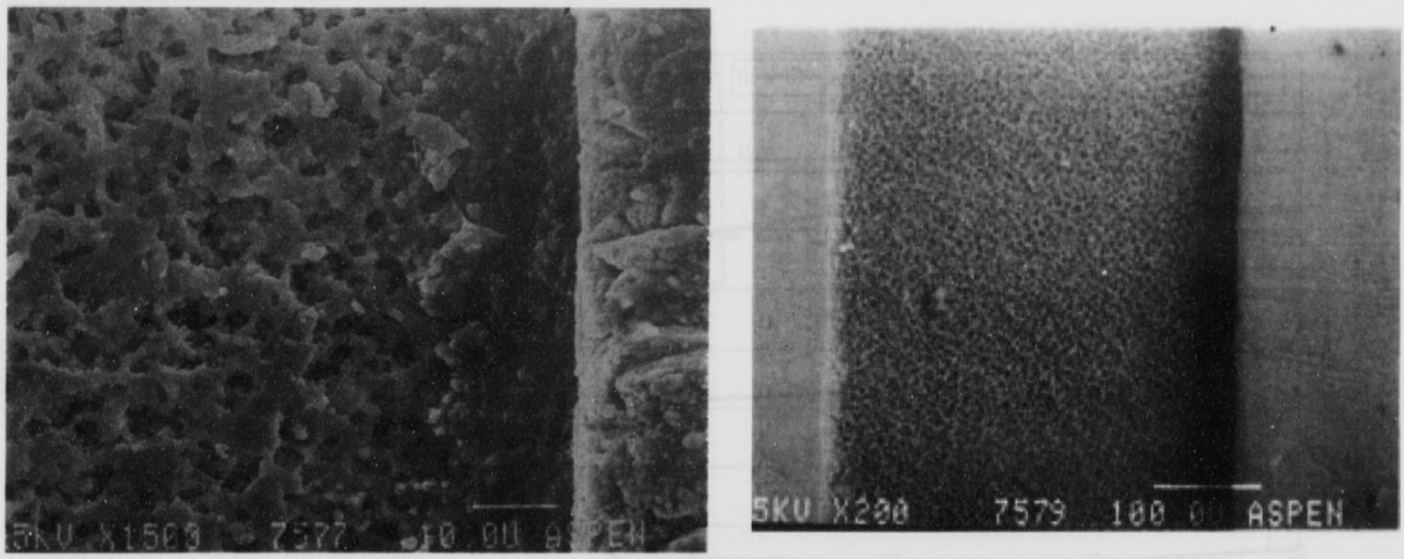

Fig. 6A and 6B. Electromigration of copper into semiconductor film evidenced by the dark region near the contacts in the electron microscope photographs.

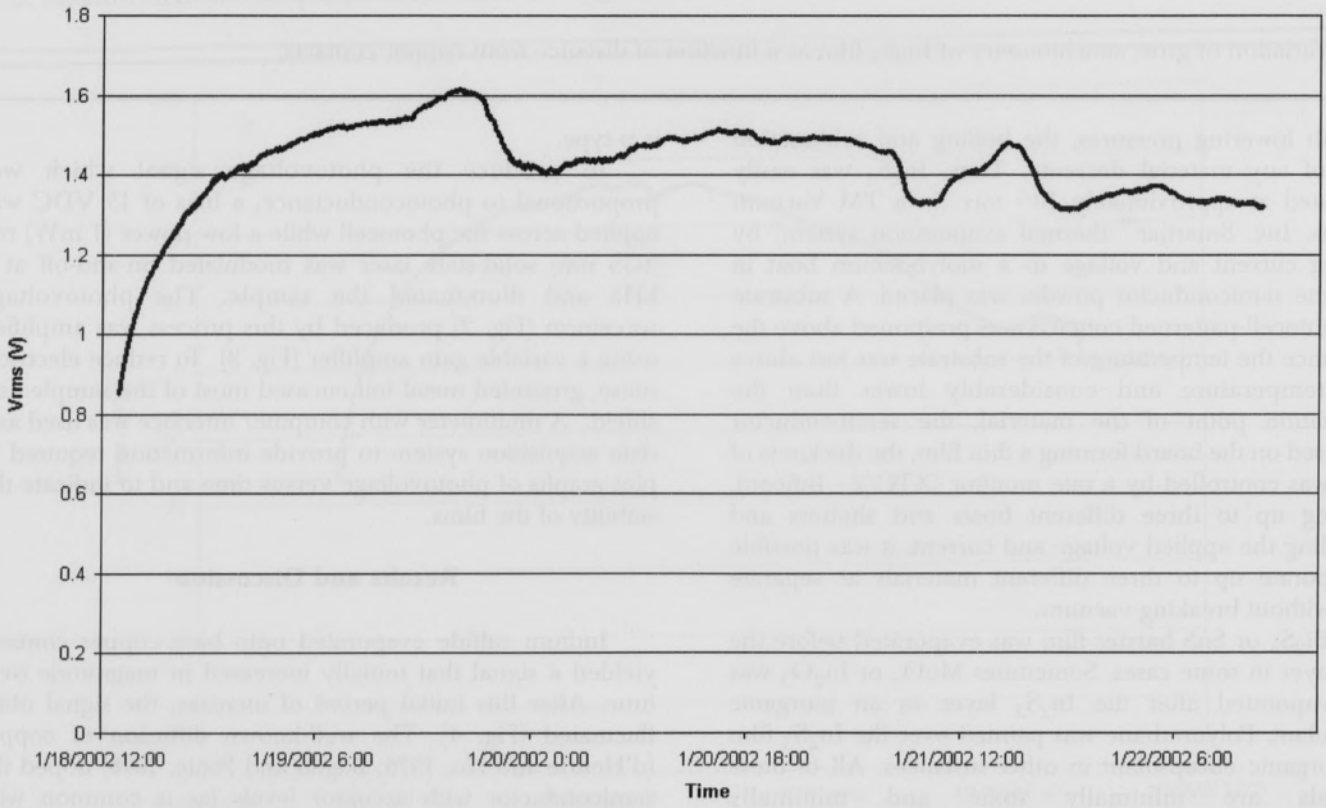

Fig. 7. Stability of photovoltage for In_2S_3 on solder-coated copper contacts over time.

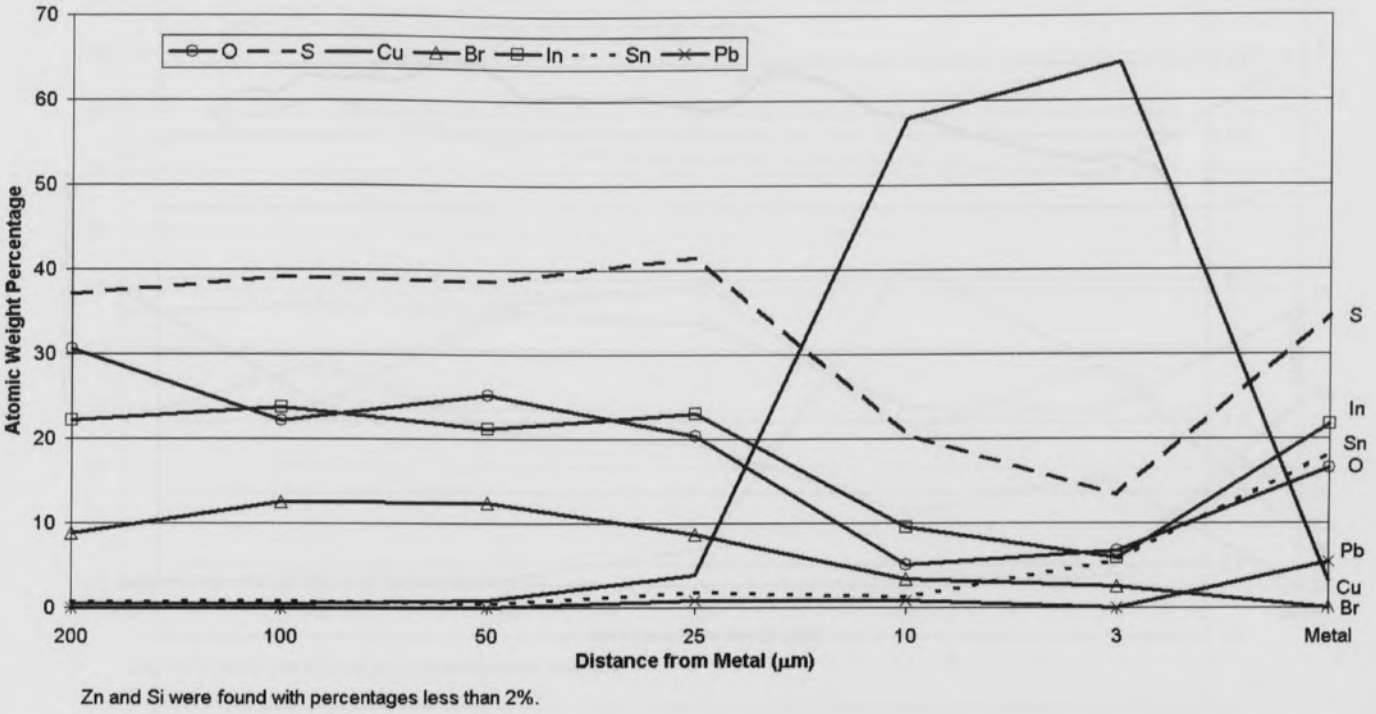

Fig. 8. Variation of gross stoichiometry of In_2S_3 film as a function of distance from solder-coated copper contacts.

copper sulfide bridge across the contacts, shorting the photocell. To further investigate the diffusion and electromigration of copper into the film, energy dispersive X-ray analysis/spectroscopy (EDS) was performed by Dr. Susan Kerber, Material Interface, Sussex, WI. Figure 5 shows the atomic percentages of different elements in the semiconductor film at various distances from the copper contacts. The EDS analysis confirmed the suspicion that the copper diffused into the film. At 3 and 10 μm from the metal contacts, the atomic percentages of copper were surprisingly high (48.43% and 14.35%, respectively). Scanning electron microscope photographs (Fig. 6A and 6B) illustrate the diffusion of copper; the copper/copper sulfide region can be seen as a dark area close to the metal contact. The percentages of oxygen were also significant throughout the film. This indicates the possibility that In_2S_3 reacted with or absorbed/adsorbed atmospheric moisture or oxygen, which could have contributed to the fluctuations of the photosignal over time.

In an attempt to block the copper diffusion into the film, In_2S_3 was evaporated onto solder-coated copper contacts. The same initial increase and fluctuations were observed, but the magnitude of the signal decreased slightly over time (Fig. 7). EDS analysis was also performed on this sample (Fig. 8). It indicated that copper was still diffusing into the film, which is consistent with the previous assumption that the copper was doping the semiconductor, causing the signal to increase initially. Tin and lead also diffused into the film to a much lesser extent and could be responsible for the subsequent slight decrease in signal. Once again, oxygen was detected in the film.

Gold and nickel are known to be more stable chemically than copper and more effective than solder in preventing copper diffusion, thus In_2S_3 was evaporated onto gold-on-nickel-coated copper contacts. Once again, the sample exhibited an initial increase followed by minor fluctuations of the photosignal (Fig. 9). It is possible to see in the EDS data of Fig. 10 that copper was still diffusing into the semiconductor film. Also, the large amounts of oxygen again indicate a potential partial oxidation or hydrolysis of the film into In_2O_3, $In(OH)_3$, and/or $In_2S_xO_{3-x}$ as was seen in previous EDS analyses.

Bi_2S_3 and SnS were investigated as underlying photoconductive barrier films for the In_2S_3 film. This was an attempt to further block the copper diffusion and increase overall photoconductance. Plots of photovoltage versus time

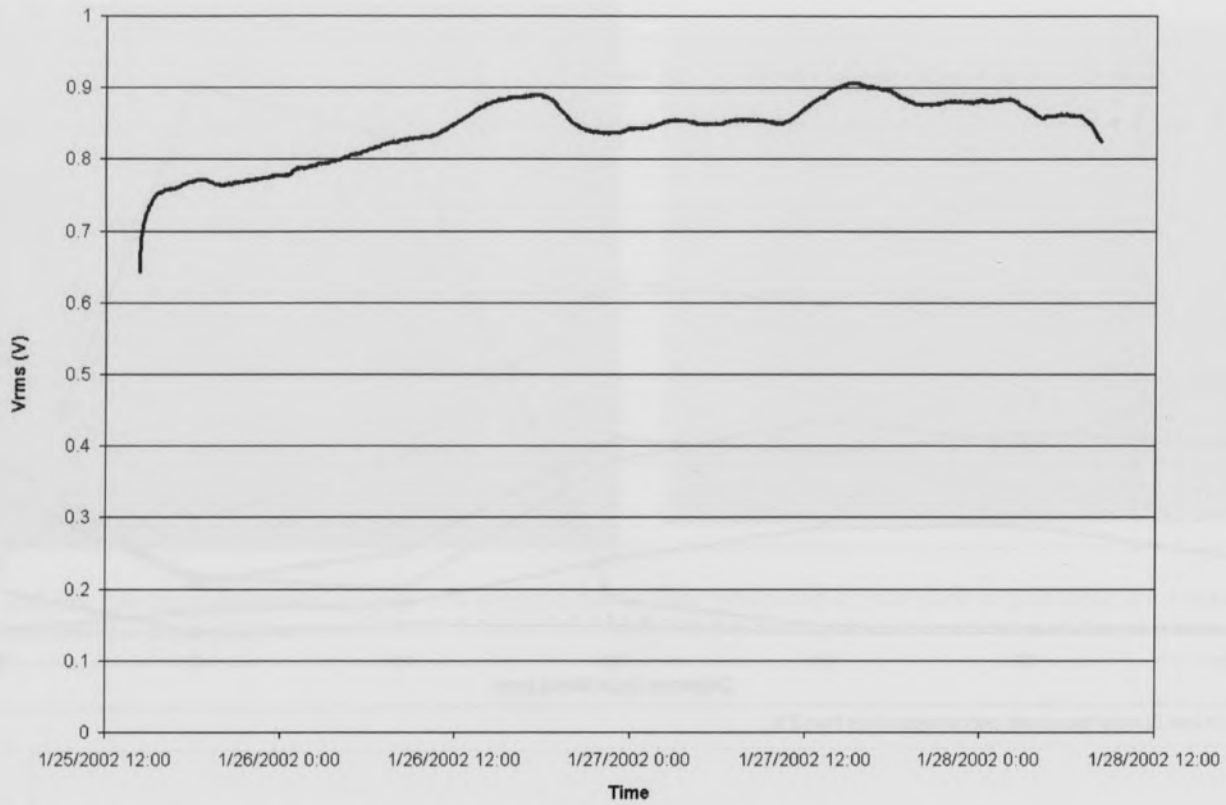

Fig. 9. Stability of photovoltage for In_2S_3 on gold-on-nickel-coated copper contacts over time.

for a Bi_2S_3/In_2S_3 film on bare copper and solder-coated copper contacts are shown in Fig. 11. Photovoltage versus time data for these films behaved similarly to that for In_2S_3 films on bare copper and solder-coated copper contacts films. SnS as a barrier film yielded an initial decrease of photovoltage followed by a considerably more stable signal (Fig. 12). The sharp peaks seen on the graph are transient electrical/electromagnetic noise spikes interfering with the photosignal.

Since copper diffusion could not be conclusively eliminated using coatings of various metals or semiconductor barrier films, In_2S_3 was evaporated onto ITO-on-glass contacts (Fig. 13). This film yielded an initial increase in signal, as had the films with copper contacts. This indicates that the copper diffusion wasn't solely responsible for the initial transient increase in signal. Another plausible explanation for the initial increase in photosignal could be the transient filling of an impurity or defect level ("trap state") within the bandgap by the photo-excited electrons and/or holes that fall from the conduction band and/or valence band and get trapped in this band, thus decreasing the initial free carrier concentrations (Rose, 1978). As increasing numbers of trap states become filled, less-and-less additional free carriers become trapped, more stay in the bands as free carriers, and the conductivity increases. Once the impurity or defect level is filled, there is no further increase in signal, since the concentrations of free holes and electrons remain the same under steady state conditions. This conjecture is supported by the fact that the photosignal decreased in magnitude when the laser was moved from the illuminated area to a previously unilluminated location on the same photocell.

Indium sulfide on graphite contacts produced a small steady increase in signal over time (Fig. 14). Very small fluctuations of the signal were due to electrical noise.

Polyurethane was applied to an In_2S_3 film on solder-coated copper contacts after evaporation (Fig. 15). The initial decrease in photosignal illustrated on the graph was probably due to the drying of the polyurethane. After this initial decay, it was once more possible to see a slight increase of the photovoltage over time. The polyurethane coating prevented reactions with the atmosphere, and the small fluctuations that were common on the unencapsulated In_2S_3 on solder-coated copper contacts vanished.

In_2O_3 was evaporated onto In_2S_3 on solder-coated copper contacts as an inorganic encapsulating film. This

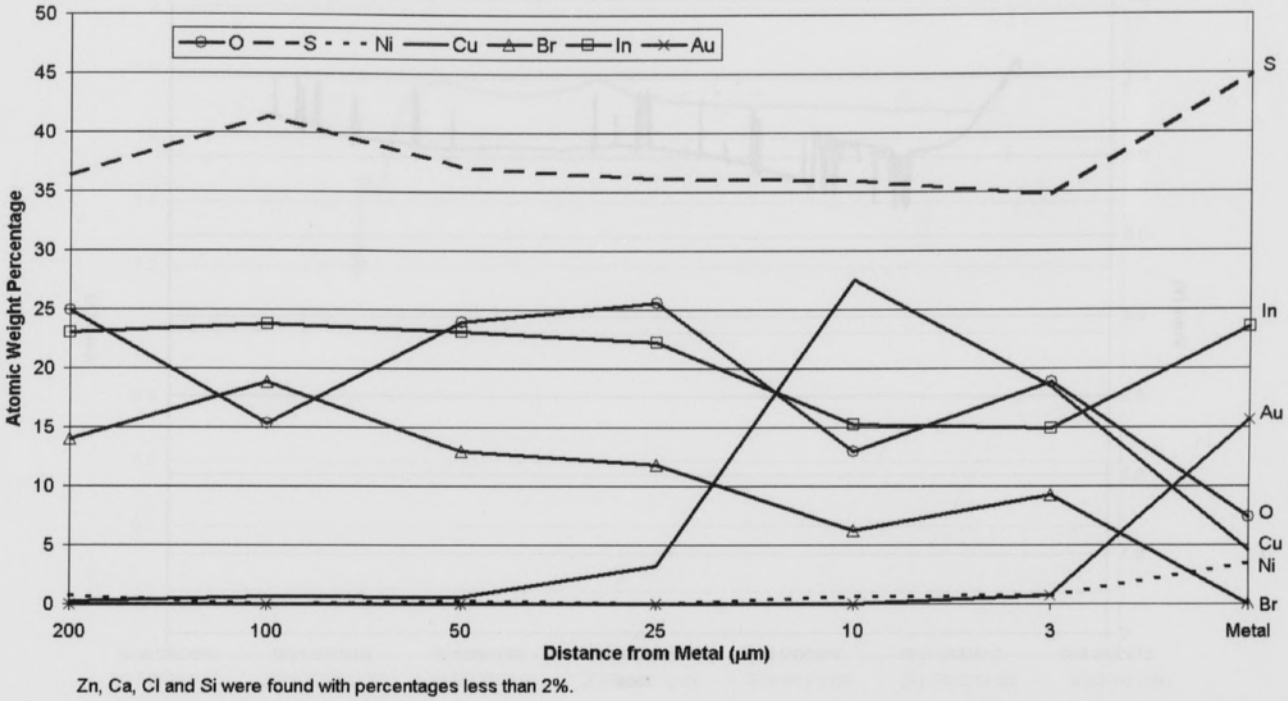

Fig. 10. Variation of gross stoichiometry of In_2S_3 film as a function of distance from gold-on-nickel-coated copper contacts.

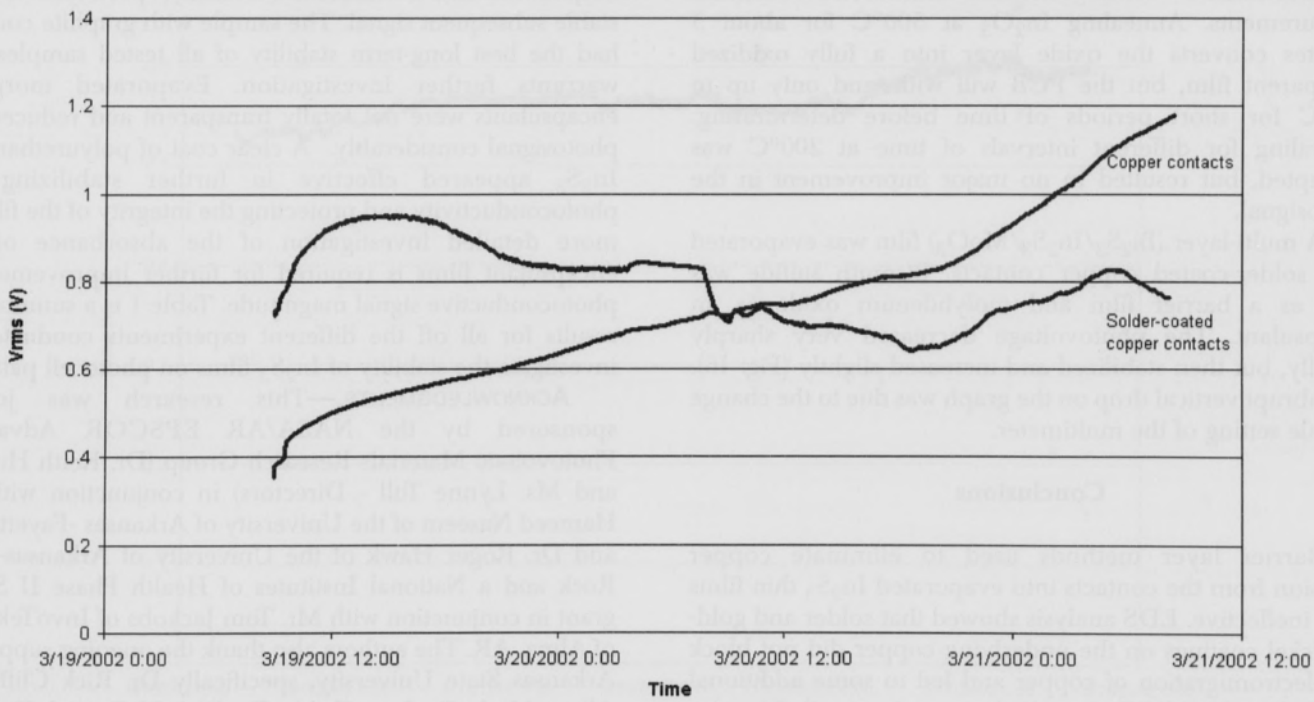

Fig. 11. Stability of photovoltage for In_2S_3 on bare copper and solder-coated copper contacts over time with Bi_2S_3 as a photoconductive barrier film.

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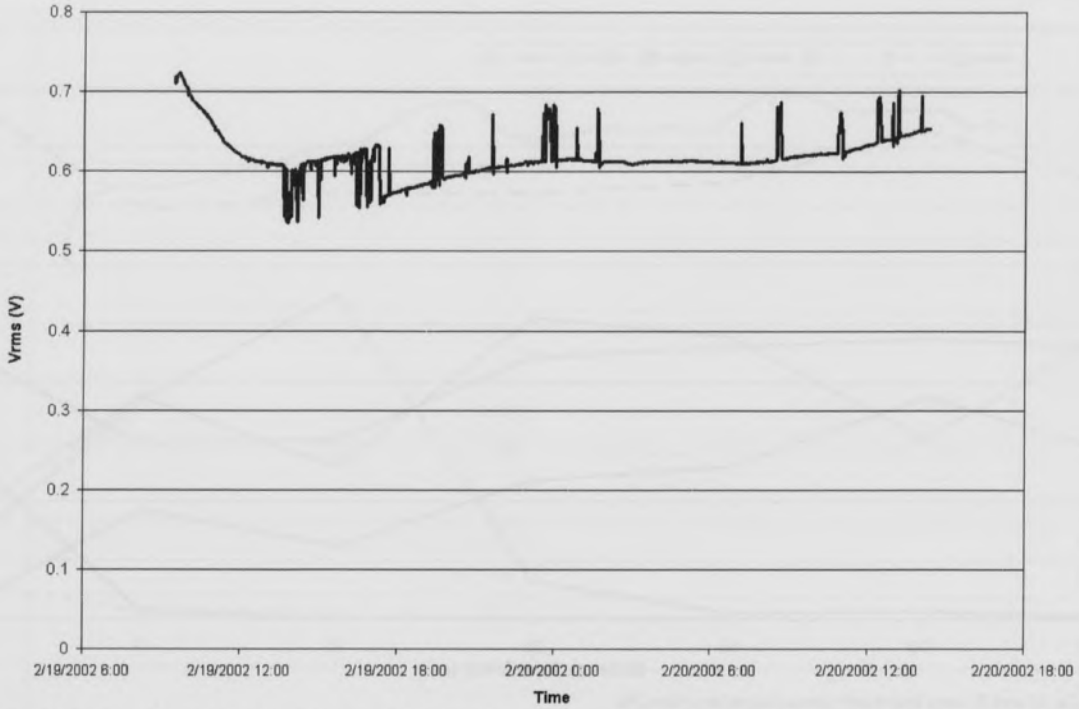

Fig. 12. Stability of photovoltage for In_2S_3 on solder-coated copper contacts over time with SnS as a photoconductive barrier film.

sample produced a very small photovoltage with a poor signal-to-noise ratio which hindered accurate measurements. Annealing In_2O_3 at 500°C for about 5 minutes converts the oxide layer into a fully oxidized transparent film, but the PCB will withstand only up to 200°C for short periods of time before deteriorating. Annealing for different intervals of time at 200°C was attempted, but resulted in no major improvement in the photosignal.

A multi-layer ($Bi_2S_3/In_2S_3/MoO_3$) film was evaporated onto solder-coated copper contacts. Bismuth sulfide was used as a barrier film and molybdenum oxide as an encapsulant. The photovoltage decreased very sharply initially, but then stabilized and increased slightly (Fig. 16). The abrupt vertical drop on the graph was due to the change in scale setting of the multimeter.

Conclusions

Barrier layer methods used to eliminate copper diffusion from the contacts into evaporated In_2S_3 thin films were ineffective. EDS analysis showed that solder and gold-on-nickel coatings on the underlying copper did not block the electromigration of copper and led to some additional tin, lead, and gold diffusion. A photoconductive SnS barrier film underneath the In_2S_3 film reduced photovoltage fluctuations, whereas the Bi_2S_3 barrier film resulted in no improvement in long-term stability. ITO-on-glass contacts, despite the initial transient instability, produced a very stable subsequent signal. The sample with graphite contacts had the best long-term stability of all tested samples and warrants further investigation. Evaporated inorganic encapsulants were not totally transparent and reduced the photosignal considerably. A clear coat of polyurethane on In_2S_3 appeared effective in further stabilizing the photoconductivity and protecting the integrity of the film. A more detailed investigation of the absorbance of the encapsulant films is required for further improvement in photoconductive signal magnitude. Table 1 is a summary of results for all off the different experiments conducted to investigate the stability of In_2S_3 films on photocell patterns.

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Fig. 13. Stability of photovoltage for In_2S_3 on ITO-on-glass contacts over time.

Fig. 14. Stability of photovoltage for In_2S_3 on graphite contacts over time.

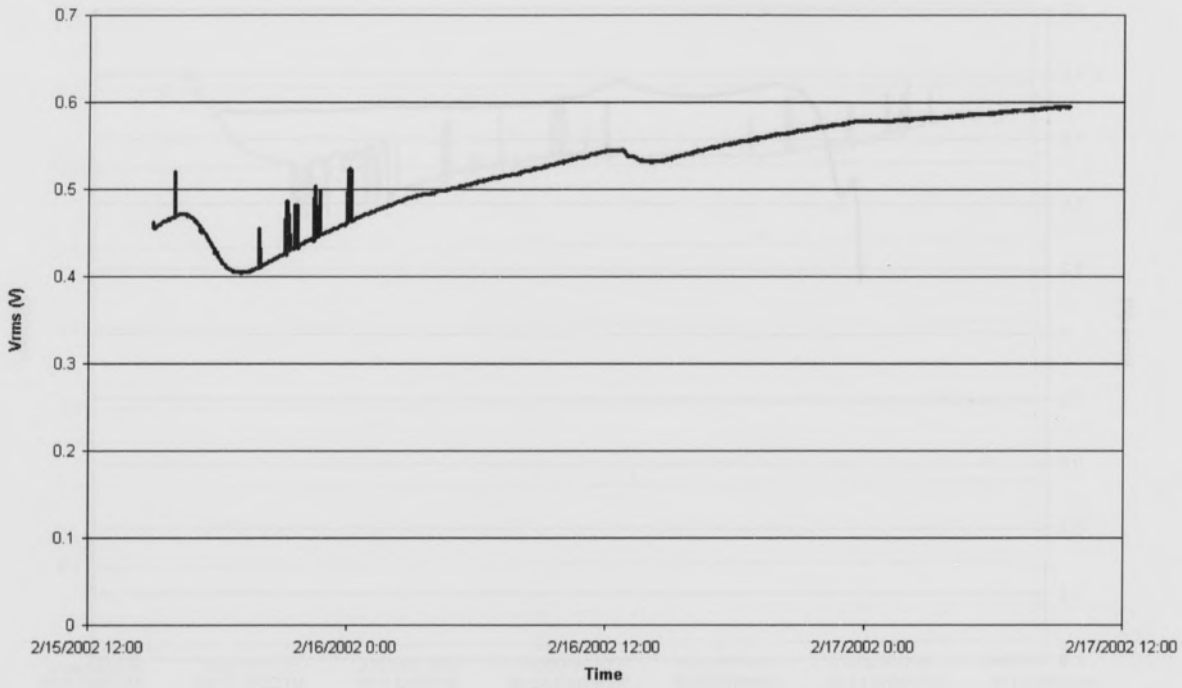

Fig. 15. Stability of photovoltage over time for In_2S_3 with polyurethane encapsulation.

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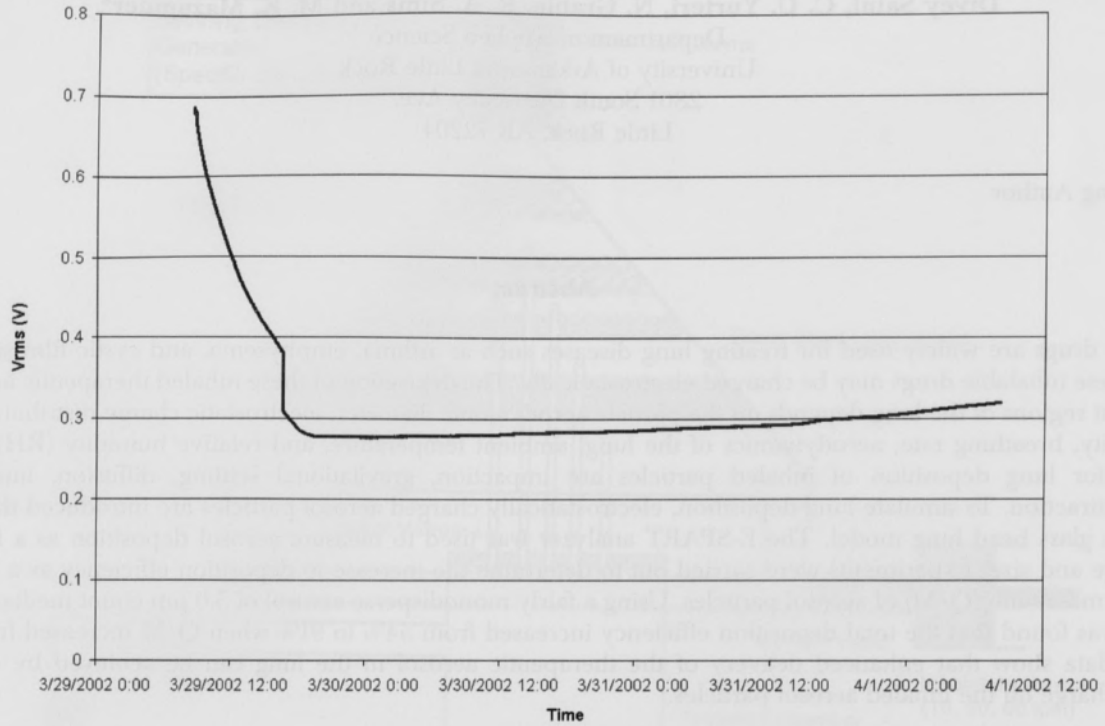

Fig. 16. Stability of photovoltage over time for In_2S_3 with Bi_2S_3 as a photoconductive barrier film and MoO_3 as an encapsulant.

Table 1. Summary of Experiments and Results.

Contact Material	Signal Stability
Bare copper	Initial increase/decrease
Solder-coated copper	Initial increase/fluctuations
Gold-on-nickel	Initial increase/fluctuations
ITO-on-lgass	Initial increase/stable
Graphite	Stable
Solder-coated copper with Bi_2S_3 barrier film	Initial increase/fluctuations
Bare copper with Bi_2S_3 barrier film	Increase
Solder-coated copper with SnS barrier film	Initial increase/fluctuations
Solder-coated copper with polyurethane encapsulant	Initial decrease/increase
Copper with Bi_2S_3 barrier film and MoO_3 encapsulant	Initial decrease/stable