International Materials Institute for New Functionality in Glass
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Effect of annealing on the Temperature dependence of photoconductivity of As_2S_3 films

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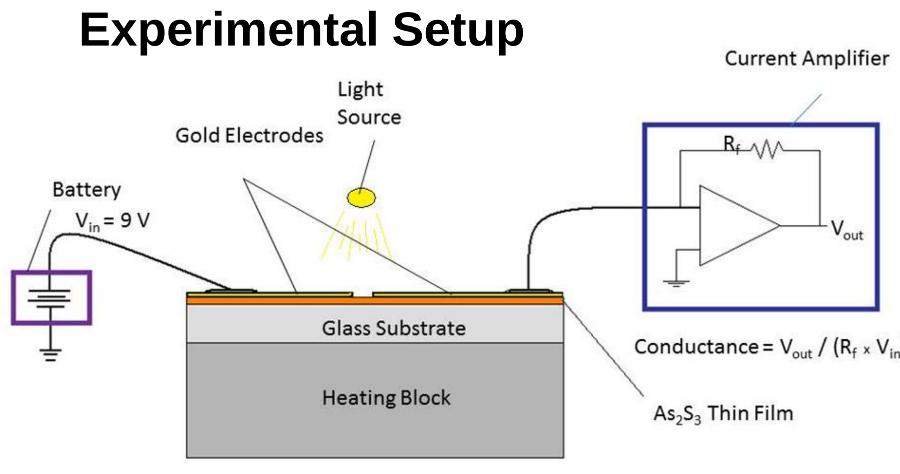
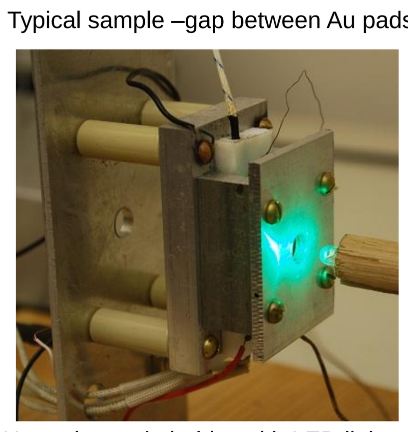
Educational Objective: Chalcogenide glasses represent an important class of active glasses whose properties such as optical absorption, electrical conductivity, volume and chemical reactivity can be changed with light illumination. Consequently they have many interesting applications, yet students typically have little experience with these materials. As part of our effort to develop low-cost experiments for students to explore glass science, we used a previously described[1] student built electrometer to measure electrical conductivity and associated photoconductivity in thin film arsenic sulfide chalcogenide glass samples. The entire apparatus from heated sample holder to illumination sources was student constructed.

Abstract: of Results: We measured conductivity under alternating dark and light exposure as a function of temperature. Both virgin and annealed thin film samples were examined, as well as, the changes through an annealing sequence. The fresh, as-prepared films reveal considerable dark and light conductivity at lower temperature (20-70 C) with a region of negative temperature coefficient. This anomalous behavior disappears after heating to 170 C. Fully annealed samples show negligible photocurrent at room temperature; the photocurrent increasing gradually with temperature reaching a maximum near 100 C. The changes in photoconductivity during annealing provide a meaningful experiment in chalcogenide glasses and demonstrate the significance of defect structure and relaxation.

Experimental Setup



Typical sample –gap between Au pads

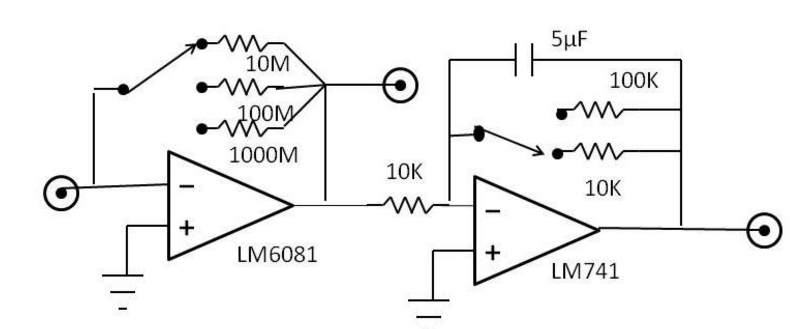


Heated sample holder with LED light

Sample Preparation and Student-Built Apparatus

Samples were prepared by thermal evaporation of high purity As_2S_3 (AMTIR-6 from Amorphous Materials Inc.) on a glass slide, to an nominal thickness of 400 nm. Thin Au was sputtered on top to form the contacts , using a thin strip of Al foil (~ 1.25 mm wide) as a mask to form the gap. Silver paste was used to attach wires to the Au pads as shown. Estimated cell constant of gap region is ~ 4 x 10^{-3} mm. Sample mounted on an aluminum block with 2 embedded 30 W cartridge heaters. Simple heating profile achieved using manual adjustment of a variable transformer (Variac) to achieve heating rates of approximately 1º C/minute. Electrical shielding of apparatus from 60 Hz noise was essential and achieved with aluminum foil.

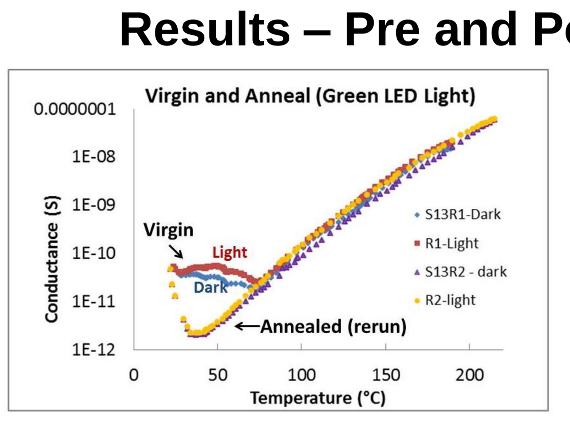
Low-Cost Electrometer for DC Conductivity



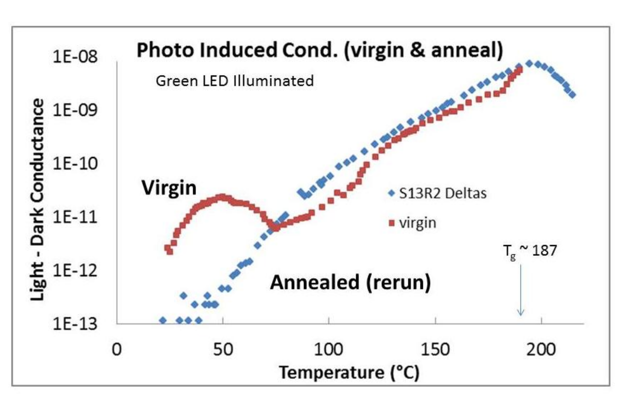
Input stage:
LMC6081 - Precision CMOS Operational Amplifier
High Impedance input > 10 Tera Ω
Ultra low input bias current: 10 fA
Low offset voltage: 150 µV
Cost < $5 in 8pin DIP package (DigiKey)
2nd Stage
Isolation, filtering and additional gain
0.05 sec time constant for 60 Hz suppression

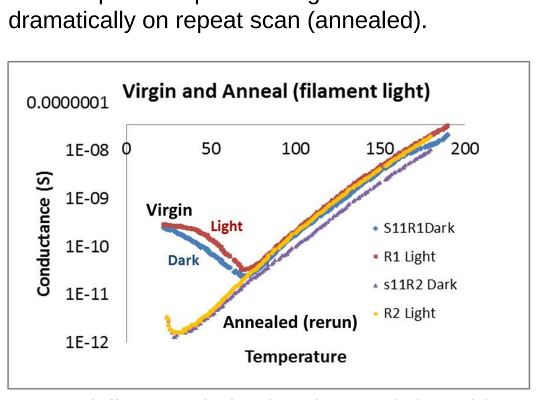
Other experimental issues –
Light sources : Both white (filament) and green LED light used (Cree led, C503, wavelength =527 nm.). The LED is chosen close to the bandgap while the white light contains also components above and below. Busse[2] reports Tg of bulk As_2S_3 as approximately 460 K = 187 C.
Details of results shown below.

Results – Pre and Post Anneal

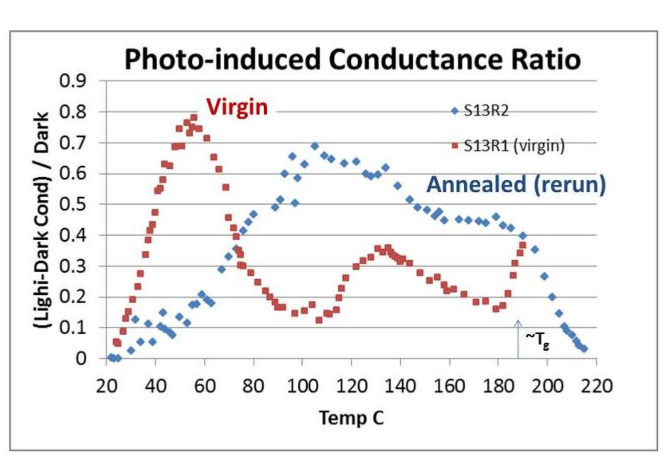


Virgin film show initial decrease in conductance with subsequent rise above ~ 70 C.
Low temperature plateau region decrease dramatically on repeat scan (annealed).

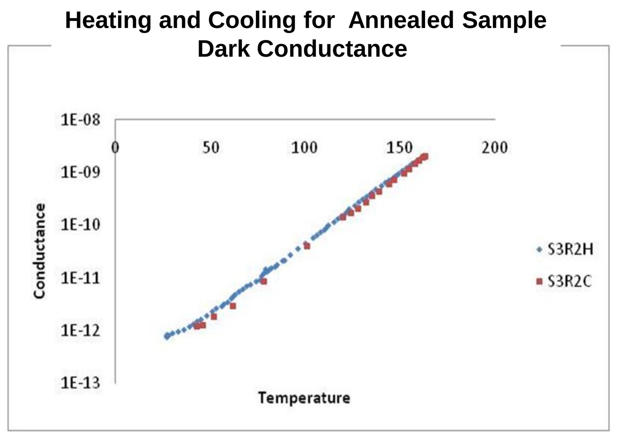




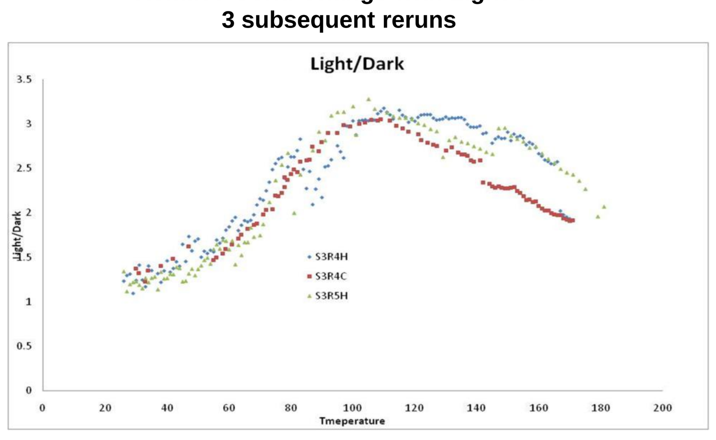
Essentially same behavior observed for White Light illumination as for green LED.



Good Repeatability of Post Annealed Samples

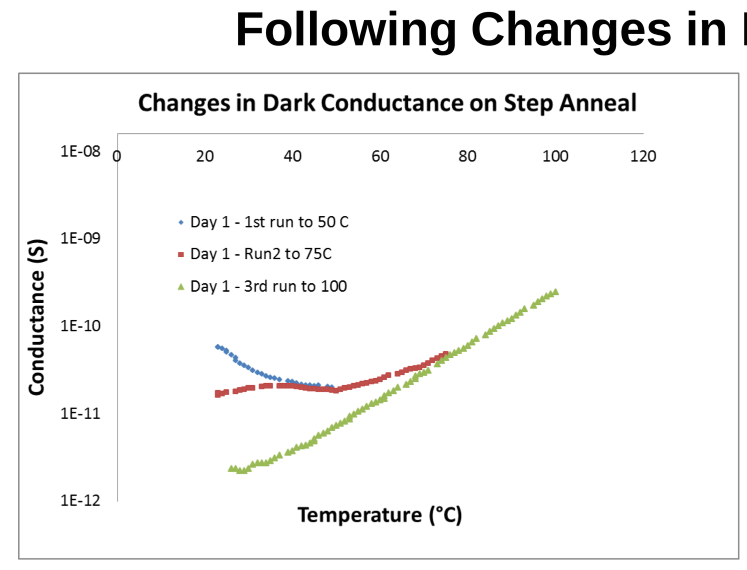


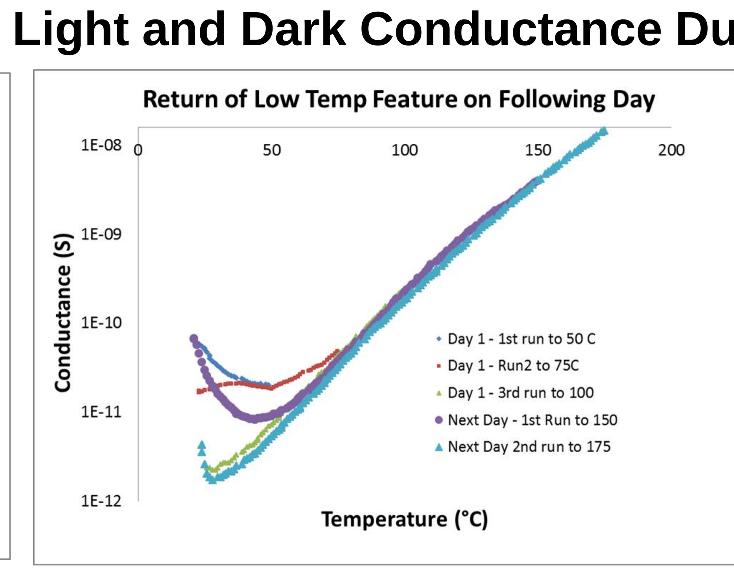
Dark conductivity behavior remains stable after the initial change – during course of the heating cooling.

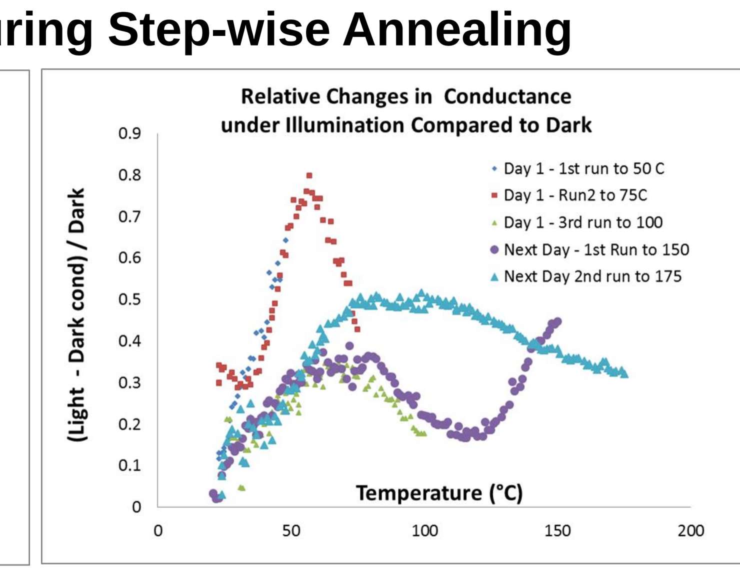


Increase in relative response to light remains relatively constant after the initial change on annealing.

Following Changes in Light and Dark Conductance During Step-wise Annealing

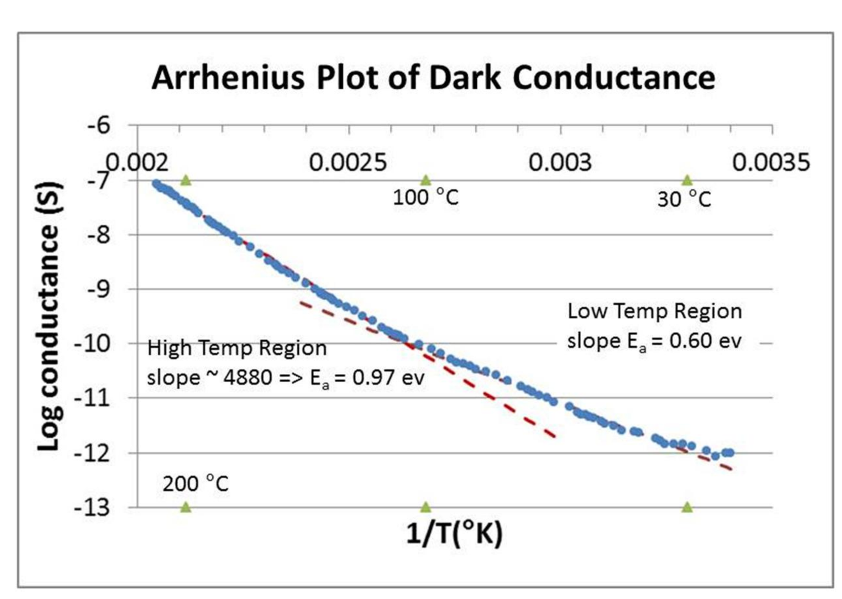






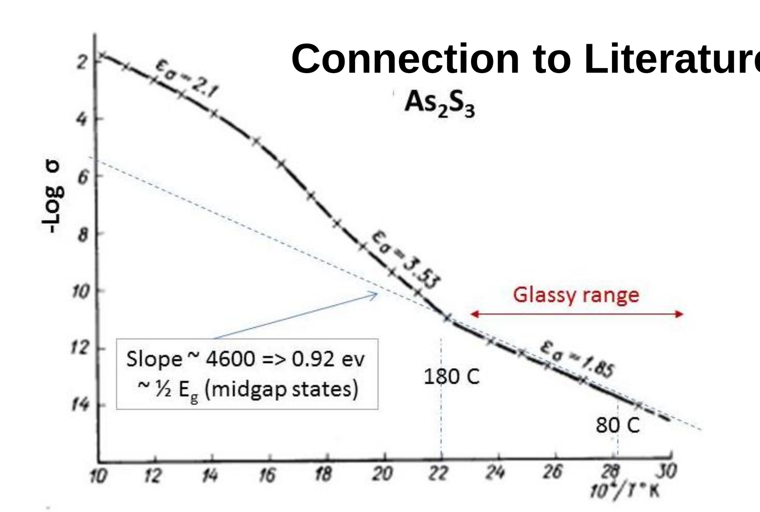
Figures above depict the changes in the dark and light conductance with heating to increasingly higher temperatures (50, 75, 100, 150 and 175º C). The annealing sequence demonstrates that heating to 75º C is sufficient to cause a major reduction in the low temp conductivity and associated peak in relative light to dark response (right) near 50º C. However much of this low temperature elevation returns after an overnight rest (suggesting moisture effect). Heating again to 150º C is sufficient to produce the single broad peak near 100º C observed in all other annealed samples.

Arrhenius Behavior in Dark Current and Connection to Literature



Connection to Literature

As_2S_3



Electrical Conductivity of As_2S_3 glass over a large temperature interval
Figure 78. from Z.U. Borisova, Glassy Semiconductors, Plenum Press, 1981

The Arrhenius plot of the dark conductance data suggests two distinct regions of nearly constant slope. In the higher temperature region (above ~100 C) the slope is in close agreement with that obtained by Borisova [3] for bulk As_2S_3. She attributes the observed E_a as arising from near mid-band states.
The lower temperature region has a lower slope and may be associated with either surface conduction or unannealed defect states, closer to the band edge. This is the region that exhibits significant changes with annealing and was shown unstable, suggesting moisture adsorption.
The maxima in photocuducatnce observed near 100 C was similarly reported for As_2Se_3 by Adriaanssens[4] and Veralan[5], which they attributed to the competing influence of donor and acceptor level states within the bandgap.

Accomplishments :
We have developed a simple method for experimental studies of photo conductivity in chalcogenide glasses. Our preliminary measurements on the thin film As_2S_3 model system show a complex and unexpected temperature dependence of photo conductance with significant changes between fresh and annealed films.
Virgin samples show high photoconduction response in the temperature range below about 70 C, which disappears on annealing. In contrast the annealed samples show little photo conductance at lower temperatures, but gradually rises to a maximum near 100º C, followed by a slowly falling plateau above this maximum. Moisture absorption appears to make significant contribution to the high conductance of virgin films at low temperatures, as may other defect states, to a lesser degree. The maximum in photo conductance observed near 100 C has been attributed to competing effects of both donor and acceptor states on the conductance. This low-cost apparatus can be used in the undergraduate laboratory to examine basic properties of disordered glassy semiconductors.

As follow-up REU we propose:
- Improve apparatus chamber to separate possible atmospheric /moisture effects
- Study spectral dependence off the photo conductance in this system
- Extend measurements to higher temperature (~ 300 C) and examine other light intensities
- Extend investigation to spin coated chalcogenide films - as more accessible preparation procedure

References:
1. W. Heffner, "A Low-Cost Student Built DTA for Exploring the Glass Transition", 2010 GOMD, Corning, NY. Also on IMI website at http://www.lehigh.edu/imi/.
2. L. Busse, Phys Rev. B, 29, 3642, 1984.
3. Z.U. Borisova, Glassy Semiconductors, Plenum Press, 1981.
4. G. J. Adriaenssens, and A. Stesmans, Journal of Optoelectronics and Advanced Materials,. 4, p. 837, 2002.
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