

Spectroelectrochemical Study of Carbon Nanotube and Indium Oxide Thin Films

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Abstract:

Two related spectro-electrochemical experiments were performed. In the first experiment voltages applied to a single walled carbon nanotube (SWCNT) thin film induced changes in the transmittance spectrum of the film. The changes are attributed to a voltage-modulated shift in the Fermi level of the nanotubes in the film. From this study the intrinsic doping level of the semiconducting carbon nanotubes was also determined. In the second experiment, an Indium Oxide thin film was subjected to varying voltages to change the film's free carrier electron density and thereby also modulate the film's transmittance. A spectroelectrochemical cell with high chemical resistance was designed for use in these experiments.

1. Introduction:

Spectroelectrochemistry is a field of study that combines spectroscopy with electrochemistry. Spectroelectrochemistry can provide valuable information about thin films, such as the effects of different applied voltages on the optical transmittance of the thin film. Aqueous electrolyte is commonly used in many electrochemical applications. However, water is not ideal in spectroelectrochemistry because it has strong absorption

bands that make it almost impossible to gain information about a thin film at certain wavelengths. Additionally, water has a narrow potential window. Water can only be taken to -0.81V or +1.23V before it breaks down into its byproducts (H₂ gas and OH⁻ ions at negative voltage, O₂ gas and H⁺ ions at positive voltage) [1]. To circumvent these types of problems, a nonaqueous solvent must be used.

Two experiments were performed using the nonaqueous solvent acetonitrile. The first involved a single walled carbon nanotube (SWCNT) thin film. In this experiment potentials were applied to the thin film (versus a platinum wire counter electrode using a silver wire pseudoreference electrode) while changes in the transmittance spectrum were monitored. We infer that these changes in the spectrum occur as a consequence of changes in the Fermi level. From this inference, we are able to locate the intrinsic doping level of the semiconducting nanotubes. The second experiment dealt with a transparent conducting film of Indium Oxide. In this experiment we tried to shift the free carrier electron density by applying different voltages and observing the changes in the transmittance spectrum.

A chemically resistant cell and identical reference cell were developed for use in these experiments. One of these cells is displayed in Fig. 1. The bodies of the cells are composed of Teflon®. They use Simriz® SZ485 O-rings and have quartz optical windows. All of these components have high chemical resistances to most substances. Nylon tubing was used for getting solutions into and out of the cells. Additionally, Teflon® valves were used to control the flow of the solution, and a steel poppet valve was attached so that any gasses produced would be able to leave the cells without allowing atmospheric contaminants to enter. There were three types of electrodes used in

the cell. The working electrode was the film under study contacted by a graphite rod, the counter electrode was platinum, and the reference electrode was silver. A Perkin-Elmer {model} potentiostat supplied the potentials in a three terminal set-up, where-in the counter electrode voltage is varied to make the voltage difference between the working electrode and reference electrode the desired value. The benefit of this is that the desired potential on the working electrode is maintained versus a well-defined reference independent of any Faradaic electron transfer occurring at the working electrode. The cells were designed in an attempt to keep out water vapor and air. The cells served their purpose well, and substantial impurity peaks were only observed after the cells were exposed to the environment for periods of over 24 hours.

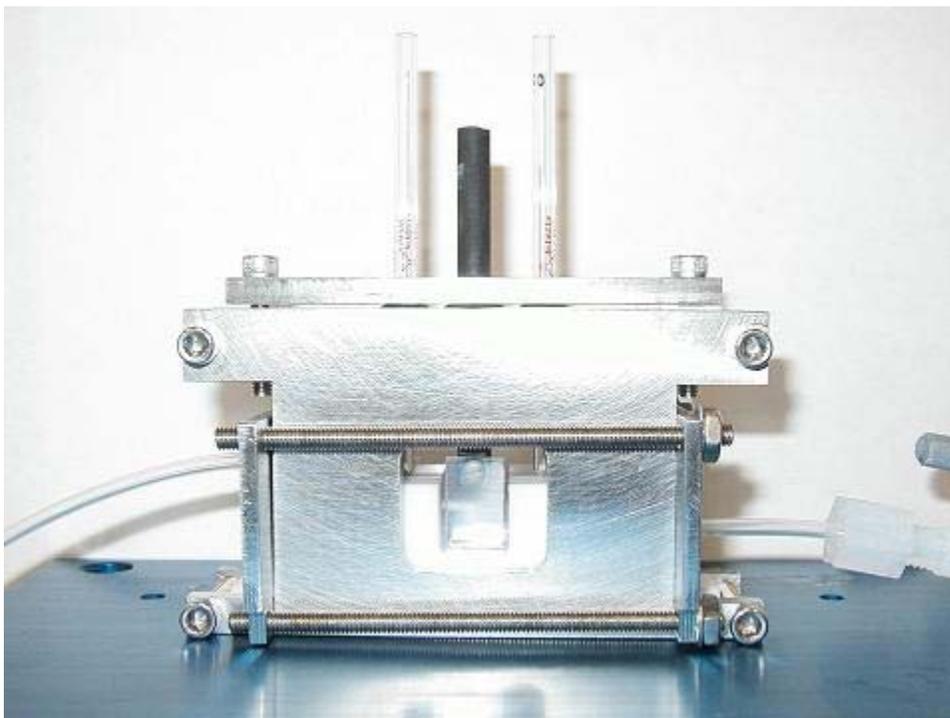


FIG. 1: The spectroelectrochemical cell used in the experiments.

2. Carbon Nanotube Experiment:

2.1 Introduction

Carbon nanotubes are self-assembling structures that can be induced to form under appropriate conditions. Multi-walled carbon nanotubes were discovered in 1991 by Sumio Iijima [2]. Several coaxial nanotubes of different diameters comprise one of these multi-walled carbon nanotubes. Single walled carbon nanotubes (SWCNTs) were first produced in 1993 by D.S. Bethune et al. [3]. SWCNTs can be thought of as one sheet of graphene rolled up into a cylinder. Depending on how the sheet is rolled up, the resulting carbon nanotube can be either semiconducting or metallic.

When taking a transmittance spectrum of a thin film of SWCNTs one observes three broad peaks. Our study focuses on the peak centered at 1650nm. This peak corresponds to photons absorbed during electronic transitions from the highest occupied semiconducting valence band (V1) to the lowest unoccupied semiconducting conduction band (C1).

Figure 2 shows that the valence and conduction states for carbon nanotubes have sharp peaks in the density of states known as Van Hove singularities. This would imply very sharp absorption bands. However, a thin film of SWCNTs is composed of semiconducting nanotubes of different diameters and chiralities. As a result of this assortment of types of nanotubes, the peaks in the transmittance spectrum end up being broad and smooth.

By applying a voltage to the SWCNT sample, one can shift the Fermi level. One can see in Fig. 2(a.) that if the valence state (V1) becomes more depleted, then fewer electrons will be available to undergo the transition to the conduction state (C1).

Therefore there will be less absorption of photon energy, and the absorbance peak will diminish. Similarly, if the Fermi level is increased as in Fig. 2(b.) so that some electrons already occupy the conduction state (C1), then there will be fewer available states for the remaining valence state electrons to move into and the peak will also diminish. Based on this knowledge, one can then determine the intrinsic doping level of the semiconducting nanotubes. If the peak is largest at 0V then the semiconducting nanotubes will be intrinsically undoped. Using this method, one can only determine the amount of doping qualitatively.

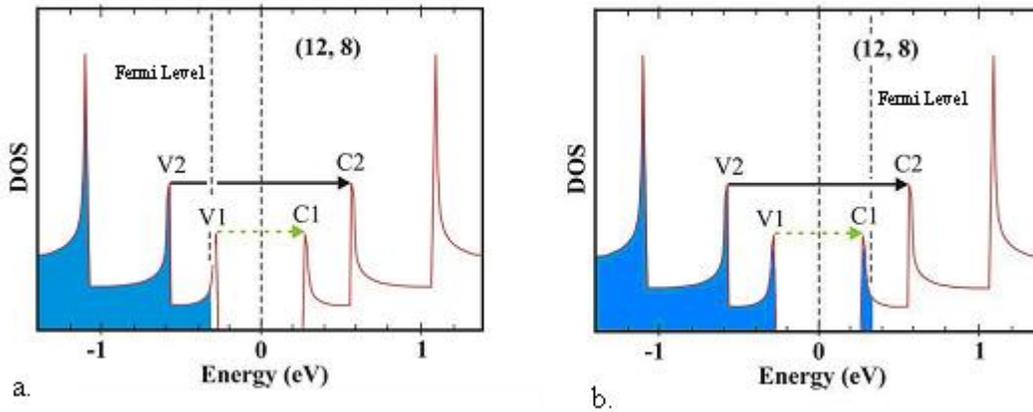


FIG. 2: Diagram of the Fermi Level of a semiconducting (12,8) SWCNT that is (a.) p-doped or (b.) n-doped

2.2 Experimental Section

This experiment is similar in nature to an experiment performed by Ladislav Kavan et al. [4]. Our experiment mainly differs from that one in that the SWCNT thin film that we use is mounted directly on quartz instead of ITO (Indium Oxide doped with Tin Oxide). We can do this because the nanotube samples also contain metallic nanotubes and we have learned how to make ultrathin (and hence transparent) films of

SWCNTs that are in contiguous electrical contact with each other. Methods for producing these films will appear elsewhere [5].

A SWCNT film was prepared and attached to a piece of quartz. This sample was baked in flowing argon gas in a Thermolyne 79300 tube furnace to drive off chemical dopants. The temperature was ramped at 5°C per minute until it reached 110°C, stayed at 110°C for 30 minutes, and then ramped at 1°C per minute to 600°C. The temperature remained here for 2 hours. A reference piece of quartz was also baked in the same way to be used in a reference cell.

Once the two pieces of quartz were allowed to cool, they were removed from the tube furnace and attached to the graphite working electrodes inside the electrochemical cell and reference cell described in the introduction. Next, both cells were heated to 75°C under flowing argon atmosphere for approximately 24 hours. Upon removal from the tube furnace, the cells were sealed by closing their Teflon® valves. The cells were then placed inside of an argon glove box and allowed to remain in there for 24 more hours with their valves open. This argon glove box had 1-2ppm Oxygen.

Inside the argon glove box, the solvent and electrolyte were added to the two cells. The solvent we used was Acetonitrile obtained from Fisher Scientific, and the electrolyte was 0.5 M LiBF₄. This solution was also placed inside glass tubes which held the reference and counter electrodes. Once the solvent and electrolyte were added, the cells were resealed, and removed from the argon glove box. Potentials were applied with a Perkin-Elmer Model 283 Potentiostat, while transmission spectra were recorded with a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer. With the reference cell (no nanotube film but including the quartz plate, cell windows and electrolyte) in the

reference beam of the spectrometer, and the sample cell in the sample beam, the absorbance of the sample cell itself (windows, electrolyte, quartz substrate) could be normalized out, leaving only the spectrum of the nanotube film.

2.3 Results and Discussion

Voltage was only applied to the cell with the nanotube thin film. We applied voltages ranging from -1.0V to +0.8V and recorded their spectra. The spectra observed at positive voltages are displayed in Fig. 3, and the spectra at negative voltages are displayed in Fig. 4. As can be seen in Fig. 3, the transmittance peak is smaller at +0.2V than it is at 0.0V. However, one can see in Fig. 4 that the peak size is the greatest at -0.4V. After +0.2V and -0.6V the transmittance peaks change dramatically with a change in voltage.

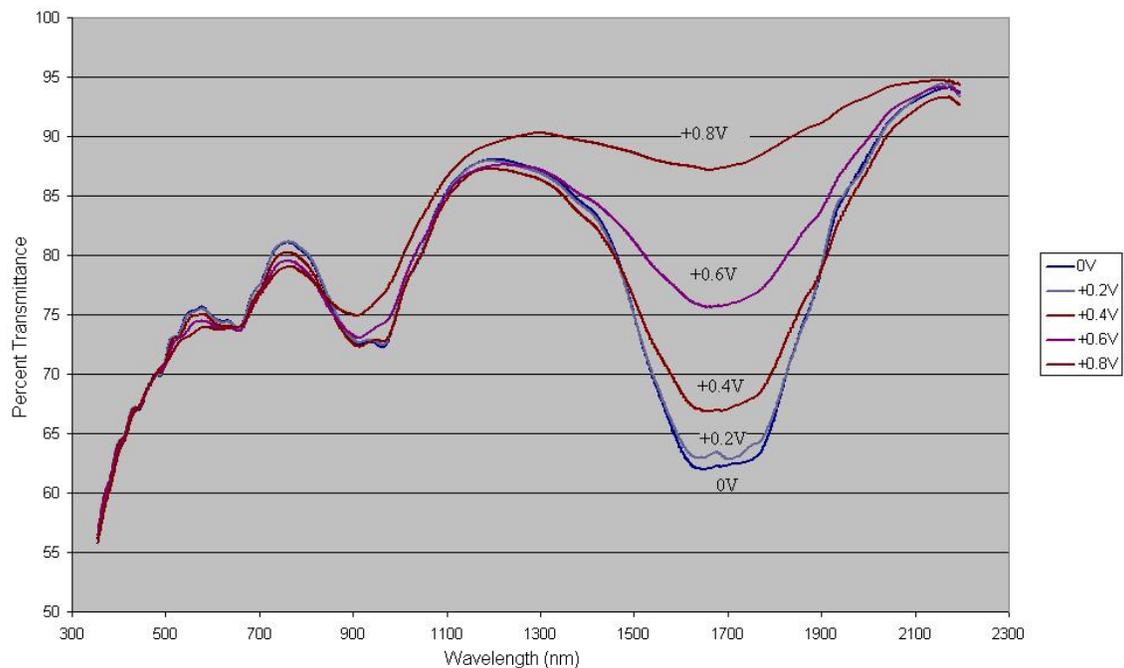


FIG. 3: Percent Transmittance vs. Wavelength for SWCNT thin-film at various positive applied potentials.

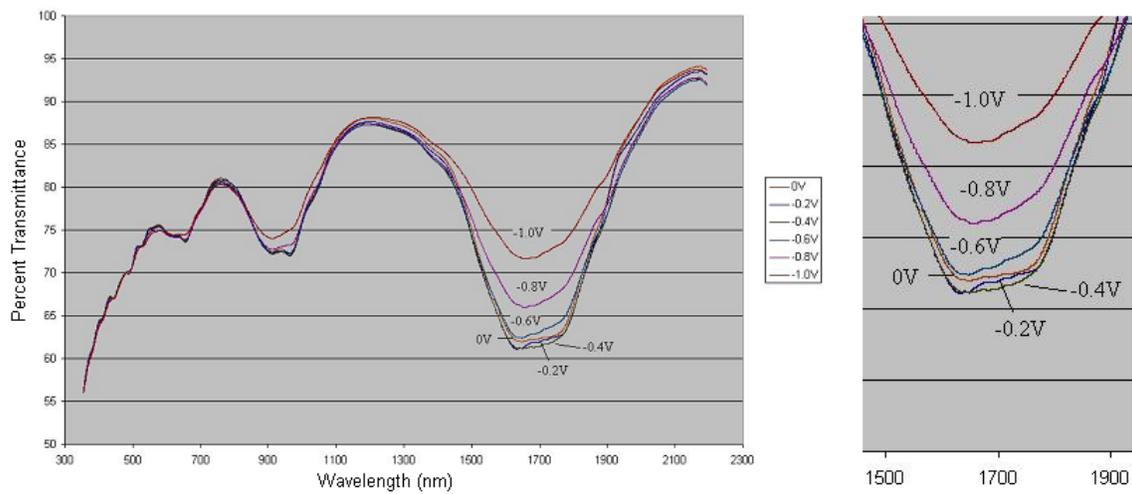


FIG. 4: Percent Transmittance vs. Wavelength for SWCNT thin-film at various negative applied potentials.

One problem encountered with the two cells was that they were not exactly the same thickness. We could only minimize the difference to within 0.2mm. This variance caused some acetonitrile peaks to show up in the spectra. Since these peaks were the same in all spectra, they were removed and the figures were smoothed prior to presentation in Figs. 3 and 4.

2.4 Conclusions

We determined that the maximum size of the transmittance peak occurs at -0.4V. At this voltage, the Fermi level is in the band gap between the first valence state and first conduction state of the most semiconducting nanotubes. This conclusion indicates that at 0.0V, the Fermi level has been shifted toward the positive side. Therefore the nanotube film is intrinsically slightly p-doped. There is some uncertainty in the measurement of the maximum of the transmittance peak because we incremented our voltage by 0.2V each time. A better approach would have been to slowly ramp the voltage from -1.0V to +0.8V while performing a time drive measurement (measuring the changes as a function of time) of the transmittance peak at 1650nm. This method will be explored in future experiments.

3. Indium Oxide Experiment

3.1 Introduction

Indium Oxide is a commonly used transparent conductor. It is usually doped with Tin Oxide to form ITO (Indium-Tin Oxide). However, the Tin Oxide mostly provides stability to the thin film only and does not substantially change its optical properties. ITO

films are currently being used in flat-panel displays, window defrosters, and as transparent electrodes on which other thin films are mounted [6]. Since many of these applications utilize the optical properties of the Indium Oxide thin film, it is important to understand the changes in the optical properties of this substance as different voltages are applied.

As is shown in Fig. 5, the transmittance drops from about 80% at 10000 cm^{-1} (1000 nm) to near zero at 2000 cm^{-1} (5000nm). This is ascribed to the free carrier absorption in the ITO film. In this experiment, we try to add or deplete the amount of free carrier electrons by changing the voltage. At negative voltages more electrons should be added to the ITO film, the film should become more absorbent, and the transmittance should decrease. Similarly, at positive voltages the film should contain less free carriers, it should become less absorbent, and its transmittance should increase. However, since this effect only occurs at wavelengths between 1000nm and 5000nm, we should see less change in the spectrum as 1000nm is reached.

This experiment is important to perform because there are many applications for Indium Oxide thin films. It is important to know about the effects of different voltages on the transmittance of the Indium Oxide film.

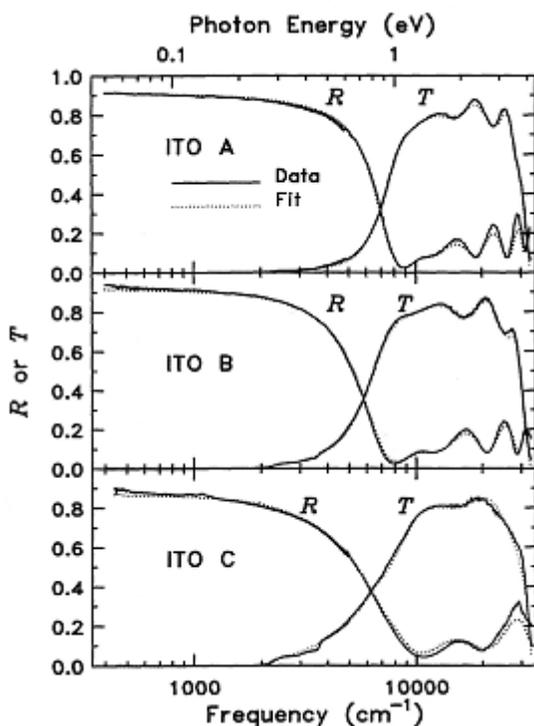


FIG. 5: Reflectance and Transmittance of ITO A (2870 Å thick), ITO B (2430 Å thick) and ITO C (1242 Å thick): data and fits [7]

3.2 Experimental Section

The setup for this experiment is similar to the setup described for the Carbon Nanotube experiment in Section 2.2. The Indium Oxide film was sputter deposited on a quartz substrate. The thin film was approximately 100Å thick. After deposition, the quartz piece with the Indium Oxide film was attached to the working electrode inside of the cell described in Section 1. A second piece of quartz (no InO_x) was used in the reference cell. The bake out and electrolyte (0.1 M LiBF₄ in acetonitrile) fill procedures were the same as described above. Since only small changes in the transmittance were anticipated, spectra with voltage applied to the film were recorded using a baseline

consisting of a spectrum recorded with no potential applied to the film. This meant that only changes from the baseline spectrum were monitored.

3.3 Results and Discussion:

As is shown in Fig. 6, at positive voltages the transmittance increases, and at negative voltages the transmittance decreases. Also, from Fig. 6 one can see that the effect on the transmittance increases from 800nm to 2200nm. These results indicate that we have been able to shift the density of the free carrier electrons. The results displayed in Fig. 6 have been smoothed so their effects at lower wavelengths can be observed more easily.

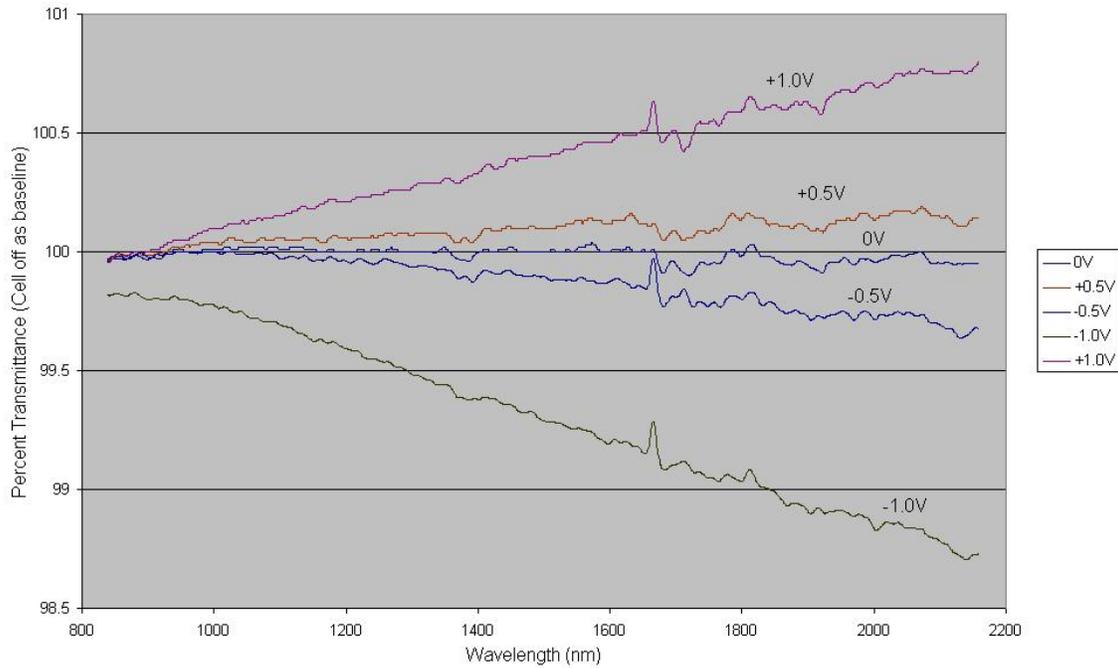


FIG. 6: Percent Transmittance (using cell off as the baseline) vs. Wavelength of an Indium (III) Oxide Film at various Voltages.

Another interesting result that we observed is that when going from positive voltage back down to zero volts, the film's transmittance remained at approximately the same level it was when it was at positive voltage. When negative voltage was applied and returned to zero volts, the film was able to recover more easily. However, the film never completely recovered its initial transmittance in either case. When the film was driven back and forth between positive and negative voltages, there was no drift in the percent transmittance, indicating that the process was reversible. These results are illustrated in Fig. 7.

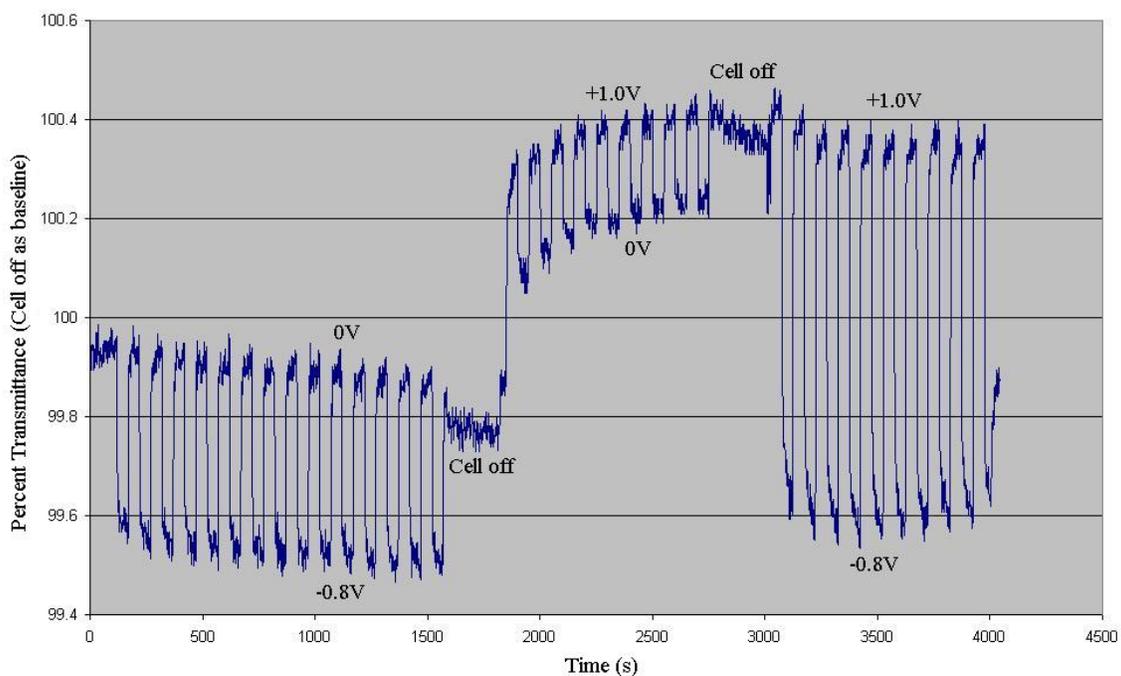


FIG. 7: Time-drive measurement of the percent transmittance of an Indium Oxide thin film at 2050nm. Voltages are changed every 50 seconds except for when the cell is off.

As is seen in Fig. 7, the transmittance at 0V is different depending on whether it is reached from positive or negative voltage. Since the process appears to be reversible, this difference in the transmittance at 0V suggests that some sort of hysteretic behavior is occurring. On a second run of this experiment we decided to look for this hysteretic behavior in the percent transmittance while ramping from negative to positive and back down to negative voltages over a long period of time. Although we were able to see some hysteresis, we unfortunately discovered that if voltage was applied to the thin film for long periods of time (as was the case in our time-drive measurements), then irreversible damage was done to the film. We noticed that during our time drive measurements, the percent transmittance would slowly decrease over time. Upon removing the Indium Oxide film from the cell, we noticed that the film had become discolored.

3.4 Conclusions:

We were able to change the percent transmittance of the Indium Oxide thin film by applying voltage to it. We believe that the result that we obtained is due to a shift in the density of free carrier electrons. Additionally, we conclude that it is more difficult for the thin film to recover from an applied positive potential than an applied negative potential. This type of film, which can have its percent transmittance changed by just applying a positive voltage and returning it to zero volts, could have many practical applications. However, one must remain cautious about applying a voltage for too long to one of these thin films, or else irreversible damage may occur.

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