Use of AC Faraday rotation as a complementary technique in material characterization

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ABSTRACT
Magnetic measurements like Hall Effect, etc. have a long history of providing useful information related to material characterization. Here, we study glasses using a very sensitive AC Faraday rotation (FR) setup to show that magneto-optic techniques can also be utilized to study types of samples that are not necessarily known for their magnetic response. Samples included in this study are widely used in technological and research applications ranging from microscopy to solar cell applications. The experimental setup employs a stabilized He-Ne lase (633 nm) along with AC magnetic field that enables lock-in detection. We investigate a series of glass samples that include borosilicate glass (BSG) and quartz subjected to UV treatment and glass with transparent conducting oxide films (TCO). The TCO samples include the more widely used Indium Tin Oxide (ITO) and the relatively newer Fluorine doped Tin Oxide films, usually referred to as FTO. Various other measurements like absorbance, four-point probe, and ellipsometry have been conducted on these samples as well. We mention the results of these measurements in conjunction with FR measurements, where needed. This work is focused on reporting novel results. A much more comprehensive manuscript is under preparation that explores the deeper connections between FR and the above-mentioned measurements.

I. INTRODUCTION
Glass as a material is generally well understood. It has proven to be remarkably versatile as a substrate material. From biological and polymer samples to solar films, many disciplines make use of glass for film deposition. Transparent glass is often characterized optically by using straightforward transmission-based measurements. Polarization based measurements like ellipsometry are also employed routinely to characterize glass in terms of its index of refraction, dispersion, extinction coefficient, etc. In this work we focus on a different type of transmission-based measurement for glass characterization. Glass is not widely known for its magneto-optic response. Glasses can exhibit a weak, and therefore difficult to measure, diamagnetic or paramagnetic response.

So, while glass substrates may have a difficult to measure magnetic response, many films on these substrates that are of technological and scientific significance have magnetic properties that are important to characterize. An important and relevant example would be that of TCO films that have a magnetic response due to the presence of free carrier concentration. While the response may be strong in relative terms (as in per unit length of the film), it is still challenging to measure it given the thickness range of these films which is usually tens of nanometers (nm) to hundreds of nm. In this work we present the details of an AC version of FR, along with lock-in detection that allows us to characterize the magnetic response of TCO films with a high degree of confidence. To our knowledge this is the first report of FR measurements for one of the types of TCO films we have analyzed (Fluorine doped ITO films).

In addition to film properties, glass substrates are often cured by subjecting them to ultraviolet (UV) light. This treatment changes the surface chemistry of the glass substrate and renders the surface more amenable to applications like wetting or adhesion. UV exposure also ensures cleaning for glass slides and semiconductor substrates that may be used for biological films, or other semiconductor processing. We examine two different types of glass substrates by exposing them to UV light for different times (fixed intensity). We compare results from FR measurements to absorbance
measurements for these samples. Again, to our knowledge, this is the first such report of its type.

II. THEORY

FR can be described as the rotation of the electric field vector of light as the sample is subjected to an external magnetic field along the direction of propagation of light. For linearly polarized light, this phenomenon can be explained by the simple equation

$$\theta = VBd,$$  \hspace{1cm} (1)

where $\theta$ is the angle of rotation of the electric field vector of linearly polarized light, $V$ is the Verdet constant of the sample, $B$ is the magnetic field, and $d$ is the length of the sample that the light passes through. Recall that this study applies an AC magnetic field and thus $\theta$ will also be sinusoidal. It can be shown that by placing an analyzer at 45° with respect to the initial polarization right after the light exits the sample, the amplitude of the FR is maximized and can be calculated by

$$\theta = \frac{1}{2} \frac{V_{AC}}{V_{DC}},$$  \hspace{1cm} (2)

where $V_{AC}$ is the amplitude of the AC voltage signal occurring at the frequency of the B-field (1f signal), and $V_{DC}$ is the DC offset voltage detected by the photodiode. Eq. (1) can be expanded to include magnetization for samples where magnetization is strong one can expect non-linear response to the applied magnetic field, and analysis of higher harmonics becomes important. In this work we are not dealing with such samples but in prior work it has been shown how this measurement can be utilized in those cases as well.\(^5\) Two other well-known expressions for FR relate this technique to more fundamental properties of samples under investigation. For transparent materials like glasses or for material being investigated far away from any absorption band, the Verdet constant can be related\(^1\) to the refractive index ($n$) and its dispersion ($dn/d\lambda$).

$$V = \frac{e}{2mc} \frac{dn}{d\lambda}.$$  \hspace{1cm} (3)

The pre-factor involves the mass and charge of the electron along with the speed of light. For films (like TCO) where free carriers provide the dominant contribution to the FR, the relevant expression for angle of rotation is as follows.\(^1\)

$$\theta = \frac{\hbar^2 n^2 \lambda^2 B l}{2 \pi e^4 n (m_e)^2}.$$  \hspace{1cm} (4)

In the above expression, $N$ represents the free carrier density and $m_e$ is the effective mass for the carrier (electrons or holes). The effective mass can show strong dependence along crystallographic direction.

III. EXPERIMENTAL DETAILS

The typical setup used to measure FR is shown in Fig. 1 which employs an AC magnetic field (typically ~800 Hz) provided by a calibrated solenoid, that is longitudinal with respect to the direction of propagation of light. Details of the measurement (Fig. 1) have been reported elsewhere\(^8\) but here we include a self-contained summary. Linearly polarized light (He-Ne 633 nm) is transmitted through the glass sample (on the order of 1.0 to 3.0 mm) and subsequently passes through an analyzer oriented at 45° with respect to the initial polarization. The sample is located at the center of a solenoid that is part of a resonant circuit. Transmitted light is detected by a photodiode (Thorlabs DET110) in conjunction with a lock-in amplifier (Stanford Research Systems SR830 DSP) that is locked to the reference provided by the magnetic field signal. Our measurement protocol consists of ramping the current (field) from 0 to some pre-determined value that allows us to construct a plot of angle ($\theta$) vs. the product of field and sample path length ($B \cdot d$). The slope of this graph directly yields the Verdet constant for the sample.

At each field value during the ramping up phase, five values of AC and DC voltages along with solenoid current values are collected.

![FIG. 1. Schematic of the typical setup to measure FR using an AC B-field.](image-url)
TABLE I. Sample descriptions.

| Sample | Description                        | Sheet resistance (ohm/square) | Film thickness (nm) |
|--------|-----------------------------------|------------------------------|---------------------|
| BSG    | Borosilicate glass slides         | ...                          | ...                |
| Quartz | Quartz glass slides               | ...                          | ...                |
| ITO 1  | Float glass substrate (1.1 mm)    | 10.5                         | ~150 nm ITO        |
| ITO 2  | Float glass substrate (1.1 mm)    | 69.7                         | ~15 nm ITO         |
| FTO 1  | Float glass substrate (2.2 mm)    | 6.50                         | ~15 nm FTO         |
| FTO 2  | Float glass substrate (3.0 mm)    | 10.5                         | ~15 nm FTO         |

and averaged over. This data also provides the standard deviation of the mean value of the rotation angle. The rotation of the light is measured from a 1f voltage signal where \( V_{AC} \) and \( V_{DC} \) can be obtained from the lock-in amplifier and the rotation angle \( q \) due to the sample can be calculated via Eq. 2. Samples used in the first set of results discussed in the next section are glass substrates (quartz and BSG) purchased from Sigma-Aldrich. All samples were cleaned with acetone and methanol before UV exposure and FR measurement. UV exposure was carried out using a UV lamp (Novascan PSD UV4) that allows for two UV wavelengths, 185 nm and 254 nm. Different samples (for either quartz or BSG) were cut from the same glass substrate and were used for different exposure times.

Thickness values for these quartz and BSG samples are 2.00 cm ± 0.05 cm and 1.05 cm ± 0.05 cm, respectively. ITO and FTO samples are also purchased from Sigma Aldrich. They are selected to represent different thickness and resistivity values. Resistivity is obtained from 4-point probe measurements and thickness of ITO/FTO films is obtained from ellipsometry. Both methods yield values that are consistent with the ranges provided by the manufacturer. Table I summarizes this information.

IV. RESULTS AND DISCUSSION

A typical data set is shown in Fig. 2 that allows for easy extraction of the Verdet constant. Measurements typically used around a tenth of an arc minute of rotation which can be measured very reliably due to a lock-in arrangement! Verdet constant results for quartz and BSG are shown in Fig. 3, respectively.

For quartz it is interesting to note that unlike absorbance measurements where there is no measurable difference in the absorbance measurements for different exposure times, here FR reveals not only a dependence on curing time, it also shows the presence of a threshold value of thirty minutes after which the effects become noticeable. Identification of a threshold can then lead to implications for the correct curing time for applications ranging from wetting to adhesion.

In this preliminary report we can, with certainty, point to the existence of a threshold that is worth investigating in terms of changes in surface chemistry.

On the other hand, there are no measurable changes in absorbance in the visible range as a function of curing times for...
BSG. FR measurements however show that the changes in curing time decrease the Verdet constant. We suspect that this is indicative of the fact that the effect of UV curing is more uniformly distributed throughout BSG and results in a lower index dispersion for the entire sample, in line with Eq. 3. Additional detail can be extracted from Fig. 3 (right panel) by way of comparison with the quartz sample. There is no threshold value for BSG beyond which a linear dose response is evident. Instead, for the same dose of UV light, changes happen around 15 minutes (∼half the time) and are more of a stepwise nature.

We also present a preliminary discussion of ITO and FTO results. As evidenced from Table I, techniques like the 4-point probe and ellipsometry can yield important information regarding resistivity and film thickness for these samples. The method for measuring FR as applied to glass substrates is employed here as well. We do verify that there are no higher harmonic signals due to free carriers. Although the Verdet constant of the ITO (or FTO) film is expected to be much higher than glass, given the relatively small values of the ITO and FTO film thickness, compared to the glass substrate, it is expected that most of the rotation that is measured will be due to the substrate. Results for the ITO and FTO samples (film + substrate) along with the float glass results by themselves which serve as baseline are summarized in Table II.

The most important point that the reader is expected to take away from this summary of results is that for all samples the FR measurement yields a result that is significantly different from that of the float glass substrate. This fact suggests that FR can be employed to learn more about the nature and density of the carriers. While we are still refining our ellipsometry models to extract the film thickness and index and its dispersion with greater confidence, it is clear that once that task has been accomplished one can employ Eq. 4 to either get the carrier density with a known value of effective carrier mass or go the other way and knowing the carrier mass with confidence, work out a carrier concentration. The angle used in Eq. 4 would be the one determined experimentally from using Eq. 1. Once a reliable film thickness has been established, we plan to proceed in the manner suggested by Eq. 1. The overall rotation angle is broken down into contributions from the substrate (known) and from the film (θf). This angle along with the appropriate value for film thickness can then be used to calculate the Verdet constant for the film alone. From there, as stated earlier, one can employ Eq. 4 to either get the carrier density or the carrier mass with confidence. While that work will be reported in detail in the near future, we point out that Table II contains some very interesting trends. In both the ITO and FTO samples, greater doping (or lower the resistivity), leads to higher Verdet constant. This observation clearly suggests that there is an optimum range of doping for which FR will prove to be most helpful.

V. CONCLUSIONS

We have shown that the magneto-optic technique of Faraday rotation, unlike absorbance, can provide a sensitive probe for changes in surface chemistry of glass substrates due to UV exposure. Absorbance measurements in visible range are unable to do so and

![FIG. 3. Verdet constant for quartz (left panel) and BSG (right panel) as a function of curing time showing evidence of threshold and stepwise changes, respectively.](image-url)
in UV where slight differences are shown, absorbance is unable to provide nuanced information like the onset of change as a function of time, etc.

We also show that ultrathin TCO films can be analyzed using this technique. More work is needed to extract additional information like carrier density and carrier effective mass from these results, but we have shown the feasibility of the technique beyond doubt. We feel that this approach has the potential to make FR an important and eventually, routine characterization measurement in the highly important areas of transparent and conducting substrates, and semiconductors in general.

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