Resistance Anisotropy in Transparent Conductive Films Containing Silver Nanowires

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Introduction

Transparent conductive films for touch screen applications using silver nanowire electrodes have been widely researched over the past few years. Silver nanowires are considered especially promising as transparent conductive film electrodes by virtue of silver having the highest conductivity of any metal. Films comprised of silver nanowires can also be mechanically flexible and possess attractive optical properties such as low haze and high transparency. One drawback, however, of silver nanowire films produced in a roll-to-roll coating process can be differences in sheet resistance (hereafter referred to as resistance) measured in the machine (downweb or MD) direction versus the transverse (crossweb or TD) direction. Typically, the resistance in the transverse direction, R_{TD}, is higher than the resistance in the machine direction, R_{MD}. Values of R_{TD}/R_{MD} of 1.5 – 2.0 are not uncommon. This resistance anisotropy can create inefficiencies in the touch screen module fabrication process. For instance, film yields can suffer if it is necessary to orient the conductive film in a particular direction to accommodate the anisotropy. In addition, anisotropy that is too large can cause problems with the operation of the touch controllers and can lead to errors in touch accuracy. For these reasons, it is desired to have values of R_{TD}/R_{MD} less than 1.3 and ideally less than 1.1.

This manuscript describes experimental work aimed at developing fundamental understanding of the causes of resistance anisotropy in transparent conductive films containing silver nanowires as well as experimental results on the effect of key process and formulation parameters.

Experimental

In order to measure resistance anisotropy, a pattern is etched into a 6 inch x 7 inch film using a Delphi laser. The pattern, shown in Figure 1, consists of four groups of eight channels. The channels are 39 mm long by 1 mm wide. Two groups of channels are oriented in the MD (machine) direction and two are oriented in the TD (transverse) direction. The channel ends are inked with silver paste and the resistance across the channels is measured with a Fluke multimeter.
For the experiments described below, a transparent conductive film of the construction shown in Figure 2 was used. The silver nanowire layer was coated on unprimed 100 – 125 micron PET that contained a previously applied UV curable hardcoat layer. The silver nanowire layer was slot die coated from a formulation comprised of a silver nanowire dispersion (23 nm diameter wires in isopropanol) along with binders, dispersants, surfactants, and water. The aim wet laydown was approximately 45 microns and the viscosity was about 5 cP. The silver laydown was in the range of 19 -20 mg/m² in order to achieve an average sheet resistance of approximately 50 ohms/square. A UV-curable acrylic top coat was applied to the silver nanowire layer in a separate coating operation.

**Results**

One of the causes of resistance anisotropy in coated films containing nanowires is thought to be preferential orientation of the nanowires due to shear flows in which the long dimension of the nanowires align in the downweb (MD) direction. Such shear-
induced alignment of particles with high aspect ratios is well known in fluid mechanics and is the mechanism by which solutions of many polymeric materials exhibit shear-thinning rheological behavior. For films of conductive nanowires, it is postulated that this alignment, shown schematically in Figure 3, can create $R_{TD}/R_{MD}$ values greater than 1 due to a longer range of connectivity of nanowires and reduced contact resistance.

Using the image analysis capabilities in MATLAB, it was possible to roughly measure the degree of wire alignment on experimental samples. In this analysis, -90 degrees corresponds to perfect alignment in the MD direction and 0 and -180 degrees correspond to perfect alignment in the TD direction. Figure 4 shows the distribution of measured wire alignment angles with a film sample having $R_{TD}/R_{MD} = 2.0$. Visual inspection of the image does reveal a clear orientation of the nanowires in the MD direction.

**Figure 3.** Schematic depicting nanowire alignment in the MD direction. It is hypothesized that such alignment can result in lower values of $R_{MD}$ compared to $R_{TD}$.

**Figure 4.** Photograph of film sample having $R_{TD}/R_{MD} = 2.0$ with corresponding distribution of wire alignment angles using Matlab image analysis. An angle of -90 degrees corresponds to alignment in the MD direction.
It has been found that lower values of anisotropy correspond to a distribution of nanowire alignment angles that are less oriented in the MD direction as indicated by larger standard deviations of nanowire alignment angles around the mean as shown in Figure 5 for experimental data obtained for slot die coatings described in the previous section.

Figure 5. Correlation between $R_{TD}/R_{MD}$ and standard deviation of nanowire alignment angles. Lower values of anisotropy are associated with nanowire distributions that are less oriented in the MD direction as measured by higher standard deviations.

The coating solution exhibits different shear rates as it moves through the slot die process. This is shown in Figure 6 using expressions for representative shear rates described by Schweizer\(^1\). Relatively high shear rates in an orientation that may promote downweb wire alignment exist close to the coating point, specifically in the narrow die slot and the coating bead.

Figure 6. Representative shear rates in various locations of slot die coating process. High shear rates occur in the die and at the coating point. The coating conditions are: coating speed, $S=102$ cm/s; slot height, $h=127$ microns; lip-to-web gap, $G=127$ microns; solution delivery line radius, $R=0.95$ cm; volumetric flow rate, $Q=3.6$ L/min; coating width, $W=1350$ mm.

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\(^1\) Schweizer, P.M., “Viscosity vs. Rheology,” Converting Quarterly, Quarter 3 2016, pp. 86-89.
As shown in Figure 6, the shear rate in the narrow die slot is a strong function of the value of the slot height. Figure 7 shows the result of an experiment to investigate the effect of the slot height on resistance anisotropy. In this experiment, the slot height was varied from 50 - 250 microns. This 5x change in slot height results in a 25x variation in wall shear rate in the slot. Given this large change in shear rate, it might be expected that there would be a large change in anisotropy with lower anisotropy occurring at the large slot heights. While the anisotropy does decrease with slot height, the decrease is modest. It may be that even the relatively low die slot shear rate at large die slot heights is sufficient to provide significant alignment in the downweb direction. In fact, Zhou et al.² visualized silver nanowire solutions on a microscope slide after processing in a rotational rheometer. They demonstrated that silver nanowire alignment can occur due to shear flows as low as 10 sec⁻¹.

![Figure 7. Effect of die slot height on resistance anisotropy. Anisotropy decreases only slightly with increasing slot height despite the large change in slot shear rate with increasing slot height.](image)

Drying conditions were found to have a significant impact on resistance anisotropy. In particular, higher air flows early in the dryer were found to reduce the Rₜₖ/Rₘₖ ratio. This is shown in Figure 8 for an experiment in a two-zone dryer in which the fan speeds that feed the dryer distribution slots in each zone were varied. Lower anisotropy was obtained when the fan speed in the first dryer zone was increased. Increased fan speeds correspond to an increase in air velocity in the TD direction as shown in Figure 9a. It is postulated that higher air flows in the TD direction early in the drying process may act to reorient the nanowires to be less aligned from their initial downweb orientation as a result of the die flow and coating processes.

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In order to avoid excessive direct air impingement that could lead to coating thickness differences, baffles were installed on the slot distributors in the first dryer zone. A schematic of the distributor and baffle design is shown in Figure 9b.

Conclusions and Recommendations for Future Work

Nanowire alignment in the downweb (MD) direction has been proposed as a cause of resistance anisotropy in transparent conductive films (TCFs) containing silver nanowires. While more work is needed, initial image analysis has shown a reasonable correlation between nanowire alignment and resistance anisotropy. Drying conditions were found to have a significant effect on anisotropy. Increased air flows early in the dryers were found
to reduce anisotropy, possibly through air driven randomization of nanowires after coating.

Given the strong effect that dryer conditions have on anisotropy, it is recommended that future work include studies of formulation parameters that influence flow after coating such as viscosity and wet laydown as well as dryer air flow parameters such as direction of air relative to the web (concurrent, countercurrent, and crosscurrent). Experiments should also include investigations of fundamental nanowire characteristics such as diameter and length. Finally, there should be a focus on studying additional coating methods that may have a lower propensity to orient the wires in the downstream direction. Preliminary lab investigations of spray coating and Mayer rod coating indicate that these methods show promise with respect to reducing wire alignment. As shown in Figure 10, the wire alignment distribution angles are distinctly different than the samples generated from our slot die experiments shown previously.