[Electronic materials Experiment]

Nanowire-based transparent electrodes for flexible electronics

1. Experiment summary and objectives
	1. Experiment summary

Electronics have a close relationship with our everyday lives. People use smart phones, tablet PCs, desktop computers, laptops, etc. on a daily basis. These devices have in common the fact that they need high-performance, high-resolution display panels, highlighting the need for highly transparent and conductive thin film electrodes.

ITO(tin-doped indium oxide)s are conventionally used in these thin film electrodes. However, ITO glasses are very brittle, have limited flexibility, and are increasing in price due to high demand. Therefore, new materials have to be considered for these uses.

Materials that meet the required conditions include conductive polymers, graphene, metal nanowires and carbon nanotubes. Out of all metal nanowires, silver nanowires have the biggest potential as silver has the highest conductivity of all metals and has a relatively low cost, 1/80 of that of gold. Also, silver is very flexible, lowering the probability of brittle fracture taking place. As can be seen in [Fig 1], having a high conductivity and a low cost is a big advantage when compared to ITO. On the other hand, there is room for improvement when using silver nanowires for electrodes. Many works focus on solving problems such as conductance changes coming from junctions between nanowires, low adhesion with the substrate material, decreased efficiency coming from empty spaces between the nanowires, and oxidation or melting from annealing.

Figure 1: Cost vs Conductivity of many electrode materials

Finding an efficient yet simple way to improve the conductance of flexible electronics is very important as flexible substrates experience rupture in temperatures higher than 200 degrees. In this experiment, we aspire to find an optimal silver nanowire solution concentration, spin coating and annealing conditions for highly conductive transparent thin films.

* 1. Experiment objectives

The objectives of this experiment are to:

• Study how to synthesize silver nanowires and succeed in synthesis.

• Make a transparent electrode on a glass substrate using silver nanowires.

• Improve the efficiency of transparent electrodes by changing the silver nanowire solution concentration, spin coating and annealing conditions.

• Understand how 4-point probe measurement works, and use a 4-point probe to measure the sheet resistance of a transparent electrode.

• Know how to use a UV-vis spectrophotometer and measure the transmittance of a transparent electrode.

• Know what the definition of Figure of merit(FOM) is and calculate the figure of merit of your own transparent electrode.

1. Theoretical background



Figure 2 : Mimetic diagram of spin coating

* 1. Spin coating

Spin coating is a technique used to make a homogeneous thin film on top of a flat surface. After dropping a solution on a substrate surface, the substrate is rotated at a high speed, evaporating the solvent using centrifugal force. When the solvent evaporates, a thin film remains on the substrate. The thickness of the thin film depends on the coating materials characteristics (viscosity, density, concentration, surface tension, etc.) and spin coating conditions (spinning speed, etc.).

The theoretical background of spin coating lies in fluid mechanics, and analysis is carried out using models based on physics and mathematics. For a basic physical analysis, we choose a simple model where a viscous fluid is applied to a spinning disk. This model has the following assumptions:

1. The disk is level with the surface and is not subject to gravity.
2. The thickness of the liquid film is small enough to ignore the gravitational potential perpendicular to the surface.
3. The radial speed is small enough to ignore the Coriolis force.

A few more assumptions are added to further simply the model:

1. The rotating disk is infinitely large.
2. The liquid layer is symmetrical in all directions.
3. The liquid shows Newtonian behavior.
4. The shear resistance is only considered for the horizontal plane.
5. The wetting of the surface of the disk is sufficient.

Although these assumptions are not exactly defined, they provide a means for an efficient quantitative analysis.

1. UV-vis spectroscopy

Figure 3: Mimetic diagram of UV-vis measurement

A quantitative, qualitative analysis of an unknown sample can be made by using the UV-VIS Spectrophotometer, using the light absorbing phenomena when exposing UV/visible light. When external energy is given to an atom or molecule, many different things happen depending on the size of the given energy. When a molecule absorbs UV-vis, the ground state of a bounded/unbounded electron turns into an excited state, releases its energy through a variety of methods, and returns back to its ground state. If we know the absorbing wavelength, we can predict the structure of the atom or molecule.

The radiant rays are converted into a single or narrow wavelength by using a spectroscope such as a color filter or prism. This resulting ray is passed through the sample solution and are measured for analysis. If we know the exact amount of absorbance the concentration of the atoms or molecules can be calculated. This can be expressed as the beer-lambert equation $A=log\frac{I\_{0}}{I}=εlc$. (A : absorbance, $ε$ : extinction coefficient l : path length, c : concentration)

1. 4-point probe measurement

Figure 4: Image of a 4 Point Probe

The 4-point-probe is widely used to measure the sheet resistance or resistivity of silicon wafers and conductive thin films. It consists of 4 probes placed side-by-side in a row, and carries out measurement by contacting the probes with a sample surface. The 4-point-probe first measures the sheet resistance by factoring in the sample size and probe distance, and multiplies it by the sample thickness to measure the resistivity.

The sheet resistance using the 4-point-probe is measured by flowing a current through probe A and D, and measuring the voltage between probe B and C, as can be seen in [Figure 4] and the following equation:



The sheet resistance  can be expressed as the following:



$K\_{s}$ is a constant and defined as the following:



The reisistivity($ρ$) can be obtained by multiplying the sheet resistance by the thickness of the sample:



The F(D/S) in the equation above is the correction factor for the sample size D relative to the probe distance S. If the sample size D is infinity large relative to the probe distance S, the correction factor F(D/S)=4.5324. The correction factor F(t/S) is 0.9995 when the Probe Distance S is 1mm and sample thickness t is 0.4mm.

F(T) is a correction factor related to the measured temperature, which is needed because resistors such as silicon wafers are affected by temperature. If possible, measurement should be carried out in a laboratory environment where the temperature is fixed.

 is a correction factor related to the distance of the probes as the following:



S2 is the distance between the measurement probes; F(S) has an error of below 0.1% when . Conventionally, the error coming from F(S) is given from the manufacturer. When  is below 0.3%, we apply a correction factor of 1.

In the case of a nanowire thin film, the thickness of the film is usually hard to measure; in which case we use the sheet resistance having the unit [Ohm/square]. Here, the area of the square does not affect the overall resistance of the square, and as a result, if the number of squares are the same, the overall resistance is also the same. This can be seen in [Figure 5].

1. Figure of merit(FOM)

The Figure of merit(FOM) provides a means to quantitatively compare the performance of a device, system, or methodology. In transparent conductors, the following equation is used for the figure of merit, where T is the transmittance and Rsh is the sheet resistance:

Figure 5: Two samples having the same sheet resistance and total resistance values

$$ϕ\_{TC}= \frac{T^{10}}{R\_{sh}}$$

1. Experiment schedule

|  |  |  |
| --- | --- | --- |
| Time | Objective | Content |
| Ch. 1 | Study how to synthesize silver nanowires and succeed in synthesis | Synthesis of silver nanowires through pre-investigated methods |
| Ch. 2 | Make a transparent electrode on a glass substrate using silver nanowires. | Glass cleaning *via* sonicationTransparent electrode fabrication on glass substrate *via* spin-coating |
| Ch. 3 | Improve the efficiency of transparent electrodes by changing the silver nanowire solution concentration, spin coating and annealing conditions. | Improvement of electrical characteristics of transparent electrodes by annealing *via* Hot plate |
| Ch. 4 | Understand how 4-point probe measurement works, and use a 4-point probe to measure the sheet resistance of a transparent electrode. | Sheet resistance measurement of transparent electrodes *via* 4-point probe |
| Ch. 5 | Know how to use a UV-vis spectrophotometer and measure the transmittance of a transparent electrode. | Transmittance measurement of transparent electrodes *via* UV-vis spectrophotometer(Will be evaluated by measuring the transmittance at 550nm) |
| Ch. 6 | Optimize your transparent thin film electrode | Optimization of transparent electrodes and calculation of figure of merit |

1. Apparatus
	1. Experiment Apparatus
		1. Sonicator

|  |  |
| --- | --- |
| Apparatus name | Apparatus picture |
| Sonicator |  |
| Model(Company name) |
| POWERSONIC405(화신테크) |
| Usage | • Uses supersonic saves to clean the surface of a substrate |
| ApparatusInformation | • Oscillation frequency: 40KHz• Power consumption: 350 Watt• Can control the power of sonic waves by 3 levels |

* + 1. Spin coater

|  |  |
| --- | --- |
| Apparatus name | Apparatus picture |
| Spin coater |  |
| Model(Company name) |
| NSF-100DP(랍도스) |
| Usage | • Deposits silver nanowires on top of a glass substrate |
| ApparatusInformation | • Programmable rotation speed: 40~10000RPM• Programmable time: 1~1000s• Maximum number of steps: 100 |

* + 1. Hot plate

|  |  |
| --- | --- |
| Apparatus name | Apparatus picture |
| Hot plate &Magnetic stirrer |  |
| Model(Company name) |
| HS180(미성과학기기) |
| Usage | • Used to anneal the silver nanowires on top of a glass substrate  |
| ApparatusInformation | • Max temperature: 380℃• Temperature error: 1℃• Heater output: 680W |

* 1. Characterizing apparatus
		1. UV-vis Spectrophotometer

|  |  |
| --- | --- |
| Apparatus name | Apparatus picture |
| UV-VIS-NIR Spectrophotometer |  |
| Model(Company name) |
| Cary 5000(Agilent Technologies) |
| Usage | • Measures the absorbance/transmittance spectrum of organic/inorganic materials• Measures the refraction of a power sample• Measures the refraction or transparency spectrum of a film• Measures the Energy band gap of a sample |
| ApparatusInformation | • Wavelength range: 175-3300nm• Limiting resolution: <0.048 nm at UV-vis• Monochromator: Double out-of-plane Littrow monochromator• Detectors: R928 PMT for UV-vis |

* + 1. 4-Point probe

|  |  |
| --- | --- |
| Apparatus name | Apparatus picture |
| 4-point probe  |  |
| Model(Company name) |
| CMT-SR2000N |
| Usage | • Measures the sheet resistance of a given sample |
| ApparatusInformation | • Measurement range: 1mohm/sq ~ 2Mohm/sq• Resistivity measurement range: 10.0 uohm•cm ~ 200.0 kohm•cm• Measurement error: 0.5% |

1. Experiment methods and result analysis
	1. Substrate cleaning

 1) Cut a number of 1”x3” slide glasses into 1”x1” glasses depending on your need.

 2) Put the cut glasses into a glass staining jar. Put in acetone into the jar and sonicate for 5 minutes.

 3) Repeat 2) using DI water and Isopropanol instead of acetone.

4) Before spin coating, use the air gun connected to the nitrogen gas canister to blow of any residual solution on the surface of the glass. Lock the air gun by turning the gas canister nozzle in a clock-wise direction.

* 1. Spin coating

1) Fix the substrate material by putting it on the vacuum chuck and turning the vacuum on.

2) Apply silver nanowire solution so as it covers the substrate material.

3) Use the spin coater for about a minute so that the solvent is all evaporated, at an rpm of your choice.

4) After turning the vacuum off, use tweezers to move the sample to a sample container.

5) Turn of the Spin coater by pressing the power switch.

* 1. Annealing *via* hotplate

 1) Turn the hot plate on.

 2) Press on the “MD” button until a blinking “Su” display appears. Designate the target temperature by pressing the arrow buttons.

3) When pressing on the “MD” button again, the temperature will begin to rise. Wait for approximately 5 minutes for the temperature to rise to the intended temperature.

4) After annealing the sample for 10 minutes, remove the sample from the hot plate. Before moving the sample to the sample container, cool the sample in open air for 1-2 minutes.

5) Following the same procedures for designating a high temperature, set the temperature to below 20 degrees. After confirming that the temperature is below 30 degrees, turn the hot plate off.

* 1. 4-point probe measurement

1) Place your sample on the middle of the apparatus. Turn on the measurement program and set it to “Sheet resistance measurement mode”.

2) Measure the sheet resistance after designating the measurement spot.

3) Turn of the computer and the apparatus.

* 1. UV-vis measurement

 1) Turn on the UV-vis apparatus, and position your sample in the device.

 2) Set the mode to “Single front”, and the measurement range to the visible range (300-700nm)

3) After measurement, save your data as a .csv file and later analyze the penetrance at 550nm, using origin.

4) Turn off the UV-vis apparatus and the computer. Make sure you don’t leave anything behind.

1. Results and discussion
2. By changing the concentration of silver nanowires, annealing temperature and time, optimize the figure of merit for your transparent electrode. Include a table with information regarding silver nanowire concentration and annealing temperature in your final report.
3. If there is a tendency in sheet resistance relative to annealing temperature, time, or the concentration of silver nanowires, present your findings in your final report with a brief explanation on why these trends appear.
4. Evaluation Criteria and must-haves in your reports
	1. Evaluation criteria

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Initial report | Final report | Experiment results | Attendance | Participation |
| Percentage | 30% | 40% | 20% | 10% | +ɑ  |

* 1. Must-haves in your initial report
		1. Read the following research paper and give a brief summary of how to synthesize silver nanowires. (Search the following paper in scholar.google.com)

**Li, Bo, et al. "Synthesis and Purification of Silver Nanowires To Make Conducting Films with a Transmittance of 99%." *Nano letters* 15.10 (2015): 6722-6726.**

* + 1. Find, if any, other Figure of merits that determine the performance of transparent electrodes than the one given in this manual, and give a brief explanation about it. (Make sure to include the reference)
	1. Must-haves in your final report
		1. Processes and pictures of transparent electrode fabrication
		2. Calculate the Figure of merit of your electrodes, and compare them to other works. (Make sure to include the reference. By works, you have to search for other research papers.)
		3. Think and write about methods to realize transparent electrodes with higher Figures of merit.

1. Reference
1) G. Haacke, “New figure of merit for transparent conductors,” Journal of Applied Physics, vol. 47, no. 9, pp. 4086–4089, 1976.

2) Emslie, Alfred G., Francis T. Bonner, and Leslie G. Peck. "Flow of a viscous liquid on a rotating disk." *Journal of Applied Physics* 29.5 (1958): 858-862.

3) Schwartz, Leonard W., and R. Valery Roy. "Theoretical and numerical results for spin coating of viscous liquids." *Physics of Fluids (1994-present)* 16.3 (2004): 569-584.

4) Smits, F. M. "Measurement of sheet resistivities with the four‐point probe." *Bell System Technical Journal* 37.3 (1958): 711-718.

5) Swclrizendruber, Lydon J. "Correction factor tables for four-point probe resistivity measurements on thin, circular semiconductor samples." (1964).

6) Khaligh, Hadi Hosseinzadeh. "Silver Nanowire Transparent Electrodes: Fabrication, Characterization, and Device Integration." *University of Waterloo*(2013).

7) Sergio B. Sepulveda-Mora1 and Sylvain G. Cloutier “ Figures of Merit for High-Performance Transparent Electrodes Using Dip-Coated Silver Nanowire Networks”. Hindawi Publishing CorporationJournal of Nanomaterials Volume 2012, Article ID 286104, 7 pages