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DEPOSITION AND CHARACTERIZATION OF DOPED CARBON NANOTUBE THIN FILM ON GLASS SUBSTRATE

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ABSTRACT: *The carbon nanotubes (CNTs) as transparent conducting films is the most promising aspects of CNT-based applications due to its optical and electrical properties. The films were prepared using chemical vapour deposition method (CVD).The fabricated thin films were characterized using the profilometry machine, UV-Spectophotometry and Hall effects machine to investigate its optical and electrical properties, thickness of the thin films, sheet resistance, and conductivity. We observed that higher thin film thickness produce higher conductivity. For the wash and dry samples with the highest thickness of 0.26 nm at 106^{0}C temperature exhibits the highest maximum conductivity σ of 2E 1/Ωcm with relatively smallest sheet resistance of 2.5E + 08Ωcm while the wash at 400^{0}C doped and dry sample show the smallest thickness of thin films of about 0.4 nm with temperature of 101^{0}C. It was observed that the conductivity was 2E-04 1/Ωcm and has a higher sheet resistance of 4.6E + 08Ωcm.*
KEYWORDS: transparent conductive films, carbon nanotube, chemical vapour deposition method, UV-Spectophotometry, profilometry machine.

INTRODUCTION

Transparent conductive films (TCFs) are films of electrically and optically transparent conductive materials. Currently, indium tin oxide (ITO) is the prevailing material used for large industrial-scale transparent conductive films application. Indium tin oxide (ITO) does not only have excellent properties with a sheet resistance of 10 Ω/square at around 90% optical transmittance, but also exhibits high compatibility and stability with both wet and dry device processes (Hua et al, 2017). However, future optoelectronics require TCF materials which are automatically bendable, lightweight and low cost of fabrication. The growing need for ITO due to the development of solar cells may lead to an increase in considerable cost because of the relatively rare element of indium. ITO suffers from poor involuntary suppleness, which reduces its application for emerging bendable, wearable and stretchable electronic applications. These important limitations of ITO have been motivating research for alternative TCF materials for large industrial-scale use including novel metal oxides, conducting polymers, metal nanowires, metal grids and carbon nanomaterials (Chkoda et al, 2000).The best TCFs using Cu NWs gives a sheet resistance of 100 Ω/square and 95% transmittance. The stability of Cu NWs against oxidization is a dispute (Minami, 2005). Graphene shows very good electrical and optical properties in theory, and therefore it can be an ideal material for TCF application. However, the electrical properties strongly depend on the quality of graphene. The best TCFs using four or five layers of mechanically exfoliated graphene show a low sheet resistance of 8.8 O/square at transmittance of 84%. Solution processed graphene TCFs generally show a sheet resistance of above 1000 O/square at transmittance of 85% (Tung et al, 2009). Carbon nanotubes (CNTs) are high aspect ratio conducting nanomaterials that demonstrate

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excellent optical and electronic properties. The ideal building blocks are arranged in a randomly oriented, highly connected nanoporous and thin continuous network. . CNTs are built from sp2 bonds carbon units and present a seamless structure with hexagonal honeycomb lattices (Jackson, 2009). Basically, there are two types of CNTs: Single-walled carbon nanotubes (SFWCNTs) and Multi-walled carbon nanotubes (MWCNTs). SWCNTs are single graphene rolls with diameters of 0.8 to a few nanometers while MWCNTs are concentric grapheme tubes whose diameters range from a few to more than a hundred nanometers. Many experimental and theoretical works have exposed the outstanding properties of CNTs. Single-walled carbon nanotubes (SWCNTs) display a metallic or semiconducting electronic property which depends on the chirality of the nanotube (Jorio et al., 2008). When a network of separated metallic SWCNTs is deposited on a substrate forming a thin film with thickness in the range of 10-250 nm, it exhibits some properties of transparent conducting film; tin-doped indium oxides (ITO) are important material for many electronic device applications (Mizuhashi, 1980). The demand for transparent conductors is expected to grow continuously as electronic devices, such as displays, solar cells and touch screens are becoming more interactive and seen everywhere. However, commonly used transparent conductor materials such as Indium tin oxide (ITO) are scares, expensive, and also suffers from thermal degradation. Consequently, there is a need for alternative materials that are cheaper with high performance. Such materials are carbon nanotube thin films that have high potential performance transparent conductor.

METHODOLOGY

A SWCNTs source used were obtained from a research institute synthesized by chemical vapour deposition (CVD).

Figure 2.1: Single walled carbon nanotube used

A microscopic glass slide is a thin flat piece of glass, typically 76.2 ×24.5mm, and 1.2mm thick, used to hold objects for examination under a microscope.

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Figure 2.2: Sample of Glass Slide

The syringe was used to control the dispensing of the carbon nana tube (CNT) (flowmetering). It was used to control the pressure of the flow of the CNT.

Figure 2.3: Sample of syringe used.

Figure 2.4: Thermocouple

The thermocouple was used to regulate the temperature at which each sample was consider, the hot plate was also controlled by the thermocouple to dry the soda lime glass which was deposited with the CNT and the nitric acid.

Figure 2.5: Experimental Setup

The spray nozzle is a precision device that enhances the dispersion of liquid. The spray nozzle was used for itemization.

Six samples of CNT film were grown at various volume, at various temperatures, the samples were characterized at Sheda Science and Technology Complex, Abuja (SHETSCO) using UV-Avec 2048 Spectrometer, profiler.
The first sample was considered unwashed and unannealed, the soda lime glass which was not conducting is place on the Robert machine to spray, after which it was tested with a multimeter to check if it was conducting, thereafter it was doped with(Nitric Acid) for about 30 minutes at 70 ^{o}C.

Figure 2.6: Processed Sample

The second sample that was carried out was washed and dried at 400 ^{o}C which was also tested to know if it was conducting. This sample was also doped for about 30minutes.

The third sample was washed and dried at 400 ^{o}C and then doped with Nitric acid.

The fourth samples was just only washed and dried with soda lime glass of 76.2 mm of length with the width of 24.5 mm.

The fifth samples was washed and dried at 400^{o}c with the soda lime glass of 76.2 mm with the width of 24.5 mm for each of the samples has different temperature and time.

The last Sample was washed and dried, making used of the soda lime glass, thereafter, it was tested to check if it was conducting using the multimeter.

Film preparation Process

The concentration of CNTs used was typically 1.1 mg / 2 ml. Then the solution was bath sonicated for 12 hour, followed by centrifugation at 16,000 rpm for 60 minutes. During centrifugation residual metal catalysts and impurities from the manufacturer and any large undissolved aggregates and bundles were forced to the bottom of the solution due to centrifugal forces created during the process. The CNTs were grown on a slide measuring about 76.2 × 24.5mm, and 1.2mm thick. The CNT deposit on the silicon was mechanically removed for the characterization and the purification processes. The dispersion of CNT thin films, involved a lot of technology. The first is the flow metering rate which is the ability to determine the flow rate of the CNT thin films; this was done by dispersing the CNT. The syringe pump which is programmable was also used in the process of dispersing of the CNT thin films and to control the pressure to enable the CNT to flow at a required rate. This syringe was used to reduce the air that is in the system. The carbon nanotube was dispersing with sodium lauryl surface, which was also used as the solvent to make the result accurate. The syringe pump was programmed to pump at about 1000μL/hr.

A test run was done on the surface slide for the Robert machine to spray on to check properly if sprayed the way it should be. We consider a repeatable method to slidize the shape from the software. A total of six (6) samples were used for the experiment.

Figure 2.7: Snap shot across the six (6) sample on a petri-dish.

Table 2.1 represent each of the samples, the time of spraying, temperature and the thickness involved.

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Six (6) Samples	**Volume (ml)**	**Sprayi ngTim e (Min)**	**Temperature**	**Thickness**
Unwashed& Unannealed	13	10	84°C	0.15μm
W@400°C	19	18	98°C	0.1μm
W+Dr	24	16	101°C	0.26μm
W+D@400°C	34	20	102°C	0.2μm
W+D+Dr	39	18	105°C	0.2μm
W@400°C+D+Dr	44	28	106°C	0.14μm

W = Wash
D = Doped
Dr = Dry
The thermocouple was used to regulate the temperature at which each sample was consider, the hot plate was also controlled by the thermocouple to dry the soda lime glass which was deposited with the CNT and the nitric acid.

The infrared thermometer was use to check the temperature, for each of the sample that was carry out. There were other glasses like the borosicate glass which is more superior to the soda lime glass, it contains more than the soda lime glass but it has a deficiency; it is very fragile.

Characterization Process

In this study, the profilometer was used to estimate the surface roughness and film thickness by measuring the step size between thin film edge and glass surface of the six (6) samples, the optical properties were obtained using UV-Spec machine and was also used to estimate the transmittance of the transparent film within the visible light wavelength range. Two terminal I-V electrical measurements was done using the Ecopia HMS-3000 Hall Effect Measurement system to estimate the resistivity, ρ, conductivity, σ and sheet resistance, R*s* of the six (6) samples.

RESULTS AND DISCUSSION

A profilometer was used to characterize the surface roughness of the CNT films. A total of 29 random line scans of 500 – 2000 μm in length were taken over six (6) samples. The characterization micrographs are shown in figure 3.1(a-f):

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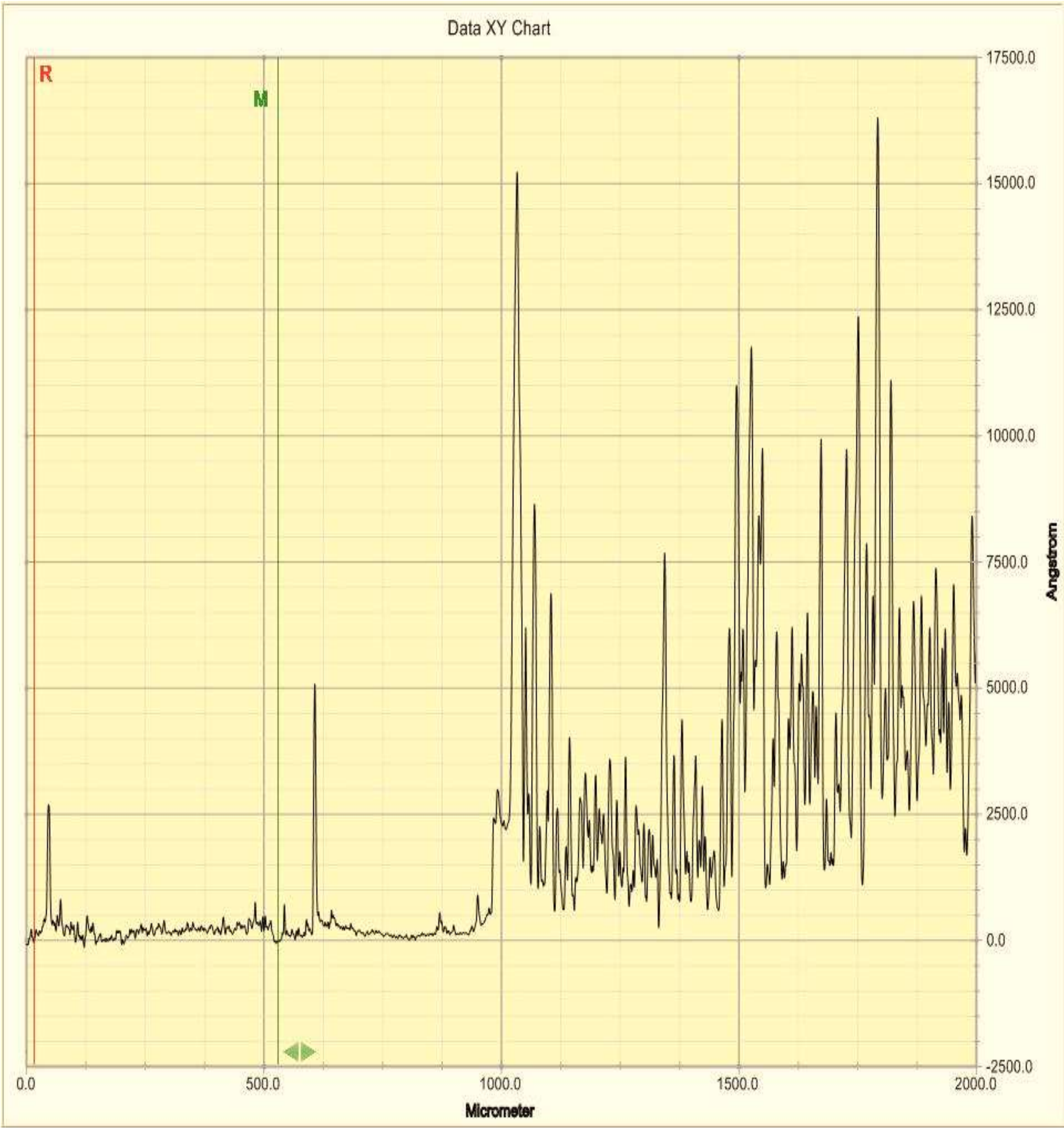


Figure: 3.1(a): Surface height profiles for samples, unwashed and unannealed;

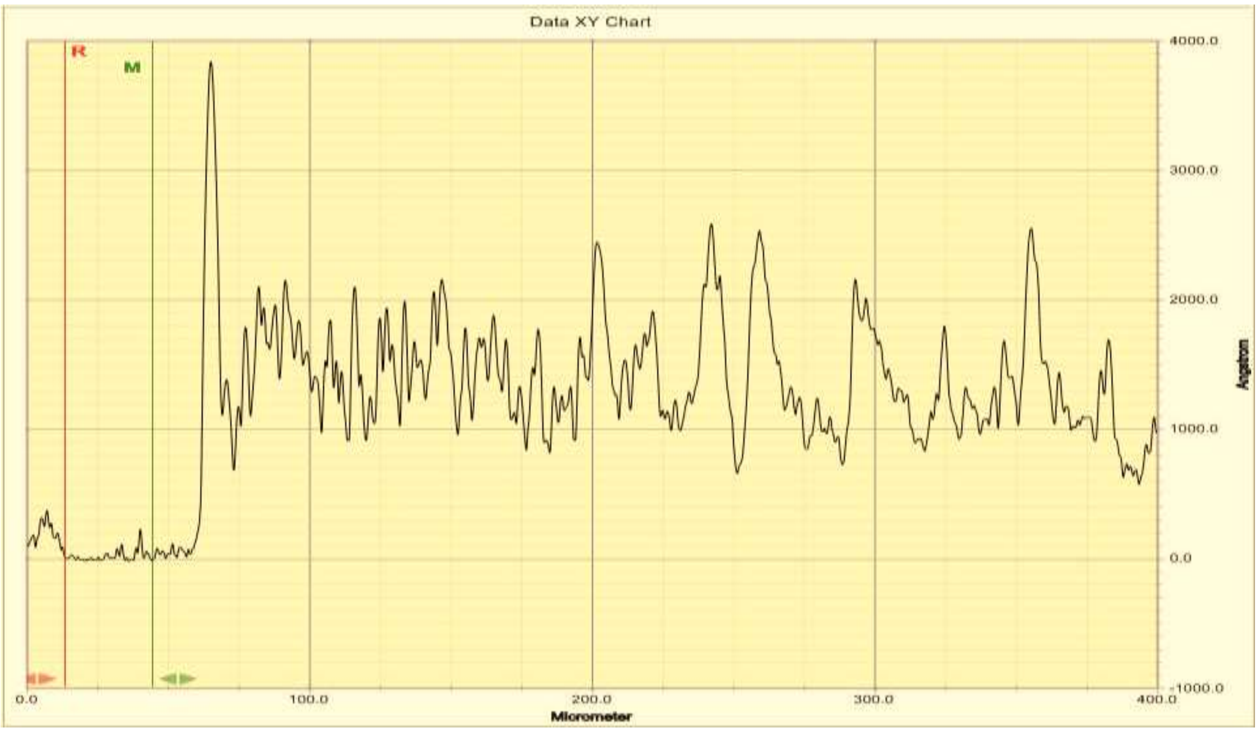


Figure 3.1(b): Surface height profiles for the washed samples

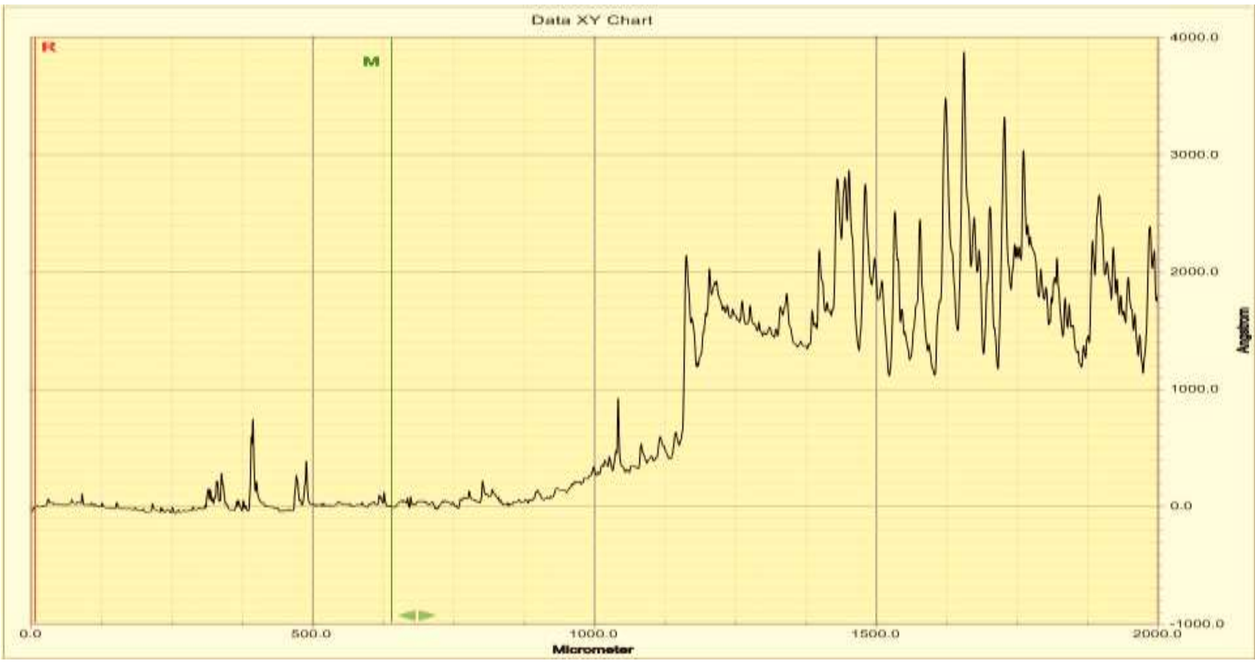


Figure 3.1(c): Surface height profile for sample Washed @ 400^oC, Doped and Dried

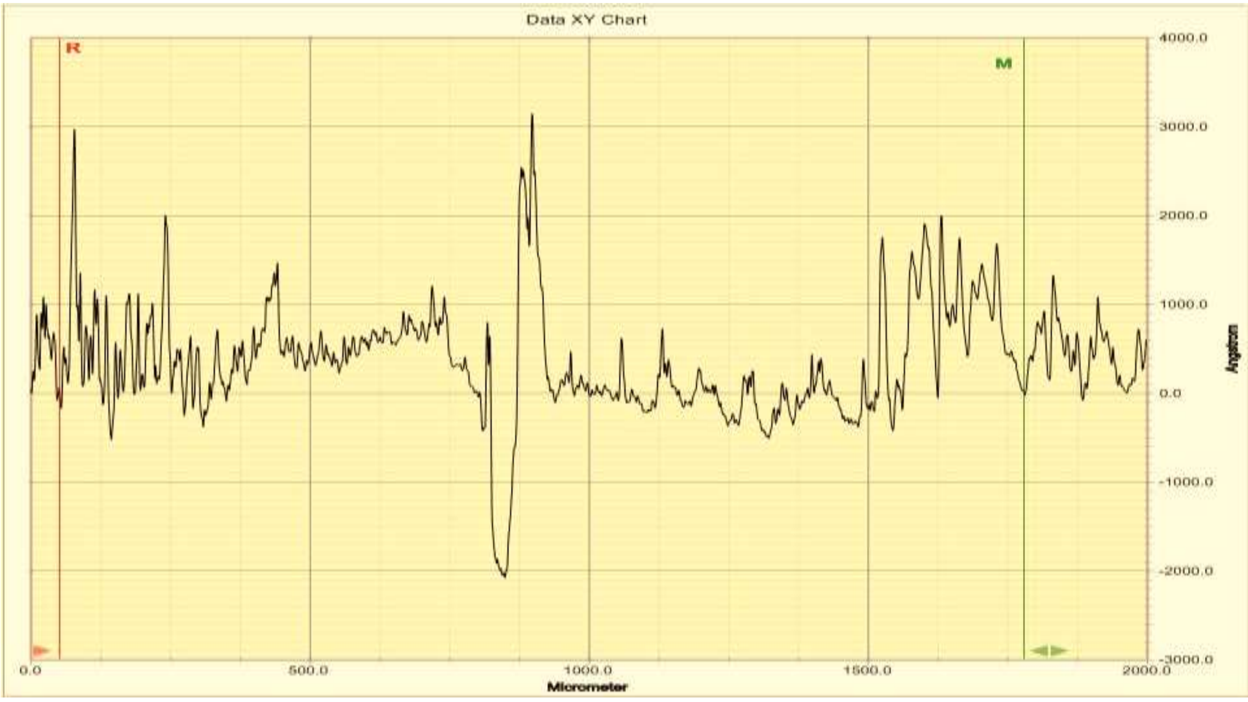
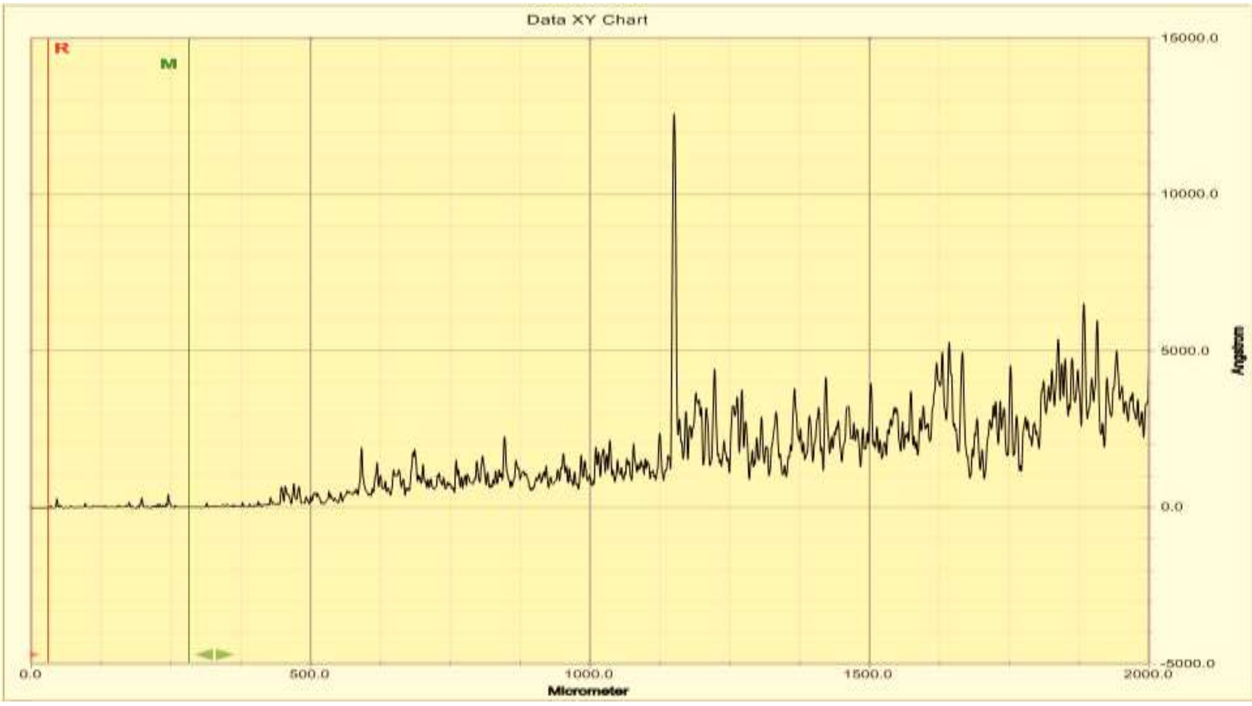


Figure 3.1(d): Surface height profiles for the Sample Washed, Doped at 400^{o}C

Figure 3.1(e): Surface height profiles for Sample Washed, Doped and Dried



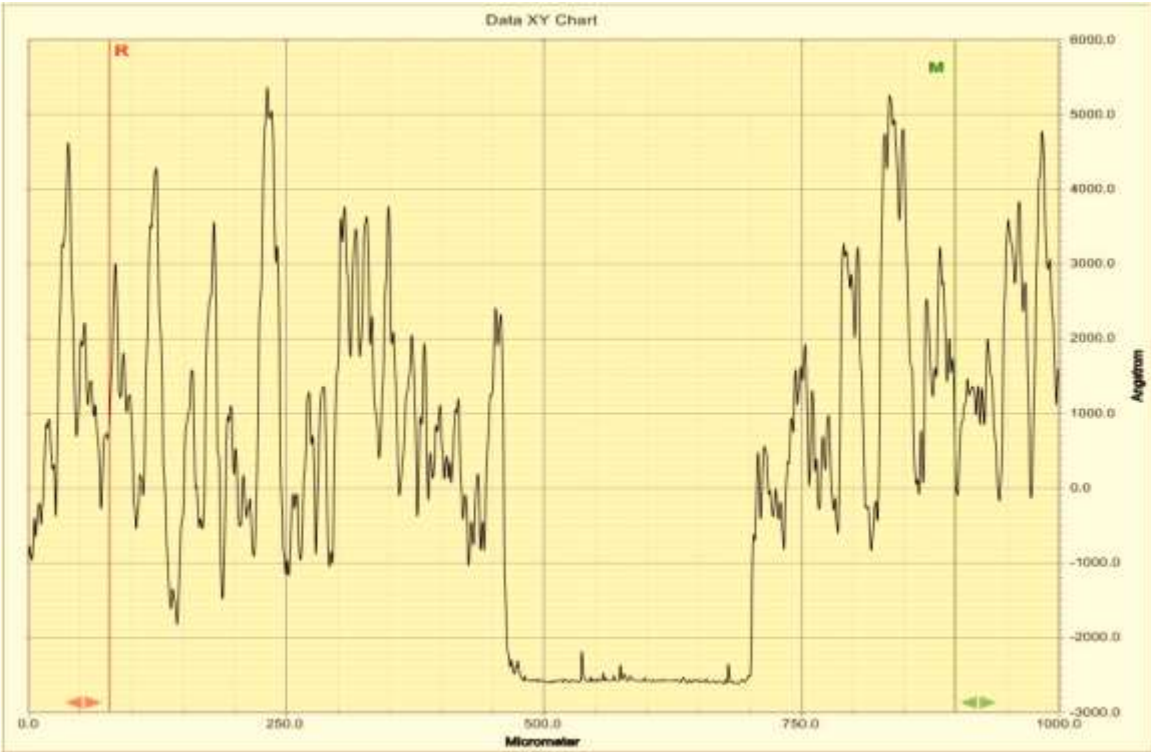


Figure 3.1(f): Surface heights profiles for Sample Washed and Dried

From the graphs 3.1(a-f), It was observed that the various samples have different Thickness, Temperature, Conductivity, Sheet resistance, Bulk concentration, Mobility etc. This was as a result of different techniques used in the samples which show that various techniques have constantly increased the various thin films as expected.

Optical Characterization of the Film.

The ultra-ultraviolet-visible spectroscopy (UV-Vis) spectrometers optical absorption spectra for all six (6) sampled film are shown in Figure 3.2 The transmittance and optical absorption measurements are shown in Figure 3.2 (a) and 3.2(b), respectively.

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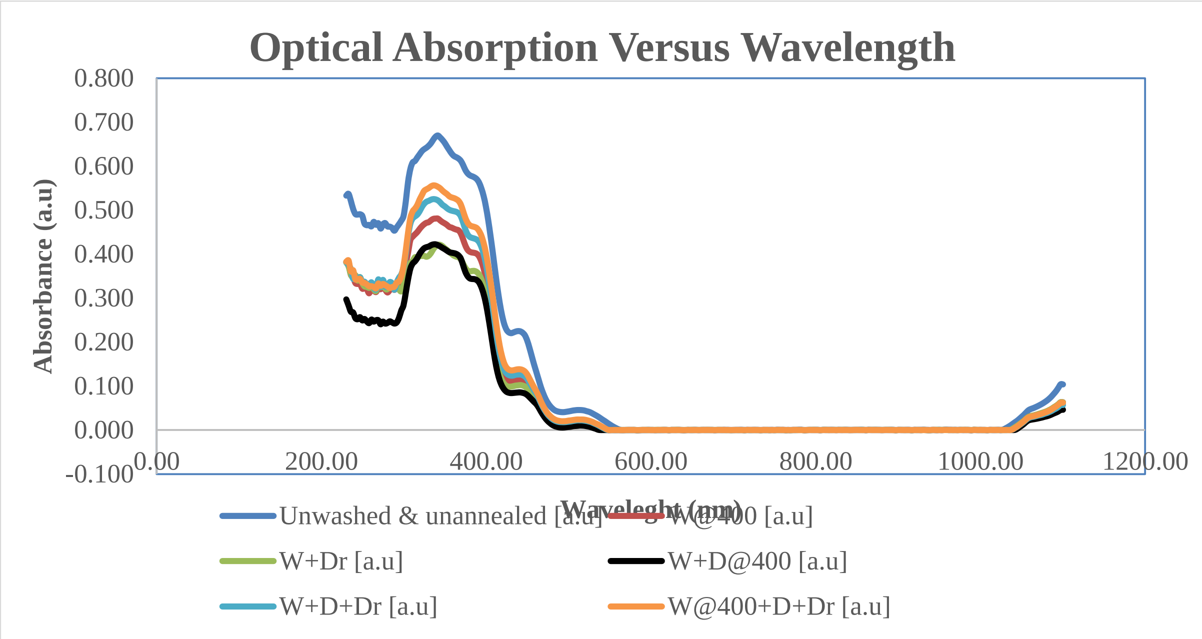

Figure 3.2a: The UV-Vis spectrometers optical absorption measurement spectra of all six (6) samples film.

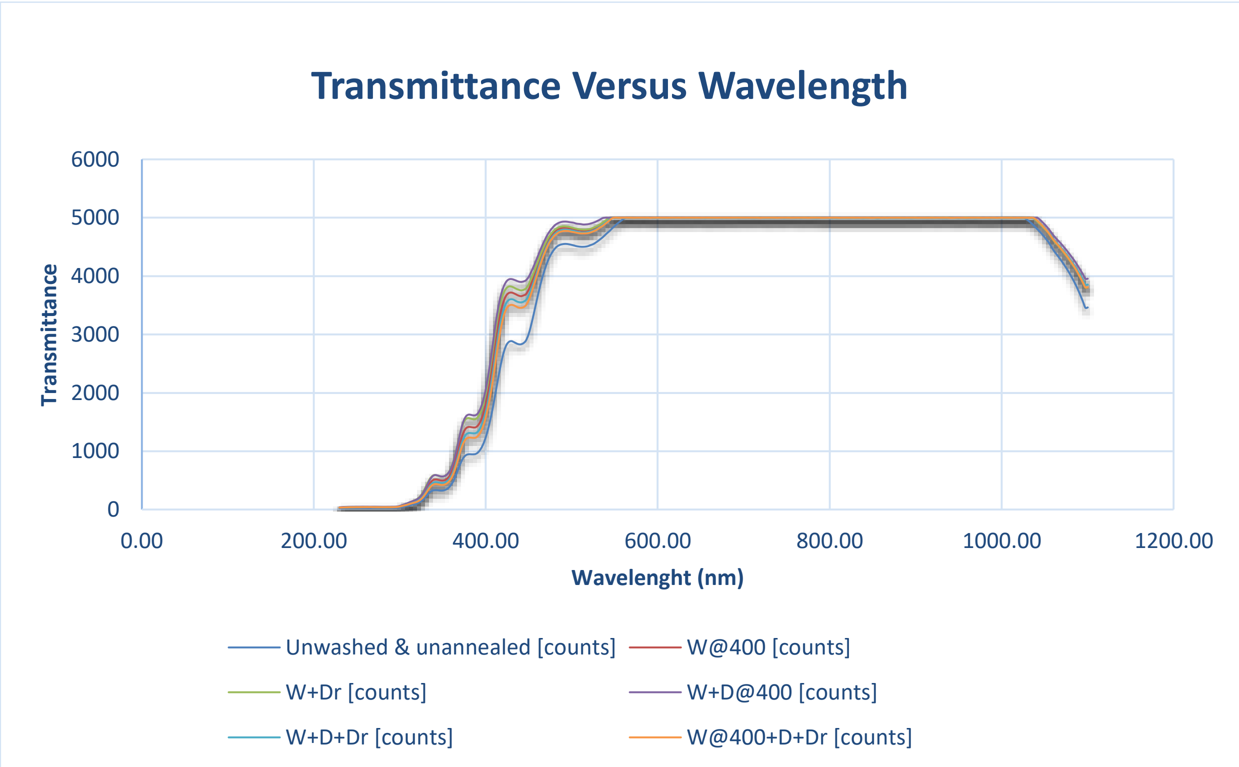

Figure: 3.2b: Relationship between Transmittance Versus Wavelength

The optical absorption measurement of the films, it is expected that all three spectra show identical curve with respect to wavelength owing the fact that the films were fabricated from the same SWCNT source. However, this is not the case as evident of the spectra in Figure 3.2(a). The curve profile for the unwashed and unannealed film

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shows expected ripple peaks associated to SWCNTs of different chirality and diameter, hence the band gap. The same cannot be said for the washed, doped and dried samples curves most probably due to the low absorption resulting from them having relatively small film thickness compared to unwashed and unannealed film. This is not an issue as far as transparent conductors are concerned and only important if the films were to be fabricated into thin film transistors. For the application of the films as a transparent conductor. The TM measured for all films fall within acceptable limit as practical transparent conductor applications.

Table 3.1: Electrical characterization parameters of single wall carbon nanotubes (SWCNT) films.

↓ Parameters	unwashed_ unannealed	w_400°C	W_400°C_D_DR	W_D_400°C	W_D_DR	W_DR
Bulk Concentration /cm^3	2.07E+13	-2.559E+14	6.745E+13	1.933E+13	-2.573E+14	-5.454E+11
Mobility cm^2/Vs	4.78E+02	-6.683E+02	1.452E+01	8.042E+01	4.231E+01	1.788E+03
Sheet-Resistance (Ω/□)	4.20E+07	3.651E+06	4.552E+08	2.008E+08	2.868E+07	2.462E+08
Resistivity (Ωcm)	6.31E+02	3.651E+01	6.372E+03	4.016E+03	5.735E+02	6.401E+03
A-C cross Hall Coefficient cm3/C	5.89E+05	-5.079E+02	1.689E+06	-5.095E+05	-8.553E+03	-2.164E+07
Magneto-Resistance (Ω)	2.87E+06	7.309E+05	1.614E+08	3.726E+07	1.72E+06	1.558E+08
Sheet-concentration /cm^2	3.11E+08	-2.559E+09	9.443E+08	3.865E+08	-5.146E+09	-1.418E+07
Conductivity (1/Ωcm)	1.59E-03	2.739E-02	1.569E-04	2.490E-04	1.744E-03	1.562E-01
Average Hall Coefficient (cm3/C)	3.01E+05	-2.440E+04	9.255E+04	3.230E+05	-2.426E+04	-1.144E+07
B-D Cross Hall Coefficient (cm^3/C)	1.40E+04	-4.829E+04	-1.504E+06	1.155E+06	-3.997E+04	-1.251E+06
Ratio of Vertical/Horizontal	5.69E-01	-2.285E-02	-1.407E+01	-3.022E-01	3.814E-01	1.649E-01

The Electrical Characteristics of the Film

The I-V electrical measurements were carried out for the six (6) samples tested. The resulting measurement curves by the Ecopia HMS-3000 machine are shown in Figure 3.3(a-f).

From the I-V characteristics, key electrical characterization parameters can be calculated, which are resistivity, ρ, conductivity, σ and sheet resistance, Rs. Table

3.1 shows the electrical characterization parameters for all the six films sampled at different conditions.

From all six film samples, it is observed that the conductivity, σ, and sheet resistance, Rs, varies with varying thin film conditions. A uniform film should exhibit fixed σ and Rs, which corresponds to continuous and homogenous thin films. The varying σ and Rs along thin film surfaces demonstrated here can be ascribed to the non-uniform intermolecular single wall carbon nano tubes (SWCNT) electrical contacts and film surface roughness.

Samples	**Sheet Resistance (Ω□)**	**Conductivity $\Omega^{-1}cm^{-1}$**	**Film Thickness (μm)**	**Temperature**
Unwashed unannealed	4.2E+07	2E-03	0.15	84°C
W_400°C	3.7E+06	3E-02	0.2	98°C
W_400°C_D_DR	4.6E+08	2E-04	0.14	101°C
W_D_400°C	2.0E+08	2E-04	0.2	102°C
W_D_DR	2.9E+07	2E-03	0.2	105°C
W_DR	2.5E+08	2E-01	0.26	106°C

Table 3.2: Optical and electrical characterization parameters of single wall carbon nano tubes (SWCNT) films i.e. film thickness (t), conductivity (σ) and sheet resistance (Rs).

Coincidentally, W_400°C_D_DRfilm sample at 101°C with the lowest film thickness shows the highest degree sheet resistance with lower conductivity. Therefore, key in producing homogenous and high quality conducting thin films is to minimize Rs. It can also be observed that higher film thickness, t, produces higher conductivity. Sample W_DR with film thickness of 0.26μm exhibits the highest maximum Conductivity (σ) with relatively smallest sheet resistance as seen in Table 3.2. It should be noted that the correlation between thickness and conductivity is not linear and largely dominated by the deposition technique used. Therefore, the deposition technique and the adopted procedures used in forming thin single wall carbon nano tubes(SWCNT) films outweighs the film dimension effects in determining the film's electrical performance. It is expected that given the same film dimensions, the wash and dried film (W_DR) technique yields the best thin film performance compared to the rest techniques.

Overall, there are certain trade-offs between optical performance and electrical performance of single wall carbon nano tubes (SWCNT) transparent thin films produced using different techniques. From the results shown in Table 3.1, and Table 3.2, higher thickness produces lower electrical performance and vice versa. Finding the balance between optical and electrical performance will depends largely on the device application for optimum device operation. It is also shown here that high quality surface topology plays a significant role in determining the material and hence device performance. For large surface area applications such as organic light-emitting diode (OLED), single wall carbon nano tubes (SWCNT) film deposition method that produces the lowest surface roughness, whilst the electrical performance can be improved by increasing film thickness.

CONCLUSION

Carbon Nano tubes (CNTs) were discovered over a decade ago, the progress of preparation and application of CNTs based thin films was initially hindered by the high cost. Recent innovations in experimental techniques have greatly advanced the development of these films. Achievements on synthesis, characterization, and device applications of CNTs based thin films. The chemical vapour deposition (CVD) techniques was employed in this study to synthesize Carbon Nano tube transparent electrode (CNT) thin films at various conditions to determine its electrical and optical properties with a focus on their transparent conductive film applications. Six samples of same thin film where prepared at various conditions of wash, doped and dried where investigated. Characterization of the films where investigated. The profilometer, was used to determine the thickness and roughness of the film, the UV-Spectrometry was used to investigate the optical properties of the film and the four point probe machine was used to investigate the electrical properties of the film.

Further study

1. It would be interesting to observe how the argon (Ar) annealed Single wall carbon nano tube (SWCNT) electrodes compares to the nitric acid doped SWCNT electrodes.
2. It is suggested that using different deposition techniques allows researchers to compliment different result and build up a full understanding of the thin film.

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