

Electrical Conduction Mechanism Of Volume And Surface Resistivities Of Multi-Walled Carbon Nanotubes Doped Polyvinyl Alcohol (PVA) And The Pyroelectric Behavior Of Polyvinylidene Difluoride (PVDF) Thin Films

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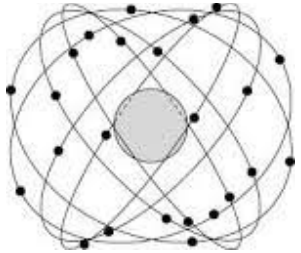
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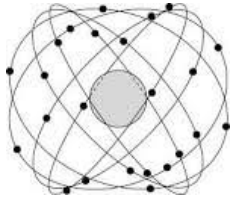
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Outline



- Introduction and Background
- Motivation
- Objectives
- Experimental
- Results
- Summary/Conclusion
- Acknowledgements

Abstract



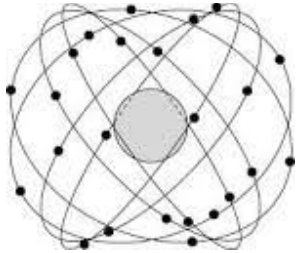
- we have reported measurements of the temperature-dependent surface resistivity of pure and multi-walled carbon nanotubes doped Polyvinyl Alcohol (PVA) thin films.

- In the temperature range from 22 ^{0}C to 40 ^{0}C, with a humidity-controlled environment, we have found the surface resistivity to decrease initially but to rise steadily as the temperature continued to increase.

- we report recent volume resistivity measurements and address the electrical conduction phenomenon that contributes to both surface and volume resistivities of pure and doped PVA thin films.

- we have measured the temperature-dependent pyroelectric coefficient of doped PVDF thin films.

Motivation



- To Continue property characterization doped polyvinylidene difluoride (PVDF) thin films for pyroelectricity/IR sensors
- To measure bulk and surface resistivity of PVDF as a function of temperature
- To consider doped polyvinyl alcohol (PVA) thin films and measure their resistivity properties as well
- To consider the application of the electrical temperature coefficient for sensing

Dielectric thin film samples have been prepared with the solvent evaporation procedure as shown in Fig. 1a and 1b

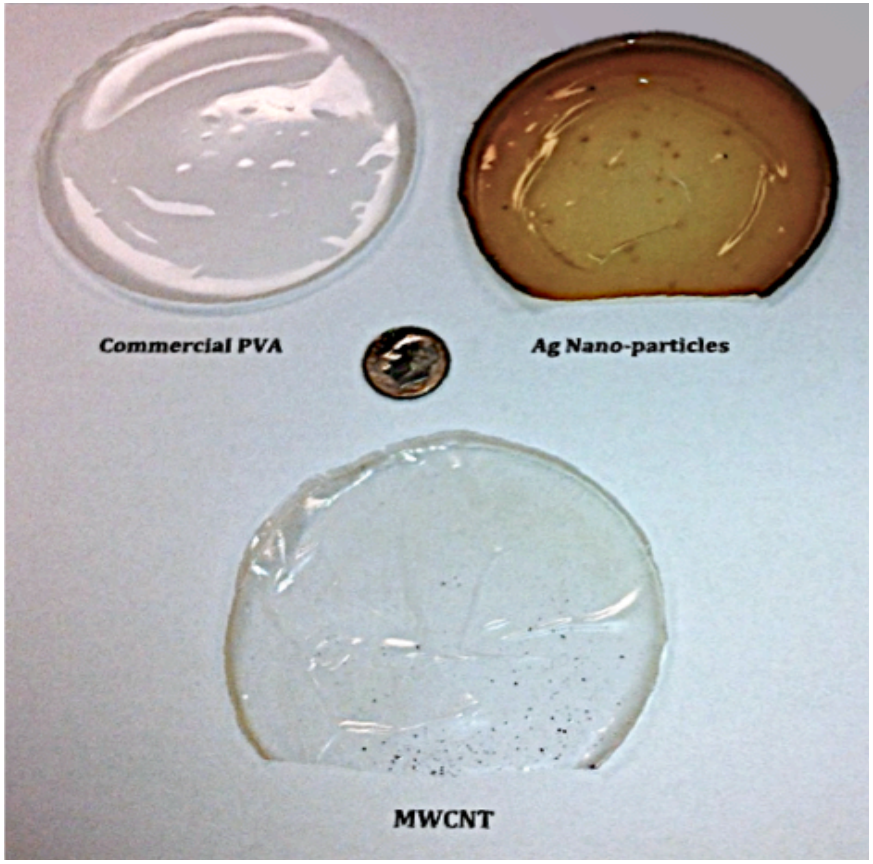


Fig. 1a. Image of samples

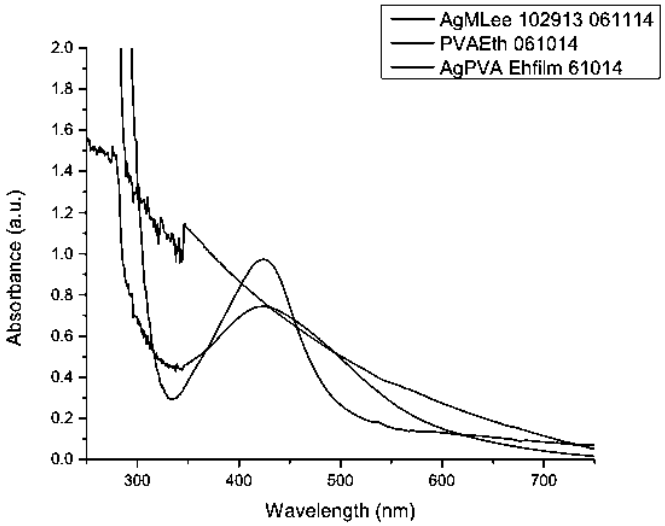


Fig. 1b. UV-VIS spectrograph of Ag-nano-particles in PVA film

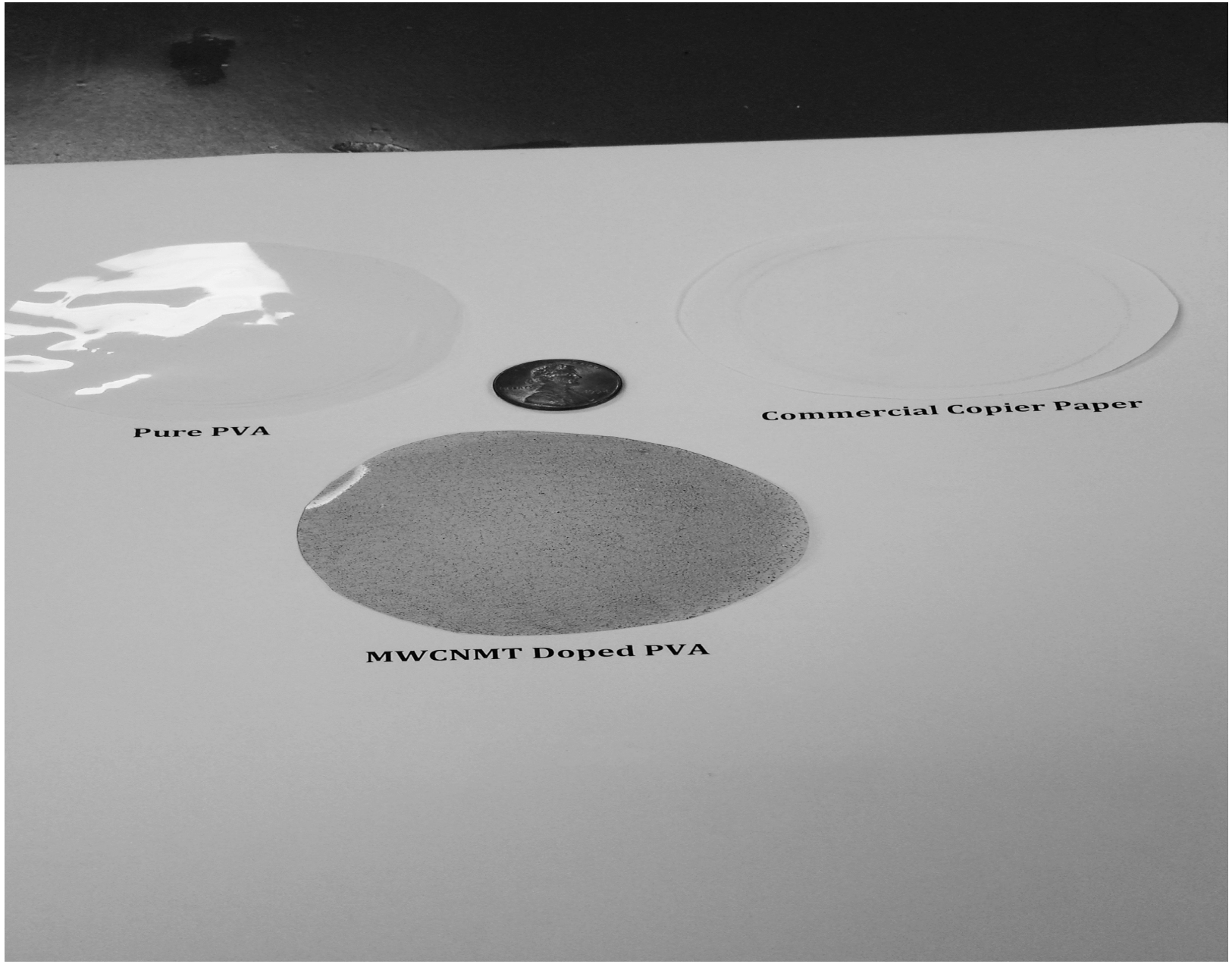


Figure 1c. Pure And Doped PVA Films And Commercial Paper



- For testing purposes, we have used Keithley Model 6517 Electrometer and Keithley Model 8009 resistivity test fixture with the Amprobe wireless thermometer when using the J-type thermocouple .

- Humidity, another important factor in surface resistivity measurements, was monitored with a commercial grade humidifier.

- In this research, we specified humidity as normally low, normally medium or normally high.

- All of our reported measurements were made at normal medium humidity at approximately 70%.

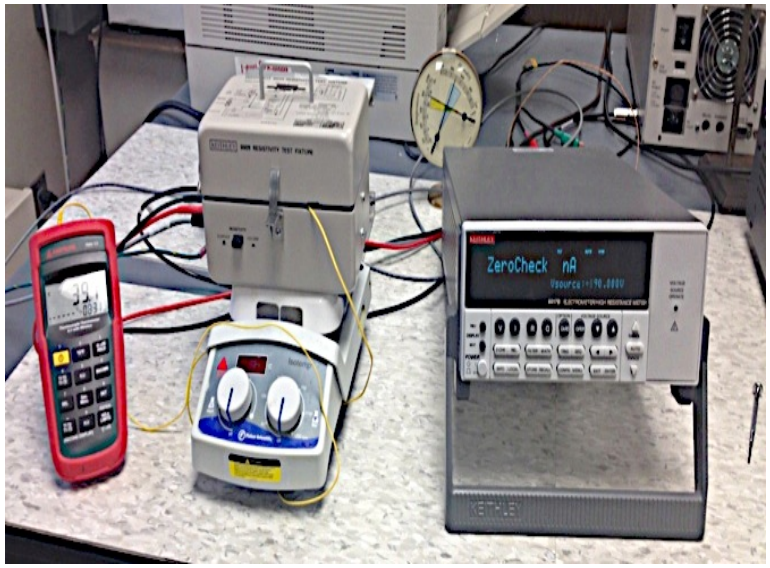


Fig. 2a. Experimental setup #1

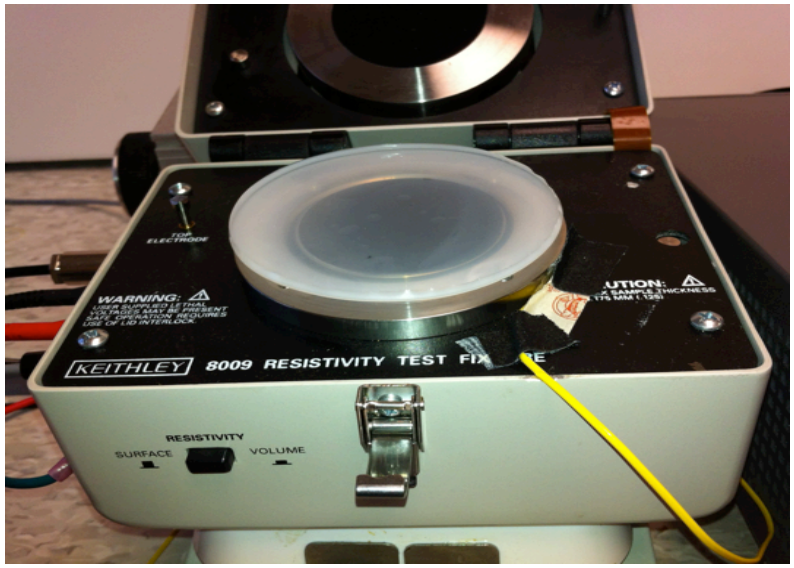


Fig. 2b. Interior view of fixture with commercial PVA film

Fig 2a, 2b, 2c and 2d show our setup resistivity measurements, consisting of a combined Keithley electrometer and Keithley test fixture, with the Amprobe wireless thermometer



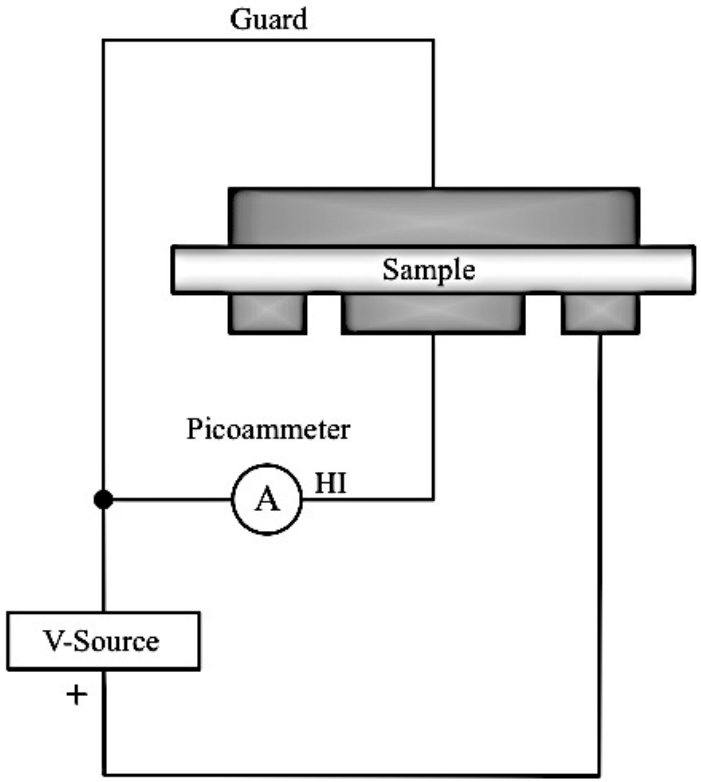


Fig. 2c. Illustration of current path with sample and electrodes

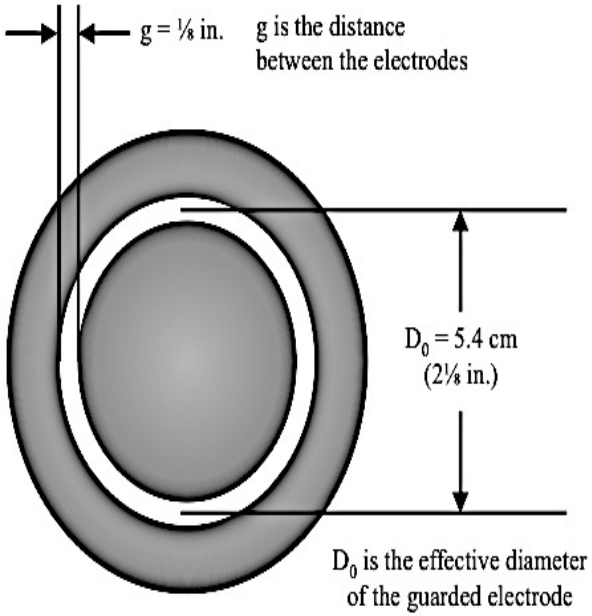
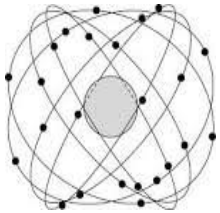


Fig. 2d. Close-up showing circular electrodes with dimensions



Figure 2e. Experimental Setup #2, Dielectric Constant, Dielectric Loss, and Other Measurements



- Table 1 that follows gives important conduction mechanisms in dielectrics.

- The methods to distinguish these conduction mechanisms are essential because there are several conduction mechanisms that may all contribute to the current through the dielectric or on its surface at the same time.

Electrode-Limited Conduction Mechanisms	Bulk-Limited Conduction Mechanisms
1. Schottky emission	1. Poole-Frenkele emission
2. Fowler-Nordheim tunneling	2. Hopping conduction
3. Direct tunneling	3. Ohmic conduction
4. Thermionic-field emission	4. Space-charge-limited conduction
	5. Ionic conduction
	6. Grain-boundary-limited conduction

Table 1. Important Conduction Mechanisms In Dielectrics



- See Fig. 3a – 4b below, which show the temperature dependent surface resistivity measurements of PVA for the commercial films, for the doped Ag nano-particles or for the doped MWCNT, and the copier paper films.

- All of the resulting graphs have the same characteristic behavior: the surface resistivity is only slightly high at low temperatures, but decreases initially as the temperature increases reaching a minimal resistivity value where upon the surface resistivity increases as the temperature continues to increase to our experimental limit of 40^{o}C.

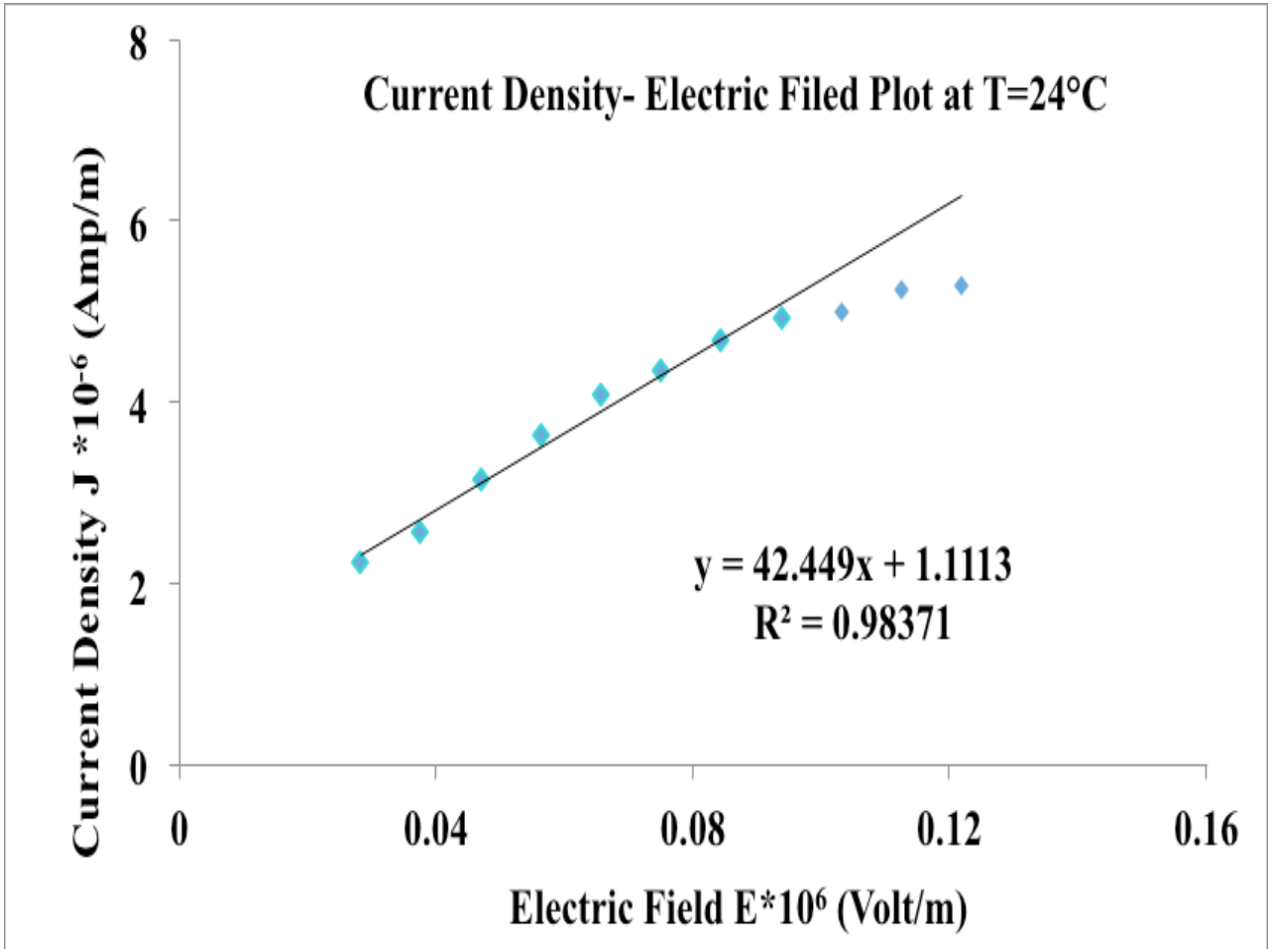


Figure 3a. Doped Sample: Current Density Vs. Electric Field

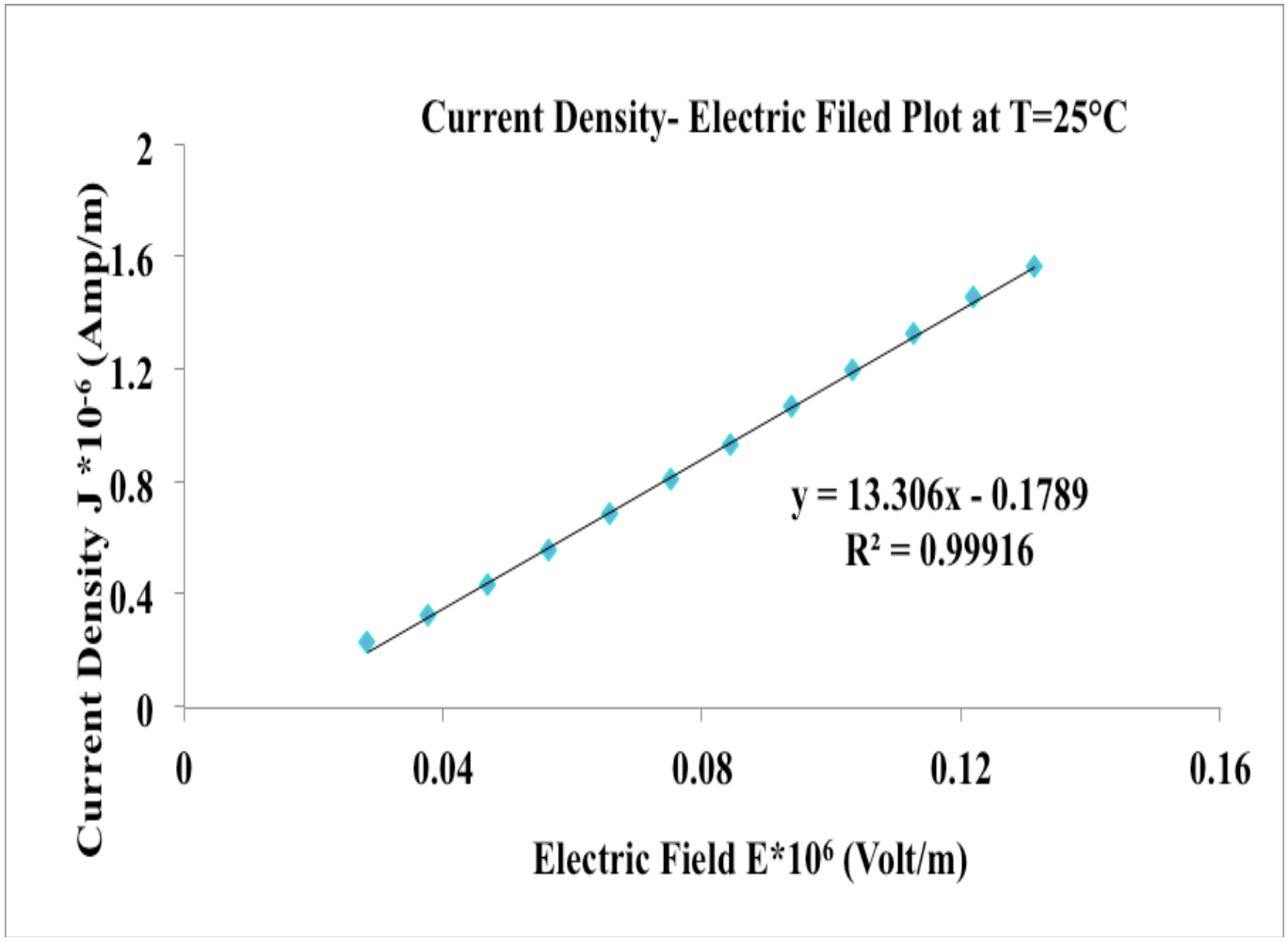


Figure 3b. Undoped Sample: Current Density Vs. Electric Field

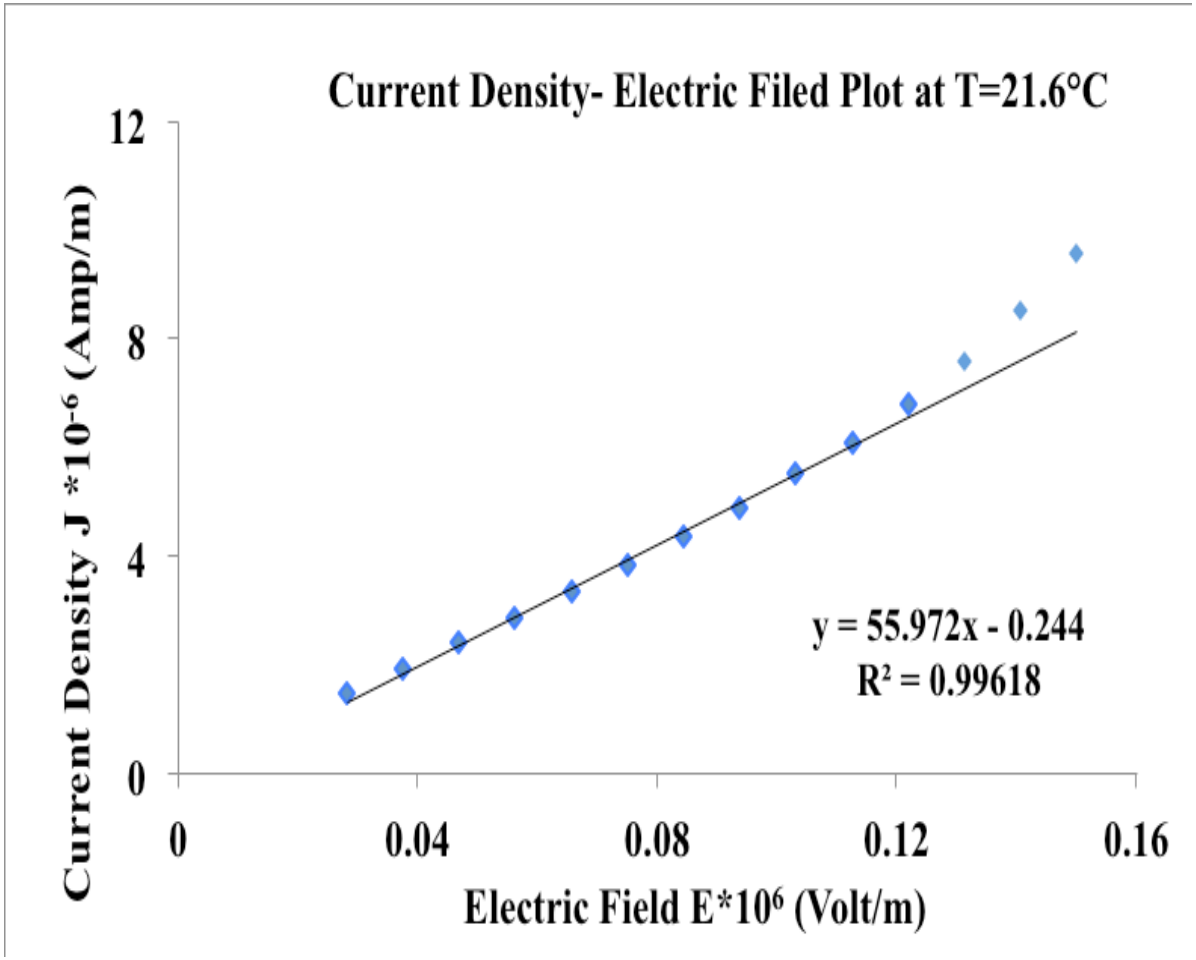


Figure 3c. Commercial Copier Paper: Current Density Vs. Electric Field

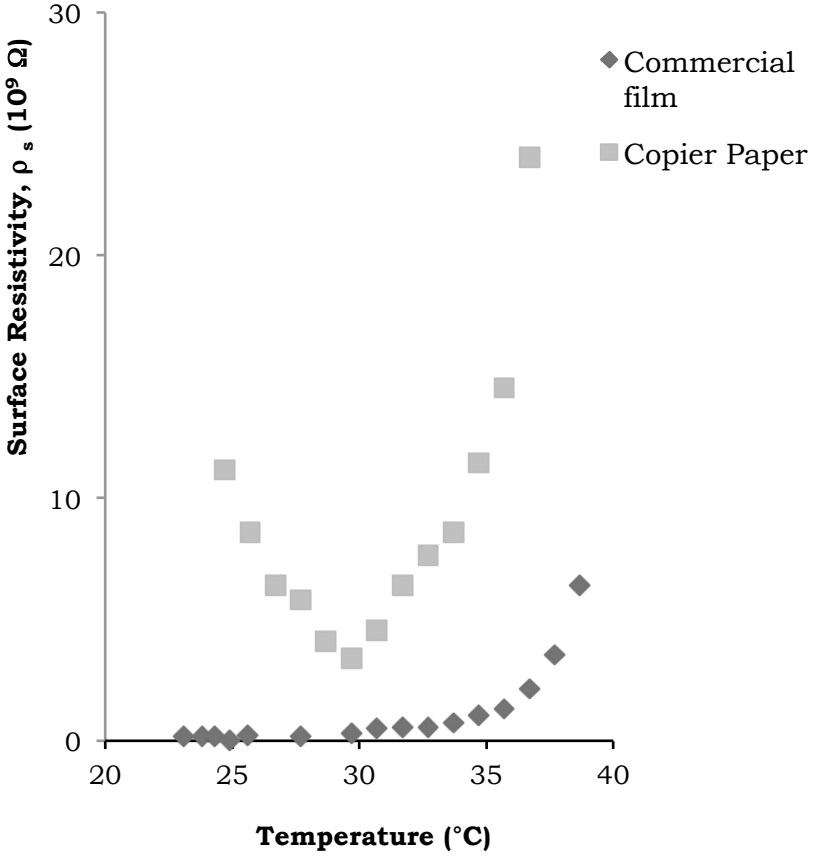


Fig. 4a. Surface resistivity graphs of commercial film and copier paper

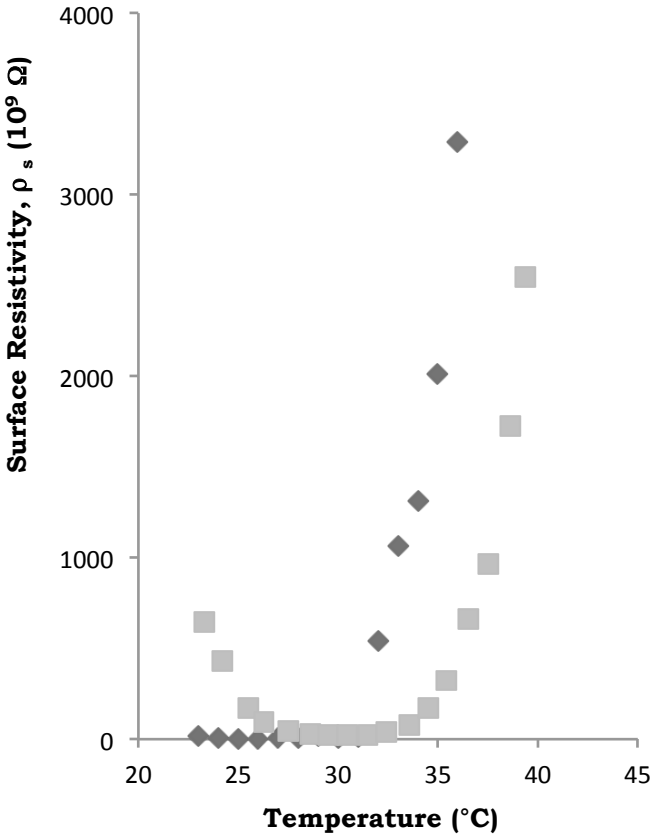


Fig. 4b. Surface resistivity graphs of Ag nano-particle and MWCNT

Discussions and Conclusions For PVA Films



- The preliminary experimental results obtained from this investigation can be summarized as:

- PVA thin films, doped and commercial, can be developed with the solvent evaporation method.

- The combined system of Keithley Model 6517 electrometer, Keithley Model 8009 test fixture and the amprobe thermometer can be used readily to measure surface resistivity of commercial PVA films, of Ag nano-particle or MWCNT doped PVA films and of copier-paper films, but cannot in the present configuration be used to measure the surface resistivity of PVDF films.

- Surface resistivity of Ag nano-particle doped PVA films is generally higher in value than that of commercial PVA and varies the most greatly in the temperature range from 22^0C to 40^0C, followed in order of that of MWCNT PVA films and copier-paper.

PVDF Films

◆ The authors have determined the dielectric and conductance properties of multi-wall carbon nano-tubes (MWCNT) in polyvinylidene fluoride (PVDF) nanocomposite thin films as a function of temperature and frequency

◆ Film Thickness was from ranging from 15 – 280 microns and measurements were made in the temperature range from room temperature to 20 to 90^0C and frequencies from 50Hz to 110MHz

◆The samples were prepared by the solution casting technique

◆Measures indicate that at constant temperatures, the real dielectric constant decreases at lower frequencies, stays steady at low frequencies but rise at higher frequencies over towards the strong resonance

◆ The dielectric loss decreases also at lower frequencies but rise at higher frequencies with a steeper slope in each case

◆The pyroelectric coefficient in the same temperature range, compared the pyroelectric coefficient results with previous measures made on silver nanoparticle in PVDF thin films

◆ MWCNT:PVDF thin films yield higher figures of merit than that indicated by pure PVDF thin films and results indicate a usage of MWCNT:PVDF thin films in infrared uncooled sensors and vidicon technology.

Methods to Measure The Pyroelectric Coefficient

- Direct Techniques (Byer & Roundy)
  (Present Method at AAMU)
- Dynamic Method (A.G. Chynoweth)
- Charge Integration Method (A. M. Glass)
- All-Optical Technique (Jacopo Parravicini)

Important Mathematical Relationships

◆The real (ε') and imaginary (ε") parts of dielectric constant were calculated by measuring capacitance C_p and dielectric loss D(=tanδ) .

$$\varepsilon' = C_p \varepsilon_0 \left(\frac{d}{A}\right), \quad \varepsilon'' = \varepsilon' D$$

d is the film thickness, and A is the electrode area

◆ The pyroelectric current I_p was measured, and the pyroelectric coefficient (p) was calculated using the relationship:

$$p = \left(\frac{I_p}{A(dT/dt)}\right)$$

where A is the electrode area (identical areas for the opposite electrodes used in each sample) and dT/dt is the rate of temperature change with time, which was kept to 1ºC/minute.

Pyroelectric Coefficient from the Effective Medium Approach:

$$p = \left(\frac{\varepsilon' - \varepsilon_m}{\varepsilon_i - \varepsilon_m}\right) p_i - \left(\frac{\varepsilon_i - \varepsilon'}{\varepsilon_i - \varepsilon_m}\right) p_m$$

ε' for the composite, ε_i the inclusion, ε_m the matrix

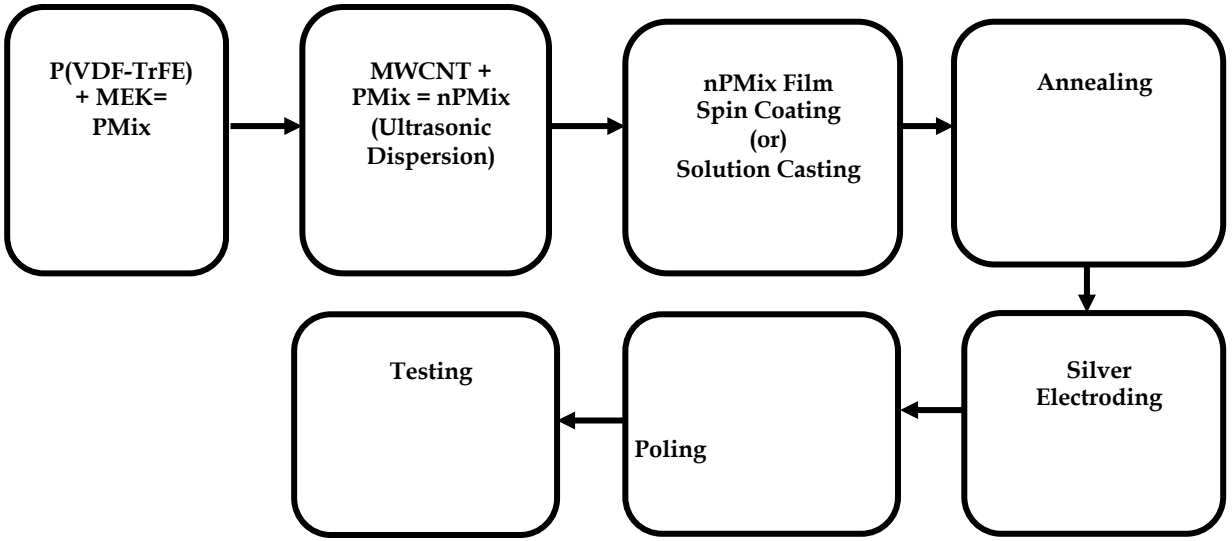
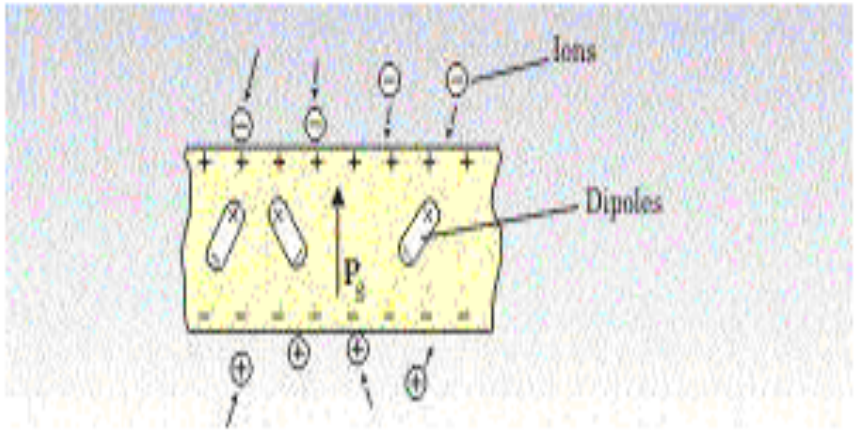
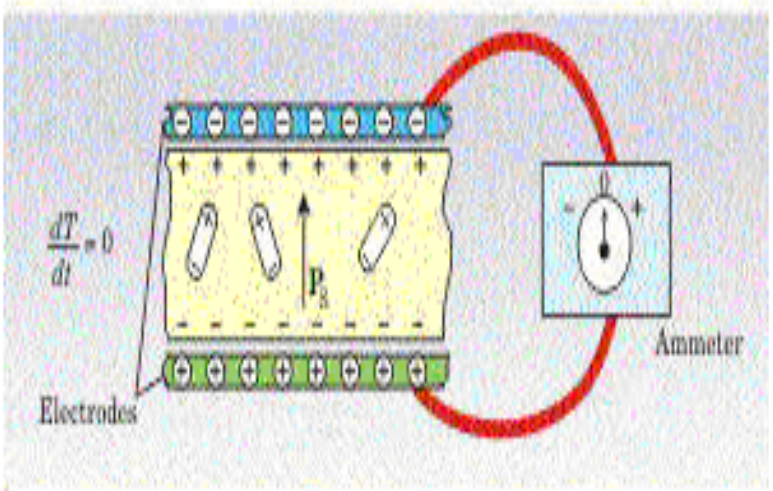
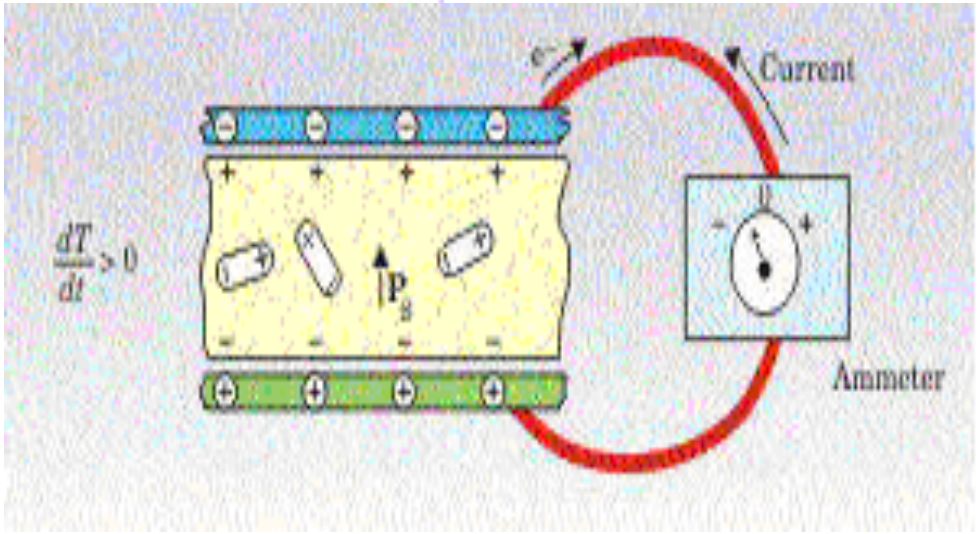


Figure 1. Summary of Composite Film Fabrication Process

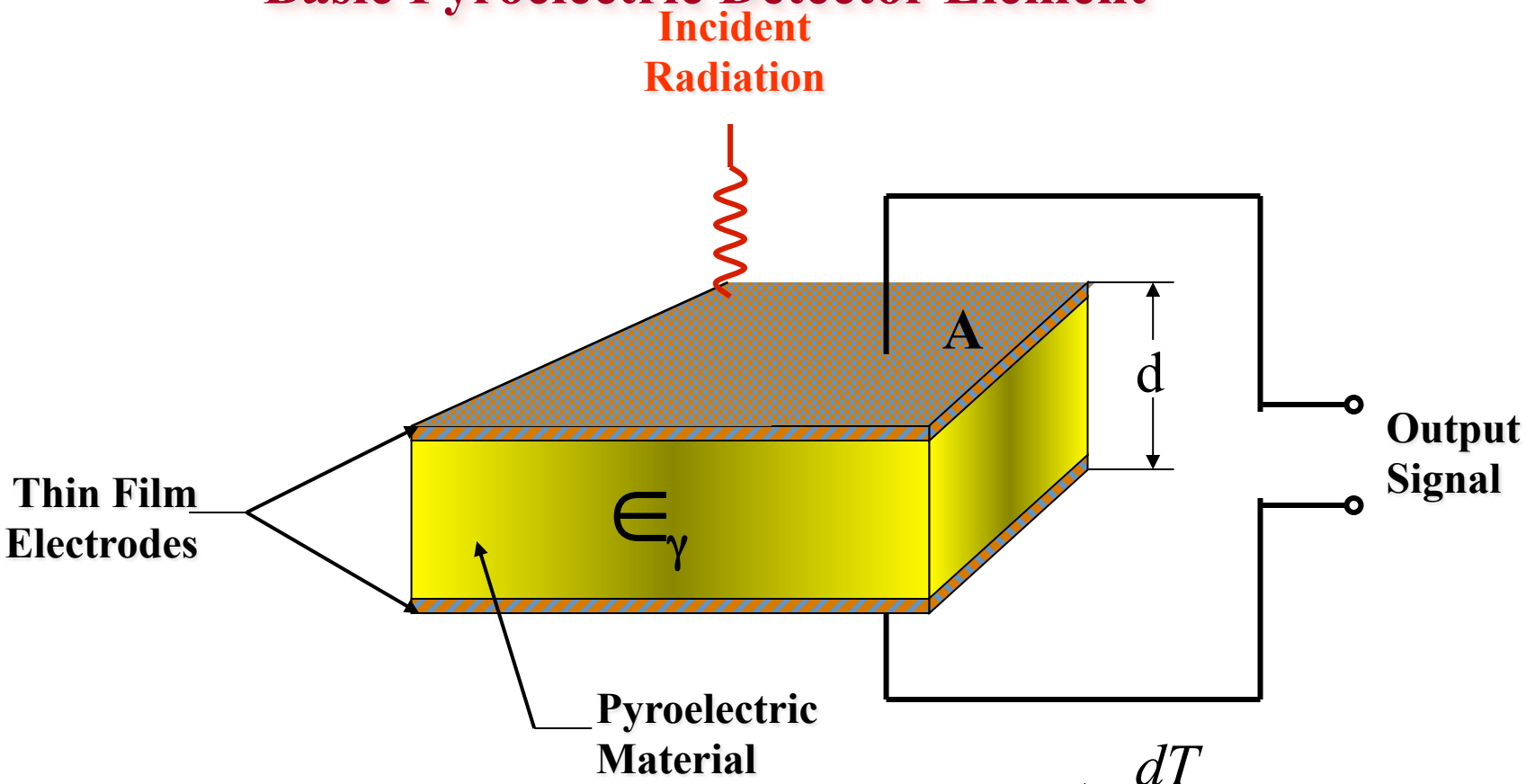
PYROELECTRIC CRYSTAL SHOWING THE CHANGE IN POLARIZATION







Basic Pyroelectric Detector Element



$$i_p = Ap\frac{dT}{dt}$$

Room-temperature Properties of Various Pyroelectric Detector Materials and Some Figures of Merit" for Detector Operation.

Material	p ($nCcm^{-2}K^{-1}$)	$\varepsilon'/\varepsilon_0$	c_p ($Jcm^{-3}K^{-1}$)	p/c_p ($nAcmW^{-1}$)	$p/(c_p\varepsilon')$ ($Vcm^{-2}J^{-1}$)	$p/(c_p\varepsilon'')$ $(cm^3J^{-1})^{1/2}$
TGS	30	50	1.7	17.8	4000	0.149
LiTaO3	19	46	3.19	6.0	1470	0.050
$Sr_{1/2}Ba_{1/2}Nb_2O_6$	60	400	2.34	25.6	720	0.030
PLZT(6/80/20)	76	1000	2.57	29.9	340	0.034
PVDF	3	11	2.4	1.3	1290	0.009

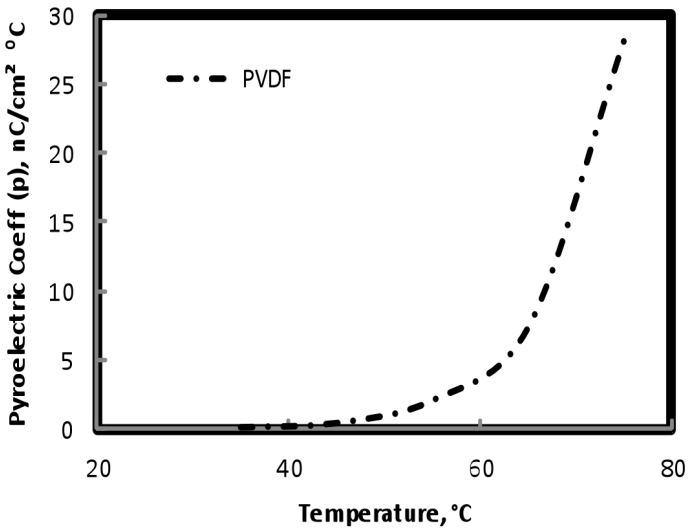


Figure 2. Pyroelectric Coefficient Vs Temperature of PVDF Film

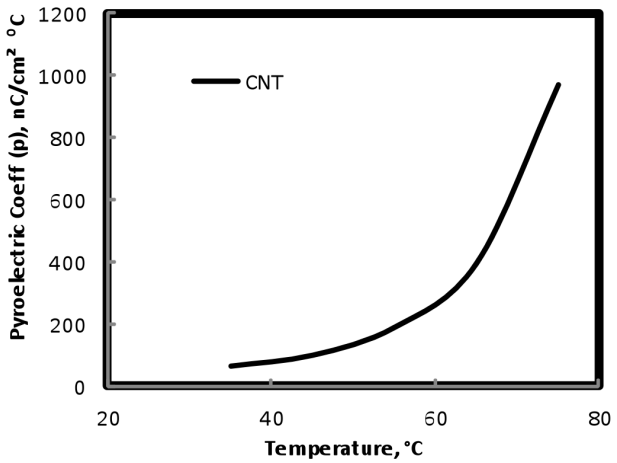


Figure 3 Pyroelectric Coefficient Vs Temperature of PVDF/MWCNT Film

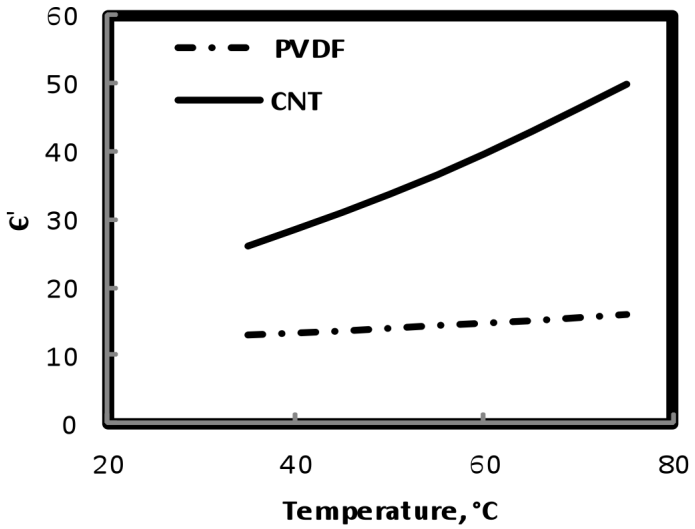


Figure 4. Real Part of Dielectric Constant (ε´) Vs Temperature of PVDF and PVDF/MWCNT Films

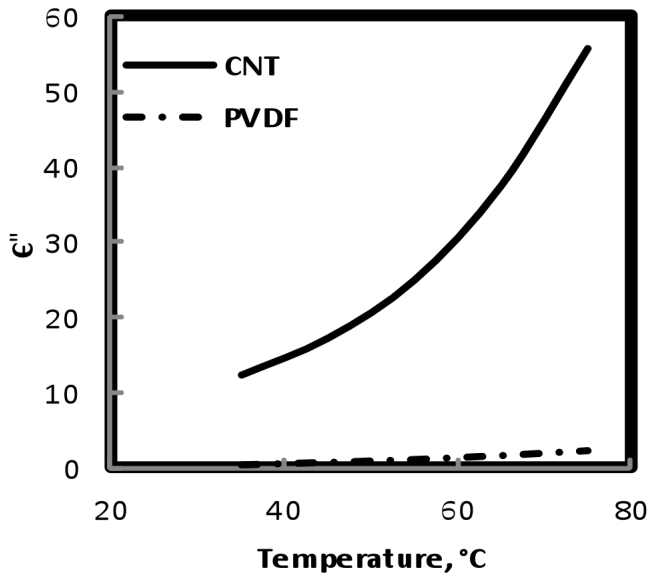


Figure 5. Imaginary Part of Dielectric Constant (ε´´) Vs Temperature of PVDF and PVDF/MWCNT Films

Table 1. Dielectric, pyroelectric and figures-of-merit of PVDF and composites films

Temp. (°C)	Pyroelectric Coeff. (p) ; F_I (nC/cm² °C)	Dielectric Cont. (ε′)	Dielectric Loss (ε")	*Pyroelectric-voltage (V)*	$FM_V=p/\varepsilon'$ (nC/cm² °C)	$FM_{vid}=p/(\varepsilon')^{1/2}$ (nC/cm² °C)
PVDF Film						
35	0.1175	12.924	0.4702	3.16	.00909	.03271
45	0.4345	13.540	0.7785	3.31	.02975	.10458
55	2.0943	14.378	1.1059	3.51	.13759	.52346
65	7.4164	15.093	1.5894	3.69	.45585	2.0942
75	28.302	16.026	2.1629	3.92	1.7665	7.0674
PVDF:MWCNT Film						
35	63.971	26.175	12.329	10.19	2.4564	12.4689
45	99.137	31.115	17.245	12.12	3.2943	18.1295
55	189.07	36.578	24.985	14.24	5.4329	32.1958
65	394.56	42.897	37.487	16.70	9.7286	66.2146
75	968.41	49.767	55.724	19.38	19.4752	137.2829
P(VDF-TrFE) Film						
60	0.28	17.58	2.21	-	0.02	0.07
70	0.637	18.97	3.35	-	0.03	0.15
P(VDF-TrFE)+LT+Ag Nanoparticles Film						
60	44.9	40.99	29	-	1.09	7.01
70	132	48.28	40.73	-	2.73	18.99

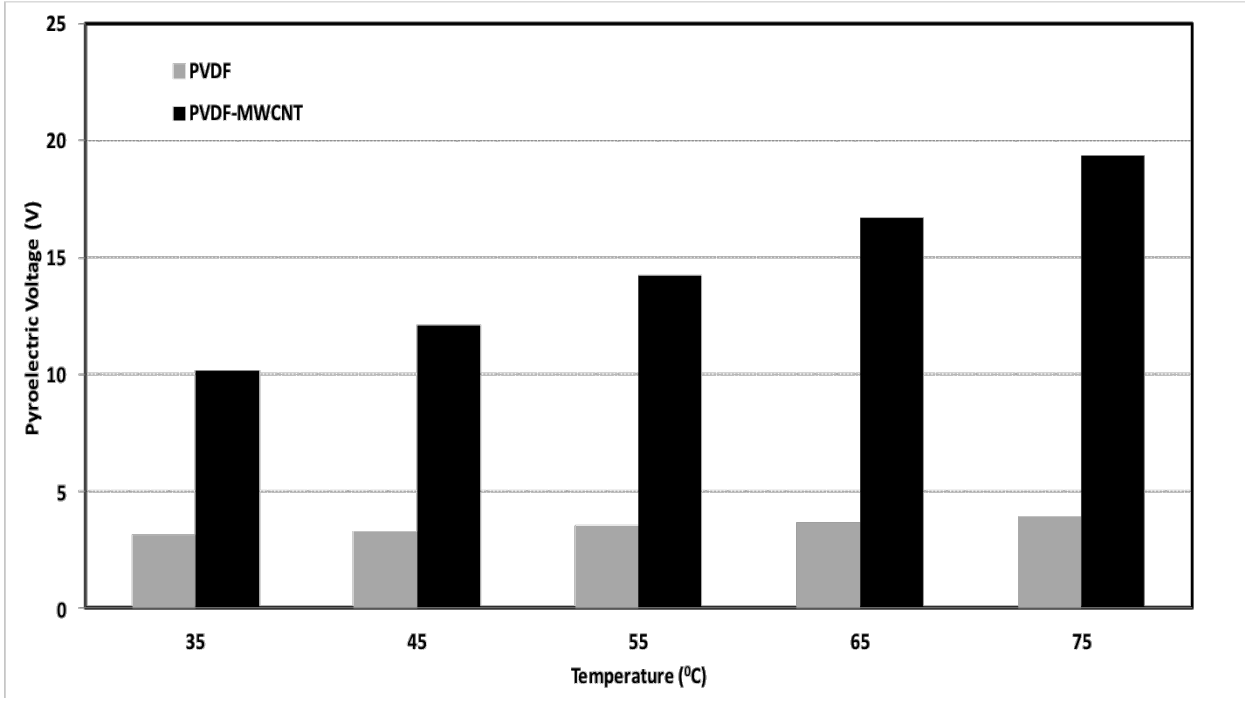


Figure 16. Comparison of pyrovoltage generated for PVDF and PVDF- via 1ºC increase in temperature

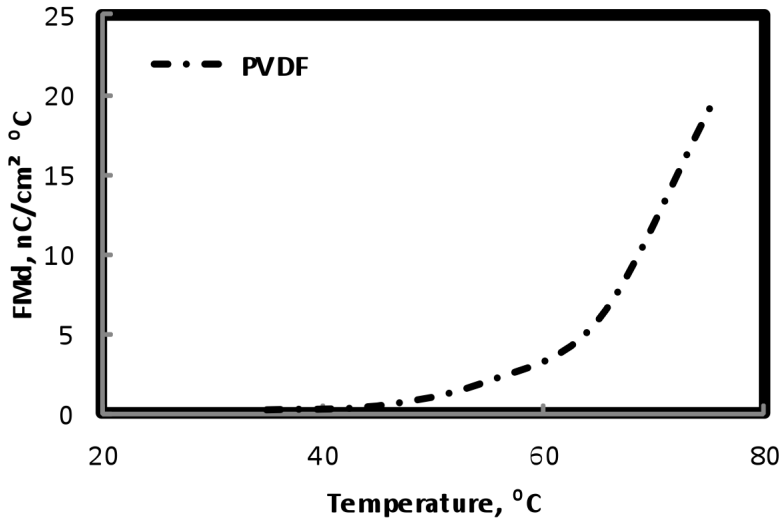


Figure 9. Figure-of-Merit for Detector Applications Vs Temperature of PVDF Film

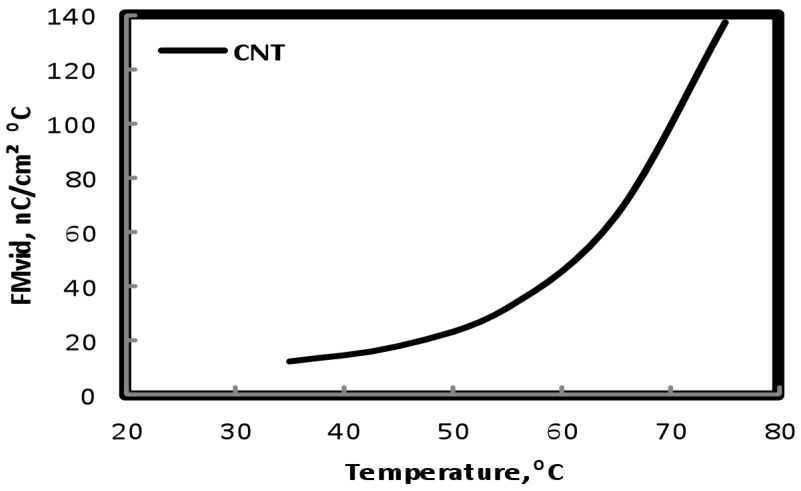


Figure 10 Figure-of-Merit for Vidicon Application Vs Temperature of PVDF/MWCNT Film

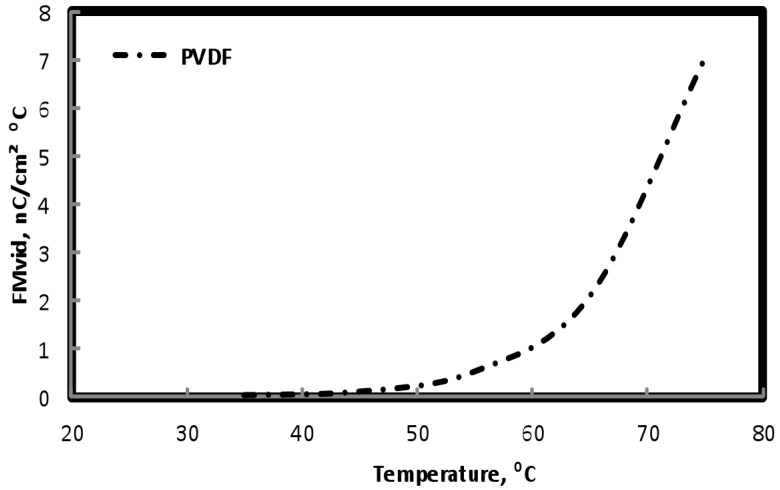


Figure 11. Figure-of-Merit for Vidicon Application Vs Temperature of PVDF Film

Summary/Conclusions

Flexible And Homogeneous Films Have Been Prepared— LT Or MWCNT Composites;

The Incorporation Of MWCNT Have Enhanced Both Dielectric Constants And The Pyroelectric Coefficient;

Further Work Is In Progress To Grow Thinner Films With Larger Amounts Of MWCNT Or LT In PVDF;

Phenomenal And Synergistic Understanding Of The Effects Of MWCNT In Composite Thin Films;

Resolve Issues of Using Parallel Plates Versus Electrode Metallic Coating

Development Techniques to Reduce Internal Stress In The Films;

Development of IR Devices Remain To Be Completed.

Further Studies



- Further study is needed on PVA to ascertain the surface resistivity temperature dependence in greater temperature ranges, and to determine conduction mechanisms that are involved as a function of temperature

- Further study is needed on PVDF films to ascertain surface resistivity properties more conclusively that what are reported here

- Further studies are needed to determine sensors and other detection applications

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- Adedotun Ayokanmbi, Kelso Kwyntero, and Jade Douglas, Undergraduate Research Students

Some References



- [1] Malikov, E. Y., Muradov, M. B., Akperov, O. H., Eyvazova, G. M., Puskas, R., Madarasz, L., Kukovecz, A., and Konya, Z., "Synthesis and characterization of polyvinyl alcohol based multiwalled carbon nanotube nanocomposites," Physica E., 61, 129-134 (2014).
- [2] Renoux, P., Jonsson, S. A., Levente, K. J., Hamann, H. F., and Ingvarsson, S., "Sub-wavelength bolometers: uncooled platinum wires as infrared sensors," Optics Express, 19(9) (2011).
- [3] Chiu, Fu-Chien, "A review on conduction mechanisms in dielectric films," Advances in Materials Science and Engineering, Hindawi Publishing Corporation, Article ID 578168, 1-18 (2014).
- [4] Maryniak, W. A., Uehara, T., Noras, M. A., "Surface resistivity and surface resistance measurements using a concentric ring probe technique," Trek Application Note, 0623/MAN Rev. 1b(1005) (2003).
- [5] Wong, C. K., and Shin, F. G., "Electrical conductivity enhanced dielectric and piezoelectric properties of ferroelectric 0-3 composites," J. Appl. Phys., 97, 064111 (2005).
- [6] Nye, J. F., "Physical Properties Of Crystals," Oxford Science Publications (1985).
- [7] Edwards, M. E., Batra, A. K., Ashwith, C. K., Guggilla, P., and Curley, M., "Pyroelectric properties of PVDF:MWCNT nanocomposite film for uncooled infrared detectors," Materials Sciences and Applications, 3, 851-855 (2012).

Additional References

1. Edwards, M.E., Batra, A.K., Chilvery, A., Guggilla, P., Aggarwal, A., “Pyroelectric Properties of PVDF:MWCNT Nanocomposite Film For Uncooled Infrared Detectors”, Journal of Materials Sciences and Applications, Vol. 3, Pages 851-855, 2012.

2. Batra, A. K., Aggarwal M. D., Edwards, M. E., and Bhalla, A. Present status of polymer:ceramic composites for pyroelectric infrared detectors Ferroelectrics 2008; 366: 84-121.

3. Aggarwal, M. D., Batra, A. K., Guggilla, P., Edwards, M. E., Penn, B., and Currie, J. R. Pyroelectric materials for uncooled infrared detectors, NASA Technical Memorandum-NASA/TM, 2010, 2164373, 1-71.

4. Seminara, L., Capurro, M., Cirillo, P., Cannata, G., and Valle, M. Electromecahnical characterization of piezoelectric PVDF polymer films for tactile sensors in robotics applications, Sensors and Actuators A. Physical 2011, 169, 49-58.

5. Graz, I., markus, K., Simona B-G, and et al.: Flexible active-matrix cells with selectively poled bifunctional polymer ceramics nanocomposites for pressure and temperature sensing skins J. Appl. Phys., 2009, 106: 034503-1-034503-4.

6. Batra, A. K., Corda, J., Guggilla, P., Aggarwal M. D., Edwards, M. E. A Electrical properties of silver nanoparticles reinforced


Q&A