

# Raman Effect Studies of Electrochemical Synthesized Quartz Crystal of Poly-O-Phenylenediamine for Piezoelectric Application.

## Abstract

Microelectronics arose from the desire for miniaturization of electrical devices, while Nano-electronics arose from subsequent study. Researchers have developed and modeled energy harvesting technologies based on the conservation law of energy over the last two decades to produce an alternative power source for small size electronics (nano-electronics) and low power electronic devices that can replace traditional power sources like batteries. The ambient energy, which is typically in the form of solar, thermal, vibrational, and other types, can be converted into a variety of different forms. Electrical energy can be harvested from vibrational energy in materials and other man-made materials using piezoelectric, electromagnetic, electrostatic, and nano-electric generators. Poly-o-phenylenediamine (PoPD) Quartz (silicon dioxide) Crystals were electrochemically produced at varied percentage ratios of silicon dioxide and Poly-O-Phenylenediamine samples in this study (sample A represents 20:80 percent, sample B with 50:50 percent, and sample C has 60:40 percent respectively). The Raman Effect and Scanning Electron Microscopic (SEM) analysis were used to characterize the material and forecast its Piezoelectric effect. All of the samples have their maximum peak record at a raman shift of  $2872\text{cm}^{-1}$ , however the raman intensity varies. Sample A produced a peak intensity of 1250, Sample B produced a peak intensity of 1700, and Sample C produced a peak intensity of 2700. As the doping concentration of silicon dioxide increases, the raman peak intensity for Poly-o-Phenylenediamine doped with silicon dioxide increases. The SEM images show that Sample A forms a fine cluster with little or no distinctive morphology, Sample B is ball-shaped with grain-like structure, and Sample C shows a flat, thin leaf-like shape. From sample A to C, the intra-particle separation rises, which corresponds to an increase in  $\text{SiO}_2$  concentration.

**Keywords:** Piezoelectric, Quartz Crystal, Poly-O-Phenylenediamine, Electrochemical and Synthesization

## Introduction

The quest on the miniaturization of electronic device has paved way for microelectronics and with further research gave rise to Nano-electronics. Thus, the appearance of nanotechnology has inspired industries such as internet, mobile devices, and robotics towards its achievement on electric source and other electronics, where some notable research discovery had indicated that the material shows good novel property at nanoscale quite different from the bulk material properties. The miniaturized dimensions offer unique electrical, structural, optical, thermal, and mechanical properties; The reduced dimensions enable them to show high surface area and quantum size effect. (Dong *et al*, 2016)

Microdevices have recently become more popular in new technologies that demand less power and can run on alternative power sources. The concept of harvesting energy from the surrounding environment, in particular, is gaining traction as a way to extend the life of portable gadgets, wearables, and sensor equipment (Bowen *et al*, 2014).

Raman spectroscopy is a useful characterization tool in electronics that may be used to examine crystal structures, domain textures, crystallographic misalignments, and residual stresses in piezoelectric materials and devices on a local and quantitative level. (Gantschi.,2002) Despite this, a promising method is used to record the raman spectra of a material that has been subjected to an external field below its destruction threshold. The materials that change their properties significantly when exposed to external stimuli, such as semiconductors, ferroelectrics, piezoelectrics, pyroelectrics, and so on, are the most fascinating (Anastassakis, 1980).

On an atomic scale, the precise symmetry of the unit cell dictates whether or not the material can experience piezoelectricity, with the symmetry of the crystal structure reflecting the symmetry of the material's extrinsic

piezoelectric qualities (Kholkin *et al.*, 2008). As a result, Raman spectroscopy has become a popular tool for establishing phase diagrams and elucidating phase transition mechanisms in piezoelectric materials (Venkateswaran *et al.*, 1998; Haines *et al.*, 2003; Souza *et al.*, 2001; and Haines *et al.*, 2003). This kind of experimentation takes advantage of Raman spectroscopy's simplicity in revealing complex phase transitions. The development of an internal structure/texture of fine crystallographic domains is, nevertheless, directly linked to the macroscopic piezoelectric capabilities of the material. The shape and spatial distribution of heat fields, as well as the accompanying residual strain tensors, influence domain textures, which in turn influence the fabrication process (Okai *et al.*, 2011). This now widely held belief contradicts the previously held (and long held) belief that sintered ceramics could not be piezoelectrically active because they include a large number of randomly oriented crystallites, cancelling out any existing internal dipole. A turning point in understanding piezoelectricity was the phenomenological discovery of the unusually high dielectric constant of BaTiO<sub>3</sub> and, more precisely, the successive understanding that the origin of such high dielectricity was actually related to the ferroelectric nature of this material (Jona and Shirane, 1962). Such progress ultimately inspired the identification of a completely new class of materials: such as the ABO<sub>3</sub> perovskites (in which A is an alkali or rare-earth element and B may represent different transition metal elements). A growing number of devices (such as capacitors, transformers, igniters, power generators, ultrasound and acceleration sensors, actuators, valves, micromotors, printer heads, frequency filters, and so on) now include piezoelectric ceramics in their core components, as well as their complex assemblies to metallic parts (Nakamura *et al.*, 2002; Kuwajima *et al.*, 2002). There is also a strong tendency toward optimizing performance, decreasing bulk, multiplying functionality, and extending the lifetime of such gadgets. The structural compatibility criteria for multi-step processing techniques, on the other hand, are very strict. The optimization of the thermal and mechanical cycles by which the selected ceramics are brought together with other parts composed of metallic materials (i.e., having completely different physical properties) pose actual technological hurdles, for example. As feature sizes grow larger, practical implementations are frequently limited by a lack of process compatibility (Swartz, 1990). This has led to the development of new and exciting research areas aimed at solving compatibility problems, but has also summoned the search for efficient and exhaustive analytical tools, which could promptly serve technologists in performing hybrid crystallographic and mechanical characterization (Giuseppe, 2013).

In the study, for the first time, the characterization on piezoelectric effect in monolayer WS<sub>2</sub> by Ling *et al.*, 2021. Subsequently, monolayer WS<sub>2</sub> was artificially stretched by applying in-plane uniaxial deformation. Consequently, the Raman anisotropy increased as evidenced from the angle-resolved polarized Raman spectra, and the band gap decreased from the red-shift of the PL emission. Raman spectroscopy result which is based on Intensity and wavenumber changes towards the characterization of materials.

This research is capitalized on the most suitable concentration of quartz crystal (silicon dioxide) and Poly-O-phenylenediamine towards the fabrication of piezoelectric device. Its raman effect, bandgap and the SEM structure for the best piezoelectric energy harvesting at the conversion of its potential energy to kinetic energy under external field (anisotropic field).

## Material and Methods

**Materials:** - Monomer o-Phenylenediamine of CAS NO:95-54-5, Ammonium persulphate, silicon dioxide with CAS NO:148087-60-7 and Hydrochloric acid were product of India marketed in Nigeria. Other chemicals were for analytical reagent grade and were used as received without any further purification.

## Methods.

Monomer of O-Phenylenediamine was polymerized via oxidation process using Ammonium Persulphate as the oxidant to obtain Poly-o-Phenylenediamine as found in literature. Then, Poly-o-Phenylenediamine and Silicon dioxide (SiO<sub>2</sub>) was dissolved in the 1mole of HCl, on the application of heat at a constant temperature of 40°C. using the magnetic stirrer and heater, PoPD was first measured out with an electronic weighing balance at 8.0g and then put into beaker with 5ml of 1MHCl then heathered and stirred for 5mins before adding silicon dioxide of 2.0g (0.033mole) and stirred until a homogenous mixture is obtained. This was repeated for different ratio of PoPD : SiO<sub>2</sub> at the ration of 80:20% for sample A, 50:50% for Sample B and 40:60% for Sample C respectively.

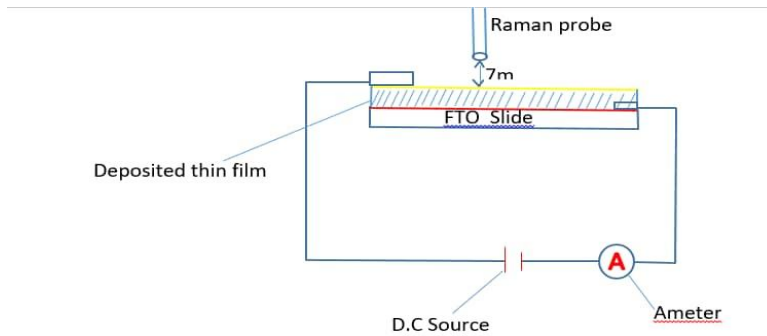


Image 1 Schematic step up for the Raman Spectroscopic Experiment under the influence of Electric field.

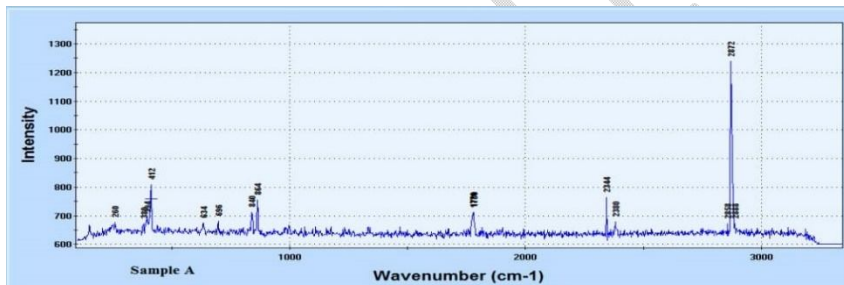
A constant voltage of 20v was used to excite the deposited substrate while about 7mm under the raman spectroscopy probe, as shown in the figure 1. The raman spectroscopic machine was run to obtain the phonon readings.

## Results and Discussions

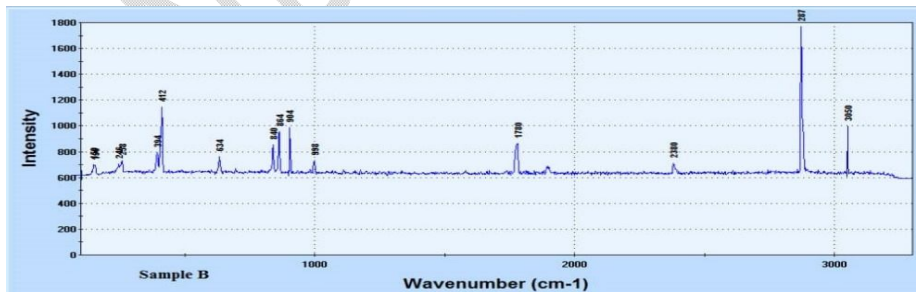
The experimental results obtained from raman spectroscopy and scanning electron microscopic characterization were as follows:

### Raman Spectroscopic Analysis

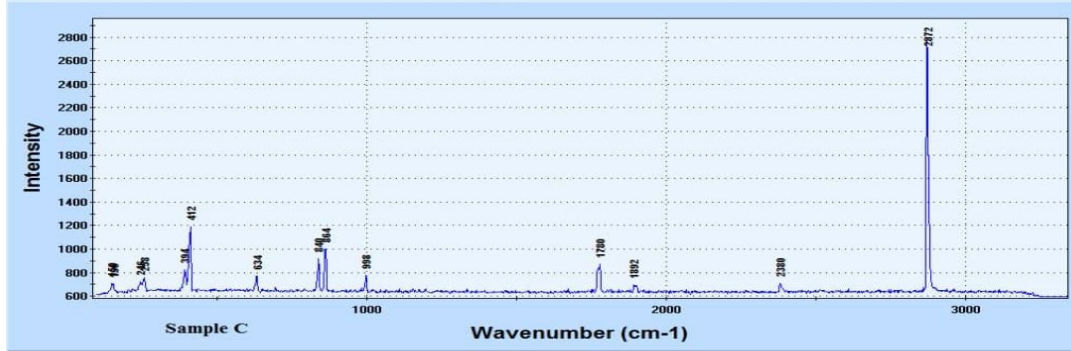
The Raman Effect on raman spectroscopic intensity variation is always proportional to the material's mechanical stress/strain. Because piezoelectric energy harvesting is dependent on the material's mechanical stress/strain and vice versa, the intensity change in the raman spectra effect tends to provide a better knowledge of the appropriate doping concentration for piezoelectric device construction. The findings of raman at various percentage doping ratios of Poly-o-Phenylenediamine and silicon dioxide are shown in the figure below.



a



b



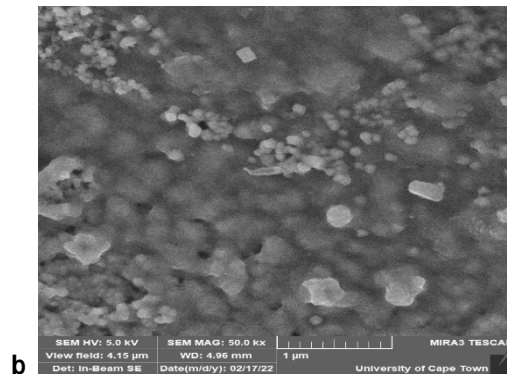
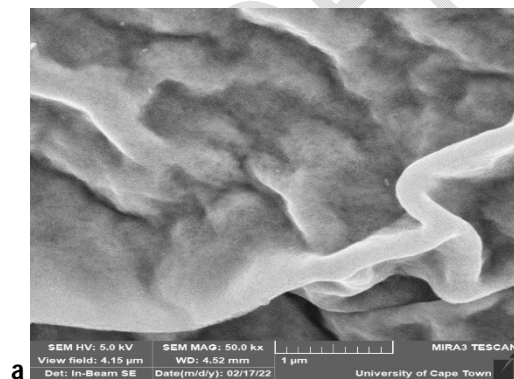
C

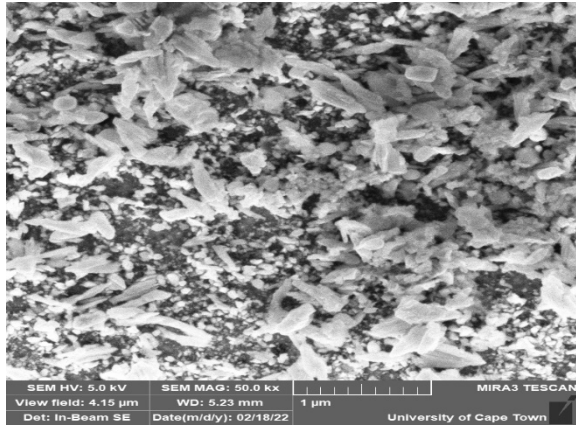
**Fig. 1.** The Raman Spectroscopic graphical result of Poly-O-Phenylenediamine doped at various percentage of silicon dioxide (a) 80% of Poly-O-Phenylenediamine to 20% of Silicon dioxide for sample A (b) 50% of Poly-O-Phenylenediamine to 50% of Silicon dioxide for sample B (c) 40% of Poly-O-Phenylenediamine to 60% of Silicon dioxide for sample C.

In the figure 1, it was observed that all the samples have its highest peak record at raman shift of  $2872\text{cm}^{-1}$  but with different raman intensity. The sample A has its peak intensity at 1250, Sample B, obtain a peak intensity of 1700 and Sample C. gave a peak intensity of 2700. Thus, the raman peak intensity for Poly-o-Phenylenediamine doped with silicon dioxide increase with and increase in the doping concentration of silicon dioxide.

### Scanning Electron Microscopy (SEM)

The SEM images of PoPD:  $\text{SiO}_2$  deposits are shown in Figure 2a – c for different composite ratio. In Figure 2a, the SEM image appears to form a finer cluster with little or no distinctive morphology for sample A (20%  $\text{SiO}_2$ ). The SEM images with 50% and 60% of  $\text{SiO}_2$  particles for sample B and C respectively as shown Figure 2b – c is observed to have a grain-like clusters with distinctive morphology. Figure 2b shows a ball shape with grain-like structure and Figure 2c has flat, thin leaf-like structure. It can also be observed that in Figure 2a, the clusters appear tightly bound and in Figure 2b, the intra-granular separation becomes slightly obvious with respect to Figure 2a while Figure 2c has wider separation when compared to Figure 2a and b. It can be stated that the intra-particle separation increases with increase in the concentration of  $\text{SiO}_2$ . While sample B has a similar texture and crystallography with SEM of  $\text{BaTiO}_3$  nanoparticle investigated by (Sagadevan and Jiban., 2015)





c

**Fig. 2. Scanning Electron Microscopic (SEM) results of Poly-o-Phenylenediamine doped with silicon dioxide at different Percentage ratio concentration. (a) 80% of Poly-O-Phenylenediamine to 20% of Silicon dioxide SEM for sample A (b) 50% of Poly-O-Phenylenediamine to 50% of Silicon dioxide SEM for sample B (c) 40% of Poly-O-Phenylenediamine to 60% of Silicon dioxide SEM for sample C.**

### Conclusion

By electrochemical deposited approach, Poly-o-Phenylenediamine (PoPD) doped with Quartz Crystal (Silicon Dioxide) at various concentrations of the thin film was created; reveals distinct characteristic features as the doping concentration increases. Sample B and C exhibit a relative and similar crystallographic, Domain, and textural structure of a piezoelectric material like as  $\text{BaTiO}_3$  when PoPD and Silicon dioxide are mixed at a ratio of 50:50 percent and 40:60 percent, respectively. As a result, the optimal doping concentration for piezoelectric device manufacturing is between 50:50 and 40:60 percent PoPD and Silicon Dioxide, respectively.

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