Ionizing organic compound based nanocomposites for efficient $\gamma$–ray sensor

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composites have great potential for low cost alternatives to semiconductor approach
Ionizing organic based nanocomposites for efficient $\gamma$-ray sensor

Outlines..

- Objectives
- Previous studies
- Current approach
- Thin film approach (Well established by Arshak and his group)
- Composite approach
- Results
- Summary

Ionizing organics have some advantages
Ionizing organic based nanocomposites for efficient $\gamma$–ray sensor

Our previous work in this field:

- **Semiconductor crystals**
  - Bulk CZT and CdTe crystals
  - Ternary selenide crystals
- **Heavy metal halides**
  - Mercurous Halides
  - Thallium lead halides
- **Thin film unusual oxides**
  - Pure and doped oxides
- **Nanoengineered Indium** (Cherinkov radiation)
- **Ionizing organic composites**
Ionizing organic based nanocomposites for efficient $\gamma$-ray sensor

Objectives:
Develop nanoengineered composites for radiation sensors

Approach:
\textbf{Base Material:} Nickel oxide
Ionizing organic for matrix: Ethylene carbonate
\textbf{Dopants:} TiO$_2$
Other materials under investigation: MnO$_2$, KMNO$_4$, K$_2$Cr$_2$O$_7$

\textbf{Approach:} Determine I-V curve as grown and radiation exposed composite

\textit{Monolithic NiO$_2$ has been utilized for instrumentation}
Composites have potential for applications where low cost large volume is required.

Chip based detector can be used on every platform.
Cerenkov radiation (emission) is based on nanoparticles

- Idea is to prepare desired size of nanoparticles so that emission is in region where we can observe.
- Emission will depend on particle size

Cerenkov radiation can be used for detection using emission in near IR region
Several novel features will improve performance of detectors

• **What is lacking to make it reality**
  - Materials Red-Ox characteristics must be studied for improvement
  - Materials with different nano- and micro morphology should be evaluated to see effect of morphology
  - Materials with different transparent substrates should be evaluated to enhance sensitivity
  - Electrodes effect is unknown, it will affect sensitivity
  - No data is available for Low cost PVD vs sputtering methods for pure and doped NiOx performance
  - Novel design of diodes may also enhance sensitivity
  - NiOx based devices with at least three modified characteristics will provide better selection for performance
Current status of NiO$_x$ based technology.

• Work done by Prof. Khalil Arshak: Published famous paper Nickel oxide as gamma ray sensor
  • He was the first one to show that NiO$_x$ works

Microstructures have pronounced effects,
There data shows that NiOx does work,

No attempt was made to understand and enhance materials parameters for device and sensor performance

NiOx must be engineered and improved to enhance efficiency
Preliminary work showed feasibility of NiOx based devices, but properties, processes to control microstructures and fabricate diodes must be investigated and improved to make a practical detector.

Preliminary one shot data on effect of thickness and time of exposure.

Measurement of different exposure time showed feasibility, but sensitivity with pure NiOx was low and higher exposure was required.

Design of materials (Red-OX), film quality enhancements, design of electrodes and diodes ill enhance performance suitable for system.
Preliminary work showed feasibility of NiOx based devices, but properties, processes to control microstructures and fabricate diodes must be investigated and improved to make a practical detector.
Composites of Nickel Oxide

Structure of Nickel Oxide
- \( \text{NiO}_x \) mixed in matrix of Ethylene carbonate
- Effect of \( \text{TiO}_2 \)
- \( \text{MnO}_2, \text{K MnO}_4 \) or \( \text{KMnO}_4 \)
- Both together \( \text{MnO}_2 + \text{K MnO}_4 \) together
- Sample 1:
  - Ethylene Carbonate: 9.52g
  - Nickel Oxide: 1.28 g
- Sample 2:
  - Ethylene Carbonate: 10.96g
  - Nickel Oxide: 0.8 g
  - Titanium Oxide: 0.57

- Mixed in molten \( \text{ETCO}_3 \) by melt freeze method
- Evaluate C-V behavior
- Exposed to gamma ray and determine C-V
- Morphology of both pre and post exposed
Relevance for applications of composites

- The significant difference in the I-V characteristics due to radiation source of monolithic and composites based on ionic organics can be explained based on contribution of organic ionic matrix.

- Pair production due to ionization is the major mechanism in organic compounds. The $\gamma$- and $\beta$-radiations easily break the chemical bonds and prevent bond recombination.

- The radiation, $\gamma$-rays or other charged particles lead to ionization process and hence can alter the current-voltage characteristics compared to monolithic oxides.

- This results in larger change in current (high resistance) for the composites compared to monolithic film. Most of the film based NiO$_2$ sensors involve growth of film by high temperature process on desired substrates.
Shaped composites can be designed

Ethylene carbonate composites containing (a) NiO$_2$ and (b) NiO$_2$ and TiO$_2$

(a) (b)

Shaped composites containing (a) NiO$_2$ and (b) NiO$_2$ and TiO$_2$
Processing has significant effect on morphology

- NiO$_2$ and TiO$_2$ doped ETC composites processed at slow cooling rate
- Large crystals are possible at slow cooling

Morphology controls the performance
Sources used in present study

**Alpha, beta and gamma source**

**Cs-137**: 0.25 µCi, 30.2 years, β, γ radiation

https://www.pasco.com/prodGroups/radioactive-sources/index.cfm

- Silver pastewas used as electrode
- LCR meter was used for electrical characterization
- Measurements were taken at 50, 100, 250, 500, 1nd 1,000mV
- 100, 120, 1,000 10,000 100, 000 and 1000,000 Hz was used for each bias voltage
- Radiation exposure of 48 hours was used with commercial Cs-137 source

Radiation source was placed within mm distance
I-V curve showed large difference in slope of virgin and radiated samples

I-V for as prepared NiO₂ composite

I-V for radiated NiO₂ composite at different frequencies

I-V for different frequencies: Radiated composite had lower current

I-V for as prepared and radiated NiO₂ composite at 100Hz

I-V curves for NiO₂ composite before and after radiation exposure at 1000Hz

Frequency and radiation had higher resistivity and hence lower current
I-V curves at all frequencies showed that radiation had similar effect at all frequencies.

Performance of composite at 100 and 10,000Hz.
Effect of TiO$_2$ doping on performance

As prepared TiO$_2$ containing composite showed lower current
Effect of TiO$_2$ doping on performance

As prepared and radiated samples showed identical behavior at all frequencies.

I-V characteristics of TiO$_2$ composite before $\gamma$-ray radiation exposure

I-V characteristics of TiO$_2$ composite after $\gamma$-ray radiation exposure

As prepared and radiated samples showed identical behavior at all frequencies.
I-V characteristics for pure NiO$_2$ TiO$_2$ doped samples

Addition of TiO$_2$ increased the hardness, but decreased the sensitivity.
Resistivity of NiO$_2$ composite

There is no tunability as function of voltage
Resistivity of TiO$_2$ doped composite: TiO$_2$ raises the resistivity and hence lowers the sensitivity.

There is no tunability as function of voltage.
Effect of organic matrix and dopants

- TiO$_2$ had pronounced effect on performance
- I-V curves showed similar behavior at all frequencies
- Current at certain voltage were higher for frequencies
- Ionizing organics have different sensitivity for identical doping
- Processing is very important for the sensitivity
- Effect of particle size on sensitivity is to be studied

Effect of parameters are unknown on sensitivity
Summary

- Ionizing organics have significant advantage
- Commercial source Cs-137 for was used radiation for testing the composite
- It was clear that we observed very significant difference in as prepared sample and radiated sample.
- The data on $\gamma$-radiation interaction with the composite showed that I-V exhibits a linear response that can be used in the development of real-time radiation sensors for the low $\gamma$-ray dose range.
- All samples showed higher resistivity after $\gamma$-radiation.
- The ionic organic ethylene carbonate is a low melting material and has some problems for applications above 38°C.
- We are performing experiments with other organic matrix materials suitable for applications above 50°C and increase mechanical hardness of the composite.

Other ionic organics show similar effect with better mechanical properties.
Thank you for your attention
Topic