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THE PIEZOELECTRICITY AND THE NANOTECHNOLOGIES – A POSSIBLE FUTURE

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Abstract: *Starting by observing the mechanical phenomenon of tensioning – relaxing that repeatedly takes place within the surrounding environment (the example of a leave that moves due to the slightest breeze thus creating a tension into its tail) it has been analyzed the possibility of harvesting those tensions and turning them into electricity. As the idea was new but the phenomenon known for the last several decades (the transformation of mechanical work into electricity = the piezoelectricity and the piezoelectric effect) it has been identified the possibility of designing devices made of materials with known piezoelectric proprieties and adapting them to the original desired applications. The nanogenerators own characteristics so offer new opportunities having multiple field applications: medical, communications, auto industry, electronics, research and lab applications and last but not least the development of new materials, having usage within the construction industry.*

Key words: *nanotechnologies, nanogenerators.*

1. Introduction

By observing the behaviour of naturally occurring mechanical systems, we noticed the phenomenon of tensioning – relaxing that repeatedly takes place within the surrounding environment, so the question arose whether the surface occurring tensions could somehow produce electricity – the methods that could be used to make use of the abundance on tensions and to have them converted to electric power. The phenomenon of tensioning – relaxing mostly observed was the movement of leaves due to the slightest breeze – followed by the appearance of the tensions in their tails. [1], [4]

2. A New Idea with not Such a Shy Past

Following the research was proven that, although original – transforming into electricity the tensions that appear within the tail of a moving leaf and the harvesting of such produced electricity – the notion of "*piezoelectricity*" or the manifestation of electricity within materials subjected to mechanical work has been observed to take place both within naturally occurring materials and the manmade once (Fig. 1, Fig. 2, Fig. 3) , [2].

The naturally occurring materials comprise:

- Quartz, Berlinite (a rare phosphate mineral structurally identical to quartz),

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- Sugarcane, Rochelle Salt, Topaz (a fluoride and aluminium silicate mineral), Tourmaline (a boron silicate mineral crystal),

The man made piezo materials include:

- Artificial crystals – quartz analogue crystals ($GaPO_4$ si $LaGaSIO_{14}$)
- Artificial ceramics – ceramics' family having either perovskite structure or Bronze – Tungsten structure,[3].
- Barium titanate ($BaTiO_3$); Lead titanate ($PbTiO_3$); Lead zirconate titanate – named "PZT"

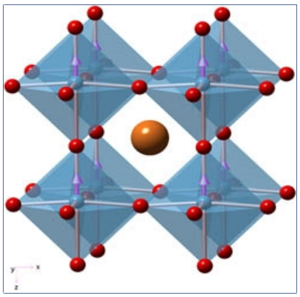


Fig. 1. *Atomic structure - Barium Titanate*

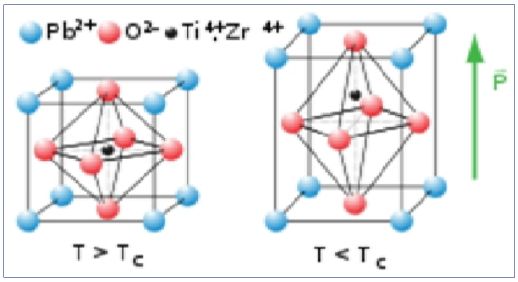


Fig. 2. *Unit cell of Tetragonal Lead Titanate*

- Ceramics without lead
- Potassium sodium niobate (NaKNb); Bismuth ferrite ($BiFeO_3$); Sodium niobate ($NaNbO_3$).
- Polymers - Polyvinylidene fluoride or **PVDF**

We refer to all the above listed substances as materials displaying piezoelectric characteristic.

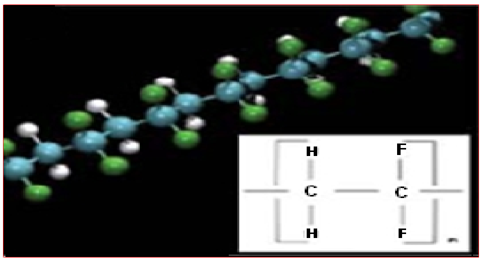


Fig. 3. *PVDF is a high-molecular weight polymer with repeat unit [CH_2–CF_2]*

2.1. The Piezoelectricity[6],[9]

The piezoelectricity refers to the electricity resulted from pressure. The term's origin comes from the greek "*Piezo*" = to squeeze, to press and '*electron*' which refers to amber, an ancient source of electric charge.

The Piezoelectricity is the direct result of the *Piezoelectric effect.*

Although initially discovered by Jacques and Pierre Currie in 1880, the piezoelectric effect displayed by the Quartz has been widely used with applications in sonar technology since the First World War.

During the Second World War the Quartz had ceased its place in favour of Barium Titanate ($BaTiO_3$) for usage in sonar technology, the latter subsequently becoming the most used piezoelectric material.

Currently both the Quartz (SiO_2) and the Barium Titanate are frequently used in many applications.

2.1.1. The Piezoelectric Effect [10], [12]

2.1.1.a. The Description of the Process:

When in a perfect equilibrium, the constituent positive protons, negative electrons and neutral neutrons of any material, do not make possible a measurable electric charge within the material despite the fact that their atoms have a high electric potential.

A separation of electric charges through the removal of atoms from their equilibrium (result of an external applied force – the bending of the material) will cause net electrical charges to appear (the case only applies to crystals having their unit cells asymmetrically arranged), Fig. 4.

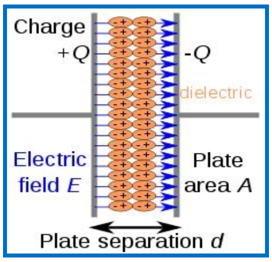


Fig. 4. *An upset of the balance of atoms will cause a spatial separation of positive and negative charges. It will appear on opposite, outer faces of the crystal*

2.1.1.b. Mechanism:

The nature of the piezoelectric effect is closely related to the appearance of strong electric dipole moments in solids. The electric dipole moments can be induced for ions on crystal lattice sites with asymmetric charge surroundings (as in $BaTiO_3$ and PZTs).

For crystals, the dipole density (polarization) "***P***" may be calculated by summing up the dipole moments per volume of the crystallographic unit cell.

Of crucial importance for the piezoelectric effect is the alteration of polarization "***P***" when a mechanical stress is being applied.

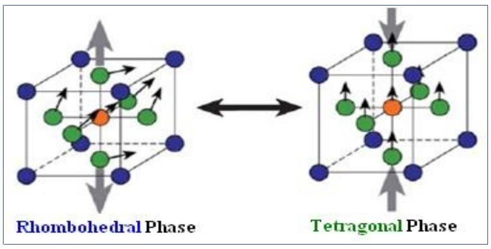


Fig. 5. *Stress-induced phase transition in PZT. Blue = Pb atoms. Green = O atoms. Orange = either Ti or Zr atoms*

In Fig. 5 the displacements of positively charged metal atoms compared to the negatively charged oxygen give a large spontaneous polarization in the PZT crystal at room temperature.

The changing of the polarization '***P***' may have one of the following causes:

- A shifting of the dipole molecular moments under the influence of an external effort (the shape changing of the ceramic disc when pressed – see Fig 7); [11]
- A reconfiguring of the polarisable surroundings due to exposure to an electric field.

Fig. 6. *Piezoelectric ceramic disc attached to a thin flexible metallic disc*

The piezoelectric effect is a reversible process. If an electric current is applied to the same piezoelectric material, the electricity generates an internal mechanical force leading to the deformation of the material, such characteristic leading to extremely useful applications (Fig 6)

3. The Nanotechnologies – The New Wave Overcoming the Old Technological Barriers [5], [8], [13]

3.1. The Nanomaterials

The development of technologies that allowed creation of nano dimensional materials, by atom manipulation, has opened a new perspective for the piezoelectric materials' domain, Fig. 8.

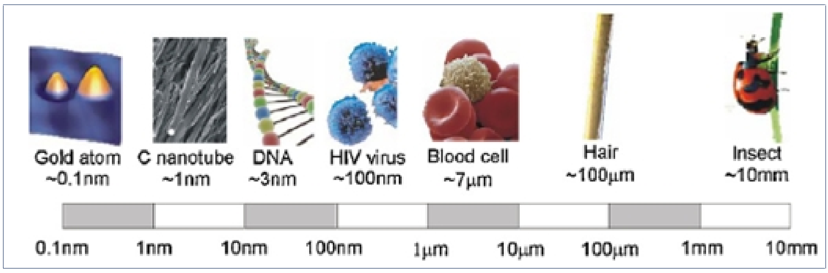


Fig. 7. *Comparison of diferent sizes*

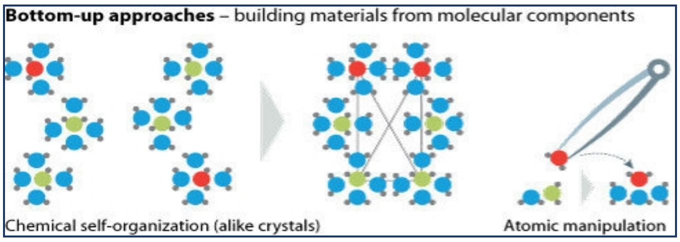


Fig. 8. *The synthesizing of materials from molecular components (metal oxides in particular)*

Out of the new nanomaterials category of particular interest for piezoelectricity are both those obtained from Gallium nitride (GaN – used in making of the blu-ray technology) and those synthesized from different metal oxides – TiO_2, Al_2O_3, ZnO, SnO_2, CuO – all of them presenting notifiable piezoelectric properties. [7]

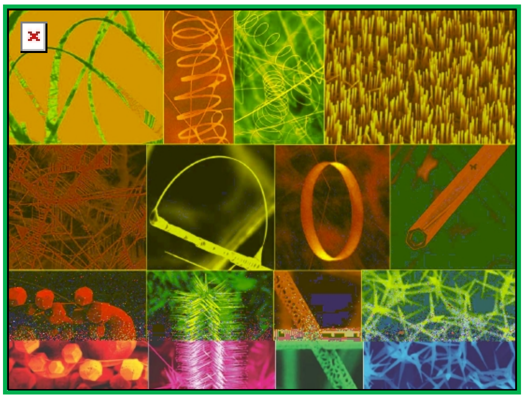


Fig. 9. *ZnO nanostructures (nanocombs, nanorings, nanohelixes/nanosprings, nanobows, nanobelts, nanowires, nanocages)*

In Fig. 9 are shown ZnO nanostructures synthesized under specific growth conditions using a solid-vapor phase thermal sublimation technique. Most of the pictured structures can be obtained having 100% purity.[11]

These nanomaterials having controlled composition, surface endings and crystal structures are of importance in the realization of innovative devices – the *NANOGENERATORS.*

3.2. The Nanogenerators[

Are integrated nanosystems obtained from metal oxides nanowires (Zn, Ti) having particular piezoelectric properties, assembled (grown or printed) on flexible substrates and allowing electricity generation by harvesting and transforming mechanical energy, a process that becomes much more efficient no longer being restricted by the limitations imposed by the traditional piezoelectric materials, Fig. 10 a, b. [14], [16].

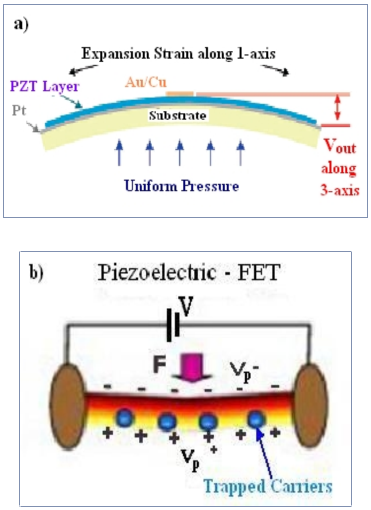


Fig. 10. *a) A PZT layer having the substrate, the top and base electrodes indicated;*
b) The piezoelectric field (FET) produced across a nanowire by an external force F.

In Fig. 11, the key innovation leading to the emergence of the nanogenerator was the designing of a new zigzag shaped electrode coated with Pt, having parallel peaks and valleys alternately arranged.[13]

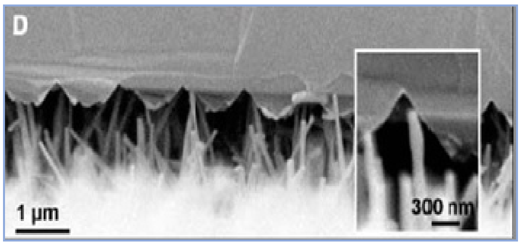


Fig. 11. *The top zigzag electrode interacting with vertically aligned array of ZnO nanowires*

The top zigzag electrode, having beneath the vertically arranged arrays of ZnO nanowires, causes the compression and bending of a large number of nanowires when moving, thus generating the electric current that the conductive bottom electrode collects simultaneously,[15].

3.3. Advantages

The piezoelectric coefficient displayed by the nanowires having a diameter of 2.4 nanometers is 20 times higher for ZnO nanowires and 100 times higher for GaN nanowires when compared to the coefficient displayed by the same materials at macro scale, Fig. 12.[17]

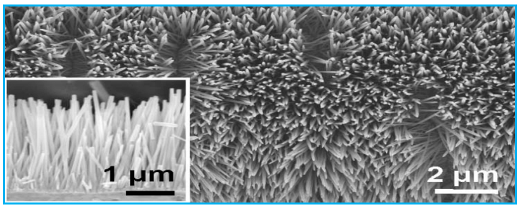
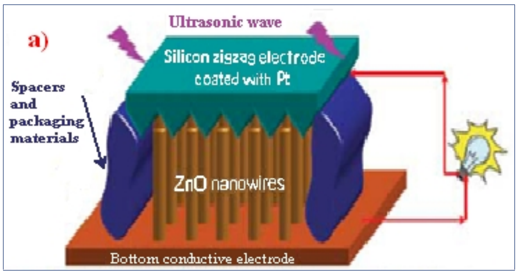


Fig. 12. *Arrays of ZnO nanowires grown either on a GaN substrate or sapphire substrates that are covered by a thin layer of ZnO film, serving as a common electrode for directly connecting the nanowires with an external circuit.*

As the entire nanosystem is totally encapsulated, the nanogenerators can be used in a variety of environments, Fig. 13.



a) Graphic sketch

b) The experimental built device
Fig. 13. *A totally encapsulated nanogenerator*

The entire nanowires system can be grown both on flexible and on stretchable substrates at relatively small temperatures (< 100º), making it economical, reliable, with low manufacturing costs, and suitable to a multitude of substrates, Fig. 14. The lack of mobile, constitutive parts significantly increases the usage life of nanogenerators, depending only on the ageing of the used substrates.

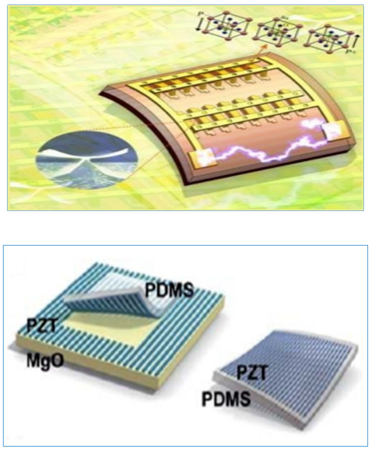


Fig 14. *Flexible nanogenerators thin film type, without moveable, quick wearable constitutive parts[19]*

4. Remarks

The excellent performance of ribbon type piezoelectric nanodevices coupled with biocompatible, flexible substrates suggests various applications starting with their introduction in both our everyday activities for the purpose of supplying with power electric mobile devices (phones, MP3's) and medical usages where the biomechanical energy offered by the human body's regular movement (organs) could be harvested and transformed in useful electric energy supplying a range of implantable medical devices (pacemakers, insulin delivery pumps, magnetic valves serving as urinary sphincters).

The generator's small dimensions are opening the road for the designing of new devices functioning without batteries, devices supplied by the surrounding's harvested mechanical energy, therefore the nanogenerators are emerging as a new, viable alternative of today's energy sources. Of the total possible usages we refer to the following:

- The nanogenerators are functioning at frequencies lower than 10Hz, in the range of the conventional mechanical vibrations (such as stepping, heart beating) therefore substantially expanding the areas of the piezoelectric devices' applications:

a) The naturally occurring energy sources (wind, vibrations, sound, waves) and the biomechanical forces produced by the human body (the heart beating, swinging arms, bending knees, lung and cavity expansion during respiration) could produce inexhaustible, clean energy;

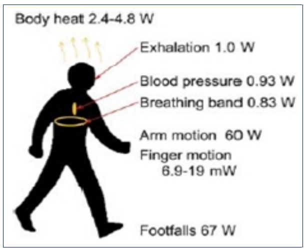


Fig. 15. *The total available power for every day bodily activities[18]*

b) By making use of ZnO nanowires grown on textile fibers it has become possible the designing of pliable, bendable, wearable, robust energy sources made of textile materials in any shape – as an example a shirt or power generating pair of trousers, Fig. 15 ;

- In ***Nano Letters*** in a published document doctor Zhong Lin Wang demonstrated the ability of five stamp sized nanogenerators stacked together, when squeezed between fingers, to produce about 1 μAmpere output current at 3 volts – similar to the voltage of 2 regular batteries of 1.5 V each, Fig. 16.

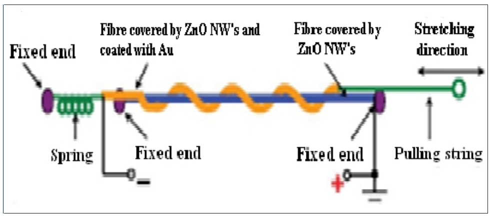


Fig. 16. *ZnO nanowires grown on textile fibers*

- The possibility of creating independent nanosystems made of nanosensors coupled to ZnO nanogenerators, having the following usages:

a) The detection of pH and UV;

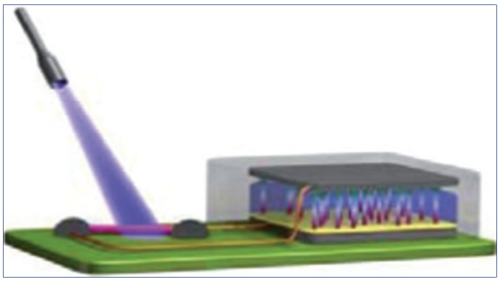


Fig. 17. *A ZnO based UV nanosensor coupled with a nanogenerator in an energetic independent nanosystem*

b) Creating environment sensors powered by nanogenerators motioned by wind;

c) Ultrasound sensors;

d) Wireless hermetically encapsulated sensors, powered by bridges' vibrations, that could collect data for long periods of time without the need for maintenance, offering a continuous monitoring of different parameters such as icy conditions, cracks or corrosion, traffic flow etc;

e) Creating chemical sensors without batteries, sensors that take advantage of the dynamic interaction between molecules and the semiconducting nanowires' surfaces (interaction that induces an electrical charge) Fig. 18.

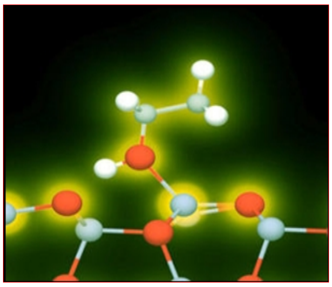


Fig. 18. *A chemical sensor without battery. The nanosensor responds selectively for different types of chemical categories and concentration levels.*

Due to their extreme precision and fast response, the piezoelectric nanomaterials have found applications in the field of nanopositioning, designing of mechanisms and control systems for accurate movement, domain that requires the control of vibrations, positioning errors and shifts to less than 0.1 nm;

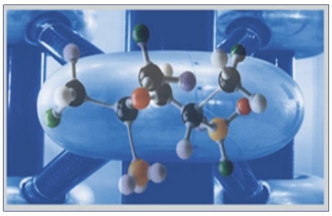


Fig. 19. *As the conventional positioning systems do not offer the required stability and accuracy, a fast response and high precision is offered by the nanosensors with usage in measuring motion as accurate as the sub-nanometer range.*

The inherent properties of the new nanogenerators are offering new opportunities with applications in multiple fields: medical, - auto, - electronics, - research and laboratory applications and not least in the development of new materials for construction purposes, Fig. 19.

The potential offered by the nanogenerators is therefore limited only by everyone's imagination.

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