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**Inaugural Lecture Series 192**

**MATERIALS, THE BASIS OF THE  
BEAUTY OF MODERN DAY ELECTRONIC  
SYSTEMS.**

**By**

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*Professor of Electronic Materials and Devices*



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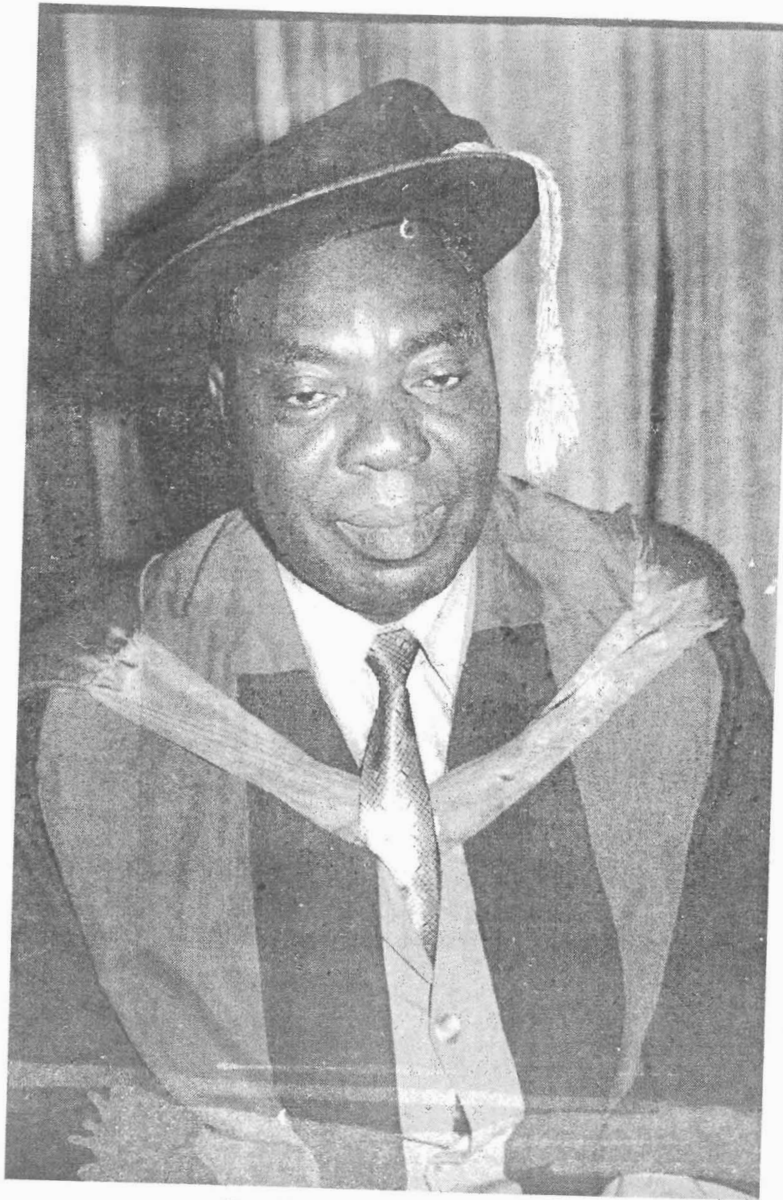
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*Professor of Electronic Materials and Devices*

**An Inaugural lecture Delivered at Oduduwa Hall,  
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## INTRODUCTION

We encounter the use of electronic devices and systems in our everyday life, from the simple radio set to the television set, the mobile phones, electronic cameras, electronic computers and the whole electronic gadget world. The improvement in the presentation (or apparent attractiveness), usefulness and complexity of these gadgets are common knowledge. Gone were the days when a computer system was big enough to fill this auditorium, but what is the situation today? We can hold in our palms a computer system that will equate the functions of the room filling one and even perform better, faster and more reliably.

When we talk about the "beauty" of the electronic system, we are not talking about the apparent beauty of the packaging (and we all know that these days they are real pretty to look at), but rather, that of the component devices that are packaged in the system we see. Many a time the actual devices within the core of the packaging are not visible. While you see the transistor radio blasting nice music to you, what you see mostly is the packaging, but not the active device components like the integrated devices, the discrete transistors or the passive resistors and capacitors, etc, that have been put together as circuit elements to build up the transistor radio as an electronic system.

This talk will be more on the "beauty" associated with the development of those devices that make the electronic systems tick.

What is important to appreciate is that those inner core devices are made with specialized materials, the processing and

development of which are carried out in modulated fashions to make their use in system development through the assemblage of these devices realizable to give the effects that we perceive. We must also state that for the finesse of the packaging, materials development across the years have also led to improved presentation, ruggedness and the attractiveness we see with the package.

What are materials? Why have they become so useful to have become the basis of the beauty of the electronic systems in today's use? According to Moris Cohen (Cohen, 1979), "materials are a part of the matter in the universe, but more specifically, they are substances whose properties make them useful in structures, machines, devices or products". The category of materials include metals, ceramics, semiconductors, polymers, vinyl plastics, glasses, dielectrics, fibers, wood, water, sand, stone and many composites. Materials are in essence the working substance of our society. They play a crucial role not only in our way of life, but also in the well-being and security of our nations. The role of materials in the evolution of technology is exemplified in the story of the discovery and exploitation of the transistor. The transistor is often considered to be the base technology for the Information Age. The ability of this single device to have such unique characteristics-and, as a result, such an overwhelming impact-was due in no small part to the very special materials properties of silicon and its oxide. We find that the use of materials cut across all the bodies of knowledge and especially engineering and science, which has led to the development of an area of knowledge called Material Science and Engineering. To the Electronic mind however, interest is in such materials that can

be classified as "Electronic Materials", which are more related to the development of electronic devices and systems.

There is a wide and expansive spectrum of electronic materials and devices. This talk is not going to give a compendium of all electronic materials, devices and systems, but will relate more to my exposure within the wide area of the electronic materials world.

My research interests have been specifically directed to the development, characterization and device application of materials towards the fabrication of electronic devices and hence system build-up. This talk would therefore be focused on my contributions to the development of semiconductor electronic devices. Since the trend these days is to be able to have the devices and their powering units in the same assembly or package, the talk will also address my contributions towards the realization of power producing devices like solar cells and all solid state batteries within the framework of electronic system build-up.

### **From Microelectronics to Nanoelectronics and Molecular Electronics**

Microelectronics is a special field of engineering that has evolved over the past 60 years. It encompasses the design, fabrication, and testing of electronic circuits based on semiconductor structures of submicrometer feature size. Through its entire history, the development of microelectronics was driven by a rapid succession of inventions that permitted revolutionary



improvements in the performance and reliability of electronic circuits accompanied by a drastic reduction of their cost.

Until about 45 years ago, electronic devices including the early computers depended on the use of vacuum tubes or valves which were relatively bulky components and relatively power-hungry. The origin of microelectronics may be traced back to the invention of the point contact transistor by John Bardeen and Walter Brattain in 1947 (Barden and Brattain, 1948), and of the junction transistor by William Shockley in 1950 (Shokley, 1952) at Bell Telephone Laboratories. These devices were originally made from germanium, which has been almost totally replaced by silicon which shares a common diamond crystal structure with it.

In 1958, Jack H. Kilby of Texas Instruments (Kilby, 1954) added to the invention of the transistor the concept of the integrated circuit (IC), setting the stage for modern microelectronics (Augarten, 1983). An IC consists of internally interconnected transistors and passive elements, such as resistors and capacitors, and is fabricated on a single semiconductor chip, keeping the length of input and output lines to a minimum. This provides for high reliability and the economic use of materials, minimum resistive power loss, and minimum delay by the minimization of the RC constants associated with the device elements and connecting metal lines. However, an understanding of the design and function of the devices that are used in their implementation is essential for the selection of materials and processing options, which is an important point in the discussion of the materials science of microelectronics. With advances in technology, the integrated devices have gone smaller and more complex. Today,

the closely packed integrated circuits, made with the concept of the ultra large scale integration (ULSI), containing not only transistors but also components such as resistors and diodes, contain more than 1,000,000 (1 million) components in a chip measuring 5 millimeters across and with aluminium connection 100 times thinner than human hair, as against the earlier concept of the very large scale integration, (VLSI), that had about 100,000 transistors per chip. Concomitantly, the computing power has drastically increased, and the cost per operation has significantly declined. As a consequence of this development, the cost of the products of the electronic industry has dramatically decreased. For example, the cost of electronic calculators declined between 1980 and 2000 by over 3 orders of magnitude. There has been extremely rapid development of the industry in the US, Europe and Asia. The world market value of semiconductor ICs alone is predicted to be about \$3 trillion in year 2000, and is currently the world's largest industry.

As stated earlier, the first set of devices were built with germanium. These have however now been mostly replaced with silicon, which incidentally derives from quartz sand. Apart from silicon, studies have shown that semi conducting materials deriving from compounds formed between elements of the Groups III and V of the periodic table, such as GaAs, InAs, InP, InSb, GaSb, AlN, etc (Fornari, 2001) have adequate characteristics for the development of semiconductor devices, and are so largely applied either in their single crystal form or more especially in their thin film forms, when the planar techniques utilized for silicon devices production are also employed. Consequently, recent interests have been with the

development of thin film transistors "and associated devices.

As the complexity of the semiconductor devices increased especially in the late 1970s, when the move was from Large Scale Integration (LSI) to Very Large Scale Integration (VLSI), the need arose for multilevel interconnection of the metal lines to device points. Usually, aluminum metal lines, generated through vacuum evaporation or by a sputtering process, were mostly used, while silicon dioxide or silicon nitride were found to be adequate for monolayer isolation of device surfaces from metal lines. The thermal cycling associated with the deposition of these dielectric films was found to affect device performance. Consequently, research into multilevel devices connection studies that would eliminate the thermal cycling problems were undertaken. My modest contribution then involved the development of a two level metallization system (Kuku, 1978) and involved the partial anodisation of the aluminum interconnection film, such that the ensuing aluminum oxide can be used as a dielectric, and hence an adequate electrical isolation medium between layers of conducting aluminum interconnects. More recent developments have however involved the use of Chemical Vapour Deposited (CVD) silicon dioxide, or silicon nitride, or polyimide (Gong *et.al*, 1990).

As stated above, metal deposition was achieved by the evaporation or sputtering of the metal layer. Metal delineation or patterning was by chemical etching with integrated photolithographic and photoresist processes or by a high energy ion etching process. Since it was discovered that these processes had some telling effects on the performances of devices, a simpler

and somehow more efficient photo-fabrication process was developed and it involved the photolysis of metal halides in vacuum or air to give the oxides, and the subsequent reduction of these to metal in hydrogen plasma (Green and Kuku, 1983, Kuku and Green, 1986). Using appropriate masks, metal lines of micron dimension could be delineated. An example of such patterns are as shown in Fig 1, where line resolutions of 2.5 micron are defined, the lines obtained here were limited by the resolution of the chrome/glass mask used.

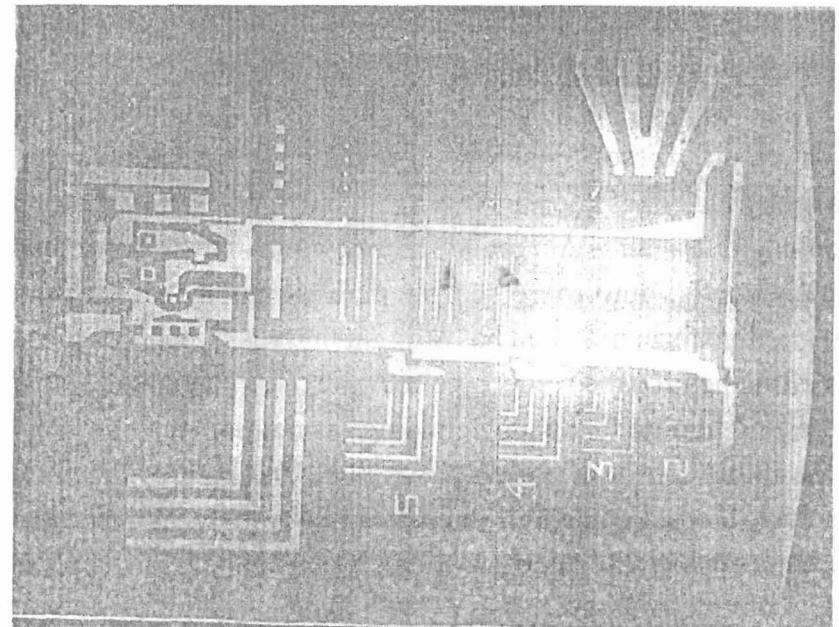


Figure 1: Tin Metal Pattern Generated from the Photolysis of Tin diiodide thin films

Across the globe, the technology of devices development has gone beyond the stages of VLSI to ULSI, and currently, realizations are for nano devices or nanoelectronics.

Nanostructures are assemblies of bonded atoms that have dimensions in the range of 1 to 102 nanometers ( $1 \text{ nm} = 10^{-9} \text{ meter} = 10 \text{ \AA}$ ). To Solid State Physicists, Material Scientists and Electrical Engineers, nanostructures are very small. For decades, microelectronic researchers were happy to think of electrons as particles - miniature ping-pong balls that bounced around between energy bands and pelted through switches and wires. Now by making ever more miniature semiconductor structures, they're discovering the other side of electron's quantum-mechanical duality: their wave nature. Material Scientists are now building devices so small that they cramp electron waves, forcing them into specific wavelengths and energies.

As a result, these "quantum structures" -nanoscale layers, channels, and boxes known as quantum wells, quantum wires and quantum dots- turn the broad energy bands of conventional semiconductors into more sharply defined energy levels. And that is a transformation that has brought into reality greater speed and efficiency for the resulting circuits and optical devices. It is interesting to note that nanotechnology is no more a technology of the future, but it is presently with us. One kind of quantum structure, the quantum well, has already found its way into the transistors in satellite microwave receivers and the lasers in some fiber - optics communication system and in the run-of-the-mill compact disc players we mostly have in our living rooms. It may also be noted that nanoscale technology has entered important energy conversion and storage fields such as nanocrystalline photovoltaic cells, photo-electro-catalytic fuel generation, materials treatment, photo-electrochromic devices, fuel cells,

modern batteries, supercapacitors, sensors, etc (Sebastian, 2003). By a way of comparison, we have below (Fig. 2), the picture of the first transistor, and that realized using nanotechnology, in which we have only three atoms of gold serving as the interconnection between the source and drain of the transistor device. The source-drain separation is 30nm (300  $\text{\AA}$ ) (Durkan and Welland 2000). With this sort of structure, we all can therefore imagine the level of complexity that is now possible to be achieved with circuit developments, and hence, the improved miniaturization of electronic devices and systems all being based on material manipulations!

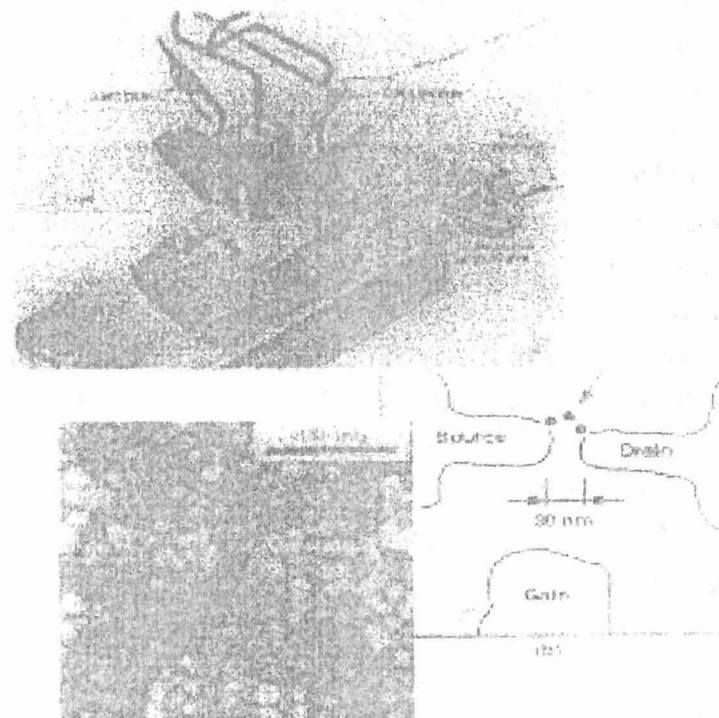


Figure 2. (a) The first solid-state transistor and (b) a single electron transistor, illustrating the extent to which devices dimensions have decreased over last 50 years.



The semiconductor industry has seen a remarkable miniaturization trend, driven by many scientific and technological innovations. But if this trend is to continue, and provide ever faster and cheaper computers, the size of microelectronic circuit components will soon need to reach the scale of atoms or molecules—a goal that will require conceptually new device structures. The idea that a few molecules, or even a single molecule, could be embedded between electrodes and perform the basic functions of digital electronics—rectification, amplification and storage—was first put forward in the mid-1970s. The concept is now realized for individual components, but the economic fabrication of complete circuits at the molecular level remains challenging because of the difficulty of connecting molecules to one another. A possible solution to this problem is 'mono molecular' electronics, in which a single molecule will integrate the elementary functions and interconnections required for computation. Molecules have not historically played a prominent role in electronic devices. Ten years ago, chemical applications were limited to the use of small molecules such as silanes ( $\text{SiH}_4$ ) and germanes ( $\text{GeH}_4$ ) as thin-film precursors or as the components of etching processes, resist precursors, packaging materials, and the like. However, over the next 10-20 years, molecules may be increasingly viewed not just as the starting points for bulk electronic materials, but as the active device components within electronic circuitry. Although this possibility is hardly a foregone conclusion, a number of fundamental issues favour the development of a true molecular-based electronics. At device areas of a few tens of square nanometers, molecules have an inherent attractiveness because of their size, because they represent the ultimate in terms of atomic

control over physical properties, and because of the diversity of properties—such as switching, dynamic organization, and recognition—that can be achieved through such control. Although molecular electronics has been the subject of research for some time, over the past few years a number of synthetic and quantum chemists, physicists, engineers, and other researchers have sharply increased the ranks of this field (Heath and Ratner, 2003). Several new molecular-electronic systems, analytical tools, and device architectures have been introduced and explored. As a result, the basic science on which a molecular electronics technology would be built is now unfolding, and the science and applications that are emerging are tremendously exciting. For example, current research is using molecules in such electronics applications as interconnects, switches, rectifiers, transistors, nonlinear components, dielectrics, photovoltaics, and memories. The essential science in these areas reflects the broader field of molecular electronics, and although certain fundamental challenges have been faced, many others must still be overcome.

### Photovoltaic Materials and Devices

Our flourishing twenty first century civilization is based on large scale consumption of precious and irreplaceable reserve of fossil fuel that has taken eons of ages to build up. Nowadays, two kinds of crisis are frequently discussed: one is the exhaustion of these precious fuel resources, and another is the rapid corruption of the global environment.

Though it may be debatable which of the two crises will come to a head earlier, it is certain that both have arisen by the too rapid, and

in a sense thoughtless, waste of underground fuel resources. Some experts say that the proved recoverable resource (PRR) for oil will expire in 35 years with the present speed of consumption. If this is really true, we should panic right now, especially for us in Nigeria that our whole existence depends on the oil money. Some other oil experts are more optimistic and estimate that fuel resources, including natural gas, but not including coal, may last more than 100 years. However, even a prediction of 100 years does not comfort us as much, when we consider how many years it will take to transform our present civilization, as typified by automobile and air transportation, into a much more energy-conservative one, or to establish the way of getting new, clean, and sustainable energy. The use of coal and nuclear energy cannot be sufficient to save the situation, and the development of nuclear fusion is uncertain.

What this speaker believes is that the only sustainable source of energy that our descendants will be able to rely on is solar energy, which is the ultimate source of all the energy that mankind has depended on from the beginning. By using solar energy as our future source of energy, we can certainly avoid both the two crises. In this talk, I shall take up solar cells as one of the most attractive and important techniques of solar energy utilization. Emphasis shall be on the materials aspect that has made the utilization of this energy source a reality.

The devices that convert solar energy to electricity are called solar cells. The silicon solar cell was first developed by Chapin, Fuller, and Pearson of RCA in 1954 (Chapin, 1954). Since then, the development of solar cell technology has been remarkable. Efficiencies have improved, manufacturing cost has decreased,

and production has increased.

The major elements of the junction-type solar cell include: (a) the top metal (grid or finger) electrode, which must be partially open in order to allow the light to reach, (b) the top semiconductor layer which is n type silicon. The junction is made to the (c) base silicon semiconductor, of opposite polarity (p-type) to (b). An ohmic metal contact is made to this base, and the top and bottom contacts are connected to the external load. Usually an antireflection coating  $\mu\text{m}$  is deposited on the top semiconductor to minimize loss of radiation by reflection. In its basic form the solar cell is composed of these five layers.

For even the most complex and largest photovoltaic energy generation installation, the single-component solar cell is the basic building block. These individual devices are connected into series (to provide increased voltage) and parallel (to provide increased current) combinations in a module that encapsulates the cells, protecting them from the environment. The connection into a single structure is called an array. An array field is the grouping of such arrays with support structures to provide the needed electricity. This hierarchy of photovoltaic system is shown in Fig 3. The full photovoltaic system is composed of the array field, any necessary power conditioning (inverters to provide AC, voltage regulators, etc.) and any needed storage components (e.g., batteries).

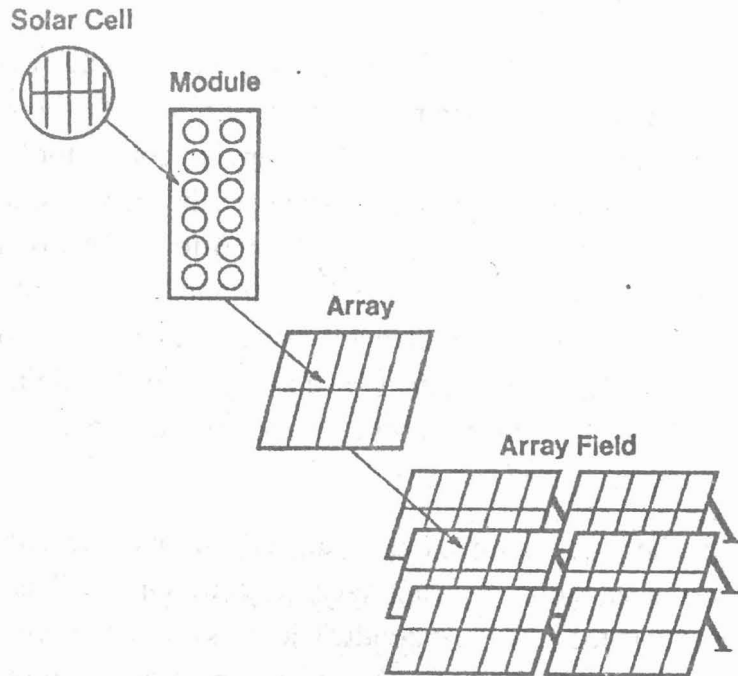


Figure 3: Hierarchy of photovoltaic terms

To give an idea of the amount of solar energy, let us take an example. The total annual world consumption of energy now is about  $32 \times 10^{16}$  kJ. The solar insolation in the Sahara Desert is of the order of  $7.5 \times 10^{12}$  kJ/km<sup>2</sup>/year. Therefore, we can provide all the world's energy needs (not only electrical energy but all energy, including that of petroleum, coal, hydropower, and so on) by placing solar cells of 10 % efficiency in an area about  $42.7 \times 10^4$  km<sup>2</sup>, that is, about 5 % of the Sahara Desert.

To realize such a dream, we must work hard not only to improve our solar cell efficiency, but also to reduce the cost of solar cells.

Contemporary solar cell technology is dominated by crystalline silicon. The annual rate of growth of cell reached 40 % in the year 2000, with around 80-90% of cells being based on crystalline silicon. The current primary goal is to continue this successful development, and to reach a few GWp of installed power production at the end of the present decade (*Gasheva et al, 2003*)

Promising alternatives for solar energy utilization are thin film technologies involving various new materials (Deb, 2002). The stimulus for thin film photovoltaic technology development is supplied by the advantages which it offers in : (i) decreasing the amount of expensive semiconductor material required, (ii) using low-cost substrates, and (iii) fabrication of large area cells and modules. A substantial reduction in the manufacturing cost of solar cells is expected via this approach. Various materials other than crystalline silicon are being considered for the preparation of solar cells. The energy gap of the absorbing material is considered the first indication of performance potential for a photo voltaic material. Since the solar spectrum is not constant, but varies with wavelength, then the matching of the energy gap to the solar spectra has led to a number of calculations of the optimum energy gap for a photo voltaic material, and predicts an optimum energy gap of 1.5-1.6 e V for a semiconductor to be used for solar cell fabrication. Such materials include CdTe, GaAs, CuInS<sub>2</sub>, InP, Cu<sub>2</sub>S.

Currently, the highest efficiency solar cells have been fabricated using III-V materials, especially GaAs. A conversion efficiency higher than 25% has been achieved on single junction solar cells fabricated in epitaxially grown GaAs on a single crystal substrate.



Efficiencies over 30% (actually 33.3%) at AM 1.5 have been achieved in a monolithic tandem cell device consisting of GaInP<sub>2</sub> (top cell) and GaAs (bottom cell) with a low resistivity tunnel junction interconnect. Cells with over 50% conversion efficiency using a Braggs reflector base has been proposed for the future (Yamaguchi, 2002).

So far, amorphous silicon (a-Si:H), cadmium telluride (CdTe) and copper indium diselenide (CIS) thin film PV technologies have been commercialized.

The technology of a-Si:H for PV is based on two types of device design: a single junction and multijunction p-i-n structure. It is generally recognized that any significant increase in efficiency can only be achieved by using multijunction devices. This has indeed been the case as shown by the achievement of a world record stable efficiency of 13% (initial efficiency of 14.6%) in a triple-junction structure (Yang *et al*, 1997). It has also been shown that a combination of amorphous and microcrystalline material can be used to fabricate a tandem structure called the "micromorph" cell with a stable efficiency around 13% (Meier *et al*, 1998).

Thin film silicon also offers exciting opportunity for the development of efficient low cost solar cells. The most exciting new development is the achievement of 9.8% efficiency in a 3.5  $\mu$ m film and 9.3% in a 1.5  $\mu$ m poly-Si film with the structures glass/back reflector/n-i-p p-Si/ITO/Ag grid and it has been named the "STAR" cell (surface textured-enhanced absorption with back reflector) (Rath, 2003)

A notably successful technology is that using copper indium diselenide (CIS), where conversion efficiency of the order of 18.8% has been reached using the physical vapour deposition (PVD) technique (Contreras, 1999). The deposition of a high quality copper indium gallium selenide (CIGS) absorber layer is the crucial processing step, and thus far, the PVD technique appears to be the preferred method. Cell efficiencies exceeding 16% are achieved routinely. Recently, Siemens Solar Industries started to market CIGS modules of world record efficiency of 12.1 % for an aperture area of 3651 cm<sup>2</sup>.

Thin film solar cells based on the cadmium telluride (CdTe) have recorded efficiencies close to 16% for small area devices at laboratory level. Module efficiencies are however mostly quoted as being between 8% and 10% (Mathew *et al*, 2003).

Two of the major problems in the use of CdTe for cell fabrication are the doping of the material to obtain low resistivity films as well as the growth of films with improved grain sizes. I was able to join with other researchers to develop an innovative method of doping CdTe films with atomic nitrogen, produced by a plasma process (Romeo *et al*, 1989, 1991) as well as growing films with improved grain sizes by using cadmium chloride treatment. Such films gave solar cell devices of about 10 % efficiency (Romeo *et al* 1994) An industrial plant to produce cells and modules commercially is currently (as I talk) being set up in Parma, Italy, and is based on these processes (Romeo, 2005).

Apart from the celebrated materials being currently utilized in the

development of solar cells and modules, interest continues to be put actively on the study and device realizations from new materials that have absorptive characteristics similar to the proven materials.

As stated earlier, materials having optical energy gaps in the range 1.4 to 1.6 eV could be very adequate for solar cell development. Our interest in my laboratory at Ife has been therefore directed towards the development of new materials for electronic devices realization. A number of novel materials have been developed. These include  $\text{Cu}_2\text{SnS}_3$  (Copper tin sulphide) and  $\text{PbSnS}_3$  (Lead tin sulphide). The fundamental properties of  $\text{Cu}_2\text{SnS}_3$  were studied and the material was found to have its optical direct edge at 1.51 eV, with high absorption coefficient across the visible (Kuku and Fakolujo, 1987, Kuku *et.al*, 2004). The thin film was subsequently applied for solar cell devices development (Kuku and Azi, 1993, 1994) with appreciable efficiency.  $\text{PbSnS}_3$  was also found to be very absorptive with its optical edge at 1.44 eV, and its other fundamental properties indicating the possibility of its use for solar devices development (Kuku and Azi, 1992, 1994, 1998, Kuku, Azi and Osasona, 2006). Further studies of the behaviour of the material in built up devices is currently being pursued.

The antireflection coating listed as a part of the solar cell structure is made up mostly of conducting and spectrally selective tin dioxide,  $\text{SnO}_2$  film. Such materials could be deposited using chemical vapour deposition, sputtering or evaporation techniques. We have however developed other simpler

techniques here at Ife for the deposition of such films using a photolytic process, and involved the photolysis of the halides involved with subsequent oxidation in air atmosphere at relatively low temperatures (Kuku, 1986a, 1986b, 2006).

It may be remarked that the technology of the solar cell development has advanced remarkably, and its application has been many and varied from the powering of hand held calculators to the establishment of solar array farms for electricity production into national grids, to architectural inclusion in highway side structures, to being part of the roof or facades of buildings

### Thin Film Solid State Batteries

Demand for low power, battery operated devices is on the rise, particularly in portable equipment needing longer operating life with high reliability. Most of the electrochemical generators manufactured today were discovered at the end of the 19th century. This is the case of the manganese dioxide cell (Leclanche, 1868), the Lead accumulator (Plante, 1859) and the ferro-nickel accumulator (Edison, 1900). The characteristics of these batteries and accumulators were considered to be acceptable by users for a long time. For the past 20 years or so, mass production of industrial objects with their own sources of power (computers for the popular market, Communications (cellular phones), medicine, photography, watch making, space, etc.) has led to a new growth in research on new, essentially solid state types of energy sources. Efforts have therefore been intensified in these years to synthesize solid electrolytes with very advantageous features (good ionic conductivity, charge

carrier selectivity, very low electronic transport number, etc.). All solid state electrochemical systems (batteries) have thus been developed. These have many advantages over systems using liquid electrolytes: no problems of liquid seal, no passivation and corrosion, etc. These capabilities, linked with an ever increasing need to integrate electrical circuits using the miniaturization of components have led to the emergence of a branch of research called "microionics" by analogy with microelectronics. The initial idea was to profit from the knowledge and skill available in the microelectronics field (thin film fabrication techniques and characterization) to make miniaturized batteries.

Like all electrochemical devices, these systems use the reactions which occur at the interfaces between electronic and ionic conductors, i.e. between electrode and electrolyte (ion transport, charge transfer at interfaces). The main problem in microionics, and more generally in all solid state electrochemical systems, lies in choosing the combination of electrolyte/electrode materials which displays the best features (low internal resistance, good charge transfer, etc).

The first set of solid state micro batteries were fabricated with silver ion  $\text{Ag}^+$  conducting materials and principally  $\text{AgI}$  and  $\text{RbAg}_4\text{I}_5$ . After this, many other superionic conductors were tried. Many of these are ternary or multinary halide materials with very high anionic or cationic activity. Generally for these superionic conductors, the ions that are mostly labile are the  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ , or  $\text{O}^{2-}$  ions. Again the, interest in my laboratory has been geared towards the development of novel

materials whose properties can be assessed to see if they can be adaptable for the production of all solid state battery structures. To this end, number of novel ternary halide materials have been developed, and include  $\text{CuPbBr}_3$ ,  $\text{CuPbI}_3$ ,  $\text{CuSnI}_3$ ,  $\text{KPbI}_3$ ,  $\text{CuCdCl}_3$ ,  $\text{PbSn}_4$  etc. Since these materials are of novel synthesis, the contributions to the literature have been a combination of their solid structural properties (X-ray, DSC, TG, SEM, TEM etc), optical and electrical (ionic and electronic) conductivity characteristics (Kuku, 1986, Salau et al, 1987, Kuku, 1987, Kuku and Salau, 1987, Kuku and Adeosun, 1988, Kuku *et al* 1989, 1990, Kuku 1992).

Also, all solid state microbatteries have been developed from  $\text{CuPbI}$  and  $\text{PbSnLi}$  with the cell configurations  $\text{Pb/CuPbI}/\text{AgI}/\text{Ag}$ , and  $\text{M/PbSnLi}/\text{AgI}/\text{Ag}$  ( $\text{M}=\text{Sn}, \text{Pb}$ ), with all the film structures achieved by vacuum evaporation of the different materials (Kuku 1998, Kuku 1999). The discharge characteristic of  $\text{Pb/CuPbI}_3)/\text{AgI}/\text{Ag}$  microbattery is as shown in Fig. 4.

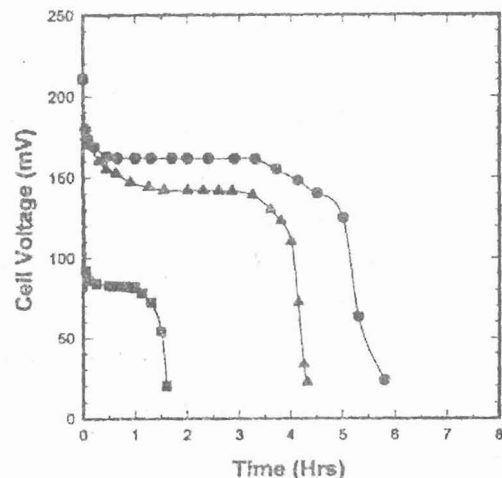


Fig. 4 Variation of cell potential with time for a galvanic cell of the form  $\text{ph/CuPI}_3/\text{AgI/Ag}$  when different loads of (a) ● 500 k $\Omega$  (b) ▲ 200 k $\Omega$  ■ 35 k $\Omega$  are applied at room temperature.

Apart from the use of polycrystalline materials that have the inherent disadvantage of grain boundaries and allotropic transformations, especially with the  $\text{Ag}^+$  conductors, another class of materials, ionic conductive polymers have been developed (Sekido *et al.*, 1981). These removed the two disadvantages which put limits to the possibilities of electrochemical systems: there are no grain boundaries, thus the intrinsic conductivity of the material is conserved and, above all, polymers have high plasticity ensuring excellent contact with the cathode material (whose volume varies during the cycles). Unfortunately, a high anionic transport number (around 0.5) has restricted the development of devices in which these materials are used.

Interest these days is being concentrated on the development of

vitreous ionic conductors. They have very good conductivity, wide choice of compositions, high suitability to thin layer technology, etc.). In addition, choice of glasses can make it possible to achieve considerable reduction of problems of electrolyte/electrode interface (large contact area, quasi-delocalization of the interface by using the same glass former). The microionics approach is justified when the requirements and features of the market are compatible with the use of advanced technological means, as in the following fields:

- 1 microstorage of power
- 2 displays
- 3 miniaturized chemical or electrochemical sensors.

Lithium batteries are recognized as the most viable rechargeable battery system, since lithium is the lightest and the most electropositive element, producing the highest specific capacity. Efforts have therefore been directed to the development of anode and cathode materials that can reversibly intercalate lithium ions, in a configuration labeled "rocking chair" structure (Scrosatti, 2005). For this, materials with "open" structures that can conveniently intercalate lithium atoms, without much change to their structural volume are considered. Such materials include the lithium spinels,  $\text{Li}[\text{M}_2]\text{O}_4$  where  $\text{M} = \text{V}, \text{Ti}, \text{Mn}$ , are attractive electrode materials for Li batteries.  $\text{LiMn}_2\text{O}_4$  is particularly interesting, since it can reversibly intercalate one Li ion per mole, without altering the  $\text{MnO}_2$  framework. This system has a 4V operating voltage versus Li metal negative electrode and good electrochemical behaviour due to the favourable kinetics for fast  $\text{Li}^+$  diffusion through the three dimensional channels of the  $\text{Mn}_2\text{O}_4$  spinel structure.

A number of glassy ionic conductors are now available in the literature and many of them have been applied in the realization of workable thin film rocking chair microbatteries. The speaker has in recent times been involved with the development of such batteries with other researchers in Pavia, Italy. For our cell design, the negative electrode was  $\text{LiMn}_2\text{O}_4$ , the electrolyte is 1:1 ratio compound composition of lithium borophosphate glass ( $\text{LiB}_3\text{O}_3\text{:LiPO}_3$ ) while molybdenum trioxide ( $\text{MoO}_3$ ) and Vanadium oxide ( $\text{V}_2\text{O}_5$  that can also intercalate lithium ions reversibly have been chosen as the positive electrode, (cathode), of our cell. The cell was realized by the sputtering of the thin films of all the component materials to give a total cell thickness of about  $2\mu\text{m}$ . A thin film micro battery based on  $\text{Au/LiMn}_2\text{O}_4/\text{LiB}_3\text{O}_3\text{:LiPO}_3/\text{MoO}_3/\text{Au}$  is as shown in Fig 5 (Magistris *et al*, 1998, Kuku *et al*, 1999). The running and discharge characteristics of the cell are currently being followed in Pavia.

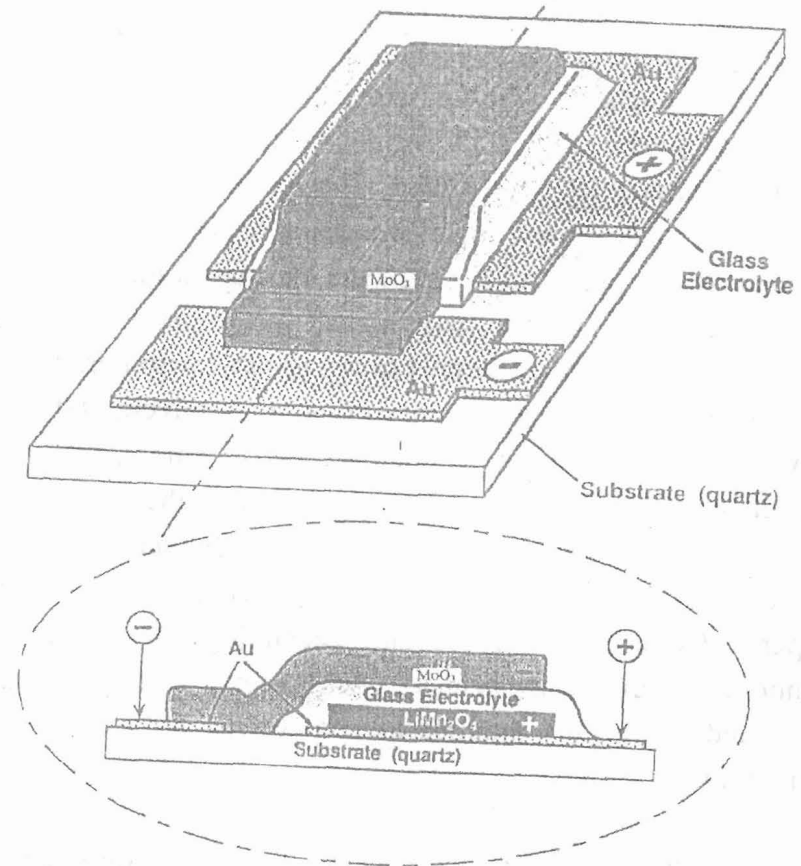


Figure 5: Thin film micro battery based on  $\text{Au/LiMn}_2\text{O}_4/\text{LiB}_3\text{O}_3\text{:LiPO}_3/\text{MoO}_3/\text{Au}$

### General Remarks and Recommendations

It may be remarked that a semiconductor technology (microelectronics) programme was started in this University in the Department of Electronic and Electrical Engineering, in 1973 by Prof V. A. Williams. The established laboratory succeeded



with the production of discrete diode and transistor devices as well as stabilized tin dioxide thin film and carbon composite resistors. Products from the laboratory were widely displayed at a number of Science and Trade Fairs, and exhibitions across the country between 1975 and 1986. The technology was silicon based. Also, the research team was multidisciplinary in nature being made up of Electronic Engineers, Physicists and Chemists. Mr Vice Chancellor Sir, it may interest you to know that I was actually invited to be a Chemist to the group, having graduated from the Chemistry Department of this great university. I have however had to convert to engineering by going through a conversion course in Electronics at MSc level at the Department of Electronics, University of Southampton, England. This was topped up with a PhD in Electrical Engineering Materials at the Imperial College of Science and Technology, University of London, England. I have been a COREN registered engineer and continued to find the practice of engineering profession very stimulating.

As regards the semiconductor laboratory, it may be said that the laboratory came ahead of its time, when we consider the situation of things in the Nigerian environment. Laboratories of this nature have mostly become the bedrock of national scientific developments in other nations of the world, but not so in Nigeria! For example, a laboratory of same character was started in Tunisia about the same time in 1973. The end products of that laboratory today are complete built up systems of television and radio sets. Unfortunately, the Ife laboratory was starved of funds, and has become a ghost of what a lively devices laboratory should be like.

Apart from being able to make active and passive devices in the laboratory in the 1970s, since the technology was silicon material based, and since the silicon ingots used for device processing were bought from abroad, and with the politics that surrounded the availability of such ingots from world market suppliers at that time, an ambitious attempt was made to produce our own silicon. This was to a good extent achieved by the production of silicon from Igbokoda quartz sand (Williams *et al*, 1977). We succeeded to a level, silicon was successfully extracted, but resources were not immediately available to ensure the realization of pulled single crystal silicon ingots. It is the same resource problem that has to a level "killed" the laboratory, and hence the only silicon devices fabrication effort ever made in this country.

This has been possible because till date, Nigeria lacks a definite policy on electronic materials/devices production. Half hearted attempts were made in the 1980s to compile potentials across Nigeria for human and material resources for the establishment of national microelectronic capabilities. I remember the beautiful reports put together and presented to the Federal Government by the Prof Buraimoh-Igbo led committee. In the report, a number of Institutions, and Ife especially, were marked out and recommended for establishment or reinforcement as Centres of Excellence in the pursuit of microelectronics devices and Science development. Unfortunately, nothing has come out of that report.

As a Fellow of the Materials Society of Nigeria, I am aware that a policy document is currently before the Federal Government tagged "The National Policy on Materials Development". I wish



to plead with the Federal Government to have a quick look at this policy document, and approve it for implementation, so that as a nation, we can start to have a guided focus on materials development, and hence be able to be in league with the developed nations of the world.

Also, am aware that the Energy Commission of Nigeria has put together a policy document on the adoption of Renewable Energy Sources in Nigeria. This also is before the Federal Government. The use of photovoltaic devices as an energy sources is a component / of this document. Since this would to a good extent encourage the development of the required base for solar cell production in Nigeria, I very much plead with the Federal Government to as a matter of urgency also give assent to the document.

It may be noted that apart from our efforts at Ife one or two other agencies of Government are however already working towards ensuring some materials development for devices build up. One may wish to commend the efforts of the Engineering Materials Development Institute, Akure, for their work on polymeric materials for electronic devices. Also of note is the recent announcement by the Director General of Nigerian Agency for Science and Engineering Infrastructure (NASENI), that they would soon put together a 5 MWp production facility for amorphous silicon solar cells in the country. This is a most welcome development. I do hope that more of such developmental projects will be conceptualized and seen to fruition across our national landscape.

### Concluding Remarks

Mr Vice Chancellor Sir, I have endeavoured in this lecture, to give a synopsis of some of the activities of our laboratory here at Ife in the pursuit of electronic materials studies towards devices realization. Although our laboratory was started with the pursuit of developing devices based on silicon technology, it has been possible for us to extend this into other materials and consequently devices build up from the new and upcoming materials. While one is happy that we have been able to make considerable contributions in terms of study and device development from these new materials, it would still have been our joy to see the laboratory active in its major silicon based devices effort. What is required is adequate funding, and presumably a lot of it. I remember that during my days at the Imperial College of Science and Technology, London, the semiconductor laboratory used to have an annual budget of about two million pounds sterling (£2,000,000.00). This money came mostly from Government, the Military and Industries.

I am sure the budget must be much more than the above currently. We can therefore understand why there is so much growth of science and technology culture in such an institution because of the encouragement she is able to get from the sponsors. I do hope the Nigerian Government would also take the bull by the horns, encourage scientific development more consciously, so as to allow us have adequate materials development towards devices build-up and hence develop in house electronic system within the nation, so as to appreciate even better the beauty in such systems.

Mr Vice Chancellor Sir, but for the strict instruction from the University that acknowledgement should not be contained in this lecture, it would have been my greatest pleasure to acknowledge a number of individuals and institutions who have played very prominent and positive roles in my academic growth. A number of them are in fact seated in this auditorium. I am grateful to them all from the depth of my heart. My love and appreciation go to them.

Mr Vice Chancellor Sir, I thank you all for listening.

### References:

1. Augarten S. State of the Art: A tographic history of the integrated circuit", New Haven and New York: Ticknor and Fields 1983
2. Azi S. O. and Kuku T. A., "Photovoltaic potentials of PbSnS<sub>3</sub> thin films" *Proceedings of the ISES Solar World Congress*, Budapest, Hungary, 23 to 27 August, 1995.
3. Barden J. and Brattain W. H., "The Transistor, A Semiconductor Triode" *Phys Rev.* 74 (1948) 230, US Patent No 2,524,035, October, 1950.
4. Chapin, D. M., Fuller, C. S. and Pearson, G. L. "A New Silicon pn Junction Photocell for Converting Solar Radiation into Electrical Power" *J. Appl. Phys.* 25 (1954) 676.
5. Cohen M *Element of Materials and Engineering* .Fourth Edition by L. H. Wesley, Amsterdam: Van Vlack Addison

6. Contreras M., Egass B, Ramananthan K, Hiltner J, Swartzlander A, Hasoon F, Noufi R, "Progress toward 20% efficiency in Cu(In,Ga)Se<sub>2</sub> polycrystalline thin-mm solar cells" *Prog In Photovoltaics*, 7 (1999) 311.
7. Deb S. K., "Current Progress and Future Oppurtunities for Thin Film Solar Cells" in *Proceedings of World Renewable Energy Congress VII*, edited by A. A. M. Sayigh, 2002.
8. Durkan C, and Welland M. E., "Nanometer Scale Electrical Characterization of Artificial Mesostructures" *Critical Rev in Solid State and Material Science*, 25 (2000) 1.
9. Fornari R. in *Proceedings of the International School on "Crystal Growth of Materials for Energy Production and Energy Saving Applications"*, edited by Fornari R, and Sorba L, ICTP, Trieste, 2001, pp39 - 50.
10. Gesheva K. A., Dimova-Malinovska D, Marshall J. M. and Maud. J. M. "Photo voltaic and photoactive materials-properties, technology and applications" *Solar Energy Materials & Solar Cells*, 76 (2003) 429.
11. Gong S. F, Hentzell H. T. G and Robertson R. A, *Mat Res Soc. Proc.* 181 (1990) 487.
12. Green M, and Kuku T. A., "The Kinetics of the Photolysis of thin of Tin diiodide" *J. Phys Chem. Solids* (1983), 44,999 - 1008.

13. Heath J. R. and Ratner M. A. "Molecular Electronics", *Physics Today*, (May, 2003), pp43-49.
14. Kilby J. S. "Miniaturised electronic circuits", US patent No 3,138,743, 1964.
15. Kuku T. A., "Two level metallization System", MSc Thesis, University of Southampton, Southampton, England, 1978.
16. Kuku T. A. - "Physical properties of thin  $\text{SnO}_2$  and  $\text{SnO}_2 : \text{Sb}$  films obtained by a photolytic method", *Thin Solid Films* (1986), 142, 241 - 250.
17. Kuku T. A. - "Heat mirror characteristics of Prototypically produced Indium Tin Oxide thin films" *Solar and Wind Technology*. (1986), 3, 53-58.
18. Kuku T. A. - "Ionic Conductivity of  $\text{SnI}_2$ ", *Solid State Ionics* (1986), 20, 217 - 222.
19. Kuku T. A. and Salau A. M., "Electrical Conductivity of  $\text{CuSnI}_3$ ,  $\text{CuPb}_3$  and  $\text{KPb}$ ", *Solid State Ionics* (1987), 25; 1 - 7.
20. Kuku T. A. "DC Electrical Conductivity of Evaporated  $\text{CuPbBr}_3$  and  $\text{CuCdCl}_3$  thin Films", *Physica Status Solidi (a)* (1992), 129, K27.

21. Kuku T. A., "Ionic transport and galvanic cell discharge characteristics of  $\text{CuPbI}_3$  thin films" *Thin Solid Films*, 325 (1998) 246 - 250.
22. Kuku T. A., "Ion transport studies on vacuum deposited  $\text{PbSnI}_4$  thin films" *Thin Solid Films*, 340 (1999) 292 - 296.
23. Kuku T. A. "Preparation and optical properties of transmission selective thin films of cadmium stannate by a photolytic process" *Proceedings of World Renewable Energy Congress IX*, Florence, Italy, 2006.
24. Kuku T. A., Adeosun O. S., Akande A. R. and Adiguzel O., "Transport Properties of  $\text{PbSnI}_4$ ", *Solid State Ionics*, (1988), 31, 73 - 78.
25. Kuku T. A., Akande A. R., Erharhine P.O., Chiodelli G. and Adiguzel O. "Structure and ionic transport properties of some,  $\text{A}_2\text{BX}_4$  ( $\text{A}=\text{Cu}$ ,  $\text{B}=\text{Pb}$ ,  $\text{Sn}$ ,  $\text{X} = \text{Br}$ ,  $\text{I}$ ) Compounds", *Solid State Ionics* (1990) 44, 99 - 105.
26. Kuku T. A. and Azi S. O. "Growth and Physical Properties of Vacuum Evaporated  $\text{PbSnS}_3$  Thin Films - *Renewable Energy Technology and the Environment* (A.A.M. Sayigh ed.) Pergamon Press (1992), Vol. 1, 297 - 302.
27. Kuku T. A. and Azi S. O. "Thin Films of  $\text{Cu}_2\text{SnS}_3$  for solar cell development" *Proceedings of the /SES Solar World Congress*, Budapest, Hungary, 23 to 27 August, 1993.

28. Kuku T. A. and Azi S. O. - "Photoconductivity of PbSnS<sub>3</sub> thin films". *Renewable Energy* (1994),5(3), 1725.
29. Kuku T. A. and Azi S. O., "Photovoltaic characteristics of CdS/Cu<sub>2</sub>SnS<sub>3</sub> thin films heterostructure solar cells", *Renewable Energy* (1994),5(3), 1722.
30. Kuku T. A. and Azi S. O. "Optical properties of evaporated PbSnS<sub>3</sub> thin films" *Journal of Material Science*, 33(1998) 3193 - 3196.
31. Kuku T. A., Azi S. O. and Osasona O. "Transport properties of Cu<sub>2</sub>SnS<sub>3</sub> thin films" - *Nigerian Journal of Pure and Applied Physics*, 3(2004) 75-78.
32. Kuku T. A., Azi S. O. and Osasona O., "Electrical properties of vacuum evaporated PbSnS<sub>3</sub> thin films" *Journal of Material Science*, 41(4)(2006).
33. Kuku T. A., Chioba E. R. and Chiodelli G, "Electrical Properties of CuPbBr<sub>3</sub>", *Solid State Ionics* (1989) 34, 141 - 147.
34. Kuku T. A. and Fakolujo O. A. - "Photovoltaic Characteristics of thin films of Cu<sub>2</sub>SnS<sub>3</sub>" - *Solar Energy Materials* (1987), 16, 199 - 204.

35. Kuku T. A. and Green M. "Photochemical Fabrication of SnO<sub>2</sub> and Sn micropatterns from SnI<sub>2</sub> thin films", *Thin Solid Films* (1986), 144, L 119 - 120.
36. Kuku T. A., Mustarelli P., Tomasi C. and Magistris A., "Thin film deposition of borophosphate glasses as ionic conductors", *Proceedings of the 50th International Society of Electrochemistry Meeting, Pavia, Italy, 5 to 10 September, 1999.*
37. Kuku T. A. and Salau A. M., "Electrical Conductivity of CuSnI<sub>3</sub>, CuPbI<sub>3</sub> and KPbI<sub>3</sub>", *"Solid State Ionics"* (1987),25; 1 -7.
38. Magistris A., Mustarelli P., Sberveglieri G., Tomasi C. and Kuku T. A. "Materiali per batterie a film sottile", XXIX Congresso Nazionale Di Chimica Fisica, University of Catania, 5 to 9 October, 1998, Taormina, Italy.
39. Mathew X., Thompson G. W., Singh V. P., Mc Clure J. C., Velumari S., Mathews N. R. and Sebastian P. J., "Development of CdTe thin films on flexible substrates- a review", *Solar Energy Materials & Solar Cells*, 76 (2003) 293.
40. Meier J., Keppner H., Dubail S., Ziegler Y., Feitknecht L., Torres P, ch Hof, U. Kroll U. , Fischer D, Cuperus, J., Anna Selvan A, Shah A, Proc 2nd World Conf on PV Solar Energy Conversion, 378 (1998).

41. Rath J. K., "Low temperature polycrystalline silicon: a review on deposition, physical properties and solar cell applications", *Solar Energy Materials & Solar Cells*, 76 (2003) 431.
42. Romeo N. "Thin film solar cells based on CdTe: Towards industrial production-Workshop on "Physics of Renewable Energy", ICTP, Trieste, Italy, October 2005.
43. Romeo N, Bosio A., Canevari V. and Kuku T. A. "Low resistivity CdTe thin films" - 2nd EUROLAD Meeting, University of Parma, Parma, Italy, 13 - 14 September, 1991.
44. Romeo N., Bosio A, Canevari V. and Kuku T. A., "Crystallization of CdTe thin films by CdCh treatment at high temperature" - Proceedings of 12th European PV Solar Energy Conference, Amsterdam, The Netherlands, 11 to 15 April, 1994, pages 662 to 663.
45. Romeo N., Canevari V. and Kuku T. A. "Nitrogen doped CdTe thin films for photovoltaic applications" - Proceedings of the International Conference Applied Optics III" Prague, Czechoslovakia, 2 - 6, October 1989.
46. Salau A. M., Kuku T. A. and Akinnifesi J. O. "Vacuum deposited KPbI<sub>3</sub> films for use in photothermal conversion" *Solar and Wind Technology* (1987), 4, 151 155.

47. Scrosatti, "Batteries", Workshop on the "Physics of Renewable Energy", ICTP, Trieste, Italy, October 2005.
48. Sebastian P. G., "Structural and optical properties of hot wall deposited CdSe thin films", *Solar Energy Materials & Solar Cells* 76 (2003) 223.
49. Sekido S., Yoshinoro Y., Mori H., *New Mater & New Proc.* 1(1981) 184.
50. Shockley W., "A unipolar field effect transistor," *Proc I R: E.* 40 (1952) 1365.
51. Williams V. A., Aliu S. A., Osasona O. and Kuku T. A., "Preparation of Silicon from Igbokoda Sand", Internal Report, Semiconductor Laboratory, University of Ife, 1977.
52. Yamaguchi M., "Towards 50% super-high-efficiency multijunction solar cells", *Proceedings of World Renewable Energy Congress VII* (WREC) 2002, Ed. A. A. M. Sayigh.
53. Yang'l., Banerjee A., . Glatfelter T., Sugiyama S. Guha S., "Recent progress in amorphous silicon alloy leading to 13% stable cell efficiency", *Proc 26th IEEE PVSC*, 1997, Anaheim, 1997, 563-568