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Edited by Visakh P.M., Artem Semkin,
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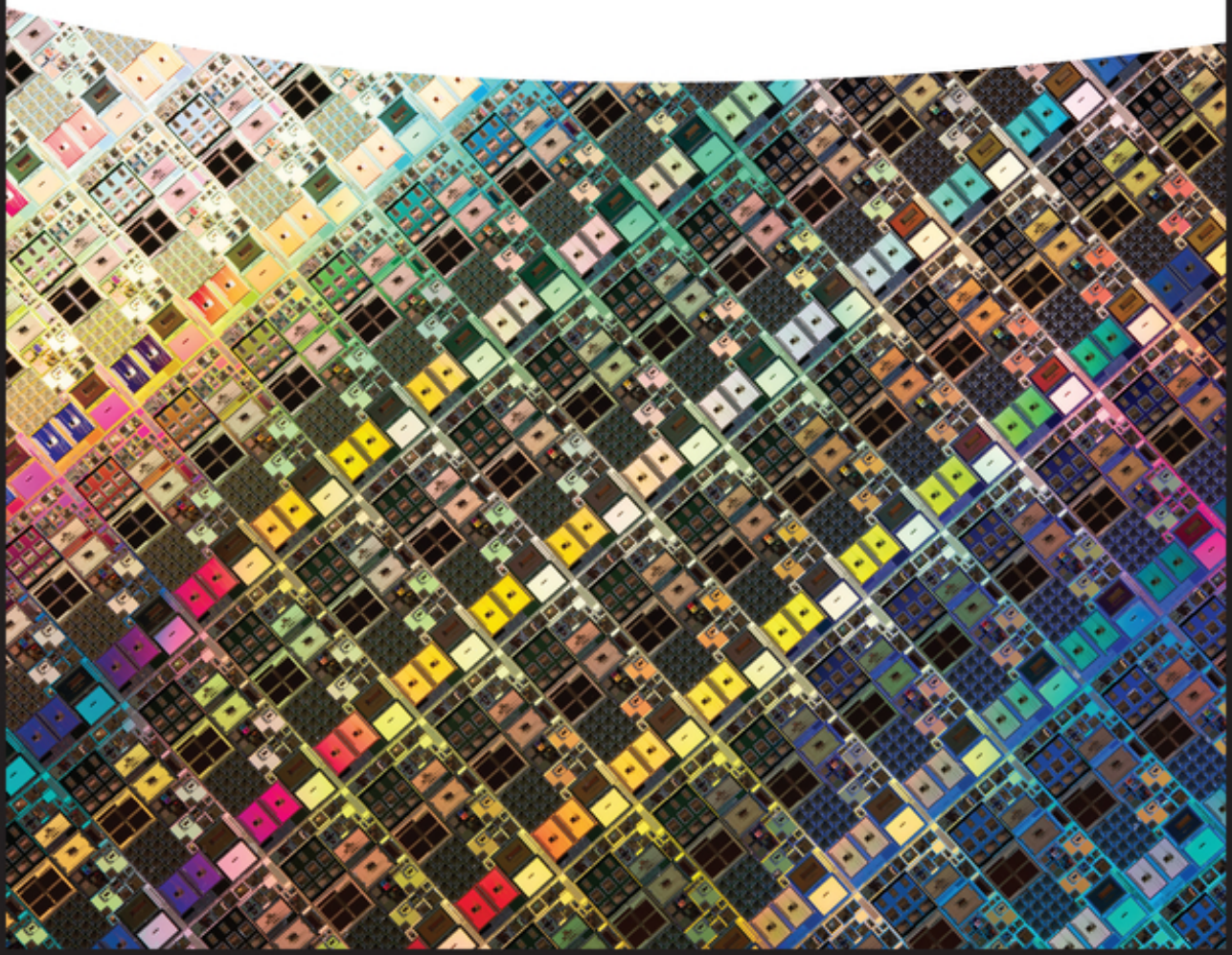
Materials, Properties, Devices



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Preface

Nanotechnology is one of the most talked about technologies today. The application of nanotechnology in modern electronic devices, especially memory devices, nanoscale transistors, nanosensors, etc., improves the devices' functionalities. Not only is the power consumption in nanoelectronic devices reduced drastically but also the weight and thickness of the devices are decreased. This book summarizes recent research accomplishments in the area of nanotechnology-based electronics, its properties, and applications.

A brief description of the book content and an introduction to nanotechnology in electronics and current challenges are given in the first chapter. The second chapter offers a review of graphene-based nanoelectronic biosensors. This chapter covers the introduction to graphene, its properties, and some novel potential applications as biosensors. Zinc oxide piezoelectric nanogenerators for low-frequency applications are described in Chapter 3. Different types of ZnO nanostructure-based nanogenerators are discussed. Chapter 4 deals with the investigation of hot carrier-induced degradation in nanoscale junctionless MOSFETs. The fifth chapter discusses the electrostatic and dispersion forces in nano-electromechanical systems. In addition, the effects of different electric fringing field corrections and other effects related to the Casimir force are separately reported. The sixth chapter deals with nanomaterials that can be used as wearable, flexible, and stretchable strain/pressure sensors. A detailed review of conductive nanomaterials for printed and flexible electronics applications is covered in the seventh chapter, with the fundamentals, features, and progress in various printing technologies.

The application of different metal oxide semiconductors for the non-invasive diagnosis of breast cancer is discussed in Chapter 8. This review outlines breast cancer-related volatile organic compounds and the detection mechanisms currently used for diagnosis. The ninth chapter presents the down-conversion photoluminescence properties of ZrO_2:Ln^{3+} (Ln = Eu, Sm, Er, Tb, Ho, Tm, Pr, Gd, Dy) films formed by plasma-electrolytic oxidation. Chapter 10 provides an overview of multiferroics for spintronics applications. This chapter reviews the fundamental aspects and applications of multiferroic-based spintronic devices. The eleventh chapter covers many of the latest research accomplishments in quartz tuning fork-based nanosensors.

In this book, chapter authors have reviewed different aspects of nanotechnology in the field of electronics and related advancements. This book is a valuable reference source for faculties, professionals, research fellows, senior graduate students, and researchers working in the field of nanotechnology/electronics. The use of nanomaterial in electronics is considered as a promising area of research, a lot of research activities are going on, and some knowledge of nanoelectronics is helpful to bring a change in the current techniques and applications. Finally, we would like to express our sincere gratitude to all the contributors of this book, who made excellent support to the successful completion of this venture. We also thank the publisher Wiley for recognizing the demand and importance of nanotechnology in the field of electronics.

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Nanotechnology in Electronics, Materials Properties, and Devices: State of the Art and Future Challenges

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1.1 Graphene-based Nanoelectronic Biosensors

Graphene is the thinnest, strongest material, with one-particle thickness, and is 200 times stronger than steel. Graphene exhibits outstanding electrical and thermal conductivity with remarkable light absorption capability. Graphene is a material that could change the world in the true sense, with its infinite potential for integration practically in any industry. Graphene has diverse forms and can be combined with other materials to form various materials of extraordinary characteristics. Researchers are very keen to explore and patent graphene and gain expertise about its various properties and potential applications, mainly in cells, transistors, computer chips, supercapacitors, energy production, etc.

The common graphene derivatives are pristine graphene, reduced graphene oxide, graphene quantum dots (GQDs), and polycrystalline graphene, which are extensively used in biosensing applications. Pristine graphene consists of single crystalline grains that have flawless lattices made up of defect-free hexagonal ring networks of sp^2 hybridized carbons atoms [1]. Graphene oxide also mainly consists of covalently bonded sp^2-hybridized carbon atoms but has some defects due to the following reasons: disrupted sp^3-hybridized carbon atoms and the oxygen functional groups like carboxyl group located at the edges and the basal plane are saturated with hydroxyl and epoxy groups [2]. The presence of these groups makes graphene oxide hydrophilic depending on their oxidation state [3].

Nanoelectronic devices are made up of nanomaterials such as nanowires, graphene, carbon nanotubes (CNTs), and transition metal dichalcogenides. These nanomaterials must possess extraordinary characteristics such as high surface-area-to-volume ratio, low power consumption, high charge mobility, and excellent compatibility to fit in modern electronic devices. As nanomaterials display unusual properties that are not obtainable at the micro scale, nanoelectronics holds

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significant importance. Graphene is a recently discovered nanomaterial known for its outstanding mechanical, electrical, and optical properties [4–6]. To develop an efficient graphene-based electrochemical biosensor, the graphene oxide nanosheets were decorated with Au NPs by aryldiazonium bridges fabricated on glassy carbon electrode (GCE). Then, the glucose oxidase enzyme was immobilized on the graphene oxide–Au NP nanocomposites. The biosensor showed a high sensitivity of about 42 $\mu A\, mM^{-1}\, cm^{-2}$ with a wide detection range of 0.3–20 mM. This glucose biosensor showed excellent selectivity for glucose detection [7].

N-doped graphene–chitosan–glucose oxidase biosensors showed an excellent sensitivity of 226.24 $\mu A\, mM^{-1}\, M^{-2}$ 120 due to high porosity of graphene and high conductivity of graphene sheets, which facilitate enhanced electron transfer. The CuO nanoparticle (NP) composites with graphene oxide have shown a high sensitivity of 262.52 $\mu A\, mM^{-1}\, cm^{-2}$ with an LOD of 0.69 μM. This biosensor was also used for human serum detection and showed a sensitivity of 285.38 $\mu A\, mM^{-1}\, cm^{-2}$ [8]. Similarly, biosensors based on Pt-NiO–reduced graphene oxide nanocomposites showed a sensitivity of 832.95 $\mu A\, mM^{-1}\, cm^{-2}$ and an LOD of 2.67 μM. This high performance was attributed to porosity of Pt-NiO–reduced graphene oxide nanocomposites [9]. Moreover, the Cu-Co–reduced graphene oxide nanocomposites were electrochemically deposited over the pencil graphite electrode and showed a high sensitivity of 240 $\mu A\, mM^{-1}\, cm^{-2}$ and an LOD of 0.15 μM [10].

1.2 Zinc Oxide Piezoelectric Nanogenerators for Low-frequency Applications

Nanoparticles can be fabricated through solid-phase, liquid-phase, and gas-phase methods. Chemical bath deposition [11], green chemistry synthesis [12], and wet chemical methods [13] are other recently used techniques for the synthesis of ZnO NPs. Vertical ZnO nanorods were grown hydrothermally on a gold-coated PTFE (polytetrafluoroethylene). Spin coating was used to deposit 0.005 M zinc acetate dehydrated in ethanol on the surface of gold-coated PTFE film. Then, the substrate was heated at 90 °C for 30 minutes. The seed layer was uniformly deposited in a two-step process of deposition and decomposition to cover the substrate. ZnO nanorods were hydrothermally grown on the seed layer. Zinc nitrate hexahydrate and hexamethylenetetramine (HMT) were used to hold the seed layer at 90 °C for three hours [14].

Masuda et al. [15] demonstrated a simple liquid-phase synthesis method to control the morphology and crystal size of ZnO. ZnO nanowires of 100 nm long and about 50 nm wide were successfully synthesized at 50 °C. They also found that nanowires had no branches without aggregations. Several techniques have been explored to synthesize and develop both direct and alternating current zinc oxide piezoelectric nanogenerators [16]. Controlled precipitation is typically used to produce ZnO NPs in large quantities with reproducible properties for use in industrial products. In this process, zinc salt solution is spontaneously reduced by a reducing agent.

Breaking down of agglomerations is an important process in this method. Therefore, temperature, pH, type of aqueous media, time of precipitation, and the raw materials are most important parameters in the precipitation of ZnO NPs, which have impact on the size and final characteristics of the nanoparticles [17]. Aladpoosh et al. [18] used the ZnO-controlled precipitation method, a green synthesis method using natural plant source, namely, Keliab and zinc acetate. Wurtzite structure and nanorod shapes result from in situ synthesis of ZnO on the cellulosic chains of cotton using the green synthesis method. The principle of nanogenerators was first used by Wang's research group in 2006 [19]. They used a conductive tip of an atomic force microscope (AFM) to deflect the aligned semiconductor ZnO nanowires and successfully obtained a measurable piezoelectric voltage output of around 10 mV. They grew ZnO nanorods on a sapphire substrate using a vapor–liquid solid method, which caused the gold particles to remain on the top of each rod after their growth.

A Schottky contact was formed between the conductive AFM tip and the semiconductor ZnO nanowires, which is a key factor in current generation by piezoelectric nanogenerators. The stretched side of the rod with a positive potential produced a reverse bias with the Schottky junction, leading to no current to screen the polarization. When the contact between the tip and the compressed, negatively polarized side of the rod was disconnected, the junction was forward biased, and the current was able to flow and screen the polarization. Monitoring the open-circuit voltage reflects an uncertainty in the measurement of this type of device [20]. Zinc oxide is an environmentally friendly multifunctional semiconductor possessing outstanding piezoelectric effect, piezoelectric coupling coefficient, and thermal and mechanical stability at room temperature. Owing to its non-centrosymmetric hexagonal wurtzite crystal structure and polar Zn—O bonds, ZnO has unique piezoelectric properties as the core of studies in the ceramic industry [21, 22]. For the first time in 2009, Xi and coworkers [23] fabricated a ZnO-nanotube-based piezoelectric nanogenerator. They used a solution chemical method to synthesize hexagonal ZnO nanotube arrays at temperatures below 100 °C.

ZnO-based nanogenerators can be incorporated into various substrates. In 2012, Khan et al. [24] grew ZnO nanorods on a silver-coated cotton fabric using a low-temperature, aqueous chemical growth method. An external force was applied on ZnO nanorods via an AFM tip, where the flow of charges was taken into account and a Schottky barrier formed between the electrode and the nanorods.

1.3 Investigation of the Hot Carrier–induced Degradation in Nanoscale Junctionless MOSFETs: A Reliability-based Analysis

In the past decades, reliability of MOSFET devices was a major concern in the electronics industry: the aging phenomenon degraded the device operation and lifetime severely. Extensive research has been carried out to identify the causes of aging and to seek viable solutions. Channel and substrate hot carrier injection

(HCI and SCI), channel hot electron/hole (CHE/H), drain avalanche injection, and radiation were found to be the main degradation mechanisms[25–31]. Hot carrier–induced degradation is of prime interest for designers as the process aggravates with downscaling. Degradation is essentially due to the enhancement of the electric field with dimension reduction, in the lucky electron model representation, providing the carriers enough energy to be injected through the oxide layer. These carriers are most likely to be captured by the existing oxide traps or to break the silicon bounds and thus giving rise to a localized and nonuniform pile-up of interface states near the drain–channel junction [32]. A energy-driven paradigm proposed by Rauch et al. suggests that the electron–electron scattering mechanism, governed by energy rather than the electric field, is responsible for aggravation of hot carrier degradation in downscaled devices [33].

The concept of junctionless transistor was proposed by Lee et al. [34] as a simple way to overcome process limitations. Indeed, as downscaling of channel lengths trends toward less than 10 nm, controlling process-induced variability becomes imperative to conserve the properties of transistors. At these scales, inherent scattering and diffusion of shallow-extension impurities into ultra-short channels pose a serious problem. As high doping concentration gradient is primordial, the extension formation with the actual process techniques implies additional complex and costly operations [35]. Contrary to IM MOSFETs, measures highlighted an enhancement in the effective mobility with the increasing gate bias [36]. The enhancement is so significant that the effective mobility exceeds the corresponding bulk mobility especially in the accumulation regime [37]. Surface mobility also significantly improved in the accumulation layer of heavily doped devices, which indicates a higher current in the accumulation regime of the junctionless field-effect transistor (JLFET). This effect is attributed to the impact of the accumulation layer on screening of ionized impurities, yielding a reduction of Coulomb scattering [38]. In heavily doped devices, measurements highlight a correlation between the carrier density and the Coulomb scattering limitation, where a significant improvement in the effective mobility with respect to the carrier density is observed [39, 40]. Also, it was demonstrated that enhanced electrostatic controllability provided by multigates and thinner equivalent oxide thickness (EOT) yielded higher carrier density and improved mobility.

1.4 Study of Electrostatic and Dispersion Forces in Nanoelectromechanical Systems (NEMS)

Due to the outstanding electrical and mechanical properties of nanostructures, researchers are interested in novel generations of ultrasmall devices such as micro- and nanoelectromechanical systems (MEMS and NEMS, respectively), which are used in switches, actuators, sensors, AFMs, mass and force detectors, etc. New effects appearing due to the scale alteration in geometry introduce several additional terms into the theory of nanoscale structures, while their influence on other scales is negligible. One of these effects is dispersion forces. Dispersion

forces or quantum interactions, including the Casimir and van der Waals (vdW) regimes, play a key role in the behavior of nanodevices [41–43], related to the structure dimensions/configurations and the gap between electrically actuated electrodes [44]. The total electromagnetic Casimir energy is the sum of energies of the Dirichlet and Neumann modes. However, in large separations, the Dirichlet mode is dominant, while the Neumann mode is negligible [45]. It should be noted that the large separation assumption is valid for most real nano-tweezers since the gap between the arms is relatively larger than the radius of the arms ($D \gg R$). Typically, for ($D < 100R$), the contribution of the Neumann mode is negligible compared to the Dirichlet mode, and the asymptotic approximation provides an excellent estimation of the Casimir force [46]. In this section, practical mathematical models by assuming the large separation approximation (Dirichlet mode) are developed.

1.5 Nanomaterials for Wearable, Flexible, and Stretchable Strain/Pressure Sensors

Hardness and rigidity of micro and smart electronics cause mechanical deformation because of brittleness and inflexibility of their material components. This has restricted the application of non-flexible electronics that were replaced with electronic devices containing polymer and plastic substrates as flexible electronics in the past decades. In electronic devices, flexibility implies lightweight, elasticity, non-brittle, ductility, and easy fabrication [47]. Flexible electronics aroused great interest among researchers, industries, organizations, and military sectors to design and manufacture hybrid composite structures with lightweight flexible electronic devices [48]. On the other hand, the rapid growth of technologies, especially Internet in our daily life, has resulted in the advent of wearable technology in recent years [49]. Wearable and flexible sensors and biosensors have been widely explored in research and industry [50–52]. Sensors convert one form of energy into another form for processing [53]. Sensors detect environmental changes using conductive materials and send data to the computer for processing [54]. Conventional detection methods have been replaced by wearable and stretchable sensing electronics with nanomaterials [55]. Structures and designs of wearable sensors as well as nanomaterials determine sensor applications and their performance. Nanomaterials and nanocomposites depending on their properties, shape, size, structure, porosity, and fabrication method impart different sensor properties to wearable substrates. Strain/pressure sensors measure deformations, pressure stimuli, and mechanical properties [56, 57]. Metallic and semiconducting films were conventionally used as strain sensors and exhibited brittleness and rigidity with low stretchability [58]. These bulk materials could not attach to wearable substrates.

Nanomaterials including metal and metal-oxide nanoparticles and nanowires, conducting polymers (CPs), graphene, and CNTs have been explored due to their larger surface area compared to bulk materials. Superior mechanical and electrical properties and use of lower active materials are some of the advantages of the

integration of nanostructures and hybrid nanomaterials with flexible supports. The supports can also maintain their stretchability, wearability, and flexibility [59–64]. Flexible wearable piezoresistive strain/pressure sensors are composed of conductive sensing elements in addition to elastic polymers or other flexible/stretchable substrates. The contact resistance of the conductive part changes with strain/pressure stimuli, detected by electrical measuring systems. Different conductive nanomaterials have been explored as conductive fillers of elastomer composites including metal nanoparticles, nanowires and thin films, CPs, and carbon nanomaterials due to their desirable electrical and mechanical properties [65–71]. PDMS, polyurethane (PU), silicon rubber, Ecoflex, and Lycra are also explored as elastic substrates or components for conductive nanomaterials [72, 73]. On the other hand, incorporation of metallic nanomaterials, CNTs, and graphene with flexible wearable substrates propose desirable gauge factor ranges, introducing different structures and resulting in strains inside the matrix during stretching [74, 75]. Disconnection between nanomaterials decrease the contact area between them, leading to higher electrical resistance.

Graphene is another impressive carbon-based nanomaterial for resistance-based strain sensors due to its high electrical conductivity and mechanical properties [76–78]. Applied strain can change and partially destroy the hexagonal structure of the edges of graphene films [79]. Graphene can be combined with elastic polymers, which are generally grown through chemical vapor deposition or derived from exfoliated graphite. The shape and structure of graphene determine the flexibility and stretchability of sensors. To increase the stretchability and sensitivity of graphene in strain/pressure sensors, certain structures and engineering strategies were designed [80, 81]. In another work, macroscopic, flat, uniform graphene ribbons were fabricated through a modified wet spinning method [82]. Carbon black (CB) and graphite were also integrated with textiles to show piezoresistivity [83–85]. Natural biomaterials including natural textiles such as silk and cotton can be converted into conductive carbon materials via hydrothermal and pyrolysis processes [86, 87]. Carbonized silk nanofiber membranes integrated with PDMS film were also reported as skin-like pressure sensors.

1.6 Conductive Nanomaterials for Printed and Flexible Electronics Application

Printing is a process whereby formulated inks are deposited on the top of the substrate material for data transfer just as graphics, images, text, and the forms reappear as an image-carrying medium called substrate. Accordingly, printed and flexible electronics follow a set of printing methodologies to build electronic devices on flexible substrates. In the bubble-jet printing model, there is a print head with a heating unit. This heating unit is responsible for the preparation of ink bubbles and also forces the ink drop out of the nozzle. In the piezoelectric printing model, the nozzle

has a ceramic piezoelectric tile that gets expanded into the ink reservoir inside the print head and forces the ink drop out of the nozzle. The technology that enables to print inks on a variety of substrates with flexible or rigid structure materials is called screen printing. The entire process is relatively simple, flexible, and economical. The ink passes through a stencil made of a porous material during printing and gets deposited onto the substrate material. A delicate mesh made of nylon is used as a whole screen and stretched over a wooden or aluminum frame with a fitness of 150–400 fiber in.$^{-1}$

A high-resolution printing technique that uses an electric field to produce an essential fluid flow for ink delivery onto a substrate is called an electrohydrodynamic printing. It produces two to five smaller droplets compared to the nozzle size. The positive impact on the shape regulation of nanoparticles in the droplets developed for printing is due to the electric field existing between the substrate and the nozzle. It is also preferred in 3D structure additive manufacturing. Magdassi et al. prepared concentrated citrate-reduced silver nanocolloids as ink for inkjet printing on surfaces such as glass and paper. The material was prepared by redispersion following lyophilization of newly prepared colloids. Carboxymethyl cellulose, a polymer stabilizer, was used as a binder and stabilizer. The material was characterized by its high electrical conductivity, reactivity, and optical properties [88]. Shankar et al. [89] synthesized Ag NPs by a reduction method using tin acetate as a reducing agent with a passivating shell of dodecylamine (DDA). This process was carried out in the toluene medium. The aim was to formulate nonaqueous conductive ink to print circuits for antennas and radio frequency identification (RFID) tags on surfaces such as Epson photo paper through aerosol jet printing. Lai et al. presented a review article on synthesis of silver NP and inks. Also, control of chemical concentration is significant to maintain the size and morphology of nanoparticles. The most suggested method to synthesize nanoparticles is chemical reduction, which requires a reducing agent to decrease the ion solution to the physical nanoparticle form. The authors concluded that most printing metal inks in the market are silver based owing to its remarkable electrical properties [90]. Zhou et al. performed a study on DDA-protected Ag NPs by modifying a small amount of dodecanethiol as the co-protective agent to formulate conductive silver ink for inkjet printing. The study revealed that electrical properties of silver can be enhanced quickly by heat treating at 90 °C, thus proving its suitability to print electronic circuits [91]. A similar team also synthesized water-dispersible Ag NPs using polyacrylic acid as a capping agent to inkjet print on paper substrates. Following the treatment of the Ag NPs with the poly(diallyldimethylammonium chloride) [PDAC] solution at room temperature, the nanoparticles coalesced together after the detachment of polyacrylic acid (PAA). The films showed changes in the morphology and electrical properties. Which is significant identification for printed electronic devices [92]. Zhang et al. synthesized Ag NPs for paper-based electronics through inkjet printing. Conductivity of the printed silver tracks was enhanced by a multiple-step room temperature (RT) post-processing method. Electrical properties, mechanical flexibility, and strain sensitivity of the material are proven effective to serve the 3D

electronics in future [93]. Kastner et al. and Shahariar developed Ag NPs for inkjet printing of conductive lines on textiles. The reactive silver ink contained silver in the complexed form, and no dispersions were found. The inkjet printer electronic circuit paths on the fabric were found to withstand washing tests, moisture, and heat [94, 95]. Liang et al. developed water-based Ag nanowires to fabricate wearable thin-film transistors and stretchable conductors through screen printing on polyethylene terephthalate (PET) sheets. A new water-based Ag nanowire ink was prepared using a mixture of (hydroxypropyl) methylcellulose, fluorosurfactant, distilled water (DI) as a solvent, and an antifoaming agent as an organic binder. Investigations were carried out to connect the rheological properties of the ink with its composition [96].

Patil et al. performed a study on inkjet printing of silver nanowires synthesized by the polyol method. The study focused on conductivity improvement printed pattern stability on flexible surfaces and techniques followed. The process was optimized by varying the concentration of isopropyl alcohol and the Ag nanowire mixture suspended in ethylene glycol, which was synthesized. The printed patterns obtained using the developed ink demonstrated high conductivity and strength [97]. Zhao et al. performed their study on selective dopamine determination in human serum using inkjet-printed multi-walled CNT chips. The CNT ink was examined with homogeneous double layers to increase the efficiency of dopamine detection. This method successfully resulted in the demonstration of the samples. The low-cost approach for the ink formulation paves a way for futuristic applications in printed sensors [98].

1.7 Metal-oxide Semiconductors for Noninvasive Diagnosis of Breast Cancer

In recent years, research in biomedical engineering has enabled clinicians to achieve early medical diagnosis with help of advanced technologies. Although these conventional diagnostic techniques help in diagnosis of cancer, they have certain drawbacks: high cost, painful to patients, and may not always give accurate results, especially in the early stage of the disease.

Recent research has revealed that the overall cost of cancer diagnosis and treatment is indeed decreasing for patients treated in the early stages; hence, the prognostic management of cancer remains a topic of key interest in the scientific community, from fabrication of devices to even machine learning [99]. Over the past few decades, advances in molecular biology and biotechnologies have achieved significant milestones to identify cellular changes at the molecular level, which may be a promising approach for early disease detection. Moreover, present technologies can quantify cellular changes at an early phase of disease development. This may help in identifying particular pathophysiological processes and underlying conditions to build more accurate devices [100–103]. The early diagnosis of cancer is crucial for patient survival; therefore, sensitive and specific methods are required for early cancer diagnosis. These methods aid clinicians in successfully diagnosing and treating patients, thus, increasing their chances of survival [104].

The conventional diagnostic methods for cancer detection involve histological characterization such as staining based on cell morphology and analyzing the slides using microscopic techniques. These are invasive techniques that require human sample collection by taking a biopsy sample followed by sample processing techniques that involve cell fixation and further analysis using a microscope to detect cancer cells [105–107]. Breast cancer is a result of interplay of various factors that lead to genetic mutations. Hereditary and environmental factors play a major role in causing these mutations, which inactivate the DNA repair genes in the breast cells [108]. The main biomarkers associated with targeted therapy of breast cancer are estrogen receptor and progesterone receptor. Growth factors such as epidermal growth factors, mainly ErbB-1 (EGFR) and ErbB-2 (ERBB2, HER-2/neu, HER2), are also regulated in breast cancer tumorigenesis [109, 110]. EGFR overexpression is correlated to overexpression of HER-2, levels of which are used for targeted therapy by using the drug trastuzumab [111]. However, breast cancer type is classified based on gene expression profiling, which requires a large amount of tumor tissue for analysis and is highly expensive and also a difficult procedure. Moreover, gene expression in an individual is subject to changes due to post-transcriptional modifications and may lead to upregulation or downregulation of certain genes [112]. The diagnosis of breast-cell-related diseases requires an extensive biopsy and sampling for confirmation. These invasive diagnostic techniques cause distress until the diagnosis is confirmed through biopsy, and sometimes even after treatment there is a high chance of relapse; therefore, the patient has to get a biopsy done every few months. Some benign tumors, such as premalignant hyperplasia, when left untreated can also lead to invasive breast cancer, which is one of the most common malignancies diagnosed in women.

Breath analysis is widely being explored as a noninvasive diagnostic test for detection of breast cancer [113]. Increased oxidative stress is a key factor regulated in breast cancer, which causes damage to the cellular DNA, lipids, and proteins. Also, cytochrome P450 enzyme, expressed in breast cancer, causes lipid peroxidation of polyunsaturated fatty acids and leads to overexpression of volatile organic compounds such as alkanes and alkane derivatives in breath [114, 115]. Apart from lipid peroxidation, free radical–induced oxidation of certain amino acids, proteins, and peptides has also produced hydrocarbons and monoaldehydes [116, 117]. Recently, implementation of optical fibers in sensor application is rapidly increasing due to their ease of fabrication, low cost, and immunity to electromagnetic interferences. Especially in volatile organic compound (VOC) gas sensor applications, optical fibers are widely used because of their fast response and sensitivity toward gas molecules. Different types of optical fibers have been reported in sensor applications such as plastic optical fibers, silica optical fibers, fiber Bragg grating optical fibers [118], photonic crystal optical fibers [119]. In addition to the geometry and types of optical fibers, various sensing mechanisms have been reported, including absorption-based sensors, evanescent mode [120], plasmonic mode optical sensors such as surface plasmon resonance [121], localized surface plasmon resonance [122], and lossy mode resonance [123].

1.8 Down-conversion Photoluminescence Properties of ZrO_2: Ln^{3+} (Ln = Eu, Sm, Er, Tb, Ho, Tm, Pr, Gd, Dy) Films Formed by Plasma Electrolytic Oxidation

In recent years, plasma electrolytic oxidation (PEO) is a very convenient process for formation of Ln ion–doped metal-oxide semiconductor films such as ZrO_2 [124–132], Al_2O_3 [133–139], TiO_2 [140, 141], Zn [142], Nb_2O_5 [143], HfO_2 [144], Y_2O_3 [145], and Gd_2O_3 [146] by PEO of pure Zr, Al, Ti, Zn, Nb, Hf, Y, and Gd metals, respectively, in an electrolyte containing suitable lanthanide oxide (Ln_2O_3) particles. The formation mechanism of the PEO film is complex, as it involves electro-, thermo-, and plasma-chemical reactions in the electrolyte and metal–electrolyte interface, due to locally high temperature (10^3–10^4 K) and pressure ($\sim 10^2$ MPa) at the micro-discharge sites [147].

During the PEO process of zirconium in an alkaline electrolyte containing Ln_2O_3 particles, ZrO_2 films are formed by PEO as a result of the oxidation of zirconium substrate via a sequence of localized micro-discharging events. Zr^{4+} ions formed at the zirconium/oxide interface ($Zr \rightarrow Zr^{4+} + 4e^-$) enter the micro-discharge channels and react with O^{2-}/OH^- ions from the electrolyte. Metal oxides are eminent host matrices for Ln^{3+} due to their outstanding physicochemical characteristics such as good thermal, chemical, and physical stability, wide bandgap, broad optical transparency, low phonon frequency. Among them, zirconium oxide (zirconia, ZrO_2) is an excellent host material because its low phonon energy of about 470 cm^{-1} can increase the probability of radiative transition occurrence and reduce non-radiative multiphonon relaxation of excited Ln^{3+} throughout the vibrational bands of the ZrO_2 host lattice, thus foreseeing a high yield of intra-4f transitions from the Ln^{3+} [148–150].

The Ln_2O_3 particles take part in PEO process through the electrophoretic and micro-discharging mechanisms [151]. Ln_2O_3 particles have a negative zeta potential in alkaline media; thus, its particles are negatively charged. Due to the electrophoretic effect, the Ln_2O_3 particles move toward the zirconium anode. Melting point of Ln_2O_3 particles ($\sim$2400 °C) is much lower than locally high temperatures ($\sim$7000 °C) which induced at the micro-discharging sites [152], allowing the molten Ln_2O_3 particles to react with ZrO_2 and form Ln^{3+} ion–doped ZrO_2 films.

1.9 Multiferroics for Spintronic Applications

Multiferroics are a special class of materials that simultaneously possess two or more primary ferroic order parameters in the same phase such as ferroelectricity, ferromagnetism, ferroelasticity, and ferrotoroidicity [153]. In the last few decades, a significant number of research works have been done on multiferroics. A material that simultaneously possesses multiferroic orders is not sufficient. There should be a strong coupling interaction between different orders to achieve potential applications. Magnetoelectric coupling refers to the linear magnetoelectric effect [154]. One