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Pyrazoline Derivative as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium: Experimental and Theoretical Approach

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A new pyrazoline derivative, 1-[5-(4-bromophenyl)-3-(6-methoxypyridine-3-yl)-4-5-dihydro-1H-pyrazol-1-yl]-ethane-1-one (BMDP) was synthesised using chalcone derivative. The FTIR, 'HNMR and mass spectral analysis were performed to validate the synthesised compound. The electrochemical impedance spectroscopy and potentiodynamic polarization techniques were performed to evaluate BMDP as a corrosion inhibitor for mild steel. The corrosion inhibition was observed to rise with an increase in BMDP concentration and decline with an increase in temperature. The maximum inhibition efficiency of

91.1% was reported at 303 K in 40 ppm of BMDP concentration. Activation and adsorption parameters were found with statistical thermodynamic calculations. The surface investigation of the metal surface was performed by SEM, AFM and EDX techniques. UV-visible spectroscopy was used to realise the inhibitor-metal complex formation. The quantum chemical computations were performed by density functional theory using Gaussian 16 software, and the theoretical calculations confirm the outstanding anticorrosive property of BMDP at the diminutive level as analysed in electrochemical studies.

Introduction

Iron and its alloys dominate most of the oil, petrochemical and machinery industries due to their extraordinary mechanical strength, physical properties and low cost. The advancement of metallurgical technologies enhanced the use of iron-based materials in harsh industrial conditions. It is known that metal attains stability in its oxidised form, and oxidation of metal by corrosion is an inevitable process. Along with the natural tendency of the metal, the rapid environmental pollution accelerates the rate of electrochemical reactions resulting in a shortening of the life span of the metal. As corrosion potentially affects machinery and equipment, the infrastructure assets thus have become a global issue. The prevention of corrosion always becomes challenging and employing organic compounds as corrosion inhibitors is the most feasible and easiest way of corrosion protection. Tatal

The various derivatives of heterocyclic organic compounds were synthesised to study the effect on the corrosion inhibition process. Usually, the corrosion process is studied in the hydrochloric acid medium as it is used as the pickling agent in most of the industries. A moderate acid concentration and

temperature range are preferred as mild steel undergoes embrittlement at high temperatures and pressure. Studies have shown that the pyrazoline derivatives are proven to be good antimicrobial agents and corrosion inhibitors which enable a researcher to synthesise eco-friendly anticorrosive pyrazoline derivatives. Pyrazoline derivatives with sulphonamide scaffolds were used as antitubercular and antimicrobial agents. [5] The various pyrazoline moieties are proven less toxic, which is confirmed by the minimum inhibition concentration used in antimicrobial studies.^[6,7] The most convenient method to synthesise environment-affable pyrazoline derivatives is through the chalcone intermediates, which allows the researcher to modify the pyrazoline scaffold with varying substituents. The hydroxy-based pyrazoline derivatives behaved as excellent corrosion inhibitors where the effective inhibition is due to the interaction of protonated pyrazoline with the metal surface. [8] The introduction of a methoxy group in pyrazoline derivatives enhances the inhibition efficacy.[9] The donor-acceptor interaction between the antibonding orbitals of phenoxy acetic acid pyrazoline and d electrons of the metal effectually prevents the dissolution of the metal.[10] The investigation of the substituent effect on pyrazolines confirms that both positive and negative inductive groups arrest corrosion effectively. The literature review on pyrazole and bipyrazole derivatives gives evidence about the stability of these compounds as a corrosion inhibitor in all kinds of corrosive media like H2SO4, HCl, HNO3 and salt water.[12] Water-soluble pyrazole-pyrimidine hybrids bearing various anchoring groups functioned as mixed-type inhibitors with multi-functional heteroatoms and halides. P.S.

The present research involves the synthesis of 1-[5-(4-bromophenyl)-3-(6-methoxypyridine-3-yl)-4-5-dihydro-1H-pyrazol-1-yl]-ethane-1-one (BMDP). This newly synthesised pyrazoline derivative possesses a methoxy-bearing pyridine ring and a bromine-bearing phenyl ring. These molecules are known to

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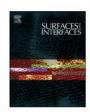
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Clitoria ternatea flower extract: Biopolymer composite-based triboelectric nanogenerator as a self-powered smart counter

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ABSTRACT

The development of biopolymers-based high-performance triboelectric nanogenerators (TENGs) for powering innovative electronics is crucial for green energy technologies. Herein, a novel TENG composed of polyvinyl alcohol (PVA) functionalized with electron-donating groups from *Clitoria tematea* (CT) flower extract is proposed. The compatibility of composite film in energy harvesting devices is tested through various characterizations, including structural, surface, electrical, and bioassay. Interestingly, the enhanced tribopositivity of the composite is attributed to intermolecular hydrogen bonding between taraxerol and PVA, substantiated by Hartree-Fock-DFT calculated vibrational spectrum, frontier molecular orbital energy gap, and electrostatic potential maps. TENG with PVA-CT: Polyurethane generated an open-circuit voltage ($V_{\rm OC}$) of 14.8 times and short-circuit current ($I_{\rm SC}$) of 32.7 times, more significant than PVA TENG and several bio/non-biodegradable tribonegative polymers. The long-term stability test of PVA-CT TENG is confirmed by an observation of constant $V_{\rm OC}$ for eight consecutive months. Additionally, humidity studies reveal that output increases with an increase in relative humidity of 30–100%. Further, the PVA-CT TENG is efficient in charging capacitors, powering LEDs, and acts as a self-powered smart counter. Overall, this study contributes new insights into developing eco-friendly synergistic materials for TENG fabrication and extending its applications in the Internet of Things, facilitating to build of futuristic smart cities.

1. Introduction

Powering electronic devices and sensor networks requires continuous functioning of many batteries, which need to be replaced frequently and therefore result in system unreliability and environmental contamination [1,2]. To counter these issues, Wang and his co-workers invented the triboelectric nanogenerator (TENG) as a viable green technology that harvests energy efficiently from the environment by combining triboelectrification with electrostatic induction [3–5]. Contact between frictional layers generates electrostatic charges of the

opposite polarity, creating an electric field that drives electrons through an external circuit [6–9]. Thus, triboelectric frictional materials are vital in determining TENG's efficiency. Traditionally, TENGs are fabricated using polymers, viz PTFE (polytetrafluoroethylene), PDMS (polydimethylsiloxane), PVDF (polyvinylidene fluoride), PMMA (polymethyl methacrylate), FEP (fluorinated ethylene propylene), nylon, and metal electrodes, which are of high-cost and non-biodegradable leading to e-waste and finally hazardous to the ecosystem [10–16]. Thus, it is necessary to promote low-cost green technologies that will effectively overcome the environmental risk factors along with large-scale

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RESEARCH ARTICLE

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Polyaniline grafted pullulan: Optical, thermal, structural, and electrical characterization studies in combination with density functional theory calculations

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Abstract

Polyaniline (PANI), a conducting polymer, has great interest for a large number of applications. However, poor processability and mechanical properties limits its usage and many methods like blending, grafting etc. are used to overcome this disadvantage. We have carried out grafting of PANI onto pullulan (PULL) via chemical oxidative polymerization technique. The percentage of grafting is favored by increasing concentration of aniline monomer. The formation of PANI is confirmed through UV-Vis spectroscopic studies. The possible grafting mechanism is studied using Fourier transform infrared spectroscopy and validated by Hartree-Fock density functional theory (HF-DFT) calculations. Further, thermal properties of grafted polymers are studied using differential scanning calorimetry and thermo gravimetric analysis. Using FESEM and x-ray diffraction, structural properties of graft polymer were studied. DC electrical conductivity of grafted polymer is measured from I-V characteristics, shows a significant conductivity which is the highlight of this work.

KEYWORDS

DFT calculations, FTIR, grafting, polyaniline, pullulan

INTRODUCTION

Polyaniline (PANI) is widely used organic conducting polymer, has significant applications in biomedical field due to its high electrical conductivity, biocompatibility, low toxicity and high environmental stability. The conductive PANI-based nanocomposites and blends are used in the biomedical fields including antimicrobial therapy, biosensors, drug delivery, artificial muscles, nerve regeneration, neural prosthesis interfaces, scaffolds, tissue engineering, wound healing, nerve regeneration, cardiac tissue engineering etc.1,2 In biomedical fields such as electrotherapy, antimicrobial

clothing, electromagnetic devices for monitoring health etc., the antimicrobial conducting PANI has been used. The PANI shows good thermal and chemical stability, pH-switching behavior, electrical and optical properties. Recently, development of PANI based ion exchange membrane for fuel cell is of interest to researchers, due to its hygroscopic nature and high proton conductivity.3 While, usage is limited due to the lack of solubility in common organic solvents and film forming ability. The grafting is one of the procedures adapted to improve its processability. This allows the formation of functional groups to polymer backbone by covalent binding of a molecule.4-6

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Etching of micro-channels in fused quartz for novel device applications

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ABSTRACT

Glass and fused-quartz are commonly used in microfluidic and optical sensor devices due to their chemical inertness and optical transparency. This study focuses on the etching of glass and fused-quartz using chemical etching and electrochemical discharge machining (ECDM) techniques. The aim is to compare their effectiveness and identify the most suitable technique for micro-channel formation. Chemical etching with hydrofluoric acid /Buffered hydrofluoric acid solution is commonly used for deep etching in silicon dioxide, but becomes challenging for long etching periods beyond 100 µm depth. There are primarily two problems: a) the integrity of the mask used for defining micro-channels; b) undercut below the mask edges. These two problems seriously limit the chemical etching process beyond 100 um depth. A mask made of evaporated Au/Cr has been found effective in protecting borosilicate-glass during etching to a depth of 148 µm. However, etching of fused-quartz is much slower than borosilicate-glass while the mask integrity remains the same. Hence obtaining micro-channels beyond 100 µm depth is extremely challenging in fused-quartz. This study compares our results of chemical etching and ECDM of fused-quartz, concluding that electrochemical discharge machining is the effective and reliable technique for micro-channel formation on fused-quartz. The results showed a significant enhancement in surface quality as proven by UV-vis transmission data obtained after well-optimized BHF treatment on ECDM samples. Specifically, this treatment involved subjecting ECDM etched fused-quartz samples to a 1:1 BHF treatment for duration of 5 min. Following this optimal BHF treatment, the UV–vis transmission data showed an increase from 36% to 44% thereby meaning the surface roughness caused by ECDM has been smoothened during 5 min 1:1 BHF treatment. These findings provide valuable insights into the etching processes, masking materials, and techniques for micro-channel fabrication, with potential applications in microfluidics and optical sensing

1. Introduction

Fused quartz and glass, due to their unique properties such as transparency, corrosion resistance, temperature resistance, and hardness[1], find widespread applications in microelectromechanical systems (MEMS), microfluidics, and lab-on-chip devices. To define patterns in glass and fused quartz, controlled etching in HF-based etchant is commonly employed [2,3]. Chemical etching and electrochemical discharge machining are known as superior techniques for etching glass and fused quartz. Notably, recent studies have investigated the

machining of fluidic channels on borosilicate glass using grinding-aided electrochemical discharge engraving (G-ECDE) and process optimization methods [4]. The integration of such innovative approaches enhances the capabilities of glass machining, opening up new avenues for advanced microfluidic device fabrication. Electrochemical discharge machining (ECDM) has been proven to be a successful method of fabricating micro features in fused silica and glass substrates. Electrochemical machining (ECM) and electro-discharge machining (EDM) are combined in ECDM. Material removal happens by thermal melting, anodic dissolution and vaporization in the ECM and EDM processes,

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Degradation mechanisms in PEM fuel cells: A brief review

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ABSTRACT

One of the most important features of polymer electrolyte membrane (PEM) fuel cells is durability. Improving fuel cell life and membrane electrode assemblies (MEA) durability translates to significant cost savings for fuel cells. This review is about the study of the degradation mechanisms of PEM fuel cells. The Degradation mechanisms include chemical, mechanical, catalyst, and thermal degradation. The reason for degradation also may be due to the presence or formation of contaminants during dynamic conditions. From the review, it has been observed that Pt catalysts made of Pt or Pt-alloy catalyst value superior to those required for complete Pt oxide.

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1. Introduction

Energy sustainability is a critical challenge due to the depletion of fossil fuels and the release of large amounts of CO2 into the air which causes global warming. So alternatively, fuel cells are among the most essential energy devices because they can directly transfer chemical energy from fuel (such as methanol, hydrogen, etc.) to electrical energy with great efficiency and zero carbon emission in the case of hydrogen fuel. Depending on the electrolytes and fuels employed, there are many distinct types of fuel cells such as polymer electrolyte membrane fuel cells (PEMFC), direct methanol fuel cells (DMFC), solid oxide fuel cells (SOFC), molten carbonate fuel cells (MCFC), phosphoric acid fuel cells (PAFC), alkaline fuel cells (AFC), and alkaline anion exchange membrane fuel cells (AEMF) [1-4]. Among all, PEMFCs are the most sustainable with a variety of applications [5] in particular, for automotive applications [6]. The main benefit of PEMFC is that it operates at low temperatures below 100 degrees Celsius.

The PEMFC's key component is the MEA. A PEM fuel module is composed of two catalyst layers and two gas diffusion layers

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(GDL): because of their superior proton conductivity, mechanical and chemical stability nafion membranes are the most used electrolytes.

One of the most serious obstacles to the commercial use of PEMFCs is the high cost of electro-catalyst platinum (Pt) and fabrication process. One technique to reduce the cost is to expand the surface area of the Pt catalyst and use it more efficiently without sacrificing cell performance. It will assist in reducing the fuel cell's size, and its high cost. The factors which reduce the PEM fuel cell performances are temperature control and water control capabilities, ohmic resistance, and rate of long-term performance deterioration of PEMFCs which are all determined by the membrane, catalyst degradation, and efficiency. The performance is impacted by a variety of input factors and output factors of a PEM fuel cell which encompass both design and construction of fuel cells, material deterioration, impurities or pollutants, and operating situations. The long-term endurance of PEM fuel cells is a major roadblock to their commercialization in stationery and transportation applications. Improved fuel cell component durability is required for commercial viability. Individual components must be thoroughly described to determine and quantify deterioration mechanisms to expand fuel cell durability. In this review, we summarise some of the progress made in identifying chemical, mechanical and thermal degradation mechanisms in PEM fuel cells over the years, as well as a solution to the degradation due to contaminants.

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FTIR signal assignment in Chitin using density functional theory calculations – A monomer approximation

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ABSTRACT

Density functional theory (DFT) calculations are performed on Chitin to investigate the geometry and vibrational properties under monomer approximation. Vibrational spectra of chitin have been analysed using the DFT monomer approach, and complete assignments of experimental FTIR signals are being reported in the present work. DFT calculations with the 6-311G basis set produces results for vibrational modes that reasonably agree with the experimental FTIR results.

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1. Introduction

Chitin, the second most abundant natural polymer[1] after the cellulose, is a linear polymer composed of repeating $\beta(1,4)$ -Nacetylglucosamine units. Chitin exists in the shells of arthropods such as crabs, shrimps, and insects and is also produced by fungi and bacteria[2,3]. Chitin and its blends of polymers have wide range of application from conducting polymers[4], sensors[4] and other biodegradable medical applications[5]. The Fourier Transform Infrared Spectroscopy (FTIR) is a characterization technique applied widely from small organic molecule to a macromolecule, to have an estimation of structure through vibrational modes of the chemical groups present in the system. FTIR signals of the chemical groups present in the Chitin viz., -NH2, -CH3, -OH and most importantly -OCH3 and their analysis forms the indicative markers for structural validation.[6] Typically, the IR signals arising out of the polymers are quite complex due to conjugated vibrations and are quite tedious for analysis.

Though experimental IR, an established spectroscopic technique for initial assignment of the chemical groups that are present in the macromolecule and a tool to render a structural validation, pans out as a strenuous process in the case of polymers. Consequently, a theoretical dimension that supplements the experimental IR analysis and facilitates the process of assignment of FTIR

signals, thereby providing a robust structural validation of polymers using a monomer approximation.

Here in this work, we show the possibility of nearly complete and precise assignment of experimental FTIR signals to their respective chemical group in a unit of Chitin macromolecule using density functional theory (DFT) calculations with monomer approximation.

2. Methodology

2.1. Experimental FTIR

Chitin (purchased from HIMEDIA, Mumbai) with Mol. Wt. 400,000 g/mol used for recording FTIR using a Perkin–Elmer spectrophotometer (model 1000).

2.2. Density functional theory (DFT) calculations

The single monomer unit of Chitin is subjected to density functional theory (DFT) calculations using GAUSSIAN 16 (G16)[7] program. The G16 program on Bewoulf type (Configuration: 2.3 GHz processor, 16 GB RAM) computational facility at IMMM, Le Mans, France was used for the DFT work. We utilized 4 nodes composed of 8 nodes, out of which 4 nodes was used for Gaussian 16 (G16) calculation.

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A novel cross-linked PVA-Chitosan composite membrane for heavy metal filtration applications

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ABSTRACT

A novel glutaraldehyde cross-linked Chitosan-PVA (GCP) polymer composite membrane is used to create a water filtration device. The GCP polymer membrane is synthesised using the solution casting process. GCP membranes are characterised using different techniques. The results showed that this filtration unit developed using GCP membrane is effective in reducing the Lead, Cadmium, Sodium and Iron content by 99.32%, 98.1, 88.21% and 78.9% respectively. The creation of nano-pores in GCP membrane, the adsorbent property of GCP and the thermal and chemical stability of GCP are the key factors leading to high performance filtration of major metal contaminants in ground water.

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1. Introduction

Water is extremely important for life on earth. Especially potable water is a global challenge and the problem is more specific to developing countries. The large water bodies such as lakes and rivers get contaminated by Industrial effluents and improper disposal of sewage and other urban pollutants. On land, the soils get polluted by untreated wastes. The contaminants from the soil get infiltrated into the Ground water when there is precipitation, resulting in irreversible changes to underground water. The human body uses water to regulate temperature and maintain routine bodily functions in all its cells, tissues and organs. Hence, consuming polluted water would cause various waterborne diarrheal diseases and other severe diseases such as typhoid, Guinea worm disease and dysentery [1]. One of the most common sources of contamination are the Dumpyard sites which, especially in the developing countries, are used for dumping of several materials like plastics, waste from industry and medical wastes. Hence, these areas pose a great threat to the ground water and other water bodies. Thus, it is a considerable challenge to purify the contaminated underground water. Water treatment processes employ multiple

membrane types. They include microfiltration membranes, ultra/ nano-filtration and reverse osmosis. The largest pore sizes of the microfiltration membranes generally block large particles and different micro-organisms [2]. Ultra/nano-filtration membranes are better to block bacteria and soluble macromolecules such as proteins due to their smaller pore sizes compared to microfiltration membranes. Reverse osmosis (RO) is specifically a pressuredriven membrane diffusion/filtration process in which membranes are generally non-porous and thus eliminate low molar mass particles such as organics [3], whereas ultra/nano-filtration membranes are relatively new and are often referred to as reverse osmosis "loose" membranes. These are porous membranes with pore sizes of the order of ten angstroms or less and they show filtration efficiency almost similar to reverse osmosis. Membrane technology is generally being used for the production of drinking water based on reverse osmosis process [4]. However, reverse osmosis process is a high-pressure driven process. Hence, it is useful to have a low pressure processsuch as ultra-filtration/nano-fil tration process. In this case removal of heavy metal contaminants becomes an issue. Here the principle of removal of metal ion contaminants based on adsorption process becomes important. The most favoured methods for removing heavy metal ion contaminants from ground water have been adsorption processes that are very simple, economical, efficient and flexible. Comparatively,

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Chitosan-Polyvinyl Alcohol blend as beta-ray attenuator

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ABSTRACT

Living organism exposure to radiation beyond certain limit is dangerous, while handling the radioactive materials. High Z- materials give proper shielding to this radiation, but the associated production of external bremsstrahlung, high cost of materials, hazardous nature of materials like lead (Pb) make us to choose low Z polymer as shielding material. Present work investigating on the beta attenuation properties of Chitosan-Polyvinyl Alcohol blend films. The films of individual polymers and their blends in different ratios having different thickness were prepared and attenuation study has been carried out with the help of G M Counter and Tl-204 beta active radiation source. FTIR, XRD, DSC, TGA, SEM characterisation shows that blend with 10–90(CH-PVA) and 30–70(CH-PVA) ratios have good attenuation property because of good miscibility of polymers in the blend. Miscibility of blend reduces as chitosan content increases and hence attenuation values also decreases. These results suggest the feasibility of using CH-PVA blend as low energetic beta attenuator.

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1. Introduction

Nowadays, the production and application of nuclear radiations are increased due to their wide applications in the areas like industry, food processing, security devices, household products, space technology, medicine etc. [1]. Due to this, extra care has to be taken while handling the nuclear radiation sources, because exposure to those radiations, beyond some extent, is dangerous to living organisms. So, it is very important to have proper shielding or packaging materials for these radiation source while handling them. A variety of shielding materials are available today, provided their selection depends on the ionization power of nuclear radiation and range it can travel through the matter. Further, attenuation ability or attenuation coefficient (μ) is another important parameter of the shielding material. The linear attenuation coefficient has direct dependence on the atomic number (Z) of the shielding material. Which suggest the use of high -Z material like Pb, Sb, Sn etc. [1,2], but in future the protection from the harmful radiation is a kind of issue due to unavailability of high-Z materials. Now it is the time to think about such shielding materials that can be used

at large scale and will be available at low-cost, non-toxic in nature and made up of low -Z material. So, the best alternative is feasibility of using polymer. Polymers have a low Z, high resilience and toughness, are easy to produce, are less expensive, require less maintenance, and are thermally stable. These characteristics make it ideal for making containers, pipes, electrical insulation, corrosive fluid valves and pumps in nuclear technology, as well as protective coatings and base materials for nuclear radiation shielding. The polymers are employed in dosimetry services, radiation detector calibration, and tissue equivalence.[3].

Several studies are carried out to check the efficiency of some low-Z polymer materials that can be used at large scale as a radiation shielding material. N.Govinda Nayak et.al studied effective atomic numbers of few polymers and other materials for photoelectric process at 59.54 keV from the measured total attenuation coefficients, for gamma ray attenuation. They have used the mixture rules to find the attenuation coefficient and found that hygroscopic nature affects the attenuation for gamma ray interaction in materials. At lower γ energy (10 keV \ll E $\gamma \ll$ 100 keV) the measured photoelectric cross sections match with the theoretical values for polymers having low Z elements as its constituents [4]. Absorption Coefficient of Polymers (Polyvinyl Alcohol) at various concentrations by using Gamma Energy of 0.39 MeV is found to

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Optical and photoluminescence studies of precursor stabilised Aluminium-Gallium Zinc oxide thin films

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ABSTRACT

A low cost, versatile, and cost-effective ultrasonic spray pyrolysis approach was used to generate aluminium and gallium doped Zinc Oxide thin films on stretchable corning glass substrates at 400 °C temperature. Ammonium acetate is employed as a stabilizing ingredient in the precursor solution. According to X-ray diffraction patterns, high quality polycrystalline films on glass substrates grew successfully. As Ga doping levels rose, photoluminescence spectra showed an increase in exciton peak emission. As time passes, photoluminescence spectra show a strong emission peak centred at 3.24 eV that is progressively pushed toward higher wavelength. When Aluminum and Gallium were added into the Zinc Oxide lattice, the crystalline size was reduced and the thin film residual stress was raised. In the visible area, all films were extremely clear, with an average transparency of 80%. The optical energy band gap increased from 3.12 eV to 3.3 eV when the doping concentration increased.

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1. Introduction

Zinc oxide thin films have recently been studied by many researchers for promising applications in many opto-electrical and electronic products [1], including thin film transistors for display device applications. It is also well known that thin films which are transparent are the majority use in a variety of applications that is ITO films [2]. Due to its rarity in nature indium is a highly costly metal; as a result, strategies have been created to replace indium-based thin films with advantages like abundance in nature [3], non-toxicity and its stability in hydrogen plasma [4,5], ZnO is an effective candidate. Due to an imbalance of oxygen sites pure zinc oxide films are essentially n-type semiconductors, resulting in the generation of ions, positive vacancies and free electrons. ZnO has a high electrical resistance when it is not doped with group 3 trivalent elements, which can be readily overcome. Among the most frequently researched dopants, Ga is the most powerful. (Al, Ga and In stand for Alabama, Georgia, and Indiana respec-

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tively.) Rapid Al oxidation and low heat stability are two disadvantages of Aluminum doped ZnO films (AZO). Gallium doped ZnO (GZO) films are less durable and more costly than AZO films in humid conditions [6]. Co-doping with Aluminium and Gallium thus offers a solution by complementing the limits of each single dopant. There are many techniques for AGZO film growth, some of them are RF-magnetron sputtering [7], pulsed laser deposition [8] and molecular beam epitaxy [9], expensive techniques are also included. Due to their simplicity and low cost, chemical methods are helpful. These techniques include deposition of chemical baths [10], hydro-thermal [11], spray-pyrolysis [12], and sol-gel [13]. Due to the fact that spray-pyrolysis AGZO films provide a number of benefits over other chemical techniques, they have not been widely used [7,14-16]. Chemical homogeneity can be easily achieved in a multi-dopant system, and can be simply modified for the development of large area coatings [17]. Using this process, good quality polycrystalline thin films were generated at comparatively low temperature [18]. By taking ZnO as an ultra-thin buffer layer and also by using ammonium acetate as a precursor solution, best AGZO films were grown and its properties are discussed in this paper. AGZO thin films of various compositions were made



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Simulation & analysis of PZT/ P (VDF-TrFE) cantilever beams for health monitoring of building and structures

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Piezoelectric
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P(VDF-TrFE)
Vibration sensors

ABSTRACT

The design of a piezoelectric PZT/P(VDF-TrFE) based Microelectromechanical system cantilever beams for a very low frequency applications, using silicon bulk-micromachining technology is described in this paper. The natural frequencies of cantilever beams were calculated using the COMSOL software. For signal output, the cantilever-beam structure contains a layer of PZT/P(VDF-TrFE) as well as chrome-gold interdigitated electrodes. According to the simulation results, the cantilever-beam with dimensions of 10mmx3mmx5µm has a lowest resonant frequency of 95.56 Hz, implying that PZT/P(VDF-TrFE) is an appropriate piezoelectric material for really low frequency uses such as building and structure health monitoring.

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1. Introduction

MEMS based instruments have found uses in a various technology over the last few years, such as navigation devices [1], health-care products [2], radio transmission [3], pressure transducers [4], inertial sensors [5], and others. Piezoelectric materials are required for purposes such as pressure sensors and accelerometers. Inorganic piezoelectric materials like [6] lead zirconium titanate (PZT), organic/polymer piezoelectric substances like Polyvinylidene fluoride (PVDF) and their co-polymers important among the most prevalent piezoelectric materials. Regardless of the fact that piezoelectric ceramic substances have seen usage in MEMS instruments [7,8,9] application of lower frequencies application [10,11,12,13] is limited because of its higher electromechanical coupling factor k, which will end up having higher resonant frequencies.(See Table 1.).

Due to their favorable qualities such as small size, reduced energy consumption, long lifespan, and low cost, micro-electromechanical systems (MEMS) are discovering ever more application areas every day [14]. In recent years, micro power generating devices have been one of the most significant application areas for MEMS structures. MEMS energy harvesters are used in various

cations equipment. Traditional energy sources, including such cells, fail to match the size and charging demands of wireless networks [15]. The goal of current research is to develop more sustainable power sources in order to reduce wireless networks and enhance device performance. Thermoelectric, vibrations, and Radio Frequency energy production systems are all being researched, with the power harvesting methodology chosen particular application [17]. Because to their elastic character, which leads to lower resonant frequency, piezoelectric polymer materials substances have been getting popular for lower frequencies uses such as accelerometers and power harvesters. Moreover, these have reduced electromechanical coupling coefficients, a low dielectric constant, and excellent piezoelectric properties. The actual application of stress to a piezoelectric material result in formation of an electrical charges. While some found naturally piezoelectric materials, such as crystal, showcase piezoelectric properties including materials such as lead zirconate titanate (PZT), PVDF, and P(VDF-TrFE).

research, mainly to supply sensor networks and related communi-

Among the most familiar piezoelectric materials are polymers such as PVDF and ceramics such as PZT. While polymers are soft and flexible, with low dielectric and piezoelectric properties that result in lower natural frequencies, PZT seem to be rigid but also have good piezoelectric properties and naturally higher frequencies. They too are fragile, which restricts their use in applications.

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Effect of precursor dilution solvents on the growth of V₂O₅ thin films using spray pyrolysis

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Keywords: Spray pyrolysis ACM Thin films V₂O₅ thin films

ABSTRACT

Using the ultrasonically nebulized spray pyrolysis of the aqueous combustion mixture (UNSPACM) technique, the effect of precursor dilution solvents on the growth of V_2O_5 thin films is reported. V_2O_5 thin films are grown by spraying an aqueous combustion mixture (ACM) onto glass substrates at 400°C. Methanol and ethanol are used to dilute the ACM. FESEM, XRD, and FT-Raman spectroscopic analysis are used to examine the surface microstructure, crystallographic information, and functional groups of the grown thin films respectively. The results show that thin films grown by diluting ACM with methanol produce the best results.

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1. Introduction

The molecular combination of vanadium and oxygen is extremely complex owing to the multivalency of vanadium with the least contribution being at V^{2+} and the highest being at V^{5+} [1]. Because of their propensity to undergo a reversible metal-insulator transition (MIT), vanadium oxides have gained a lot of attention, which could cause their electrical conductivity to change significantly [2]. They are of significant technological interest due to their ability to undergo MIT with different oxides exhibiting transition behavior at their respective different temperatures. For example, at 68 °C, VO2 undergoes an MIT, as well as a significant change in its optical characteristics, which makes vanadium dioxide ideal for optical switches, smart windows, and optoelectronics [3–5]. In lithium-ion batteries, gas sensors, and other wide range of industrial processes, V2O3 and V2O5 are commonly employed as catalysts [6-8]. Electrochromic layers made of V2O5 can also be found in electrochromic devices [9,10], micro-batteries, smart windows [11-13], photochromic devices [14,15], color memory devices, electronic information displays [14-17], optical/electrical switching, chemical sensing, and catalysis [18-21].

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Because of its high oxygen-to-vanadium ratio, V_2O_5 is the most stable vanadium-oxide compound. As a result of atmospheric oxygen absorption, V_2O_5 is the most common compound formed as a result of the natural aging of vanadium oxides [22]. V_2O_5 is composed of multiple layers of distorted VO_6 octahedra held together by weak bond interactions [23,24]. High-capacity solid-state batteries [1,25,26] can be developed by taking advantage of this V_2O_5 structure since the intercalation of lithium ions (Li⁺) can be easily done between VO_6 layers.

However, growing vanadium oxide thin films with a single stoichiometry remains a challenge. This is due to the multivalency of vanadium, which complicates the vanadium–oxygen system. The phase diagram of vanadium oxide has approximately twenty stable phases, including V₂O₃, VO₂, VO, V₄O₇, V₂O₅, V₆O₁₁V₆O₁₃, and V₄O₉, with each oxide being stable only within a small window [10,27]. Vanadium oxide thin films can be grown by sol–gel [28,29–31] anodic deposition [32], sputtering [33], electron-beam evaporation [34,43], electrodeposition, hydrothermal growth, doctor-blade [35–39], flash evaporation [40], pulsed laser deposition [17,41], thermal evaporation [42], chemical vapor deposition [43,44], and sputtering [18,45,46].

Spray pyrolysis is another processing technique to grow thin and thick films, powders, and ceramic coatings [47]. In comparison to many other thin film growth techniques, spray pyrolysis is both fairly simple and inexpensive. This method has been used for dense



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Optical and photoluminescence studies of precursor stabilized gallium zinc oxide thin films

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ABSTRACT

Precursor stabilized Gallium doped ZnO thin films were grown using spray pyrolysis on glass substrates. UV-vis spectrophotometry and an X-ray diffractometer were used to characterise the GZO thin films. Gallium is doped with a concentration ranging from 1 at% to 4 at% and its effects on structural and optical features were studied. XRD studies found the thin films to be polycrystalline with a hexagonal wurtzite structure. In the visible range of wavelength (400–800 nm), all GZO films exhibit average transmittance above 90%, with a pronounced absorption edge in the UV area. The PL emission spectra show the Nearband-edge emissions at about 389 nm and strong deep-level emissions from oxygen defect states at about 545 nm are observed in all the films. With increase in concentration of Ga, the intensity of these two bands decreased.

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1. Introduction

ZnO is a semiconductor material of n-type and because of their potential for technological improvement of novel nano-devices, ZnO thin films have been investigated extensively. High refractive index, low resistivity, high optical clarity and a large band gap which make ZnO a promising candidate for optoelectronic devices like LCDs, light-emitting diodes, solar cell anti-reflection coating, and transparent thin film transistors (TFTs) among others. ZnO thin film is a better substitute to Indium tin oxide (ITO) thin film transparent conductive oxide (TCO) due of its low cost. Depending on the technique of synthesis, the structural and optical properties of ZnO thin films change and therefore it is important to choose the appropriate technique for deposition in order to adjust the properties for technological application. To enhance the quality of thin films of ZnO, apart from doping, for its economic and productive technical applications, the effect of conditions of preparation must be analysed. Metal oxide semiconductors are extremely convenient among the flexible thin films for thin film

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transistor technologies, due to their high optical transparency [1-4] high electrical efficiency [electron carrier mobility of 10 cm² V⁻¹s⁻¹ even at room temperature as well as outstanding mechanical properties (large bendability and strong strain insensitivity down to 25 µm radii) [5,6]. Several synthesis routes have been successfully used, such as spin coating [7], dip coating [8], RF magnetron sputtering [9], electron beam evaporation [10,11] and spray pyrolysis [12,13], to deposit thin films of metal doped ZnO, primarily Gallium doped Zinc oxide (GZO). Among these techniques, the benefits of spray pyrolysis include simple deposition procedure, lowcost preparation, non-requirement of high vacuum and adaptation for large area coatings. Three main parameters are considered such as pre-coating, coating and post-coating parameters which affect the thin film properties deposited by the spray pyrolysis. The method of spray pyrolysis, however, requires several process parameters, such as the temperature of the substrate, the distance of the spray gun substrate, spray speed, spray time, pre and post heat treatment, influencing the efficiency of thin films directly or indirectly. Optimization of the deposition parameters is also important for obtaining a high-quality thin film. In addition to enhancing their electrical properties and optical properties, the doping of ZnO with metals, namely aluminium, gallium and

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Optical band gap and photoluminescence studies of precursor optimized Indium-Gallium Zinc oxide thin films

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ABSTRACT

Spray pyrolysis at an optimal substrate temperature of 400 °C produces thin layers of pure and Indium-Gallium doped Zinc oxide on glass substrates. In the growth of precursor solution, ammonium acetate is used as a stabilizing agent. Polycrystalline films with hexagonal shaped crystalline structures are deposited in all cases. We have investigated the optical band gap and photoluminescence behavior of Indium and Gallium doped Zinc oxide thin films. Powder X-ray diffraction studies show that the deposited thin films are polycrystalline structure, with a hexagonal crystal structure with (002) orientation. In the visible wavelength range, all thin films have a transmittance of around 85% and a strong absorption beginning of about 375 nm, which corresponds to the fundamental absorption edge of 3.3 eV of Indium-Gallium doped ZnO. UV-Vis-NIR results along with tauc's plot show that energy gap decreases with the increase of Indium-Gallium doping concentration. Photoluminescence results indicate the effect of indium-gallium dopants at of various concentrations plays a significant role in the defect chemistry in the films.

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1. Introduction

Metal oxide amorphous Indium-Gallium Zinc Oxide (a-IGZO) semiconductor thin films are proved to be a better material for channel layers in thin film transistors (TFTs) which are used in flexible display device applications [1–4]. a-IGZO semiconductor thin film channel layers in TFTs have better field effect mobility than a-Si and organic semiconductor channel layers, a-IGZOs have gained a lot of interest as a potential contender for an active matrix flat panel displays [5]. Many n-type oxide semiconductor thin films, such as Al-Sn-Zn-O (ASZO) [6], ZnO[7], and IGZO [8], have recently gotten a lot of interest in the large size flat panel display sector because these materials could solve the problems with amorphous hydrogenated silicon α -Si:H and polycrystalline silicon thin film transistor device applications [9].This is mostly related to the unique features of TAOS thin-film transistors, which include

optical transmittance in the visible range region, large-area homogeneous thin film coating at room temperatures, and excellent electron carrier mobility. Because the mobility of IGZO thin film transistors is greater than that of a-Si, they may be utilized as the backplane of FPDs. There are many reports on the thin film deposition and field effect mobility studies of a-IGZO semiconductor thin films on polymer substrates. The a-IGZO semiconductor thin films were coated at room temperature on polyethylene terephthalate polymer substrate and had a good Hall effect mobility [8]. Hosono et al initially created a-IGZO TFTs in 2003 for crystalline IGZO thin film transistors [9] and in 2004 for a-IGZO TFTs [3]. n-type a-IGZO TFTs have significant Hall mobility (>15 cm²/ V-s) and these TFTs were discovered with a molar ratio of 1:1:1 and also preferred for constructing electronic devices. Zan et al. stated that they created a porous gate structure out of polystyrene polymer spheres with 200 nm diameter with Argon plasma treated via the porous gate metal formed dot-shaped Indium and Gallium doping on a-IGZO TFT channel area. They claimed that an a-IGZO semiconductor thin film channel layer show electron mobility of

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Growth of precursor stabilized IZO thin films and study of their optical and photoluminescence properties

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ABSTRACT

ZnO thin films doped with Indium were produced on glass substrates by the process of spray pyrolysis. XRD results showed a polycrystalline hexagonal wurtzite structure. The structural, PL and optical characteristics of IZO thin films were investigated with increasing doping concentration. X ray diffraction studies with increasing Indium doping concentration show a change in the preferential orientation from 0 0 2 to 1 0 1 crystal planes. UV-vis-NIR spetra was collected and the results show that the band gap of the IZO thin film was found to be 3.5 eV. The optical transmittance spectra for thin films coated with 3 at% Indium concentration revealed high transmittance of 80–90% in the visible region. Other than the characteristic blue-green emission in In-doped thin films three more PL emissions were observed. Copyright © 2022 Elsevier Ltd. All rights reserved.

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1. Introduction

ZnO, because of its special optical properties, is a multifunctional n-type semiconductor material. In the visible field, ZnO possesses low resistivity, high optical clarity, high refractive index and wide band gap make them a bettercandidate for optoelectronic devices such as organic LEDs, solar cell, liquid crystal displays, anti-reflection coating and transparent thin film transistors (TFTs). ZnO thin film is considered to be an alternative to expensive Indium Tin Oxide thin film transparent conductive oxide (TCO) material and is extensively studied because of its cost effectiveness, non-toxicity, minimal deposition temperature and high chemical and thermal stability. The optical and structural properties of thin films of ZnO are influenced by thetechnique of synthesis, so selecting the right deposition technique is critical for tailoring properties suitable for technological applications. Apart from doping, the effect of preparation methods and factors on characteristics must be investigated in order to enhance the quality of ZnO thin films for economic and productive technical applications. Metal oxide semiconductors are extremely convenient among flexible thin films for TFT technologies, because of their

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high optical transparency [1-4] and good electrical properties [5,6]. Several synthesis routes have been successfully used, such as spin coating [7], dip coating [8], rf magnetron sputtering [9], electron beam evaporation [10,11] and spray pyrolysis [12,13], to deposit thin films of metal doped ZnO, primarily aluminium doped ZnO, indium doped ZnO and gallium doped ZnO. Among these techniques, the benefits of spray pyrolysis include, simple deposition procedure, low-cost preparation, no high vacuum requirement and well adaptation for large area coatings. Three main parameters, such as pre-coating, coating, and post-coating parameters affect the properties of thin films deposited by spray pyrolysis process. Spray pyrolysis on the other hand, necessitates a number of process parameters, including substrate temperature, spray gun substrate distance, spray speed, spray time, and pre and post heat treatment, all of which influence thin film efficiency directly or indirectly. Optimization of the deposition parameters is important for obtaining a high-quality thin film. Doping ZnO films with metals including aluminium, gallium, and indium improves their electrical and optical properties while also making them more stable. The atomic radius is commonly used to select dopants. To avoid lattice distortion, the dopants' atomic radius must be equal to that of ZnO. In addition, doping concentration is also essential for the improvement of thin film mobility. Therefore, the optimal dopant dose is important. Moreover, oxygen desorption at the grain



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Spray pyrolysis deposited aluminium-indium zinc oxide thin films and study of their electrical and photoluminescence properties

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ABSTRACT

The structural, optical, photoluminescence and electrical behaviour of aluminium and indium doped ZnO (AIZO) thin films are investigated for different dopant compositions. AIZO thin films were grown on glass substrates using an ultrasonic nebuliser spray pyrolysis process at 400 °C substrate temperature. Ammonium acetate is used as a stabiliser as well as a binding agent in the precursor solution. It was found that a shift in crystalline nature as the deposition time increases. Further, these thin films show hexagonal nanostructures, according to XRD investigations. Optical studies show that AIZO films have transmittance of more than 70%. Electrical study reveals that resistivity of AIZO thin films range from 2.35 to $4.591 \times 10^{-3}~\Omega cm$.

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1. Introduction

The films are optically transparent and electrically conductive with transparent conductive oxides (TCO). Many applications are involved, such as LCD (liquid crystal displays), window thermal coatings, solar cells and LED's [1-5], TCOs are widely investigated. Zinc oxide, a large band gap semiconductor, is favoured over other transparent conductive oxide materials, such as CdO, SnO2, CuO, PdO, In₂O₃ and NiO [6], for its high availability, non-toxicity and low-cost. Intrinsic ZnO, however, is extremely resistive. gallium (Ga) Aluminium (Al) or indium (In) are the favoured dopants for develop the electrical behaviour of zinc oxide thin films, as their ionic radii is similar to that of zinc (Zn) [7-9]. Zn²⁺, Ga³⁺, Al³⁺ and In3+ ions have an ionic radii of 0.074 nm, 0.062, 0.054 and 0.080 nm respectively [10,11]. For the growth of ZnO thin films, different growth techniques/parameters are pursued, such as pyrolysis spray (USP), sol-gel, sputtering, chemical vapour deposition (CVD) and thermal evaporation, ultrasonic pyrolysis spray (USP) [12-16]. Among these, there are numerous advantages of ultrasonic spray pyrolysis, such as wide area depositions, easy

experimental setup and cost efficiency [17-19]. Many researchers/authors documented single element ZnO doped (Al/In/Ga) coated using spray pyrolysis technique [20-27]. Minimum resistivity was obtained for Aluminum doped ZnO (AZO) is 5×10^{-3} , for Indium doped ZnO (IZO) is 3.4×10^{-3} and Ga-doped ZnO is $9.3 \times 10^{-3} \Omega$ cm. In recent years, prosecutors have favoured the enhancement of co-doping properties [28]. It can also be said that the study of photo-luminescence (PL) emission spectra is the greatest field of research on this perspective material; most emission wavelengths from ZnO nanoparticles, can show from blue-green wavelength region [29]. One of the most notable problems is the emission of light tuned to longer wavelengths [30]; This emission zone, most probably used in displays and medical therapies [31-33], is relatively hard to reach. This associated ZnO emission is also less commonly recorded [30,34-36]. In addition, the achievement of a small and solid emission band for monochromatic emission devices remains a further challenge [37]. Novel PL properties can be obtained by regulating the additives, band gap engineering, morphology and scale [38,39]. For instance, co-doping makes it possible to add the advantages of two dopants simultaneously. In:ZnO and Al:ZnO composite materials with better optical properties exhibited at room temperature were presentedin few earlier reports [39-44]. The results of Indium and Aluminum co-doping

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A review on chemi-resistive human exhaled breath biosensors for early diagnosis of disease

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ABSTRACT

Human breath analysis provides a non-invasive and fast method for identifying numerous volatile organic compounds that are disease markers. Breath analysis on a small device that is connected to the Internet of Things and uses chemi-resistive semiconductor with extremely low energy usage will build new roads for detection of diseases and monitoring patients. Nano-structures of various forms, synthesized by diverse nano-meter-scale synthesis methods, can be utilized to achieve this aim. Metal oxide nano-structures allow a well-built gas-sensing layer interaction and, as a result, show a higher sensitivity than traditional materials due to features such as high surface-to-volume ratios and, consequently a large number of surface sites exposed to gas. This paper provides an overview of advances in chemi-resistive nano-structures as gas sensing materials for exhaled breath detection, with the goal of assisting patients with various conditions in their disease screening. The many types of chemi-resistive materials utilized in breath sensors have been discussed, as well as their limits and future prospects also presented. Copyright © 2022 Elsevier Ltd. All rights reserved.

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1. Introduction

Treatment of illnesses in their early stages enhances the chances of survival while lowering medical costs. Medical diagnostics, in comparison to conventional blood testing methods, is to provide a technique that can rapidly anticipate and, if necessary, non-invasively monitor illnesses like diabetes, lung cancer, renal disease and breast cancer at their initial stages, when the chances of recovery are significantly greater. Human breath analysis is currently a potential contender for meeting this demand. Gas chromatography (GC) in combination with other techniques which include mass spectrometry (MS), ion mobility spectrometry (IMS), or flame ionisation detector (FID) which provide a reliable examination of exhaled gases. Nonetheless, it is challenging to accomplish portable and real-time disease detection which would substitute several diagnosis methods which involve long diagnosis time and high cost [1]. Emerging wearable electronics technolo-

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gies, which are distinguished by their comfort, compact size, low weight, and robustness, might be an appealing option for portable health surveillance [2,3].

Nano-materials which include metal oxides and noble metals have lately been recognized as appealing components in clinical diagnostics via breath analysis due to their porosity, high specific surface area, quick response and cost-effective production [4–6]. The enhanced gas reaction sites on the surface of nanostructured metal oxides (NMOs) require a large surface to volume ratio to attain high sensitivity. These basic chemical sensors have advanced into potential sensing devices for wearable breath diagnostics that can not only monitor breathing habits but also test for illnesses characterised by exhaled gases. Chemi-resistive biosensors offer faster electron transit than bulk biosensors due to their high surface to volume ratio, biocompatibility, non-toxicity, robust electron transfer ability, and free-exciton binding energy. Breath analysis is an important method for assessing the physiological condition of the human body that has a number of advantages, including non-invasiveness, comfort, and ease of use. Ammonia (NH₃), nitric oxide (NO), hydrogen sulphide (H₂S), and volatile



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A review on metal-oxide based trace ammonia sensor for detection of renal disease by exhaled breath analysis

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ABSTRACT

Breath sensors have the potential to transform medical diagnostics by providing non-invasive and customised on-demand detection and monitoring of health indicators. The nanostructured film's gas sensing capacity is impressive in terms of response time, detection limit, & reversibility. In this work, we present advances in the detection of trace level ammonia vapor in breath, a bio-marker for renal disorders, using extremely selective, sensitive, and stable sensors at sub-ppm levels. This painless, efficient method will enhance the existing gold standard for detecting renal disease, allowing for speedy and early identification. At the end, we present an outlook for the upcoming development of efficient ammonia sensors. Copyright © 2022 Elsevier Ltd. All rights reserved.

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1. Introduction

The fingerprints of a variety of pathophysiological states and illnesses may be seen in exhaled human breath. By volume, inhaled air contains 78 percent nitrogen, 20.95 percent oxygen, and trace quantities of argon, carbon dioxide, neon, helium, and hydrogen. Exhaled human breath includes around 79 percent nitrogen [1], 3.6-16 percent oxygen, 4-5 percent carbon dioxide (nearly a 100-fold increase over inhaled quantity), 5.0-6.3 percent water vapour, and 1% Argon. hydrogen in parts per million (ppm) from microbial metabolic activity in the large intestine [2], carbon monoxide in ppm from heme protein breakdown, and ammonia in ppm. Furthermore, the exhaled breath of a healthy individual has relatively low amounts of ammonia, carbon monoxide, nitric oxide, and hydrogen dioxide. Hundreds of volatile organic molecules, particularly isoprene and acetone, can be traced. Certain chemical molecules are indicative of disease [3,4]. Oxygen O2 and hydrogen sulphide H2S, as well as acetone, ethanol, and other chemicals. The existence of various illnesses in the patient is indi-

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cated by a significant increase in the concentration of last gases. Increased acetone content in breath, for example, has been linked to diabetes [5], whereas ammonia concentration is used as a biomarker for liver and kidney illness [6].

An otherwise healthy person's typical exhaled breath ammonia content is about 250 ppb. However, as kidney-related diseases progress, its concentration rises, reaching up to 4.88 ppm in Last-stage renal disease (LSRD). Portable and user-friendly exhaled breath sensors are required for daily breath analysis in large populations. Chemoresistive sensors are particularly appealing for this purpose because of their small size [7], low power consumption and cheap cost [8], making them suitable for incorporation into hand-held devices [9]. LSRD necessitates time-consuming, costly, and uncomfortable hemodialysis, lowering patients' quality of life substantially. Kidney transplantation should be considered if the nephron function is entirely gone. However, selective, sensitive, and precise sensing methods for ammonia gas detection have become increasingly prevalent in recent years. Renal disease has become one of the world's most serious health issues, with a significant death rate among patients with kidney illness. As a result, ammonia sensors with excellent selectivity and sensitivity are critical for detecting renal illness. The fabrication processes for NH3







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Chemical etching of glasses in hydrofluoric Acid: A brief review

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ABSTRACT

The removal of material, selectively or non-selectively, from the surface of glasses by using acidic, caustic, or abrasive chemicals is referred to as glass etching. Wet and dry etchings are extensively used for variety of applications, including flow channel designs in fuel cell electrodes. Since precise micro-level etching is challenging, optimization of the etching parameters is important. This paper reviews wet etching of glasses including fused quartz for formation of microchannels and microstructures for a variety of applications. The review also discusses different etch mechanisms including etch parameters and surface microstructure of the etched glass. It is found that HF concentration and etching time play a major role on the resulting surface microstructure of glass materials. The paper also describes the use of HF buffered with NH₄F solutions to improve the quality of the etched surface.

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1. Introduction

Glasses are frequently utilised in everyday life due to their distinctive characteristics. The most remarkable of their qualities are optical transparency and the capacity to endure a wide range of environmental effects. Due to their unusual viscositytemperature relationship, glasses can be moulded into any required form with relative simplicity. Further, glasses are resistant to most gases and liquids. At room temperature, they can only be dissolved in hydrofluoric acid and other HF-containing aqueous solutions [1]. Hence, for a number of applications, controlled dissolution in HF-based etchants is used to etch away material from glass. In glass etching, three types of methods are used: mechanical, wet, and dry. Ultrasonic drilling, traditional drilling, and powder blasting, electrochemical discharge are all mechanical techniques. Smooth surfaces, on the other hand cannot be created using such techniques. Li et al discussed dry etching of glass in ICP reactors by using SF₆ plasma and Ni mask or bulk silicon as a masking layer and C₄F₈/He plasma [2] or C₄F₈/CHF₃plasma [3]. Because the process is slow (etch rate 0.5 nm/min [4]), it will only be

utilised for profiles with vertical walls. Aside from that, wet etching is acost-effective option.

Etching solutions like concentrated HF (49%) [5,6], HF/HCl [7], or traditional HNA (HF/HNO₃/H₂O) [8] have widely been employed for etching glass. Despite its non-vertical profiles, wet etching of glass continues to interest micro fluidic researchers because of its benefits such as simplicity, cost effectiveness, outstanding etch selectivity and low surface roughness. Glass is primarily composed of SiO₂, with small amounts of metals such as Ca, Mg, K, Na and related oxides, as well as modest additions of Al₂O₃ and B₂O₃. Because different additives have different etch rates, the etched profile and etch rate for the glass substrate vary with different compositions [9].

Wet chemical etching of glasses in aqueous HF solutions is a subject that has studied for many years. Scheele et al. reported about the discovery of HF in 1771 [10] and then is being studied more extensively, Microfluidic components for a micro-peristaltic pump to be integrated in a tiny polymerase chain reaction (PCR) device are made via deep etching. Through holes for liquid access and electrical contacts, as well as a 200 m thick pump diaphragm, are among the components. This novel masking approach expands the options for fabricating microfluidic devices on glass surfaces. In various fuel cells, wet/dry etched glass surfaces with various patterns may be utilised as cathode and anode of fuel flow channels.

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