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RESEARCH CENTRE IN PHYSICS

Ph.D PUBLIC VIVA VOCE

As per the regulations of Madurai Kamaraj University, Madurai, **Mrs.A.Mathi Vathani, (Reg. No. F9630),** Full Time Research Scholar, Department of Physics, V.H.N. Senthikumara Nadar College (Autonomous), Virudhunagar, will defend her thesis at a Public Viva-Voce examination through Video Conference mode using Google Meet Platform.

Title of the Thesis

STUDIES ON METAL DOPED TiO_2 THIN FILM ELECTRODES FOR SENSOR APPLICATION

Date & Time

29.06.2020 (Monday) at 11.00 A.M

Venue

Research Centre in Physics, V.H.N. Senthikumara Nadar College (Autonomous), Virudhunagar

Video Conference Platform

Google Meet

Meeting ID

https://meet.google.com/gih-fxav-gmy

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The Synopsis of the thesis is avilable in the College Website and a copy of the thesis is available in the Department Library, for reference. Faculty members, Scholars and Students are most welcome to attend the Viva-Voce.

ALL ARE CORDIALLY INVITED

Place : Virudhunagar
Date : 16.06.2020

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Studies on metal doped TiO_2 thin film electrodes for sensor application

Synopsis submitted to Madurai Kamaraj University in partial fulfillment of the requirement for the Degree of

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SYNOPSIS

We are living in the world of sensors. In our daily life we generally utilize a variety of sensing devices and machines. Early and accurate diagnosis of the diseases plays a very significant role in recent medicine. Now a days biosensors become necessary due to an increase in demand for diagnostics and monitoring the various diseases, increasing healthcare needs. New generation biosensors are made up of thin film electrodes to make compact devices. Sensitivity, selectivity, fast response time, easy handling and low cost are the chief advantages of thin film electrode biosensors.

Thin films play a principal role in recent device technology. Thin film is a material layer having thickness from fractions of a nanometer to several micrometers. Thin films contain very large surface-to-volume ratio and therefore the surface generally influences the properties of the film significantly. Due to the compactness, better performance and reliability together with the low cost of production and low weight, thin film devices are favored more than its bulk counter parts.

Transparent conducting oxides (TCOs) are a unique kind of materials that attain high value of electrical conductivity, concurrently maintaining a high transmittance of visible range of the electromagnetic spectrum. Metal oxides are considered as the best candidates for transparent conductors due to their excellent stability at all temperatures, cost effectiveness and enhanced opto-electronic uniqueness. Oxides of zinc, tin, cadmium, indium, gallium and titanium are commonly recognized as efficient component of transparent conducting electrodes when doped with other metal oxides.

Transparent metal oxide thin films are broadly used materials in various applications now a days. The metal oxide semiconductor thin films such as TiO_2, ZnO, and SnO_2 are widely researched and extensively considered for various applications with high performance. Among these TiO_2 has been investigated widely and used in many applications for its good crystalline structure, larger surface area, chemical stability, non-toxicity and low cost. Anatase TiO_2 is a suitable compound for TCOs because of its wide band gap (3.2 eV) and comparatively low effective mass of ~1 m_o (m_o - free electron mass). With its good biocompatibility and immobilizing ability TiO_2 got interest in the field of biosensor.

For fabrication of TiO_2 thin films with good surface, optical and structural properties it is important to choose the deposition technique. Spray pyrolysis is a simple and low-cost technique for the preparation of semiconductor thin films. The basic principle involved in spray pyrolysis technique is pyrolytic (endothermic) decomposition of salts of a desired compound to be deposited onto a substrate maintained at higher temperatures and forming a single crystalline or cluster of crystallites as a product. It has ability to generate large area and high quality adherent films with uniform thickness. The deposition rate and the thickness of the films can be easily controlled by varying the spray parameters and operating at moderate temperature (100 ºC – 500 ºC). Doping is easy in this method with any element in any quantity and can be done simply by adding it in some form to the spray solution. Due to the simplicity, cost effectiveness and the high-quality productivity on a large scale of this technique, it attracts the researchers for the fabrication of thin films of metal oxides.

Many researchers have made the synthesis and modification of TiO_2 thin film electrode for enhancing the electrochemical performance. The major difficulty happened when using metal oxide semiconductors as electrodes is poor charge transport. An efficient method to increase charge transfer rate in semiconductors is to add very small amounts of preferred additives to them, usually not more than a few parts per million. These additives are referred to as impurities (dopant) and the process of adding them into the crystal lattice is called doping. Doping of impurities in semiconductors induces modification in structural, surface morphological and optical properties. The intention of doping in semiconductor is to increase charge transfer rate between the electrolyte and the electrode which also enhances the detection performances of the biosensors.

Selection of doping material plays vital role for the improvement of the TiO_2 lattice. The dopant material should have same ionic radii as the TiO_2 lattice. Copper (Cu), zinc (Zn) and aluminium (Al) causes more effective doping with TiO_2 thin films electrode since ionic radius of these are similar to that of TiO_2. The ionic radius of Cu^{2+}, Zn^{2+} and Al^{3+} is 0.87 Å, 0.88 Å and 0.68 Å respectively while Ti^{4+} is 0.75 Å. Hence Cu^{2+}, Zn^{2+} and Al^{3+} ion can easily replace Ti^{4+} ion in TiO_2 lattice without destroying the crystal structure, thereby stabilizing the anatase phase of TiO_2.

In the present research work an attempt has been made to deposit TiO_2 and metal doped TiO_2 thin films over glass substrates by spray pyrolysis technique and a detailed study on the structural, surface morphological, optical and electrochemical properties has been done. The study on sensing property of TiO_2 and metal doped TiO_2 thin films electrode on Ascorbic acid, Urea and Uric acid was also done in view of its application as a biosensor.

Objectives of the present work

The major objectives of the present research work carried out are,

- ❖ To synthesis TiO_2 and Al, Cu and Zn metal doped TiO_2 thin film electrodes by the Spray pyrolysis technique.

- To optimize the Spray pyrolysis parameters such as nozzle to substrate distance, substrate temperature and number of coatings to get good quality films.
- To dope Al, Cu and Zn metal in various concentrations with TiO_2 and to study their effect on the structural, surface morphological, optical and electrochemical properties of TiO_2 thin films.
- To study the sensing performance of TiO_2 and Al, Cu and Zn metal doped TiO_2 thin film electrodes on Ascorbic acid, Urea and Uric acid.

TiO_2 thin films were deposited via spray pyrolysis technique, which is unique thin film preparation for large area with uniformity. The different spray pyrolysis parameters such as nozzle to substrate distance, substrate temperature and number of coatings were optimized for fabrication of high-quality thin films. The prepared TiO_2 thin films were subjected to a variety of characterization studies such as X-ray diffraction study, Scanning electron microscopic study, Contact angle measurement study, UV-Visible spectroscopic study, Photoluminescence study and Reflectance study.

To prepare TiO_2 precursor solution, titanium tetra isopropoxide (TTIP, $Ti\{OCH(CH_3)_2\}_4$) was used as a precursor material and ethonal (C_2H_5OH) was used as the solvent. For stabilizing the precursor solution acetylacetone (AcAc, $C_5H_8O_2$) was used. For preparing TiO_2 precursor solution the molar ratio of TTIP, ethanol and AcAc was maintained as 1:10:1. 4 ml of TTIP was dissolved in 20 ml of ethanol in a beaker and stirred for 10 minute using magnetic stirrer. Transparent solution was obtained. To this mixture 4 ml of acetylacetone was added and stirred for 10 minutes. Now an orangish yellow solution was obtained. Again 20 ml of ethanol was added to the solution and stirred vigorously for 1 hour in a closed manner. The obtained TiO_2 precursor solution was atomized into spray pyrolysis for film growth.

TiO_2 thin films were deposited by varying the nozzle to substrate distance as 10, 15 & 20 cm. The XRD study reveals that the TiO_2 films were in anatase phase of preferred orientation (1 0 1) with tetragonal structure. It is concluded from the XRD study that the crystalline size is highest and the dislocation density and strain are lowest for the sample deposited with 15 cm nozzle to substrate distance. The UV-Visible absorbance of the sample with 15 cm nozzle to substrate distance was high. The optical band gap value, reflectance, contact angle value and PL emission peak intensity are lowest for 15 cm nozzle to substrate distance sample. SEM micrographs show that the TiO_2 thin films contain mostly spherical grains. EDX confirms the presence of titanium and oxygen. Hence TiO_2 nanocrystalline thin film prepared with 15 cm nozzle to substrate distance at 350 ºC is found to have better structural and optical properties.

TiO_2 thin films were deposited also by varying the substrate temperature as 300 ºC, 350 ºC, 400 ºC and 450 ºC. XRD study reveals that the crystalline size is highest and the dislocation density and strain are lowest for the sample deposited with 350 ºC substrate temperature. The absorbance was high for 350 ºC substrate temperature sample. The optical band gap value, reflectance, contact angle value and PL emission peak intensity are lowest for 350 ºC substrate temperature. Hence TiO_2 thin film was obtained with better structural, surface and optical properties for 350 ºC substrate temperature.

Six different TiO_2 films were deposited by spray pyrolysis technique by varying the number of coatings as 2, 4, 6, 8, 10 and 12. The thickness of the thin films found to increase with increase in number of coatings. From XRD analysis it is clear that the crystalline size is highest and dislocation density and strain are lowest for the TiO_2 films with 10 number of coatings. SEM analysis revealed that the particle size increases visibly as the number of coatings increases. EDX study indicates the purity of the film. The contact angle value shows that the TiO_2 films are hydrophilic in nature and its value decreases with increase in number of coatings. The UV-Visible absorbance increases with increase in number of coatings and it was high for TiO_2 films with 10 number of coatings. The optical band gap value, reflectance and PL emission peak intensity decreases with increase in number of coatings and lowest for TiO_2 film with 10 number of coatings. The structural, surface morphological and optical studies reveal that as the number of coating increases the quality of the film also increases.

The present study clearly showed that the nozzle to substrate distance, substrate temperature and varying number of coatings has influence on the film properties. The better quality and uniform TiO_2 thin film was yielded by coating with 15 cm nozzle to substrate distance at 350 ºC substrate temperature with 10 number of coatings. The good quality TiO_2 thin film prepared with these optimum conditions was used for further studies.

To prepare Al doped TiO_2 (Al-TiO_2) precursor solution aluminium nitrate was added at various concentrations such as 0.1 wt%, 0.3 wt%, 0.5 wt% and 1 wt%. Al-TiO_2 thin films were successfully fabricated using spray pyrolysis technique. The XRD study shows that the Al-TiO_2 films are in anatase phase with tetragonal structure. The crystalline size and UV-Vis absorption were highest for the 0.5 wt% Al-TiO_2 thin film. The dislocation density, strain, optical band gap and PL intensity were lowest for the 0.5 wt% Al-TiO_2 thin film. SEM micrograph reveals the aggregation of the particles and EDAX image confirms the presence of Al. Contact angle measurement shows the hydrophilicity of the Al-TiO_2 thin films.

In the present study, Cu doped TiO_2 (Cu-TiO_2) thin films were deposited on glass substrate by spray pyrolysis technique with various concentration of Cu such as 0.025 wt%, 0.05 wt%, 0.1 wt% and 0.5 wt%. The XRD analysis reveals that all the films are polycrystalline in nature with anatase and also less intense rutile phases with tetragonal structure. The crystalline size and UV-Vis absorption was higher for the 0.05 wt% Cu-TiO_2 sample. The dislocation density, strain, optical band gap and PL intensity were lower for the 0.05 wt% Cu-TiO_2 sample. SEM micrograph shows the agglomeration of the particles and EDAX image confirms the presence of Cu. Contact angle measurement reveals the hydrophilic nature of the Cu-TiO_2 thin films.

In the current work, Zn doped TiO_2 (Zn-TiO_2) thin films with various concentration of Zn such as 0.05 wt%, 0.1 wt%, 0.3 wt% and 0.5 wt% were deposited on glass substrate by spray pyrolysis technique. Zn-TiO_2 thin films were successfully deposited by Spray pyrolysis technique by varying the Zn concentration. The XRD study shows that all the thin films were of dominantly anatase phase and nanocrystalline in nature with tetragonal structure. The crystalline size is highest and the dislocation density and strain is lowest for the 0.1 wt% Zn-TiO_2 sample. The UV-Vis absorption is high and optical energy gap value and PL emission peak intensity is low for 0.1 wt% Zn-TiO_2 sample. This is in correlation with the XRD results. SEM image shows the aggregation of particles and EDAX image confirms the presence of Zn. Contact angle measurement shows the hydrophilic nature of the Zn-TiO_2 films.

The structural, surface morphological and optical properties of the TiO_2 thin films were modified by Cu, Zn and Al doping. The good crystallinity, surface morphological and optical properties of 0.5 wt% Al-TiO_2, 0.05 wt% Cu TiO_2 and 0.1 wt% Zn-TiO_2 thin films show that these films are optimum for fabrication of electrode material.

Electrochemistry is a powerful tool to investigate reactions involving electron transfers. Electrochemistry explains the mechanism of electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. The cyclic voltammetry (CV) is a simple and easy technique used to examine all types of electrochemical reactions.

In the present work the electrochemical analysis was carried out using CHI604E electrochemical work station. The electrochemical studies were performed using three electrode cell systems with TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 thin films as working electrode separately. Ag/AgCl (KCl) electrode served as reference electrode and polished glassy carbon electrode (GCE) served as counter electrode. The electrolyte solution used to perform the study was 0.1M Phosphate buffer solution (PBS) with pH 7.

Electrochemical analysis was successfully carried out by cyclic voltammetric method in basic media for TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 electrodes by varying the number of cycles and also scan rates as 50 mV/s, 75 mV/s, 100 mV/s and 150 mV/s. TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 electrodes with a scan rate of 150 mV/s is observed to have high current response and also good shift in anodic and cathodic peaks. So the scan rate of 150 mV/s was considered as the optimized scan rate. The CV study of TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 electrodes illustrates that there is a good linear relationship between the peak currents and the scan rates and it signifies that the redox process is surface-confined.

The electron transfer rate between surface of the electrode and electrolyte becomes high for Cu-TiO_2 and Zn-TiO_2 electrodes compared to TiO_2 electrode it indicates that the Cu-TiO_2 and Zn-TiO_2 electrodes have more oxygen vacancy. The electron transfer rate is lesser for Al-TiO_2 electrode. The higher direct electron transfer between the electrolyte and transition metal doped electrode surface gives rise to enhanced voltammetric response than that of TiO_2 electrode. Thus the electrochemical analysis reveals that the electrode performance was improved by addition of the transition metal dopant in TiO_2 lattice. The electrochemical response of these electrodes reveals high stability and good linearity which is necessary for sensor devices.

In recent years the electrochemical analysis have gained attention in the investigation of important biological molecules and drugs because of their simplicity, cost effectiveness, easy handling and highly sensitive compared to other methods. The objective of the work is to fabricate a metal doped semiconductor electrode material for electrochemical biosensor to sense biomolecules.

Ascorbic acid is an essential antioxidant in humans, capable of search oxygen-derived free radicals. Excess intake of ascorbic acid enhances the risk of kidney stones. Urea is the key end product of nitrogen metabolism in humans. Increased level of urea leads to loss of kidney function. Thus determination of urea is important in analysis of kidney diseases. Uric acid is biomedically important compound that plays a vital role in human metabolism. Abnormal level of uric acid in human body causes several diseases including gout, hyperuricemia, lesch-nyan disease, cardiovascular and chronic renal sickness

Electrochemical biosensing activity for Ascorbic acid, Urea and Uric acid was carried out using CHI604E electrochemical work station. The electrochemical biosensing activity was done by cyclic voltammetry (CV) method with three electrode cells by using Ag/AgCl (KCl) as reference electrode, glassy carbon electrode (GCE) as counter electrode and TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 thin films as working electrodes, separately. 0.1M Phosphate buffer solution (PBS) with pH 7 was the electrolyte.

To the best of our knowledge, there are no reports on use of Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 thin films as electrode material for the electrochemical sensing of Ascorbic acid, Urea and Uric acid biomolecules.

TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 based electrochemical biosensor were successfully designed. Using TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 as working electrodes, their electrochemical responses for ascorbic acid, urea and uric acid in different concentrations were studied in detail. Zn-TiO_2 exhibited excellent electrocatalytic activity towards the ascorbic acid, urea and uric acid than TiO_2, Al-TiO_2 and Cu-TiO_2 electrodes which may be due to the introduction of more oxygen vacancy by Zn doping, which could effectively enhance the electron transfer. Uric acid biomolecule response is high in all electrodes due to the immobilization of uric acid on the electrodes and so that the effective binding of the uric acid enzyme on the surface of the electrodes improving the response. The tendency of sensing ascorbic acid, urea and uric acid by TiO_2, Al-TiO_2, Cu-TiO_2 and Zn-TiO_2 electrodes is good with better sensitivity and linearity.

The future prospects of the present work are doping TiO_2 with other noble or rare earth metals and the characterization studies may be performed. TiO_2 and Al, Cu and Zn-TiO_2 thin films may be employed to various applications such as solar cells, super capacitors, diodes, photocatalytic and antimicrobial activity studies.