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TiO_2–CU Thin Film Material for Optical Hydrogen Gas Sensor Applications

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Abstract

Purpose: Several scientific researches are underway to investigate the possibility of using various green energies. Hydrogen gas is a candidate of such research, since its use as a fuel in automobiles releases pure water, a recyclable biproduct. But, the leakages of the gas are detrimental to its application due to its low auto ignition energy of 20 μj, wider air flame limit of 4-75 % and high flame velocity of 3.46 ms^{-1}. This study involved fabrication of an optical gas sensor for sensing the leakage levels of hydrogen gas to a surrounding.

Methodology: Titanium dioxide thin films of thicknesses 47.7, 56.2, 82.3, 100.4 and 120.5 nm were deposited on both microscope and FTO glass slides using DC magnetron sputtering technique and characterized as primate and annealed at 400 and 500^{o}C. Copper (Cu) catalytic layers of 5.6, 10.2, 17.3 and 21.0 nm were deposited using EDWARDS AUTO 306 Magnetron sputtering system on an optimized 100.4 nm TiO2 sample, annealed at 400^{o}C. Optical properties were deduced from transmittance and absorbance spectra measured using 1800 Shimadzu spectrophotometer in the optimum range of 280-800 nm through simulation. The optical behavior of the films was generated using SCOUT software and analyzed using ORIGIN 9.1 64-bit software.

Results: The energy band gap decreased with material thickness from 4.2±0.05 eV for 47.7 nm film to 3.9±0.05 eV for 100.4 nm films. 120.5 nm films showed higher energy gap of 4.0±0.05 eV. Transmittance decreased with increase in thickness probably due to agglomeration of film particles. The energy gap of the 100.4 nm, TiO2 thin films annealed at 400^{o}C was 3.9±0.05 eV. This is a material quality of the anatase phase. The copper surface layer increased absorption in the higher wavelength region. The energy band gaps were reduced from 3.9 to 3.8±0.05 eV with increased coverage. Self-limiting at 17.3 nm copper overlayer realized increased energy gap to 4.1±0.05 eV. A lower energy band gap range of 3.9-3.8±0.05 eV was realized when FTO substrates were used. The transmittance decreased with increased H2 gas concentration. The optical energy gap reduced from 4.1±0.05 eV in 0 ccm to 3.9±0.05 eV in 50 ccm of hydrogen gas concentration. The sensitivity increased from 0.3 % in 0ccm to 3.9 % in 50 ccm hydrogen gas concentration. An average sensitivity of 2.0 % was realized for films fabricated on FTO substrate. This is higher than 1.7 % reported earlier. The material gas sensing potential was done at room temperature. The fabricated sensor material showed higher sensitivity and lower temperature operation and is furthermore, expected to be cheaper and safer

Unique Contribution to Theory, Policy and Practices: Though, in order to realize a more portable stand-alone gas sensor, an investigation on an ideal photon type source that incorporates

the material is recommended. Further, extension of this study on structure and morphology of the film is essential to understand its sensing behavior.

Keywords: *TiO_2–CU, Thin Film Material, Optical Hydrogen Gas Sensor, Applications*

1.0 Introduction

1.1 Background of the Study

In the recent past, hydrogen has been extensively studied as a source of fuel due to its potential recyclable biproducts after combustion. Nevertheless, its safety, storage, handling and transport have prevented it from becoming a reliable source of energy. Safety is a primary concern for wide practical use of any source of fuel, hydrogen inclusive. Hence, design and implementation of new optoelectronics technologies for monitoring and detection applications is vital.

The H2 safe keeping, particularly in the automotive industry is seen as inadequate by many scientists as a result of its low diffusion coefficient as well as substandard leakage detection system. From statistics, fourteen million loss of lives and several material corrosions are documented in the world more so due to unavailability of appropriate H2 sensing equipment (Kang et al., 2012). This becomes a main hindrance in implementing H2 powered technologies to minimize air pollution and fossil fuel dependency. If a repeatable H2 sensor with the enlisted qualities cannot be realized, convincing the general public to embrace new technology becomes a daunting task. This can lead to strenuous use of nonrecyclable fuels which pose to be more expensive in future. This will result to rising cost of living and inflation, as the available fuel will be overstrained.

Detection techniques for H2 sensors have been explored and many conventional sensing techniques are mostly used in the industry, (Gaspera et al., 2011) notably sensing bead, chromatography and conductivity. Although these platforms enable accurate sensing of H2, they are costly, complex and not suitable for in-situ usage (Yaacob et al., 2009). Moreover, semiconductor sensors from oxides of metal have been made and have become popular as actual and highly sensitive devices to low percentage concentration of chemicals. These oxides are accurate in high or low temperature applications, based on method of preparation and deposition parameters used. The semiconductor sensors are made using different types of transducing platforms (Yaacob et al., 2009), namely, conductance, surface platforms acoustic, piezoelectric and pyroelectric. Electrical sensing methods are widely used in designing hydrogen sensors, unlike optical transducing platforms.

1.2 Statement of the problem

The design and fabrication of opto-film gas detectors is less studied. However, it offers a low overall cost technology which operates at lower temperatures. The sensors realized are less affected by external environment, effectively operating in ragged environments. It is less corrosive, reactive and flammable environments (Sekimoto, 2000) make it ideal for H2 sensing applications.

1.3 Objectives of the Study

The general objective of the study was to investigate TiO2-Cu thin films for optical gas sensing applications.

1.4 Significance of the Study

Use of conventional energy sources like fossil fuels has led to emission of toxic gases which are harmful to both animals and human beings. Green energy sources such as hydrogen gas, in automobiles have been widely hindered by storage issues. Sensing the leakage of hydrogen gas is essential. However, the sensors currently used employ electrical methods in their operation. Few studies on optical hydrogen sensors have used palladium and platinum as TiO2 surface modification. These materials are scarce, expensive and toxic. There is need for a more sensitive, repeatable, durable, affordable and low temperature and electromagnetic resistant sensor that analyses the levels of exposure to this gas. This research aims at investigating TiO2 –Cu system as an optical sensor transducer for sensing hydrogen gas.

2.0 LITERATURE REVIEW

2.1 The nano-scale materials for optical gas sensing applications

The deployment of semiconductors as hydrogen detector materials was done by Zakrzewska et al. (1997). The findings illustrated that diffusion of the gas on the surface of germanium changed its conducting ability. A report by Lundstrom et al. (1975) on the sensing ability of a semiconductor material towards hydrogen formed the foundation of the semiconductor sensing material. Upto 1990's, majority of studies on metal oxide semiconductors concentrated on Pd/SiO2/Si material, with little study on other materials. The hydrocarbon sensed was hydrogen sulfide and methanol (Tobias et al., 2003). The sensor developed lacked repeatability which is a vital property of a perfect sensor.

CeO2, TiO2, Ga2O3-ZnO, Ga2O3, WO3, CoOx, MoO3, In2O3, TiWO and Pt catalyzed TiO2 were studied, including their behavior towards various gases (Kandasamy et al., 2007). Generally (Korotcenkov, 2007), these materials were found to be n and p-type of conductivity. The later accept and give out electrons when subjected to higher valent and lower valent gases, respectively. However, the former act opposite (Li et al., 2002) to their counterparts when exposed to similar gas. The gas detection ability of the oxide-based gas sensors relates to three independent parameters, namely, the film characteristic, transducer function and complexity of sensor construction (Gopel et al., 1990).

Wide range of nanomaterials is compatible with opto-transducers for gas detection and monitoring applications. Three main categories i.e. Inorganic, Organic and composite materials are used to realize a gas sensor. Despite their use, there is no record of the comparative efficiency of all the materials when used for gas sensing (Korotcenkov, 2007). Hence, with a number of categories of nanoscale materials, the major setback in the field of inventions is the best material identification. Through this work, sensing potential of TiO2-Cu thin films towards hydrogen gas was comprehensively studied. Capone et al. (2003) noted the cheaper version of sensing technology when metal oxide was employed in fabricating sensors. This resulted due to a low temperature

operation device which could easily be employed together with different types of transducing platforms.

2.2 Titanium dioxide (TiO2)

Titania is a relatively large energy band gap (2.5–3.2 eV) metal-oxide commonly known for the photocatalysis applications, sunscreen, electrochromic and photochromic device fabrication (Sadek et al., 2009). The photosensitivity of Titania material was invented by Fujishima and Honda in 1972 (Chen and Mao, 2007). The material has been widely studied for numerous applications including gas sensors. TiO2 proved to be sensitive towards oxygen gas and has been since used as lambda sensor in combustion engines to control air to fuel ratio (Gopel et al., 1990).

Fergusona et al. (2009) studied PL spectra of TiO2 thin films synthesized by PLD. Thin films were annealed at varied temperatures. A large PL signal between 380 and 420 nm was due to the band to band PL transitions with the light of energy relatively equal to the band gap energy of the anatase and rutile. The energy band of anatase and rutile were 3.2 and 3.0 eV, respectively. Hotov´ et al. (2009) deposited TiO2 films using DC reactive sputtering method. A mixture of oxygen and argon was used to realize the films on silicon and oxidized silicon substrates. The films were hence annealed and characterized. The result of post-deposition annealing (300, 500 and 700ºC for 8 h in air) on the properties of TiO2 thin films were studied. Crystallization occurred within 300 to 500ºC.

Fasaki et al. (2009) prepared TiO2 thin films by DC reactive magnetron sputtering in a mixture of oxygen and argon on glass and oxidized silicon substrates. The result of platinum layer addition (0, 1, 3 and 5 nm) on sensing potential of hydrogen was studied. Heat treatment between 300 °C to 500 °C initiated crystallization and the nano-film structure changes from amorphous to crystalline (anatase phase), for samples on glass. Films with 0,1, 3 and 5 nm Pt surface partial coverage were tested as hydrogen sensors after thermal activation by heating in dry air for 10 h. TiO2 as a gas sensitive layer operated at temperatures between 180–200 °C. As for the material with 5 nm Pt coverage, no gas response was recorded. The materials with 1 and 3 nm Pt surface coverage, the Pt overlayer caused a greater response at relatively low temperatures. The samples with surface coverage of 3 nm of Pt responded to hydrogen with highest sensitivity.

Nasution et al. (2009) used modified-impregnation method to synthesize cu-TiO2. TiO2 absorption shifted towards visible region upon adding copper. Optical band gap changed from 3.3 eV to 2.7 eV, with optimum cu-loading of 3 wt %.

Haidry et al. (2012) studied hydrogen gas detection potential of titanium dioxide thin films deposited by means of unbalanced dc magnetron sputtering and the change caused by the post deposition annealing. Films with a hundred nanoscale of thickness were prepared by this method. The thin films were deposited on sapphire substrate from the metal target in oxygen atmosphere. The samples were then post-annealed in air in the temperature range 600 °C – 1000 °C. Absorption of the resulting material was studied by UV-Vis spectroscopy. It was found that the phase gradually

changed from anatase to rutile, the grain size and roughness tended to increase with increasing post-annealing temperature. The optical band gap of anatase and rutile was 3.3 and 2.9 eV, while activation energy was 0.318 and 0.934 eV, respectively. This decreased from 0.934 to 0.76 eV with increase in substrate temperature during deposition from 350 °C – 450 °C, resulting from increased crystallinity with substrate temperature. Sensitivity ranged from 101 to 104 at operating temperature below 200 °C and 10000 ppm of H2 concentration. They found direct correlation between the sensitivity of TiO2-pt and activation energy EA obtained from Arrhenius plots corresponding to temperature range 250 - 350 °C, it was observed that the anatase samples with lowest value of EA= 0.318 eV has the highest sensitivity.

Bedikyan et al. (2013) presented some work on the properties of TiO2 thin films. Ti films were deposited by common thermal evaporation and cathodic arc plasma deposition and after that were annealed to TiO2. Transmittance spectra were obtained and refractive 27 indices and band gaps of TiO2 films were evaluated. The TiO2 film showed a higher visible transmittance, up to 80 %. The forbidden energy gap, ΔEg for thermally (TE) evaporated samples was 3.42 eV at Tann= 450 ºC and 3.47 eV with the increase of annealing temperature up to Tann = 600 ºC. The band gap energy, ΔEg for cathodic-arc (CAD) deposited samples was 3.55 eV at Tann = 600 ºC. The refractive indices of 2.3-2.25 for thickness of 150-300 nm respectively, were recorded.

Carlos et al. (2013) prepared TiO2 using sol gel method. Cu surface layer was deposited on the film using spin coating. The depletion gap reduced from 3.25 to 2.9 eV on copper loading as the absorption shifted to higher light wavelengths. This was attributed to perfect crystallinity and low defect density near the band edge. Low energy gaps enhanced charge recombination. The deposition method used also lacked reproducibility.

Nguu et al. (2018) deposited TiO2 .by electrophoretic deposition on microscope glass substrate. Highest transmittance of 55 % was reported with the forbidden band gap of 3.932 eV. This was within 3.25-4.14 eV reported in his literature.

Despite several attempts by researchers to fabricate an ideal hydrogen gas sensor that conform with DOE in USA specifications, the sensors realized, the catalytic bead, piezoelectric and electrical conductivity sensors realized explored use of electricity through the fabricated material. This caused the material decomposition resulting from heating effect of electric current. The repeatability of the sensor realized has been compromised as well as increasing the overall running cost of the sensor. Few studies on optical conductivity sensors used gold, palladium or platinum as catalytic layers (Kandasamy et al., 2007). These materials are scarce, expensive and poisonous to handle. The films realized optimally operate at temperatures between 150 to 200 oC (Haidry et al., 2012) The chemical deposition methods used yielded films that lacked reproducibility of the fabricated films.

In this research work, synthesis of the TiO2 material was carried out by vacuum reactive dc magnetron sputtering technique. The catalytic Cu layer was realized by deposition of copper on the TiO2 film surface through sputtering coater technique.

3.0 METHODOLOGY

3.1 Substrate cleaning process

The microscope glass and fluorine-doped tin oxide (FTO) substrates (Pyrex East Africa supplies, Kenya) were used. Prior to deposition, the following procedure was used to clean the slides. The slides were initially cleaned using soapy water then subjected for sonication in de-ionized water within half an hour at 25^{o}C. Distilled water was hence used to rinse the substrates before drying in the open. Thereafter they were stored in a desiccator ready for use.

3.2 Preparation of TiO2 nanostructured thin films

DC reactive sputtering system was used with pure titanium target (99.99 % pure, Kurt J Leasker Company, USA). Ti target was fixed 12.0 cm from the substrates (microscope glass or fluorine doped tin oxide), which were pre-cleaned.

The machine was initially run for 15 minutes in argon atmosphere to eliminate contaminated surface layer of titanium target, as the substrate was covered to prevent predisposition of the film. Oxygen and argon were separately let into the system, both at the rate of 100 sccm. The shutter was then removed to allow the deposition of TiO2 film on the substrates. Films of ranging thicknesses were realized by changing the deposition time.

During the deposition process, the chamber was maintained at a base pressure of 4.5×10^{-5} mbar, oxygen partial pressure of 1.9×10^{-2} mbar. Total chamber pressure of 6.0×10^{-3} mbar, which was the optimum sputtering pressure for TiO2 thin films (Karunagaran et al., 2002). Sputtering power of 250 W was maintained. The films realized were annealed at temperatures between 400^{o}C to 500^{o}C.

3.3 Deposition of Cu catalytic surface layer on TiO2 nanostructured thin films

The surfaces of 100.4 nm TiO2 thin film on microscope glass and FTO substrates and annealed at 400^{o}C (optimized) were sparsely copper (Cu) coated to form TiO2-Cu thin film, using DC magnetron sputtering. Copper target of purity level 99.99 % and diameter 5cm was used (Kurt J Leasker Company, USA). The substrate was maintained at 12.0 cm from the target during the experiment. The machine was run for 15 minutes to eliminate contaminated surface, as the substrate covered to prevent pre-deposition. Pure Argon was then pumped into the chamber until preferred sputtering pressure of $1.9\text{x}10^{-2}$ mbar (Yaacob, 2012), was maintained at room temperature. Sputtering power of 250 W was maintained. 5.6 nm thickness of copper overlayer was attained on TiO2 surface of optimized thickness. The sample was left for one hour in the chamber to minimize chances of oxidation of copper catalytic surface layer when out of the chamber. Other samples of varied copper catalytic surface layer thicknesses 10.2, 17.3 and 21.0 nm were deposited on 100.4 nm TiO2 film.

3.4 Optical characterization

The optical properties were studied based on transmittance and absorbance measurements using UV-VIS 1800 Shimadzu spectrophotometer, located at the department of chemical sciences,

Technical university of Kenya laboratories. Transmittance and absorbance data were taken within the photon wavelength range of 280-800 nm.

The transmittance data were simulated using SCOUT software and graphs drawn using ORIGIN 9.1 64-bit software. Tauc relation $(\alpha hv)1/n = \beta(hv-Eg)$ was used, since TiO2 was a direct band gap semiconductor (Shinen et al., 2018), extending the linear part of (αhv) 2 against hv gave the band gap energy. Transmittance, refractive indices and optical energy band gaps were studied.

3.4.1 Characterization of fabricated FTO and glass/TiO2-Cu thin film

Pre-prepared optimized FTO and glass/TiO2-Cu samples of different copper aspirates surface layer thicknesses as mentioned in 4.4 were optically characterized, with special interest on effect on multilayer energy band gap with different proportions of copper catalytic aspirates layer. The characterization was done in the range of 280-800 nm. Effects of copper catalytic aspirates on the electronic properties of TiO2 was analyzed from the graphs realized.

3.5 Customized gas chamber fabrication

Fabrication of customized gas chamber was done at the University of Nairobi, College of Biological and Physical Sciences, Chiromo campus science workshop. Perspex glass was used to fabricate the customized gas chamber shown in figure 1.

Figure 1: Pictorial diagram of customized gas chamber

3.5.1 Customized chamber layout design

Corel connect ×6 programme was used to draw a coreldraw ×6 of customized gas chamber slot of dimensions 26.0×76.0×9.0 mm from 42.0×85.0×9.0 mm Perspex glass plate. M3 bolt holes were drawn at each corner. The soft chamber design was saved as AI-Adobe illustrator as curves in the desktop. The design was imported in RD worksv8 programme, as acrylic Perspex parameter power of 95 W and laser head speed of 10 m/s set. The work was then saved to the U-file (flash disk) and copied onto the memory of the laser engraving machine. Another plate of dimensions

42.0×85.0×2.0 mm was designed and saved onto the laser machine memory. This was used to make two identical lids of the customized chamber.

3.5.2 Cutting the designed customized chamber

Laser engraving machine in figure 2 was used. The laser head was set at a desired position on the Perspex plate and tested within the material surface. Both water pump and control 58 switch were switched on. The laser was hence switched on and okay button pressed to continue cutting.

Figure 2: Pictorial diagrams of a laser engraving machine

3.5.3 Engraving of gas hole

The engraving machine applying copy milling principles was used to shape the Perspex plate into a circular rod of diameter 6 mm. Gas hole of diameter 3 mm was drilled in the rod to form a fitting tube on the side of the chamber, this was done using a drill bit of 3 mm. Perspex glasses of thickness 2 mm were fixed as top and bottom lids using M3 bolts, with gas casket in between to bring an airtight condition. A 6mm pipe was fitted to the chamber with the other end to the air flow valve.

3.6 Testing the optical gas sensing potential of glass/TiO2-Cu thin film

The optimized FTO and glass/TiO2-Cu were tested for gas chromic properties. The samples were mounted one after the other in the chamber slot, tightly covered and 10 ccm of the gas pumped into the chamber, positioned along the photon path within the spectrophotometer. Different static gas responses of the sample were realized from the transmittance measurements. The analyte test gas concentration by volume was varied to 20, 30, 40 and 50 ccm and the transmittance measurements taken. The optical behavior of the films was generated using SCOUT software and analyzed using ORIGIN 9.1 64-bit software, more particularly with the presence of copper aspirates layer.

3.7 Analysis of elemental composition of TiO2-Cu material

Energy dispersive X-ray fluorescence spectrometer, located at the University of Nairobi, physics laboratory, consisting of an X-ray source, sample irradiation area, a detector, and a pre-amplifier, amplifier and multi-channel analyzer was used in this study. The experimental measurements were conducted using the Shimadzu Senes EDX-800 Hs type Energy Dispersive X-Ray Spectrometer comprising of Rh X-ray tube source with Pd anode target, 220W highest power and 50 kV highest voltage. Shimadzu Senes EDX-800Hs model comprise of new qualitative and quantitative analytical software that features Profile Fitting (PF) technology. The software allows partial quantitative analysis of elements without standards – and complete quantitative analysis with standards. Machine operational sensitivity, high peak/background ratio spectra was determined using copper as secondary target with polarized optics instead of usual direct excitation optics in a wide energy range (Alvaro et al., 2017). The target radiation produced by the elements was realized by irradiating the sample for 100 s. The fluorescent X-rays were collected by a silicon drift detector (SDD) allowing very high-count rate capability with perfect spectral resolution of 140 eV for $MnK\alpha$ at 5.9 keV and data acquisition dead time of less than 25 %. The film composition was determined by using fundamental parameter method inbuilt software in which matrix effects was counted for.

4.0 RESULTS

4.1 Elemental analysis of TiO2-Cu material

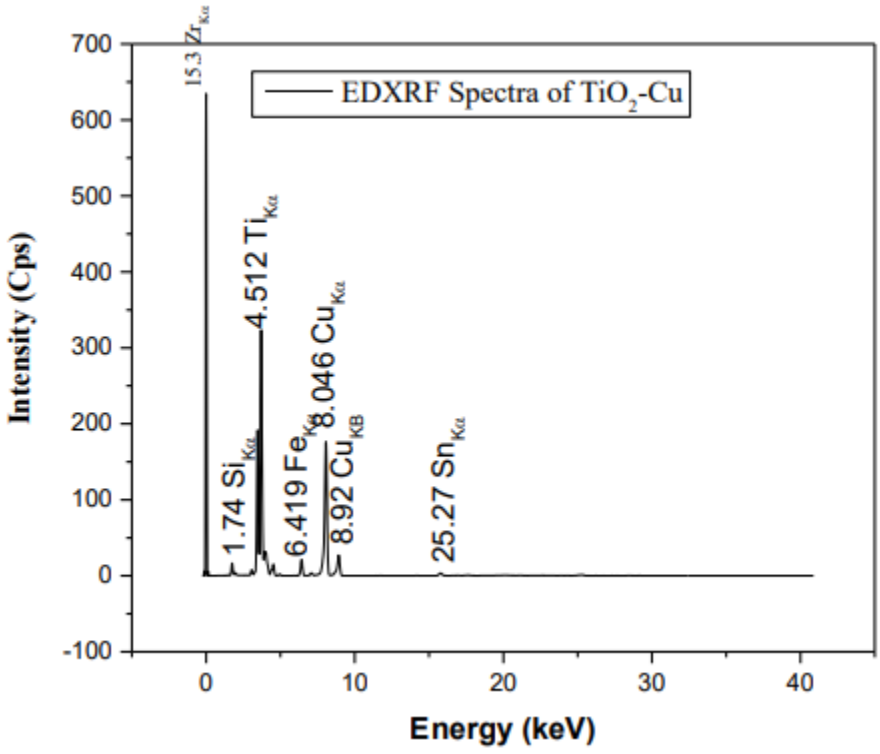

Figure 3: EDXRF Spectrum of the fabricated TiO2-Cu material

Figure 3 shows the elemental composition of the sample determined using energy dispersive X-ray spectroscopy. In these spectra, the characteristic X-ray energy emitted from 33.3 % titanium are observed on 4.512 (Kα) keV, characteristic signals of 2.58 % copper are observed on 8.046 (Kα) and 6.92 (KB) keV. In the sample, the presence of 0.574 % tin and 62.3% silicon was identified on 25.27(Kα) keV and 1.74 (Kα) keV, respectively, which were due to the substrate used. There were peaks associated with 0.924 % iron on 6.419(Kα) keV and 0.24 % zirconium on 15.3(Kα) keV. These lines were attributed to the equipment used for the analysis or impurities (Alvaro et al., 2017).

4.2 Optical characterization

4.2.1 TiO2 characterization

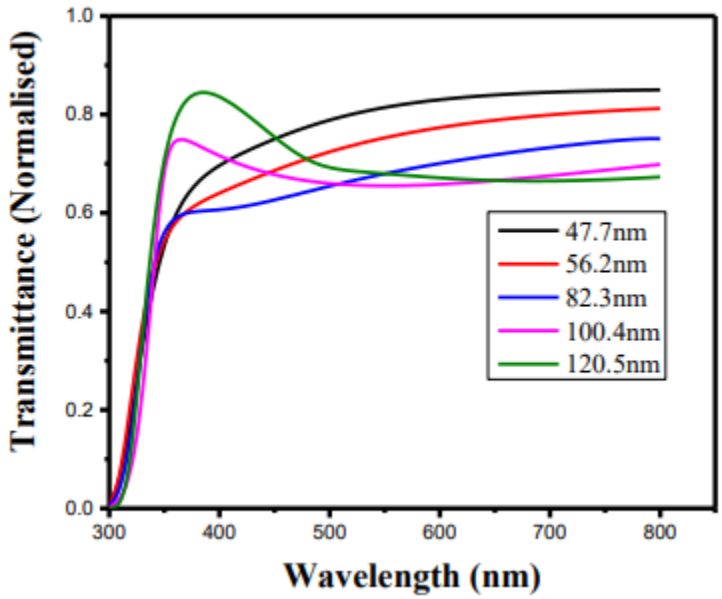

Figure 4: Transmittance spectra of TiO2 films of thickness 47.7-120.5 nm

Transmission of the films reduced with thickness as shown in Figure 4. This may be attributed to agglomeration of film particles, increasing the absorption edge towards higher photon incident wavelength. At 120.5 nm, the material transmittance increased abruptly within the visible region. The film four-fold coordination resulted due to increased crystallinity and reduction of surface defects with thickness could have resulted to the observation.

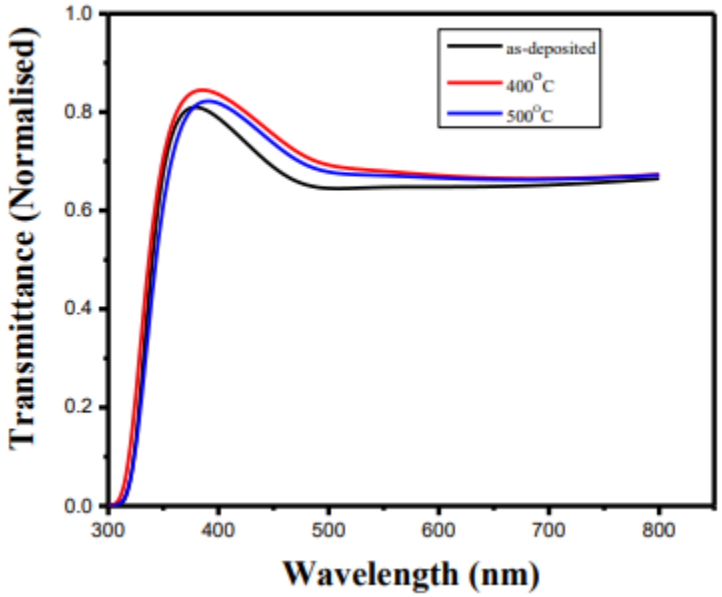

Figure 5: Transmittance spectra of TiO2 120.5 nm film at varied temperatures

Annealing shifted the transmittance of thin films to higher photon wavelength. Higher transmittance within the visible region in annealing was realized, probably due to reduction in dislocation densities (Gayathri et al., 2012). This is depicted in Figure 5. This increases as the film thickness increase probably as a result of increased crystallinity with temperature.

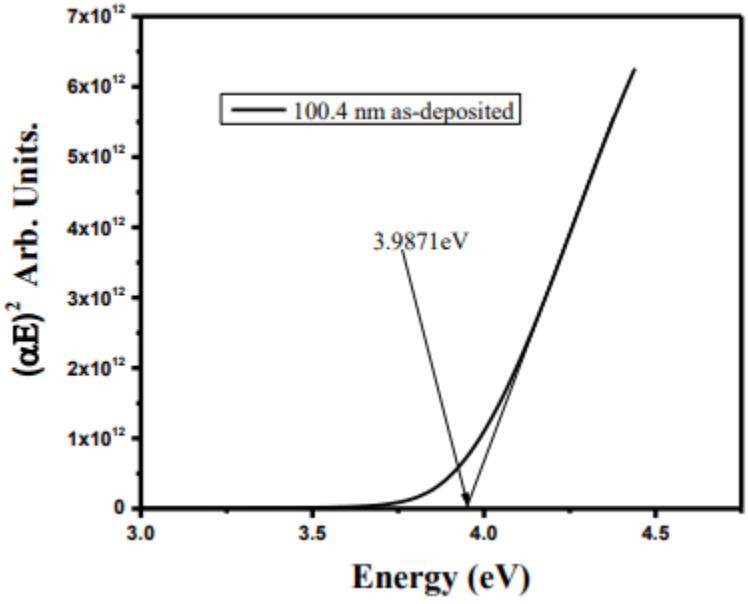

Figure 6: Tauc plot of the 100.4 nm as-deposited TiO2 sample

The optical energy band gap reduced from 4.1±0.05eV for 47.7 nm thin films to 3.9±0.05eV for 100.4 nm TiO2 film as deposited. This was determined from Tauc plots as in figure 6. The energy

band gaps changed from 4.1±0.05eV for 47.7 nm film to 3.8±0.05 eV for 100.4 nm films upon annealing. Post deposition annealing probably improved crystallinity and oxygen deficiency, enhancing a reduced optical energy band gap. This was in line with the 3.9 eV of TiO2 anatase reported by Nguu et al. (2018). At 120.5 nm, the optical band gap increased to 4.1±0.05eV. This could be attributed to Moss-Burstein effect.

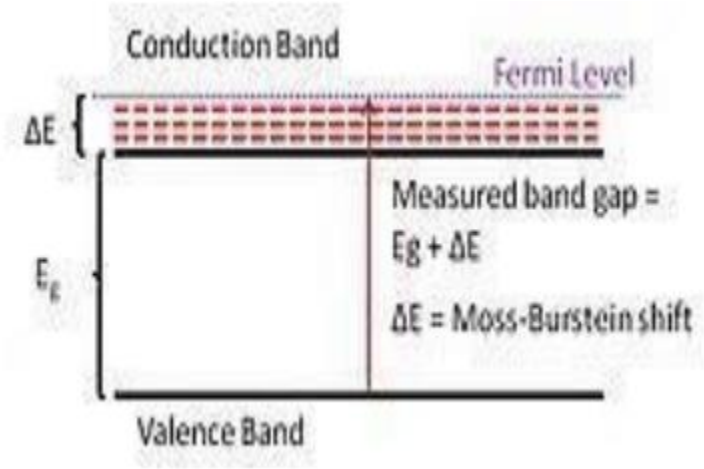

Figure 7: Fermi energy shift in an n-type catalyzed semiconductor (Marius, 2006)

The effect occurs when the electron carrier concentration exceeds the conduction band edge density of states, which corresponds to degenerate doping in semiconductors. In nominally doped semiconductors, the Fermi level lies between the conduction and valence bands. For example, in n-doped semiconductor, as the doping concentration is increased, electrons populate states within the conduction band which pushes the Fermi level to higher energy. The apparent band gap becomes higher (Marius, 2006), as the absorption edge is moved to higher energies probably due to some states nearer to the conduction band being populated as in Figure 7.

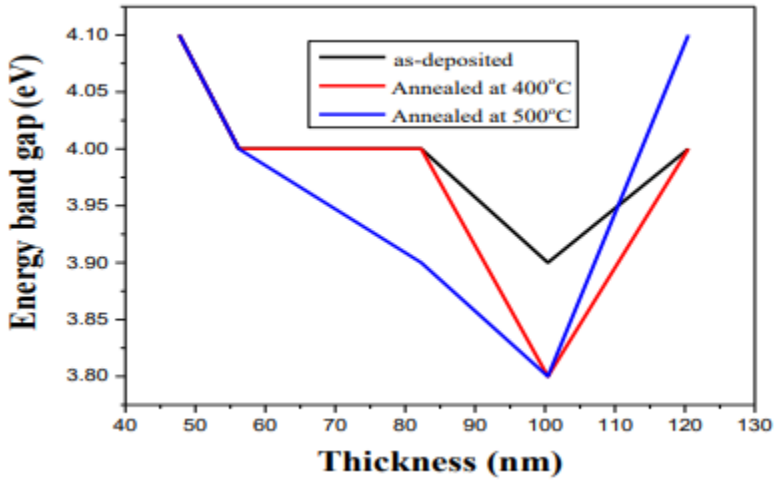

Figure 7: Variation of energy band gap with thickness at different temperatures

Annealing increased crystallinity, enhancing a reduced optical energy band gap with thickness as shown in Figure 7. The lowest energy band gap value of 3.8± 0.05 eV was obtained from a film of thickness 100.4 nm, thereafter Moss-Burstein effect resulted at 120.5 nm. There was no significant change in annealing films of thicknesses 47.7 nm and 56.2 nm. This could probably result due to the amorphous nature of the film as it takes the structure of the substrate.

4.2.2 TiO2-Cu thin films characterization

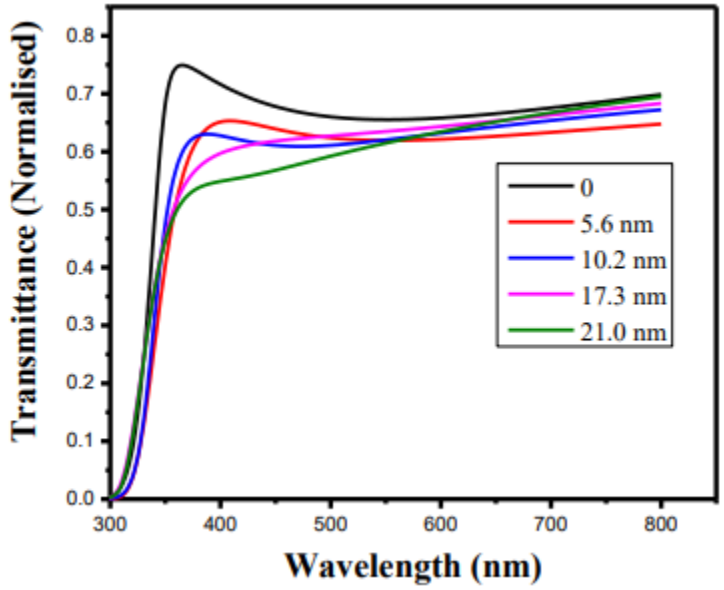

Figure 8: Transmittance spectra of optimized TiO2 and TiO2-Cu with different copper layer thicknesses

Reduced transmittance was witnessed with increased copper surface layer, as atom number per film area increased as in Figure 8. A fall in transmittance due to reduced interference shows uneven thin film realized due to island to island mode of growth of copper layer on the surface of TiO2. This increases surface area for the gas active site interaction with the material.

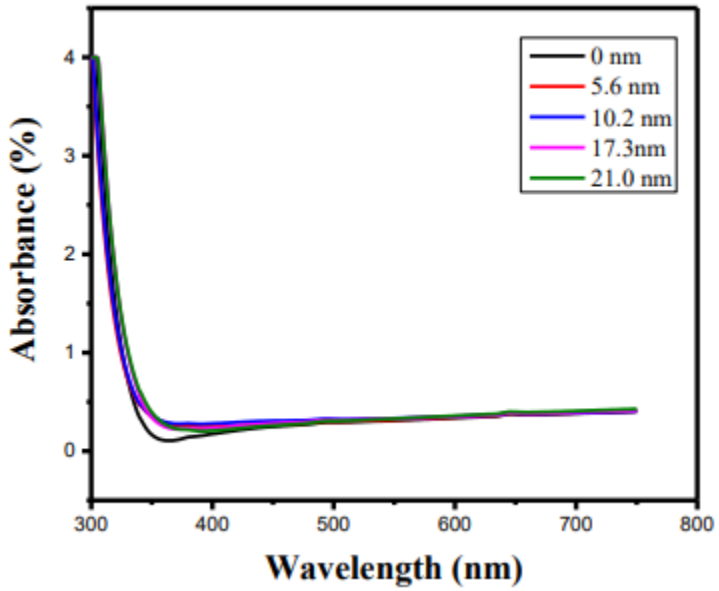

Figure 9: Absorption spectra of various thicknesses of Cu overlayer on TiO2 thin film

Figure 9 depicts higher absorption was realized within the higher photon wavelength region with copper surface loading in both films on FTO glass and microscope glass substrates probably due to some states induced near the top of the valence band (Álvaro et al., 2017). The same observation was made at very low copper coverage since implanted ions modified electronic behavior of the catalyst.

4.2.3 TiO2-Cu characterization in varied hydrogen gas concentration

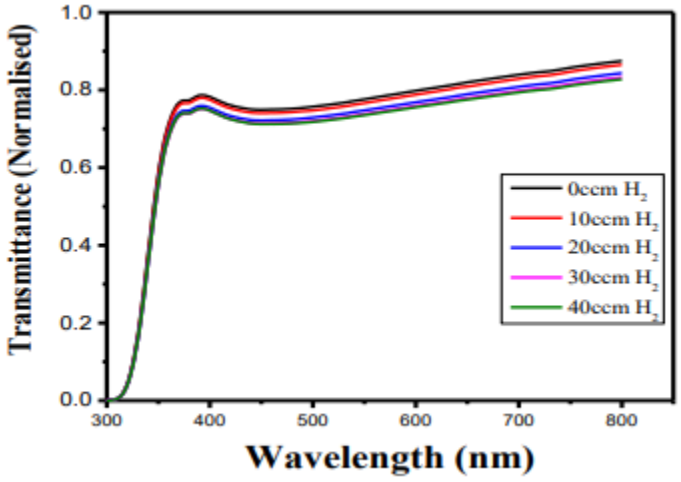

Figure 10: Transmission spectra of 100.4 nm film with 10.2 nm copper layer in different hydrogen concentrations

Optical transmittance decreased with increased hydrogen concentration in the chamber as in figure 10. This could have resulted from interface oxide layer formation, inhibition of diffusion of cations from substrate towards the TiO2 layer, hence increased photocatalytic efficiency under UV radiation.

5.0 CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

TiO2 layers of various thicknesses 47.7, 56.2, 82.3, 100.4 and 120.5nm were deposited by reactive DC magnetron sputtering. The films were characterized as-deposited and as annealed at 400^{o}C and 500^{o}C. 100.4 nm thin films annealed at 400^{o}C showed characteristic of anatase phase of TiO2, with energy band gap of 3.8 eV, ideal for photocatalytic activities. Annealing the films improved crystallinity of the deposited thin films. The energy band gap of the resulting films varied from 3.9 to 3.8 eV for 100.4 nm thin film upon annealing.

Copper layers of thicknesses 5.6, 10.2, 17.3 and 21.0 nm were deposited on optimized TiO2 sample. Both microscope and FTO glass slides were used. Increased absorption and reduced optical energy gaps were realized using FTO glass substrate, a precursor of effective photocatalytic layer.

The copper aspirates surface layer on TiO2 surface lead to decrease in optical band gap and refractive index until a certain level, with surface equilibrium at 10.2 nm surface layer thickness. Absorbance was also shifted to higher wavelengths.

The exposure of the fabricated TiO2-Cu thin film to analyte hydrogen gas increased the photon absorption edge. The energy band gap decreased with increased hydrogen concentration, from 4.1 eV for 0ccm to 3.9 eV for 50 ccm. The highest sensitivity of 2.0 % was achieved in the optimized film. This was higher compared to 1.7 % realized earlier. The fabricated material sensor showed improved properties for gasochromic sensor applications. From the above discussion, 100.4 nm TiO2 thin films annealed at 400^{o}C on FTO glass substrate with 10.2 nm copper layer was recommended for use as optical gas sensor material. The material sensor had cheaper fabrication cost and operation; this is due to absence of electrical decomposition. The test results realized at room temperature proved its optimum operation, as heating could cause oxidation of catalytic surface layer, inhibiting the material active sites.

5.2 Recommendations

Though, in order to realize a more portable stand-alone gas sensor, an investigation on an ideal photon type source that incorporates the material is recommended. Further, extension of this study on structure and morphology of the film is essential to understand its sensing behavior.

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