This indicates that the Au/*T*-ZnO sensor exhibited the highest sensor response. Therefore, the Au nanoparticles doping would result in the higher reaction rate constant and exhibits an excellent catalytic ability [10, 17-19].

Conclusion

The hexagonal wurtzite *T*-ZnO has successfully synthesized by thermal oxidation technique. The enhancement of the sensor response of the Au/*T*-ZnO sensors is considered in terms of an increase of the adsorbed oxygen density, O_{ads}^{ion} and the reaction rate coefficient, $k_{Eth}(T)$ in the rate equation for an ethanol adsorption reaction on the ZnO surface.

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Sensitivity Improvement of Ethanol Sensor Based on ZnO Nanostructure by Metal Impregnation

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Chemical sensors based on ZnO nanostructure were fabricated and studied toward ethanol vapour. The adding metal by metal impregnation technique was used for sensitivity improvement of ethanol sensor based on ZnO nanostructure. ZnO nanostructures were prepared by thermal oxidation technique under normal atmosphere and exhibited diameter of 40–300 nm and length of several micrometers. The ethanol sensing properties of sensor based on ZnO nanostructure with platinum and gold nanoparticle were investigated. The improvement of sensitivity due to metal adding was observed and found that adding metal with both Au and Pt resulted in the highest sensitivity of 85 at 1000 ppm. The sensitivity improvement by metal impregnation is due to catalytic properties of metal in both ethanol adsorption reaction $k_{Eth}(T)$ and oxygen adsorption reaction $k_{Oxy}(T)$ at the surface as described in sensitivity formula.

Keywords: Sensors, ZnO, Nanostructure, Metal Impregnation.

1. INTRODUCTION

ZnO nanostructures have potential for various applications such as gas sensor,[1–3] solar cell[4] and optoelectronic device.[5] Gas sensor based on ZnO nanostructure has been widely investigated. However, ethanol sensor based on ZnO nanostructure exhibited typically low sensitivity unless the nanostructure size was less than about 10 nm.[6] Thus, the techniques for sensitivity improvement were intensively studied. Adding noble metal such as platinum (Pt),[7] palladium (Pd),[8–10] silver (Ag),[11] and gold (Au)[12–13] is also one of the techniques commonly used to improve sensor sensitivity. Typically, the metal acts as a catalyst to modify surface reactions of metal oxide semiconductors toward sensing gas and results in higher sensitivity than that of pure ZnO.

Many researchers have reported the sensitivity improvement of ZnO nanostructure by adding noble metal. Wang et al. have reported the sensitivity improvement of ammonia sensor with Pd-doped ZnO nanotetrapods that was better than pure ZnO.[14] While, Li et al.[11] coated gold on ZnO nanorods of 15 nm diameter and found an increase of the sensitivity. Moreover, our group has reported the enhancement of ethanol sensor by impregnating platinum on surface of ZnO tetrapods and found that the sensitivities of platinum impregnated ZnO tetrapod sensors were higher than that of pure ZnO tetrapod sensors.[7] Also, we have found that the sensitivity of the sensor based on Au-doped ZnO nanowires exhibited higher value than that of the sensor based on undoped ZnO nanowires.[12–13]

Thus, in this work, adding metal by metal impregnation technique was used for sensitivity improvement of ethanol sensor based on ZnO nanostructure. The ethanol sensing properties of sensor based on ZnO nanostructure with platinum and gold nanoparticle were investigated.

2. EXPERIMENTAL DETAILS

ZnO nanostructures were prepared by thermal oxidation technique under normal atmosphere. Zn powder (purity 99.9%) was evaporated on alumina substrate under pressure of 4×10^{-5} Torr. Then, the film was thermal oxidized at the temperature of 500 °C for 24 h under normal atmosphere. Then, they were impregnated by gold colloid and platinum colloid. Gold colloid was prepared by wet chemical method as described in our previous report.[12] The platinum colloid was obtained from 0.5-mM Hydrogen hexachloroplatinate (IV) Hydrate, $Cl_6H_2Pt \cdot aq$ (38% Pt, Fluka), in acetone solution.

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The ethanol sensor based on pure ZnO nanostructure is called ZnO sensor. While, sensor based on ZnO nanostructure dropped by 0.1 ml of gold colloid and platinum colloid onto the area of 5×5 mm^2 is called ZnO:Au sensor and ZnO:Pt sensor, respectively. Moreover, sensor based on ZnO nanostructure dropped by 0.1 ml of gold colloid and again dropped by 0.1 ml of platinum colloid is called ZnO:Au + Pt sensor. After dropping, all sensors were heated at the temperature of 300 °C for 48 h. The morphology was observed from field emission scanning electron microscopy (FE-SEM). The sensors were fabricated by putting gold paste interdigital electrodes on the top of ZnO surface with a heater putting underneath the alumina substrate. The ethanol sensing characteristics of ZnO, ZnO:Au, ZnO:Pt and ZnO:Au + Pt were tested in ethanol atmosphere at the ethanol concentration of 50, 100, 500 and 1000 ppm at the operating temperature ranging from 280–400 °C.

3. RESULTS AND DISCUSSION

After thermal oxidation, the color of thin film changed from grey to white color indicating change of zinc to zinc oxide under the chemical reaction as $2Zn + O_2 \rightarrow 2ZnO$. From FE-SEM image with magnification of 10,000, the nanostructure of ZnO was observed with diameter of 40–300 nm and length of several micrometers as shown in Figure 1(a). After metal impregnation, it was observed that ZnO:Au, ZnO:Pt, and ZnO:Au + Pt had the different morphology comparing to ZnO as shown in Figures 1(b–d). This is due to acidic property of metal colloid solution that corroded the surface of ZnO. However, the diameter of nanostructures after metal impregnation was about the same. The diameter was in range of 50–350 nm, 50–270 nm, and 80–300 nm for ZnO:Au, ZnO:Pt, and ZnO:Au + Pt, respectively.

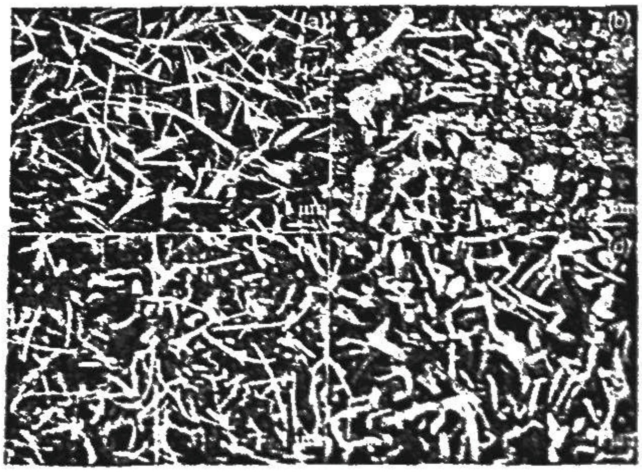

Fig. 1. FE-SEM images of pure ZnO (a), ZnO:Au (b), ZnO:Pt (c) and ZnO:Au + Pt (d).

The resistance change of sensors based on ZnO at 300 °C, ZnO:Au at 340 °C, ZnO:Pt at 380 °C, and ZnO:Au + Pt at 380 °C in air and in ethanol atmosphere of 1000 ppm at optimum temperature were shown in Figure 2. A decrease of resistance was observed in ethanol atmosphere. It should be noted that the optimum temperature of ZnO:Au, ZnO:Pt and ZnO:Au + Pt sensors are higher than ZnO.

The sensitivities as a function of operating temperature were plotted in Figure 3. It can be seen that metal impregnation resulted in improvement of sensitivity and ZnO:Au + Pt exhibited the highest sensitivity. The sensitivities of ZnO:Au, ZnO:Pt and ZnO:Au + Pt sensors at optimum temperature were 27, 75, and 85, respectively while the sensitivity of ZnO sensor was 9.

The improvement of sensitivity due to metal adding can be considered by using sensitivity formula from our previous report[6] as:

$$S = \frac{R_{air}}{R_{gas}} = \frac{\Gamma_r k_{Eth}(T)[O_{ads}^{ion}]^b}{n_0} C_g^b + 1 \tag{1}$$

where Γ_r is proportional constant, $k_{Eth}(T)$ is a reaction rate constant between adsorbed oxygen species and the ethanol vapor that depends on the operating temperature, $[O_{ads}^{ion}]^b$ is adsorbed oxygen species concentration, C_g^b is the ethanol concentration, and n_0 is electron concentration of sensor in air.

The improvement of sensitivity due to metal adding may be explained by using two parameters in sensitivity formula: reaction rate constant $k_{Eth}(T)$ and adsorbed oxygen species concentration $[O_{ads}^{ion}]^b$. First, metal can act as a catalyst to enhance reaction rate constant in ethanol adsorption reaction $k_{Eth}(T)$ as given in Eq. (2)

$$CH_3CH_2OH_{ads} + O_{ads}^{2-} \xrightarrow{k_{Eth}} C_2H_4O + H_2O + 2e^- \tag{2}$$

and resulted in enhancement of sensitivity as seen in Eq. (1). The evidence for having higher $k_{Eth}(T)$ can be

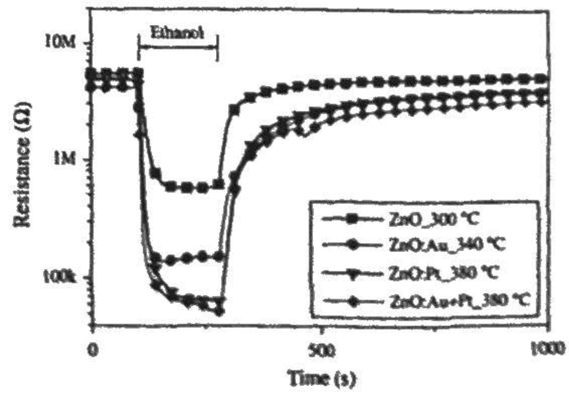

Fig. 2. The resistance change of sensors based on ZnO at 300 °C, ZnO:Au at 340 °C, ZnO:Pt at 380 °C, and ZnO:Au + Pt at 380 °C in air and in ethanol atmosphere of 1000 ppm.

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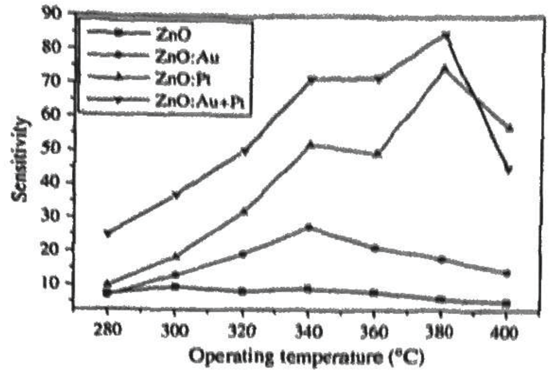

Fig. 3. Sensitivities as a function of operating temperature for sensors based on pure ZnO, Au:ZnO, Pt:ZnO, and Au + Pt:ZnO sensors under ethanol concentration of 1000 ppm.

observed by the sensor resistance in the ethanol ambient. It is clearly seen in Figure 4(b) that the sensor resistance in the ethanol ambient of the metal adding sensor is lower than that of ZnO sensor suggesting the higher reaction rate constant in ethanol adsorption reaction.

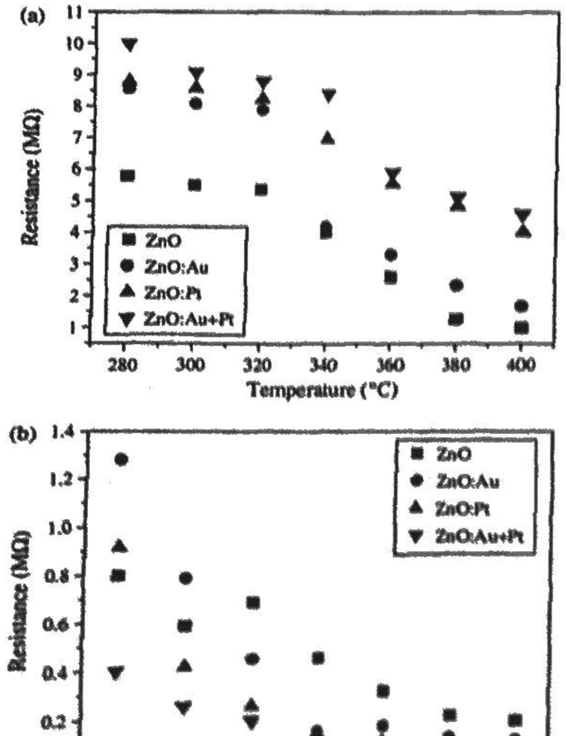

Fig. 4. Sensor resistance versus the operating temperature for all sensors in air (a) and under ethanol concentration (b) at the ethanol concentration of 1000 ppm.

Second, metal can also act as a catalyst to enhance reaction rate constant in oxygen adsorption reaction $k_{Oxy}(T)$ as given in Eq. (3).

$$\frac{1}{2}O_2 + 2e^- \overset{k_{Oxy}}{\Leftrightarrow} O_{ads}^{2-} \tag{3}$$

The increase in $k_{Oxy}(T)$ resulted in an increase of $[O_{ads}^{ion}]^b$ and finally, resulted in enhancement of sensitivity as seen in Eq. (1). The evidence for having higher $k_{Oxy}(T)$ can be observed by the sensor resistance in the air. As seen in Figure 4(a), the sensor resistance in air of the metal adding sensor is higher than that of ZnO sensor suggesting the higher reaction rate constant in oxygen adsorption reaction. Therefore, the sensitivity improvement by metal impregnation is due to catalytic properties of metal in both ethanol adsorption reaction and oxygen adsorption reaction at the surface.

4. CONCLUSIONS

The adding metal by metal impregnation technique was successfully used for sensitivity improvement of ethanol sensor based on ZnO nanostructure. The improvement of sensitivity due to metal adding was observed and found that adding metal with both Au and Pt resulted in the highest sensitivity of 85 at 1000 ppm. Therefore, the sensitivity improvement by metal impregnation is due to catalytic properties of metal in both ethanol adsorption reaction and oxygen adsorption reaction at the surface. The evidences for the enhancement of $k_{Eth}(T)$ and $k_{Oxy}(T)$ can be observed from sensor resistance that indicated by the resistance decrease in ethanol ambient and the resistance increase in air, respectively, after metal impregnation.

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Contents

Chapter 1

Metal-Oxide Nanowires for Gas Sensors

Supab Choopun, Niyom Hongsith and
Ekasiddh Wongrat

Additional information is available at the end of the chapter

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1. Introduction

In past decades, gas sensors based on the metal oxide semiconductors (MOSs) have been studied in diverse field for wide applications. A gas sensor is a device that can be used to detect various gas such as ethanol, LPG, CO_2 and CO gases etc. The gas sensors based on MOSs such as SnO_2, TiO_2, WO_3, ZnO, Fe_2O_3, and In_2O_3 have an important role in environmental monitoring, chemical process controlling, personal safety (Q. Wan et al., 2004), industrial process controls, for the detection of toxic environmental pollutants in human health, and for the prevention of hazardous gas leaks, which comes from the manufacturing processes (K. Arshak&I. Gaidan, 2005), wine quality monitoring, and traffic safety (X.F. Song et al., 2009).

The first generation of MOS gas sensors were based on thick films of SnO_2 since 1960s which was firstly reported by Taguchi (E. Comini et al., 2009). The MOS gas sensors have some advantages such as small size, low-power-consumption (E. Comoni et al., 2009), simple construction, good sensing properties (K. Arshak&I. Gaidan, 2005), and high compatibility with microelectronic processing (E. Comini et al., 2002). So, they have rapidly gained attention over the years.

Recently, various morphologies of MOS nanostrcutures such as wire-like, belt-like, rod-like, and tetrapods have been widely investigated for gas sensor applications. It is well-known that the sensitivity characteristics of these sensors strongly depend on the morphology of MOS. Especially, one-dimensional nanostructures such as nanowires, nanobelts, nanoneedles have gained a lot of interest for nanodevice design and fabrication (Wang et al., 2008). The sensors based on MOS nanowires are promising due to feasibility for ultrahigh sensitive sensors or ppb-level sensors. These nanowires can be prepared by various techniques such as pulse laser deposition (PLD), chemical vapor deposition (CVD), thermal evaporation, metal-catalyzed

NANOSTRUCTURED OXIDES, INTERFACES, HETEROSTRUCTURES AND DEVICES

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A7.1-2

Nanomolding of Zinc Oxide Nanostructures and Its Application to Efficient Light Trapping in Thin-film Solar Cells

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The ability to pattern functional materials at the nanometer scale has become of crucial importance in many fields of nanoscience and nanotechnology. In particular for photovoltaics, nanopattering has gained tremendous importance, as absorption of sunlight may be enhanced drastically by proper engineering of photonic nanostructures.

Currently zinc oxide (ZnO) is one of the key functional materials for advanced optoelectronic and photonic applications, including photovoltaics. Approaches, so far explored to increase light trapping in solar cells, include the growth of ZnO films with randomly-oriented pyramids via chemical vapor deposition or wet etching of crater-like structures into sputtered ZnO films. Also solution-based methods have been extensively investigated for the synthesis of nanopillar-type ZnO structures.

Although these approaches provide a certain degree of freedom in designing the surface morphology of ZnO films, the basic feature morphology is dictated by the underlying growth and etch kinetics. Experimentally, one desires a method capable of implementing arbitrarily designed surface morphologies. Here we demonstrate that nanomolding of ZnO provides exactly such a platform. We use ultraviolet nanoimprint lithography (UV-NIL) for mold fabrication from an arbitrary master structure. ZnO films are subsequently grown on the mold via chemical vapor deposition and anchored on glass substrates using an UV-curable sol-gel lacquer. Finally the mold is detached, leaving a nanostructured ZnO film. We demonstrate the power of our method by fabricating one-dimensional periodic gratings, two-dimensional quasi-periodic dimple arrays, and randomly-oriented pyramid networks.

We further present first experimental results on high-efficiency thin-film silicon solar cells grown on these substrates. We anticipate a strong potential for other thin-film technologies, including cadmium telluride, copper indium gallium diselenide, and organic solar cells, as well as for other optoelectronic and photonic applications as our method provides a versatile tool to study nanophotonic effects of a large variety of nanostructures directly on the device performance.

A7.1-3

Impedance Spectroscopic Analysis of Aluminum-doped Zno Transparent Conduction Layer for Dye-sensitized Solar Cells

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Al-doped ZnO thin films were deposited on glass substrate by radio frequency magnetron sputtering technique. The optimum thin films have low sheet resistance of 8.56 W/Sq and average transmittance values of 82% in visible region and also, exhibit good thermal stability in electrical conductivity. For dye-sensitized solar cell application, Al-doped ZnO thin films were used as a transparent conducting oxide layer (TCO). The DSSCs structure is Al-doped ZnO thin films/ZnO+dye/LiI+I_2/Pt/FTO. The DSSC employing this layer as TCO layer showed a photon to electron conversion efficiency of 1.02% compared to 0.73 and 1.13% for the reference cells which employing the FTO and ITO layer, respectively. The charge transport properties were measured by using electrochemical impedance spectroscopy (EIS). It was found that the DSSCs which employing Al-doped ZnO thin f. have an excellent electron transport by decreasing the electron lifetime of the conductio. band in ZnO. This result demonstrated that Al-doped ZnO thin film is a promising TCO for large scale DSSCs.

A7.1-4

Influence of Carbon Nanotubes in Gel Electrolyte on Photovoltaic Performance of Zno Dye Sensitized Solar Cells

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Dye-sensitized solar cell (DSSC) has attracted much attention thanks to its low cost, ease to fabricate and high efficiency at low light intensity. However, problems such as evaporation and leak of liquid which are caused by liquid electrolytes are considered main reason that limit the long-term performance and practical use of DSSCs. In this work the polymer gel electrolyte was used to replace the liquid electrolyte. Polymer gel electrolyte-based cell using the PEG polymer gel electrolyte has low current density and fill factor. The effect of addition of multiwalled carbon nanotubes (MWCNTs) in different %wt into the PEG gel electrolyte has been investigated. Current density-voltage characteristics and impedance spectroscopy showed that use of MWCNTs with PEG gel electrolyte increases current density and fill factor. It was found that 5%wt of MWCNTs in PEG gel electrolyte exhibited the highest photo conversion efficiency. The role of MWCNTs for charge transport and charge recombination is discussed in terms of charge transport resistances and back electron resistance. With respect to stability, devices tested for 1000hr maintain over 80% of its initial performance.

A7.1-5

Metal-O-Metal Linked NIR Dyes for Nanoporous SnO2 Based Dye-sensitized Solar Cells

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Dye sensitized solar cells (DSSCs) have attracted significant attention in the recent past owing to light-to-electric power conversion efficiencies of 10–11% with simulated sunlight. Further enhancement in the efficiency of such devices, development of new sensitizers having strong absorption in near infrared (NIR) wavelength region is currently a hot topic in the area of solar cell research. Panchromatic sensitization over a wide wavelength region is desired for further enhancement in the photoconversion efficiency. We have recently reported that multi electron injection occurs from linearly linked two dye molecules where the first dye is bonded to SnO2 surface with a Sn-O-Sn linkage, without having conventional carboxylic groups [1].

Naphthalocyanine (Nc) and phthalocyanine (Pc) dyes with different central metals such as Sn, In, Ga, Si, and Al were synthesized using reported methodology. A perusal of absorption spectra of these dyes reveals that they possess sharp absorption in NIR wavelength region indicating the possibility fabrication of hybrid DSSC with visible dyes for panchromatic photosensitization. It is interesting to note that Ga, Si and Al phthalocyanines were not stacking on hexagonal close-packing lattice structure. Each sample has a fundamental absorption edge lying in the near-ultraviolet part of the visible spectrum. Optical measurements revealed that the Honeycomb structures exhibited the maximum haze values up to 93% at wavelength range 400nm to 850nm.We believe that this honeycomb structures could be applied in optoelectronic applications such as grating, gas sensor, solar cell, dye sensitive solar cell (DSSC), and photodetectors.

A-PO4-38

Effect of Synthesis Parameters on Phase Formation, Magnetic and Electric Properties of Bifeo3 Material

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Bismuth ferrite ($BiFeO_3$) has emerged as a new multifunctional material with concomitant presence of electric/magnetic ordering and photovoltaic response sustainable over a wide temperature range. Several studies have indicated that the multiferroic properties of $BiFeO_3$ are intimately linked to its structure and strain generated in thin film form. The bulk compound can represent the properties as a whole material. However, synthesis of single phase material has been difficult due to diverse nature of constituent elements, particularly volatile nature of bismuth oxide. The immediate consequences are impurity phases and vacancies. The impurity phases often account for the excess magnetic moment and vacancies act as centers for leakage currents.
We have systematically studied the structural, magnetic and ferroelectric properties of $BiFeO_3$ phase as a function of synthesis parameters. We synthesized several polycrystalline samples with stoichiometric composition using solid state reaction method. The synthesis parameters like sintering temperature, duration were varied and quenching sequence was used to stabilize single phase. The phase evolution and structural variation were studied using powder X-ray diffraction technique. We confirmed single phase nature and rhombohedral structure in the samples synthesized under optimized conditions. The characteristic low magnetic moment resulting from antiferromagnetic ordering was observed using vibrating sample magnetometer. It also indicated that iron based impurities were absent in the samples. We also studied microstructure and ferroelectric behavior of these samples. Detailed results on structure-property relationship will be presented.

A-PO4-39

Ethanol Sensing Characteristics of Sensors Based on ZnO:Al Nanostructure Prepared by Thermal Oxidation

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ZnO:Al nanostructures with Al 1-3 % by mol were synthesized by thermal oxidation technique on alumina substrates. The heating temperature and sintering time were about 600°C and 24 h respectively under normal atmosphere. The structural characteristics of ZnO:Al nanostructure were studied by using field emission scanning electron microscope (FE-SEM). From FE-SEM images, the diameter and length measured at the middle of the wire-like structure were in range of 100-500 nm and several micrometers, respectively. From TEM analysis, it was suggested that the ZnO:Al nanostructure grew along (11-20) direction on [0001] plane. From, XRD analysis, it was suggested that ZnO:Al can be formed and has no segregation phase of Al after thermal oxidation. At room temperature, a resistance of ZnO:Al is lower than that of pure ZnO. The lowest resistance of 1 MW was observed in ZnO:Al with Al 1% by mol compared to 8 MW of pure ZnO. The ethanol sensing characteristics of ZnO:Al nanostructure were investigated from the resistance change in ethanol atmosphere at concentration of 50-1000 ppm and an operating temperature of 280-380°C, respectively. It was found that the sensitivity of ZnO:Al nanostructure sensors was higher than that of pure ZnO nanostructure sensors. The highest sensitivity of 32 was obtained in ZnO:Al nanostructure sensors with Al 1% by mol compared to 14 of pure ZnO nanostructure sensor at optimum temperature of 300°C. The sensitivity improvement of ZnO:Al can be explained by an increase of oxygen vacancy-related defects which increase the surface depletion thickness and potential barrier height at the contact.

A-PO4-40

Asymmetric Hysteresis Loop and Leakage Current Behaviors in Au/PZT/Pt/Al2O3/SiO2/Si Ferroelectric Thin Films

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The characteristics of hysteresis loops and leakage currents, and capacitance versus voltage were investigated on a ferroelectric structure consisting of a platinum bottom electrode, a vapor-deposited gold top electrode, and PZT films. The P-V hysteresis loops, the J-V characteristics, and the C-V characteristics were measured after performing a rapid thermal annealing (RTA) process. A Precision LC Radiant Technology was used to measure their electrical properties with a 90-nm PZT thickness and an area of 7.1x10-4 cm2. The measurements were taken by connecting a Pt bottom electrode to the drive of the precision LC and the Au top electrode to the drive of the precision LC. The P-V hysteresis, the J-V and C-V curves of PZT samples showed the asymmetry for both measurements. The asymmetric hysteresis loops, the J-V and the C-V curve were shifted in the positive direction when the drive was applied to the Pt electrode, while being negatively shifted in the converse case. The asymmetric behavior of the polarized state in the hysteresis loops due to the electrode configuration resulted from different work function between the Pt and Au electrodes, further influencing the leakage current behavior and the capacitance voltage.

Keywords: PZT films, Pt bottom electrode, Au top electrode, work function, P-V Hysteresis and asymmetric

A-PO4-41

Sensitivity Enhancement of ZnO Nanostructure Sensors by Palladium Impregnation

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ZnO nanostructure sensors were fabricated and studied toward ethanol vapor. ZnO nanostructure was prepared by thermal oxidation technique. Zn powder was screened on alumina substrates and sintered at 600°C for 24 h. The structural characteristics of ZnO nanostructure were studied by using field emission scanning electron microscope (FE-SEM). FE-SEM images showed needle-like and wire-like structure. The diameter and length of nanostructure were 75-500 nm and 3-18 mm, respectively. For sensor fabrication, ZnO nanostructure sensors were impregnated by palladium solution (1001 PPM of Pd in 5.1 wt%

HCl). ZnO nanostructure sensors were dropped with palladium solution for 2, 4, 6, 8 and 10 ml. The ethanol sensing characteristics were studied from the resistance change in air and target gas at ethanol concentration of 50-1000 ppm. It was found that the highest sensitivity is about 38.51 at 1000 ppm for sensor with 6 ml of palladium solution. The sensitivity enhancement can be explained by catalytic effect of palladium nanoparticle on ZnO nanostructure surface.

A-PO4-42

Efficiency Improvement of ZnO Dye-sensitized Solar Cells by Using Double-layer of Zno Nanoparticle/zno Powder

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In this work, the photoelectrochemical characteristics of ZnO dye-sensitized solar cells (DSSCs) with double layer of ZnO nanoparticle/ZnO powder were investigated. The structure of DSSCs was ZnO nanoparticles/ZnO powder as a semiconductor, Eosin Y as a dye sensitizer, iodine/iodide solution as an electrolyte and Pt/FTO as a counter-electrode. The photo-electrode was fabricated by screening ZnO nanoparticles as underlayer and ZnO powder as upper layer. The ZnO double-layers with thickness ratio of 1:1, 1:2, 1:3, 2:1, 2:2 and 3:1 were studied. The films were characterized by FE-SEM, Raman spectroscopy and UV-visible spectroscopy. The photoelectrochemical characteristics of ZnO DSSCs were measured under stimulated sunlight AM 1.5 from a solar simulator with the radiant power of 100 mW/cm^2. It was found that DSSCs with thickness ratio of 1:3 exhibited the highest photoconversion efficiency of 1.10%. The improvement of photoconversion efficiency with double layer can be explained in term of low transfer resistance.

A-PO4-43

Effect of Metal to Citrate Ratio on Architecture of Cobalt Ferrite Nano-materials by an Shs Route

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Cobalt ferrite (CoFe2O4) is a well-knownmagnetic material with high coercivity and moderate magnetization. These properties, along with their great physical and chemical stability, make CoFe2O4 nanoparticles suitable for magnetic recording applications such as audio and videotape and high-density digital recording disks etc. Magnetic nano particles of $CoFe_2O_4$ have been synthesized by auto combustion method by varying nitrate to citrate ratio (1:X, where X= 0.5, 1.0, 1.5 and 2.0). As burnt powder was calcined 950° C for 4 hrs in order obtain mono phase of spinel ferrite.The prepared samples characterized using FTIR, XRD, SEM and Dielectric measurements.X-ray Diffraction (XRD) confirmed the formation of single phase cobalt ferrite nanoparticles in the range 22-30 nm depending on the metal to citrate ratio.

FTIR spectroscopy also confirm the formation of stable SnO_2 phase as annealing temperature increases.

The gradual transformation of Sn(OH) to SnO_x and ultimately SnO_2 are clearly demonstrated. Moderate annealing leads to reduced crystallite size, while maintaining the oxygen deficiency We demonstrate that Raman spectroscopy is a single metrology to determine the parameters relevant for sensing.

A-PO4-46

Self Quasi-beaded SnO2 Nanowires and Their Ethanol Gas Sensing Properties

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Tin dioxide, SnO_2, is an attractive wide-gap semiconductor due to its potential for use in various applications. The ability to control the size and shape of SnO_2 nanostructure would lead to an even broader range of applications. In this work, self quasi-beaded SnO_2 nanowires were synthesized using carbothermal reduction process on gold-coated alumina substrates. The products were characterized with electron scanning microscopy and x-ray diffractrometer. Result showed ultra long nanowires beaded with particles. The nanowires had the diameter of 50-150 nm and the length of a few ten micrometers. The size of the particles was about 300-1000 nm. The SnO_2 nanostructures were pure tetragonal rutile structure. Gas sensing characterization showed that the optimal temperature was in the range of 340^{o}C and maximal sensor response was about 28 for 100 ppm of ethanol gas.

A-PO4-47

Constructive Photovoltaic Effects for Ultraviolet (UV) Detector

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Ultraviolet (UV) detectors are widely used to measure the intensity and dosages of UV light in solar radiation for health care and in various industries with UV radiation for materials processing, sterilization, and medical treatments. For semiconductor photovoltaic detectors, the photovoltaic outputs are typically generated at an interfacial space charge region (SCR), such as at a Schottky junction between metal and semiconductor materials or a p-n junction of two semiconductor materials. The output photovoltage magnitudes in these semiconductor photovoltaic devices are limited in principle by the energy barrier height at the interfaces. In this work, a photovoltaic multilayer structure was designed with incorporating a photovoltaic output generated in the bulk region of a ferroelectric oxide thin film as an add-on effect to the response at the interfacial Schottky barrier. An improved photovoltaic output was demonstrated in the resulting UV detector on the basis of the constructive photovoltaic effect.

It should also be noted that in many of UV detector applications, continuous monitoring of high intensity UV radiation over a long duration is essential. UV detectors with high stability and durability are highly demanded. The use of stable metal oxides of the ferroelectric thin film and also the electrodes as presented in this work was also promising to achieve improved durability under strong UV intensity for a long duration.

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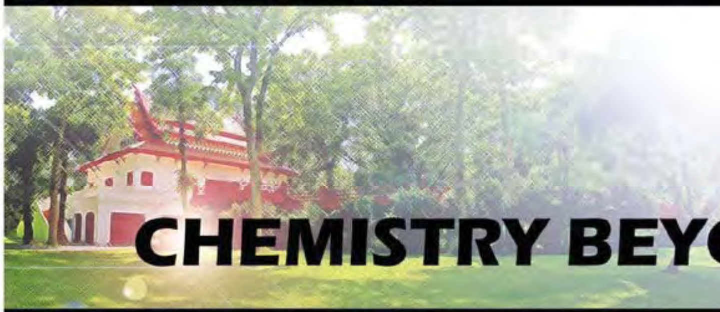

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e-ABSTRACT

DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CHIANG MAI UNIVERSITY
& THE CHEMICAL SOCIETY OF THAILAND UNDER THE PATRONAGE OF
HER ROYAL HIGHNESS PRINCESS CHULABHORN MAHIDOL

MNT-P-124

GROWTH OF ZINC OXIDE NANOWIRES BY THERMAL OXIDATION OF ZINC FILMS ON GLASS SUBSTRATES UNDER ARGON-ACETONE VAPOR

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ABSTRACT

ZnO nanowires (NWs) were grown by thermal oxidation of Zn films under flow of Ar gas and acetone vapor. The Zn films were deposited on glass substrates by thermal evaporation process with film thickness of 150 nm, 300 nm and 450 nm. Then, the substrates were heated at 425-625^{0}C for an hour at a center of the tube furnace under flow of Ar gases and acetone vapor with a flow rate of 1000 ml/min and 5 ml/min, respectively. The as-grown ZnO NWs were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy and X-ray diffraction (XRD). The results showed that the ZnO NWs were wurtzite hexagonal structure with diameter ranging from 25–75 nm depending on the growth temperature whereas the length increased linearly with the growth time. The ZnO NWs with smallest diameter were obtained at growth temperature of 475^{0}C for all Zn film thickness. The density of the ZnO NWs depended on the thickness and growth temperature. As the Zn film thickness increased, the growth temperature of ZnO NWS was higher in order to obtain the maximum density of ZnO NWs. In addition, a growth mechanism for ZnO NWs formation on the substrates will be discussed.

Keywords Zinc oxide; Nanowires; Thermal oxidation

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MNT-P-279

PREPARATION AND CHARACTERIZATION OF ZINC OXIDE-GOLD NANOCOMPOSITE BY PHOTODEPOSITION TECHNIQUE

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ABSTRACT
ZnO-Au nanocomposite was prepared by photodeposition technique. Firstly, ZnO powder was mixed with 10 wt% of polyethylene glycol (PEG) solution in the ratio of 1:2. Then, mixed powder was screened with area of $1\times1 cm^2$ on the glass substrate and baked to remove organic compounds at 500 °C for 1 hr. Then, 20 μl of 0.5 mM hydrogen tetrachloroaurate ($HAuCl_4$) as metal precursor was dropped on ZnO film and kept to dry. After that, $HAuCl_4$ dropped ZnO was loaded to quartz chamber and Ar mixed water vapor was flowed to the chamber with flow rate of 0.5 l/min. Finally, 20 W/m^2 of UVA lamp (365 nm) was irradiated to film for 30 minutes for photocatalysis which ZnO acts as a photocatalyst. After deposition, the color of film was changed from white color to red color indicating the formation of ZnO-Au nanocomposite. The red color was due to the formation of gold nanoparticles. ZnO-Au nanocomposite was investigated by transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), and photoluminescence (PL) spectroscopy. It was found that Au nanoparticles were formed on ZnO surface with small diameter less than 15 nm. Moreover, photoluminescence spectra show that the defect emission of ZnO at around 500 nm for ZnO-Au composite was less than that of pure ZnO. This also confirmed the formation of Au nanoparticles on ZnO surface.

Keywords Nanocomposite; Photodeposition; Gold Nanoparticles

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Growth of ZnO Nanowires by Oxidation of Zn in Acetone Vapor

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Surachet Phadungdhitidhada **, Auttasit Tubtimtae* and Supab Choopun**
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Abstract

In this work, size-controlled growth ZnO nanowires by oxidation of Zn layer in acetone vapor ambient at low pressure with temperature of 850 °C. The Zn films were deposited on FTO glass substrate by thermal evaporation. The ZnO nanowires were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction and UV-vis spectroscopy for morphology, crystal structure, optical properties, respectively. The diameter of ZnO nanowires was found to depend on thickness of Zn layer and acetone flow rate. It was observed that the ZnO nanowires had diameter ranging from 45 to 319 nm. Also, the energy gap of ZnO nanowires was found to be 3.26 eV. In addition, a growth mechanism of ZnO nanowires on the FTO substrate was discussed.

Keywords: ZnO Nanowires, FTO Glass, Zn Layer, Acetone

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Effect of ZnO Anti-reflection Layer on Efficiency of ZnO Dye-sensitized Solar Cells

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Abstract

In this research, we investigated the effects of ZnO thin films as an anti-reflection layer for ZnO dye-sensitized solar cells (DSSCs). ZnO thin films were prepared by thermal evaporation and sparking technique with 0.5, 1.5 and 2.5 sparking cycles onto glass substrates. Surface morphology were investigated by field emission scanning electron microscopy (FE-SEM) and showed that sparking ZnO thin films have roughness surface with nanoparticles compared with thermal evaporation. The optical properties were measured via transmittance and reflectance using UV-vis spectroscopy. The optical reflective index and thickness of the films were obtained via ellipsometry. It was found that the films prepared by sparking technique can reduce reflection and also increase transmission of light more than that of the reference film and the film prepared by thermal evaporation. Also, the optical reflective index of the sparking films has value between that of the substrate and air. The thicknesses of sparking films are in the range of 20-100 nm. For the ZnO DSSCs assembly, the photoelectrochemical parameters of DSSCs were monitored under stimulated sunlight AM 1.5 with the radiant power of 100 mW/cm^2. The results showed that the solar cell with sparking film 1.5 cycles has a short circuit current density (J_{sc}) of 4.34 mA/cm^2 and the maximum efficiency (E_{ff}) of 0.8%, compared with the reference cell of 3.00 mA/cm^2, 0.43%, respectively. Moreover, the DSSCs with sparking films exhibited higher efficiency, suggesting an efficiency improvement due to anti-reflection layer.

Keywords: Anti-reflection coating, Dye-sensitized Solar Cells, Sparking Technique, Thermal Evaporation, ZnO Thin Films.

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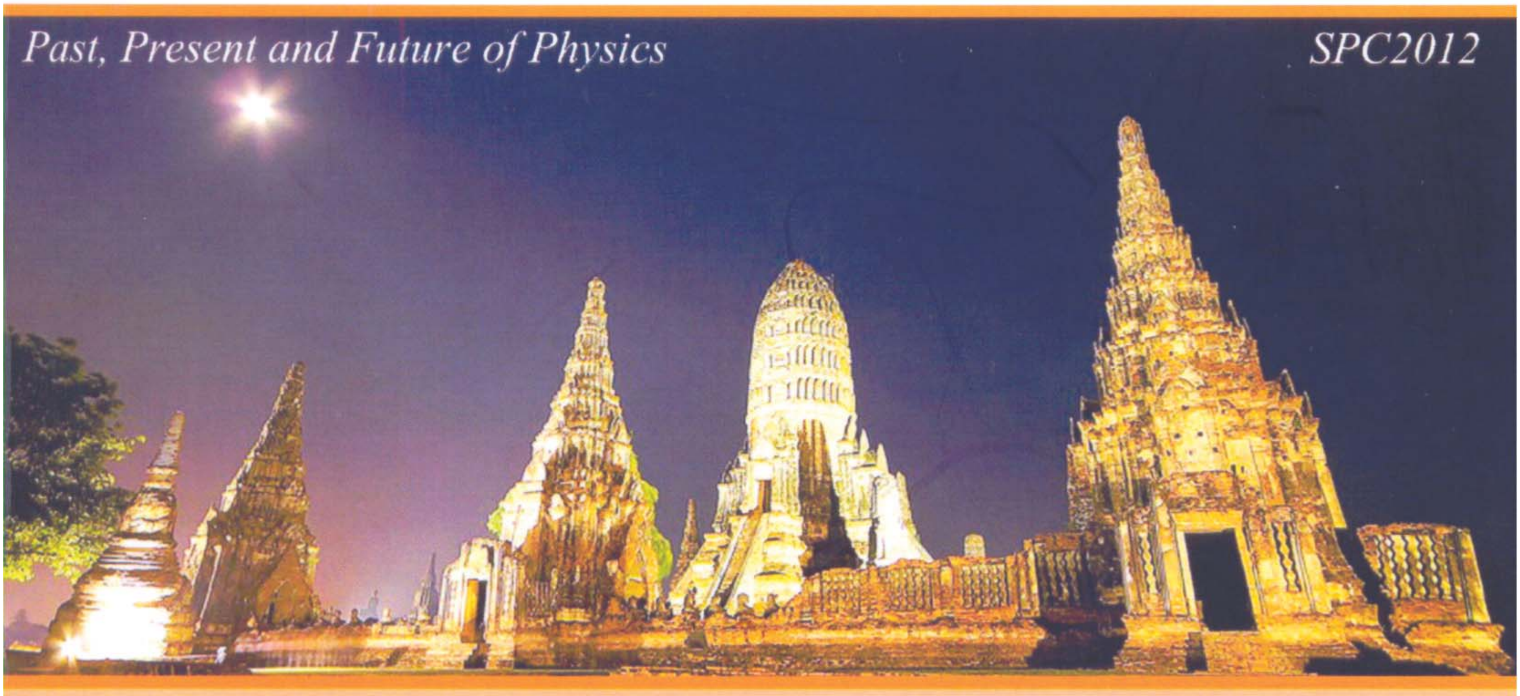

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BOOK OF ABSTRACTS

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Gas Sensors Based on ZnO Nanostructures

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Abstract

The conductometric gas sensors based on ZnO nanostructures were investigated. ZnO nanostructures with various morphologies such as nanowires, nanobelts, nano-tetrapods were synthesized by radio frequency sputtering and thermal oxidation techniques. The sensing properties of gas sensors were mainly studied for ethanol vapor in order to develop alcohol breath analyzer. The sensitivity is a key parameter for gas sensor and several techniques such as using nanostructure and adding noble metal have been used for sensitivity improvement. Moreover, the sensitivity formula was successfully developed in order to explain the sensitivity improvement due to nanostructure and metal adding.

***Keywords*:** Gas Sensor, ZnO, Nanostructure

Copper Oxide Nanoparticles as a Barrier in ZnO Dye-Sensitized Solar Cells

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Abstract

Dye-sensitized solar cells (DSSCs) with CuO nanoparticles (CuO NPs) on the top of ZnO were studied. The CuO NPs used as a barrier layer were prepared by pulsed Nd:YAG (1064 nm) laser ablation and then characterized by transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), UV-visible spectrophotometry (UV-vis), and photoluminescence spectroscopy (PL). It was found that the CuO NPs were rather spherical in shape with diameter of about 26.8 nm and the energy gap is approximately 2.38 eV. The photoconversion efficiency of ZnO DSSCs was measured under illumination of simulated sunlight obtained from a solar simulator with the radiant power of 100 mW/cm^2. The results showed that the ZnO DSSCs with the CuO NPs exhibited higher power conversion efficiency than that without CuO NPs and has the optimum power conversion efficiency up to 1.03%.

Keywords: CuO Nanoparticles, Dye-Sensitized Solar Cells, Laser Ablation, ZnO DSSCs

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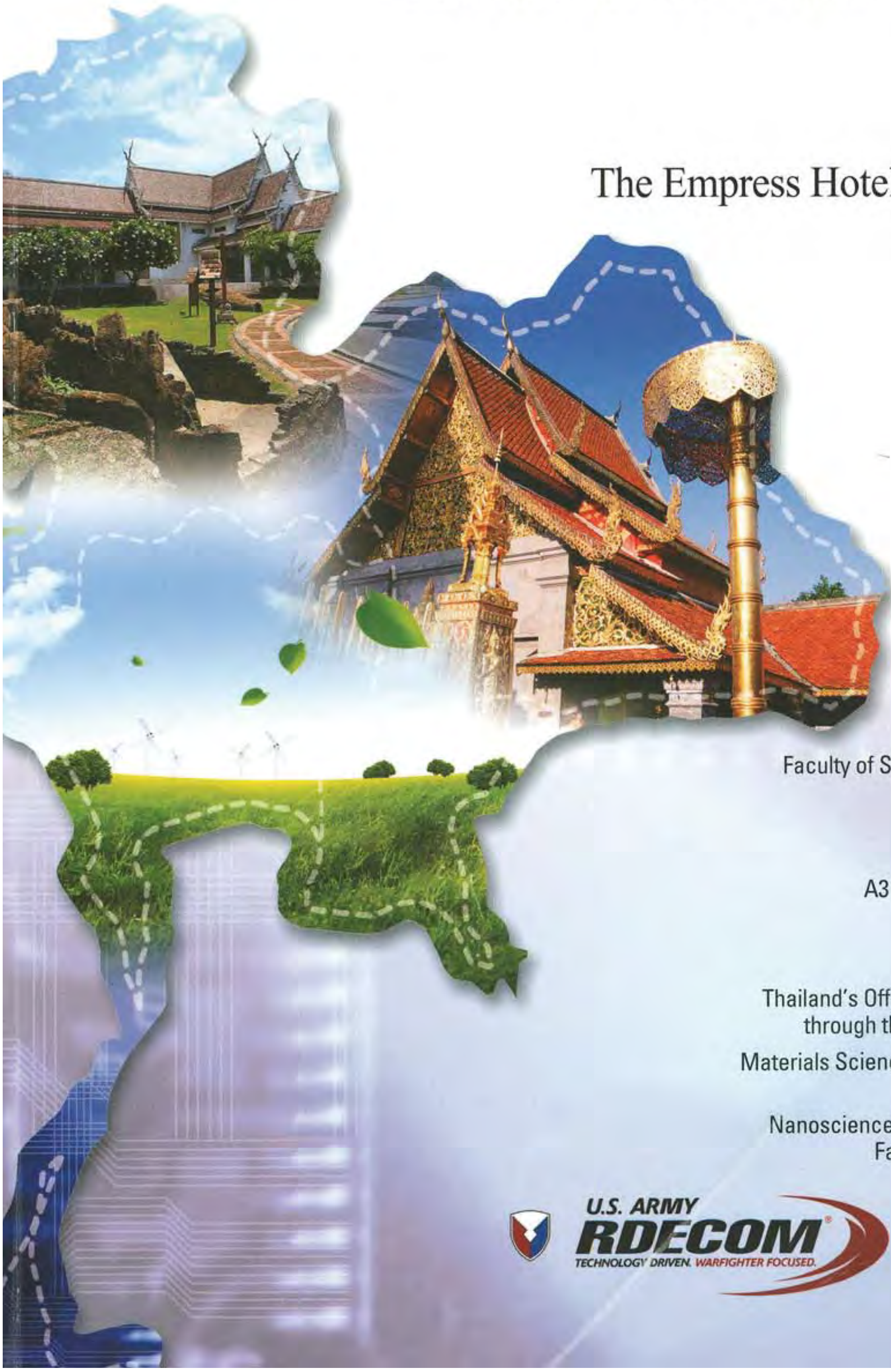

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O - C 08

Size Reduction of Gold Nanoparticles by Pulsed Laser Ablation and Re-irradiation in Water Media

Pichitchai Pimpang, Supab Choopun, Duangmanee Wongratanaphisan, Atcharawan Gardchareon
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Gold nanoparticles (Au NPs) were prepared by using pulsed laser ablation with and without cover slide. The cover slide was used to confine atoms/ions in order to reach supersaturation condition. Au NPs prepared by laser ablation with and without cover slide were investigated by UV-vis spectroscopy, transmission electron microscopy (TEM), and zeta potential measurement. The absorbance spectra exhibited its absorption peak at around 520 nm for both Au NPs ablating with and without cover slide. It was found that Au NPs ablating with cover slide exhibited smaller size and size distribution (10.6±5.9 nm) than those of without cover slide (34.1±21.5 nm) at laser power of 5.00 mJ/pulse. This is due to supersaturation effect and re-irradiation effect caused by cover slide that trapped atoms/ions of gold and trapped Au NPs, respectively. Also, the zeta potential of Au NPs had a negative value suggesting negative surface charge. The lowest zeta potential was observed for Au NPs ablating with cover slide at 5.00 mJ/pulse and it was in consistent with an observation of the highest pH value. In addition, the Au NPs ablating with cover slide at 5.00 mJ/pulse showed the least change with time indicating the most stable Au NPs which was in consistent with the lowest zeta potential results. Thus, pulsed laser re-irradiation could be used for size reduction of Au NPs prepared by pulsed laser ablation in water media.

Keywords: Gold nanoparticles, Pulsed laser ablation, Size reduction, Zeta potential

O - G 02

Efficiency Improvement of ZnO Dye-Sensitized Solar Cells by ZnO Passivating Layer and CuO Thin Film Barrier Layer

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In this work, we reported on efficiency improvement technique of ZnO dye-sensitized solar cells (DSSCs) by using double blocking layer of ZnO passivating layer and CuO barrier layer as a photoelectrodes to block black electron transfer. The general structures of ZnO DSSCs were FTO/ZnO as a photoelectrode, Eosin Y as a dye sensitizer, iodine/iodide solution as an electrolyte and Pt/FTO as a counterelectrode. ZnO passivating layer was deposited on the conducting glass substrate by RF magnetron sputtering technique with different sputtering time (5, 10, 20 and 40 min) and characterized by scanning electron microscopy (SEM) for morphology. CuO thin film barrier layer was deposited by thermal evaporation of copper on the top of ZnO upper layer and then copper was thermally oxidized to form copper oxide. The photocurrent, photovoltage and power conversion efficiency characteristics for DSSCs were measured under illumination of simulated sunlight coming from a solar simulator with the radiant power of 100 mW/cm^2. It was found that the DSSCs with CuO barrier layer exhibited higher efficiency than those of without CuO barrier layer for the same ZnO sputtering time. In addition, the DSSCs with CuO barrier layer exhibited the highest efficiency of 1.1% for sputtering time of 5 min. Thus, CuO barrier layer and ZnO passivating layer has combining effect to improve the efficiency of ZnO DSSCs.

Keywords: Dye-sensitized solar cell, Photoconversion efficiency, Zinc oxide, Copper oxide, Blocking layer

O - G 03

Improved Photo Electrode of Dye-sensitized Solar Cell Using a ZnO/Zn2TiO4

Warut Koonnasoot, Duangmanee Wongratanaphisan, Atcharawon Gardchareon, Supab Choopun
Physics and Materials Science Chiang Mai University, Thailand

Zinc titanate nanostructures were prepared by oxidation reaction technique. Here Zn mixed with 0, 10, 20 and 30 mol% of TiO2 powder was screened on alumina and FTO substrate, and then sintered at 400~600°C for 12 hrs under normal atmosphere. Through a detailed field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD) indicated that the nanostructures were found to have belt-like shapes of Zn2TiO4 phase. Moreover, the belt-like nanostructures of Zn2TiO4 were studied in terms of optical properties by the UV-vis spectroscopy to obtain band gap energy (Eg). The results showed that the Eg gap energy ranged from 3.57 eV to 3.63 eV as the mol% of TiO2 In addition to the characterization of the nanobelts, the synthesized Zn2TiO4 nanostructures were applied as a bilayer semiconductor electrode in ZnO-based DSSC and the results show that the Zn2TiO4 nanostructures with 10 mol% of TiO2 had the highest efficiency.

Keywords: Dye-sensitized solar cell, Thermal oxidation, Zn2TiO4, ZnO

O - G 05

Effect of Nickel Oxide Thin Films on Photoconversion Efficiency in Zinc Oxide Dye-sensitized Solar Cells

Surat Futemvong, Atip Pengpad, Niyom Hongsith, Duangmanee Wongratanaphisan, Atcharawon Gardchareon, Supab Choopun
APRL, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, 50200, and ThEP Center, CHE, Bangkok 10400, Thailand

ZnO dye-sensitized solar cells (ZnO DSSCs) with different thickness of NiO thin films coated in photo-electrode and counter-electrode were investigated. NiO thin films were prepared by thermal evaporation of NiO onto FTO glass substrate. The films were characterized by FE-SEM. The general structures of ZnO DSSCs were FTO/ZnO as a photo-electrode, Eosin Y as a dye sensitizer, iodine/iodide solution as an electrolyte and Pt/FTO as a counter-electrode. For the photo-electrode, NiO thin films were coated on ZnO with 0.2, 0.6, 1.1 and 2.2 mg to form a barrier layer. For the counter-electrode, NiO thin films were coated on FTO glass with 5.4, 10.8, 16.2 and 21.6 mg in order to increase a surface-to-volume ratio. The photoconversion efficiency of ZnO DSSCs was measured under illumination of stimulated sunlight obtained from solar simulator with the radiant power of 100 mW/cm^2. It was found that ZnO DSSCs coated with 0.6 mg NiO in photo-electrode and 10.8 mg in counter-electrode exhibited the highest photoconversion efficiency of 1.00% and 0.92%, respectively. The enhancement of photoconversion efficiency with NiO coating maybe explained by decreasing of charge recombination in photo-electrode and increasing of active surface area in counter-electrode.

Keywords: Dye-sensitized solar cell, Photoconversion efficiency, Zinc oxide, Nickel oxide, Thermal evaporation

O - J07

Enhancement of Sensor Response by Au Nanoparticles Doping on ZnO Tetrapod Sensor

Chawalit Bhoomanee, Duangmanee Wongratanaphisan, Atcharawon Gardchareon, Niyom Hongsith, Supab Choopun
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Zinc oxide tetrapods (T-ZnO) were synthesized using thermal oxidation technique under normal atmosphere. It starts with Zn powders mixed with hydrogen per oxide (H2O2). Through a detailed field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD) showed that the T-ZnO with needle-like shape exhibited single crystalline hexagonal wurtzite structure. The leg tip of the T-ZnO is about $8.17\pm1.17\ \mu m$ in length and 47.80 nm in diameter. The ethanol sensors, based on the T-ZnO and the T-ZnO doped with Au nanoparticles (Au/T-ZnO), were fabricated and investigated for the ethanol sensing properties. The ethanol sensor response of the T-ZnO and the Au/T-ZnO sensors was tested at the operating temperature of 260-360oC with the ethanol concentration of 50, 100, 500, and 1,000 ppm. The results showed that the Au/T-ZnO sensors exhibited higher sensitivity than that of the pure T-ZnO sensors for entire ethanol concentration with optimum temperature of 340^{o}C and 320^{o}C, respectively. This enhancement can be explained in terms of the electron concentration of sensor in air, n0 and the reaction rate constant, kEth between the adsorbed oxygen species and the ethanol vapor due to the increase of effective surface for adsorption of ethanol on the surface. With an excellent catalytic ability, the Au nanoparticles doping would result in the higher reaction rate constant. Therefore, the T-ZnO doped with Au nanoparticles, has a potential application as an ethanol sensor.

Keywords: Gas sensor, Gold nanoparticles, Thermal oxidation, ZnO tetrapod

P - G01

Copper Oxide Nanoparticles for ZnO Dye-Sensitized Solar Cells

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CuO nanoparticles (CuO NPs) were prepared by pulsed Nd:YAG (1,064 nm) laser ablation. The CuO NPs were characterized by transmission electron microscopy (TEM), UV-visible spectrophotometry (UV-vis), and photoluminescence spectroscopy (PL), respectively. It was found that the CuO NPs were rather spherical in shape with diameter of about 26.8 nm and the energy gap is approximately 2.38 eV. The different amounts of the CuO NPs were applied in ZnO dye-sensitized solar cells (DSSCs). The photocurrent, photovoltage and power conversion efficiency characteristics for DSSCs were measured under illumination of simulated sunlight obtained from a solar simulator with the radiant power of 100 mW/cm2. It was found that the ZnO DSSCs with the CuO NPs exhibited higher power conversion efficiency than without CuO NPs. The optimum power conversion efficiency of the ZnO DSSCs with the CuO NPs was 1.03%.

Keywords: CuO nanoparticles, Dye-sensitized solar cells, Laser ablation, ZnO DSSCs

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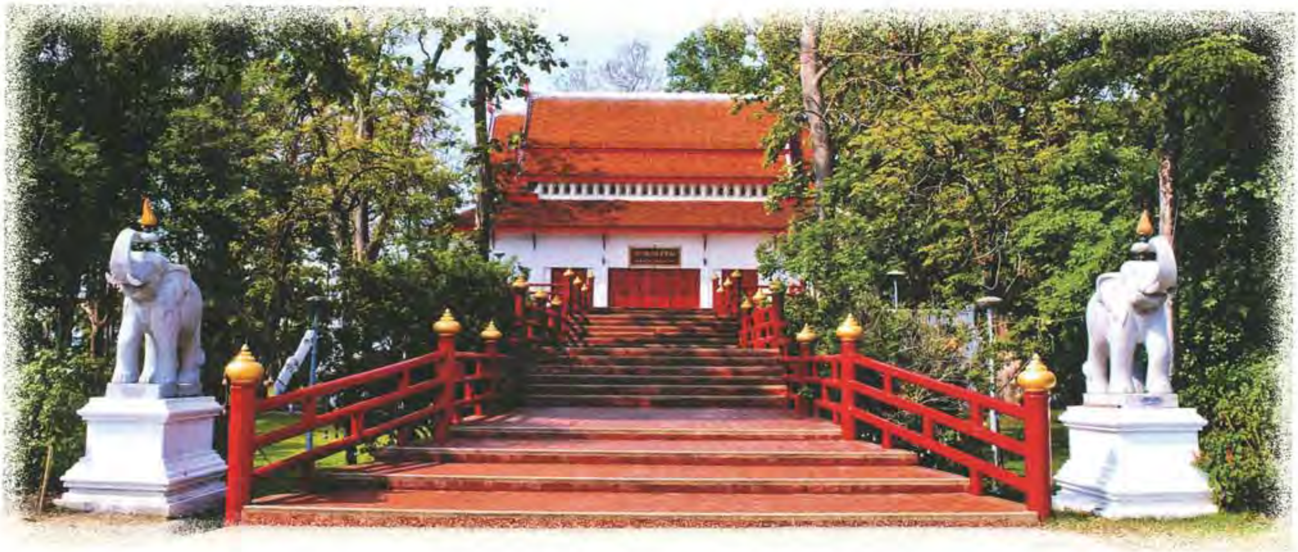
Program & Abstracts



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Zinc Oxide Nanostructures for Ethanol Sensors and Dye-Sensitized Solar Cells

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Keywords: zinc oxide, nanostructure, sensor, dye-sensitized solar cell

ABSTRACT

ZnO nanostructures were prepared by thermal oxidation technique for using as ethanol sensors and dye-sensitized solar cells. To improve sensitivity of the sensor based on ZnO nanostructures, gold was impregnated by gold colloid. The gold colloid is the solution prepared by chemical reduction technique; it appeared red color for gold nanoparticle solution and yellow color for gold solution. The ethanol sensing characteristics of gold colloid:ZnO nanostructures and ZnO nanostructures were observed from the resistance change under ethanol vapor atmosphere at concentrations of 50, 100, 200, 500, and 1000 ppm with the operating temperature of 260-360 °C. It was found that the sensitivity of sensor depends on the operating temperature and ethanol vapor concentrations. The sensitivity of gold colloid: ZnO nanostructures were improved comparing to pure ZnO nanostructures. The mechanism analysis of sensor revealed that the oxygen species on the surface was O^{2-}. For dye-sensitized solar cell application, the dye-sensitized solar cell structure based on ZnO as a photoelectrode was FTO/ZnO/Eosin-Y/electrolyte/Pt counter electrode. ZnO with different morphologies of nanobelt, nano-tetrapod, and powder were investigated. It was found that DSSCs with ZnO powder showed higher photocurrent, photovoltage and overall energy conversion efficiencies than that of ZnO nanobelt and ZnO nano-tetrapod.


มหาวิทยาลัยเชียงใหม่
ขอมอบโล่เกียรติยศนี้ เพื่อเชิดชูเกียรติ แก่
ผู้ช่วยศาสตราจารย์ ดร.สุภาพ ชุพันธ์
ที่ได้รับการคัดเลือกให้ได้รับ
รางวัลมหาวิทยาลัยเชียงใหม่ 'ช้างทองคำ'
'นักวิจัยดีเด่น'
ประจำปีการศึกษา ๒๕๕๕
ให้ไว้ ณ วันที่ ๒๕ มกราคม พ.ศ. ๒๕๕๖
ขอให้ประสบแต่ความเจริญก้าวหน้าในหน้าที่การงาน
และเป็นกำลังสำคัญในการพัฒนามหาวิทยาลัยตลอดไป


วช.
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ในฐานะอาจารย์ที่ปรึกษาหลักที่ให้คำแนะนำและควบคุมการจัดทำวิทยานิพนธ์
เรื่อง
"โครงสร้างนาโนซิงก์ออกไซด์สำหรับการประยุกต์ใช้เป็นอุปกรณ์นาโน"
ของ ดร.นิยม โอ่งสิทธิ์
ที่ได้รับรางวัล ระดับดีเด่น
ให้ไว้ ณ วันที่ ๒ กุมภาพันธ์ ๒๕๕๖
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ขอมอบโล่ประกาศเกียรติคุณแด่
ผู้ช่วยศาสตราจารย์ ดร. สุภาพ ชูพันธ์
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ขอมอบโล่ประกาศเกียรติคุณแด่

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