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Synthesis and Gas Sensing Properties of Sno_2 Nanostructures in Ethanol and Carbon Monoxide Gases

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ABSTRACT

The study focused on synthesis and investigation on gas sensing properties of tin oxide (SnO_2) nanostructures (NS) toward ethanol and carbon monoxide gases. The nano SnO_2 sensing materials were prepared by thermal evaporation method grown on silicon substrates by varying three different parameters. These parameters were temperatures (650 °C, 750 °C and 850 °C), nickel catalyst concentrations (0, 5 and 10 milimoles) and tin powder source to substrate distances (2cm, 4cm and 6cm). Another catalyst used was Aurum (Au) coated silicon substrates. The parameters were found to affect the size and morphology of the synthesized nanostructures. Scanning Electron Microscope (SEM) showed that the SnO_2 formed nano-spheresnano-needlesandnano-wires. Growth temperatures had a significant effect on morphology and size of NS; catalyst concentration affected the porosity and growth of the nanostructures; source to substrate distance affected the nanostructures predominately on homogeneity and particle size. The presence of tin and oxygen in all NS were validated by Energy dispersion X-ray (EDX) analysis. X-ray diffraction (XRD) also showed the formation of SnO_2 phase in all conditions. At the growth temperature of 850 °C significant formation of SnO_2 nanowires (NW) was observed. By using this synthesized nanowires, gas sensing properties towards ethanol (C_2H_5OH) and carbon monoxide (CO) gas was measured at 450 °C with different volume concentration. It was found that SnO_2 NW has good sensing properties for C_2H_5OH at 100 ppm and at 25 ppm for CO.

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INTRODUCTION

Over the past decade, a lot of researchers are studying metal oxide NS materials due to their unique properties. Metal oxides NS have been extensively utilized in various technological applications. For examples they are used as gas sensors, bio-sensors, nanoelectronics, nanogenerators, electrochromic devices, light-emitting diodes, field emitters, supercapacitors and photo-detector. Due to its enhanced surface-volume ratio and possible quantum confinement effects, metal oxide NS materials have added advantages in chemical, electrical, mechanical, optical and thermal properties than other materials (Castillo *et al*., 2012). The large surface-to-volume ratio of semiconducting metal oxide nanostructures make them highly sensitive to surface chemical processes(Kolmakov *et al*., 2005).For example, absorption of certain gases on surface of metal oxide NS such as SnO_2 results in significant electrical conductivity changes(Wan Normiza *et al*., 2013).

The gas sensing mechanism involves the change in the electrical conductivity when the active gases are adsorped on the surfaces. Since nanomaterials offer advantage in large surface to volume ratio which are much larger than metal oxide thin films sensitivity of specific gases are enhanced. When comparing the metal oxide nanostructures like nanowires with the thin film, nanowires may lead to have favourable sensing properties.

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Single crystalline properties of nanowires can provide the short response and recovery time, leading to ultra high chemical sensitivity.

In comparison to NW, a sputtered thin film is composed of columnar grains made of fine crystallites which has narrow voids between columnar grains as well as grain boundaries between the crystallites. When the active gases passed through the sputtered film sensor, the adsorbed species spreads into the voids and boundaries, being accompanied by atomic diffusion. Such a diffusion process may delay the sensing properties(Yamazaki, 2012).

Recently, SnO_2 semiconductor has been widely used in gas sensor due to its high capacity to adsorb gaseous species and change its surface conductivity while promoting the reactions(Wan Normiza *et al*., 2013). SnO_2 is an n-type semiconductor metal oxide which have properties of wide band gap of 3.6 eV (at 300 K), high optical transparency in the visible range, high achievable carrier concentration (up to $6x10^{2°}$ cm^{-3}), low resistivity (10^{-4} to $10^{-6}\Omega$-cm), and chemical and structural stability (Castillo *et al*., 2012). The wide band-gap semiconductors are ideal for gas sensing because it can provide numerous advantages such as the ability to operate at high temperatures, radiation and environmental stability and mechanical robustness (Pearton and Ren, 2013). Very small tin oxide nanorods with 3 nm in diameter can give ultrahigh gas sensitivity for detection of ethanol, a sensitivity of up to 83.8 at 300 ppm ethanol vapor in air(Comini *et al*., 2002). Furthermore, $SnO_2$with nanobelt-based morphology can act as gas sensors for polluting gases such as CO and NO_2 , as well as for ethanol for exhalation analyzers. For example, the sensor responses are 41.6 for 250 ppm for ethanol and –15.5 for 0.5 ppm NO_2 at 400 ° C (E. Comini 2002).

Different synthesizing condition of SnO_2 will give different types of SnO_2 NS, thus will affect the mechanical, electrical as well as thermal properties. It is important to investigate the effect of parameters involved (growth temperature, catalyst concentration and tin powder to substrate distance) to the responses of morphology, size, porosity and density of NS. This is to ensure the desired properties of functional nanomaterials as a gas sensor can be obtained. By understanding the growth mechanism of SnO_2 nanowires, the sensitivity of SnO_2 can be modified and optimized, thereby possibly allowing detection of gases at a lower concentration such into the parts per billion (ppb) level.

Experimentation:

SnO_2 NWs were synthesized by via chemical vapour deposition (CVD) technique. The CVD process was carried out in a horizontal tube vacuum furnace as shown in the Fig. 1(a). The source material was 1.0 g of Sn powder with 99% of purity and it was loaded on a quartz boat and positioned at the hot zone of the furnace. The substrate used in this study was a boron doped p-type silicon wafer with orientation of (001). Also the substrates were coated with two type of catalysts which are nickel nitrate ($NiNO_3$) and gold (Au) to accelerate the formation of tin oxide nanowires. The wafer that was coated with $NiNO_3$ was spin coated on the surface of silicon substrate. On the other hand, the gold coated substrate was done by sputtering method. In the first step argon gas with flowrate of 150 sccm was introduced into the horizontal tube in order to purge the system. The Ar gas was also used during the heating of the furnace to synthesis temperature.

After the growth temperature was achieved, high purity oxygen gas with 50 sccm was introduced and kept at this temperature for 2 hours. The flow rate of argon (150 sccm) and oxygen (50 sccm), synthesis time (2 hour), weight of tin powder (1.0 g), spin coating speed (7000 rpm) and time (30s) were made constant throughout the experiments. The variables in this research which were growth temperature, distance between the source to substrate and catalyst usage. By varying these three parameters, the products of this synthesis process (NS and NW) were characterized by XRD (Bruker AXS diffractometer D8) and SEM/ EDX (Zeiss Gemini Supra 35VP). For gas sensing characterization, the test was done at ITIMS, Hanoi University. Dilution of pure ethanol and carbon monoxide gas to 25-100 ppm was carried out by three mass flow controllers from an initial concentration of 1000 ppm. The resistance on the NW was measured by Keithley 2700 multimeter with data acquisition card, which measures V/I profile with respect to time. The measurement mechanism was done by 2-point probe and shown in Fig. 1b.

RESULT AND DISCUSSION

Fig. 2 shows SEM images of typical synthesized nanostructures grown by thermal evaporation process at different temperature (650°C, 750°C and 850°C) and with and without Ni catalyst when the tin powder were placed 2cm from the substrate. From the figure, it can be seen thatthe growth temperature affectedthe morphology and size of nanostructures. At 650 °C, the nanostructure possesses spherical like shape with high porosity. As the temperature increased to 750 °C, nanostructure possesses facet structure with lower porosity compared to nanostructures formed at 650 °C. Besides that, at 850 °C, the NS possesseda needle/wire-like morphology with large diameter and short width. The growth temperature determined how much the reactive vapor could be generated and the surface diffusion length of the adsorbed vapor species (Dalal *et al*., 2006). As the temperature increase the condensation of vapor will increase and thus will increase the growth rate of SnO_2 NS. At high temperature (850°C) the growth species had enough energy to diffuse and move to the energetically

favorable plane of growth. Furthermore, the ample energy from higher temperature caused a high rate of desorption and re-evaporation which led to dense, and short nanowire arrays (Fang *et al*., 2008).

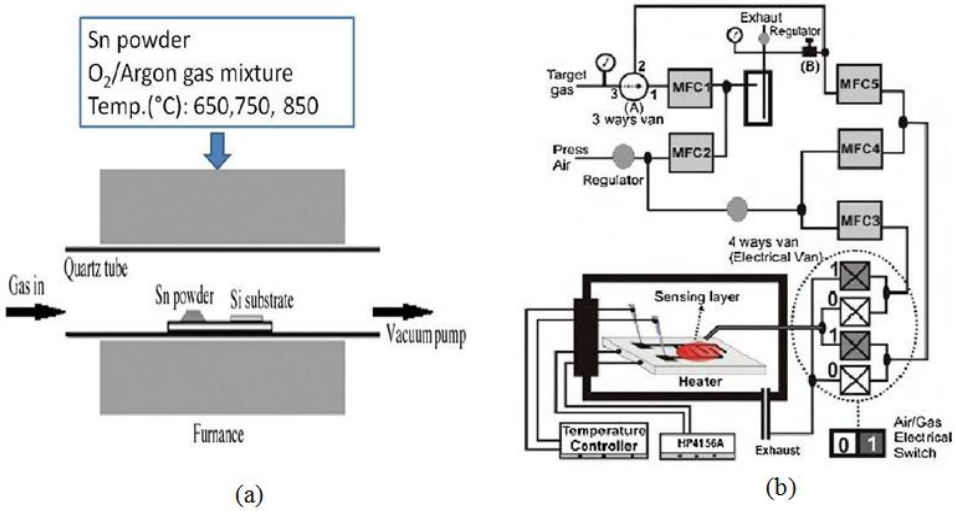

Fig. 1: a) Furnace setup at USM. b) Gas sensor testing systems at ITIMS, Hanoi University.

The use of Ni-based catalyst produced NSthat have smaller size with higher concentration and denser appearance than NS without Ni catalyst. The metallic seeds (catalyst) act as nucleation sites that promote the growth of SnO_2 NS by VLS mechanism. However, without seed, oxide particles sometimes can be as large as micron size. This oxide seed will deposit during the initial stage of the condensation process and large structure will formed by means of VS mechanism. The effect of distance between tin powder and substrate can be seen on the distribution and particle size of NSs. Formation of NSs at 2cm smaller in size compared to at 4cm and 6cm. This is due to the condensation of Sn vapours which was higher at shorter distance. Fig. 3 shows the SEM image and EDX spectra ofSnO_2 NS withAu catalyst at 850°C. NSs with Au catalyst possesses wire-like structure with small diameter average 71nm (Fig. 3b).NW with small diameter and large surface to volume ratio will give high sensitivityfor gas sensor.From EDX analysis, it can be observed qualitatively that a high percentage of tin atoms compared to oxygen (Fig. 3b). XRD analysis shows that all diffraction peaks for the product indicate the typical feature of the rutile structure of SnO_2 naowires(Fig. 4).

Fig. 5a & 5b show the gas sensing resistance in air and ethanol (C_2H_5OH) and in air and carbon monoxide respectively. The resistance decreases upon exposure to C_2H_5OH and CO at 450°C. For ethanol gas, the decrease in the resistance is increases with increasing C_2H_5OH concentration. On the other hand for carbon monoxide (CO) gas,the resistance increase as CO concentration increases. Sensitivity of the NWs to the absorbed gases can be calculated by the ratio of $R_a/R_g$where R_a and $R_g$are the resistance before and after exposure to a particular gas(Xia *et al*., 2003). Table 1 and 2 summarizes the gas sensitivity data for C_2H_5OH and COgases at different concentrations. From Table 1 it can be demonstrated that the sensitivity tend to increase with rising of gas concentration whereas Table 2 shows the resistance changes reversibly upon introduction of CO. Different type of gases will give different changes to gas sensing resistance and sensitivity at different gas concentration. This is the results of the electron transferred from SnO_2 nanowires to adsorb C_2H_5OH and CO gas molecule. For ethanol, higher sensitivity can be achieved at 100 ppm with sensitivity of ~2.4. For carbon monoxide, gas concentration as low of 25 ppm will gave the highest sensitivity (1.68). The gas sensor shows a good reversibility of property since the resistance recovers to its initial value at shorter time after ethanol and carbon monoxide gases was removed. Tin oxide is a typical n-type semiconductor and its gas sensing property was mainly governed by the surface. When placed in a gas atmosphere with certain concentration, gas molecule will absorbed on its surface first, and then the resistance and conductance of the surface would be modified (Chen *et al*., 2012). Some researchers have foundPd doping can increases the sensitivity and lower the operating temperature at which the gas sensing properties can be maximized (Yamazaki, 2012)

Table 1: Sensitivity of SnO_2 NWs at different ethanol concentrations.

	25 ppm	50 ppm	100 ppm
R_a (kΩ)	3.68E+05	3.68E+05	3.68E+05
R_g (kΩ)	2.71E+05	2.15E+05	1.55E+05
S	1.36	1.71	2.37

Table 2: Sensitivity of SnO_2 NWs at different CO concentrations.

	25 ppm	50 ppm	100 ppm
R_a (kΩ)	2.44E+05	2.44E+05	2.44E+05
R_g (kΩ)	1.45E+05	1.69E+05	1.82E+05

S	1.68	1.44	1.34

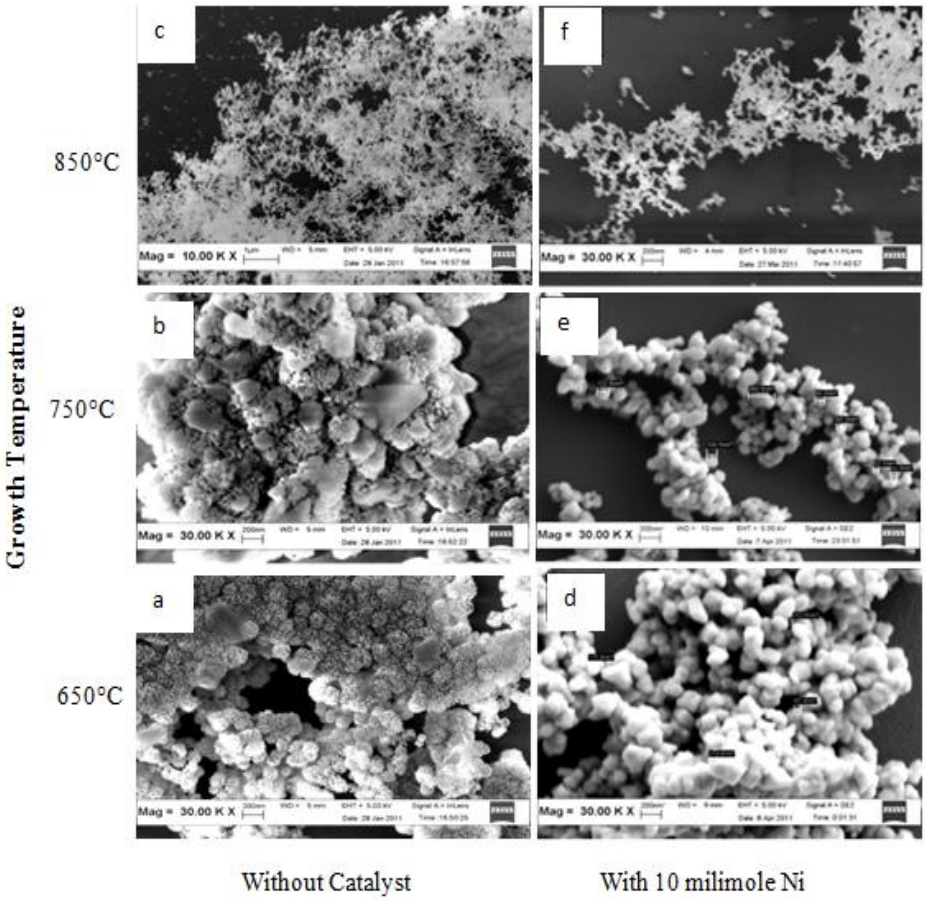

Fig. 2: SEM images of SnO_2nanostructures at different temperature (650°C, 750°C & 850°C), with and without Ni catalyst at 2 cm distance from source.

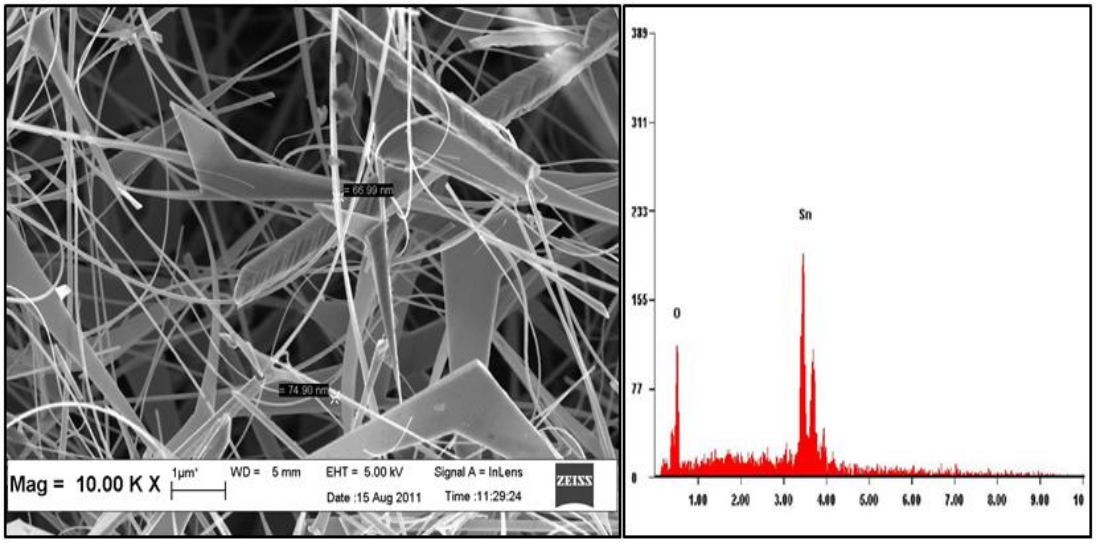

Fig. 3: (a) SnO_2 NW formation at 850°C with Au catalyst. (b) EDX analysis of SnO_2 NW formation at 850 °C with Au catalyst.

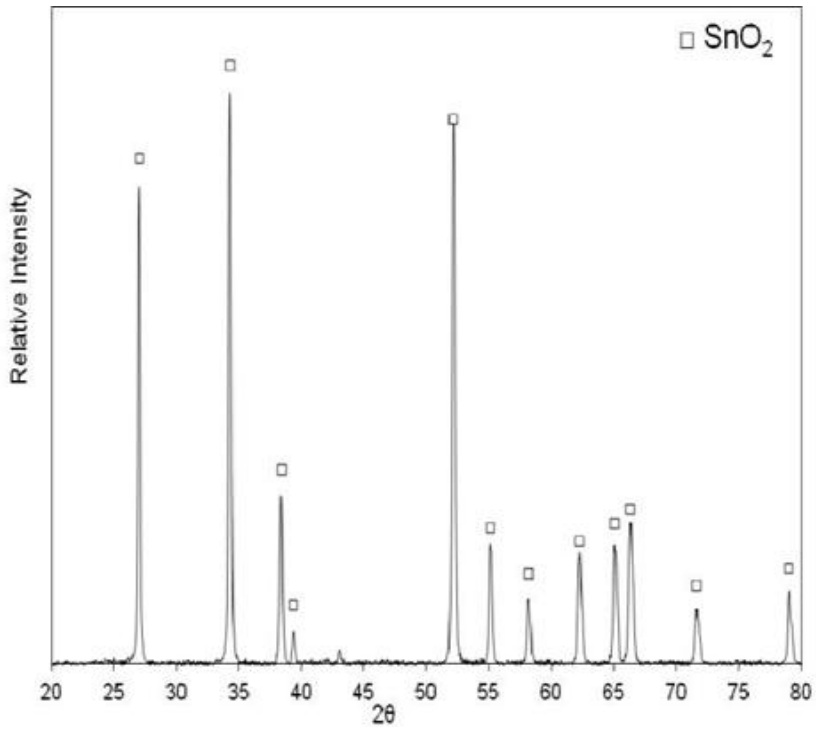

Fig. 4: XRD spectra of SnO_2 NW with Au catalyst.

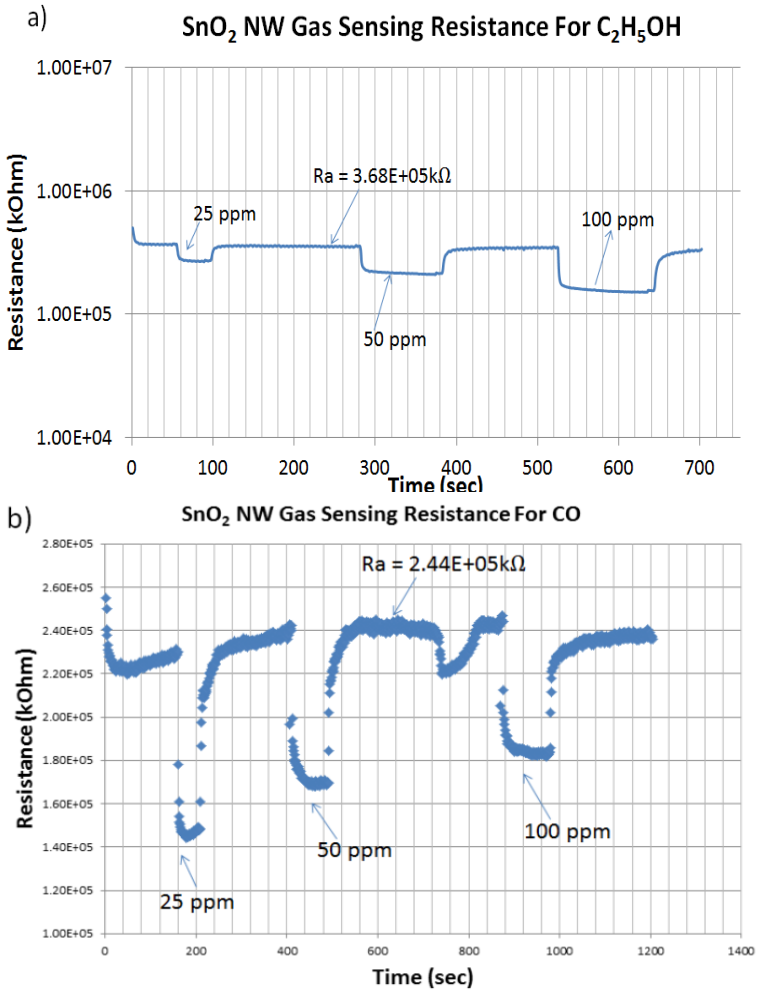

Fig. 5: Gas sensing properties of SnO_2 NW formed at 850 °C with Au catalyst to a) C_2H_5OH b) CO at 450°C.

Conclusion:

In summary, synthesis ofSnO_2 nanowires using tin powder at temperature of 850°C was feasible. Other than NWs, formation of nano-needles and nano-spheres are also had obtained under different synthesis conditions. The use different temperature and catalyst will affect the morphology and size of NWs. SEM/EDX and XRD results show the present of SnO_2. Nanowires that were produce at 850°C using Au catalyst had been used as gas sensor. At 450°C, ethanol showed high sensitivity at concentration of 100 ppm whereas for carbon monoxide, it showed high sensitivity at 25 ppm. The gas sensing properties can be enhanced by doping the NWs with other rare earth elements i.e. Pd doping.

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