CHAPTER 5

CONCLUSIONS

The undoped ZnO and Sn-doped ZnO (0.5–5 at% of Sn) nanostructures were successfully produced by FSP using zinc naphthenate and tin (II) 2-ethylhexanoate as Zn and Sn precursors, in a single step under 5/5 (precursor/oxygen) flame condition. The XRD results revealed that Sn doping could reduce the crystallite size in the (002), (100) and (101) planes of undoped ZnO wurtzite structure, predominantly in reducing of (002) plane. This is because Sn^{4+} ions limited the extent of the ZnO crystal expansion during the FSP synthesis process by substituting Zn^{2+} into the ZnO lattice due to the similarity in their ionic radii. It was also found that, when ZnO was doped with Sn from 0 to 5 at%, the trend of SSA_{BET} unveiled a tendency increment from 95 to 194 m^2/g. However, for raw data, the d_{XRD} of 5 at% Sn-doped ZnO sample is smaller than that of 3 at% Sn-doped ZnO while the d_{BET} of 3 at% Sn-doped ZnO is slightly smaller than that of 5 at% Sn-doped ZnO. TEM micrographs of samples showed rod-like and hexagonal/spheroidal morphologies, and confirmed the decreasing of particle sizes particularly the diameter of rod-like morphology according with the clear decreasing of d_{XRD} in the (002) plane. High resolution-TEM revealed that the nanorods were grown along with the $\langle 2110 \rangle$ direction. FESEM-EDS analysis of Sn-doped ZnO nanostructures confirmed that the agglomerated nanostructure size increased as the intended Sn doping concentration increases, and the atomic composition ratio of Zn:Sn was similar to that ratio of the mentioned doping.

The film sensors were successful fabricated by spin coating with the nanostructures on Al_2O_3 substrates composing of interdigitated Au electrodes. The cross-section FESEM-EDS revealed the thickness of the sensor films as approximately 2.2 µm and the compositions of the films. The optimal operating temperature of the sensors towards C_2H_5OH and H_2 gas sensing was 400°C while towards $(CH_3)_2CO$ and CH_4 gas sensing was 350°C. Change in the conductivity of the sensors happened as the current increased when the sensors interacted with $(CH_3)_2CO$, C_2H_5OH and CH_4 gases, but the conductivity decreased when interacted with H_2 gas at the high concentration and operating temperature, which confirming p-type to n-type conversion. The gas sensing characteristics of the sensors were compared, 5 at% Sn-doped ZnO showed the best response towards C_2H_5OH under the consideration of its detection limit (4.9 ppm) which calculated from the power law equation with the lowest limitation response value ($S = 1.1$). The concentration of Sn doping in ZnO exhibiting the highest gas response was 5 at% for C_2H_5OH ($S = 38$ at 400 ppm) and H_2 ($S = 8$ at 50,000 ppm), while 3 at% for $(CH_3)_2CO$ ($S = 20$ at 1,000 ppm) and CH_4 ($S = 15$ at 50,000 ppm), under the optimal operating temperatures. Therefore, it can be concluded that 3−5 at% Sn-doped ZnO sensor exhibited the best gas-sensing performance due to its very small grain size. However, the selectivity of Sn-doped ZnO showed at 5 at% of Sn doping for C_2H_5OH in this study.

The UV-vis spectra suggested an enhancement of absorption intensity in UV region as an increase in Sn doping level. The bandgap of the nanostructures were found to be 3.31 eV and 3.32 eV for 0, 0.5 and 2 at% Sn doped ZnO, and 3 and 5 at%

Sn doped ZnO, respectively, from calculating with the first derivative of UV-vis absorption spectra. However, doping with Sn did not help improving the C_6H_5OH and CH_3OH degradation activity of ZnO in our study. This might be due to the formation of deep states in ZnO bandgap energy as described in the references [171] and [183]. The C_6H_5OH photodegradation kinetics over undoped ZnO was found to follow first order whereas the reaction over all Sn-doped ZnO samples was consistent with zero-order kinetic scheme. The C_6H_5OH degradation rate constants of undoped ZnO was 0.1220 min^{-1}, while 0.5, 1, 2, 3 and 5 at% Sn-doped ZnO were 0.2913, 0.2360, 0.2925 and 0.1828 (mg C/l).min^{-1}, respectively. The rate on the degradation of CH_3OH was rather critically slower than that of C_6H_5OH in the case of undoped ZnO (approximately 6 times) and Sn-doped ZnO (approximately 9 times) nanocatalysts. This is because the photodegradation of CH_3OH took place by direct holes transfer at metal oxide surface while the photodegradation of C_6H_5OH took place through attacking with $OH^{\bullet}$ radicals.

Suggestion for future work

1. To investigate abundantly the gas selectivity of Sn-doped ZnO nanostructures synthesized by FSP, more gases should be tested with the same condition in a gas sensing measurement.
2. To gain more understanding the physiochemical characteristics of Sn-doped ZnO nanostructures synthesized by FSP, it should be also characterized with X-ray photoelectron spectroscopy (XPS) technique or other techniques for pinpointing Sn ion states and locations in ZnO structures, including their bandgaps. These analyses will confirm all

reasons about gas sensing and photocatalytic properties, which relative to the physiochemical characteristics.

3. From literature survey, another application of Sn-doped ZnO nanostructures, which is very interesting, is applying it to a conducting film [76, 78, 81−83, 189, 192−193]. It can be used as a candidate for ITO, antireflecting coating and window material in solar cells due to its prominent electrical and optical properties and its rather cheaper cost.