CHAPTER 3

Copper oxide for ethanol sensor application

Recently, chemical sensor is under great interesting for new properties, since the problems with conventional semiconductor gas sensors such as insufficient gas selectivity, inability to detect very low gas concentrations, and degradation of the sensor performance by surface contamination still persist. Metal oxides are often used as gas sensors because their electrical conductivity depends on the composition of the ambient atmosphere. The sensing mechanism of conductance sensors based on electrically active grain boundaries of semiconductor compounds is ascribed to variations of majority carrier surface concentration under the influence of adsorbed substances. A gas sensor is a device which detects the presence of various gases. Usually, a gas sensor is used to warn about gases which might be harmful to humans or animals. Such a device can be used to detect combustible, toxic, gases etc. Ethanol, also known as ethyl alcohol, drinking alcohol or grain alcohol, is a flammable, colorless, slightly toxic chemical compound, and is best known as the alcohol found in alcoholic beverages. In common usage, it is often referred to simply as alcohol. Its molecular formula is variously represented as CH_3CH_2OH, C_2H_5OH or as its empirical formula C_2H_6O. An ethanol vapor gas sensor is a necessary component for the alcohol breath meter used to detect drunk drivers. The legal threshold of blood alcohol content is about 50 mg% for Thailand, according to local law. Similar prohibitions exist for drunk sailing. CuO is one of the materials which can be used to detect ethanol gas.

3.1 Literature review of CuO gas sensor

Kim and co-workers[21] grew CuO nanowires (NW) by the thermal oxidation of Cu foil at 400°C and gas sensors were fabricated by the deposition of a solution containing the CuO nanowires. At 300–370 °C, the sensor resistance increased upon exposure to 30–100 ppm CO. The gas sensor was contained within a quartz tube for the high temperature ambient atmosphere gas sensing measurements. Prior to the gas sensor measurements, the sensor within the quartz tube was heat treated at 600°C for 2 h in order to remove some organic content. The temperature of the furnace was kept at 400°C and the gas concentration was controlled by changing the mixing ratio of the parent gases (100 ppm CO, 5 ppm NO_2, and 100 ppm NO_2, all in air balance). Figure 3.1 shows (a) Sensor structure and (b) sensing temperature as a function of heater power. Figure 3.2 shows dynamic gas sensing response of CuO nanowires sensors toward CO and NO_2 at heater powers of 300 and 400 mW: (a) CO at 300 mW, (b) NO_2 at 300 mW, (c) CO at 400 mW, and (b) NO_2 at 400 mW. Figure 3.3 shows gas sensing transient of the CuO nanowires upon exposure to 5ppm NO_2 at 200, 300, and 400°C. Figure 3.4 shows Gas sensing transient to the emissions from a: (a) gasoline engine, 300 mW, (b) diesel engine, 300 mW, (c) gasoline engine, 400 mW, (d) diesel engine, 400 mW. The resistance of the CuO NW sensor increased upon exposure to 10–100 ppm CO at 300–370°C. By contrast, the NO_2 sensing characteristics were not simple and varied according to the NO_2 concentration. The resistance decreased upon exposure to 30–100 ppm NO_2 but increased upon contact with ≤ 5 ppm NO_2. This indicates that the interaction between the NO_2 and the surface oxygen changes with decreasing NO_2 concentration. The ability of this single gas sensor to increase its

resistance upon contact with CO and ≤ 5 ppm NO_2 provides a potential method for detecting the pollutant gases emitted from gasoline and diesel engines.

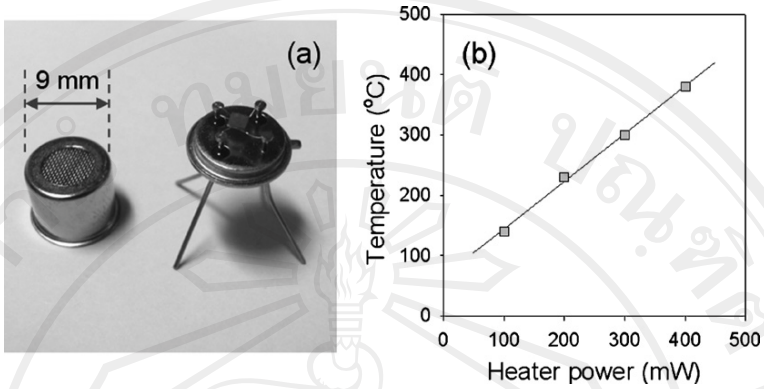

Figure 3.1 (a) Sensor structure and (b) sensing temperature as a function of heater power[21].

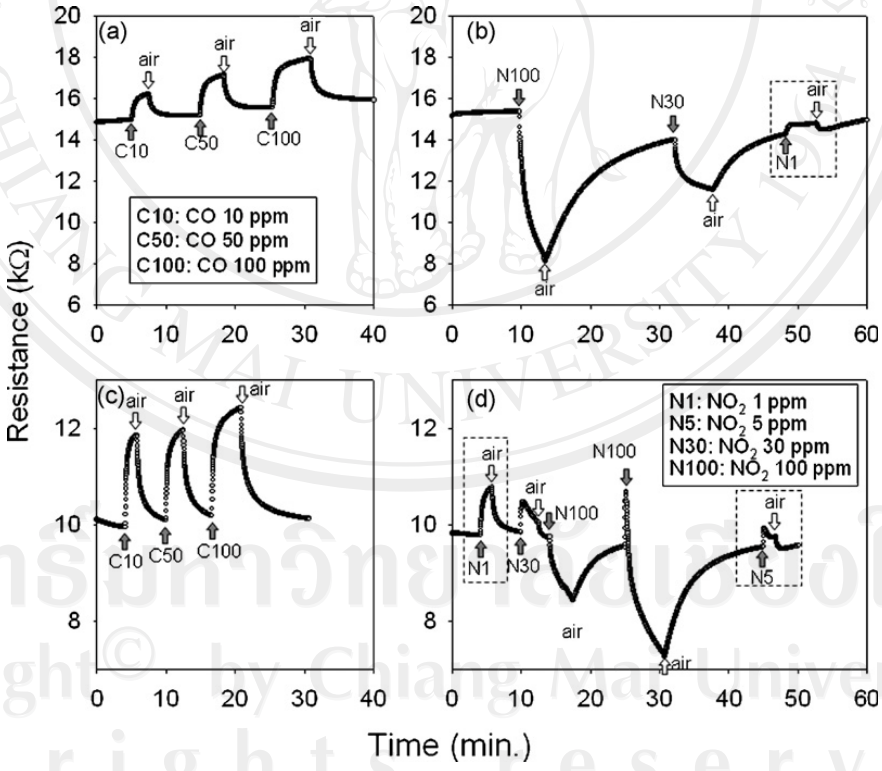

Figure 3.2 Dynamic gas sensing response of CuO nanowires sensors at heater powers of 300 and 400 mW toward: (a) CO at 300 mW, (b) NO_2 at 300 mW, (c) CO at 400 mW, and (b) NO_2 at 400 mW[21].

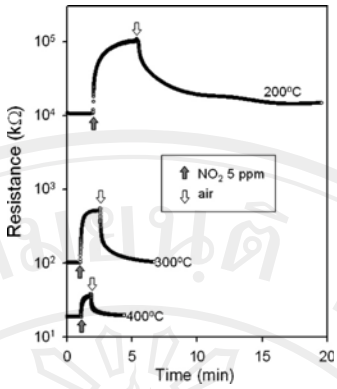

Figure 3.3 Gas sensing transient of the CuO nanowires upon exposure to 5 ppm NO_2 at 200, 300, and 400°C[21].

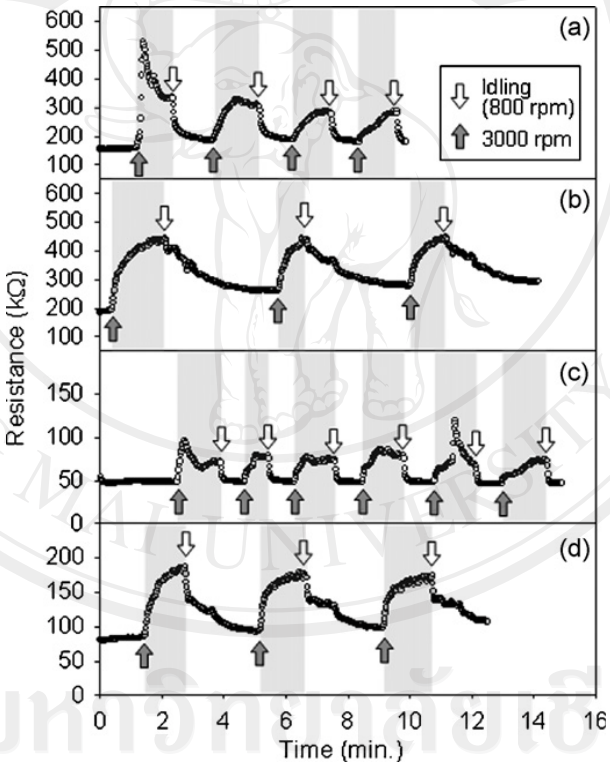

Figure 3.4 Gas sensing transient to the emissions from a: (a) gasoline engine, 300 mW, (b) diesel engine, 300 mW, (c) gasoline engine, 400 mW, (d) diesel engine, 400 mW[21].

Li and co-workers[22] reported the synthesis of CuO particles, CuO plates and their gas sensing properties for NO_2 and alcohol. The results show that the as-

synthesized CuO particles and plates have potential in the sensor application for NO_2 gas detection. The results showed that the as-prepared CuO behaved as a p-typed semiconductor. It was found that suitable operating temperatures for CuO plates to detect NO_2 and alcohol were about 200°C and 350°C, respectively. The sensitivity of CuO plates was better than that of CuO particles. This research suggested that the low-cost CuO plates had potential application to detect NO_2 with low energy consumption due to their good sensing properties and low operating temperature. Figure 3.5 shows conduct-metric response curves to 50 ppm NO_2 of gas sensors made of (a) CuO particles and (b) plates at different temperatures. Figure 3.6 shows curves of R_{air}, R_{gas} to 50 ppm NO_2 for gas sensors made of (a) CuO particles and (b) plates at different temperatures. Figure 3.7 shows typical response curves of gas sensors made of (a) CuO particles and (b) plates to NO_2 with different concentrations at 200°C. Figure 3.8 shows typical response curves of gas sensors with (a) CuO particles and (b) plates to alcohol with different concentrations at 350°C.

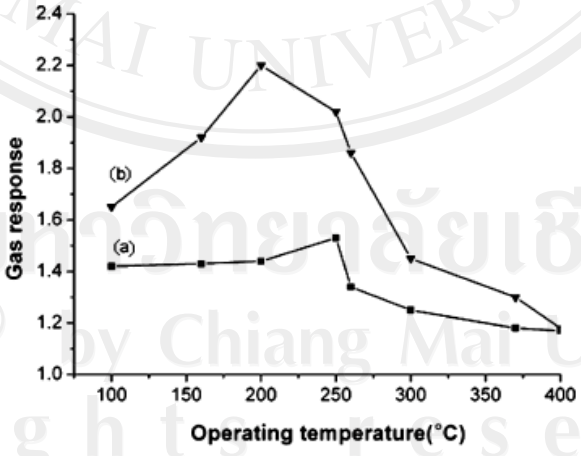

Figure 3.5 Conduct-metric response curves to 50 ppm NO_2 of gas sensors made of (a) CuO particles and (b) plates at different temperatures[22].

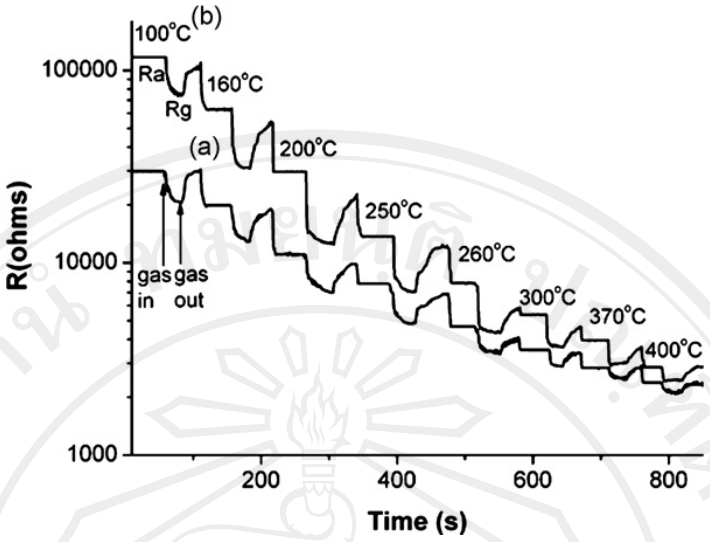

Figure 3.6 Curves of R_{sensor} to 50 ppm NO_2 for gas sensors made of (a) CuO particles and (b) plates at different temperature[22].

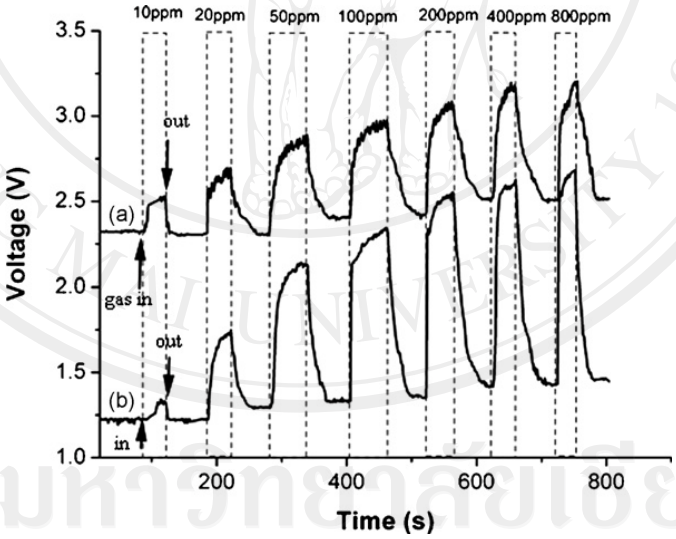

Figure 3.7 Typical response curves of gas sensors made of (a) CuO particles and (b) plates to NO_2 with different concentrations at 200°C[22].

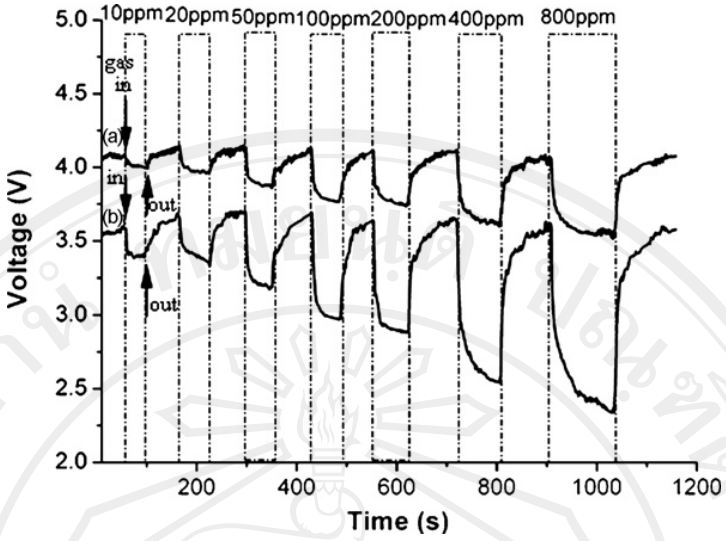

Figure 3.8 Typical response curves of gas sensors with (a) CuO particles and (b) plates to alcohol with different concentrations at 350°C[22].

3.2 Ethanol sensing properties of CuO nanowires

3.2.1 Preparation of CuO nanowires for ethanol sensing

CuO nanowires which were prepared by oxidation reaction of copper plate were separated from the copper plate for fabrication of an ethanol sensor as shown in Figure 3.9. It should be noted that the black plate (black product) substance was composed of CuO layered with CuO nanowires. The black plate was cut into a square shape with dimensions of 5×5 mm before silver paint was applied at the diagonal corners of the black square to be silver electrodes, sized 1×1 mm. A heater for the ethanol sensor was made from a nickel-chromium coil and wound around an alumina plate, resistance 80 Ω, and placed beneath the CuO plate. Finally, copper wires were attached to the silver electrodes for resistance measurement to complete the ethanol sensor.

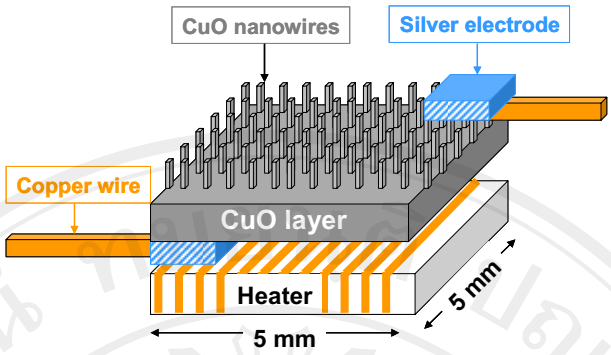

Figure 3.9 Schematic diagram of a sensor fabricated from CuO nanowires and a layer of CuO.

3.2.2 Experimental system for ethanol sensing properties

The sensor was put in the chamber and the ethanol simulator (figure 3.10) which can produce ethanol with concentration of 100, 200, 500 and 1000 ppm was heated to 34°C for propelling ethanol atmospheric to the chamber. The sensing properties were studied by recording the current in the range of μA, for an supplied voltage of 5 V and calculating the change of resistance from air to ethanol ambient for ethanol concentration of 100, 200, 500 and 1000 ppm, and at working temperatures of 200, 220, 240, 260 and 280°C. The response and the recovery characteristics were monitored and recorded via an interfaced personal computer. The schematic diagram of the ethanol sensing simulation is shown in figure 3.10.

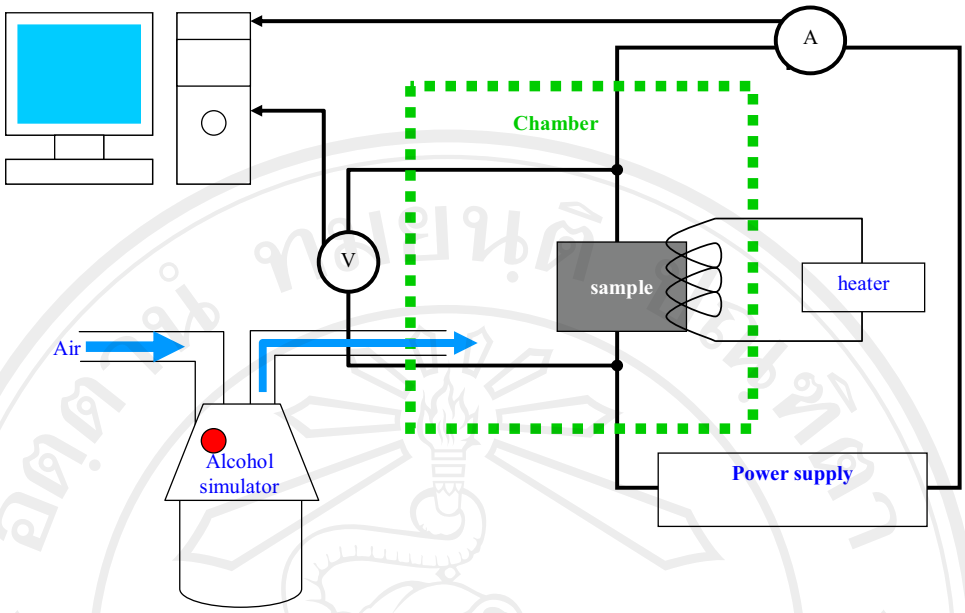

Figure 3.10 Schematic diagram of ethanol sensing simulation.

The ethanol sensing properties of the gas sensor based on CuO nanostructure was observed from the change of resistance under air and ethanol vapor atmosphere as shown in figure 3.11.

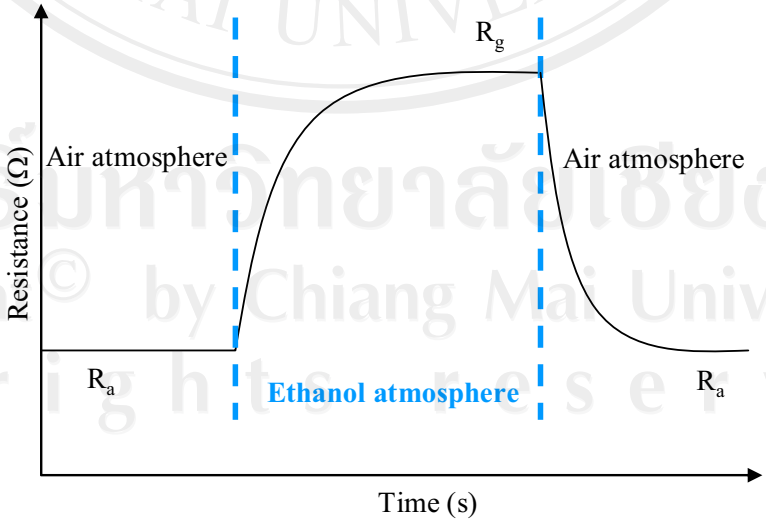

Figure 3.11 The typical resistance change of an ethanol sensor based on CuO nanostructure.

The electrical resistance of the sensor was steady in an ambient atmosphere (R_a is the electrical resistance of the sensor in air). The resistance of the sensor increased when ethanol vapor was injected into the chamber (R_g is the electrical resistance of the sensor in ethanol-air mixed gas) and the resistance decreased when ethanol vapor was removed.

The sensitivity, S_g, of the sensor is defined as the ratio of R_a and R_g. In addition, the sensitivity of the semiconducting oxide gas sensor can usually be empirically represented as

$$S_g = 1 + aC^b \tag{3.1}$$

where *C* represents ethanol concentration. The sensitivity *Sg* is characterized by the constants *a* and *b*. The value of the constant depends on the sensor material, the type of gas sensor is exposed and the working temperature. The value of the constant *b* is normally around either 0.5 or 1, depending on the charge state of the surface species. It was reported that for b of 0.5 the adsorbed surface oxygen species is O_2^- and for *b* of 1, the adsorbed surface oxygen species is O^-.

3.2.3 Ethanol sensing result for CuO nanowires

CuO nanowires fabricated as in 3.2.1 were tested as an ethanol sensor. Figure 3.12 shows the response and the recovery curves of a sensor based on CuO nanowires being exposed to an ethanol concentration of 1000 ppm at working temperatures of 200-280^{o}C. At the beginning, the measured resistance was steady in an ambient atmosphere. But when ethanol vapor was injected into the chamber, an increase of resistance was observed; and when ethanol vapor was removed out of the chamber, a decrease of resistance was observed. The increase of resistance under an ethanol vapor atmosphere is due to the p-type conductivity of CuO. It can be clearly seen

from Figure 3.12 that the characteristic of the sensor depends on the working temperature. It should be noted that the lower resistance of CuO nanowires at higher working temperatures is due to the common semiconductor property of CuO.

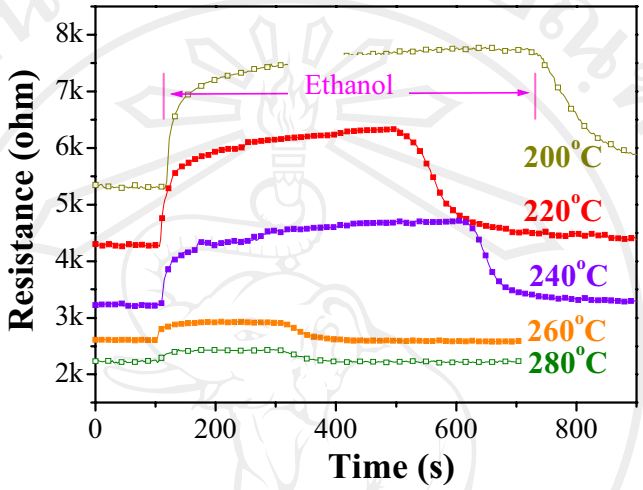

Figure 3.12 The response and recovery curves of a CuO nanowires sensor at an ethanol concentration of 1000 ppm, working at 200-280°C.

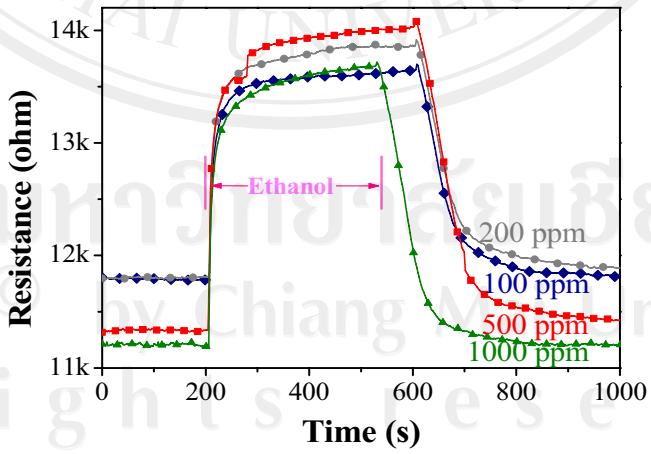

Figure 3.13 The response and the recovery curves of the CuO nanowires sensor at ethanol concentration of 100-1000 ppm working at 240°C.

The sensitivity of the sensor is defined as R_g/R_a. The sensitivity obtained for the CuO nanowire sensor at different working temperatures at the ethanol concentration of 1000 ppm is listed in Table 3.1. The highest sensitivity was obtained at the working temperature of 220 and 240°C, however the working temperature of 240°C shows shorter recovery time than 220°C, suggesting the optimum working temperature. In addition, the response time and the recovery time also depended on the working temperature in the range of 30-235 s and 60-245 s, respectively.

Figure 3.13 shows the response and the recovery curves of ethanol sensors based on a CuO nanowire sensor when exposed to an ethanol concentration of 100-1000 ppm at the working temperature of 240°C. It was found that the sensitivity only slightly depended on the ethanol concentration.

Table 3.1 The ethanol sensing properties of a CuO nanowire sensor at an ethanol concentration of 1000 ppm and a working temperature of 200-280°C.

Working temperature (°C)	**Steady resistance (R_g, Ω)**	**Ethanol ambient resistance (R_a, Ω)**	**Sensitivity**
200	5314	7749	1.4
220	4290	6302	1.5
240	3232	4690	1.5
260	2610	2925	1.1
280	2229	2428	1.1

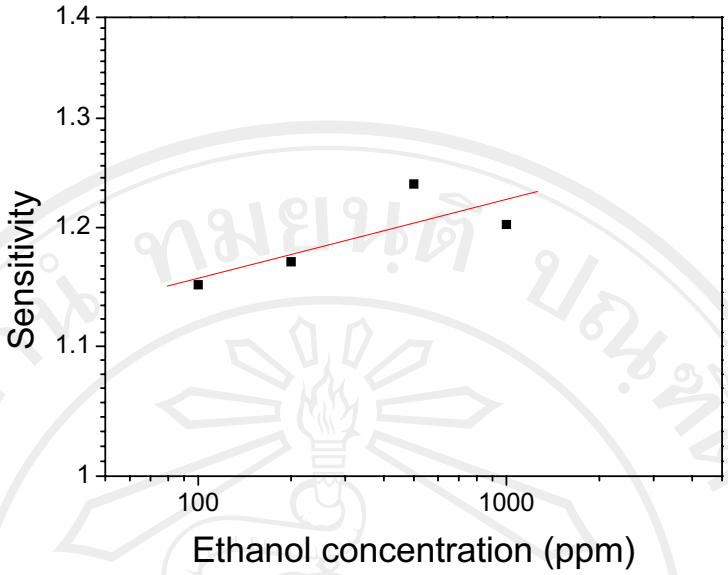

Figure 3.14 Log–log plot of gas response and ethanol concentration for CuO nanowires.

The plot of gas response and ethanol concentration from 100 to 1000 ppm for CuO is shown in figure 3.14. The logline graph shows a nearly linear line supporting Equation (3.1). This confirms that the CuO nanowires can be used as ethanol sensor.