CHAPTER IV

THE DEVELOPMENT OF GAS SENSOR FOR CARBON MONOXIDE MONITORING USING NANOSTRUCTURE OF Nb-TiO_2

4.1 Abstract

The development of titanium dioxide (TiO_2) as a gas sensor material for combustion and exhaust air pollutants monitoring is strongly dependent on its properties such as thermal stability, grain size and surface area. In this study, nanostructured TiO_2 with its thermal stability enhanced by niobium dopant (Nb-TiO_2) was synthesized using the water-in-oil (w/o) microemulsion system of n-heptane/water/sodium bis (2-ethylhexyl) sulfosuccinate (AOT) surfactant and was compared with undoped TiO_2. It was found that the synthesized powder was of uniform size (14 nm) and high surface area (80 m^2/g). Nb-doped TiO_2 at a level of 3-5 mole% clearly hinders the anatase to rutile phase transformation and inhibits the grain growth in comparison with pure TiO_2. The nanostructure of anatase was maintained even after the powder was fired at 850°C. The results indicate that sensitivity of CO is significantly increased with an increase in the thermal stability of Nb-doped TiO_2 in comparison with that of undoped TiO_2 and thus is useful for CO sensing studies at high temperatures.

4.2 Introduction

The monitoring of toxic and flammable gases has become more important in both domestic and industrial environments. The development in this specific application requires reliable and inexpensive gas sensors. Typically, the metal oxides have been of interest for solid-state semiconductor gas sensors due to their high sensitivity to pollutant gases, small size and low cost. Among metal oxides; TiO_2 is very interesting because of its ability to monitor both indoor and outdoor air quality [1-4, 16-17].

The performance of TiO_2 as a gas sensor depends on many important factors such as the grain size, size distribution, microstructure, intrinsic properties and

crystallographic phase. Typically, TiO_2 has three crystallographic phases: brookite, anatase and rutile. The different structures influence the sensing properties. The most sensitive phase for gas sensing is found to be anatase. However, anatase can easily and irreversibly convert to the rutile phase at about 600°C. In exhaust air pollutants monitoring, TiO_2 as a gas sensor has to be operated at high temperatures necessary to reach equilibrium between the oxygen in the bulk and that in the gases in the environment. Accordingly, the phase transformation from anatase to rutile can cause a drastic decrease in sensor sensitivity. Beside the effect of phase transformation (thermal stability), sharp increase in sensitivity are expected when the grain size becomes smaller than the space-charge depth. Thus, maintaining the nanostructure of TiO_2 films in the anatase phase at high temperatures is found to be an effective way to increase the sensitivity of gas sensor for exhaust gas sensing applications [4-6, 12-15]. In this study, we have focused on synthesis of the nanostructured TiO_2 gas sensor with Nb as a dopant to enhance the thermal stability for CO monitoring. Nanostructured pure and Nb-doped TiO_2 were synthesized by a microemulsion system of *n*-heptane/water/NaCl/ sodium bis (2-ethylhexyl) sulfosuccinate (AOT). The physical properties, the thermal stability and microstructure of these TiO_2 powders were characterized. The effect of thermal stability on CO gas sensing was studied by measuring the electrical response in laboratory tests.

4.3 Experimental

4.3.1 Nano Size TiO_2: Preparation and Characterization

Pure TiO_2 was prepared by a microemulsion technique according to a procedure described in a previous work [7]; 10 g of the aqueous solution of 0.3 M $TiCl_4$ was added to 90 g of 6 wt% AOT in n-heptane solution with rapid stirring. After thorough mixing, the solution was equilibrated at 30°C for 2 h. For Nb-doped TiO_2, the procedure was slightly modified by adding $NbCl_5$ in the aqueous phase before mixing. The resulting microemulsion was stable and separated for precipitation, which was carried out by bubbling air through concentrated NH_4OH solution into the microemulsion. The as-synthesized TiO_2 was separated by high-speed centrifugation at 10,000 rpm. Then, it was washed sequentially with *n*-heptane,

twice with ethanol and acetone and finally with water to remove the remaining surfactant from the as-synthesized particles. The as-synthesized TiO_2 was dried and calcined for 5 h at various calcinating temperatures. After that, the characterization of the microstructure of the TiO_2 powders was carried out by XRD, BET and TEM.

4.3.2 Microstructural Analysis of Thick Film Sensor

After calcination at 460°C, the TiO_2 powder was formed into a thick-film sensor. Thick-film sensors were fabricated using pastes obtained by adding each powder with an organic vehicle. The pastes were painted on an alumina substrate with an activated Au electrode. The sensor was fired in air at temperatures ranging from 550-850°C and subsequently characterized by XRD. The gas sensing characteristics were examined by fixing the concentration of CO at 1000 ppm and the operating temperature at 550°C. The gas-sensitive electrical response of the films was measured. The sensitivity was defined as the ratio of R_{air}/R_{gas} where R_{air} and R_{gas} are the resistance in air and gas exposure, respectively. After gas was applied to the flow system, the oxidizing CO caused a dramatic decrease in resistance of the TiO_2. As a result, a sudden increase in current can be detected. A step response was observed by switching the flow from air to gas and gas to air.

4.4 Results and Discussion

4.4.1. Nano-Sized TiO_2 Characterization

The effect of calcination temperature on the nanostructure of TiO_2 was studied at various temperatures from 450°C to 850°C. TEM observations showed that both Nb-doped and pure TiO_2 powder had uniform morphology in the anatase structure (plane 101) with the characteristic d-spacing of 3.52 Å after heating to 450°C (Fig. 4.1(a)-(b)). However, when the temperature was increased up to 850°C, the undoped TiO_2 showed the presence of both anatase and rutile structure, while Nb-doped TiO_2 was still maintaining the anatase structure. The HR-TEM (Fig. 4.1 (c)) shows the Nb-stabilized anatase structure (plane 101) at 850°C. The average grain size of pure TiO_2 and Nb-doped TiO_2 was about 20 and 14 nm, respectively.

The effect of calcination temperature on the surface area and grain size was investigated. Fig. 4.2 shows the average grain size of powder and specific

surface area as a function of calcination temperature. The pure TiO_2 exhibited large grain growth and a drastic drop of specific surface area, whereas grain coarsening of the Nb-doped TiO_2 was negligible. This indicated that the Nb addition can inhibit the grain growth while maintaining high specific surface area of the powder.

The effect of temperature on the phase transformation from anatase to rutile of pure and Nb-doped-TiO_2 was studied by varying the calcination temperatures from 550°C to 850°C. XRD results agreed well with TEM observation showing a significant increase of the amount of rutile structure with an increase of firing temperatures for pure TiO_2. At 850°C, more than 90% of rutile structure was obtained (Fig. 4.3). In case of Nb-TiO_2, the atomic ratios of Nb to Ti were varied from 1 to 5%. The pure anatase phase was obtained even if the calcining temperature was increased up to 850°C (Fig. 4.4). This might be due to Nb^{+5} substituting for Ti^{+4} in the crystalline lattice [6, 13-15]. Doping may either hinder or anticipate the antase-to-rutile transformation. Moreover, Nb not only hindered the phase transformation but also prevented exaggerated grain growth, which was shown previously by TEM. Thus, 3% Nb-TiO_2 was the optimum loading and was used in further work as indicated in the CO gas sensing section.

4.4.2. Microstructure Analysis of Thick-Film TiO_2 Sensors

The sensors were prepared from a powder of pure TiO_2 and 3% Nb-doped TiO_2 powders. The films were fired at different temperatures varied from 650°C to 950°C. The heat conduction through the alumina substrate during the firing process for sensor preparation may accelerate the phase transformation differently in the calcination process. Thus, the effect of firing temperatures on the phase transformation from anatase to rutile structure of TiO_2 on the alumina substrates was studied again to confirm the crystallographic phases by XRD-thin film mode. The results are shown in Fig 4.5. After subtraction of the alumina substrate peaks, the percentages of anatase and rutile structures were calculated. The results showed an improvement in thermal stability. The transformation temperature from anatase to rutile structure was increased in the presence of 3 % Nb doping. At 850 °C, the Nb-TiO_2 was still in pure anatase structure.

4.4.3. Gas-Sensitive Electrical Response of Thick Films

4.4.3.1 CO response

The TiO_2-based films with and without Nb doping were tested as gas sensors at 550°C with 1000 ppm of CO. The ratio of R_{air}/R_{gas} sensor response was reported as sensitivity.

4.4.3.1.1 Sensor response of pure TiO_2

Fig. 4.6 shows the sensor response to 1000 ppm CO when firing temperatures were varied from 550°C to 850°C. The best gas response on CO was obtained when a sensor film was fired at 650°C. This might be due to the presence of nanostructured TiO_2 with a high percentage of anatase when it was fired at moderate temperatures (650°C). However, at higher temperatures (850°C), the phase transformation from anatase-to-rutile was accelerated. Moreover, grain growth (150 nm) occurred resulting in a drastic drop in surface area (37 m^2/g). When firing at low temperature (550°C), the nanostructure in the anatase phase was retained but the electrical response was low. This is possibly due to the insufficient heat providing poor adhesion between the film and electrodes with a resulting poor signal.

4.4.3.1.2 The effect of Nb-doping on TiO_2 sensing properties

For Nb-TiO_2 (Fig. 4.7), there is obviously an effect because Nb enhanced thermal stability. The existence of the anatase phase at high temperature results in a better electrical signal of the film on CO. Moreover, the resistance of the film was 10 times lower than that of the pure TiO_2. At 650°C, the Nb-TiO_2 was not in fully crystalline structure. When the firing temperature was increased, crystallinity in the anatase phase improved with average grain size of 10 to 15 nm and the specific area about 70 to 80 m^2/g. An increase in thermal stability resulted in a better CO response at 950°C. Thus, Nb doping is effective in both keeping the grain size at the nanometer level and improving CO response due to anatase phase stabilization.

In order to explain clearly the effect of thermal stability, the sensitivity of the film both with and without Nb doping TiO_2 with varied calcination temperatures was correlated with the percentage of anatase structure, as shown in Fig. 4.8. Nb-TiO_2 which had the highest percentage of anatase, stabilized at high temperatures, showed the best sensitivity at about 2.2. The pure TiO_2 which almost turned to the rutile structure at the firing temperature of 850°C

clearly showed a drop in sensitivity. The result clearly indicated improved sensitivity with an increase in thermal stability of a thick film.

4.5 Conclusion

Thermally stability, nanostructured niobium doped TiO_2 (Nb-TiO_2) was successfully synthesized using the water-in-oil (w/o) microemulsion system of n-heptane/water/sodium bis (2-ethylhexyl) sulfosuccinate (AOT) surfactant. It was compared with undoped TiO_2. It was found that the Nb doping at 3-5 mole% clearly hinders the anatase-to-rutile phase transition of TiO_2 and inhibits the grain growth. The nanostructure of anatase could be maintained even after the powder was fired at 850°C. In a CO sensing study, it was found that the sensitivity of CO is significantly increased with an increase in the thermal stability of Nb-doped TiO_2. This shows that nanostructured Nb-doped TiO_2 is promising for environmental monitoring.

4.6 Acknowledgements

I would like to thanks the following people and organizations; The Thailand Research Fund (TRF) for financial support, The National Metal and Materials Technology Center (M-TEC) and Dr. Angkhana Jaroenworaluck for TEM photographs, Professor Harold Wittcoff, Dr. Elisabetta Di Bartolomeo, Dr. Maria Luisa Grilli and all the people in sensor laboratory at The University of Rome "Tor Vergata" for help and support.

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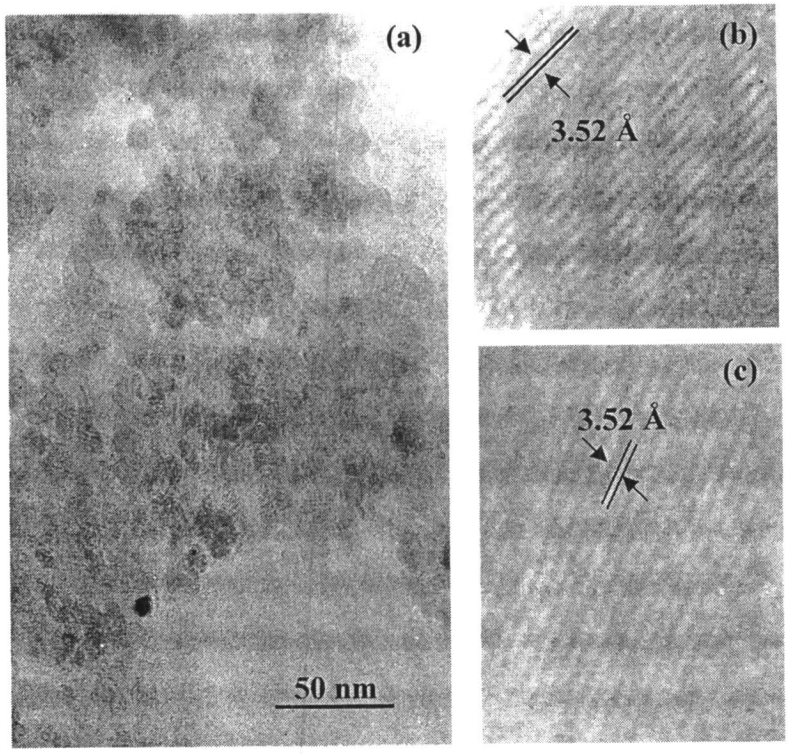
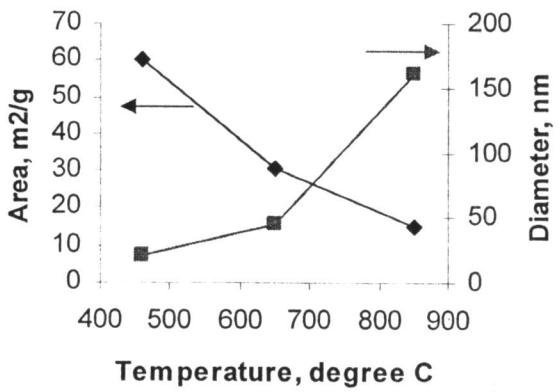
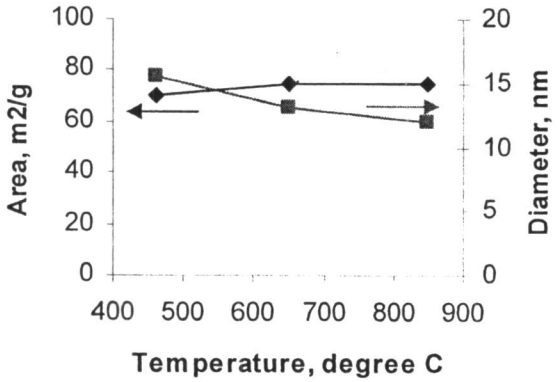


Figure 4.1 TEM image of TiO_2 powder calcined at 450°C (a), the HR-TEM of anatase structure (plane 101) of pure TiO_2 calcined at 450°C (b) and 3 % Nb-doped TiO_2 calcined at 850°C (c).



(a) undoped-TiO_2



(b) 3 % Nb-TiO_2

Figure 4.2 The effect of calcination temperature on average specific surface area and crystal size of powders.

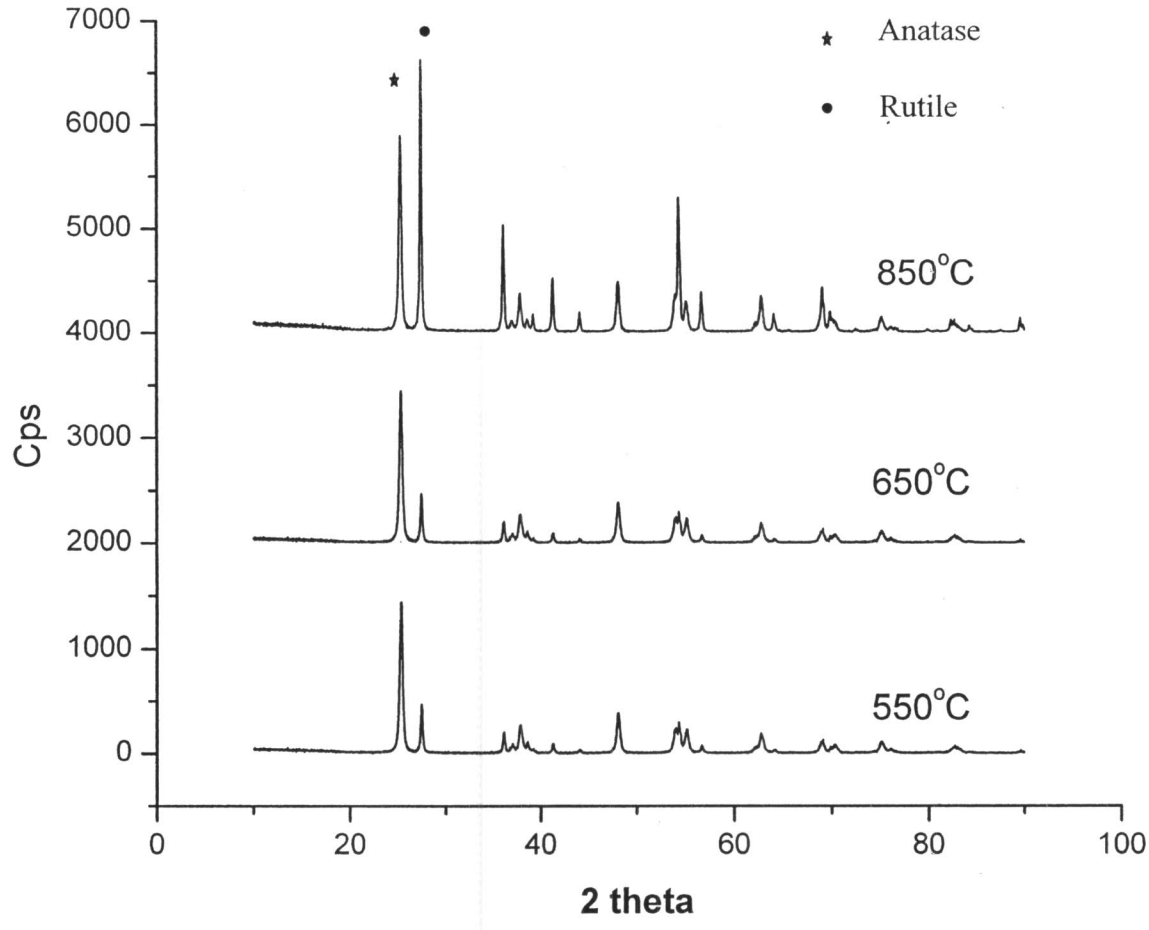


Figure 4.3 XRD pattern of pure TiO_2 with various calcination temperatures from 550°-850°C.

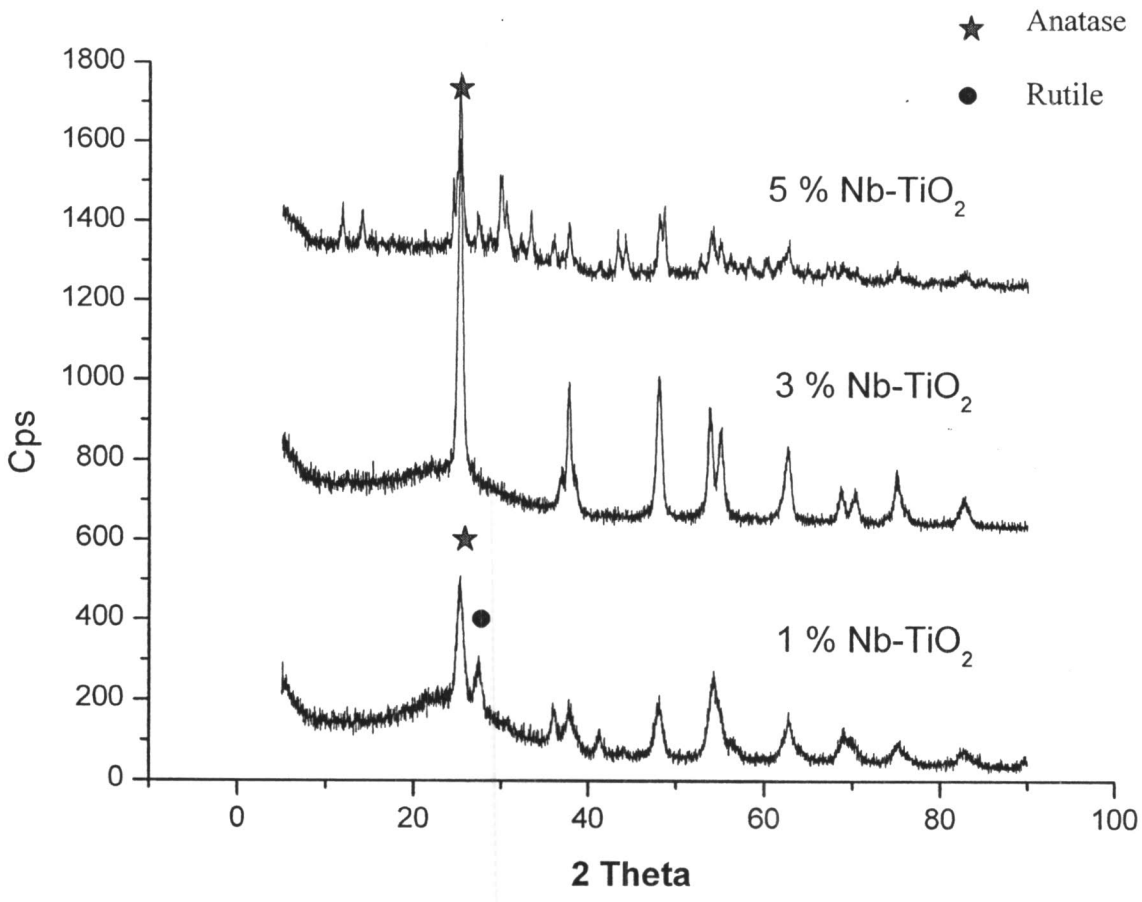


Figure 4.4 XRD pattern of Nb-doped TiO_2 at calcination temperature of 850°C.

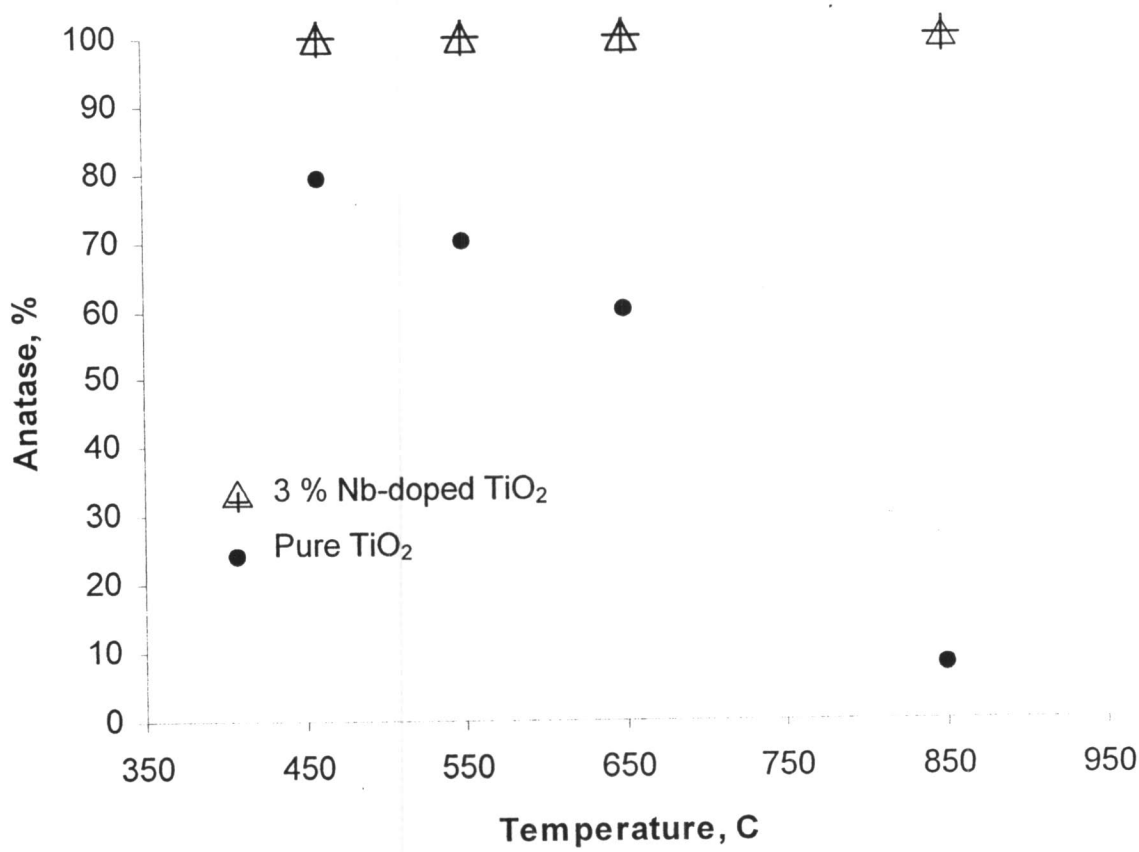


Figure 4.5 Effect of firing temperatures on a transformation from anatase to rutile structure of thick film sensors.

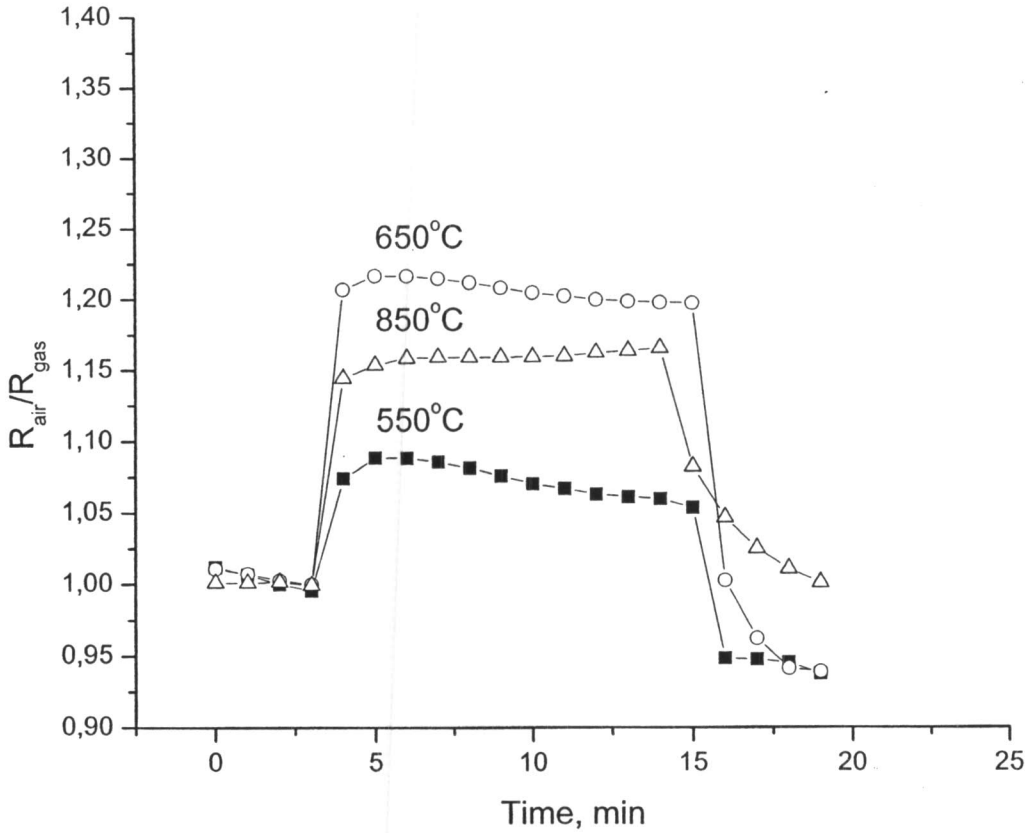


Figure 4.6 Sensor response to CO (1000 ppm) at an operating temperature of 550°C from the pure TiO_2 at firing temperatures from 650-850°C.

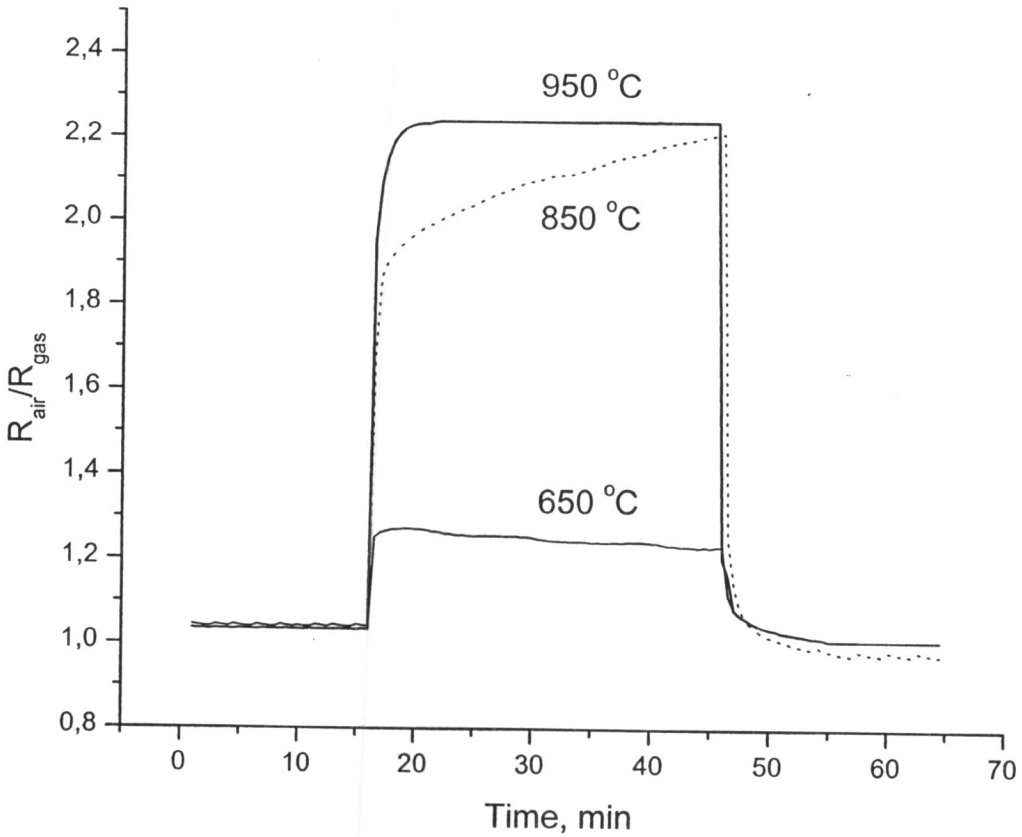


Figure 4.7 Sensor response to step of CO (1000 ppm) of 3% mole Nb-TiO_2 at the operating temperature of 550°C with firing temperatures from 650-950°C.

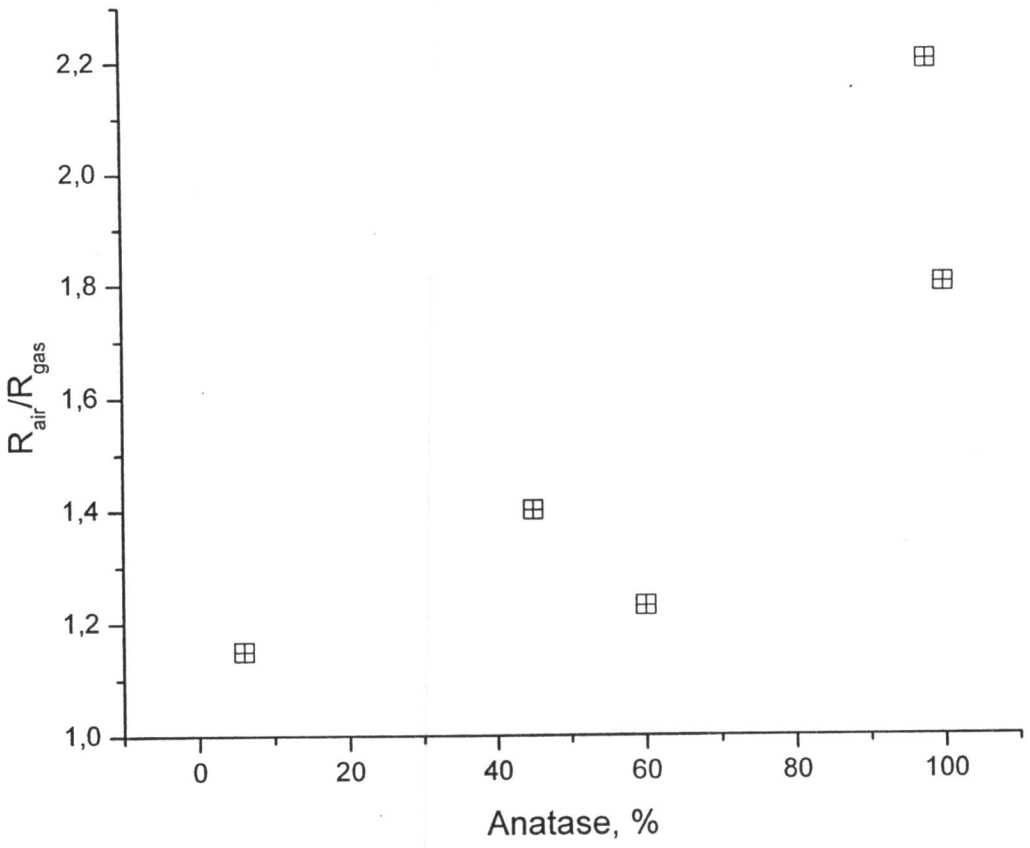


Figure 4.8 Effect of stability of anatase phase on sensitivity of CO (1000 ppm) at the operating temperature of 550°C.