Temperature effect on the H_2 Sensing Properties of Simonkolleite Nanoplatelets: Sensor Application

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Abstract. In this work, simonkolleite nano-particles were synthesized using aqueous solution by a moderate temperature solution process in view of their potential H_2 gas sensing properties. The structural properties of the platellets-like $Zn_5(OH)_8Cl_2{\cdot}H_2O$ were characterized by powder X-ray diffraction, energy dispersed X-ray spectroscopy, as well as attenuated total reflection infrared spectroscopy. The operating temperature was found to play a key role on the H_2 sensing properties of the simonkolleite nano-plettelets. The results on the sensitivity and response time as per comparison to earlier reported ZnO based sensors are indicated and discussed.

1. Introduction

Hydrogen and fuel-cell technologies are believed to be the energy solutions for the twenty-first century, enabling clean, efficient production of power and heat from a range of primary energy sources. The transition to a future "hydrogen economy" is expected to reduce dependency on oil and gassubstantially, and reduce carbon dioxide emissions. However, H_2 is a hazardous, odourless and highly inflammable gas and it is necessary to detect its leakage. A reliable and inexpensive sensor that can take advantage of nanoscale to detect hydrogen leakages is the focus of many research groups worldwide [1]. A low resistance material has lower driving power when it is used as a sensor. The sensitivity and response time of ZnO based sensors strongly depend on the porosity of the material [2]. As in the case of ZnO, the oxygen vacancies on $Zn_5(OH)_8Cl_2 \cdot H_2O$ surface should be electrically and chemically active. Hence one could expect that these vacancies would function as n-type donors as well in the case of the simonkolleite; and hence significantly increase its conductivity. The gas sensing mechanisms normally accepted for semiconductor gas sensors assume that the oxygen adsorbed on the surface of the oxide removes some of the electronic charges and thus decreases the material's conductivity. When reducing gas molecules come into contact with this surface, they may interact with these oxygens, leading to inverse charge transfer [3]. Upon the return of the electrons to the conduction band, conductivity increases. In this study and as per comparison to the ZnO nano-platellets [4], pressed films of nano/micro simonkolleite plaletellets were placed between Cu interdigitazed electrodes. The change in the pellets' resistance was carried out in 200ppm of H_2 gas at various temperatures ranging from 150 to 350°C. Both the sensitivity and response time on simonkolleite as per comparison to the earlier reported ZnO based sensors are discussed.

2. Experimental techniques

A solution containing zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), sodium chloride (NaCl) and hexamethylenetetramine ($C_6H_{12}N_4$, HMT) was used for deposition of simonkolleite plate-like structures. A bottle 100ml with autoclavable screw cap was filled with an equimolar (10^{-1} M) aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$, HMT and NaCl. The reaction solution was about 100ml. Subsequently a piece of cleansed glass substrate, with alcohol and deionised water, was immersed in the solution and heated at a constant temperature at 85°C for 24h in a regular laboratory oven. Finally, the thin film was thoroughly rinsed with deionized water to eliminate residual salts, and dried in air at the same temperature used in the oven. Powder X-ray diffraction "XRD", with $CuK_{\alpha 1}$ radiation (D8 advance Bruker X-ray diffractometer, λ=0.154060 nm at 40 kV and 40 mA), was used to investigate the surface morphology and structural properties of ZnO. Furthermore; infrared attenuated total reflection spectrophotometry was used to confirm the simonkoleitte phase structure. The gas sensing sensors based on simonkolleite nano-micro platellets were fabricated. The gas sensor was put in a cylindrical gas flow chamber with 10 cm in diameter, 15 cm in height fabricated with Cu electrodes at each end of the tube with a coil heater inserted into the tube. The gas sensor was put in a cylindrical gas flow chamber and allows the concentration of 200 ppm hydrogen gas with work temperatures from 150°C to 350 °C to pass through the chamber. The H_2 gas sensing properties were recorded using a computer controlled gas sensing characterization system. The relative concentration of the H_2 gas was measured using pre calibrated gas flow meters.

3. Results and discussion

3.1.X-Rays diffraction investigations

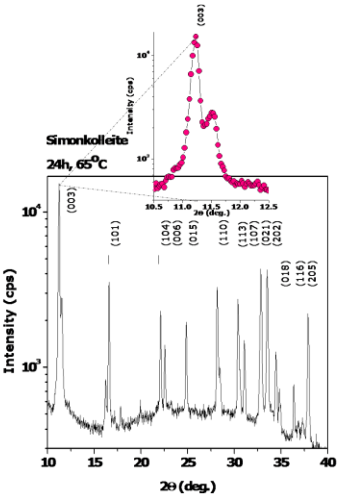

Figure 1. XRD pattern of the simonkolleite product prepared at 85°C for 24h .

The characteristic XRD spectrum of the as-synthesized product is shown in Figure 2. The Rieveldt treatment and the identification of all Bragg diffraction peaks confirmed that the crystallographic phase of the nano/micro platellets is ascribed to pure rhombohedral simonkolleite (ICSD No. 07-0155) with lattice constants <a> and <c> of about ~6.337 Å and ~23.643 Å, respectively and space group $R\bar{3}m$. The XRD analysis shows that all simonkolleite films have a strong preferential orientation along (003). The corresponding angular position of about $2\Theta_{\square 003)}$~11.25 is related to the highly ordered reticular plans characterized by an inter-reticular distance d_{003} ~ 7.881. In view of the intensity of this (003) Bragg peak for all samples, and as in the simonkolleite bulk crystals, one can conclude the lamellar structure of the synthesized simonkolleite nano/micro platellets too. This might be inferred that high concentration of chloride ions favors the formation of the lamellar simonkolleite structure.

3.2. Energy dispersed X-ray spectroscopy and infrared attenuated total reflection investigations

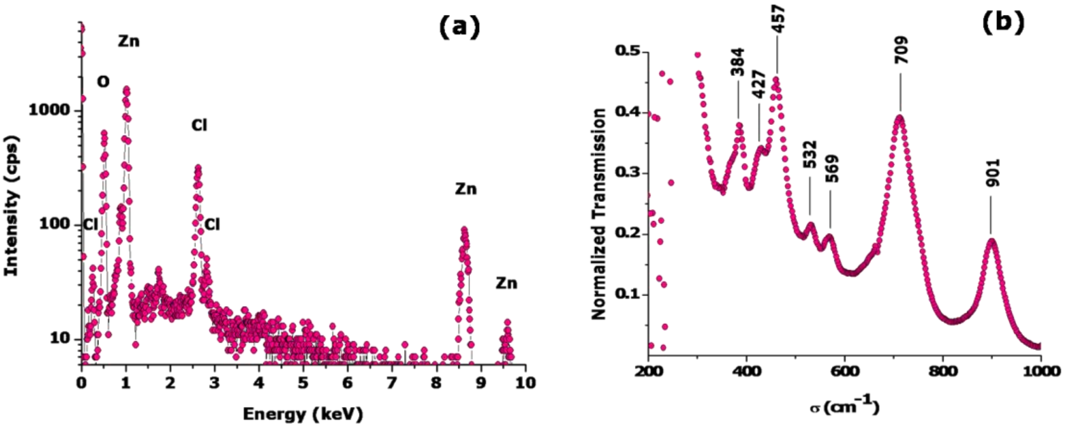

Figure 2. Energy dispersed X-ray spectroscopy (EDX) **(a)** and infrared attenuated total reflection ATR spectra **(b)** of as-prepared simonkolleite plate-like at 85°C for 24h

The electron dispersion X-rays analysis data taken from the various samples indicate the presence of Zn, O and Cl as illustrated in Figure 3. To concur again with both XRD and EDAX investigations on the purity of the simonkolleite nature of the nano/micron platellets, infrared attenuated total reflection "ATR" studies were performed. The ATR investigations were carried out in the spectral region of 4000-300 cm^{-1} focusing on OH stretches and OH librations as well as Zn-OH modes proper to the simonkolleite. The room temperature investigations were carried out on a Bruker model unit. Figure 4 reports a typical infrared attenuated total reflection spectra of the prepared plate-like $Zn_5(OH)_8Cl_2 \cdot H_2O$ samples. Besides the strong band due to deformation vibration of H_2O molecules at 1626 cm^{-1}, and an absorption band centered at 3445 cm^{-1}, characteristic of O-H stretching vibration, specific bands at lower wavenumbers are observed. The bands are due to various stretching vibration modes of chloride ion [5-7]. More accurately, and according to the structural data, hydrogen bonds are formed between the H_2O molecules (H bond donors) and the OH groups (H bond acceptors) in $Zn_5(OH)_8Cl_2 . H_2O$. The hydrogen distances are reported to have values of 2.87 and 3.10Å. The sharp bands on the higher frequency side of the spectrum "3588 and 3570 cm^{-1}" are attributed to v_{OH} of the two OH groups and those at 3495 and 3455cm^{-1} to the strech modes of H_2O. The bands at 901 and 709 cm^{-1} are assigned to ZnOH librations and those below 620cm^{-1} to lattice modes. The bands in the region below 600cm^{-1} , i.e. at 569, 532, 457, 427 and 384 cm^{-1} are attributed to translational modes of the Zn-O bonds.

3.3. gas sensing investigations

Schematic representation of the contact between the Cu electrodes and the simonkolleite sample in a cylindrical gas flow chamber connected to a cell is shown in Figure (5a). The gas sensitivity S was determined by the relative resistance, [(*R*air–*R*gas)/*R*air], where *R*air is the resistance of the sensor before passing the gas and *R*gas that after passing it. Systematic gas sensing studies were made on simonkolleite thin films, prepared at 85^{O}C, using Cu contacts. It is well known that the sensitivity is mainly determined by the dimensions of the microstructures. Figure 5(b) summarizes the typical responses of the sensor upon exposure to a gas concentration of 200 ppm H_2 and temperature of operation. Crystallite size and the gas concentration are constant while the operating temperature is varied. The sensitivity of the sample is calculated and traced as a function of operating temperature as shown in Figure 5(c). The sensitivity increases with an increase with temperature until the saturation at 300^{O}C (max. value of 67%). The latter sensitivity is even higher than the one operated at temperatures above 300^{O}C, as illustrated in Figure 5(c).

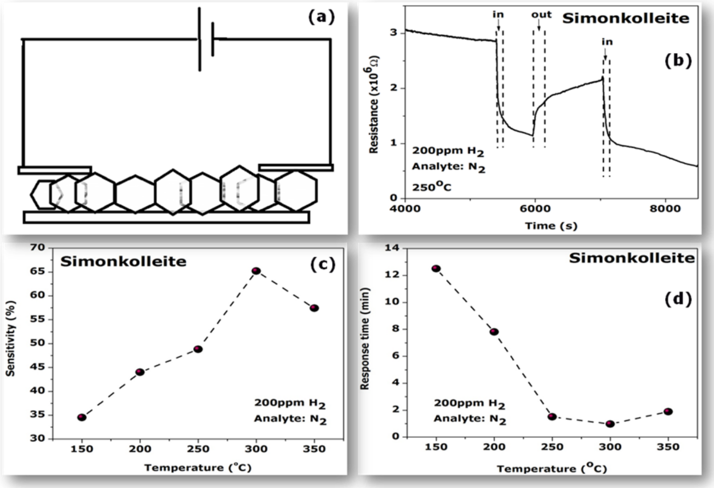

Figure 3. Schematic representation of the contact between the Cu electrodes and simonkolleite sample **(a)**, responses of the sensor upon exposure to a gas at 200 ppm H_2, and 250^{o}C **(b)** the sensitivity and response time as function of operating temperature

Figure 5(d) shows the response time as a function of operating temperature. The response time, similarly with the recovery time, decrease linearly with the increase in temperature until at 250 ^{O}C. At 250 ^{O}C and above, the response time and recovery time are 90 seconds and 180 s, respectively (Figure 5(d)). These fast responses might be due to high polarity in plate-like structure of simonkolleite sample used. As compared to ZnO with the response time and recovery time; 200 and 800s, respectively [8], simonokolleite sample has lesser response and recovery time. Moreover, the sensitivity of the 50nm diameter ZnO nanorod-arrays reaches the maximum value of 8.5 at 250^{o}C, which is around four times higher than the maximum sensitivity of the 500nm diameter arrays achieved at 350^{o}C [8]. Compared to the maximum sensitivity of simonkolleite achieved at 300 ^{o}C, simonkolleite sample is higher than the maximum sensitivity of the 500nm diameter ZnO and comparable with the 50nm diameter ZnO nanorod-arrays. It is also several times higher than the sensitivity of ZnO films operated at temperatures from 300 to 400 ^{o}C [9]

3. Conclusions

In this paper, we reported on the first time synthesis of simonkolleite nano-platellets for H2 gas sensing applications at low temperatures and low H_2 concentrations. All used probing techniques, i.e. ATR, XRD and EDAX confirmed the existence of the simonkolleite phase and its purity. The H_2 gas sensing characteristicsfor 200 ppmH_2 are: response time and recovery time are 90 seconds and 180 s, respectively t 250 ^{O}C and above.

The next step will be that of doping this material with palladium in order to enhance the sensitivity at room temperature with less concentration of hydrogen gas, 2ppm and a response time of less than 1 min.

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