CHEMICAL SENSORS BASED ON PULSED LASER DEPOSITED MOLECULAR SIEVES

Mary E. Gimon-Kinsel and Kenneth J. Balkus, Jr.
Department of Chemistry, The University of Texas at Dallas
Richardson, Texas 75083-0688 USA

ABSTRACT

Films of microporous and mesoporous molecular sieves were generated using pulsed laser deposition followed by a brief post hydrothermal treatment. Specifically, films of MeAPO-5 such as CoAPO-5 and Nb-TMS1 were made and subsequently used as the dielectric phase in capacitive-type chemical sensors. The capacitance change of mesoporous Nb-TMS1 based devices to the relative moisture in their environment makes them useful as potential humidity sensors. The CoAPO-5 based chemical sensors were evaluated for the detection of N_2 , CO and CO_2 .

INTRODUCTION

Molecular sieves comprise a class of low density metal oxides which possess highly organized one-, two- or three-dimensional pores and/or cage-like structures. The size and shape of the pores allow molecules to be discriminated based on steric properties; molecules of similar size can be differentiated based on polarity and acid/base properties. Numerous applications for these selective absorbents as sensors can be envisioned ranging from optical to mass sensitive and capacitive-type devices. These devices would benefit from the fabrication of thin films of molecular sieves.

We have developed a method for molecular sieve thin film generation which utilizes pulsed laser deposition (PLD) and a brief post hydrothermal treatment. This technique has been applied to a variety of porous metal oxide compositions some of which require a sensitizer. We refer to this modification as guest assisted laser ablation (GALA) [1]. We have demonstrated that PLD can be employed to generate thin films of microporous molecular sieves such as UTD-1 [2] and aluminophosphate molecular sieves including $AlPO_4-5$ and MeAPO (Me = V, Mn and Mg) [3, 4]. Thin films have been deposited on a variety of substrates including silicon, platinum, titanium nitride (TiN), indium-doped tin oxide (ITO), Mylar and glass. Parallel plate capacitors have been fabricated from these molecular sieve films. The absorption of small molecules (eg., CO, N_2 , H_2O , CO_2 and NH_3) result in large changes in capacitance which readily allow for the discrimination and detection of such gases at the ppm level.

Recent results for PLD of the microporous molecular sieve CoAPO-5 (pore size 7 Å) and the mesoporous molecular sieve Nb-TMS1 (pore sizes 22-33 Å) will be presented. The CoAPO-5 molecular sieves has an AFI framework topology, and the Nb-TMS1 consists of a hexagonal mesostructure (see Figure 1). This is the first time mesoporous films have been made using this laser deposition technique. The Nb-TMS1 is interesting because it possesses semiconductor properties which might be exploited in electronic devices. Results for the capacitance change of Nb-TMS1 response indicate that they are potential humidity sensors. Preliminary results using CoAPO-5 devices will also be presented.

Figure 1. (a) AFI framework structure of CoAPO-5 viewed along the 001 direction (b) hexagonal mesostructure of Nb-TMS1.

EXPERIMENTAL DETAILS

Molecular Sieve Synthesis. The transition metal oxide mesoporous molecular sieve Nb-TMS1 (pore size 22 Å) was synthesized according to the published procedure. [5] A typical preparation of the synthesis gel involved the mixing of niobium (V) ethoxide (CHEMAT Technology, Inc.) and dodecylamine (Aldrich) with a molar ratio 1:1.25. The resulting mixture was heated at 50°C for approximately 1 minute, then 10 mL ethanol followed by 10 mL deionized water were added which resulted in the precipitation of a white solid. The solid was aged in the supernatant for 72 hours. The white solid and supernatant were loaded into a 23 mL Teflon lined stainless steel autoclave and heated for 24 hours at 80°C, 24 hours 100°C, followed by 7 days at 180°C. The white product was isolated by suction filtration, washed with deionized water, ethanol and diethylether and dried overnight at room temperature.

The microporous metal substituted molecular sieve CoAPO-5 was synthesized according to the published procedure. [6] Briefly, the initial synthesis gel was made by combining 1.56 g of CoSO_4 with 1.8 mL of 85% phosphoric acid in 10 mL of deionized water. 2.08 g of $\text{Al}(\text{OH})_3$ (83.34%) was added to the cobalt phosphoric acid solution and stirred until homogeneous. 2.9 mL of triethylamine (TEA) was added to the cobalt phosphoric acid gel and stirred for 1 hour and had a reactant molar ratio of 1.5 TEA:0.8 Al_2O_3 :1 P_2O_5 : 40 H_2O :0.4 CoO . The gel was transferred to a Teflon lined stainless steel autoclave and heated under static conditions at 200°C for 20 hours. The deep blue CoAPO-5 crystals were centrifuged, washed with deionized water and dried at room temperature.

Pulsed Laser Ablation and Post Hydrothermal Treatment of Films. An illustration of the PLD and post hydrothermal treatment of laser deposited molecular sieve films is shown in Figure 2. A pressed pellet of the molecular sieve was placed in a controlled-atmosphere chamber and irradiated using a Lumonics HyperEx-400 excimer laser (248 nm (KrF*), pulse length 14 ns, repetition rate 10 Hz). The laser energy was measured using a Scientech pyroelectric head (model 380402) and found to range from 90 to 100 mJ/pulse. A computer controlled rastoring mirror (Oriol) was used to turn the laser beam 90° and move the beam across the pellet surface. A focusing lens was employed to decrease the laser beam to a spot size of ca. 0.001 cm^2 . Films were deposited by placing a substrate such as TiN (500Å) coated silicon on the heated substrate holder locate approximately 2.5 cm in front of the pellet. Typical film deposition conditions was as follows: laser power density, 100 MW/cm^2 ; substrate temperature, 150-300°; background oxygen pressure, 250-300 mTorr; deposition time, 10-20 min. Scanning electron microscopy (SEM) was used to examine the morphology and determine the thickness of the deposited films.

The laser deposited Nb-TMS1 and CoAPO-5 films were determined by XRD to be amorphous and partially crystalline, respectively. Both the Nb-TMS1 and CoAPO-5 films were then subjected to solution phase hydrothermal treatment. The solution phase treatment of the Nb-TMS1 has been described previously [7]. Briefly, the Nb-TMS1 coated substrate was positioned in the Teflon lined stainless steel autoclave at approximately 60° angle with the film side facing down. The melted niobium (V) ethoxide and dodecyl amine (molar ratio 1: 1.25) mixture was added to the Teflon liner followed by 20 mL ethanol. The resulting mixture was allowed to age for 72 hours at room temperature, 4 hours at 90°C, 4 hours at 140°C and 24 hours to 3 days at 180°C. The film was washed with deionized water, ethanol and diethylether and dried at room temperature. Because solution phase hydrothermal treatment of the CoAPO-5 films resulted in the reorganization of the laser deposited material to yield mixed molecular sieve phases (CoAPO-5 and CoAPO-34) and rapid growth in film thickness, the partially crystalline CoAPO-5 films were used as deposited.

Chemical Sensor Fabrication. A capacitive-type sensor was prepared from a hydrothermally treated/template-free Nb-TMS1 film coating a TiN/silicon substrate. The organic template was removed by washing in a solution of 3:1 isopropanol: water acidified with nitric acid to pH 1.75 for 3 hours followed by washing in ethanol. A Au/Pd alloy was patterned onto the film surface using a shadow mask. The device was then heated to 200°C to desorb water and immediately transferred to an environmental chamber under a positive pressure of high purity nitrogen where it was allowed to cool to room temperature (24°C).

Figure 2. Experimental methodology for pulsed laser deposition and post hydrothermal treatment of molecular sieve films.

The environmental chamber was equipped with two probes by which film plus adsorbate capacitance was measured. One probe made electrical contact with the bare TiN surface and the other probe made contact with a 0.184 mm^2 Au/Pd electrode. A voltage was applied and the capacitance signal was received by a WayneKerr Precision Component Analyzer 6425. A virtual instrument program written in house LabView for Windows 3.0.1 allowed the applied voltage to be stepped from 0V to 0.300V and the measured capacitance plotted as a function of applied voltage.

Figure 3. Schematic of molecular sieve thin film based sensor.

RESULTS AND DISCUSSION

SEM and Transmission electron microscopy (TEM) were used to characterize the laser deposited Nb-TMS1 films. In general, SEM images show a continuous, uniform films composed

of 30-50 nm particulates. The laser deposited film cross-section is shown in Figure 4. This film is on the order of 200 nm thick which is in the range needed to minimize leakage current while still maintaining significant capacitance changes.

Figure 4. SEM image of the laser deposited Nb-TMSI films cross-section.

The laser deposited Nb-TMSI appeared to be largely X-ray amorphous by powder XRD. However, further examination by TEM revealed areas of crystalline molecular sieve dispersed in an amorphous matrix (see Figure 5).

Figure 5. TEM of laser deposited Nb-TMSI film.

We have found that the laser deposited films can be reorganized using a post hydrothermal treatment. Figure 6 illustrates the change in the TEM images that occur following a hydrothermal treatment that was heated at 180°C for 24 hours. Larger regions of crystallinity are observed which can be described as having a “worm-like” motif [8]. The XRD pattern also reflects the increase in crystallinity with the appearance of a low angle peak between 2-3 two-theta. (data not shown).

Figure 6. TEM of hydrothermally treated Nb-TMSI film.

The crystallinity of the laser deposited CoAPO-5 films were shown to range from X-ray amorphous to partially crystalline by powder XRD. The morphology of the laser deposited CoAPO-5 films were very similar to that observed by SEM of the laser deposited Nb-TMSI films.

Capacitive-type chemical sensors were fabricated using the hydrothermally treated/template-free Nb-TMSI and/or calcined (template-free) CoAPO-5 films as the dielectric phase, the TiN substrate as an electrode and patterned Au/Pd as the other electrode. By applying a potential between the electrodes, changes in the capacitance were recorded upon adsorption of analyte molecules into the molecular sieve film. We found that the Nb-TMSI films were particularly sensitive to the relative level of moisture in the environmental chamber. When the Nb-TMSI based sensor was subjected to a flow of nitrogen containing water vapor, the capacitance measured across the hydrothermally treated film increased as the water was adsorbed. The background capacitance/area measured in flowing high purity nitrogen was on the order of 0.30 nF/mm². The capacitance/area increased to 5.2 nF/mm² when water was introduced into the flowing nitrogen. Because water can move freely into and out of the pores of the hydrothermally treated film, the capacitance response can be monitored as a function of time. For example, Figure 5 illustrates the reversible response to water of sensors based on mesoporous Nb-TMSI films which are approximately 300 nm thick. A repeat cycle (X3) of 90% humidity followed by a flush of high purity nitrogen was used to determine the reproducibility of the sensor response. During each 10 minute flush with nitrogen, the capacitance returned to its baseline within 1 minute. The average capacitance change varied no more than +/- 2.5% for the three sequential cycles.

The specificity of the Nb-TMSI based chemical sensors to water was tested on a variety of gaseous and volatile organics including CO₂, methanol and acetone. No measurable response was recorded when the sensor was exposed to CO₂. Both methanol and acetone produced a minimal capacitance change (< 1 nF/mm²) and therefore would be expected to interfere in the detection of water. The effect of other potential analytes is currently under investigation.

CONCLUSIONS

Continuous films of mesoporous and microporous molecular sieves have been prepared using pulsed laser deposition. PLD followed by a solution phase or vapor phase post hydrothermal treatment can be used to generate crystalline Nb-TMS1 and CoAPO-5 films, respectively. Capacitance-type chemical sensors can then be fabricated using these films as the dielectric phase. It was shown that chemical sensors based on Nb-TMS1 films are sensitive to the relative level of moisture in the environment which makes such sensors useful as potential humidity sensors. In contrast, CoAPO-5 is not sensitive to water but exhibits large capacitance changes upon exposure to CO. The thermal stability of the molecular sieves ($>400^{\circ}\text{C}$) suggest that sensors based on these materials may be particularly useful for the detection of combustion gases. We anticipate that the compositional variances available for both mesoporous and microporous molecular sieves will lead to more selective sensors as well as other applications for these thin films.

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Figure 7. Average reversible response for a capacitive-type Nb-TMS1 chemical sensor to the presence of water vapor in flowing nitrogen (average film thickness 300 nm).

A comparison with sensors fabricated from dense Nb₂O₅ films indicates that the accessible mesoporosity of the Nb-TMS1 results in capacitance changes which are at least 3X that observed with the dense phase devices.

The response of the CoAPO-5 based chemical sensors was measured in the presence of a number of analytes including N₂, CO₂ and CO. The CoAPO-5 based devices were found to be selective and sensitive to CO and CO₂ (see Figure 8). The background capacitance measured in the presence of high purity nitrogen was on the order of 10^{-14} F/mm². When CO₂ is added to the nitrogen flow, the capacitance increases to 10^{-9} F/mm². A change in capacitance of >3 orders of magnitude is observed when the sensor is exposed to CO indicating CoAPO-5 is a viable sensor for CO even in the presence of CO₂. The difference in the sensor response is dramatic for molecules of similar size and shape. The kinetic diameter of CO (3.8Å) is larger than CO₂ (3.3Å).

Figure 8. Capacitance response of CoAPO-5 based sensor to CO₂ and CO (film 227 nm thick).