Communication

Using Precursor Chemistry to Template Vanadium Oxide for Chemical Sensing**

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In this study, we examine the role that CVD precursor chemistry plays in the development of film microstructure. This is accomplished by using two classes of single-source precursors for vanadium oxide; a metal-organic (vanadium oxytripropoxide, $VO(OC_3H_7)_3$) and an inorganic (vanadium oxytrinitrate, $VO(NO_3)_3$). Films deposited under the same conditions but using these two precursors exhibit markedly different film microstructures. We explore the potential for using this approach for preparing selective chemical sensors on microhotplate arrays. Sensors prepared using $VO(NO_3)_3$ are more sensitive towards 1-propanol while those prepared using $VO(OC_3H_7)_3$ are more sensitive towards nitrogen dioxide.

The heightened awareness related to safety both in industrial sites and in homes has increased the demand for reliable gas detection systems. One approach that could be employed would be to use an electronic nose as the basis for real-time monitoring of various contaminant vapors in breathing air.[1] Most electronic noses use arrays of either polymer-carbon black composites or metal oxides as the sensing material.[1–3] In the case of the polymer-carbon black composites, the sensor selectivity is achieved by changing the polymer's molecular structure which can enhance a sensor's response to a given class of analytes. Metal oxides typically require either high operating temperatures, which increase power consumption, making them less likely to be successful for portable applications, or catalytic doping to enhance selectivity and reduce operating temperatures, or both to obtain a balance between sensitivity and selectivity. Metal oxides may be prepared

via a range of techniques including, but not limited to sputtering, sol-gel processing, screen printing, pressing powders and various forms of CVD. As would be expected, the method of choice for one application may not be the same for another. In one recent paper, the authors compared the results for three metal oxides (Ga_2O_3, Sb_2O_3, and SnO_2) prepared via screen printing of powders and atmospheric pressure (AP) CVD using the respective metal chlorides as the source precursor, and either methanol or ethyl acetate as the oxygen source for preparing the metal oxides.[4] The choice of metal chlorides for the source precursor limited the deposition temperatures to values higher than would have been required had single-source precursors been used. The work presented in this paper uses only the chemistry of the CVD precursors to enhance sensing film selectivity. This is made possible by differences in film microstructure that develop as a result of the precursor ligand chemistry. The microhotplate platforms used in this research have low power consumption at the operating temperatures used for fixed temperature sensing.[5–7] Power requirements may be further reduced and selectivity enhanced via pulsed temperature sensing given the devices short thermal time constants.[8-10]

Anhydrous metal nitrates have been used for the preparation of a variety of metal oxides and metal silicates.[11–13] In previous work, we demonstrated the distinct differences in microstructure in the low temperature, reaction-limiting regime and a coalescence of microstructures as the surface mobility of atoms increased.[14] Since then, we have been exploring the utility of being able to control thin film microstructure as it relates to sensor performance.[5–7] This paper explores the use of vanadium oxide thin films prepared via CVD as sensor materials for the purpose of preparing selective sensors.

We demonstrate the use of two single-source CVD precursors, one inorganic and one metal-organic, for the preparation of vanadium oxide thin films and explore the relationship between thin film morphology and precursor chemistry. Since precursor chemistry plays a pivotal role in microstructure development, an obvious starting point would be to examine whether there are any preferential surface interactions of analyte molecules with the deposited materials (molecular templating) due to the differences in film microstructure. For example, what happens when a sensor is prepared using one CVD precursor and is later tested for its sensitivity towards one of the gaseous products formed during its preparation? Our speculation was that the precursor-specific microstructures would yield lower sensitivity towards products than films prepared using a different chemical precursor under similar conditions. The rationale is simple; during film growth, deposition by-products must desorb from the surface before additional precursor

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molecules can be chemisorbed and react to form the desired product. Differences in adsorption strength amongst crystal faces leads the crystallites to propagate in low-interaction directions, because the product molecules are more likely to desorb from these crystallite faces to leave adsorption vacancies on the surface. As a result, the dominant growth surfaces of the deposited film exhibit weak binding of the reaction products.

We selected deposition conditions that enable us to make direct comparisons of sensing performance using a single sensor array. Our preliminary experiments used a broader temperature range than was used for sensor work mostly due to the minimum deposition temperatures required to obtain crack-free sensing films for the two precursors used. Although $VO(OC_3H_7)_3$ had been used for preparing vanadium oxides for sensor work, $VO(NO_3)_3$ had not. Figure 1 shows the various microstructures obtained using $VO(NO_3)_3$ in the temperature range $250-400\,^{\circ}C$.

In order to investigate whether we could employ these materials as selective chemical sensors, we prepared small arrays of sensors under a limited number of conditions. We did not make any attempt to optimize sensitivity towards the analytes, only measure selectivity in the sensor response. Sensors were tested for their responses to nitrogen dioxide and 1-propanol. In each case, the films deposited using a given precursor exhibit a lower sensitivity to the reaction products formed during its synthesis. Figure 2 demonstrates the response to nitrogen dioxide gas for vanadium oxide sensors prepared by CVD on a single microhotplate array under similar conditions.

We also examined the sensitivity of these sensing materials towards 1-propanol, a product formed via
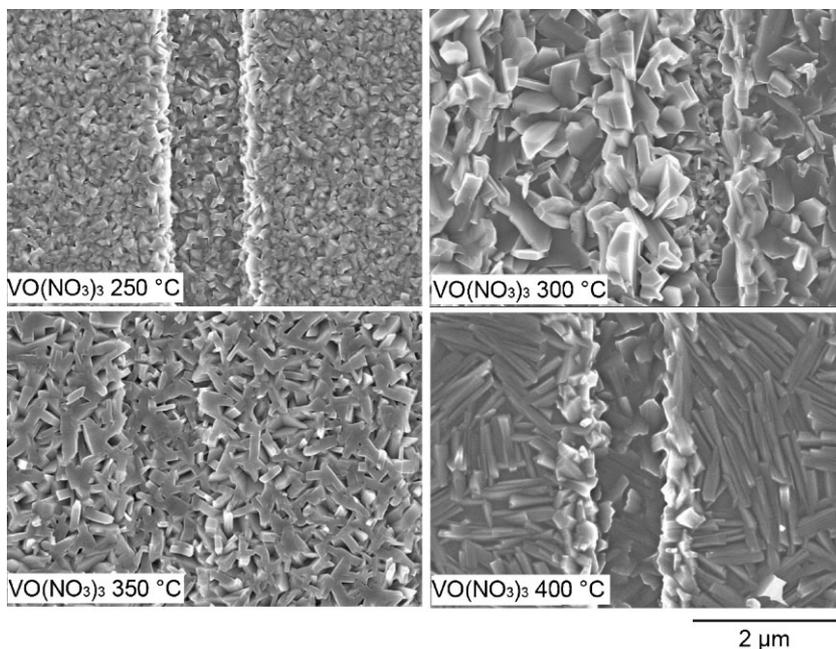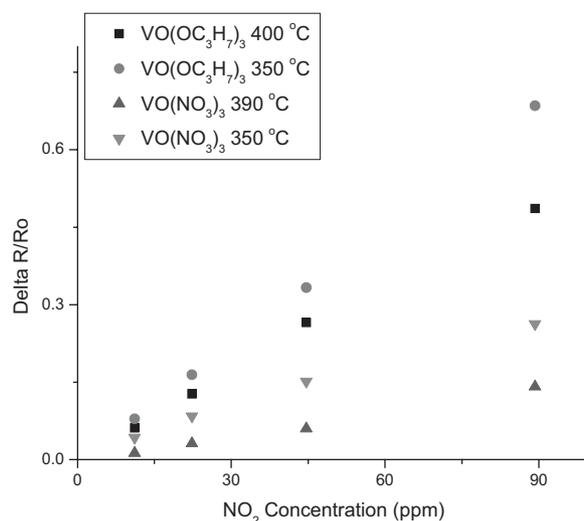

Fig. 2. Illustration of the differences in average relative response to nitrogen dioxide for vanadium oxide thin film sensors deposited via CVD on a microhotplate array. Sensors were deposited at the temperatures indicated and operated at $375\,^{\circ}C$ during sensing. The increase in relative response is characteristic for an oxidizing gas.

thermolysis of $VO(OC_3H_7)_3$. The results, given in Figure 3, were strikingly similar to those obtained with NO_2, except the chemical selectivity was reversed. The films deposited using the $VO(OC_3H_7)_3$ were more sensitive towards NO_2, and those deposited using $VO(NO_3)_3$ were more sensitive towards 1-propanol. This observation supports the hypothesis that precursor chemistry is driving this selectivity, but the mechanism by which this selectivity occurs merits some investigation.

It has been demonstrated for some time that the microstructure of thin film materials can be dictated using a judicious choice of deposition conditions, including precursor chemistry. What role does chemistry play in the overall sensing behavior observed in this work? At least three factors should be considered; effects related to surface area, chemical doping, and preferential adsorption of analytes.

One obvious question is "can the differences in sensor response be explained by differences in surface areas?" If the chemical selectivity were only a surface-area effect, then we would expect the film with the higher surface area to yield greater response towards all analytes. Figure 4 shows the microstructures for the two types of sensing films. The surface area of the $VO(OC_3H_7)_3$ deposited films were higher than the corresponding $VO(NO_3)_3$ films, but the films more sensitive to 1-propanol were actually those with the lower surface

Fig. 1. Microstructures of the vanadium oxide films obtained using vanadium (V) oxytrinitrate as the CVD precursor.
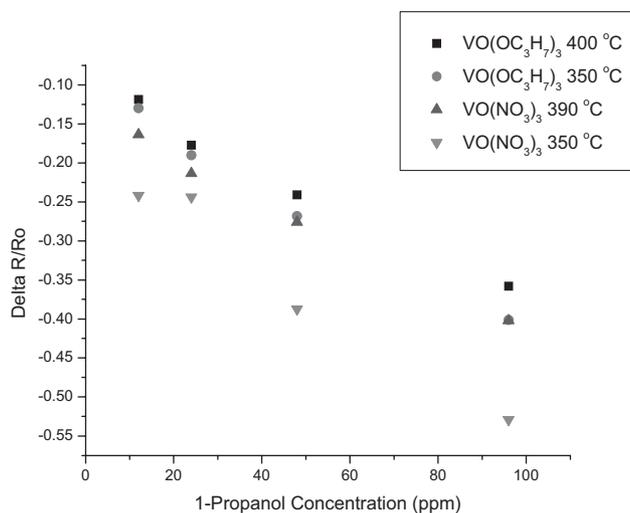
Fig. 3. Illustration of the differences in average relative response to 1-propanol for vanadium oxide thin film sensors deposited via CVD on a microhotplate array. Sensors were deposited at the temperatures indicated and operated at 375 °C during sensing. The decrease in relative response is characteristic for a reducing gas.

that TiO_2 films deposited via CVD using titanium (IV) isopropoxide as the precursor have fairly high concentrations of hydrogen entrained within the film. This entrained hydrogen adversely influences electrical conductivity and must be removed via high temperature annealing in oxygen before film conductivity falls off to acceptable levels.[15] The analogous case where titanium (IV) nitrate is used has no hydrogen incorporation, and these films require no additional thermal treatment for this application.[16] During normal operation of the microhotplate sensors used in this study, the embedded microheaters were held at operating temperatures in air until no further change in sensing film was evident. While no elemental measurements were made to evaluate whether any material was driven off during this annealing process, changes in the crystalline nature of the deposited films were observed and indicated the as-deposited films from $VO(NO_3)_3$ and $VO(OC_3H_7)_3$ were not the same, but annealing in air brought both materials to the same dominant crystallographic phase.

The small dimensions of the microhotplates made performing X-ray diffraction (XRD) measurements on sensing films problematic. In order to determine the crystallinity of the sensing films, depositions were made on oxidized silicon wafers under conditions identical to those used to create vanadium oxide sensing films. Scanning electron microscopy (SEM) was used to verify the similarity of the crystallite morphologies belonging to the fully-annealed films grown on the two different substrates. No substrate effects were observed; the film morphologies were dependent on precursor chemistry and substrate temperature but not on the nature of the substrate. Thus, the XRD data from the macroscopic samples were used to understand the nature of the film growth on the micro-hotplates.

area deposited via $VO(NO_3)_3$. One surface area-related phenomenon was apparent. In each case, the material deposited at lower temperature is more sensitive than the one deposited using the same precursor at the higher temperature and is likely related to surface area.

Is there a difference in the film doping caused by the drastically different chemistries used? It has been observed

Films deposited from $VO(OC_3H_7)_3$ were initially stoichiometrically deficient in oxygen. XRD analysis indicated the substantial presence of VO_2 crystallites in the as-deposited samples (not shown). Upon annealing at 400 °C in air, the films moved towards the fully oxidized V_2O_5 phase of vanadium oxide. No change in crystallinity was observed before and after similar annealing of the $VO(NO_3)_3$-deposited films. Figure 5 shows the XRD patterns of four fully annealed samples; two $VO(NO_3)_3$ films (350 °C and 400 °C) and two $VO(OC_3H_7)_3$ films (350 °C and 400 °C). The Raman scattering data for the same samples are presented in Figure 6.

For each technique, we observed that films deposited using either $VO(NO_3)_3$ or $VO(OC_3H_7)_3$ are substantially composed of the shcherbinaite phase of V_2O_5. The XRD results for the 350 °C sample depos-
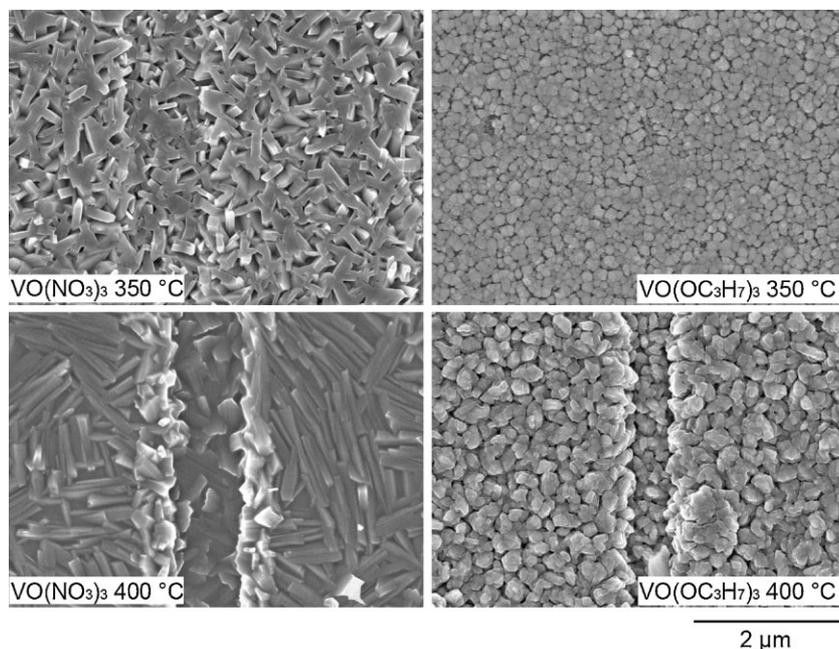

Fig. 4. Comparison of the vanadium oxide microstructures used in this work. Films were deposited via CVD at 350 °C and 400 °C. The different morphologies are the result of differences in precursor chemistry. The films on the right were deposited using vanadium (V) oxytripropoxide ($VO(OC_3H_7)_3$) and the films on the left were deposited using vanadium (V) oxytrinitrate $VO(NO_3)_3$).
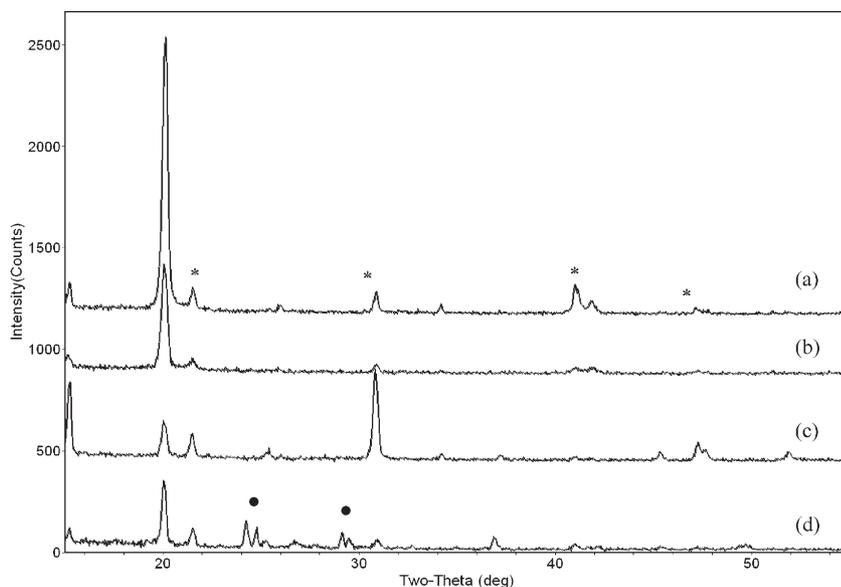
Fig. 5. XRD patterns for a) $VO(NO_3)_3$-deposited film grown at 400 °C, b) $VO(NO_3)_3$-deposited film grown at 350 °C, c) $VO(OC_3H_7)_3$-deposited film grown at 400 °C, and d) $VO(OC_3H_7)_3$-deposited film grown at 350 °C. Each film was annealed in air at 400 °C until no further changes in diffraction patterns were observed. Peaks marked with (*) originate from shcherbinaite phase crystallites of V_2O_5 and peaks marked with (•) originate from V_3O_7 crystallites.

indicated that each precursor was driving the deposition process in a different preferred orientation. It is likely that this preferred orientation leads to the difference in sensing behaviors between the two films.

We have demonstrated the use of CVD for the preparation of selective chemical sensors. The origins of the selectivity are based upon the chemistry of the CVD precursors. We see decreased sensitivity towards the products formed in the CVD process for both the films deposited using $VO(NO_3)_3$ and $VO(OC_3H_7)_3$. By judicious choice of precursor chemistry, the dominant growth faces of the deposited film can be controlled leading to the chemical selectivity desired in a sensing film. We recognize that the sensitivity of these sensors may not be as high as sensors prepared by other methods, but our approach is meant to be applied to application-specific microsensor arrays. We believe that chemical vapor deposition is the key to preparing arrays of diverse

ited from $VO(OC_3H_7)_3$ also includes some V_3O_7, a metastable phase of material which has not been fully oxygenated at the annealing temperatures. What is important to note is that all four films (which represent the four sensors under study) are mainly shcherbinaite, but the orientation of the films as observed by XRD is remarkably different. The different diffraction peak intensities observed in $VO(NO_3)_3$ and $VO(OC_3H_7)_3$ films

sensor materials in a small package. Further studies are being conducted to improve sensing film sensitivity and explore how broadly applicable this approach is in preparing selective chemical sensors using a variety of metal oxides.

Experimental

Sensing films were prepared via CVD in a low-pressure, cold-wall reactor. Sensor substrates were microhotplate arrays provided through collaborations with researchers at NIST and Aerospace Corporation and have been described elsewhere [17,18]. Additional depositions on larger substrates were performed on roughly 1 cm^2 pieces of oxidized single crystal silicon wafer (300 nm thermal oxide) cleaned by Piranha solution (3 parts 30% hydrogen peroxide and 7 parts concentrated sulfuric acid). Precursors used were vanadium (V) oxytrinitrate ($VO(NO_3)_3$) and vanadium (V) oxytripropoxide ($VO(OC_3H_7)_3$). $VO(NO_3)_3$ was prepared in-house using a method given in the literature [19], and the $VO(OC_3H_7)_3$ was purchased from Aldrich. The reactor pressure used was 40 Pa, and the total flow rate into the precursor vessel was 0.15 slm. Deposition times for the microhotplates were in the range 1 - 10 min, and depended upon substrate temperature. Deposition times for the larger substrates were 2 – 30 min. Deposition temperatures for the microhotplates ranged between 250 °C and 700 °C, although sensing results were not obtained for all films due to differences in growth modes at higher temperature. Films were deposited on larger substrates at temperatures ranging from 300 to 500 °C. Sensing films were deposited until their resistance was 5 - 10 kΩ. Sensors were annealed in air at 400 °C to bring the sensors to a constant resistance following deposition before exposure to analytes. All sensing measurements were performed using a Keithley Model 2700# digital multimeter with 7706# multichannel card in resistance mode. Sensing film microstructure and composition were characterized using a Leo DSM-982# field emission scanning electron microscope equipped with a Bruker# energy-dispersive X-ray microanalysis system. Films deposited on larger substrates were also investigated by SEM to confirm similarity of microstructure between the microhotplate films and the oxidized silicon deposited films. The phase and orientation of the films deposited on oxidized silicon substrates were analyzed both before and after annealing by XRD on a Rigaku Ultima IV# diffractometer. Raman spectroscopy was also performed to confirm the identification of the vanadium oxide phases. Raman measurements were
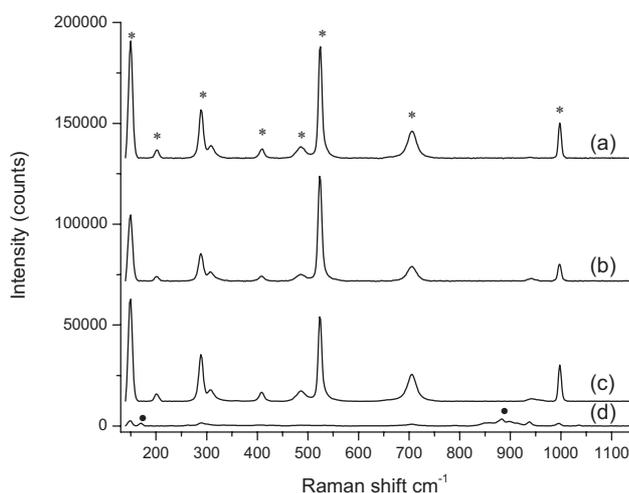

Fig. 6. Raman scattering spectra for a) $VO(NO_3)_3$-deposited film grown at 400 °C, b) $VO(NO_3)_3$-deposited film grown at 350 °C, c) $VO(OC_3H_7)_3$-deposited film grown at 400 °C, and d) $VO(OC_3H_7)_3$-deposited film grown at 350 °C. Each film was annealed in air at 400 °C until no further changes in XRD patterns were observed. Peaks marked with (*) originate from shcherbinaite phase crystallites of V_2O_5 and peaks marked with (•) are believed to originate from V_3O_7 crystallites.

carried out using a Lambda Solutions Dimension-1HR[#] spectrometer employing a 785 nm temperature-stabilized laser.

[#]Certain commercial instruments are identified to adequately specify the experimental procedure. In no case does this identification imply endorsement by the National Institute of Standards and Technology.

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