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Multiphoton-Induced Decomposition of Organometallics as a Route for Production of Doped SnO_2 Films

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A laser-assisted chemical vapor deposition scheme for SnO_2 films has been developed, based on the UV multiphoton dissociation of di (n-butyl) tin diacetate. Doped films were produced by simultaneous photolysis of other inorganic precursors. Films were characterized by UV–visible spectroscopy, room-temperature resistance measurements in the presence of a variety of gas-phase contaminants, and the temperature dependence of film resistance. These preliminary investigations demonstrate the ability to vary detection sensitivity and selectivity by changing the dopant precursor identity. © 1997 by John Wiley & Sons, Ltd.

Keywords: chemical vapor deposition; tin(IV) oxide; films; di(n-butyl)tin; photolysis; dopant.

INTRODUCTION

Development of materials which can be used as selective and sensitive detectors for toxic or irritant gases is the subject of a great deal of attention. An important class of gas sensors utilizes the change in resistance in SnO_2 as a means of detection of contaminants in air. A variety of techniques have been developed for the production of SnO_2 gas sensors.[1] Thin films of SnO_2, doped with a variety of metals, have been shown to be promising sensor materials, particularly if they are operated at elevated temperatures.[2] There have also been a few reports of SnO_2-based sensors which operate at room temperature.[3,4] Designing new techniques for production of SnO_2 thin films with good sensitivity and selectivity at room temperature continues to be an area of great interest.

Metal and metal oxide films can be deposited from volatile organometallic precursors via conventional chemical vapor deposition or by use of laser-assisted methods.[5] Laser-assisted chemical vapor deposition (LCVD) is known to occur by several mechanisms.[6] In the purely photochemical limit, the precursor absorbs the laser wavelength and gas-phase decomposition occurs. At the other extreme, the precursor does not absorb at the laser wavelength. In this case the laser serves to heat the substrate, and the film growth is termed ‘photothermal’. Both possibilities may contribute to film growth in a hybrid mechanism. In the case of SnO_2 films, there are a limited number of examples of LCVD approaches. One example is the production of SnO_2 films from the 193 nm photolysis of a mixture of $SnCl_4$ and N_2O.[7]

Multiphoton dissociation (MPD) using visible or ultraviolet wavelength lasers is a well-established route to the generation of gas-phase metal atoms which can potentially be used to generate films.[8] Previous work in our laboratory[9,10] has demonstrated that UV multiphoton dissociation of di(n-butyl) tin diacetate (DBTDA) results in extensive fragmentation. Evidence has been obtained for the formation of gas-phase Sn atoms,[9] as expected for a tetravalent tin compound,[8] as well as for the production of CH radicals from fragmentation of the ligands.[10] DBTDA is a volatile precursor which has already been utilized in chemical vapor deposition production of SnO_2 films.[11] The purpose of the work reported here is to investigate the feasibility of LCVD for the production of doped SnO_2 films via UV MPD of mixtures of organometallic precursors. Films are tested for room-temperature sensitivity and selectivity in the detection of some selected contaminants.

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EXPERIMENTAL

A Questek 2720 excimer laser, operated on either KrCl* (222 nm) or XeCl* (308 nm), was used to initiate film growth. The laser beam was focused with a 12 cm focal length cylindrical lens into a glass vacuum cell which contained a continuously flowing 100 mTorr sample of DBTDA vapor. A substrate for film growth was placed near the focus of the lens. UV-grade quartz and glass substrates were cleaned prior to use in a 1:3 mixture of concentrated HCl/HNO_3. Table 1 summarizes the number of laser shots and average laser energy/pulse used to generate films at 222 nm.

Doped films were produced simply by adding an additional precursor to the vacuum cell during the photolysis. All dopant precursors were used at their room-temperature vapor pressures for these preliminary survey studies. DBTDA (95%; Pfaltz and Bauer) samples were subjected to several freeze–pump–thaw cycles at liquid-nitrogen temperature in order to eliminate volatile contaminants. Precursors for film doping, lead (II) acetate trihydrate (99.999%; Strem), chromium hexacarbonyl (99%; Aldrich), indium (III) acetate hydrate (99.99%; Aldrich) and copper(II) acetate (98%; Aldrich) were used as supplied by the manufacturers.

Following photolysis, substrates were removed from the sample preparation cell and were tested for their resistance. Films were also treated with the acid cleaning mixture and resistances and optical spectra were found to be unchanged after this treatment. The ultraviolet–visible spectra of the films were obtained using a HP 8452A diode array spectrophotometer prior to attachment of copper wires for resistance testing.

Two-point resistance measurements were made using a Keithly 179 TRMS digital multimeter. Copper wires were attached to the end of the films with a conductive silver epoxy (Dupont 5815). The epoxy was cured at 204 °C for 1 h prior to testing the films. Film resistance measurements were made in air and in vacuum at a range of temperatures, and also at room temperature in the presence of a variety of contaminant gases.

The copper wire electrodes and epoxy were carefully removed from three films in order to test for copper content. The films were soaked in 50 ml of concentrated nitric acid for 20 min. A 10 ml portion of each wash solution was removed and was diluted to 25 ml. Samples were tested using a Perkin-Elmer 3100 atomic absorption spectrophotometer.

RESULTS

With 22 nm excitation, films were obtained on either glass or quartz substrates using laser energies of 50–80 mJ/50 ns pulse at repetition rates of 1–5 Hz. In order to obtain semiconductive films, the laser focus needed to be within 5 mm of the substrate. At 308 nm, attempts at film growth were unsuccessful even with laser energies of 180–240 mJ/pulse and

Table 1. Film production conditions and characterization results

Film Identification	F1	F2	F3	F4	F5	F6	F7
Dopant	Cu	Cu	Cr	Pb	In	None	None
$10^{-4}\times$ laser shots	8.8	4.7	4.4	5.7	5.7	5.0	6.5
Laser energy (mJ/pulse)	45	60	55	50	45	65	55
Resistance/length ($\mathrm{k}\Omega\ \mathrm{m}^{-1}$)	44	67	1100	92	6.0	13	17
Test vapor	Resistance response[a]						
Water	inc.	inc.	inc.	inc.	n.r.	inc.	inc.
Formaldehyde	inc.	inc.	inc.	inc.	n.r.	inc.	inc.
Acetone	inc.	n.r.	inc.	inc.	n.r.	inc.	inc.
Ethanol	inc.	inc.	inc.	inc.	n.r.	inc.	inc.
Ethyl formate	dec.	dec.	inc.	inc.	n.r.	inc.	inc.
2,3-Dimethylbutane	dec.	dec.	inc.	inc.	n.r.	inc.	inc.
Cyclo-octane	dec.	dec	inc.	inc.	n.r.	inc.	inc.

[a] Key to film response: inc., increase in resistance on exposure to test vapor; dec., decrease in resistance on exposure; n.r., no measurable response.

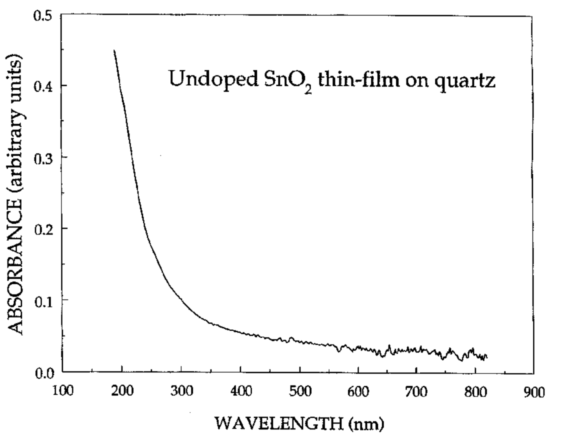

Figure 1 UV–Vis absorption spectrum of an undoped SnO$_2$ thin film on quartz. The experimental conditions for film F6 growth are listed in Table 1. The spectrum shown here was obtained prior to acid treatment or curing of the epoxy used in wire attachment.

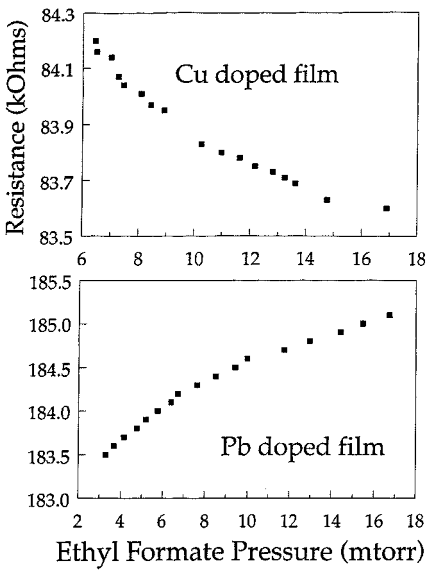

Figure 2 Film response versus ethyl formate pressure. The difference in Cu/SnO$_2$ film (F2) and Pb/SnO$_2$ (F4) film responses demonstrates the potential for selectivity in sensor behavior. Film production conditions are listed in Table 1.

glass substrates. All of the experimental results presented here were obtained using 222 nm excitation. The absorption spectrum of a typical undoped SnO$_2$ film is shown in Fig. 1. The spectrum is consistent with literature reports of SnO$_2$ thin films.[7,12,13] Addition of the small amounts of dopant materials did not make any obvious difference in the absorption spectra.

Seven different films were generated as shown in Table 1. Dopants will be identified by the metal in the organometallic precursor but no conclusions are made, in these preliminary studies, concerning the identity of dopant incorporated into the film. The resistance per unit length varies dramatically depending on dopant. The indium-doped film is the most conductive and the chromium-doped film is the least conductive. In all cases, the room-temperature sensitivities, as demonstrated by the resistance change when exposed to contaminants, were very low. Figure 2 shows typical responses for two of the films when exposed to ethyl formate. Film resistance values required approximately 10–30 s to stabilize under these measurement conditions. Table 1 summarizes the survey work done to characterize room-temperature film response. Each film was characterized by whether its resistance increased, decreased or remained the same when exposed to a variety of gas-phase samples. SnO$_2$, Pb/SnO$_2$ and Cr/SnO$_2$ films all exhibited similar selectivities but the sensitivity increased slightly when compared with undoped films with the addition of the lead and by a factor of about 5 when the chromium precursor was used. Copper-doped films had a different selectivity but similar sensitivity when compared with other films. The selectivity is shown for the two hydrocarbons tested (2,3-dimethylbutane and cyclo-octane) and ethyl formate, which led to a decrease in resistance for the Cu/SnO$_2$ film. The indium-doped films exhibited negligible sensitivity.

SnO$_2$ films are often operated at elevated temperatures. The temperature response of film resistances is shown in Fig. 3 for the same films as are described in Table 1. Responses were similar for a given film when measured in air or under vacuum. The chromium film has a significantly higher response to temperature change and is thus the best candidate for use as a sensor material at elevated temperatures. Further work is necessary to evaluate the response to contaminant gases at temperatures other than room temperature and to characterize film compositions and morphologies.

Atomic absorption measurements were attempted in an effort to obtain some information on the copper content of films F1 and F2. Film F6 was also tested in order to eliminate the possiblity of other copper sources, such as the electrodes, being the source of any observed

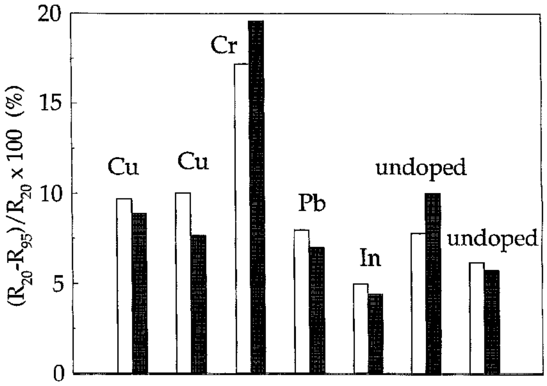

Figure 3 Temperature response of film resistances. The percentage difference between 20 °C and 95 °C responses were determined for the films F1–F7 in air (unshaded bars) and under vacuum (shaded bars).

copper signals. In all three cases, there was no detectable evidence of copper. Based on a detection limit of 0.08 mg l^{-1}, this corresponds to fewer than 10^{17} copper atoms having been removed in the acid wash process.

DISCUSSION

The precursor for SnO_2 films, DBDTA, absorbs at 222 nm but not at 308 nm. Even when substrates which absorb at 308 nm and much higher laser energies were used, no films were obtained. This indicates that there is an important photochemical component to the film growth process. In focused UV laser beams, we have previously demonstrated extensive gas-phase fragmentation of DBTDA, with observation of atomic Sn and CH radicals.[9,10] The LCVD process discussed here is also likely to require multiphoton absorption, since film growth was found to be sensitive to the distance between the laser focus and substrate surface. The fact that the film itself absorbs strongly at 222 nm indicates that the mechanism for film growth is best described as a hybrid photochemical/photothermal process since there should be some heating of the film by the laser.

The reported band gap[14] for pure, polycrystalline SnO_2 is 3.54 eV, which would correspond to a cut-off wavelength of 350 nm for transmission. The film spectrum shown in Fig. 1 is consistent with the expected optical properties of SnO_2 films. The fact that there is negligible change in the observed spectral properties or film resistances after acid treatment suggests that SnO_2 is the primary component of these films, since species such as atomic Sn and SnO are expected[7] to be etched away in this treatment.

While film sensitivities are low, there is evidence that the sensitivities increase with added dopant and that this simple one-step production scheme can lead to films which vary with respect to both sensitivity and selectivity. This provides a convenient means for generation of films with different properties which may be useful in the production of arrays of gas sensor elements. Among the materials used in this preliminary study, the copper-doped films exhibit the best potential for selectivity, since hydrocarbons and ethyl formate lead to resistance decreases while ethanol, water, acetone and formaldehyde all lead to an increase in resistance. The Cr/SnO_2 films are the most likely to have the greatest amount of dopant incorporated, since all studies were performed using the room-temperature vapor pressure of the dopant precursor and $Cr(CO)_6$ has a vapor presure of 1 Torr at 36 °C,[15] and approximately 0.35 Torr at room temperature,[16] which is significantly higher than the other dopant precursors. The Cr/SnO_2 films had the highest sensitivity and were also the most sensitive to temperature changes. In contrast, the In/SnO_2 films were the most conductive, exhibited no measureable sensitivity, and were least sensitive to temperature changes. Work is in progress to optimize film growth conditions by varying precursors and to characterize film structure and composition.

CONCLUSIONS

These preliminary survey experiments demonstrate that films with variable responses to contaminant gases can be readily produced via multiphoton laser-assisted chemical vapor deposition. The spectral characteristics of undoped films are consistent with the expected properties of polycrystalline SnO_2. Cu/SnO_2 films showed the best potential for selectivity while the Cr/SnO_2 films were the most sensitive for room-temperature detection of a variety of contaminants.

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