

# Comparison of $\text{SnBr}_4$ and Di-n-butyl Tin Diacetate as Laser-Assisted Chemical Vapor Deposition Precursors for $\text{SnO}_2$ -Based Gas Sensors

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Laser-assisted chemical vapor deposition (LCVD) was utilized to produce  $\text{SnO}_2$  films from  $\text{SnBr}_4$  plus air,  $\text{O}_2$  or  $\text{N}_2\text{O}$ .  $\text{SnO}_2$  films were successfully generated using either 222 or 308 nm laser pulses but there was evidence for film contamination when using less than 60 mJ/pulse laser energies at 222 nm. Films were characterized using ultraviolet absorption spectroscopy; the spectra of films with impurities resembled the spectrum of  $\text{SnBr}_4$ . AFM images were obtained which indicated that this LCVD route produced small and fairly uniform  $\text{SnO}_2$  grains which were 50–100 nm in size. Multi-photon ionization spectroscopy was used to verify that the dissociation of a film dopant precursor, copper(II) acetate, produced gas-phase copper atoms under conditions similar to those used in film deposition experiments. The deposition of  $\text{SnO}_2$  from  $\text{SnBr}_4$  plus an oxidant was found to be more efficient than from di-n-butyl tin diacetate but films produced via this new LCVD route, including those doped with copper, were found to be much less sensitive in preliminary gas-sensing screening. © 1998 John Wiley & Sons, Ltd.

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## INTRODUCTION

The utility of  $\text{SnO}_2$  as a gas-sensor material is well established.<sup>1</sup> The primary advantages of  $\text{SnO}_2$ -based sensors are the low cost and ease of fabrication of these simple devices. However, there is still a need to improve device selectivity, sensitivity and stability, and to lower operating temperatures. Sensors fabricated from thin films of  $\text{SnO}_2$  offer promise for addressing these critical device development issues.<sup>2</sup> The most commonly utilized deposition methods for  $\text{SnO}_2$  films include reactive sputtering,<sup>3,4</sup> chemical vapor deposition<sup>5,6</sup> and pulsed laser ablation.<sup>7,8</sup> Tin oxide sensors are also frequently doped with metals or metal oxides in order to enhance sensitivity and selectivity for target contaminant gases.<sup>1</sup> For example, copper oxide is used for  $\text{H}_2\text{S}$  detection.<sup>9,10</sup> Adding copper to platinum-doped  $\text{SnO}_2$  sensors has also been shown to improve sensitivity and selectivity for CO and  $\text{H}_2$  sensing at the relatively low detection temperature of 100 °C.<sup>11</sup>

Laser-assisted chemical vapor deposition (LCVD) provides an alternative route for generation of thin films from a variety of organometallic and inorganic precursors<sup>12</sup> which has yet to be fully exploited for sensor applications. Films are typically deposited by directing a focused, pulsed, ultraviolet (UV) laser beam onto the surface of a substrate in the presence of vapor-phase precursors. This approach has only recently been applied to  $\text{SnO}_2$  film deposition for use in gas-sensor development,<sup>13</sup> despite an earlier demonstration of the utility of LCVD for generating  $\text{SnO}_2$  films.<sup>14</sup> Film morphology is believed to be an important factor in sensor behavior<sup>1</sup> and the LCVD technique offers the possibility of growing metastable film structures via rapid heating and cooling of the film during deposition. This provides an *in-situ* film surface treatment process which is analogous to the use of,

for example, pulsed excimer laser treatment to transform single-crystal  $\alpha$ - $\text{Al}_2\text{O}_3$  to a metastable, lattice-distorted,  $\gamma$ - $\text{Al}_2\text{O}_3$  structure.<sup>15</sup>

The focus of recent work in our laboratory has been on developing new approaches, based on LCVD, for generating thin-film  $\text{SnO}_2$  gas-sensing materials with the potential for room-temperature operation. Di-n-butyl tin diacetate (DBTDA) was used as the LCVD precursor in our first study.<sup>13</sup>  $\text{SnO}_2$  films were deposited on quartz substrates from DBTDA vapor at room temperature using a focused 222 nm excimer laser beam. Films were doped by performing the same deposition procedure with lead(II) acetate trihydrate, chromium hexacarbonyl, indium(III) acetate hydrate, or copper(II) acetate vapor added to the precursor mixture. These films were evaluated for potential sensing capability by monitoring resistance changes as a function of exposure to water, formaldehyde, acetone, ethanol, ethyl formate, 2,3-dimethylbutane and cyclo-octane. With the exception of the indium-containing films, which exhibited no sensing capability, parts-per-thousand sensitivities were observed at room temperature. Films created from DBTDA and  $\text{Cr}(\text{CO})_6$  exhibited the best sensitivity as measured by resistance change per mtorr of added contaminant gas. For most of the sensor films, the resistances always increased upon exposure to any of the test gases. However, films deposited from DBTDA and copper(II) acetate mixtures did exhibit some selectivity, with resistances decreasing upon exposure to ethyl formate, 1,2-dimethylbutane, and cyclo-octane.

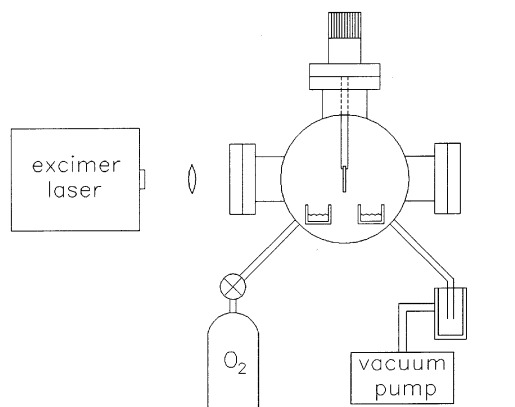
The results of the preliminary study suggest that LCVD of organometallics offers significant promise as a new method for producing sensor materials. However, the possibility of incorporating fragments of the ligands in the films must be considered since film contamination may influence sensor performance. Evidence for significant DBTDA ligand fragmentation was obtained in our laboratory using multiphoton-induced emission spectroscopy to detect gas-phase CH radicals generated under typical film-growth conditions.<sup>16</sup> Observation of gas-phase CH has been shown to be correlated with carbon contamination in LCVD,<sup>12</sup> motivating our present focus on the development of an alternative LCVD scheme which removes this possibility.

LCVD growth of  $\text{SnO}_2$  films via 193 nm photolysis of mixtures of  $\text{SnCl}_4$  and  $\text{N}_2\text{O}$  was first demonstrated by Kunz *et al.*<sup>14</sup> While  $\text{SnCl}_4$  does not absorb well at either of the excimer laser

wavelengths available in our apparatus,  $\text{SnBr}_4$  exhibits<sup>17</sup> absorption bands at both 308 and 222 nm, making it a suitable precursor for testing new gas-sensor LCVD schemes. Preliminary results are reported here for this new LCVD route. Films were deposited using  $\text{SnBr}_4$  plus an oxidant. The LCVD efficiency, degree of film contamination and sensor sensitivity and selectivity were compared with the DBTDA route. Along with the characterization of this alternative LCVD scheme, we have also continued with our assessment of the use of copper(II) acetate as a promising dopant precursor. Use of copper as a dopant material has been motivated both by our observation of some selectivity in room-temperature sensing,<sup>13</sup> as well as by other general applications of CuO and copper doping as means for enhancing sensing behavior.<sup>9,10,11</sup> As an initial step in characterizing the LCVD process, detection of gas-phase copper atoms from the UV multiphoton dissociation of copper(II) acetate is reported here.

## EXPERIMENTAL

The experimental apparatus used for film deposition experiments was similar to that used for our earlier work<sup>13</sup> and is shown schematically in Fig. 1.



**Figure 1** Experimental apparatus. The output from the excimer laser was focused into the center of the vacuum chamber and then blocked at the output side. Sample reservoirs for  $\text{SnBr}_4$  and copper(II) acetate were placed in the vacuum chamber during film deposition. A constantly flowing oxidant source was used in all experiments. Film position on the substrate was adjusted via a linear translation stage and the perpendicular substrate orientation is shown here.

The excimer laser was focused onto the surface of a substrate using a cylindrical lens of 12 cm focal length, producing films which were approximately  $1\text{ mm} \times 10\text{ mm}$  in area. Polycrystalline quartz window flats (ESCO, S1-UV grade) were used as substrates. The vacuum chamber was heated in order to vary the vapor pressures of the film precursors. Films were deposited using 1–5 Hz laser repetition rates.  $\text{SnBr}_4$  (Strem, 99%) was used as supplied by the manufacturer and was placed directly in the chamber for all experiments. The oxygen source [ $\text{O}_2$  (Amerigas),  $\text{N}_2\text{O}$  (BOC) or air] was kept continuously flowing through the chamber during film deposition and volatile products were trapped in an ethanol/dry ice bath preceding the vacuum pump. Copper(II) acetate (Aldrich, 98%) was also placed directly in the LCVD chamber for film-doping experiments.

Alternative film-deposition strategies were also tested. Experiments were performed with the substrate mounted parallel to the direction of laser propagation. The separation between the laser beam and substrate surface was approximately 1 mm for the parallel geometry experiments. Prenucleation<sup>18</sup> of films was also attempted at 222 nm. The laser was focused onto the substrate, as in the usual LCVD approach, for 600 laser shots in the presence of  $\text{SnBr}_4$  and 10 torr of air. The substrate was translated and a second position was prenucleated in an identical fashion. Following the prenucleation, the laser-focusing lens was removed and the prenucleated areas of the substrate were flood-illuminated for an additional 7200 laser shots in the presence of  $\text{SnBr}_4$  and 30 torr of air.

Films were characterized by optical spectroscopy, using a Perkin–Elmer 320 spectrophotometer. Films which appeared to contain impurities, based on UV absorption spectra, were subjected to an acid wash by dipping them several times into concentrated nitric acid, and then rinsed with distilled water. Acid-treated films were not used for the surface analysis or sensor-testing results presented here. The surface morphology of the films was investigated using atomic force microscopy (AFM). Images were obtained with a Digital Instruments Nanoscope E microscope using a silicon nitride cantilever in contact mode. The crystal structure of the films was probed using a power diffractometer with a copper tube X-ray source. Sensor performance was evaluated by monitoring film resistance as a function of pressure of contaminant gas. Copper wires were attached to the ends of the films with a conductive silver epoxy (Dupont 5815) which was cured at 204 °C for 1 h.

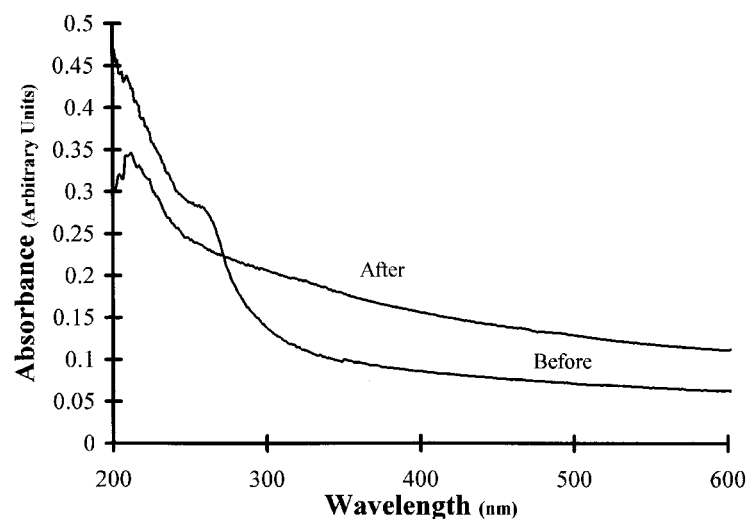
The sensors were placed in a vacuum chamber connected, via electrical feedthroughs, to a Keithly 179 TRMS digital multimeter for two-point resistance measurements.

Non-mass-resolved resonance-enhanced multiphoton ionization (REMPI) spectroscopy was utilized to verify copper atom production from copper(II) acetate. The excimer laser, operated at 308 nm, was used to pump a Lambda Physik FL 3002 dye laser. The dye laser output obtained with Coumarin 470 dye was frequency-doubled with a  $-\text{BaB}_2\text{O}_4$  (BBO) crystal housed in an InRad Autotracker. The fundamental was separated from the harmonic beam using a four-prism beam separator, and blocked. The UV laser was focused between two parallel-plate electrodes using a lens of 20 cm focal length. One of the plates was biased at +125 V and the resulting ion signal at the other plate was amplified, integrated using a home-built gated integrator (Evans Electronics) and stored in a computer for later analysis. The dye laser wavelength was stepped in 0.0015 nm increments and 50 laser shots were averaged at each wavelength.

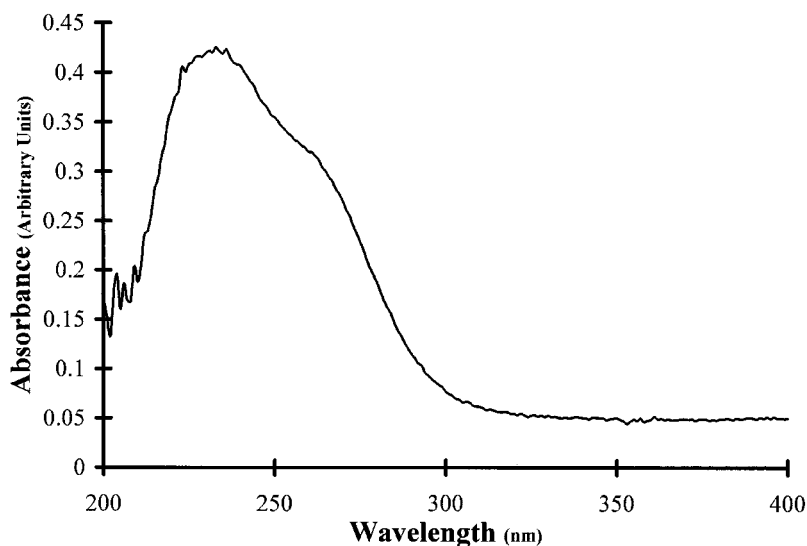
## RESULTS

### Film deposition using 222 nm radiation

LCVD films were obtained under a variety of experimental conditions. For the purpose of characterization, conducting films are defined as having a measurable, i.e. less than infinite, resistance at any position along the film axis. Conducting films were obtained using any of the oxygen sources when the laser was directly focused on the substrate and the  $\text{SnBr}_4$  sample reservoir was placed close to the substrate. Figure 2 shows the absorption spectrum, before and after acid washing, of a typical film acquired at 222 nm (45 mJ/pulse) with  $\text{SnBr}_4$  and air. The spectrum labeled 'Before' in Fig. 2 resembles that of  $\text{SnBr}_4$  shown in Fig. 3. Washing the film with nitric acid led to the elimination of the characteristic  $\text{SnBr}_4$  shoulder at 260 nm. The spectrum of the acid-washed film labeled 'After' in Fig. 2 resembled that reported previously<sup>13</sup> for films generated from DBTDA. As shown in Fig. 4 use of higher laser energies appeared to eliminate the  $\text{SnBr}_4$  shoulder without the need for postdeposition acid treatment. The spectrum of a conducting film deposited using an average 222 nm laser energy of 60 mJ/pulse is shown in Fig. 4(a).



**Figure 2** Absorption spectra of deposited film. The film was deposited, using 1/Hz, 45 mJ/pulse, 222 nm radiation, at 24 °C with 13 torr air as the oxidant. The deposition time was 4 h. The spectrum of the film immediately following deposition and the spectrum of the same film after washing in concentrated nitric acid are shown.

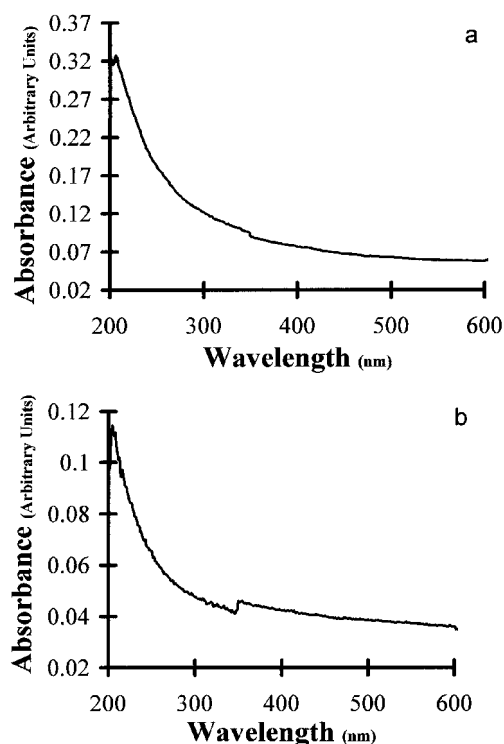


**Figure 3** Room-temperature spectrum of  $\text{SnBr}_4$  vapor in air. The spectrum was acquired using a 5 cm pathlength cell and a 1 nm slit width.

Using laser energies of 60–65 mJ/pulse, conducting films could be obtained at 222 nm with as few as 3600 laser shots. Using the procedure described above, prenucleation experiments were attempted in order to investigate the role of laser intensity during the film-growth process. Faint

traces of films were evident but there was no conductivity for either of the films deposited with this scheme.

Film growth was also attempted using a parallel geometry where the laser did not directly impinge on the surface of the substrate. A sample of  $\text{SnBr}_4$



**Figure 4** Absorption spectra of deposited films. The discontinuity in the spectra at 350 nm is due to lamp switching in the spectrophotometer. (a). Film deposited using 60 mJ/pulse, 222 nm radiation at 1 Hz for 3 h. The deposition chamber was heated to 45 °C and the oxidant was 12 torr air. (b) Film deposited using 150 mJ/pulse, 308 nm radiation at 1 Hz for 2 h. The deposition chamber was heated to 45 °C with 29 torr air used as the oxidant.

vapor with 10 torr of air was irradiated with a focused, 60 mJ/pulse, 222 nm laser beam for 10 800 shots, similarly to the conditions used to generate the films of Fig. 4. There was no evidence for conductivity and the absorption spectra resembled those of the untreated film in Fig. 2(a) and the  $\text{SnBr}_4$  spectrum shown in Fig. 3.

Figures 5 and 6 show AFM images of the surface of a conducting film. Figure 5 shows the height data for a typical 500 nm  $\times$  500 nm region of the sample. Using this image, we estimate that the RMS surface-height variations are approximately 50 nm. Figure 6 shows a top view of the central portion of Fig. 5 where the height data have been edge-enhanced to accentuate the grain boundaries at the surface of the film. Given that the lateral extent of Fig. 6 is 250 nm, we estimate the typical grain size to be of the order of 50–100 nm.

Preliminary X-ray diffraction measurements have also been performed. Despite the small volume of the LCVD films and large background scattering from the amorphous quartz substrate, weak but unambiguous peaks corresponding to the cassiterite phase of  $\text{SnO}_2$  were observed. No evidence was obtained for the presence of any other oxide of tin or of pure metallic tin.

### Film deposition using 308 nm radiation

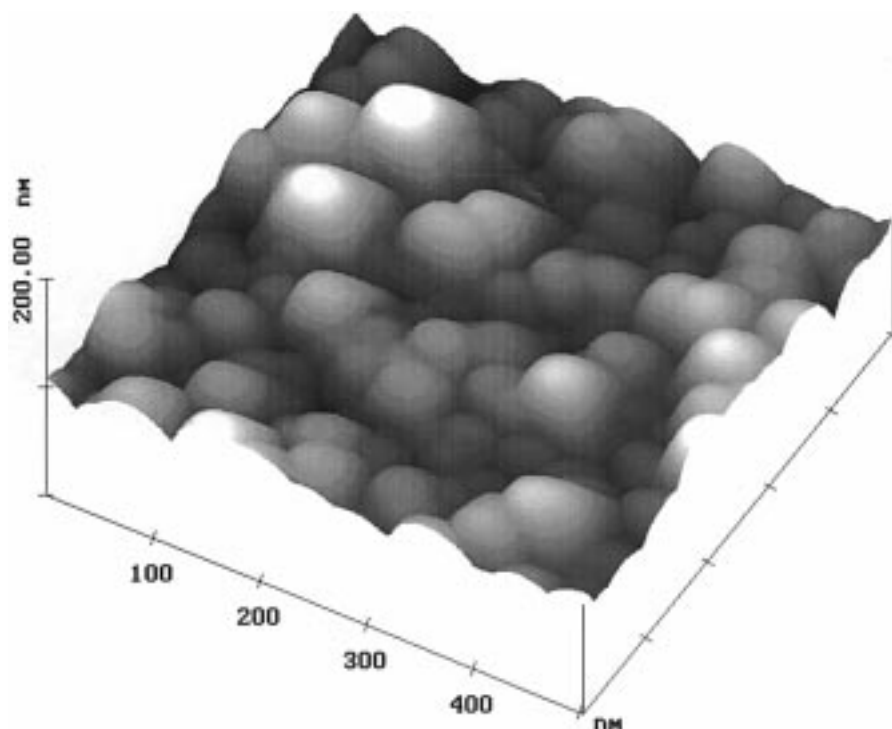
Films were also deposited efficiently using 308 nm radiation, needing as few as 1800 laser shots (170 mJ/pulse) to deposit a conducting film at 50 °C using 550 mtorr of  $\text{O}_2$ . Conducting films were readily obtained using LCVD conditions of 2–3 torr of air or 0.5–1.0 torr of  $\text{O}_2$  and laser energies of 100–200 mJ/pulse. The absorption spectra of the films deposited at 308 nm did not exhibit the 260 nm shoulder observed in 222 nm experiments performed at lower laser energies. Figure 4(b) shows a representative absorption spectrum which is similar to the high-power 222 nm spectrum of Fig. 4(a).

### Copper atom production from copper(II) acetate

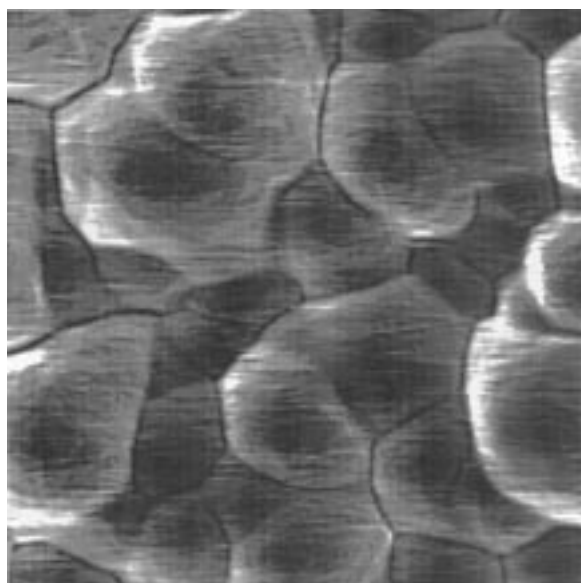
REMPI transitions due to atomic copper transitions were observed using laser energies as low as 0.1–1 mJ/pulse. An example of copper detection, using a 1 + 1 REMPI scheme, is shown in Fig. 7. The observed resonance can be assigned<sup>19</sup> to the  $^4\text{F}^{\circ}_{7/2} \rightarrow ^2\text{S}_{1/2}$  transition. Other transitions from the  $\text{Cu } ^2\text{S}_{1/2}$  state have previously been observed in our laboratory using wavelengths between 230 and 236 nm.<sup>20</sup>

### Preliminary sensor screening

Attempts were made to dope the films obtained via the 308 nm LCVD scheme. Copper(II) acetate was placed directly in the LCVD chamber along with the  $\text{SnBr}_4$  source. Doped films were deposited using 2.8 torr of flowing air, a laser energy of 200 mJ/pulse for 9000 laser shots, and a chamber temperature of 50 °C. The observed resistance of this film divided by the length of the film was found to be 26 k $\Omega$  mm.<sup>-1</sup> The film was tested for sensitivity and selectivity by placing it in a clean vacuum chamber and exposing it individually to the vapor of 2,3-dimethylbutane and 40% (v/v) formaldehyde. In both cases the resistance increased

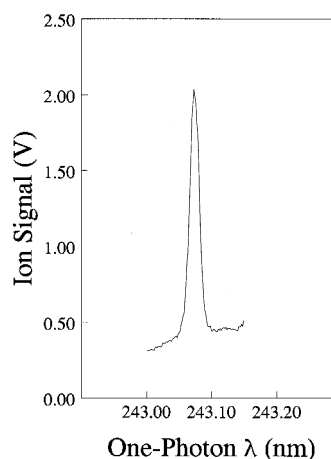


**Figure 5** Image of the raw height data obtained in a contact-mode AFM scan. The film was deposited using 70 mJ/pulse, 222 nm radiation at 1 Hz for 3 h. The deposition chamber was heated to 45 °C and the oxidant was 12 torr air.



**Figure 6** Central 250 nm × 250 nm portion of the data from Fig. 5. The data have been edge-enhanced in order to accentuate the grain boundaries.

very slightly upon exposure to the contaminant gas with changes of approximately 0.2 kΩ torr of added gas. An undoped film deposited under similar conditions also exhibited minimal sensitivity.



**Figure 7** Portion of the non-mass-resolved multiphoton ionization spectrum of copper(II) acetate.

## DISCUSSION

The primary objective of this study was to provide a preliminary exploration of the feasibility of LCVD schemes for SnO<sub>2</sub> gas-sensor materials based on SnBr<sub>4</sub> photolysis in the presence of oxidant gases. Of particular interest in this study is the evaluation of film properties and sensor response when the organic ligand is eliminated in the primary film growth scheme.

The LCVD process generated conducting films only when the laser was focused directly onto the substrate. Prenucleation experiments were unsuccessful, indicating that the multiphoton absorption of the precursor(s), and possibly heating of the film during the deposition process, were critical factors in determining the efficiency of film growth.

Use of SnBr<sub>4</sub> as the film precursor has the advantages over DBTDA of requiring shorter deposition times and allowing the flexibility of 308 nm deposition because of the longer wavelength absorption band. LCVD using DBTDA typically required ten times more laser pulses to obtain similar conductivities. One source of the efficiency of this process may be the ease of dissociation of the precursor;  $\Delta H^\circ_{\text{rxn}}$  (298.15 K) for the reaction  $\text{SnBr}_4(\text{g}) \rightarrow \text{Sn}(\text{g}) + 4 \text{Br}(\text{g})$  is calculated from tabulated thermodynamic data<sup>21,22</sup> to be 1073 kJ mol<sup>-1</sup>. This corresponds to the equivalent of approximately two photons (1078 kJ mol<sup>-1</sup>) at 222 nm and less than three photons (1165 kJ mol<sup>-1</sup>) at 308 nm. It was suggested in previous work<sup>14</sup> on SnO<sub>2</sub> LCVD deposition from SnCl<sub>4</sub>/N<sub>2</sub>O that gas-phase generation of SnOCl<sub>2</sub>, possibly generated from photochemically generated SnCl<sub>3</sub> and O(<sup>1</sup>D), is an important film precursor. In our LCVD experiments, more extensive fragmentation of the tin precursor is expected. Multiphoton ionization spectroscopy<sup>23</sup> of SnCl<sub>4</sub> indicates that atomization is an important process under focused laser conditions. Reactions of gaseous tin with N<sub>2</sub>O and O<sub>2</sub> are known<sup>24</sup> to generate SnO, which has been suggested as a key intermediate in models for SnO<sub>2</sub> CVD from Sn(CH<sub>3</sub>)<sub>4</sub>.<sup>25</sup> Preliminary multiphoton-induced emission experiments on SnBr<sub>4</sub> in our laboratory (J. A. Rzepiela and J. M. Hossenlopp, unpublished results) indicate that gas-phase atomic tin is formed during our LCVD experiments. Work is in progress to look for evidence of other potential gas-phase intermediates such as SnO.

The AFM data indicate that average grain sizes for our films are smaller and more uniform than those reported for reactive sputtering<sup>4</sup> and laser evaporation deposition<sup>7</sup>. Although the effects of

laser intensity, substrate temperature, precursor identities and partial pressures still need to be explored in more detail, LCVD appears to be a promising approach for generating grain sizes in the 10–100 nm range. Preparing such nanocrystalline grains, and investigating the correlations between morphology and sensing behavior, are areas of active interest in SnO<sub>2</sub>, thin-film sensor development.<sup>1</sup> Future experiments are also planned which will utilize single-crystal substrates and larger areas of film deposition in order to improve X-ray diffraction measurements.

There are several potential disadvantages in replacing the organometallic DBTDA with SnBr<sub>4</sub>. The first is the need for a more complex LCVD scheme which includes an additional oxidant source. The ease of generating conducting films under a variety of conditions seems to preclude this from being an important concern. A second potential disadvantage is film contamination. Minimizing carbon contamination of the films was a motivating factor for replacing DBTDA as the SnO<sub>2</sub> source. There was obvious evidence of contamination from the SnBr<sub>4</sub> when using 222 nm LCVD with laser energies which were previously found to be suitable for use with DBTDA. This appears to be consistent with reported residual intermediate species in the SnO<sub>2</sub> LCVD studies using SnCl<sub>4</sub> and N<sub>2</sub>O.<sup>14</sup>

The most important problem with the SnBr<sub>4</sub> LCVD route is the lack of sensitivity found in the preliminary gas-sensing screening. Resistance per unit length for the film used in sensor testing here was similar to those obtained in our previous work. It should be noted that the resistance/length values reported in Table 1 of Ref. 10 should be labeled with units of k $\Omega$  mm<sup>-1</sup>. The film deposited from a precursor mixture of SnBr<sub>4</sub> and copper(II) acetate exhibited three orders of magnitude less sensitivity and no selectivity. It may be possible that the reduction in efficiency of the copper doping was due to a change in either the photolysis wavelength or the photolysis time. However, we do observe film deposition from copper(II) acetate in the absence of SnBr<sub>4</sub> at 308 nm. We also note that even undoped films deposited from DBTDA exhibited better sensitivity than do those from SnBr<sub>4</sub>. Work is in progress to test film growth conditions further in order to determine whether SnBr<sub>4</sub> can be utilized as a viable sensor precursor.

Developing efficient doping schemes also requires an understanding of the gas-phase photo-fragmentation processes. Not surprisingly, copper(II) acetate generates gas-phase copper

atoms. This fragmentation behavior is similar to that observed for copper(II) acetylacetonate.<sup>26,27</sup> A review of copper LCVD using a variety of precursors and conditions can be found in ref. 12. More work is needed to understand the mechanism of copper incorporation into these films and to find the optimal conditions for deposition of doped SnO<sub>2</sub> films.

## CONCLUSIONS

LCVD at 222 and 308 nm was utilized to generate SnO<sub>2</sub> films from SnBr<sub>4</sub> with air, O<sub>2</sub> or N<sub>2</sub>O used as oxidants. Conducting films, with 50–100 nm SnO<sub>2</sub> grain sizes, were obtained with approximately one-tenth of the number of laser pulses required when DBTDA was used as the LCVD precursor. Some film contamination was evident in the 222 nm LCVD route when laser energies below 60 mJ/pulse were used. Despite concerns that carbon incorporation from organometallic precursors may potentially inhibit sensor behavior, preliminary sensitivity screening indicates that DBTDA was a more effective precursor than SnBr<sub>4</sub> for producing effective sensor materials. Finally, multiphoton dissociation of gas-phase copper acetate, under photolysis conditions similar to those used for producing doped films, was shown to produce copper atoms.

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