Direct Photopatterning of Metal Oxide Structures Using Photosensitive Metallorganics

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A novel process employing photosensitive metallorganic precursor materials is used to pattern thin-film mixed-metal oxide structures. In this process a photosensitive metallorganic precursor is coated onto a silicon substrate and exposed to ultraviolet light through a mask to form patterned oxide structures or baked at low temperatures to produce blanket metal oxide thin films. In the case of direct photopatterning, a negative-tone process occurs in which the unexposed areas can be washed away using a developer solvent. The photochemical conversion of the precursor films was monitored using transmission Fourier transform infrared (FTIR) spectroscopy, and lithographic contrast experiments were conducted to estimate the dose required to pattern mixed oxide films of barium, strontium, and titanium. It was determined that the minimum dose required to print an image with the set of precursors investigated in this work was approximately 440 mJ/cm^2 for a precursor film thickness of 800 nm. Based on FTIR data, this dose corresponds to removal of approximately 20% of the organic material from the original precursor film. Dielectric properties were measured for photochemically converted oxide films via parallel-plate capacitance testing. The composition of the oxide films produced from a given precursor stoichiometry was determined by using X-ray photoelectron spectroscopy. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1792648] All rights reserved.

Thin oxide films are required in various microelectronic applications such as infrared sensors, electro-optics, memories, and integral passives. In recent years, thin-film perovskites and ferroelectrics such as barium strontium titanate (BST) and lead zirconate titanate (PZT) have received considerable attention due to their high dielectric constants.[1-3] These materials have been primarily deposited using chemical vapor deposition (CVD), sputtering, sol-gel, and laser ablation processes, which (*i*) require either the use of costly vacuum equipment and/or high-temperature processing to deposit the films and (*ii*) subsequently require additional process steps to pattern the oxide film. Both of these characteristics translate into increased cost and process complexity which may be unacceptable in certain applications. One such difficult application is the deposition of high dielectric constant materials for integrated capacitors in system-on-a-package (SOP) or system-on-a-chip (SOC) applications where the use of high temperatures is often prohibited. Furthermore, for applications in printed wiring board (PWB) fabrication, the use of vacuum-based deposition processes is often considered too costly and time consuming. Processes that require the use of a subtractive etch, such as the conventional oxide deposition methods mentioned previously, also may not be compatible with the patterning of materials that are difficult to etch, such as BST and other mixed oxides. BST and other related materials are often difficult to etch due to the inability to form volatile etch products.[4-6]

In this paper, results on the direct-patterned deposition of amorphous oxide films via photosensitive metallorganic precursors are presented. This novel technique allows amorphous metal oxide films to be deposited at ambient temperatures and pressures. The photochemical reactions of carboxylate groups have previously been shown to result in fragmentation into carbon dioxide and an organic radical under a variety of different conditions, both in solution[7] and on surfaces.[8-10] Thus, metallorganic precursors containing this linkage group can be used to form thin metallorganic precursor films that can be directly photoconverted to metal oxides using radiation exposure. The photosensitivity of these materials allows one to selectively deposit metal oxide structures using lithographic methods, without requiring the use of the subtractive etch that is needed to pattern blanket films deposited by traditional means [*i.e.*, physical vapor deposited (PVD), CVD, sol-gel, etc.]. Low temperature (<200°C) thermal baking can also be used to convert the precursor films into the appropriate metal oxide, but only blanket oxide films

can be achieved unless direct write heating methods are used.[11-13] Since direct write methods are relatively slow due to their serial nature, no further discussion of this type of thermal patterning is discussed in this paper. However, studies are currently underway to explore the advantages and limitations of such thermal patterning methods using the materials discussed in this work. The thermal conversion of these precursor films will be the subject of a future publication. Figure 1 shows the method for depositing metal-oxide thermally or photochemically using photosensitive metallorganic precursors.

In the process investigated in this work, a metallorganic precursor is coated onto a substrate (typically by spin casting) to form a uniform film of good optical quality. The precursor can be converted to the metal oxide by UV exposure or thermal baking. Direct patterning of the precursor can be achieved by UV exposure through a mask and subsequent developer rinse to wash away unexposed regions. This process offers several advantages when compared to traditional CVD, sputtering, laser ablation, and sol-gel processes. The subtractive oxide etch required for blanket films deposited by the traditional methods is eliminated, removing the need for plasma etching equipment and avoiding the difficulties with etching some oxide materials such as BST. The simplicity of this process also leads to a relatively low cost method that may potentially be useful in a wide variety of applications. Although higher temperatures may not be compatible with all applications, the amorphous oxides deposited using this technique may also be converted to an appropriate crystalline form by following the initial patterned deposition with a thermal annealing step.

Although this process and set of materials could be used in a number of different applications that call for blanket or selective deposition of metal oxides, the focus of the current work is on microelectronic applications. Specifically, the deposition of metal oxide films using photosensitive metallorganic precursors for forming dielectric layers used in applications such as transistor gate stacks and integrated capacitors. For example, this method may be an attractive approach for fabricating capacitors for SOP integral passive applications where materials and processes must meet the low cost and low temperature requirements imposed by printed wiring board (PWB) technologies.[14-17] In addition to economic requirements such as low cost of ownership and high throughput, there are material requirements that must be met in order for a process to be considered viable in the PWB industry. For example, process temperatures must be below 200°C for applications on organic substrates such as FR4. This requirement poses a unique challenge when dealing with higher dielectric constant (*k*) materials because

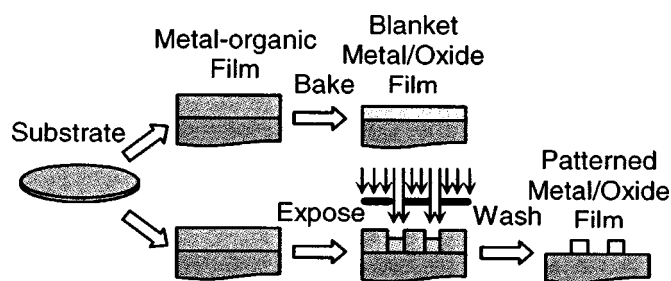[z] E-mail: cliff.henderson@che.gatech.edu

Figure 1. Deposition of metals and metal oxides using photosensitive metallorganic precursors.

these materials generally require vacuum and or high-temperature processing. By using photosensitive metallorganic precursors, amorphous metal oxide structures may be deposited at ambient conditions with no need for vacuum equipment or high-temperature processing.

To be suitable for UV patterning, the metallorganic precursors chosen should (*i*) coat to form films of good optical quality, (*ii*) undergo a desired, specific photochemistry, (*iii*) produce volatile reaction by-products, and (*iv*) possess a reasonable lithographic contrast. It is very important that the metallorganic precursors selected coat to form amorphous films so that optical scattering does not interfere with the ability to lithographically pattern the materials. In the materials chosen in this work, the presence of chiral centers in the precursor ligands prevents crystallization of the film. It is also important that ultraviolet exposure selectively cleave the ligands from the metal (as opposed to simple random bond scission events) in order to produce oxide materials with low carbon contamination. Furthermore, ideally the resulting photoproducts are sufficiently volatile so as to result in a low number of trapped contaminants in the resulting oxide film. Finally, for use with conventional lithographic exposure technologies, the material must possess a reasonable lithographic contrast in order to produce well-defined patterns of the desired size. All of these characteristics must be satisfied for a precursor to be selected for use in a photopatterning process.

In this study, the ability to produce patterned thin-film mixed oxide structures using a set of metallorganic precursors is investigated. Fourier transform infrared (FTIR) spectroscopy was used to monitor the photolytic conversion of the precursor to metal oxide. Contrast studies were performed to determine the exposure dose required to successfully pattern thin-film oxides using the particular precursor set investigated in this study. Parallel-plate capacitance testing was performed to evaluate the dielectric properties of the resulting oxides deposited by this method. Finally, X-ray photoelectron spectroscopy (XPS) was used to characterize the composition of the deposited oxide thin films.

Experimental

Materials.—All of the results presented in this work are for an amorphous mixed-metal oxide composed of a mixture of the oxides of barium (Ba), strontium (Sr), and titanium (Ti). The metallorganic precursor solution was prepared with a solution consisting of a 1:1:2 molar ratio of Ba(2-ethylhexanoate), Sr(2-ethylhexanoate), and Ti-(diisopropoxide) bis(acetylacetonoate) in methyl isobutyl ketone. Strontium and titanium compounds were obtained from Strem Chemicals, Inc., and the barium precursor was obtained from Aldrich Chemical Company, Inc. Films were prepared on single-side polished, 100 mm ⟨100⟩ n-type (1-20 Ω cm) silicon wafers unless otherwise noted. Since all of the experiments described in the paper were performed at ambient temperatures, all of the resulting oxide films are expected to be amorphous. Previous X-ray diffraction (XRD) studies on oxide films derived from these precursor materials have shown the photoconverted oxides to be amorphous and thermally converted oxides to be amorphous until annealing temperatures reach at least 550°C.[18] Although this material is not strictly a

titanate due to its amorphous nature, we refer to the mixed oxide materials produced in this work as BST throughout the rest of this paper for the sake of simplicity.

Film preparation.—Films were coated onto silicon wafers by spin casting using a CEE model 100 CB spin coat and bake unit. Unless otherwise specified, the precursor films used in this work were not subjected to a thermal bake after coating.

Ellipsometry.—Film thicknesses were determined using a V-VASE variable angle spectroscopic ellipsometer (J.A. Woollam Co., Inc.). Ellipsometer measurements were made over the spectral range from 400 to 1100 nm at three different angles (65°, 70°, and 75° from normal incidence) with a 5 nm sampling interval. All precursor and oxide films were modeled using a Cauchy dispersion model to determine film thickness and optical constants. The Cauchy model is sufficient in this case since the precursors used in this work possess no appreciable absorption in the measured wavelength range.

Fourier transform infrared spectroscopy.—Fourier transform infrared (FTIR) spectra were measured from 400 to 4000 cm^{-1} in transmission mode using a Nicolet 510 FTIR spectrometer at a resolution of 4 cm^{-1} with precursor films coated onto single-side polished silicon wafers. The spectrometer was purged with dry nitrogen for 10 min prior to data collection.

Deep ultraviolet flood exposure.—Precursor films were converted to amorphous BST for both contrast and FTIR studies via exposure to deep-UV light using a 500 W, Oriel 87000 Series Hg-Xe flood exposure tool, and a deep ultraviolet (DUV) bandpass filter with a center wavelength of 248 nm and a full width at half maximum (fwhm) bandwidth of 10 nm. The intensity of the lamp output was monitored using a Molectron EPM2000e power/energy meter and PM-3 power probe. All exposures were performed at a sample plane intensity of 2 mW/cm^2.

Dielectric measurements.—The dielectric properties of photochemically prepared BST samples were evaluated using parallel-plate capacitance testing. Mixed oxide films were prepared using the BST precursor solution in MIBK by spin casting onto aluminum (Al) coated wafers to produce a film thickness of approximately 800 nm. After conversion of the precursor film to the corresponding oxide, Al top electrodes with a diameter of 2 mm were evaporated onto the BST thin film using a CVC E-beam evaporator in conjunction with a metal shadow mask. Capacitance and leakage current values were measured in the 100 Hz-1 MHz frequency range using a Karl Suss probe station and an HP 4284A high precision LCR meter. Electrical measurements were performed by probing between two capacitor top electrodes using the underlying continuous metal film as a common ground plane (*i.e.*, two capacitors in series).

Patterning.—Patterning of BST line-space patterns was achieved using an OAI model J500/vis mask aligner, with a 1000 W DUV Hg/Xe lamp, and 220-260 nm cold mirror. The output of the aligner was measured using an OAI model 306 UV power meter. Exposures were performed in contact mode using chrome on quartz masks with line-space patterns (1:1 pitch) of varying sizes. The smallest size feature on the mask was 1 μm, which is near the practical resolution limit of contact lithography. Each precursor film was baked at 150°C for 30 s and exposed to a dose of 1.8 J/cm^2. After exposure, the unconverted (*i.e.*, unexposed) precursor was washed away using a developer solvent mixture of IPA:MIBK (20:1). Optical micrographs were taken using a Zeiss Axioscope model no. 1130 with Epiplan-NEOFLUAR objectives and a CE model no. 1.1.0 charge coupled device (CCD) camera made by Diagnostic Instruments, Inc. Scanning electron microscope (SEM) images of the oxide line-space patterns were acquired using a Hitachi S-4500 SEM. The accelerating voltage for all SEM micrographs was 10 keV. Cross-sectional images were created by first coating samples with Au/Pd using a Denton Vacuum Desk II sputtering tool to prevent sample charging.
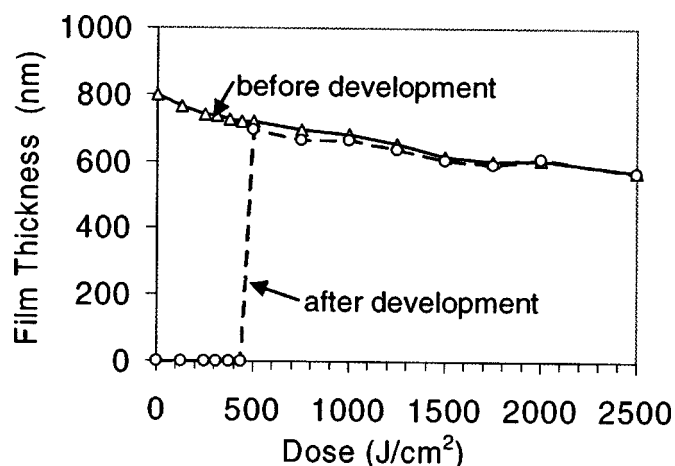
Figure 2. Ellipsometry data showing film thickness *vs.* dose for films before and after 15 s developer (20:1, IPA:MIBK) rinse.
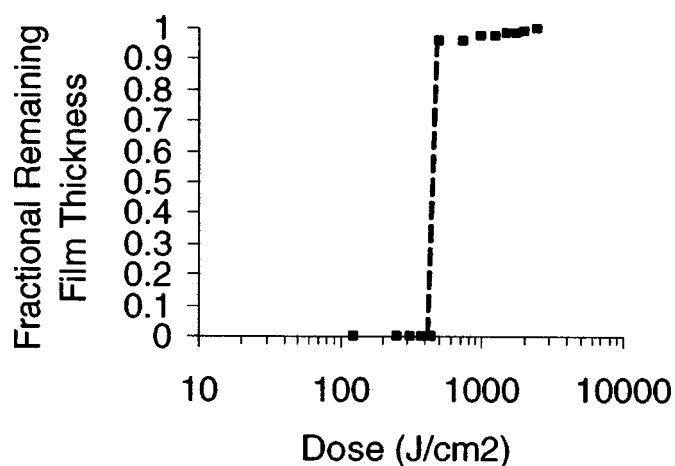

Figure 3. Photochemical contrast for BST on silicon. Fraction of postexposure film thickness remaining after 15 s developer (20:1, IPA:MIBK) rinse.

X-ray photoelectron spectroscopy (XPS).—Compositional analysis of the converted BST films was performed using XPS on a Physical Electronics PHI 1600 XPS system. Monochromatic Al K_α X-rays were generated using a water-cooled anode operated at a power of 350 W. All analysis was performed with X-rays incident on the sample at an angle of 45° from the detector axis. Chamber pressure was typically below $5 \cdot 10^{-9}$ Torr during analysis. *In situ* Ar^+ sputtering was used to remove any surface contamination in order to obtain accurate bulk material compositions.

Results and Discussion

Contrast data.—Since the goal in this work was to use lithographic methods to achieve the direct photopatterning of metal oxide films, quantification of the two common lithographic characteristics of sensitivity and contrast for this material/process combination is important. In order to evaluate these characteristics, contrast curves, which plot normalized film thickness remaining after development (defined here as the ratio of remaining film thickness after development to the film thickness before development) as a function of the log of the exposure dose, were measured. The contrast data was generated in the following manner: (*i*) metallorganic precursor films were spin coated at 4000 rpm to achieve a nominal thickness of 800 nm, (*ii*) initial film thickness was measured using ellipsometry, (*iii*) the sample was exposed to varying doses of energy at 248 nm, (*iv*) the precursor film was partially converted due to the exposure and a corresponding decrease in film thickness occurred which is measured by ellipsometry, (*v*) each sample was developed by immersion in a 20:1 solvent mixture consisting of isopropanol (IPA) and methyl isobutyl ketone (MIBK), respectively, and dried with nitrogen for 15 s, and (*vi*) the final postdevelopment film thickness was again measured using ellipsometry. This final step allows determination of the relative amount of the postexposure thickness remaining. From this data the normalized fraction of film thickness remaining can be plotted *vs.* exposure dose and two important lithographic characteristics for these materials, the lithographic contrast and sensitivity, can be evaluated. Results of these contrast experiments are shown in Fig. 2 and 3.

The contrast factor (γ), a measure of how sharp the change in the remaining film thickness is as function of change in exposure dose, is usually defined by Eq. 1

$$\gamma = \frac{1}{\log\left(\dfrac{D^0}{D^I}\right)}. \qquad [1]$$

Here D^I is referred to as the interface dose, and corresponds to the dose at which the first amount of film remains after development, while D^0 is the dose required to produce no decrease in the remaining film thickness after development (normally determined by extrapolating the linear portion of the curve to a value of 1.0 normalized thickness). The contrast gives a measure of the ability of a photosensitive material to reproduce sharp relief profiles with vertical sidewalls when exposed and developed. Depending on the contrast of a material, it may act to reproduce patterns with heights more or less proportional to exposure intensity (low contrast) or it may produce digital (high contrast) patterns with feature edges defined at some nominal threshold dose.

For negative tone materials, such as those studied in this work, the sensitivity (*S*) can be defined as the exposure dose required to obtain a standard normalized thickness after development. In this study, the sensitivity is defined, as the dose needed so that the film thickness after development is 50% of the thickness after exposure. A smaller value of *S* implies that the metallorganic system is more sensitive to UV irradiation.

Based on these experiments the sensitivity, *S*, of this set of precursors was 440 mJ/cm^2 and the contrast, γ, was 8.0. Current DUV resist materials have sensitivities on the order of 10 mJ/cm^2 and contrast values greater than 5. Modern I-line resist materials have sensitivities on the order of hundreds of mJ/cm^2 and with contrasts which can approach that seen in DUV materials. In comparing these values, it is clear that the contrast for these oxide precursors is comparatively high but the sensitivity is on the lower end of the range comparable with I-line materials. Currently, methods including both processing changes and novel precursor design are being investigated to increase the sensitivity of this set of metallorganic precursors.

FTIR monitoring of conversion.—The contrast in these materials is due to the conversion, or at least partial conversion, of the soluble metallorganic precursor to an appropriate oxide which is insoluble in the developing solvent. Thus, in terms of understanding the sensitivity of these materials, it is necessary to quantify the extent of conversion required for image formation. Therefore, the conversion of the metallorganic precursor film to the resulting metal oxide during exposure was monitored by FTIR. A summary of the absorption peaks for the precursor materials may be found in Table I. Upon conversion from the original metallorganic precursor form, the IR absorbance peaks corresponding to the appropriate precursor ligand bonds decrease and provide a method with which to monitor conversion of the precursor.

In a typical process, the metallorganic precursor film is spin coated onto the substrate and converted to the oxide by UV expo-

Table I. FTIR peak assignments for the metal oxide precursors used in this work.[a]

Complex	Wavenumber (cm^{-1})	Assignment
$Sr(O_2CC_7H_{15})_2$	1688, 1296	$\nu(CO)$ unidentate
	1558, 1416	$\nu(CO)$ bridging
	1558, 1458	$\nu(CO)$ bidentate
$Ba(O_2CC_7H_{15})_2$	1687, 1290	$\nu(CO)$ unidentate
	1543, 1460	$\nu(CO)$ bridging
	1543, 1416	$\nu(CO)$ bidentate
$Ti(O^iPr)_2(acac)_2$	1013, 993	$\nu(CO)$ isopropoxide
	930	$\nu(CO) + (CC)$ isopropoxide
	1589, 1524	$\nu(CO) + (CC)$ acac

[a] Ref. 18.

sure. The most significant absorption bands for the precursor films are the C-H stretching modes near 3000 cm^{-1} and the regions corresponding to the carboxylate groups at approximately 1400 and 1550 cm^{-1}. During conversion the intensity of the absorption peaks in both of these regions decreases.

The FTIR spectra of the photochemical conversion of the BST precursor film is shown in Fig. 4. After a dose of 10 J/cm^2, the peaks corresponding to the C-H stretching modes reduced almost to the baseline. This would indicate essentially a complete loss of the organic ligands in the original precursors. IR absorption peaks corresponding specifically to the various titanium complexes in the precursor mixture disappear even more rapidly than the bulk C-H peaks, indicative of the fact that the titanium precursor is more reactive than the barium and strontium components in the film. This conclusion is supported by previous data on the Ti precursor used as a single component film under exposure to UV light and ambient room air which have shown it to be highly photosensitive and moderately hydrolytically unstable.[18] However, even after exhaustive conversion, significant absorption is still observed in the region from 1300 to 1700 cm^{-1}. This absorption is observed even when the peak areas corresponding to the C-H stretches have diminished to approximately 1% of their original absorbance. There are many possible contributors to absorption in this region, including those due to the original precursor complexes and also those corresponding to metal carbonates. This absorption however cannot be due to the remaining unconverted precursor since virtually all C-H stretching is absent in the exposed material. Barium carbonate should produce a strong peak at approximately 1450 cm^{-1} and a smaller peak at approximately 860 cm^{-1}. The presence of many peaks in the vicinity of 1450 cm^{-1} makes it difficult to identify a single peak for barium
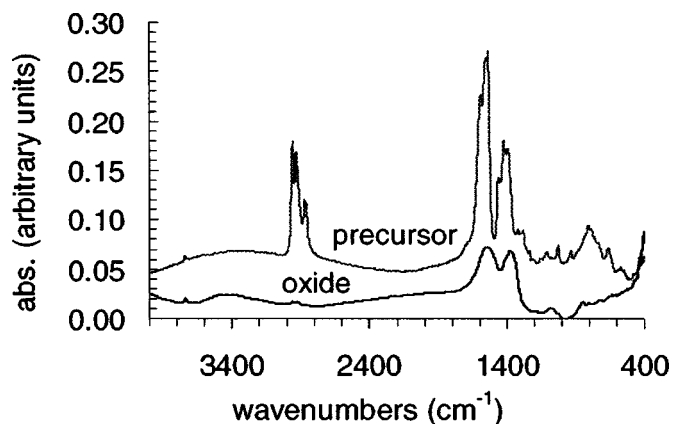

Figure 4. FTIR spectral changes accompanying the photolysis of the metallorganic precursors of BST. Oxide sample exposed to a total dose of 10 J/cm^2 (248 nm bandpass filter, nominal exposure intensity = 2 mW/cm^2). These spectra are offset for clarity.

carbonate. However, in the spectrum of the converted film, a small peak is visible at approximately 860 cm^{-1} which may indicate the formation of carbonate species in the film. A rinse in developer solvent was shown to have no effect on the FTIR spectrum of the photoconverted oxide. This suggests that the remaining materials are either insoluble in the developer solution or that they are trapped in the film. Further investigation of the nature of the species that could be contributing to this absorption in the 1300 to 1700 cm^{-1} region and the potential for carbonate formation in these materials is currently in progress.

Previous FTIR studies have shown that the photochemistry of the barium and strontium precursors in the mixture is significantly more efficient than the photochemistry of the individual components by themselves. Other work on this set of materials has suggested that the titanium precursor follows a radical-based decomposition mechanism similar to that seen for acetylacetonate complexes.[19] It is possible that the radicals produced during the decomposition of titanium precursor react thermally with the barium and strontium complexes leading to their decomposition. It is also possible that the increased reaction rates of the barium and strontium complexes in the mixture could be due to electron transfer reactions with the excited titanium complex.[18] Based on these assumptions, one might conclude that the extent of conversion would be limited by a combination of two factors, (*i*) the relative photosensitivity of each of the components in the precursor mixture, and (*ii*) the ratio of the different precursors in the mixture. If all of the titanium precursor in the mixture were to react before complete conversion of the barium and strontium complexes, the effective rate of reaction for the mixture would drop to that of the individual remaining precursors for barium and strontium. Because of the low optical absorption of the barium and strontium precursors at the exposure wavelengths used, the rate of the reaction and the maximum conversion of the precursor film would be dependent on the presence of sufficient amounts of the titanium precursor throughout the photoreaction process. Further studies on the photochemical and thermal conversion of this set of precursors are being performed to determine if such a relationship exists.

XPS analysis.—In order to verify the composition of the resulting UV converted and patterned material, the elemental composition of the resulting films was measured using XPS. Silicon wafers coated with photochemically converted BST were diced into smaller pieces for compositional analysis. For XPS studies, *in situ* Ar$^+$ sputtering was used to clean adventitious carbon and other surface contaminants from the samples. XPS depth profiling was also performed to determine the compositional uniformity of the samples.

An initial survey scan confirmed the presence of barium, strontium, titanium, oxygen, and small amounts of carbon. After the survey scan, a high-resolution scan was measured for each of the binding energy regions of interest. For the high-resolution scan, the pass energy was set to 11.75 eV and the relative compositions of the various elements in the deposited films were determined by curve fitting each spectral region, assuming all peaks to be Gaussian with a constant fwhm. According to this analysis, the photoconverted film was composed of 1.6% carbon, 60.1% oxygen, 21.2% titanium, 9.0% strontium, and 8.1% barium on an atomic basis. The carbon content found in the converted oxides is approximately an order of magnitude higher than what is typically found in crystalline BST films prepared by metallorganic decomposition.[20] However, the uncertainty of the carbon content as determined by XPS is relatively high due to the fact that the carbon levels are approaching the detection limit of the spectrometer. Furthermore, direct comparison with a crystalline BST sample is not entirely appropriate because the high temperatures used to convert the amorphous precursor film to a crystalline phase could reduce the overall carbon content.

The results of the XPS experiments are consistent with a majority of the precursor material being converted to the oxides TiO_2, BaO, and SrO. The measured ratio of the metals in the oxide is very close to that of the precursor mixture. The slight differences in the

calculated metal ratios for the oxide film may be due to a variety of factors including small fluctuations in the formulated precursor material concentrations, errors introduced by the XPS data analysis (machine sensitivity factors, etc.), and any changes in the film composition induced by the Ar^+ sputtering. The small amount of carbon remaining in the film may be the result of small amounts of unconverted precursor material or carbon contamination that is trapped in the film. These findings are consistent with the FTIR results. Depth profiling studies did not show any significant compositional nonuniformity throughout the thickness of the film.

Electrical measurements.—Since the current focus for application of these oxide films and patterns is in electronics applications, the electrical properties of the BST films produced in this work were characterized. In order to evaluate the dielectric properties of the BST samples, parallel-plate capacitor structures were fabricated. Substrates for this study consisted of silicon wafers coated with 1 μm of Al. Samples consisted of BST thin films created by UV exposure to a dose of 20 J/cm^2. The high dose was used to insure exhaustive conversion. After conversion, top electrodes were deposited by evaporating aluminum through a shadow mask. A dielectric constant of 27 was measured for a final converted BST oxide film thickness of 250 nm. Typical values for loss tangent were 0.01 and both dielectric constant and loss tangent were stable over the frequency range of 100 Hz to 1 MHz. Additional testing will need to be carried out in order to evaluate the performance of these materials at higher frequencies above 1 MHz.

A dielectric constant of 27 is in the range of previously reported values for amorphous BST films deposited by pulsed laser deposition (PLD)[21] and metalorganic chemical vapor deposition (MOCVD).[22] However, it is likely that the dielectric constant of the photochemically deposited films has been reduced due to the carbon impurities in the oxide film. Obtaining the maximum dielectric constant for this set of materials will require the elimination or reduction of such impurities. Different precursor mixtures are currently being evaluated to determine the effect of precursor composition on the resulting dielectric constant for oxide films. The crystallization of amorphous blanket films and patterned structures produced using this method are also currently being studied and will be reported in the future. The impact of precursor ligand structure on the properties of the precursor and resulting oxide films is also under investigation.

The breakdown behavior of BST oxide films was investigated by measuring current-voltage (I-V) curves using the capacitor samples built for measuring the dielectric constant of the materials. Analysis of the I-V curves showed that the samples displayed dielectric breakdown at applied field strengths in the range from 15 to 40 MV/m. The higher dielectric strength values measured for some of the films is near the range of values reported for high quality crystalline BST films deposited using other methods which are typically from 50 to 150 MV/m.[23,24] Previous authors have shown that there appears to be a general trade-off between the dielectric constant and dielectric strength in thin film dielectric materials. When the logarithm of the dielectric strength is plotted *vs.* the logarithm of the dielectric constant on a log-log scale for thin-film dieletrics, an inverse and nearly linear correlation is observed. Higher dielectric constant materials such as crystalline BST and PZT which have dielectric constants of several hundred to several thousand typically are found to have dielectric strengths in the range of 60 to 200 MV/cm. Low dieletric constant materials such as SiO_2 and Si_3N_4, which have dieletric constants in the range of 3 to 8, possess dieletric strengths in the range of 500 to 1000 MV/m. Using the fact that such dieletric strength *vs.* dielectric constant correlations appear to be somewhat general, it may then be useful to compare the breakdown strength of the amorphous BST materials produced in this work, which possess dielectric constants on the order of 30, to materials with similar dielectric constants such as Ta_2O_5. This comparison shows that the amorphous BST mixed oxides produced in this work display approximately an order of magnitude lower dielectric strength than materials such as Ta_2O_5 which have dieletric
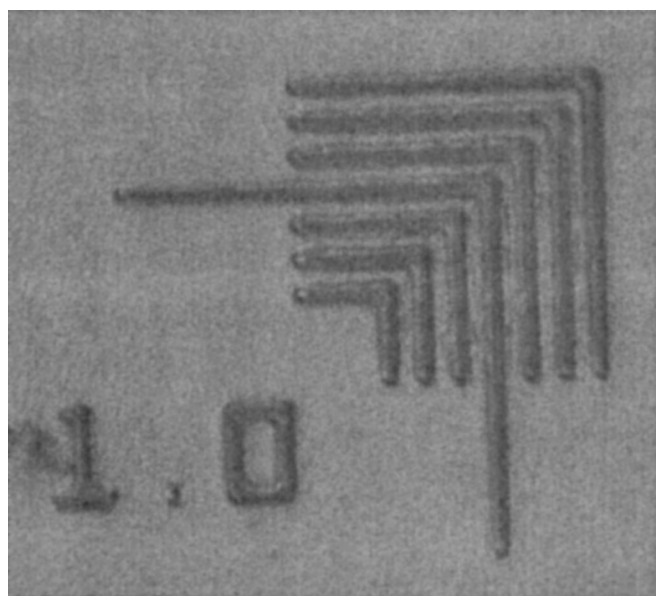

Figure 5. 1 μm line-space array patterned in BST. (150°C soft bake for 30 s followed by 1.8 J/cm^2 exposure)

strengths reported between 300 to 500 MV/m. More detailed inspection of the capacitor samples which displayed lower breakdown strengths revealed that those capacitors appeared to have particle defects in the oxide that were generated during the spin-coating process and subsequently covered by the capacitor electrodes. This would suggest that the presence of such particle defects may be one of the primary causes of the very low breakdown strength observed in some of the samples. However, further detailed capacitance *vs.* voltage (C-V) and current *vs.* voltage (I-V) measurements are in progress to draw more definitive conclusions about the electrical performance of these materials and to assess what factors, including both precursor chemistry and processing conditions, influence this behavior.

The chosen electrode material is also known to have a potentially significant impact on the measured performance of thin-film dielectrics. Reactive metals such as aluminum have a strong tendency to reduce the adjacent oxide material, especially at the elevated temperatures required for most oxide deposition processes. When placed in direct contact with an oxide dielectric, the oxygen may have a higher affinity for the metal electrode, resulting in oxygen diffusion from the dielectric into the metal and the creation of oxygen vacancy defects in the dielectric. These defects can result in greatly reduced electrical performance and large increases in leakage current. For this reason, inert metals like Pt or Au or more exotic conducting metal oxides such as Ru_2O_3 are often chosen as the electrode material for oxide dielectrics. The absence of high-temperature processing in this work should serve to minimize these interactions between aluminum electrodes and the amorphous dielectrics. Preliminary electrical tests with photoconverted oxide samples made on Pt electrodes have not displayed significantly different results than those obtained with the photoconverted oxides made on the Al electrodes.

Patterning results.—As an example of the lithographic results obtained using these materials, Fig. 5 and 6 show an optical micrograph and SEM images, respectively, of top down and cross-sectional views of BST features printed on silicon substrates. These BST line-space patterns were created by first coating BST precursor films approximately 1 μm thick onto silicon substrates. These films were baked at 150°C for 30 s to achieve partial conversion and lower the exposure dose required to form an image. The precursor film was then exposed to a dose of 1.8 J/cm^2. This combination of
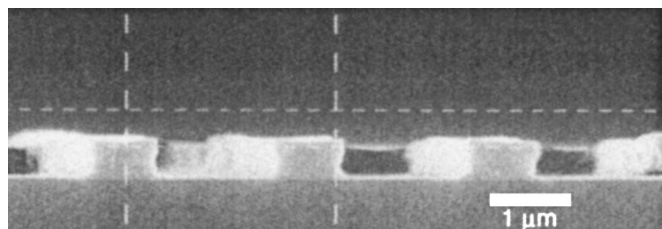
Figure 6. SEM cross section of 1 μm line-space array patterned in BST. (Same conditions as in Fig. 5)

conditions corresponds to approximately a 50% loss of the organic material in the film. This particular set of process parameters was chosen by varying the exposure dose until 1 μm lines and spaces were clearly resolved. Since 1 μm features are near the practical resolution limit for conventional contact lithography, more advanced patterning techniques would be necessary in order to evaluate the minimum feature size achievable with these materials. For most embedded passives applications, the creation of submicrometer oxide structures would not be necessary. However, the use of higher resolution lithographic exposure technologies, such as electron beam lithography, can allow these materials to be used to produce significantly higher resolution patterns. It has been demonstrated that feature sizes below 100 nm can be achieved using similar metallorganic precursor films in conjunction with electron beam lithography.[25,26]

Following exposure and development, the resulting oxide features were examined by SEM. The features were found to be slightly wider at the top than at the bottom. This behavior is typical for a negative tone material that absorbs at the exposure wavelength. Absorption of light as it passes through the film results in a decrease in the local exposure dose from the top to the bottom of the film, resulting in higher degrees of conversion near the surface of the film. This gradient in dose and conversion through the film results in the sloped sidewalls. The average feature width of the resulting oxide lines was 0.76 μm at the top, 0.71 μm at the base, and the average height was 0.45 μm. Further study of the effect of prebake and exposure conditions on the resolution and pattern profiles in these photodefinable metallorganic systems is currently in progress.

Conclusions

In this paper, the fabrication of patterned amorphous thin-film oxides using photosensitive metallorganic precursor materials has been reported. This set of precursor materials may be solution-cast onto a substrate into films of high optical quality and converted to oxide films via exposure to UV light or by baking at low temperatures. Unlike the conventional methods for patterning metal oxides, this method allows one to create patterned metal oxide structures at low temperatures and ambient pressures. These characteristics represent the potential for greatly reduced process costs when compared to the traditional methods of patterning blanket metal oxide films.

In order to determine the dose required to successfully pattern metalloxide structures using this set of metallorganic precursors, lithographic contrast experiments were performed. Using a DUV light source with a center wavelength of 248 nm, a dose of approximately 440 mJ/cm^2 was necessary to convert the precursor film to a sufficient extent that the resulting material would withstand a wash in developer solvent with no loss in film thickness. FTIR analysis showed that this dose corresponds to a 20% conversion of the precursor film. After the initial patterning and development steps, further conversion by either photochemical or thermal treatment may be performed to complete the conversion of the precursor film to the desired metal-oxide form. The impact of this final conversion method on the resulting oxide film properties is currently being studied and will be reported in the near future. Due to the relatively high doses required to pattern oxide features using the set of precursors described in this work, additional work on developing new precur-

sors and more advanced processing methods is also in progress. Nevertheless, this initial work shows that the photochemical deposition process and this class of materials offer a novel method for deposition of patterned oxide structures and that this method may be a promising alternative for creating patterned metal oxide films for integral passives and other electronics applications.

At a frequency of 10 kHz, a dielectric constant of approximately 27, and a loss tangent of 0.01 was measured for the amorphous BST thin films produced in this work. This dielectric constant is in the range of values for amorphous metal-oxides deposited using much more expensive, vacuum-based processing techniques. The breakdown strength of the amorphous BST films produced in this work was also observed to be of the same order of magnitude as that observed for other BST samples reported in the literature, but that it is substantially lower than the dielectric strength of other amorphous oxides with similar dielectric constants in the range of 30.

The physical and chemical properties of the precursor films and resulting oxides are obviously strongly dependent on the particular precursors and mixing ratios used in formulating the precursor solutions. Current work on these materials include investigations of how the mixing ratio of the individual precursors and the method of conversion (*i.e.*, thermal or photochemical) affect the lithographic sensitivity of the overall mixture, the rate and maximum extent of conversion, residual carbon contamination, and the resulting electrical properties of oxide films produced using this method.

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