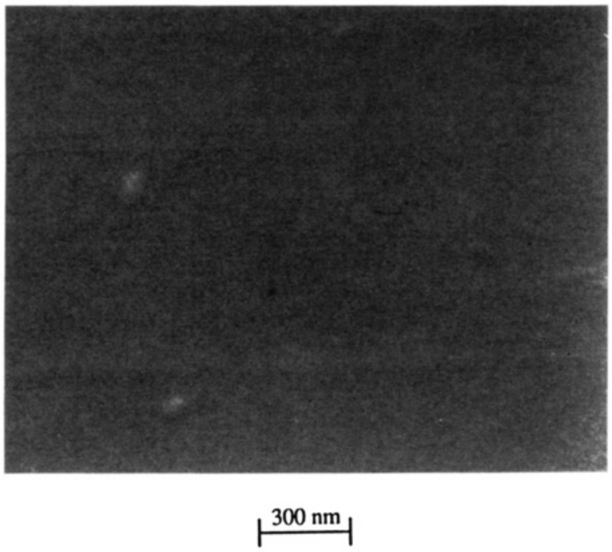

Figure 3. SEM micrograph of $ZrO_2 \cdot 4SiO_2$ thin film spun onto quartz from a 1% solution of **2** in benzene.

produced at 400 °C (2 h, O_2) is composed of 8–32-nm particles (Figure 2d). In samples heated to 1000 °C, t-HfO_2 (or cubic hafnia, c-HfO_2) is present, and samples taken to 1460 °C contain t-HfO_2 (or c-HfO_2), m-HfO_2 (in roughly equal amounts), and cristobalite.

Heating **1** to 400 °C results in amorphous $TiO_2 \cdot 4SiO_2$, from which finely dispersed anatase crystallizes at 1000 °C (by XRD). Samples taken to 1400 °C contain anatase, rutile, and cristobalite.

The low temperatures at which **2** and **3** thermally decompose allow for the convenient formation of silicate networks in solution. Refluxing **2** in xylenes for 10 h produces viscous, nearly transparent fluids and small amounts of particulate matter. Removal of the volatiles in vacuo leaves a white, amorphous $ZrSi_4O_x(OH)_y$ powder that has a BET surface area of 520 $m^2\ g^{-1}$, and looses 27% of its weight when heated to 1150 °C (by TGA). This powder is composed of ca. 0.1–3-μm agglomerates (by scanning electron microscopy) made from smaller, nonspherical 30–70 nm particles (by TEM). The dehydration of $ZrSi_4O_x(OH)_y$ was monitored by ^{29}Si NMR spectroscopy of the isolated powder (dried in vacuo), which revealed a very broak peak which moved from −99 to −110 ppm as the sample was heated from 25 to 1200 °C. Annealing this material at 1200 °C (4 h, O_2) results in a significant reduction of the surface area to ca. 3 $m^2\ g^{-1}$. At higher temperatures, the same crystallization behavior described above for $ZrO_2 \cdot 4SiO_2$ is observed.

Hydrocarbon solutions of **2** and **3** have been used to cast thin films of $ZrO_2 \cdot 4SiO_2$ and $HfO_2 \cdot 4SiO_2$ onto quartz. For example, a 1% solution of **2** in benzene was spun onto a quartz disk, and the disk was then heated to 400 °C under O_2 for 30 min. Examination of the resulting film by SEM (Figure 3) revealed a smooth, crack-free surface. Similar $HfO_2 \cdot 4SiO_2$ films prepared from a 1% solution of **3** in cyclopentanone have thicknesses ranging from 70–90 nm (Dektak 3030 profilometer).

In conclusion, the chemical thermolyses described here represent an alternative approach to the synthesis of nanocomposite silicate materials. The solid-state conversions can produce porous ceramic materials with ordered microstructures. Further investigations are in progress to probe the possibility that formation of ordered microstructures may be controlled via directionality imposed on the condensation process by the crystalline lattice of the precursor compound. The chemistry involved in this process can be applied to sol–gel-like processes in nonpolar media and should allow the homogeneous incorporation of a wide variety of dopants (e.g., polymers or additional metal ions). We are currently investigating the use of the gellike $[MSi_4O_x(OH)_y]_z$ solutions for fashioning films, fibers, and monoliths.

Acknowledgment. Funding for this work was provided by the Air Force Office of Scientific Research (Grant No. AFOSR-88-0273), the National Science Foundation, and Chevron Research Co. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988-92). We also thank Mike Sailor and Joanna McKittrick for helpful discussions.

Photoimaging of Electronically Conducting Polymeric Networks[1]

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Introduction

It is widely recognized that advances in polymer chemistry have played a pivotal role in the development of integrated circuitry. Of particular note are the advances in photolithography which have been achieved by designing high-resolution polymer photoresists for patterning semiconductors, metals, and insulators.[2,3] Polymer photoresists are chosen to exhibit the following properties: good adhesion, high thermal stability, desirable dissolution characteristics, and sensitivity to high-energy irradiation. In the majority of cases, there is little consideration of intrinsic electronic properties exhibited by the resist because it usually plays no role in device operation. In cases where the resist is an integral component of the chip, such as in multichip modules, it is chosen to have electronically insulating properties.[4]

π-Conjugated polymers are under intense investigation because of their semiconductor properties and nonlinear optical activity in the neutral state and their high electronic conductivity in the partially oxidized state. These polymers suffer from long-term stability in the oxidized state which might limit their usefulness. However, one can envisage their application in microelectronic devices where protection from the environment by encapsulation is a mature science and is critical to the stability of a device. A possible application of these materials is the formation of interconnects or channels of defined resistivity for microchips and printed circuitry. This requires their deposition in the form of thin highly defined channels. Several reports which address this challenge have appeared

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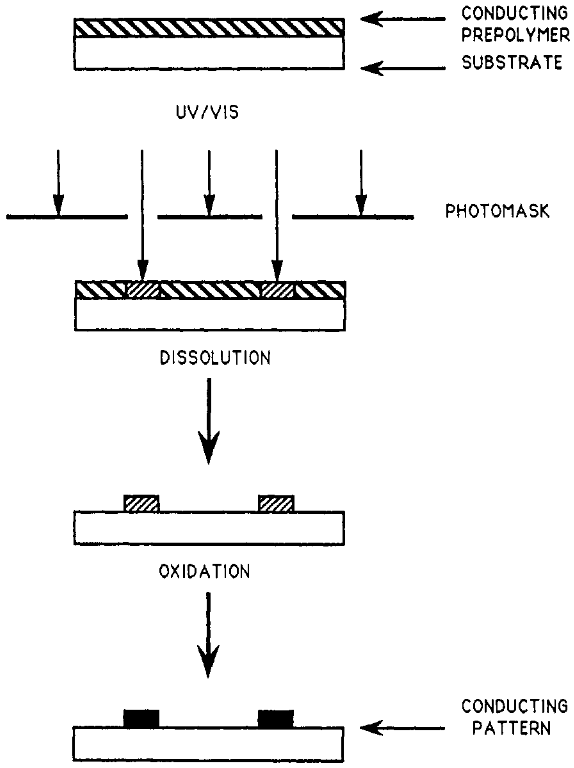
Scheme I



in the literature, but many employ "wet" photochemical or photoelectrochemical methods which are incompatible with present integrated circuit technologies.[5-7] More recently, imaging of conducting polymers has been achieved both by photochemically induced doping using photolabile sulfonium salts incorporated into the polymer films[8,9] and by the formation of a relief image in overlying conventional positive photoresists.[10,11]

We now report a simple and versatile process for fabricating electronically conducting polymeric "wires" or "channels" on solid substrates. The methodology employs a soluble π-conjugated polymer which acts as both the photoresist and a precursor to an electronically conducting pattern (Scheme I).

In the above scheme, a thin film of soluble poly(3-hexylthiophene) is irradiated with UV–vis light through a photomask. The exposed regions undergo a photochemical process which results in insolubility, whereas the unexposed regions remain soluble. Dissolution of the unexposed polymer leaves a negative image of the photomask. Chemical oxidation of the remaining polymer imparts electronic conductivity to the pattern. In this paper we describe preliminary studies on photolysis and photoimaging of thin films of poly(3-hexylthiophene).

Experimental Section

Poly(3-hexylthiophene), I, was synthesized and characterized as previously described.[6] The polymers used in this study had a number average molecular weight of 9300 and a polydispersity index of 2.3. Molecular weights were determined by size exclusion chromatography as previously described.[12]

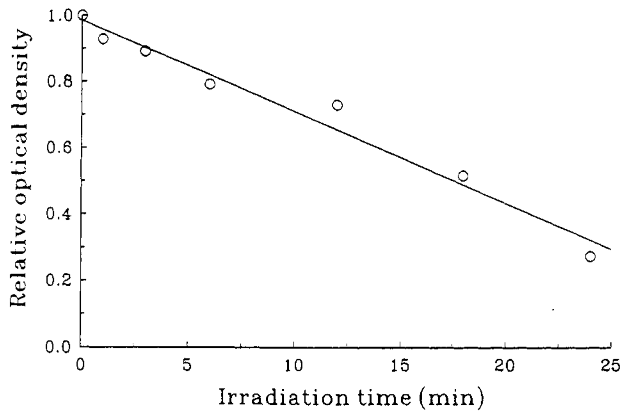
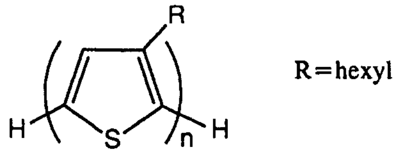


Figure 1. Relative optical density (λ = 500 nm) of poly(3-hexylthiophene) films versus irradiation time. Initial optical density = 1.102. Film thickness: 0.3 μm. Light source: 150-W Hg lamp, 280-nm cutoff filter.



I

Thin films of polymer (30–0.3 μm) were cast onto glass slides or silicon wafers from dilute solutions of the polymer in toluene. The illumination source was a 150-W mercury lamp (Illumination Industries Ltd.). The light was focused to a diameter of 3 cm. A 280-nm cutoff filter was used to eliminate high-energy irradiation. Relief images were formed in thin polymer films by irradiating through a photomask placed on top of the film. Photolysis was performed in ambient air, unless otherwise stated. Polymeric patterns were observed upon development with toluene. Neutral polymers were oxidized into their electronically conductive form by submersion of the polymer substrate into an anhydrous saturated solution of nitrosonium tetrafluoroborate in acetonitrile. Electronic conductivities were measured by the four-point probe technique. UV–vis absorption spectra were recorded on a Perkin-Elmer Lamda 3A UV–vis spectrophotometer at 25 °C. Infrared spectra were recorded on a Michelson FTIR (Bomem, 120 Series).

Results and Discussion

Poly(3-hexylthiophene), solvent cast from toluene, gave uniform, red-colored films. The wavelength of maximum absorption in the visible region was 500 nm at 25 °C, and the extinction coefficient was ~6400 mol^{-1} L cm^{-1}. The long wavelength of absorption is due to extensive conjugation of π-orbitals. The absorption maximum is red-shifted by ~60 nm compared to the same polymer dissolved in organic solvent due to restricted rotation of thienyl rings in the solid state and hence a greater degree of π-conjugation. The broad absorption profile is due to a distribution of π-conjugated segments which arises from dissimilar polymer chain lengths and thermally induced rotations of thienyl rings.

Irradiation of thin films of P3HT in ambient air causes the optical density of the film to decrease. Figure 1 shows a plot of optical density (at λ = 500 nm) against time of irradiation. Prior to irradiation the films were soluble in toluene. After 15 s of irradiation the films were rendered totally insoluble in toluene. The absorption spectra of

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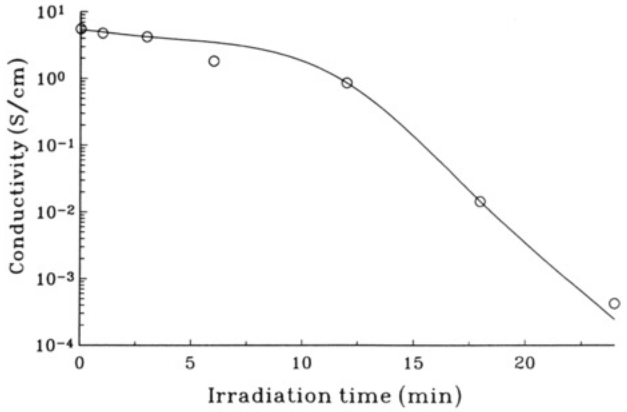

Figure 2. Logarithmic plot of conductivity of oxidized poly(3-hexylthiophene) films against irradiation time. Film thickness: 0.3 μm. Light source: 150-W Hg lamp, 280-nm cutoff filter. Oxidizing agent: nitrosonium tetrafluoroborate.

preirradiated films and films irradiated for 15 s were identical in shape, but the optical density of the latter had decreased by 3%. This indicates that a large fraction of the π-conjugated sequence lengths initially present in the film remained after photolysis. Sufficient π-conjugation should exist after photolysis, therefore, in order to impart electronic conductivity to the material upon oxidation.

Neutral irradiated and preirradiated polymer films were nonconducting ($<10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$). Upon oxidative doping by immersion of the films into an anhydrous solution of nitrosonium tetrafluoroborate the films turned blue and were found to be electronically conductive by the four-point probe technique. The initial conductivity of partially oxidized poly(3-hexylthiophene) was $\sim 5\ \Omega^{-1}\ \text{cm}^{-1}$. To determine the effect of light on the conductivity of the films, several neutral films were irradiated, each for a different length of time. Following this, each film was oxidized and the conductivity measured by the four-point probe technique. The conductivity of the film decreased in a nonlinearly with irradiation time (Figure 2) and fell by several orders of magnitude after prolonged photolysis. However, when the irradiation time was kept short (<1 min), the change in electronic conductivity was negligible. This important observation illustrates that polymer films can be photochemically insolubilized yet still exhibit high conductivity upon chemical oxidation. Thin films of poly(3-hexylthiophene) were then irradiated through a photomask. When long irradiation times were employed, exposed regions showed a distinct discoloration due to photochemical bleaching (Figure 3, top). When the irradiation time was short (<60 s) the color contrast of the relief image was barely visible yet unexposed regions rapidly dissolved when the irradiated polymer/substrate was immersed in toluene, while exposed polymer did not. The remaining polymer appeared yellow when immersed in toluene but formed a negative red image of the photomask upon drying (Figure 3, bottom). The minimum time required to form a well-developed image under the present conditions was 15 s. Upon immersion into an acetonitrile solution of nitrosonium tetrafluoroborate, the pattern immediately turned blue. The conductivity of the polymer pattern was $5\ \Omega^{-1}\ \text{cm}^{-1}$. The images shown in this paper are well developed but were only 0.5 mm in resolution. While images of this resolution are too large for microelectronic applications they do show that conducting polymer patterns are attainable by photolithography. The environmental stability of the oxidized form of the polymer is a point of concern since the polymer lost significant conductivity after 30 min of exposure to the atmosphere. However, this might be sufficiently long for encapsulation and protection. Instability is a consequence of the high oxidation potential of the polymer and not a result of the photochemical process. More stable analogues of oxidized poly(3-hexylthiophene) are under investigation.

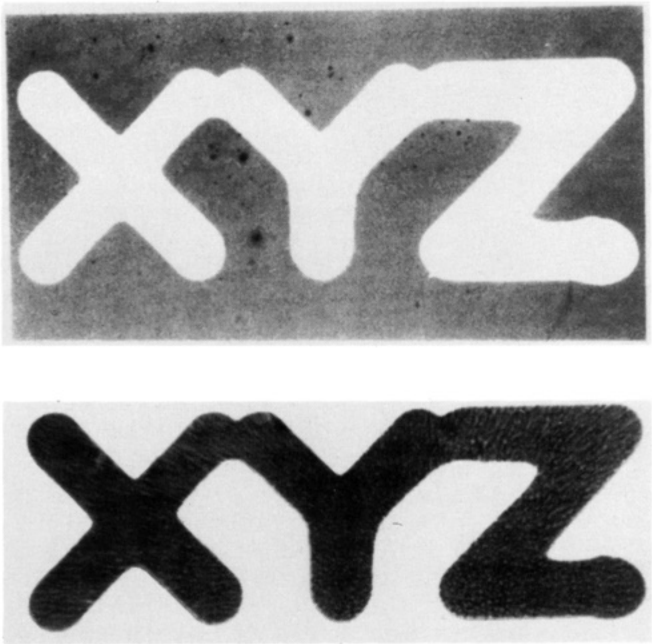

Figure 3. Micrographs of poly(3-hexylthiophene) films. Top: photobleaching after prolonged photolysis through a photomask. Irradiation time = 30 min. Bottom: photoimaging by irradiation of film through photomask (irradiation time = 30 s) and dissolution of unexposed polymer. Film thickness ~1 μm. Resolution of image = 0.5 mm.

To determine the mechanism of photolysis, IR spectra of thin polymer films were recorded before and after irradiation in ambient atmosphere. Irradiation was performed through a 353-nm broadband filter (30-nm bandpass) in order to isolate the π–π* transition. As a consequence the incident light was much weaker, and longer irradiation times were necessary. After 2 h of photolysis the IR spectrum of the irradiated polymer showed several new absorption bands: 1719, 1249, 1192, 1165, and 669 cm^{-1}. The absorption band at 1719 cm^{-1} and the bands at 1192 and 1165 cm^{-1} are assigned to a ketone and a sulfine ($C{=}S{\rightarrow}O$) group, respectively. Similar absorption bands have been observed for poly(3-hexylthiophene) and monomeric thienyl analogues irradiated in oxygen-saturated organic solutions.[13-16] The resulting polymer films were insoluble in toluene, even though excitation of the polymer had been limited to the π–π* transition.

When thin films were irradiated in an argon atmosphere, the films remained soluble in toluene and changes in the IR spectra were minimal, even after 5.5 h of photolysis. There was evidence for the formation of ketones (1760 cm^{-1}) but the relative intensity of the signal was extremely low, indicating that their concentrations were low, compared to films irradiated in air. No IR band corresponding to $C{=}S{\rightarrow}O$ was observed. Since the atmosphere above the polymer film was purged with argon at room temperature, it is believed that trapped air is the source of oxygen in this instance.

In previous papers we showed that dissolved oxygen plays a large role in the solution photochemistry of poly-

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(3-hexylthiophene).[13,14] We postulated that the polymer photosensitizes singlet oxygen formation and that addition of the latter to thienyl rings is responsible for chain scission and disruption of the π-system. Precedence for this exists for monomeric thiophenes.[15,16]

The presence of oxygen is clearly a major factor in the solid-state photochemistry of P3HT and it appears that Diels-Alder addition of singlet oxygen to thienyl units occurs, as evidenced by the formation of a sulfine. This in itself would not lead to insolubilization of poly(3-hexylthiophene). The complete mechanism of photolysis probably involves photolysis of photolabile intermediates in order to achieve insolubilization. The full mechanism of photolysis is currently under investigation.

Conclusions

We have demonstrated a simple process for depositing fine π-conjugated polymeric patterns with controlled architecture. Upon oxidation the pattern is rendered electronically conducting. This technology has broad ramifications in the design of integrated circuitry and device fabrication. Possible applications include the formation of interconnects or channels of defined resistivity for microchips and printed circuitry, the deposition of π-conjugated nonlinear active waveguide components, and hybridization of organic and semiconductor components in chemical sensor manufacture.

Acknowledgment. Financial support of this work by the Natural Sciences and Engineering Research Council of Canada and by the Science Council of British Columbia (STDF-AGAR) is gratefully acknowledged.

Preparation of Fine $PbTiO_3$ Powders by Hydrolysis of Alkoxide[†]

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Introduction

During the past few years, many fine ceramic composites with different connectivity patterns have been designed and fabricated for making new materials in which desired properties can be incorporated through the use of a combination of materials with different properties. Among the composites, the 0–3 type has a better applicability because of its versatility in forming operation and the easiness in fabricating. Lead titanate (PT) with perovskite structure is a well-known ferroelectric material. Because of its high Curie temperature, low dielectric constant at low temperature, and high pyroelectric and large anisotropy coefficients, it is a very good material for high-frequency filters, IR detectors, and photoelectronic devices. The crux of achieving a 0–3 type of PT composite is the preparation of fine PT powders with desired particle size and size distribution. Conventional methods of making ceramic powders include thermal decomposition of inorganic salts, solid–solid reaction, coprecipatation in solution, and so on. Recently, the method using precursors of organometallic compounds, including alkoxides[1,2] and carboxylates,[3] has been used to produce a wide variety of ceramic materials in powder or monolithic form, because it can offer many advantages in producing ceramics, including high purity and homogeneity, low-temperature processing, and easy to form a variety of structures (macro and micro). The present work investigates the preparation of fine perovskite PT powders by hydrolysis of alkoxide and the influence of various factors on the particle size and structure of the resulting PT powders.

Table I. Effect of Alkoxide Concentration on the Particle Size of PT Powders

no.	wt ratio alkoxide/ isopropyl alcohol	$\bar{d}$, nm hydrolysate particle	after calcination at 600 °C	wt % of particles with $d < 100$ nm
1	1:0	620	280	5.5
2	1:1	550	270	6.6
3	1:2	180	260	7.1
4	1:5	110	290	7.7
5	1:10	87[a]	250	10.4

[a] Determined by photocorrelation spectrometry.

Experimental Section

The Pb–Ti complex metal alkoxide was synthesized following the method described by Gurkovich and Blum,[2] except that tetrabutyl titanate and 2-ethoxyethanol were used instead of tetraisopropyl titanate and methoxyethanol. After removal of most of the 2-ethoxyethanol by distillation, the obtained complex alkoxide was diluted with solvent (e.g., isopropyl alcohol). The solution of complex alkoxide was added into a large amount of water under vigorous stirring, hydrolyzed to precipatate directly without an intermediate process of gelation. Therefore, this method is a modification of the sol–gel process.

The precipatates derived from the complex alkoxide were separated by filtration and dried at 80 °C for 48 h, and then the dried precipatates were calcinated in an oven using a heating rate of about 8 °C min^{-1} to 600 °C and held at this temperature for about 2 h; fine light yellow $PbTiO_3$ powders were obtained.

The crystal structure was examined with a Rigaku D/max-ra X-ray diffractometer, IR absorption spectra were measured by a Nicolet 7199 B FTIR, Raman spectra were obtained by using a Spex 1407 Raman spectrometer, the DTA and TG analyses were determined by a LCT-1 type of differential thermal analyzer. A Horiba-CAPA 500 centrifugal particle size analyzer was used to measure the weight-average particle size and size distribution of lead titanate powders dispersed in water. TEM observations were also made by using a JEM-200 CX type TEM.

The XRD pattern of the PT powders prepared according to the aforementioned method is completely consistent with that of perovskite $PbTiO_3$, and the ratio of Pb/Ti is 1.003, determined by using a Jarrell-Ash ICAP-9000 plasma spectrometer, indicating that the product is pure perovskite $PbTiO_3$. The ratio of c/a is determined to be 1.065, consistent with the theoretical value of tetragonal $PbTiO_3$.

Results and Discussion

Effect of Hydrolysis Conditions on the Particle Size of PT Powders. The effects of various hydrolysis conditions, such as manner of hydrolysis and amount of water, solvent and concentration of the complex alkoxide, temperature, pH and the addition of dispersant, etc., on the particle size of resulting PT powders have been examined. The results demonstrate that the above factors may have an apparent effect on the size of hydrolysate particles, but none of them exhibits a regular influence on

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