Published in final edited form as:

Langmuir. 2010 January 5; 26(1): 515–520. doi:10.1021/la902195k.

POLYMERIC ACRYLATE-BASED HYBRID FILMS CONTAINING LEAD AND IRON PATTERNED BY UV PHOTO-POLYMERIZATION

Huilan Han¹, John Bissell², Frank Yaghmaie³, and Cristina E. Davis^{1,*}

¹Department of Mechanical and Aerospace Engineering, University of California Davis, One Shields Avenue, Davis CA 95616, USA.

²Department of Chemical Engineering, University of California Davis, One Shields Avenue, Davis CA 95616, USA.

³Northern California Nanotechnology Center, College of Engineering, University of California Davis, One Shields Avenue, Davis CA 95616, USA.

Abstract

The development and processing of hybrid inorganic-organic thin film materials plays a critical role in advancing interdisciplinary sciences and device manufacturing. Here we present a novel approach to synthesize and deposit acrylate-containing organic/inorganic hybrid films. The material is based on a chemical solution and includes specifically desired metal dopants that are fully-integrated into the backbone of the polymer structure. The film can be deposited by simple spin coating, and we confer photosensitive properties to the material making it directly patterned by traditional UV photolithography techniques. Film thickness, chemical characterization and wet/dry etching capability of the film are also investigated. We believe this innovative material has the potential to be used in a broad range of applications for electronic, photonic, biology and other interdisciplinary fields.

Keywords

hybrid materials; polymerization; organic/inorganic; thin film

Introduction

Organic/inorganic hybrid materials have been the focus of increased investigation for micro- and nanofabrication partially due to the advantages of organizing both organic and inorganic materials on small length scales.^{1–3} These materials are traditionally deposited by chemical vapor deposition,^{4,5} atomic layer deposition,^{6,7} or spray pyrolysis.⁸ However, manufacturing costs and high processing temperatures could potentially limit their possible applications, and solution-based processing can be an alternative choice. Just as an example, the chemical vapor deposition (CVD) process requires specialized equipment containing a vacuum source, and the substrate must be held at a high voltage during the deposition process. This can cause significant temperature increases on the device that is being manufactured, and could potentially degrade organic material as well as other temperature-sensitive substrates. This is in addition to the significant cost of the specialized and complicated equipment system required for this manufacturing method. Simple solution-based deposition methods have attracted much attention in recent years because of the economy of scale for manufacturing, as well as the low

*To whom correspondence should be addressed. Tel: +1.530.754.9004; Fax: +1.530.752.4158; cedavis@ucdavis.edu.

processing temperatures that enable film deposition on a wide range of temperature sensitive substrates.

The sol gel technique⁹ is a major method used to synthesize hybrid materials from chemical solutions^{10–12} and incorporates a series of complex hydrolysis and polymerization reactions of specific precursors to form a colloidal suspension.^{13–18} While the low deposition temperature is an advantage,¹⁹ this technique can frequently suffer from rapid hydrolysis of organometallic precursors resulting in the precipitation of corresponding reaction products and phase separation due to different properties of organic and inorganic compounds.^{20,21} For example, lead-based precursors similar to those used in our current work would react rapidly with water to form lead oxide or lead hydroxide, which precipitate out of solution and cannot then be spun onto substrates for micropatterning. This example illustrates just one reason why many potential organic/inorganic hybrid formulations are infeasible using the sol-gel method.

Here, we report a novel solution-based approach to grow organic/inorganic hybrid films by using a photo-polymerization technique. Specifically, we envision that these materials could be extremely useful in developing new micro- and nanotechnologies across many disciplines. This could include optical waveguides, magnetic-based electronic devices, or biological lab-on-a-chip diagnostic instruments. Acrylate-containing monomers integrate specifically-desired metal constituents in a spin-on solution, which avoids rapid reaction of mixed precursors at the early mixing stage and solves the problem of precipitation of corresponding react products. The polymerization is quickly implemented to form UV-cured networks when the solution is subjected to the exposure. UV exposure causes free radical generation from photoactive compounds in solution, quickly transforming the liquid monomer into a solid thin film. This results in a homogeneous distribution of the inorganic particles within the organic matrix without phase separation. From device fabrication perspective, this directly patternable property also simplifies subsequent etching and other process steps since the final film product can be created in just a few simple steps. This has the potential to reduce manufacturing costs of microdevices, due to fewer steps and lack of required expensive equipment.

Experimental Section

Synthesis of organic/inorganic hybrid materials

To synthesize the organic/inorganic hybrid film containing lead, Pb(II) acrylate at 1.4 wt% from Gelest, Inc. was dissolved in 2-methoxyethanol (at 28 wt%, Sigma-Aldrich) in a brown bottle with a magnetic stirrer for 5 minutes or until the solution was completely clear. 3-(trimethoxysilyl) propyl methacrylate (TMOME) at 28 wt% from Aldrich, trimethylolpropane triacrylate about 27 wt% from Sigma-Aldrich, and less than 5 wt% 3-aminopropyltriethoxysilane and PolyFox TB are then added to the Pb(II) acrylate solution. The solution was mixed at room temperature with stirring until it's completely clear. Under yellow light, Irgacure 2022 (at 12 wt%, Ciba) photoactive compound was added to the mixture under normal class 1,000 clean room conditions. The resulting solution remained transparent. No phase separation or instability was observed for an extended period of time.

A similar process was used to formulate the iron-containing hybrid films. In a 100 mL opaque bottle, 2 g iron (II) acrylate (Gelest, Inc.) was added to 18.6 mL propylene glycol monomethyl ether acetate (PGMEA, 99% Sigma-Aldrich) and 5 mL ethanol (200 proof, Gold Shield) and mixed using a magnetic stir bar. After the salt had completely dissolved, 1 g of 2-aminopropyltriethoxysilane (99%, Sigma-Aldrich), 5 g trimethylolpropane triacrylate (TMPTA, Sartomer), and 1 g Polyfox TB (Omnova) were added while stirring continuously. After two hours of mixing, the solution was transferred into a class 100 clean room and 3 g of the same photoactive compound as the lead formulation was added. The solution was stirred for another two hours before using it for processing. Methanol was used as the resist developer.

Film deposition and patterning process

In our experiment, film deposition is conducted by simple spin coating and photolithography processes carried out in a class 100 clean room. The hybrid film substrate were generally 4-inch silicon wafers (<100> orientation, University Wafer). The solution is filtered by 0.1 μm Whatman filter before coating and no adhesion promoter was required. After coating, the soft baked wafer was exposed in a MA4-Karl Suss Mask Aligner using a binary resolution mask followed by a post exposure bake. Exposure time varied as a function of film thickness at an exposure setting of 22 mW/cm² using an i-line filter. This specific hybrid film is a negative tone photoresist and the exposure area is cross-linked after UV exposure. A number of different solvents were employed to develop the cross-linked images. Methanol or a combination of methanol and isopropyl alcohol were used in most cases. Depending on the solvent(s) used, the development time varied from 15 seconds to several minutes.

Film processing and characterization

The film thickness of our hybrid material was measured at various application spinning speeds using an Nanometrics nanospec-210 film thickness analyzer (n=15 replicates). The films were chemically analyzed using energy dispersive X-ray spectroscopy (EDX) which is a technique most commonly found on scanning electron microscopes (SEM-EDX), and the FEI XL30-SFEG SEM was used in these experiments. For the annealing experiments, the coated substrate was annealed at different temperatures in an ambient oxygen-containing air atmosphere. Again, the hybrid film was spun directly on a Si substrate and then the resultant film was gradually annealed from room temperature to 700 °C for approximately two hours in an oxygen air environment.

The hybrid films were characterized for their resistance to commonly used microfabrication processes, such as acid and base etches and reactive ion etching. Briefly, the films were exposed to 22.5% KOH solution at 60 °C for 20 minutes. They were also exposed to a buffered oxide etch for 5 minutes, and they were studied for their response to 15 minutes of reactive ion etching using CF₄ and 20 minutes of SF₆ etching (12 sccm, 120 mT, 200W with Technics 800 RIE system).

Results and Discussion

Synthesis of organic/inorganic hybrid films and film deposition

In this report, we focus on the development and characterization of a novel acrylate-containing organic/inorganic hybrid photosensitive film for micro- and nanotechnology applications. For first demonstration purposes, we use metal lead and iron as exemplary materials to demonstrate that our proposed method is simple and feasible to synthesize a wide array of organic/inorganic hybrid films. Additional metal choices could also be pursued, but were outside of the scope of this initial work. Our synthesis is based on acrylate-complexed metal compounds. Based on this approach and the availability of commercial precursors, have successfully formed organic/inorganic hybrid films containing both lead and iron. We anticipate that our method will be possible with any metal compound that is available in an acrylate form. However, gold is one example where we have not yet found a commercially available acrylate-based precursor. If a custom synthesis of gold/acrylate existed, it is possible that other researchers could form a film from that material source.

Hybrid film synthesis is completed by generating a liquid chemical solution of the precursor materials, and the film is deposited and patterned using traditional UV photolithography due to film photosensitive property. The chemical formulation of the final hybrid film consists largely of four distinct groups: (1) an organometallic group, which alters the physical properties of the film; (2) a silicone group which influences the material properties, lithographic

performance and adhesion of the film; (3) a cross-linking organic material; and (4) a light-sensitive free radical generator. These components may be present in different ratios, and may be altered to meet specific end thin film requirements. The flow chart of whole synthesis and deposition process is shown in Fig. 1. We have previously synthesized an initial film containing lead, however this current formulation is more stable than previously reported.²² In this new study, the iron formulation is particularly intriguing and has the potential to be incorporated into magnetically-actuated devices. In our experiments, we first attempted to utilize the same solvent for the iron as for the lead hybrid experiments. However, we found that only PGMEA was effective in producing a stable soluble solution, and the iron precursors did not dissolve in the other solvents. It is clear that the specific formulation details can slightly vary between metal choices for the hybrid films, and the formulations reported here work effectively, although they are not optimized.

To synthesize the hybrid film, the solution contains five common commercial starting materials that do not require further purification or filtering (Figure 1). The process begins by dissolving a metal acrylate salt precursor compound into a primary solvent and potentially a co-solvent, if required to completely dissolve a specific precursor into solution. The metal acrylate salt compounds then act as the precursors to provide the metal sources for the final film. To acquire different film properties and chemical compositions, multiple metal acrylate salt precursor compounds can be simultaneously added to the solution, which may be especially useful in generating paramagnetic mixtures of metals. Subsequently, all other chemicals in Fig. 1 are added, with the exception of the free radical generator which is added last so that the material is light sensitive and can be photo-UV patterned. The silyloxyl methacrylate compound acts as the precursor for providing a silicon dioxide source in the final film, and the acrylate compound is used for film polymerization when subject to UV exposure. The surface level agent and resist glue were found useful to improve film uniformity and film adhesion to the substrate, respectively. Finally, we added a free radical generator, which allows the film to be UV-photopatternable. The exact mass percentage of each chemical in the solution is variable and the formation can be easily altered and finely tuned by changing the ratio of these common precursor materials.

Many potential applications of hybrid materials depend on the availability of simple and feasible film deposition. In our study, this challenging problem is solved by simple spin-coating similar to traditional lithography and is possible because of our film photosensitive property. In our experiment, once the solution is formed, it may be directly spun onto commonly used substrates such as a silicon wafer or a glass substrate, in a method similar to the way that a commercial photoresist is applied. As the thin film is cured, the polymer upon exposure to oxygen plasma results in a SiO₂ passivation layer which also contains a desired metal content contained within the polymer matrix itself. An optical picture from a hybrid film containing iron (Figure 2A) and lead (Figure 2B) shows that micro-patterned devices may be created using these materials, and an scanning electron micrograph (SEM) of a patterned lead-containing hybrid film is also shown (Figure 2C).

Characterization of Hybrid Films: Chemical Composition

The characterization of hybrid materials faces special challenges and to date, and there are few reports in the literature to address how these materials may act under normal microfabrication conditions. Chemical composition, film thickness measurement, topology and periodicity are all very important areas to be considered to characterize.²³ In this study, we used the hybrid film containing lead as an example to characterize chemical composition and abundance, film thickness and etching capability to create complex topologies.

The lead structures were characterized via energy dispersive X-ray spectroscopy (EDX) to yield composition and relative element abundances immediately after coating a silicon wafer

(Figure 3A). As we expect, the film contains silicon, oxygen and lead, which is approximately 8% in this example. To increase the observed total lead content as a relative fraction of compounds found in the hybrid material, an oxygen-plasma is applied for 2 min to remove part of the residual organic portion of the hybrid film (Figure 3B). Panel 3B shows EDX data indicating the lead content of the film has been substantially increased to almost 18%. This relatively simple processing step allows us to increase the final metal content of our microstructures, which can be important for the ultimate function of devices made from these materials.

Characterization of Hybrid Films: Film Thickness

Film thickness is an important characteristic for hybrid films, and many potential device applications are limited because of the lack of a reproducible and precise deposition techniques for these materials. For example, films made using the traditional sol gel technique may often fracture due to the condensation reaction or may be too viscous to deposit reproducibly. In our material fabrication process, there is no hydrolysis and condensation reaction at the solution stage and polymerization begins only if the film is exposed to UV light, which prevents stress fractures in the film. Figure 4A illustrates the relationship between the application spinning speed and the ultimate film thickness of the hybrid film, which was obtained by spinning the material directly on a 4 inch silicon wafer at different coating speeds, again similar to the method for photoresist application. For each wafer, the film thickness was measured at 15 different locations, and we found that the thickness varies from 0.5 μm to 4.5 μm from a relatively high spinning speed to a lower speed. The variation of thickness within a single wafer was quite low, as indicated by the standard deviation plots shown in Figure 4A. For example, at 2,000 rpm spinning speed the thickness of the film was $1.546 \pm 0.098 \mu\text{m}$ ($n=15$). This suggests that the film can be deposited at a variety of thicknesses according to different device requirements, and the desired final height of the organic/inorganic hybrid microstructures. In addition, to attain varying film thickness at the same spinning speed, slight changes in chemical composition and viscosities can expand this range of film thicknesses. An alternative method to alter film thickness of the hybrid film can be achieved via annealing (Figure 4B). The coated substrate is annealed at different temperature in an oxygen-containing atmosphere. Again, the hybrid film was spun directly on a Si substrate and then the resultant film is gradually annealed from room temperature to 700 $^{\circ}\text{C}$ for approximately two hours in an oxygen air environment. The film morphology appeared the same and there were no noticeable differences from the annealing process except for a film thickness decrease. There were no cracks in the film, and no de-lamination was observed.

To explore how the film thickness is related to the chemical composition of the film, we also performed EDX experiments of the annealed samples. We can see that the annealing process does slightly increase the total lead percentage of the film (Figure 5A). By annealing at 300 $^{\circ}\text{C}$, we increased the lead content from 8% to 13%, which corresponds to an approximately ~65% decrease in film thickness (Figure 4B). However, when the samples are annealed at 400 $^{\circ}\text{C}$, we find that although the film thickness is lower, that the total lead percentage is also lower (Figure 5B). This result may indicate that some metal molecules may complex with the organic portion of the film, and may be simultaneously removed or evaporated during exposure to high temperatures.

Characterization of Hybrid Films: Etching Ability

Another important film property that is critical for device fabrication is the material etching capability. Both wet and dry etching processes may be necessary to incorporate the hybrid film into micro-structures, and we have characterized our example film under these typical processing conditions (Figure 6). First, we tested the ability of our film to function as a

protection layer for oxide etching (Figure 6A and B) and we also tested the ability of the hybrid materials to serve as a mask for silicon etching (Figure 6C and D).

To test the hybrid film ability of serving as a mask layer for oxide etching, first 0.6 μm of thermal SiO_2 was grown on a $\langle 100 \rangle$ orientation silicon wafer, and then the hybrid thin film was coated onto the silicon dioxide substrate. The film average film thickness does not decrease from 402.9 ± 7.6 nm ($n=5$) to 400.6 ± 5.5 nm ($n=5$) between the pre- and post-etch samples after exposure to a short 5 min buffered oxide etching (BOE) (Figure 6A, left and right panels). This appears to indicate the hybrid material has a high resistance to simple BOE processing steps. Besides wet etching ability of hybrid film, we also explored how the film reacts to reactive ion etching (RIE) via CF_4 gas. Prior to RIE the average thickness of hybrid film started at 430.5 ± 6.6 nm ($n=5$), and was reduced to 342.9 ± 2.5 nm ($n=5$) after the sample was etched for 15 min (12sccm/120mT/200W with Technics 800 RIE system) (Figure 6B, left and right panels). This yielded a calculated average etch rate of approximately 5.84 nm/min, which is substantially slower than the standard etching rate of 25–65 nm/min for the commercial resist SPR220, which allows our film to potentially be used as an oxide etch mask.

To test how well our example film could be applied as a mask to etch silicon, we spun the hybrid material directly onto a $\langle 100 \rangle$ orientation silicon wafer with an average thickness of $1,614.3 \pm 97.2$ nm (Figure 6C, left panel). The sample was then put into a 22.5% KOH solution at 60 °C for 20 min. After etching, the hybrid film was almost entirely etched away (Figure 6C, right panel). Because the film is not resistant to KOH etching, this indicates that it must be applied to the top surface after a major KOH etch is complete if this wet etching step is a requirement for specific device geometry. In addition, we also tested our film for resistance to silicon reactive ion etching (RIE) oxide etching by applying SF_6 gas as an etchant by using the same Technics 800 RIE System as CF_4 etching. Optical images were taken before (Figure 5D, left panel) and after SF_6 etching (Figure 5D, right panel) for 20 minutes (12sccm/120mT/200W). After etching, the average etching rate of the hybrid film is approximately 33 nm/min and this etching rate is comparable to a nominal 27 nm/min rate for silicon oxide.

Conclusion

The development and deposition of new organic/inorganic hybrid materials is a critical microsystems component enabling cutting edge interdisciplinary biological, electronic and photonic research applications. The approach reported here provides a novel method to synthesize different organic/inorganic hybrid as well as multi-metal materials into a single hybrid thin film. The synthesis process of these hybrid materials is extremely simple, and can be formulated using commercially available chemicals. Film deposition, which is generally challenging for hybrids films, is implemented by simple spin coating and photo-polymerization. Low temperature deposition provides a possibility of film formation across temperature sensitive substrates, and due to the photosensitive properties micro-patterning is achieved by traditional photolithography techniques. Two especially attractive applications of these organic/inorganic hybrid films are magnetic memory media for the electronics industry, and potentially as catalytic substrates for complex biological reactions in lab-on-a-chip devices. In both cases, the material properties and processing capabilities demonstrated here will allow functional advances in these broad categories of devices.

Acknowledgments

This project was partially supported by Grant Number T32-GM08799 from NIGMS-NIH, and by an industry/campus supported fellowship under the Training Program in Biomolecular Technology (T32-GM08799) at the University of California, Davis. Partial support was also provided by Grant Number UL1 RR024146 from the National Center for Research for Medical Research. Its contents are solely the responsibility of the authors and do not necessarily represent the official view of NCRR, NIGMS or NIH.

REFERENCES

1. Najafi SI, Touam T, Sara R, Andrews MP, Fardad MA. *Journal of Lightwave Technology* 1998;16:1640–1646.
2. Novak BM. *Advanced Materials* 1993;5:422–433.
3. Toyama T, Ichihara T, Yamaguchi D, Okamoto H. *Applied Surface Science* 2007;254:295–298.
4. Bonifield, TD. *Deposition technologies for films and coatings: developments and applications*. Noyles: Park Ridge; 1982.
5. Cho SJ, Bae IS, Jeong HD, Boo JH. *Applied Surface Science* 2008;254:7817–7820.
6. George SM, Dameron AA, Du Y, Adamczyk NM, Davidson SD. *ECS Transactions* 2007;11:81–90.
7. Park, SH.; Hwang, CS.; Chu, HY.; Lee, JI. US Patent and Trade Office. patent application #20080164476. 2008.
8. Ezhil Raj AM, Vijayalakshmi K, Selvan G, Jayachandran M, Sanjeeviraja C. *Journal of Non-Crystalline Solids* 2008;354:3773–3779.
9. Wright, JD.; Sommerdijk, NAJM. *Sol-gel materials: chemistry and application*. Amsterdam: Gordon and Breach Science Publishers; 2001.
10. Mitzi DB. *Chemistry of Materials* 2001;13:3283–3298.
11. Sayer M, Sreenivas K. *Science* 1990;247:1050–1060.
12. Que W, Jia CY, Sun M, Sun Z, Wang LL, Zhang ZJ. *Optics Express* 2008;16:3490. [PubMed: 18542441]
13. Arkles B. *MRS Bulletin* 2001:402–408.
14. Chou TP, Chandrasekaran C, Cao GZ. *Journal of Sol-Gel Science and Technology* 2003;26:321–327.
15. Li CY, Chisham J, Andrews M, Najafi SI, Mackenzie JD, Peyghambarian N. *Electronics Letters* 1995;31:271–272.
16. Llobera A, Cadarso VJ, Darder M, Domínguez C, Fernández-Sánchez C. *Lab on a Chip* 2008;8:1185–1190. [PubMed: 18584096]
17. Mackenzie JD. *Journal of Sol-Gel Science and Technology* 1993;1:7–19.
18. Zhang X, Lu HJ, Soutar AM, Zeng XT. *Journal of Materials Chemistry* 2004;14:357–361.
19. Gomez-Romero, PSC. *Functional hybrid materials*. New York: Wiley Interscience; 2003.
20. Jia QX, McCleskey TM, Burrell AK, Lin Y, Collis GE, Wang H, Li ADQ, Foltyn SR. *Nature Materials* 2004;3:529–532.
21. Schmidt H. *Journal of Sol-gel Science and Technology* 1994;1:217–231.
22. Han H, Sutherland A, Yaghmaie F, Davis CE. *Applied Physics Letters* 2009;94:144106.
23. Cassagneau TP, Sweryda-Krawiec B, Fendler JH. *MRS bulletin* 2000;25

Figure 1.

Overview of hybrid film development process. The flow chart (left) represents the entire development process of the film from the solution-based synthesis to final characterization of the hybrid thin films. The solution content information (right) illustrates the typical solution components.

Figure 2. Image of organic/inorganic hybrid films containing iron and lead which are deposited by spinning coat, polymerized and patterned into microstructures. (A) hybrid film containing iron. (B) hybrid film containing lead. (C) scanning electron micrograph of a test pattern in the lead-containing film.

Figure 3. Chemical composition of organic/inorganic hybrid film containing lead. (A) EDX analysis from the lead hybrid film. (B) EDX analysis of lead film after an oxygen plasma etch for 2 min.

Figure 4.

The change of film thickness corresponding to the spinning speed and annealing temperature (thickness is normalized). Panel A shows the film thickness can be controlled as a function of the application spinning speed. The data is shown for $n=15$ replicates across the entire wafer surface, with the average and standard deviations plotted. In panel B, film thickness changes with annealing temperature. When the temperature is higher than 400 $^{\circ}\text{C}$, the film thickness decreases dramatically.

Figure 5. Chemical composition during annealing. Panel A shows EDX data taken at the 300 °C annealing temperature, and the ~13% lead content is noticeably higher than the control (~8%, shown in Figure 3A). In panel B at 400 °C, we find the lead percentage slightly decreased along with the simultaneous reduction in film thickness, although the value is still higher than the control non-annealed sample.

Figure 6.

The characterization of organic/inorganic hybrid film responses for common standard wet and dry etching processes. The film was not effectively etched by a wet BOE solution (A), which is normally an excellent etchant for silicon dioxide. The film is slowly etched by RIE CF_4 exposure (B), which is normally a rapid etchant for silicon dioxide. Immersion in a 22% KOH bath almost entirely etches the film away (C), and RIE SF_6 exposure etches the film at a comparable rate to commercial photoresists (D).