Direct thermal-UV nanoimprint of an iron-containing organometallic hybrid film

Huilan Han, Abhinav Bhushan, Frank Yaghmaie, and Cristina E. Davis^{a)}

Department of Mechanical and Aerospace Engineering, University of California Davis, One Shields Avenue, Davis, California 95616

(Received 7 July 2009; accepted 9 November 2009; published 11 January 2010)

Direct thermal-UV nanoimprinting of an organometallic hybrid film has been demonstrated to fabricate nanoscale features into a novel organic-inorganic solution containing selected metals. The film can be patterned at low temperature and pressure, and requires only a short processing time. When analyzed by energy dispersion X-ray spectroscopy, the authors observe both organic and metal content in the final patterned features. They have also observed that film thermal stability increases after UV and oxygen plasma treatments, which may lead to devices that perform well across a wide spectrum of temperatures. © 2010 American Vacuum Society.
[DOI: 10.1116/1.3271337]

I. INTRODUCTION

Nanoimprint lithography (NIL) is an emerging and promising technology for next generation lithography due to its capacity for replicating various nanoscale patterns with low cost, high throughput, and ease of operation.¹ NIL has been widely applied in different fields ranging from magnetic data storage,^{2,3} optical tools,^{4–7} and electronics,^{8–10} to biological devices.^{11–14} Thermal nanoimprint lithography is one of the most attractive methods to manufacture nanometer sized structures among several alternative fabrication methods, such as X-ray lithography and scanning electron beam lithography.^{15,16} NIL overcomes the drawbacks of low throughput caused by series scanning over a surface or complicated mask and exposure systems that are prevalent in the above-mentioned methods.

One of the most frequent applications for NIL is the direct imprinting of organic materials due to ease of deformation for these materials at low processing temperatures and pressures. While organic materials are easy to imprint, the final device structures made from these materials may frequently have lower thermal and mechanical stability than inorganic structures. In contrast, nanoimprinting of inorganic materials is an extremely difficult process due to their high thermal durability. NIL for inorganic materials is conventionally achieved by an indirect process involving both lithography and etching steps,¹⁷ and this process is often time consuming and requires several processing steps. Direct nanoimprinting of hybrid organic-inorganic material holds the promise of incorporating metals into the organic material for final device structures, and potentially, this method is easier to implement onto hybrid materials rather than imprinting inorganic films alone. Unfortunately, to date there are relatively few papers that explore NIL pattern creation in hybrid materials, and the processes designed so far still require long processing times,⁷ high pressure, and high temperature.^{18,19} These factors can potentially lead to mold damage, pattern shifting, and pro-

cess complexity—all of which are problematic for scale up manufacturing production. Another recent report illustrated a method that uses a multistage synthesized polymer containing iron and an organic portion.²⁰ This material can function as an imprint resist, but can be limited by fairly challenging processing constraints, such as low temperature and glove-box conditions.

In this study, we provide a novel method that creates metal-containing structures down to 72 nm width and 144 nm pitch using a glass stamp previously described.²¹ We dissolved metal-containing acrylate monomer precursors into an organic matrix solution,²² using a preselected chemical ratio. The solution can be spun on and directly imprinted at low temperature and pressure, with processing parameters similar to a pure polymeric solution. We have also added a photosensitive free-radical generating compound in the material, and the film can be immediately exposed to UV irradiation after thermal NIL and before releasing the mold. This simple process addition can greatly increase the films thermal and chemical resistance.

II. MATERIALS AND METHODS

As an initial organometallic substrate, we utilize iron as a sample metal to incorporate into our hybrid film; however, a variety of metals could be used in our process. The synthesis of the iron-containing organometallic hybrid film starts with fabricating a chemical solution containing all appropriate precursor materials. The chemical formulation of the final hybrid film consists largely of four distinct groups, and the detailed chemical ratios have been previously reported.²² After the solution is synthesized, we can apply it onto the substrate for direct nanoimprint lithography.

The NIL process consists of multiple sequential steps (Fig. 1). First, the hybrid solution containing iron acrylate is spin coated onto a silicon substrate and then the substrate was heated at 90 °C to evaporate the organic solvents [Fig. 1(a)]. The mold release agent is then applied to the mold, and the mold temperature is maintained at 130 °C for 5–10 min. The glass mold is then pressed into the hybrid film at 200 psi

^{a)}Electronic mail: cedavis@ucdavis.edu

FIG. 1. Hybrid film nanoimprinting process. (a) Spinning hybrid film solution on silicon wafer. (b) Thermal imprinting mold on hybrid film. (c) UV irradiation. (d) Mold release. (e) O_2 plasma film treatment. (f) Final nanoimprinted features.

at $200\text{ }^{\circ}\text{C}$ for 3 min using a Nanonex 2000 instrument (Nanonex Corp., NJ) with an air cushion press, which allows for uniform feature formation over the entire substrate²² and enables a rapid thermal cycle [Fig. 1(b)]. Sequentially, the hybrid film is exposed to UV irradiation (365 nm) for 60 s for further curing and to increase the film's mechanical, chemical, and thermal resistances [Fig. 1(c)]. After the substrate is cooled for 1–2 min, the mold is carefully released from the substrate [Fig. 1(d)]. We then exposed the film to a 200 W oxygen plasma for 30 s to further remove a fraction of the residual organic portion of the patterned film and to harden the surface [Fig. 1(e)]. The final metal-containing patterned film is achieved [Fig. 1(f)]. It is possible that for some selected applications that demand extreme thermal and chemical properties, the film could be annealed at an appropriate temperature to form a pure metal oxide film or patterned features.²³

III. RESULTS AND DISCUSSION

The direct nanoimprinting process successfully replicated nanometer scale patterns into our hybrid film (Fig. 2). The original mold features were confirmed using a scanning electron microscope [Fig. 2(a)] to ensure that the pattern is replicated faithfully into the film. We observed that the mold pitch is 144 nm, the line spacing was equally distributed across the surface, and the linewidth was 72 nm. When imprinted into our hybrid material, the mold features are effectively transferred [Fig. 2(b)], although the dimension of the line appears to be slightly wider than that of the space. The slightly broader linewidth may be a result of trapped air or trapped moisture present during the rapid nanoimprinting process.²⁴ Further process optimization could alleviate this effect and could be explored prior to commercial use. Without optimization, further reduction in linewidth could potentially become a more serious issue, and nanostructure density and resolution could be limited due to pattern expansion. At the current feature sizes this is not yet a limitation; however, the issue should be addressed in future work.

FIG. 2. Nanoimprinting hybrid film. (A) 72 nm wide lines that are 144 nm in pitch are observed on the NIL mold. (B) These nano features are replicated into a sample coated with the hybrid film.

Once the line pattern was transferred into our hybrid film, we then examined the percent metal content using the energy dispersive X-ray spectroscopy (EDX) technique to analyze the chemical composition of the final hybrid film (Fig. 3). The data show that the hybrid film contains approximately 9% silicon and 6% iron for this specific formulation. We also see that the film contains a substantial organic portion which yields a film with lower thermal and chemical durability, similar to pure organic films. To improve the final properties of our film, we then applied an oxygen plasma to remove a large part of the organic constituents, and further annealing can remove almost all of the residual organic material, as shown in the next experiments.

The stability of our NIL imprinted hybrid film was examined under various thermal conditions, as this could potentially limit the applications of this material under demanding thermal conditions. After imprinting we annealed test films in a ceramic oven at temperatures ranging from 100 to $600\text{ }^{\circ}\text{C}$ for approximately 2 h, and this was performed on both control (untreated) and UV and oxygen plasma treated samples (Table I and Fig. 4). The untreated

FIG. 3. Hybrid film EDX analysis after spin coating onto the substrate.

TABLE I. Data showing the thickness of the film in control untreated samples and after 1 min UV and 30 s O₂ plasma etching treatment.

Temp. (°C)	Untreated samples Directly coated (measurements in nm)				Treated samples 1 min UV and 30 s O ₂ plasma etching (measurements in nm)			
	Measured average film thickness	Std. dev.	Norm. average film thickness	Std. dev.	Measured average film thickness	Std. dev.	Norm. average film thickness	Std. dev.
100	407.1	1.86	1.00	0.005	230.4	2.26	1.00	0.010
150	333.4	2.94	0.82	0.007	227.5	2.78	0.99	0.012
200	285.6	4.02	0.70	0.010	230.5	2.49	1.00	0.011
250	262.4	3.47	0.65	0.008	220.2	2.80	0.96	0.012
300	213.9	3.15	0.53	0.008	191.1	3.69	0.83	0.016
350	118.4	0.64	0.29	0.002	124.2	0.76	0.54	0.003
400	73.1	1.06	0.18	0.003	78.7	1.30	0.34	0.006
450	42.6	0.84	0.11	0.002	47.8	0.67	0.21	0.001
500	38.4	0.28	0.09	0.001	38.9	4.34	0.17	0.019
600	23.9	1.14	0.06	0.003	24.4	1.99	0.10	0.009

samples showed rapid and marked reduction in film thickness with increasing temperature, which is likely due to the removal of the organic component. Compared to the untreated samples, the UV and plasma treated samples maintained the same thickness until 250 °C, when the film thickness slowly begins to decrease with gradually increasing temperature. In both the untreated and treated cases, the organic portion of the hybrid film appears to be completely removed at annealing temperatures higher than 450 °C. From these experiments, it appears that the thermal stability of a UV irradiation and oxygen plasma treated sample has significant improvement compared to a directly imprinted sample alone. The treatment also appears to increase the metal content of the final film due to the reduction in organic component, which may also yield thermal durability improvements.

When performing NIL onto polymeric substrates, a residual resist is frequently found between the formed features

in the imprinted material. This leftover material is formed adjacent to the desired NIL features and is created as the NIL mold presses down onto the resist. The residual resist found on the substrate is a critical point, because this can potentially limit the ability to etch down between the features and into the underlying substrate for device creation. Generally, NIL users seek to remove this residual resist by using reactive ion etching; however, this becomes extremely difficult when the imprinted resist is organometallic and contains metal compounds. Acikgoz *et al.* found that residual resist removal of their poly(ferrocenylmethylphenylsilane) was extremely challenging using a variety of physiochemical properties of the hybrid material.²⁰ They developed a physical bombardment method using argon sputtering that helped to remove the residual resist in their organometallic thin film structures. This method may also prove to be useful on resists such as the one we have presented here, and shows great promise for advancing device creation using this category of materials.

FIG. 4. Hybrid film thermal stability with directly imprinted samples (blue) and after UV and oxygen plasma treatment (red). All data points represent $n=5$ sample measurements.

IV. CONCLUSIONS

We have successfully developed a process to directly nanoimprint organometallic hybrid films by combining thermal and UV technologies. We patterned 72 nm features at low temperature and pressure with a short processing time. The low processing temperature enables nanoimprinting applications on a wide array of substrates, which further expands the applications of our process. The thermal stability of the organometallic hybrid film is significantly improved by UV irradiation and oxygen plasma treatment, and provides potential applications for the film as a functional part of a final NIL-created device expected to operate at relatively high temperatures. We expect this proposed technology to provide a pathway for the development of direct nanoimprinting of organometallic hybrid films and open a door for nanopatterned device application in electronic, photonic, biological, and other interdisciplinary areas.

ACKNOWLEDGMENTS

This project was partially supported by Grant No. UL1 RR024146 from the National Center for Research for Medical Research, Grant No. 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. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the NCRR, NIGMS or NIH.

- ¹S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Appl. Phys. Lett.* **67**, 3114 (1995).
- ²S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Science* **272**, 85 (1996).
- ³W. Wu, B. Cui, X. Y. Sun, W. Zhang, L. Zhuang, L. S. Kong, and S. Y. Chou, *J. Vac. Sci. Technol. B* **16**, 3825 (1998).
- ⁴S. Moller and S. R. Forrest, *J. Appl. Phys.* **91**, 3324 (2002).
- ⁵K. Nakamatsu and S. Matsui, *Jpn. J. Appl. Phys., Part 2* **45**, L546 (2006).
- ⁶Z. N. S. Yu, S. J. Schablitsky, and S. Y. Chou, *Appl. Phys. Lett.* **74**, 2381 (1999).
- ⁷X.-C. Yuan, W. X. Yu, M. He, J. Bu, W. C. Cheong, H. B. Niu, and X. Peng, *Appl. Phys. Lett.* **86**, 114102 (2005).
- ⁸H. L. Becker and L. E. Locascio, *Talanta* **56**, 267 (2002).

- ⁹C. Kim, M. Shtein, and S. R. Forrest, *Appl. Phys. Lett.* **80**, 4051 (2002).
- ¹⁰W. Wu *et al.*, *Appl. Phys. A: Mater. Sci. Process.* **80**, 1173 (2005).
- ¹¹L. C. Glangchai, M. Caldorera-Moore, L. Shi, and K. Roy, *J. Controlled Release* **125**, 263 (2008).
- ¹²L. J. Guo, X. Cheng, and C. F. Chou, *Nano Lett.* **4**, 69 (2004).
- ¹³L. H. Thamdrup, A. Klukowska, and A. Kristensen, *Nanotechnology* **19**, 125301 (2008).
- ¹⁴V. N. Truskett and M. P. C. Watts, *Trends Biotechnol.* **24**, 312 (2006).
- ¹⁵E. Early, M. L. Schattenburg, and H. I. Smith, *Microelectron. Eng.* **11**, 317 (1990).
- ¹⁶P. B. Fischer and S. Y. Chou, *Appl. Phys. Lett.* **62**, 2989 (1993).
- ¹⁷C. M. S. Torres *et al.*, *Mater. Sci. Eng., C* **23**, 23 (2003).
- ¹⁸C. A. Harnagea, M. Alexe, J. Schilling, J. Choi, R. B. Wehrspohn, D. Hesse, and U. Gösele, *Appl. Phys. Lett.* **83**, 1827 (2003).
- ¹⁹M. T. Li, H. Tan, L. Chen, J. Wang, and S. Y. Chou, *J. Vac. Sci. Technol. B* **21**, 660 (2003).
- ²⁰C. Acikgoz, M. A. Hempenius, G. J. Vancso, and J. Huskens, *Nanotechnology* **20**, 135304 (2009).
- ²¹F. Yaghmaie, W. Nielsen, H. L. Han, A. Bhushan, and C. E. Davis, *IEEE Sens. J.* **9**, 233 (2009).
- ²²H. Han, A. Sutherland, F. Yaghmaie, and C. E. Davis, *Appl. Phys. Lett.* **94**, 144106 (2009).
- ²³H. Gao, H. Tan, W. Zhang, K. Morton, and S. Y. Chou, *Nano Lett.* **6**, 2438 (2006).
- ²⁴H. Schiff, L. J. Heyderman, M. A. D. Maur, and J. Gobrecht, *Nanotechnology* **12**, 173 (2001).