A VERSATILE METHOD FOR TUNING THE CHEMISTRY AND SIZE OF NANOSCOPIC FEATURES BY LIVING FREE RADICAL POLYMERIZATION

Timothy A. Von Werne, David S. Gernack, Craig J. Hawker*, and Kenneth R. Carter*

Center For Polymeric Interfaces And Macromolecular Assemblies, IBM Almaden Research Center, 650 Harry Road, San Jose, CA, 95120-6099

Introduction

The fabrication of nanometer-sized structures and devices is an area of increasing importance due to its commercial importance and application to the emerging field of nanoscale science. Advances in the fields of molecular-scale electronics, magnetic storage, optoelectronics, and biotechnology all depend increasingly on the ability to fashion materials with precise control of feature size and functionality. The fabrication techniques have largely been split into two broad categories, namely “top-down” approaches and “bottom-up” approaches. Classical top-down processes include well-known microfabrication techniques such as photolithography, which is currently used to make essentially all modern microelectronic devices. Bottom-up approaches are more dependent on the chemistry and functionality of the materials employed and includes the use of self-organizing materials that can undergo pattern formation at nanoscale levels to give technologically interesting structures. Both strategies for the fabrication of nanoscale structures have their own unique advantages and drawbacks. For example, top-down approaches are well understood, reproducible and scaleable, though advances become more difficult as device features drop below the 100nm level. In contrast, bottom-up approaches show promise in the ability to make sub-100 nm features, but so far the ability to utilize bottom up approaches to fashion useful devices of known architecture has proven elusive due to the inherent difficulty of directing the exact positioning of self-assembling systems over large areas.

Herein we report a new tandem, top-down/bottom-up approach for controlling the chemistry and size of nanoscopic features at the sub-100 nm level, which is both simple and versatile. In this strategy, a top-down nanocontact molding process is employed followed by the controlled growth of polymer brushes from these patterned features (bottom-up). As a consequence of this strategy, a variety of nanoscopic structures with different feature sizes and functional groups can be grown from the same, original molded template.

Results and Discussion

The primary patterning technique used in this approach is a ‘top-down’ contact molding process which involves the use of a patterned polymeric mold to template a secondary liquid photopolymer resin layer that is subsequently UV-polymerized while in contact with the mold in order to give pattern transfer (Figure 1). The patterned polymeric mold is formed by casting a photopolymer resin on a hard master, in our case either SiO₂ or Si, and photopolymerizing the resin to give a polymeric network mold that has negative features of the original master. Many molds can be made from a single master, and subsequently many imprints can be made from a single mold. As a consequence, this process allows complex and expensive, low throughput, lithographic methods, such as electron beam and x-ray lithography, to be used to fabricate a single master, which can then be used repeatedly to fabricate many replicas.

Scheme 1. Inimers, ATRP-type IN-1 and Nitroxide-type IN-2

To allow controlled graft polymerization from the surface molded polymer networks, functionalized methacrylate monomers containing a dormant living free radical initiator, termed inimers (initiators-/-monomers), were added to the photopolymer resin mixture. This resulted in the embedded inimers being covalently bound throughout the cross-linked polymer network, with a certain fraction of those groups being advantageously located at the surface of the network and available for subsequent reactions. The inimers utilized in this study, IN-1 and IN-2, are shown in Scheme 1 and are based on either atom transfer radical polymerization (ATRP) or nitroxide mediated polymerization.

Figure 2. Feature size adjustment via bottom up controlled growth

In order to ensure that the nanoscopic size of patterned features could be controllably tuned (as shown above in Figure 2), a series of ATRP reactions of MMA with varying molecular weights for the resulting PMMA chains were performed simultaneously on flat and patterned surfaces. The flat films were 30 nm thick films of IN-1 doped photopolymer and the patterned surfaces consisted of molded IN-1 doped photopolymer with a repeating series of 100 nm wide lines. AFM images of identical areas of the patterned wafers are shown in Figure 3 with the original contact molded lines being shown in Figure 3-(A/B). The line edge roughness observed in the images was intentional and an artifact of the original masters made by e-beam lithography, the roughness being reproduced in succeeding daughter images. These intentional defects were employed as a means to determine the smallest size of
features that could be reproduced and to give a range of feature sizes for subsequent growth from. In fact features as small as 5 nm have been faithfully reproduced by this patterning method.

The patterned and flat samples were then subjected to polymer brush formation by ATRP and the image is shown in Figure 3-(C/D). Comparison with the original pattern (Figure 3-(A/B)) clearly shows a dramatic change after grafting of the linear PMMA chains to the network structures. As can be observed, all of the features show an increase in size with the size increase being uniform regardless of the original feature size, which corresponds to a decrease in line-to-line separation. The molecular weight of the polymer brush was varied from 43K to 88K and the resulting thickness changes of the flat films and the increase in line width for the patterned feature sizes was in agreement with expectations and the correlation between molecular weight of the grafted chains and film/feature thickness change is excellent with a linear relationship in both cases. Of particular importance was the observation that the change in the line width was about double that of the corresponding flat films. This is expected in the case of the lines since the thickness change results from uniform film growth on both sides of the features.

As a result the size of the nanoscopic lines can be controllably varied from their initial size of 100 nm to as large as 180 nm by simply varying the reaction conditions (sacrificial initiator, reaction time, monomer concentration). Since the period of the features does not change, a corresponding change in line spacing from 100 nm down to 20 nm is obtained. This combination of “top-down” and “bottom-up” techniques now provide a corresponding change in line spacing from 100 nm down to 20 nm is obtained.

Summary

We have demonstrated the utility of combining a “top-down” contact molding process with a “bottom-up” surface initiating grafting strategy to form 3-dimensional patterns in which the chemistry and size of the nanoscopic features can be accurately tuned. Pattern replication of features ranging from 5um to <60 nm can be achieved by contact molding a photopolymer mixture containing reactive inimers which lead to surface active sites for secondary polymerization. Both ATRP-type (scheme 2) and nitroxide mediated “living” free radical polymerizations can be initiated from the inimer-embedded surfaces leading to the formation of well-defined polymer brushes consisting of polystyrene, MMA and HEMA linear chains. This leads to surfaces with different chemistries and physical properties. The grafts could be grown from either flat or nanopatterned substrates with controlled thickness ranging from 10 to 143 nm and with graft molecular weights estimated to range between 18 000 to 290 000 a.m.u.. The ability to control the growth of polymer brushes from contact molded features can then be utilized to tune the size of nanoscopic features down to 20 nm. This novel combination of “top-down” and “bottom-up” strategies now gives researchers new tools for the reproducible fabrication of nanoscopic structures. Current work focuses on creating templates for pattern replication and the development of process steps for the transfer of these patterned images into a variety of substrates for patterned magnetic media and molecular electronics applications.

Acknowledgments. nancial support from the MRSEC Program of the National Science Foundation under Award Number DMR-9808677 for the Center for Polymeric Interfaces and Macromolecular Assemblies, and the IBM Corporation are gratefully acknowledged. Assistance from Mark Hart (etching), Charles Rettner (e-beam mastering) and Gary McClelland (replication) are also noted.

References


Scheme 2. Surface-initiate ATRP reaction

Figure 3. AFM and SEM images of contact molded lines before (A) and (B) and after ATRP brush growth (C) & (D).