Fabrication of Complex Diffractive Structures in an Organic-Inorganic Hybrid and Incorporation of Silver Nanoparticles

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ABSTRACT

We report on the fabrication of photo-patterned structures with sub-micron feature sizes in a sol-gel derived organic-inorganic hybrid material. Patterns with a high level of design complexity are presented, in the form of a diffractive optically variable device. We also demonstrate how the material can serve as a matrix for nano-scale components, via the incorporation of Ag nanoparticles. It is shown that Ag nanoparticles can be used to modify the optical properties of this photo-patternable material.

Keywords: sol-gel, organic-inorganic hybrid, silver nanoparticles, photo-patterning

1 INTRODUCTION

Research activities have been expanding rapidly in recent years at the interface between micro- and nano-technologies. In particular, organic-inorganic hybrids have attracted considerable interest in this area. These materials, which are synthesized by the highly versatile sol-gel process, consist of interpenetrating organic and inorganic networks at the nano- to molecular size scale. By incorporating photo-polymerizable groups into the organic network, the material can be patterned with light in a similar way to a photo-resist [1]. Thus, micro-scale relief structures can be generated in this glass-like material. Importantly, this can be achieved without needing harsh chemical etchants such as HF.

Photo-patternable organic-inorganic hybrids have been used to fabricate simple micro-optical elements such as microlenses [2], diffraction gratings [3-5] and stacked optical waveguides [6]. Photo-patterning has been achieved by conventional amplitude masking [2-4, 6], phase masking [7], laser direct writing [8] and holographic interference methods [9, 10]. In addition, electron beam lithography has been demonstrated as an alternative patterning method [5]. Only very simple relief structures have been produced to date, with the highest resolution demonstrated in basic diffraction gratings comprised of lines ~500 nm in width [7]. In this paper, we demonstrate the fabrication of more complex diffractive structures, in the form of a diffractive optically variable device (OVD).

Another active area of sol-gel research has been the fabrication of nanocomposite materials consisting of noble metal nanoparticles embedded in the sol-gel matrix. In particular, there has been considerable interest in sol-gel glasses doped with Ag nanoparticles, due to their nonlinear optical properties [11] and surface-enhanced Raman activity [12, 13]. Such properties make these materials important in a wide range of emerging technologies, such as optoelectronics (e.g. optical switches, nonlinear waveguiding devices) and chemical sensors. Here, we demonstrate how Ag nanoparticles can be incorporated into a photo-patternable, sol-gel derived, organic-inorganic hybrid material. While there are numerous reports in the literature on Ag-doped glass films, this is the first time that photo-patterning has been demonstrated in such a material.

2 ORGANIC-INORGANIC HYBRID FORMULATION

The organic-inorganic hybrid sol was prepared by dissolving 5 mL 3-methacryloxypropyltrimethoxysilane (MAPTMS) in 25 mL isopropanol and hydrolyzing with 1.1 mL 0.2 M HCl (aq). A second solution was prepared consisting of 2.0 mL titanium(IV) isopropoxide ($Ti(OCH_2CH_2CH_3)_4$) mixed with 4.3 mL acetylacetone. Both solutions were stirred for 1 hr. The two solutions were then mixed together, 0.75 g of the photo-initiator 1-hydroxy-cyclohexyl-phenyl-ketone was added and the resulting solution stirred for 1 min. All solution preparation was carried out under dim lighting to avoid photo-polymerization. The sols were then allowed to age at room temperature for 16 hr.

3 PHOTO-PATTERNING COMPLEX DIFFRACTIVE STRUCTURES

In order to photo-pattern complex diffractive structures, aged sols were filtered through 0.25 μm membrane filters and spin-coated for 1 min at 3500 rpm onto glass microscope slides or Cu sheet. The spin-coated substrates were then baked at 80˚C for 30 min. This was done to drive away solvent, and to promote condensation polymerization reactions leading to the formation of an inorganic (≡Si–O–Si/Ti≡) network structure.

After cooling to room temperature, the spin-coated substrates were exposed through an amplitude mask in a highly collimated UV exposure unit (Hg lamp, 2.2 W/cm^2, 5 min exposure time). Exposure to UV light caused cross-linking of methacrylate groups via addition polymerization, resulting in the formation of an organic network structure.

The mask used was prepared from a standard photo-mask blank and was patterned by electron beam lithography. The design of the mask incorporated complex patterns of straight grooves of various lengths and spacing. The orientation of the lines was also varied to produce different images at different viewing angles. This type of mask design has been used in anti-counterfeiting applications and is described in detail elsewhere [14, 15]. The total image area was 2.5 × 3 cm.

Films were then developed in ethanol in order to remove unexposed material (i.e. areas devoid of organic network structure). Following development, the films were baked at 80°C for 1 hr. This was done to drive condensation polymerization reactions to completion, thereby strengthening the organic-inorganic hybrid network. The resulting photo-patterned features had a height of ~600 nm, as determined by AFM measurements.

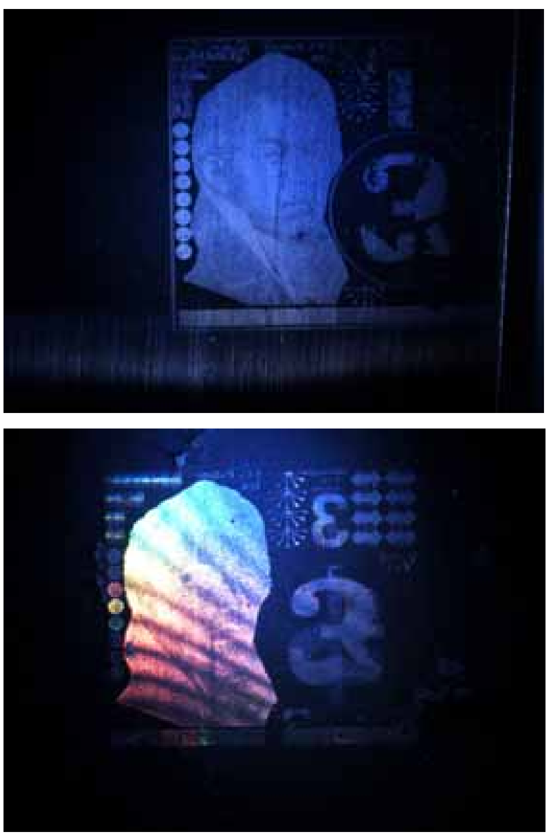

Figure 1: Diffractive OVD photo-patterned into organic-inorganic hybrid material on Cu substrate, as viewed with two different angles of white light illumination.

Figure 2: Sub-micron photo-patterned features in the organic-inorganic hybrid material on a Cu substrate.

Figure 1 shows an image photo-patterned into the organic-inorganic hybrid material on a Cu substrate, as viewed with two different angles of white light illumination. A portrait with gray-scale toning can be seen in the upper image, while diffractive effects are clearly evident in the image below. These optical effects result from the different lengths, spacing and orientation of sub-micron grooves in the photo-patterned organic-inorganic hybrid material.

A portion of the image is shown at higher magnification in Figure 2. Although some regions have delaminated due to the surface roughness of the Cu substrate, sub-micron line spacing can clearly be observed. Thus, we have achieved photo-patterned features in an organic-inorganic hybrid material with feature sizes comparable to previous work [7], but in a design of much higher complexity, and across a large image area.

4 INCORPORATING SILVER NANOPARTICLES

We have also been able to incorporate Ag nanoparticles into this photo-patternable organic-inorganic hybrid material. This is achieved by dissolution of $AgNO_3$ in the precursor sol. To the basic formulation described above, 0.15 g $AgNO_3$ (s) is added immediately after addition of the photo-initiator. The solution is then stirred rapidly for 15 min before ageing in darkness at room temperature for 16 hr.

Importantly, in the process of photo-patterning the host material, Ag^+ ions incorporated into the organic-inorganic network structure are photo-reduced, thereby producing metallic Ag nanoparticles. Figure 3 shows a transmission electron micrograph of the photo-patterned Ag-doped hybrid material. Ag nanoparticles over a range of sizes are clearly visible, with some of the larger particles displaying crystalline diffraction contrast.

Figure 4 shows the UV-visible absorption spectra of the undoped and Ag-doped organic-inorganic hybrid materials. The material incorporating Ag nanoparticles shows a weak absorption band with a peak maximum at 420 nm, which can be attributed to the surface plasmon resonance characteristic of Ag nanoparticles.

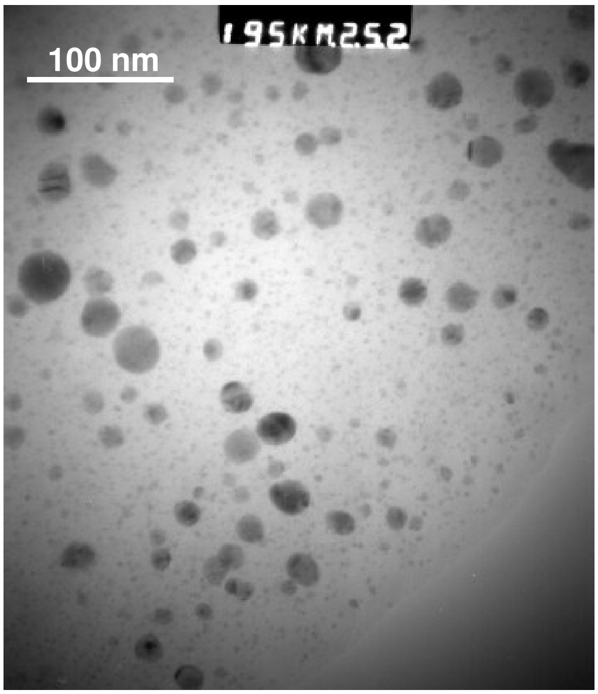

Figure 3: Transmission electron micrograph of photo-patterned organic-inorganic hybrid material doped with Ag nanoparticles.

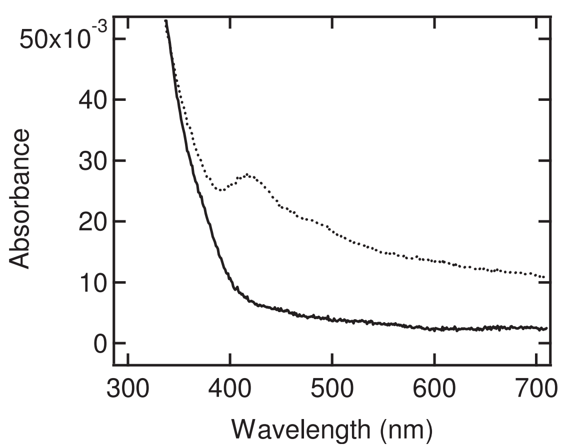

Figure 4: UV-visible absorption spectra of undoped hybrid material (solid line) and Ag-doped hybrid material (dotted line).

5 CONCLUSIONS

We have demonstrated that complex diffractive structures can be photo-patterned into an organic-inorganic hybrid material. The ability to combine both sub-micron feature sizes and a high level of design complexity in organic-inorganic hybrids may prove useful for the fabrication of a variety of devices, such as phase masks, X-ray optics and security elements.

We have also demonstrated how Ag nanoparticles can be incorporated into a photo-patternable organic-inorganic hybrid. By utilizing the unique properties of Ag nanoparticles, this novel material may find use in a range of emerging technologies such as optoelectronics (e.g. optical switches, nonlinear waveguiding devices) and chemical sensing (e.g. as a lab-on-a-chip substrate for detecting chemical species by surface-enhanced Raman scattering).

REFERENCES

[1] K.H. Haas, H. Wolter, Curr. Opin. Solid State Mater. Sci. 4 (1999) 571.
[2] H. Jiang, X. Yuan, Z. Yun, Y.-C. Chan, Y.-L. Lam, Mater. Sci. Eng. C 16 (2001) 99.
[3] P. Äyräs, J.T. Rantala, S. Honkanen, S.B. Mendes, N. Peyghambarian, Opt. Commun. 162 (1999) 215.
[4] O. Soppera, C. Croutxe-Barghorn, C. Carre, D. Blanc, Appl. Surf. Sci. 186 (2002) 91.
[5] W.X. Yu, X.-C. Yuan, Opt. Express 11 (2003) 899.
[6] U. Streppel, P. Dannberg, C. Wachter, A. Brauer, L. Frohlich, R. Houbertz, M. Popall, Opt. Mater. 21 (2003) 475.
[7] D.J. Kang, J.U. Park, B.S. Bae, J. Nishii, K. Kintaka, Opt. Express 11 (2003) 1144.
[8] W.X. Yu, X.C. Yuan, N.Q. Ngo, W.X. Qui, W.C. Cheong, V. Koudriachov, Opt. Express 10 (2002) 443.
[9] P. Cheben, M.L. Calvo, Appl. Phys. Lett. 78 (2001) 1490
[10] D.J. Kang, J.K. Kim, B.S. Bae, Opt. Express 12 (2004) 3947.
[11] P. Prem Kiran, G. De, D. Narayana Rao, IEE Proceedings: Circuits, Devices and Systems 150 (2003) 559.
[12] S. Lucht, T. Murphy, H. Schmidt, H. Kronfeldt, J. Raman Spectrosc. 31 (2000) 1017.
[13] K. Maruszewski, M. Jasiorski, D. Hreniak, W. Strek, K. Hermanowicz, K. Heiman, J. Sol-Gel Sci. Technol. 26 (2003) 83.
[14] P.W. Leech, H. Zeidler, Microelectr. Eng. 65 (2003) 439.
[15] R.A. Lee, Microelectr. Eng. 53 (2000) 513.