Direct fabrication of two-dimensional titania arrays using interference photolithography

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Two-dimensional (2D) titania arrays with periods of 0.8–2.0 μm were fabricated by polymerization of a photosensitive titanium-containing monomer film using interference photolithography. The 2D precursor arrays were prepared by exposing a mixture of methacrylic acid, ethyleneglycol dimethacrylate, and titanium ethoxide doped with photoinitiator to 355 nm, 15 ns pulses from a Nd-Yttrium–aluminum–garnet laser and then rinsing with methanol. Pure titania arrays were obtained from the precursor arrays by subsequent calcination at 575 °C. The structure of the arrays fabricated by this method was confirmed with optical microscopy and scanning electron microscopy.

While progress toward fabricating 3D photonic crystals has been rapid, it has also been recognized that two-dimensional (2D) photonic crystals have many attributes that make them more suitable for integrated photonic circuit applications. In particular, the simplicity of the 2D structure permits straightforward fabrication of photonic crystal waveguides and microcavity lasers, and integration with conventional passive and active optical components. These 2D photonic crystals are typically fabricated by defining the periodic array in a mask using an electron beam and using this mask to etch high-aspect ratio features by RIE into an underlying high dielectric constant semiconductor material. These steps are involved even though high refractive index material can be precisely obtained. Therefore, it is desirable to directly create 2D arrays with high refractive index by combining the advantages of photopolymerization and photolithography: simple fabrication of periodic materials with high refractive index.

In this letter, we report on a simple and economical alternative for direct fabrication of 2D dielectric arrays of TiO₂ by photopolymerization of a titanium-containing monomer film. The process begins by preparing a solution that contains titanium(IV) ethoxide (TE) (Aldrich), methacrylic acid (MA) (Aldrich), ethylene glycol dimethacrylate (EDMA), (Aldrich), and 2,2-dimethoxy-2-phenylacetophenone (Photoinitiator, Aldrich) components. Figure 1 shows the molecular structures of these compounds; the refractive indices of these TE, MA, and EDMA are, respectively, 1.504, 1.431, and 1.45. The TE, MA, and EDMA are mixed together in a molar ratio of 2:10:5, and then the photoinitiator is added in the amount of 2 wt. % of MA and EDMA. This film is coated on a glass substrate by spinning at about 1000 rpm under an argon atmosphere.

A three-grating interference mask was used to create a periodically modulated light intensity pattern that exposes in a single step the titanium-containing monomer film to create 2D dielectric columns or air voids by photopolymerization. The photopolymerization process results in a negative tone...
structure, with the titanium-containing polymer remaining in the regions where the light intensity is high. The interference mask was prepared by etching 4 mm long, 4 mm wide gratings with a 4 μm period into a Cr layer that was deposited onto an optically flat soda lime mask plate. As shown in Fig. 2~a!, dielectric columns were defined by positioning the sample where the three first-order diffraction beams from each of the gratings overlap. According to Berger’s method, this grating will result in a periodic array of dielectric columns with a repeat distance of 2.6 μm.24

The titanium-containing monomer film was photopolymerized by exposing it to Nd:yttrium–aluminum–garnet (YAG) pulsed laser (Spectra Physics GCR-13 Nd:YAG, 15 ns pulse duration) radiation at 355 nm, 2 mW/cm², for 7 min under an argon atmosphere as shown in Fig. 2(b). Next, the film was rinsed with methanol for 90 s to remove the unirradiated material, and 2D arrays of the patterned titanium-containing polymer were obtained as shown in Fig. 2(c).

For comparison purposes, 2D arrays made of a photore sist (SU8, MicroChem Corp.) were also fabricated by means of the same optical setup [Fig. 3(b)]. In this case, a regular 2D structure with a period of 2.6 μm, which is equivalent to the period of the original light distribution created in the film, is observed.24 Therefore, it is reasonable to conclude that shrinkage occurred in the fabrication process of the titanium-containing polymer dielectric columns. It is well known that titanium ethoxide is highly reactive with moisture in air, and that titanium dioxide is the product of the hydrolysis reaction.25–27 This process substantially reduces the volume and is the most likely cause of the shrinkage observed here. Imhof and Pine reported that the shrinkage of titanium gels reaches about 50%.28 In addition, in the preparation of 3D mesoporous polymer replicas from silica colloidal crystals, it has been shown that shrinkage of approximately 60% in linear dimensions occurs when EDMA is used as the monomer.29 The combination of these two factors can
structures can be fabricated by preparing suitable grating masks since the structure created is dependent on the interference pattern of light on the film. In fact, even with the same mask, we have observed that 2D air voids are formed in the regions of the sample where the interference pattern is created by zeroth-order and first-order diffractions from the mask [Fig. 3(f)]. Furthermore, it is possible to fabricate much finer structures by the use of gratings with smaller dimension and pitch and the shrinkage inherent in the fabrication process.

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28 Gotoh et al. reported that titanium ions introduced into poly(methylmethacrylate-co-methacrylic acid) act as crosslinkers between carbonyl groups and enhance heat resistance.27 In the present case, the strong ligation of Ti(IV) by poly(methacrylic acid) prevents it from being dissolved in methanol and washed away.

The advantage of the method described here over conventional techniques is the ability to fabricate 2D titania arrays in a simple and inexpensive manner. In addition, various

FIG. 4. Absorption spectra of (a) TE, (b) MA, (c) EDMA, and (d) a mixture of TE, MA, and EDMA in a molar ratio of 2:10:5. Only the mixture shows significant absorption at wavelengths longer than 400 nm.

easily account for the approximately 40% shrinkage observed in our 2D arrays.

In order to remove the organic components and increase the refractive index contrast of the 2D arrays, the films were heated at 575 °C for 8 h. Figure 3(c) shows the optical microscope and Figs. 3(d)–3(e) the scanning electron microscope images (Philips, XL-20) of the titania 2D arrays obtained after this calcination step. Note that although the refractive index of pure titania is 2.58, the effective refractive index of the titania array obtained after calcination was found to be ~2. Surprisingly, the uniform hexagonal 2D arrays are completely retained, even though further shrinkage occurs during calcination. The diameter and length of columns are 800 nm and 2 μm, respectively. Preliminary x-ray measurement of these titania arrays shows a small peak corresponding to the anatase phase and very large scattering corresponding to the amorphous phase, indicating that the nature of the titania arrays was amorphous.

Note that the 2D titania arrays cannot be achieved unless the TE remains in the photopolymerized organic part of the precursor structure after the unexposed resist is rinsed away with methanol. While it is possible that physical entrainment of TE in the crosslinked polymer network contributes to this effect, the dominant effect is probably exchange of ethoxide ligands with the more strongly coordinating carboxylate groups of MA, and possibly with the weakly coordinating ligands with the more strongly coordinating carboxylate effect, the dominant effect is probably exchange of ethoxide with methanol. While it is possible that physical entrainment of the TE remains in the photopolymerized organic part of the precursor structure after the unexposed resist is rinsed away with methanol. While it is possible that physical entrainment of TE in the crosslinked polymer network contributes to this effect, the dominant effect is probably exchange of ethoxide ligands with the more strongly coordinating carboxylate groups of MA, and possibly with the weakly coordinating ester groups of EDMA. Figure 4 shows the absorption spectra of each of the pure materials and the resultant mixture. None of the individual components have absorbances at visible wavelengths, but the mixture has very strong absorption to the red of 400 nm and looks yellowish. This absorption is attributed to charge transfer from the bound carboxylate ligands to titanium(IV).