

Fabrication of TiO₂-Organic Hybrid Dot Arrays Using Nanosecond Laser Interference Lithography

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Laser interference lithography is an established fabrication technique for periodic arrays such as photonic crystals (PCs). In this paper, we report the fabrication of a TiO₂-organic hybrid periodic array by nanosecond laser interference lithography. TiO₂-organic hybrid films were prepared from titanium tetra-*n*-butoxide and 2-(methacryloyloxy) ethyl acetoacetate (MEAcAc) by the sol-gel method. The films were irradiated by using 10 ns pulses of 355 nm diffracted light from a Nd:yttrium-aluminum-garnet laser. The complexes formed by the Ti alkoxide and the MEAcAc were decomposed by laser irradiation, and the irradiated parts remained as periodic dot arrays on the substrate after the development. The two-dimensional array of this TiO₂-organic hybrid material was calcined at 450°C and formed an anatase TiO₂ dot array. The refractive index measured was 2.00. These dots were crack free and adherent to the substrate.

I. Introduction

TWO-DIMENSIONAL (2-D) periodic arrays of dielectric materials with submicrometer to micrometer repeat distances have potential applications as photonic crystals (PCs).^{1–3} These arrays are fabricated by conventional lithography using X-rays, electron beams, lasers, or UV light sources depending on the lattice spacing. Laser interference lithography is a relatively new and useful technique for fabricating PCs from polymerizable materials such as photoresist.^{4–10} In this technique, photosensitive materials are exposed to a light interference pattern and are developed in an appropriate solvent, resulting in a periodic array of the photosensitive material. However, the refractive indices of photosensitive polymers are typically low and the contrast in refractive indices between the material and air is not sufficient to show outstanding properties such as a photonic band gap.

TiO₂ is among the most interesting inorganic materials for PCs because it has a high refractive index and is transparent in the visible region. We have previously studied TiO₂-organic hybrid materials as photopolymers with relatively high refractive indices.^{9,11,12} TiO₂-organic hybrids were prepared from a Ti

alkoxide modified with a β-diketonate ligand and an unsaturated hydrocarbon by the sol-gel method. When these hybrid films were exposed to UV light, the β-diketonate chelate decomposed, the unsaturated hydrocarbon photopolymerized, and the solubility in alcohol of the exposed parts decreased. Patterns with unit cell dimensions of several microns were fabricated by UV exposure through a photo mask and were developed by utilizing the difference in solubility between the exposed and unexposed parts.¹¹ When these hybrid films were exposed by interference light from femtosecond pulses, similar structural changes occurred by multi-photon absorption, and TiO₂ dot array could be fabricated successfully.¹²

Nanosecond laser interference is a more convenient technique for many researchers because of the low cost and wide use of such laser systems. We and others have previously shown that 2-D and 3-D periodic structures can be successfully fabricated by the laser interference from nanosecond pulses using different types of photo masks.^{8–10} However, in those studies, the photopolymers used had a relatively low Ti content and the 2-D TiO₂-organic hybrid arrays produced showed shrinkage by a factor of two or more in linear dimensions upon calcination.

In this paper, we report the fabrication of periodic dot arrays from TiO₂-organic hybrid films by laser interference lithography using nanosecond pulses, and the structural changes that occur in these films by laser exposure are investigated.

II. Experimental Procedure

Preparation of TiO₂-organic hybrid gel films and fabrication of TiO₂-organic hybrid dot arrays are shown in Fig. 1. The gel films were prepared by the sol-gel method. Titanium tetra-*n*-butoxide (Ti(O-*n*Bu)₄, Aldrich Co., Bellefonte, PA) was reacted with 2-(methacryloyloxy) ethyl acetoacetate (MEAcAc, Acros Organics). The molecular structure of MEAcAc is shown in Fig. 2. After stirring the solution for 15 min at room temperature, H₂O was dropped into the solution. The molar ratio of Ti(O-*n*Bu)₄, MEAcAc, and H₂O was 1:(0.5–2):2. The solution was stirred for 3 h at room temperature. The sol was spin coated at 1000 rpm for 20 s on a glass slide. After baking at 120°C for 10 min, TiO₂-organic hybrid films were obtained. The film thickness was measured by SURFCOM 1400A (Tokyo Seimitsu Co., Ltd., Tokyo, Japan).

The film was exposed to frequency-tripled light (355 nm) from a Nd:yttrium-aluminum-garnet pulsed laser (Spectra Physics GCR-13, Mountain View, CA, 355 nm wavelength, 10

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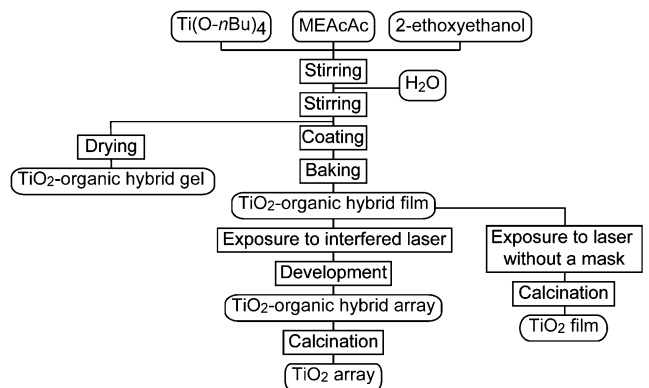


Fig. 1. Preparation of TiO₂-organic hybrid gel films and fabrication of TiO₂-organic hybrid dot arrays.

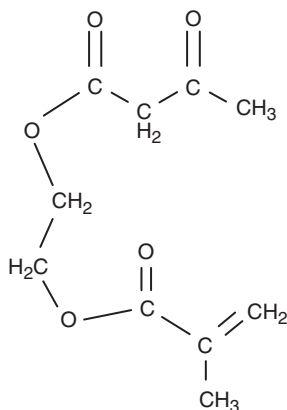


Fig. 2. Molecular structure of 2-(methacryloyloxy) ethyl acetoacetate.

ns pulse duration at 10 Hz) through a diffraction mask. The optical set-up has been previously described.⁸ The mask has three gratings oriented 120° relative to one another. Each grating was 4 mm wide and 4 mm long with a 2 μm period. The laser was expanded by a beam expander and was collimated on a film through the mask. The film was placed at the focal point of the interference pattern, which was 50 mm behind the mask. According to Berger *et al.*'s method, this grating will result in a hexagonal array of dielectric columns with a repeat distance of 1.3 μm.¹³ After laser irradiation with an integrated intensity of 100 mW/cm² for several minutes, the films were developed in 2-ethoxyethanol (Kishida Chemical Co., Osaka, Japan) for 1 min

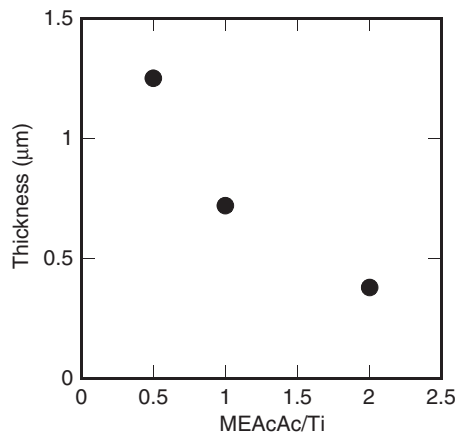


Fig. 3. Film thickness as a function of the 2-(methacryloyloxy) ethyl acetoacetate/Ti molar ratio.

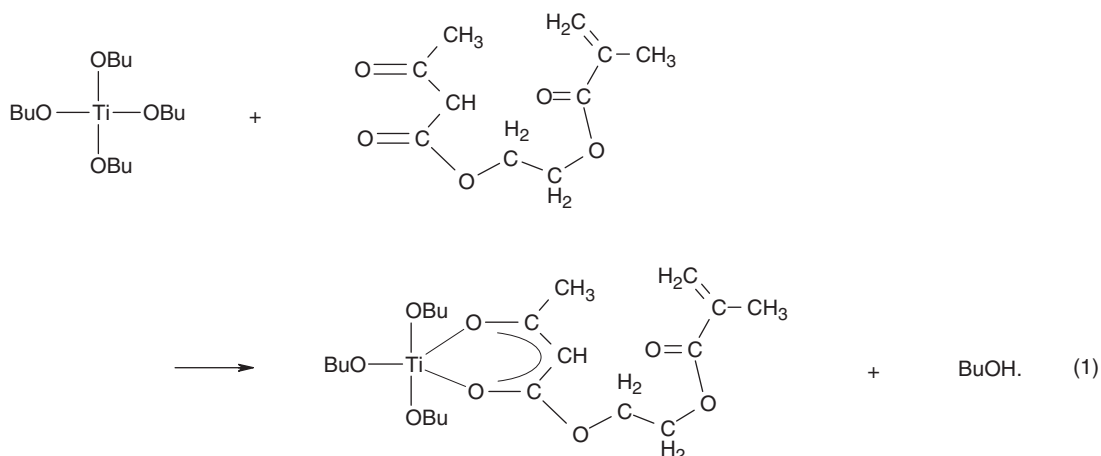
to obtain TiO₂-organic hybrid arrays. After development, the periodic arrays were calcined in air at 450°C for 1 h, and the TiO₂ arrays were fabricated. The periodic arrays were imaged by scanning electron microscopy (SEM, Philips, XL20, Amsterdam, the Netherlands).

The refractive index of the film, which was prepared by laser irradiation for 10 min and calcination in air at 450°C for 1 h, was measured at 632.8 nm using a prism coupler (Metricon 2010, Pennington, NJ). The phase composition of the calcined films was determined using an X-ray diffractometer (XRD) technique with parallel beam optics with a D8 Advance Bruker XRD (Karlsruhe, Germany) at room temperature, with monochromated CuKα, in the scan range of 2θ between 10° and 100° with a step size of 0.03 (2θ/s⁻¹). Measurements were taken under beam-acceleration conditions of 35 kV/300 mA.

After the sol with MEAcAc/Ti = 1 was dried at 120°C for 3 days, the hybrid gel was obtained. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the gel were performed at a heating rate of 10°C/min in air in order to investigate the effects of the heating process.

III. Results and Discussion

The thickness of the hybrid film is plotted as a function of the molar ratio of MEAcAc to Ti(O-*n*Bu)₄ (MEAcAc/Ti) in Fig. 3. The film thickness decreases with increasing MEAcAc content. The highest film thickness measured was 1.25 μm at MEAcAc/Ti = 0.5. Typically, a β-diketone reacts with Ti(O-*n*Bu)₄ and forms β-diketone chelate rings as shown below¹⁴:



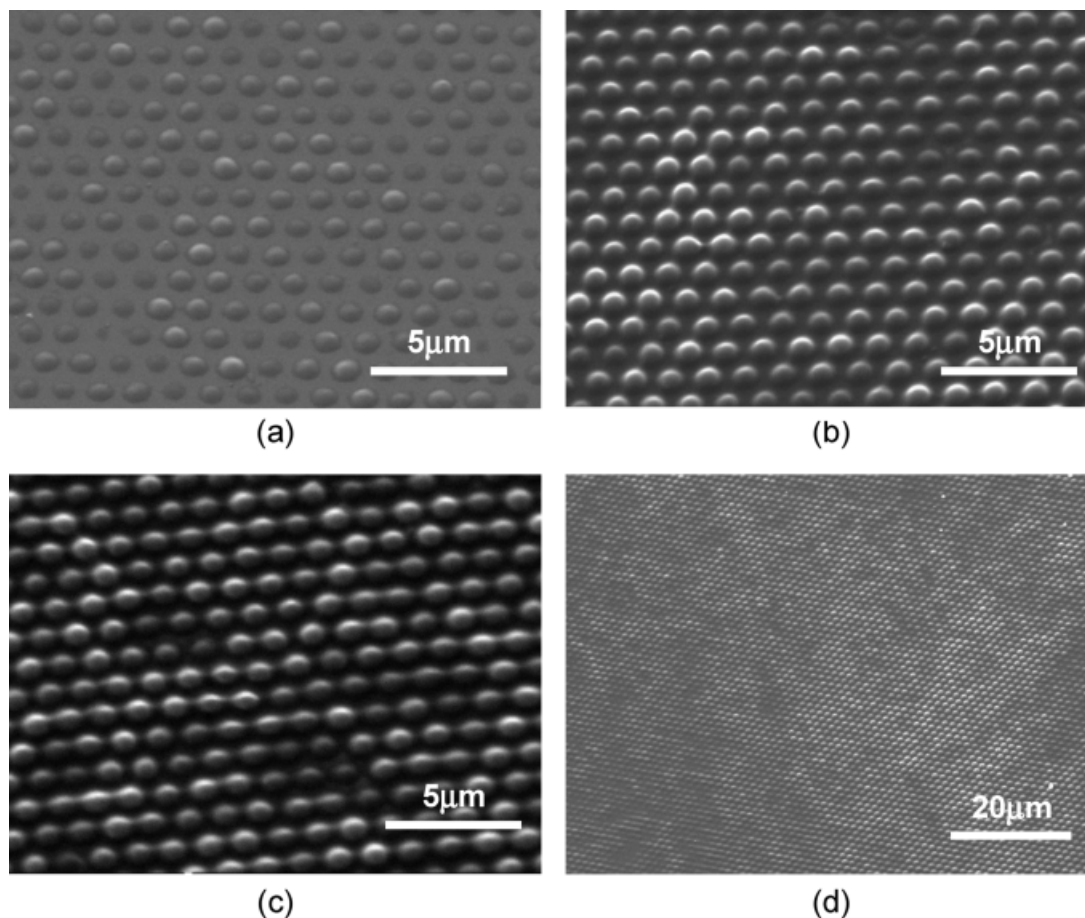


Fig. 4. Scanning electron microscopy images of periodic arrays obtained at different irradiation times; (a) 4 min, (b) 5 min, (c) 8 min, (d) wide area of (b).

when the MEAcAc/Ti ratio increases, the amount of β -diketonate chelate increases in the sol and the viscosity of sol decreases. Thus, the film thickness decreases with increasing MEAcAc/Ti ratio as shown in Fig. 3. In the following, films with MEAcAc/Ti = 0.5 were used for the experiment.

SEM images of periodic arrays, which were fabricated by different exposure times, are shown in Fig. 4. The exposure times were (a) 4 min, (b) 5 min, and (c) 8 min. In these images, whiter regions represent the part of the film that remains after development. The dots are arranged at about 1.3 μm spacing in a hexagonal lattice and correspond to the pattern expected from the mask. This suggests that the β -diketonate chelate rings as

shown in Eq. (1) react by the laser exposure and the solubility in the developer of exposed parts of the film decreases.^{11,12} The height of the dots is about 0.25 μm , although the film thickness was 1.25 μm before the laser exposure. The periodic arrays could be obtained only when the film was exposed from the substrate side. This means that the laser light is absorbed in the film and the chemical change of the film occurs only in the region of the 0.2–0.3 μm thickness. When the film is irradiated from the film side, the chemical reaction does not occur at the interface between the film and the substrate and the film is removed in 2-ethoxyethanol during development because the light does not achieve the interface. The diameter of the dots increases with increasing laser irradiation time, and neighboring dots link to each other after 8 min of irradiation as shown in Fig. 4(c). At 5-min irradiation time, the diameter of dots is 0.98 μm and the dots are well separated from each other. Figure 4(d) shows a wide-area micrograph of the periodic structure fabricated by

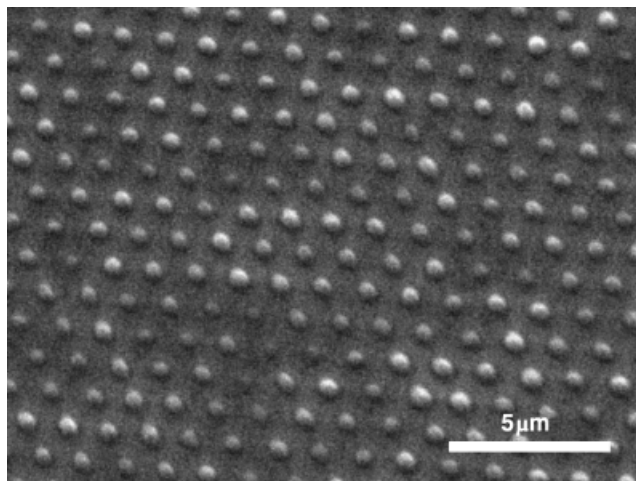


Fig. 5. Scanning electron microscopy image of a dot array prepared by calcination of the periodic array as shown in Fig. 4(b).

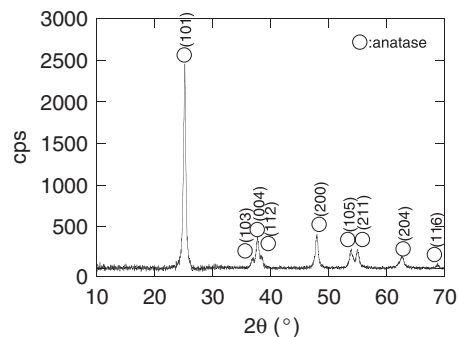


Fig. 6. X-ray diffractometer patterns of the film calcined at 450°C for 1 h. All peaks are assigned to anatase.

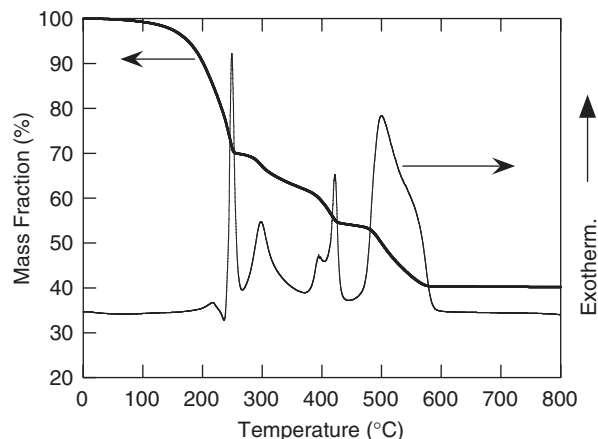


Fig. 7. Differential thermal analysis and thermogravimetric analysis traces of a bulk gel with 2-(methacryloyloxy) ethyl acetoacetate/Ti = 1, obtained at a heating rate of 10°C/min in air, after drying at 120°C for 3 days.

5-min laser irradiation. The periodic array could be obtained over the whole irradiated area, which was an equilateral triangle with 4 mm sides.

These patterned films were calcined at 450°C for 1 h to investigate morphological changes. A SEM image of a calcined dot array is shown in Fig. 5. The precursor TiO₂-organic hybrid array was fabricated by irradiation for 5 min as shown in Fig. 4(b). The individual dots do not show evidence of cracking or exfoliation from the substrate. The diameter of the dots after calcination was 0.58 μm, and the shrinkage may be attributed to loss of most of the organic fraction of the film. After calcination of the coated hybrid film under the same condition, the measured refractive index of the film was 2.00 ± 0.01.

The XRD pattern is shown in Fig. 6. The peaks are assigned to anatase, although the refractive index of the film is lower than the reported value of anatase (2.5).¹⁵ From the refractive index and the XRD patterns, the dot array calcined is found to be composed of anatase with a high refractive index.

Figure 7 shows DTA and TGA traces of the gel with ME-AcAc/Ti = 1. Several weight-loss steps corresponding to exothermic reactions were observed between 200° and 600°C. The most exothermic process occurs at 450°–600°C and can be attributed to combustion of residual organic matter in the gel networks. The calcined film might partially retain the residual organic matter. Thus, the refractive index of the calcined film is lower than that of anatase. By long duration or high-temperature calcination, the refractive index can increase to 2.5.

The fabricated TiO₂ dot arrays are useful for 2-D PCs because of the high refractive index, when the height of the dots becomes higher. The height of the dots is not high enough to show the outstanding properties of such a photonic band gap.

The height will be improved by a laser with a suitable wavelength to decompose the chelate compounds, because the thickness of the coated film is high.

IV. Conclusion

We have shown that fine patterning of TiO₂-organic hybrid films by the nanosecond laser interference lithography generates dot arrays. The dot arrays, in which the TiO₂-organic hybrid materials with 0.98 μm diameter and 0.25 μm height are arranged periodically, were obtained due to the change of the chelate rings by the laser irradiation. After calcination of the hybrid dot array, the TiO₂ dot array, which is composed of rutile anatase with a high refractive index, 2.00, can be obtained. It should be possible to fabricate 2-D arrays with higher aspect ratios by using a laser of the long wavelength, which is suitable for a chemical reaction of the chelate ring, and the 2-D arrays are applicable for 2-D PCs.

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