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Preparation and optical properties of sol–gel derived photo-patternable organic–inorganic hybrid films for optical waveguide applications

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ABSTRACT

Photo-patternable TiO_2/organically modified silane hybrid films were prepared by combining a low-temperature sol–gel technique with a spinning–coating process. A ridge waveguide pattern was fabricated by ultraviolet light irradiation through a mask placed contact with the hybrid film in direct. Optical properties and photochemical activity of the hybrid film, including refractive index, thickness, propagation mode, and propagation loss, were studied and monitored by a prism coupling technique and Fourier transform infrared spectroscopy. The change of transmittance with exposure time was also observed by ultraviolet–visible spectroscopy. These results indicate that the hybrid film is potential application for fabrication of photonic devices by ultraviolet light irradiation. The structure of ridge waveguide pattern was characterized and studied by scanning electron microscope and surface profiler. The fabrication process of the as-prepared photosensitive hybrid film as compared with traditional binary mask has a great amount of advantages of cost-effective, simple, and smooth surface over non-photosensitive material methods.

1. Introduction

Optically homogeneous and transparent organic–inorganic hybrid sol–gel materials containing organic components have been widely studied as a promising system for photonic applications over the past 10 years [1–4]. Due to the intrinsic material properties, especially, incorporation of photo-responsive organic groups into inorganic materials, this hybrid material system has been widely applied for fabrication of micro-optical elements such as diffraction gratings, channel optical waveguides and micro-lens [5–11]. To fabricate micro-optical elements, traditional methods need two steps [12,13], which include lithography process that transfers pattern structure from mask to photoresist and etching process that transfers pattern structure from photoresist to materials. Although the traditional patterning and etching fabrication method can fabricate various shape of micro-optical devices, the conventional method is time consuming and non-cost-effective. As comparison, it is simple and cost-effective to fabricate pattern by utilizing the photosensitive hybrid material as reported in this paper. As one knows, the hybrid material containing a polymerizable organic group including unsaturated hydrocarbon or epoxide substituent has been developed, which is patterned by ultraviolet (UV) light irradiation through an appropriate mask or laser writing followed by dissolving unpolymerized region. Therefore, photo-patternable hybrid materials have been extensively investigated for fabrication of micro-optical elements and optical waveguide devices in recent years, since the hybrid materials are not only favorable optical properties, but also simple and cost-effective materials for the fabrication of planar waveguide devices and micro-optical elements through UV light irradiation [14–17]. In this paper, we report the preparation of the photo-patternable organic–inorganic hybrid sol–gel thin films derived at a low-temperature and the fabrication of optical channel waveguides by one-step spin-coating process followed by direct UV light irradiation. Furthermore, we also studied the microstructural and optical properties of the hybrid waveguide films and the as-fabricated ridge waveguides by using prism coupling technique, UV–visible spectroscopy (UV–VIS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and surface profiler.

2. Preparation of photo-patternable hybrid sol–gel film and fabrication of ridge waveguide

The patternable hybrid TiO_2/organically modified silanes (ormosils) hybrid films were synthesized by three solutions. In the preparation of the solution I, 1 mole of methyltrimethoxysilane (MTES) was mixed with 4 moles of ethanol and 4 moles de-ionized water, and after being stirred for 30 min, 0.01 mole of hydrochloric acid was added into the solution as the catalyst. Then the solution was stirred for an hour again in air. For solution II, 1 mole of tetrapropyl orthotitanate was added into acetylacetone at a molar ratio of 1:4 and the solution was agitated until homogenization was attained. Solution III, 1 mole of 3-methacryloxypropyltrimethoxysilane (MEMO) was

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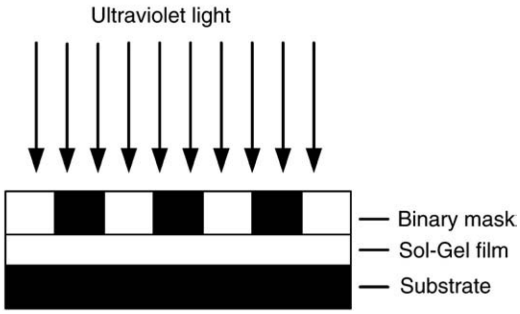

Fig. 1. Schematic diagram of the fabrication technique under UV irradiation.

mixed with 3 mole of isopropanol and 3 mole of de-ionized water, 0.01mole of hydrochloric acid was added as the catalyst, and the solution was stirred for about 1 h. Three solutions were then mixed to have a molar ratio of MTES:TiO_2:MEMO was 1:1:3. The final mixture was stirred for about one to 2 days at room temperature. It should be stressed here that before the mixed solution being used, about 4 wt. % photoinitiator of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide was added to the solution to generate plentiful free radicals at ultraviolet light irradiation. At the same time, double bond of MEMO will cut and combine with the free radicals, finally form steady polymer. Silicon and microscope slide glasses were used as substrates and they were ultrasonically cleaned in acetone and ethanol, respectively, rinsed with de-ionized water and dried. One layer of the sol–gel film was spun onto the substrate at 3500 rpm for 35 s. The coated films were then baked for about 5 min in a furnace at different temperatures.

Fig. 1 shows a schematic diagram of the fabrication process of the channel waveguide, which combines a direct-contact lithography technique with a photosensitive property of the as-prepared hybrid thin film. The channel waveguide was fabricated by UV light irradiation through a mask placed contact with the hybrid film in direct. Before UV exposure, the hybrid film was prebaked in a furnace for 5 min at 85 °C to remove the excess solvent and improve the adhesion between the hybrid film and the substrate. In the direct-contact lithography process, the hybrid film was exposed for around 20 min under a JKG-2A mask contact aligner (Shanghai xueze optical Co, Ltd,). After being exposed, the hybrid film was directly developed in ethanol for a few seconds to remove the un-exposure component and a channel waveguide structure was formed. Finally, the channel waveguide pattern was postbaked in a furnace at 150 °C for about 1 h again for further solidification of the as-fabricated pattern structure.

The refractive index and the thickness of the hybrid films were measured by a Metricon 2010 based on the prism coupling technique. It was noted that a film thickness of about 1.6 μm could be easily obtained on the silicon substrate by a single spin-coating process at the heat treatment temperature of 100 °C. The transmittance change of the hybrid film with the UV exposure time was observed with V-570 UV–VIS spectrometer from JASCO Corp, the result indicates that the hybrid film obtained under present conditions is quiet suitable for fabricating components by UV light irradiation. Photochemical property of the hybrid film was studied by FTIR. The FTIR spectra of the hybrid films heated at different temperatures and exposures were measured in the range of 4000–400 cm^{-1} by Perkin Elmer FTIR spectrometer. The surface morphology and profile of the channel waveguide were observed by SEM (Philips-FEI, Quanta 200, 20 kV operating voltage) and Dektak 6M surface profiler, respectively.

3. Results and discussion

Fig. 2 shows the propagation transverse electric (TE) modes of the hybrid planar waveguide film, which was deposited onto silica-on-silicon substrate by a single spin-coating process and baked at a temperature of 85 °C, based on the prism coupling technique at the wavelengths of 633 nm and 1312 nm, respectively. It can be seen from Fig. 2a that several dips in intensity can be observed, but only two modes of TE_o and TE_1, which their indices are bigger than the value of the substrate index (about 1.46), can be guided modes for the hybrid planar waveguide film and the other dips observed are substrate modes. Similarly, only the TE_o mode is a guided mode at the wavelength of 1312 nm. The thickness and the refractive index of the hybrid films can be determined from the measured effective refractive indices values of the TE modes. The results show that thickness and refractive index of the hybrid film derived by a single spin-coating process at room temperature are 1.67 μm and 1.5266 at the wavelength of 633 nm, 1.66 μm and 1.5119 at the wavelength of 1312 nm. It was also observed that the refractive index of the hybrid film increases and the thickness drops with increase the heat treatment temperature. For example, a thick hybrid film with a thickness of 1.67 μm can be produced on silicon substrate by a single spin-coating process at room temperature, but the thickness reduces to 1.60 μm with increase the heat treatment temperature to 100 °C. Correspondingly, the refractive index of the hybrid film increases from 1.5243 to 1.5266. The optical propagation loss of the hybrid planar film at 1312 nm, for the TE_o mode, was evaluated by a scattered-light measurement technique based on a fiber photometric detection. The loss was typically is 0.87 dB/cm. For a guided wave propagating in a planar medium, the local refractive index fluctuations in the volume of the waveguide and the deviations from a perfectly plane

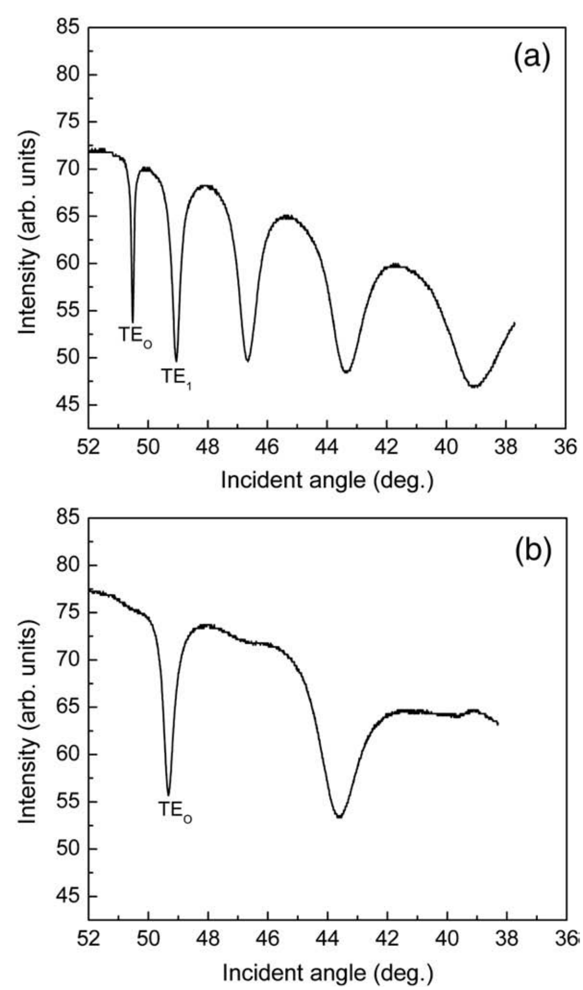

Fig. 2. Modes of the hybrid planar waveguide film. (a) At the wavelength of 633 nm and (b) at the wavelength of 1312 nm.