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Cite as: Appl. Phys. Lett. **85**, 4275 (2004); <https://doi.org/10.1063/1.1818726>

Submitted: 30 January 2004 . Accepted: 27 September 2004 . Published Online: 08 November 2004

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Direct laser writing of electro-optic waveguide in chromophore-doped hybrid sol-gel

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(Received 30 January 2004; accepted 27 September 2004)

To overcome the influence of chromophore absorption and degradation in the ultraviolet spectral range for direct photopatterning of electro-optic devices, a blue laser writing technique operating at 405 nm has been used to fabricate electro-optic waveguides from side-chain disperse red-1 doped photosensitive hybrid sol-gel films. The waveguide has good optical confinement and shows an electro-optic coefficient of about 9.0 ± 0.4 pm/V and high temporal stability. The results indicate that the hybrid sol-gel is a promising matrix for chromophores, and this technique can find applications in direct patterning of electro-optic devices from nonlinear chromophores-doped photosensitive materials including sol-gels and polymers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1818726]

There has been an increasing demand for electro-optic (EO) devices that have low optical loss, low cost, and operate at high speed with low half-wave voltage. Significant advances have been made recently in EO polymers.¹ Besides high electro-optic coefficient and stability, ease of processing and fabrication is highly desired for low-cost devices in practice. The conventional technique to fabricate electro-optic devices from electro-optic polymers is mainly based on the multistep photolithography and wet/dry etching. Direct ultraviolet (UV) irradiation has also been used to create waveguides using azo-type chromophores-doped materials.^{2,3} The index reduction in the exposed area is caused by either the reversible photoisomerization or irreversible photodecomposition of the chromophores during UV irradiation.^{4,5} However, it is difficult to fabricate steplike waveguides by UV photobleaching because the absorption of the chromophores prevents the UV photons from penetrating deep into the films of a few microns thick,⁵ so that the waveguide has poor confinement and heavy scattering.³

Photosensitive hybrid silica sol-gels have shown their potential as promising matrices for passive integrated optics because of their low-temperature processing, low optical loss, index tunability and compatibility with optical fiber. Several demonstrations have been reported on integrated optic devices fabricated by direct UV photopatterning of hybrid organic-inorganic sol-gels with a conventional I-line mask aligner at 365 nm.^{6,7} Circular waveguide has also been created with self-focusing of visible laser (514.5 nm) in passive hybrid sol-gel films.⁸ Electro-optically active sol-gels have been obtained by incorporating nonlinear optical chromophores by either guest-host or side-chain/main-chain strategy and high optical nonlinearity has been demonstrated.⁹⁻¹¹ However, direct UV photopatterning is not an effective approach for device fabrication from chromophores-doped sol-gels. One reason is that the chromophores degrade or decompose upon UV irradiation. Also, the strong absorption of the chromophores in the UV spectral range, as shown in Fig. 1, limits the proper polymerization of the materials deep through the exposed area.⁵ To overcome these limitations, we developed a blue laser writer to directly

fabricate EO waveguides. The high power of the blue laser (~15 mW) can overwhelm the absorption of the chromophores and activate and induce polymerization in photosensitive materials including both polymers and hybrid sol-gels. In the present letter, we report the direct laser writing and electro-optic effect of sol-gel waveguide doped with nonlinear optical chromophore, side-chain disperse red 1 [DR1, N-ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline].

The sol-gel material system based on hybrid precursor of 3-methacryloxypropyl trimethoxysilane (MAPTMS) doped with zirconium (IV) propoxide (ZPO) or aluminum butoxide is promising for its low optical loss, ease of processing, and photopatternability.⁶⁻⁸ In this work, MAPTMS-ZPO hybrid sol-gel was used as the matrix of the active sol. Photosensitive MAPTMS-ZPO sol was prepared following the procedure reported earlier.^{7,11} Briefly, MAPTMS was hydrolyzed with 0.01 M aqueous HCl. ZPO was dissolved in methacrylic acid (MMA) to form a stable Zr(IV)-MMA complex to avoid the precipitation of zirconium oxide.¹² The hybrid sol was obtained by mixing MAPTMS and ZPO precursors in a molar ratio of Si/Zr=78/22. A sol-gel monomer bearing the chromophore as a side chain was prepared by reacting 3-(triethoxysilyl)propyl isocyanate (TESPIC) with DR1.¹⁰ The DR1-TESPIC monomer was mixed with 0.01 M HCl before mixing with MAPTMS-ZPO. Thus, triethoxysilyls in TESPIC were hydrolyzed, generating silanols that will

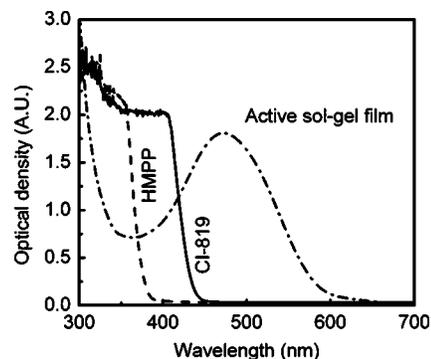


FIG. 1. The absorption spectra of active sol-gel film, photoinitiators CI-819 and HMPP.

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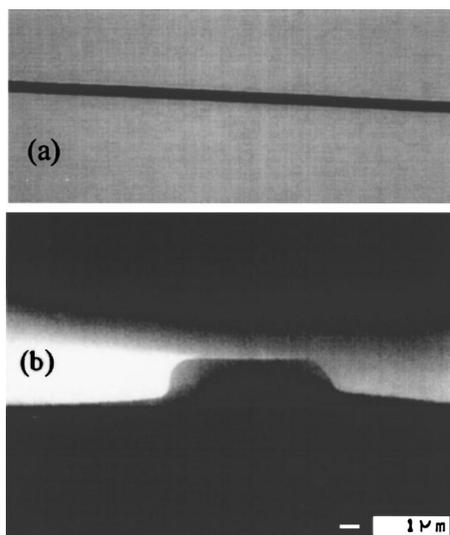


FIG. 2. Microscopic graphs of the top view (a) and cross section (b) of the sol-gel EO waveguide fabricated by direct laser writing, taken on an optical microscope (a) and scanning electron microscope (b), respectively.

be dehydrated and densified with those in MAPTMS-ZPO at an elevated temperature during poling and hard baking, resulting in rigid silica networks. For improved thermal stability, 3-glycidoxypropyl trimethoxysilane (GPTMS), which was also prehydrolyzed, was added to the active sol as a crosslinker. The final concentration of DR1 is about 10 mol %. To determine the proper photoinitiator for the polymerization of methacrylate groups in the hybrid sol, the absorption spectra of a few photoinitiators were examined in UV-visible spectral band. Figure 1 presents the absorption spectra of Irgacure® 819 [CI819, containing phosphine and phenyl bis(2,4,6-trimethyl benzoyl)] and HMPP (2-hydroxy-2-methylpropiophenone) dissolved in 2-propanol in amount of 5.0 wt %. For comparison, Fig. 1 also gives the absorption spectrum of an active sol-gel film that was spincoated onto a glass substrate and baked at 110 °C for 10 min. At 405 nm, the operating wavelength of the blue laser, CI-819 has much higher absorption than HMPP and the active sol-gel film, and can induce polymerization easily. CI-819 was first dissolved in 2-propanol and then added into the above active sol to an amount of 0.5 wt %. The sol was sealed and aged in dark at room temperature for 24 h before use. For waveguide writing, thin films were obtained by spincoating on thermally oxidized SiO₂/Si substrates ($6.0 \pm 0.05 \mu\text{m SiO}_2$) that were precoated with 100 nm indium tin oxide conducting layer as a bottom electrode. The films were soft baked at 110 °C for 10 min to evaporate the solvent.

A continuous-wave semiconductor laser operating at 405 nm was used in the blue laser writing system. The output power of the laser and the moving speed of the translation stage were computer controlled. The blue laser beam was focused onto the film surface through objective lenses with different numerical apertures to control the width of the waveguide. During writing, polymerization of the methacrylate groups occurred in the exposed area. After writing, the film was developed in acetone to remove the unexposed area. With this technique, a centimeter long waveguide can be written in a few minutes.

Figure 2 shows the photographs of the top view and cross section of the EO waveguide written with a laser power of 1.5 mW and a moving speed of 200 steps per second

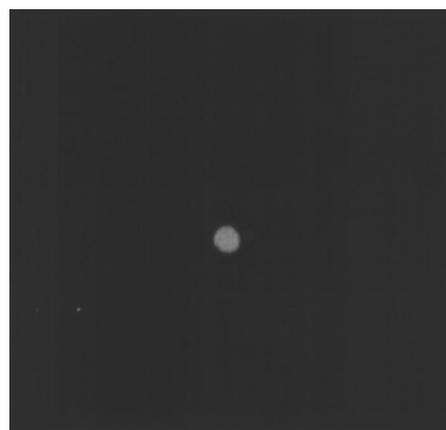


FIG. 3. Guided mode of the laser written waveguide at 1550 nm.

(30 nm per step). The waveguide was defect free, uniform, and fully polymerized deep through the bottom, which is attributed to the high power density ($\sim 2.0 \times 10^3 \text{ W/cm}^2$) of the blue laser and the strong absorption of the photoinitiator at 405 nm. The side tails of the ridge walls are mainly due to the deviation in focusing and the overdensification during soft baking. Further optimization can be achieved by fine controlling the focusing position onto the film and the soft baking temperature and time.

The ridge waveguide was corona poled and hard baked at 170 °C for 1 h with a voltage of 6 kV and a distance of 2.0 cm from the tungsten needle to the waveguide. During the hard baking, the waveguide was further densified due to the dehydration of silanols and the crosslinking of epoxy in GPTMS.¹³ With a film that was processed the same way, the refractive index of the core was measured on a prism coupler to be 1.539 at 1550 nm. A MAPTMS-ZPO cladding layer with low refractive index (1.508 at 1550 nm) was spincoated onto the ridge and then the sample was baked at 145 °C for 1 h with a 6 kV corona field being applied to maintain the alignment of the chromophore molecules. The sample was cooled down to room temperature and then coated with a silver layer of 100 nm thick as top electrode. The total thickness of the active and the cladding layers was $6.2 \mu\text{m}$. The sample was finally cleaved to a length of $L=3.0 \text{ mm}$.

The EO properties of the waveguide were tested in a transverse configuration.¹⁴ A laser beam of $\lambda=1550 \text{ nm}$, 45° polarized with regard to the poling direction, was coupled into the waveguide through a polarization-maintaining single-mode fiber. The output from the waveguide was collected with a 40× objective lens followed by a compensator and a crossed analyzer. An infrared camera and an infrared detector were used to capture the guided mode and monitor the power variation of the output, respectively.

Figure 3 presents the guided mode of the waveguide at $\lambda=1550 \text{ nm}$. The waveguide shows very good mode confinement with a very little scattering due to the imperfection of the side walls as shown in Fig. 2.

By measuring the phase shift of the output, the EO coefficient has been derived. Figure 4 shows the dependence of phase shift $\Delta\phi$ on applied dc voltage V . By linearly fitting $\Delta\phi-V$ dependence, the EO coefficient γ_{33} of the waveguide was calculated to be around $9.0 \pm 0.4 \text{ pm/V}$, which is comparable to the results of $\sim 10 \text{ pm/V}$ at 1300 nm for DR1 chromophore.¹³

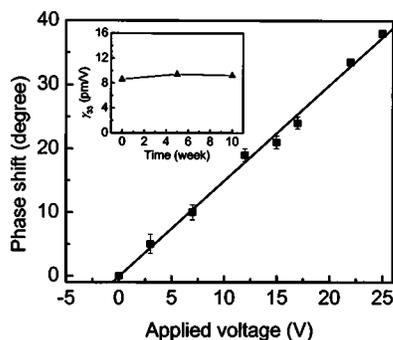


FIG. 4. Dependence of phase shift on applied voltage. The solid line is the linear fitting of the measurement. The inset shows the temporal stability of γ_{33} and the line is guide for the eyes.

The EO performance of the sol-gel waveguide also has high temporal ability. As shown in the inset in Fig. 4, in the measurement period of over ten weeks at room temperature and ambient humidity, there is no degradation observed. This is attributed to the high temporal stability of the sol-gel caused by rigid inorganic and organic networks in the material system.¹⁷

As previously demonstrated,³⁻⁵ the photobleaching of azo-type chromophores happens in a wide spectral range from UV to visible. During the process, photoisomerization and photodecomposition are induced, resulting in reduced refractive index in the exposed area. In side-chain DR1-doped polymers irradiated with $\lambda \sim 365$ nm, infrared spectroscopic and mass spectrometric measurements have indicated the photodecomposition of DR1,⁵ which means the breakdown of $-\text{N}=\text{N}-$ bonds and $-\text{NO}_2$ groups, causing the complete degradation of the nonlinear optical activity. The EO measurement shows that photodecomposition did not happen in the present active sol-gel film irradiated with 405 nm laser even at such a high power density of about 2×10^3 W/cm². We believe the photodecomposition of the side-chain DR1 in sol-gel occurs at $\lambda < 400$ nm. As a result, direct patterning of EO devices from UV sensitive chromophores-doped materials is practical by using longer-

wavelength laser sources and selecting proper photoinitiators in the corresponding spectral band.

In summary, we demonstrated the feasibility of direct laser writing in fabricating EO waveguides on photosensitive films doped with nonlinear chromophores that have significant absorption and sensitivity or degradability in UV spectral range. The waveguide written on side-chain DR1-doped sol-gel film performs well with high optical confinement. A moderate EO coefficient was obtained for the film containing 10 mol % side-chain DR1. The blue laser at 405 nm was demonstrated to be compatible with the azo-type chromophores. Moreover, by adopting different lasers and photoinitiators, this method can find applications in writing active integrated devices in photosensitive materials containing chromophores that have much higher optical nonlinearity but may degrade upon UV light irradiation.

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