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Organic-Inorganic Composite SiO_2/Al_2O_3 Films and Their Fine-Patterning by Sol-gel Process

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Organic-inorganic composite SiO_2/Al_2O_3 films were fabricated by sol-gel process from precursors of Aluminum sec-Butoxide($Al(O\text{-}sec\text{-}Bu)_3$), methacryloxypropyl trimethoxysilane (MAPTMS) and 1-Phenyl,1-3-butanedione(BzAcH). The films exhibited the photosensitivity to UV-light at around 325nm, because BzAcH and $Al(O\text{-}sec\text{-}Bu)_3$ were reacted to form chelae rings. The thicker films were obtained by introducing the MAPTMS. Such thick films were successfully patterned finely by irradiation with UV-light. Also, grating is prepared with a line-space of around 50μm and a thickness of 4.6μm.

Key words: Sol-gel, SiO_2/Al_2O_3 thick films, Organic-inorganic composite, Chemical modification, Fine-patterning

1. INTRODUCTION

The SiO_2 and Al_2O_3 films both have the excellent optical performance such as high transparence and low loss, furthermore the SiO_2/Al_2O_3 composite films can attain the different refractive index in the rang of 1.43~1.68 by adjusting the composite proportion.[1,2] Hence it is able to be applied to the integrated optic devices including multimode interference power splitters and wavelength division multiplexer.[3] The fabrication of these devices requires the waveguide film not only with the excellent optical performance but with the film thickness of 3~10μm as well.

Presently, the numbers of the fabrication techniques can be applied to the film such as thermal oxidation and sputtering.[4,5] However, these methods can not afford the required film-thickness. Some unique advantages over these techniques, for instance the low cost, the simple equipment and easily adjusting refractive index, are given by sol-gel technology, but the film thickness is still a difficult problem. The maximum attainable thickness of inorganic film is usually 0.1-0.3μm by sol-gel method,[6] but the channel waveguide compatible with single mode fibre requires the thickness of usually over 1μm.[7] To increase the film thickness, the iterative coating is required, which is costly and time consuming, but the required film thickness can't be achieved.[8]

In our present work, by sol-gel method, the organic groups are introduced to the inorganic backbone, whereby reducing the brittleness of the gel network and preventing from cracking, therefore allowing the thicker film. Further, the photosensitive chelate rings are formed in the gel film by the chemical modification, the fine patterns of the thick SiO_2/Al_2O_3 films can be simply achieved by the UV light imprinting,

2. EXPERIMENT

2.1 Sol - gel film preparation

The fabrication process was based on the hydrolysis and polycondensation of the precursors methacryloxypropyl trimethoxysilane(MAPTMS) and aluminum sec-Butoxide (($Al(O\text{-}sec\text{-}Bu)_3$), isopropanol (i-PrOH) was used as solvent and 1-Phenyl, 1-3-butanedione (BzAcH) as chemical modifier, the above chemicals were mixed in a molar ratio of 1:1:5:0.5, followed by adding the hydrochloric acid catalyst (HCl) drop by drop, the molar ratio of MAPTMS:HCl up to 1:0.05. then the solution was stirred for 8hrs and was aged for 24hrs, so that the solution was prepared.

Films were fabricated by a one-step dip-coating on quartz glass for optical absorption or silicon substrate for FTIR spectrum and fine patterning, respectively. The above processes were all finished in glove box with humidity<30%.

2.2 Fine patterning

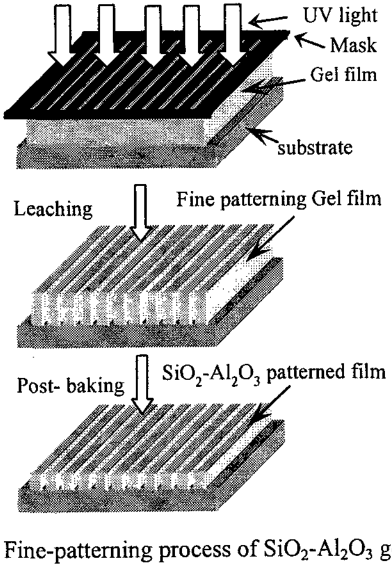


Fig.1 Fine-patterning process of SiO_2-Al_2O_3 gel film

Gel films on Si substrate were baked at 80℃ for 15min to stabilize them prior to UV exposure. An appropriate mask was placed in contact with the gel films and a He-Cd laser (λ=325nm, intensity=10 mw/cm^2) was used to define the fine patterns by photolysis through the opening in the mask. UV-exposure time was about 90min, then the irradiated part became insoluble in some organic solvent (ethanol), thereby the films were immerged into ethanol to dissolve and wash out the unexposured parts, a post-baking following at 200℃ for 2 hrs, and then the fine pattern was obtained. The fine-patterning procedure is schematically illustrated in fig.1.

3. RESULTS AND DISCUSSION

3.1 Photosensitivity of SiO2/Al2O3/BzAc gel films

BzAcH shows that the absorption bands at around 250nm and 310nm are characterized by the phenyl group and the π-π* transition in β-diketonate ligands, respectively.[9] When BzAcH reacts with aluminum sec-Butoxide to form the chelate rings with photosensitivity, the absorption band at around 310nm can shift by 15nm toward longer wavelength side to 325nm.[9,10] In this work, fig.2 shows the absorption spectra in the UV range of the obtained SiO_2/ Al_2O_3/ BzAc gel films, which is similar to that derived from Al_2O_3/BzAc in references.[9,10] It proves that MAPTMS has not affected the photosensitivity of the chelate rings. The SiO_2/Al_2O_3/BzAc gel films (about 0.3μm in thickness) were irradiated using the laser beam (intensity=10mw/cm^2) at 325nm corresponding to the absorption band. With an increase in irradiation time, the intensity of the absorption band decreases , as shown in fig.2. The band at 325nm almost disappears after 6min irradiation, indicating that the photosensitive chelate rings have been decomposed and that the gel films show photosensitivity. Fine patterning of the gel films can be simply made using such character.

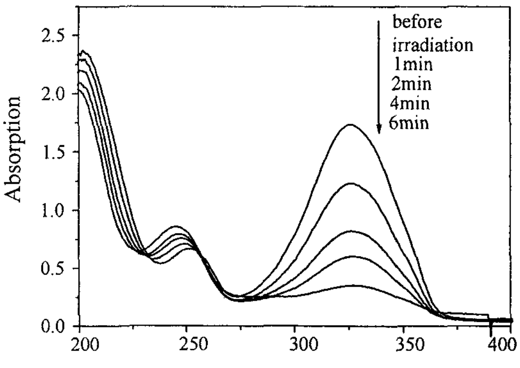


Fig 2 UV-Vis absorption spectra of Al_2O_3/SiO_2 gel

The photosensitivity of the gel film is also able to be confirmed by the change in the FT-IR spectra with UV-irradiation. Fig.3 shows the FT-IR spectras of MAPTMS and SiO_2/Al_2O_3/BzAc films, including the gel film(about 1μm in thickness) , the film irradiated for about 30min and the film post-baked at 200℃ for about 2hrs. For the gel film, a number of sharp absorption peaks are observable in a range of 1400cm^{-1} to 1715cm^{-1}. The peaks at 1600cm^{-1} and 1530cm^{-1} are ascribable, respectively to C···O and C···C bonds of the photosensitive chelate ring and the peaks at 1562cm^{-1} and 1486cm^{-1} to the phenyl group. The peaks 1458cm^{-1} is due to C-H bending and C···O stretching. By UV irradiation, the absorption peaks ranging from 1600cm^{-1} to 1400cm^{-1}, characteristic of the chelate ring, decrease. The above is consistent with the previously reported references.[9,11] compared to these references, a new sharp peak appears at 1715cm^{-1} matching with the FT-IR spectra of MAPTMS (Fig.3.A). The peaks ranging from 1600cm^{-1} to 1400cm^{-1} decrease with UV irradiation, but the peak at 1715cm^{-1} has no change. the peak at 1715cm^{-1} corresponds to the free C=O bond in MAPTMS.[12] The peaks at around 1100 cm^{-1} and 900cm^{-1}~700cm^{-1} are assigned to Si-O and Al-O-Si bonds,[11] these absorption bands become broad by UV irradiation and post-baking. Via which, a large number of organic substances have been decomposed, and the corresponding absorption peaks have almost disappeared, while the peaks at 1600cm^{-1}, 1530cm^{-1} and 1458cm^{-1} still remain partly, indicating that a small quantity of organics has not been eliminated and the SiO_2/Al_2O_3/ BzAc films are organic-inorganic composite after post-baking at 200℃.

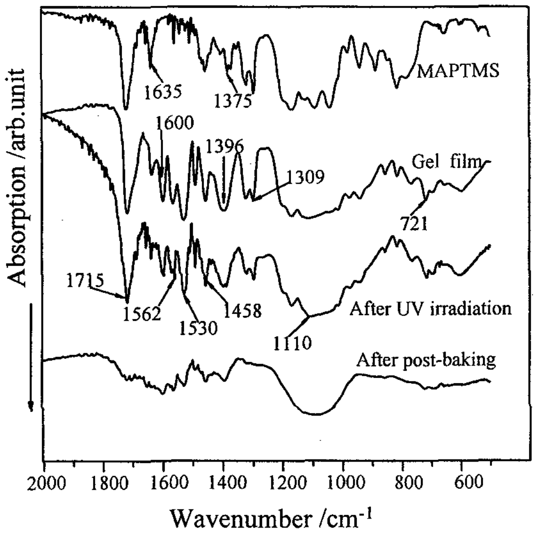
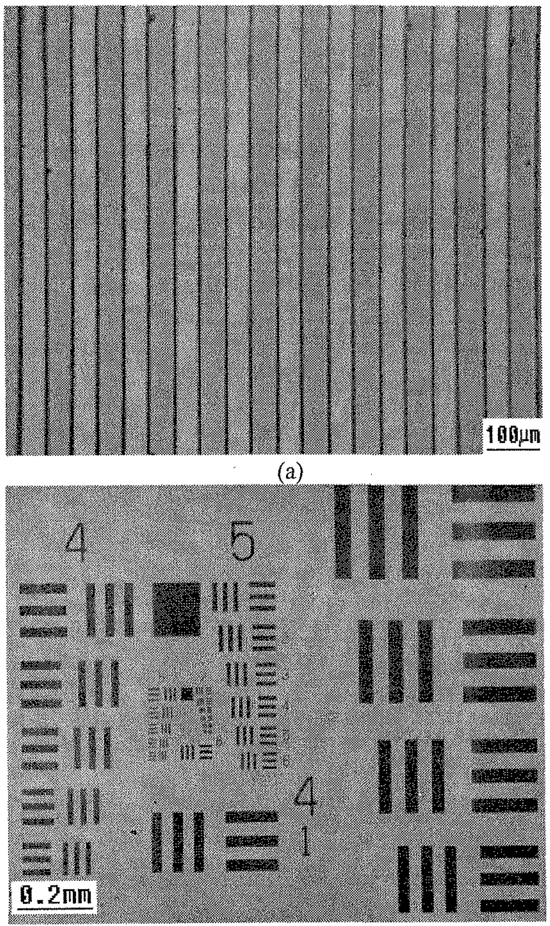


Fig 3 FTIR spectra of Al2O3/SiO2 film

3.2 Fine patterns of SiO_2/Al_2O_3 films

Due to the photosensitivity of the gel films, the fine patterns are available with the procedure shown in Fig.1. Fig.4(a,b) shows the optical microscopic photograph for the fine patterns of SiO_2/Al_2O_3 films. As shown in fig.4, the unirradiated parts have completely dissolved, while the irradiated parts have perfectly remained as a result of the declining of solubility in ethanol, because the photosensitive chelate rings have been decompose with UV irradiation.

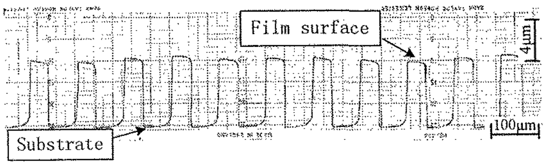
The thickness of the fine pattern of SiO_2/Al_2O_3 film in Fig.4(a) was measured by surface profilometry (Surface Measuring Instrument) , the line profile after UV irradiation and dissolving the nonirradiated regions are shown in Fig.5(a), and that of the post-baked is shown in Fig.5(b). The former thickness is around 6μm, but the latter is only about 4.6μm. The elimination of the organism is the main reason of the film thickness decreasing after post-baking. Compared to the inorganic film in reference[11], the film thickness is more effectively increased, mainly because that MAPTMS introducing the organic groups to the inorganic backbone decreases the brittleness of the inorganic network and the tensile stress, so that the thicker film is available.[13,14,15]



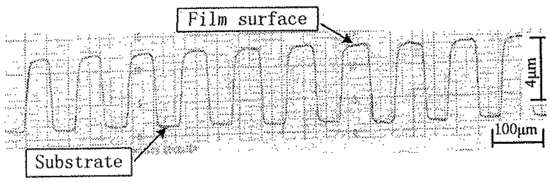
(a)

(b)

Fig.4 Optical microscopic photograph for the patterned SiO_2/Al_2O_3 film (Bright and bark areas represent silicon substrate and SiO_2/Al_2O_3 film, respectively)



(a) After UV irradiation and dissolving the unexposed parts



(b) after post-baking

Fig.5 Line profile of SiO_2/Al_2O_3 films

4. CONCLUSIONS

In our present work, by chemical modification with BzAcH and introducing of MAPTMS, the thick film was achieved through a single dip-coating step, photo-sensitive to UV light at around 325nm. Due to the photosensitivity, the fine patterns of the thick SiO_2/Al_2O_3 films were simply achieved by the UV light imprinting. The grating about 4.6μm in thickness was obtained by this technology.

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