

## Sol-gel Preparation and Optical Properties of TiO<sub>2</sub>/Organically Modified Silane Hybrid Material Containing DR13

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### Abstract

Disperse red 13 (DR13) azoaromatic chromophores were incorporated into sol-gel derived TiO<sub>2</sub>/organically modified silane matrix to achieve a hybrid material doped with dye molecules. Nonlinear optical properties of the as-prepared hybrid material were investigated by an optical Kerr shutter technique with an 800-nm femtosecond laser. It is obtained that the response time of the bulk sample doped with 0.1% DR13 molecules is less than 208 fs and the third-order nonlinear refractive index is estimated at about  $1.141 \times 10^{-15} \text{ cm}^2/\text{W}$ . It is also found that the sample of material with higher DR13 content could be with higher third-order nonlinear susceptibility. The linear refractive index and the thickness of the hybrid films derived by a spin-coating process were also studied by a prism coupling technique. It is found that with an increasing of the baking temperature, both the refractive index and the thickness of the hybrid films decrease. Absorption spectra, microstructural and morphological properties of the hybrid films were also characterized by UV-Vis absorption spectroscopy, thermal gravimetric analysis, Fourier-transform infrared spectroscopy and atomic force microscopy. Results indicate that the as-prepared hybrid material is expected to be potential in ultrafast photonic applications.

**Keywords:** Disperse red 13; Hybrid material; Sol-gel process; Non-linear optics; Kerr effect

### Introduction

Over the past few decades, photochromic materials have been proven to be potential in technological applications, including optical lenses and smart windows, holographic recording media, high-density memory devices, and nonlinear optics [1-3]. Photochromic molecules have been incorporated into various different matrices, including polymers, inorganic materials, and organic-inorganic composites. Especially, photochromic organic-inorganic hybrid materials have been extensively investigated owing to its excellent advantages of combining organic with inorganic materials to obtain upstanding properties, which are appropriate for optical applications. Actually, it has been also proven that the simultaneous existence of organic and inorganic compounds not only can preserve or even improve the features of the components, but also can confer new properties upon the material systems [4], for example, those matrixes with porous structure can provide enough space for doping photochromic molecules. Organically modified silane (ormosils) is one of such excellent organic-inorganic materials as a matrix, for it not only has all the advantages discussed above, but also be with controllable refractive index by simply adjusting the proportion of organic to inorganic component. All such properties make it have a great potential in modern optical transmission and devices [5-7].

Azobenzene is an important kind of photochromic compound, for which can generate various kinds of photoreponsive properties, including nonlinearity. Materials with nonlinear properties can be used in passive-mode optical limiting and potential switching applications. Here, two main parameters, which include a large third-order optical nonlinearity and a fast response time, are important for the realization of such optical switching. Several methods have been raised for investigating nonlinearity, for example, femtosecond optical Kerr shutter (OKS) technique is one of the most convenient nonlinear optical (NLO) measurements due to its precision, easy operating, and sensitivity [8] and can be used to investigate optical nonlinearity and ultrafast response simultaneously. Generally, the femtosecond OKS

technique is used to study the liquid and gas materials [9,10], inorganic glasses [11,12], organic or polymeric materials [13], semiconductors [14], etc. In our present work, the femtosecond OKS technique is employed to measure the nonlinearity and ultrafast response of the organic-inorganic hybrid material doped with disperse red 13 (DR13). In order to obtain the third-order nonlinear refractive index of the as-prepared samples, quartz glass was used as reference in the measurement and calculation.

Herein, we reported on the sol-gel preparation of the TiO<sub>2</sub>/γ-glycidioxypropyltrimethoxysilane (TiO<sub>2</sub>/GLYMO) organic-inorganic hybrid material doped with a kind of azobenzenes-DR13 (4'-[ethylamino]-2-chloro-4-nitroazobenzene). Femtosecond OKS technique was employed to study nonlinear property and ultrafast response. Prism coupling technique and UV-Vis absorption spectroscopy were employed to investigate the optical planar waveguide and absorption properties of the hybrid films. Thermal gravimetric analysis, Fourier-transform infrared spectroscopy and atomic force microscopy were used to study the microstructural properties of the hybrid materials.

### Experimental

DR13 azodye-doped organic-inorganic hybrid material sols were individually prepared by two solutions. For solution I, γ-glycidioxypropyltrimethoxysilane (GLYMO), ethanol and de-ionized water were

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mixed at a molar ratio of 1:4:4. After being stirred for about 30 min, 0.01 mole hydrochloric acid (HCl, 37 wt. % in water), which is used to catalyze the hydrolysis, was added into the solution. The solution was then further stirred for about 60 min in air at room temperature again. For solution II, tetrabutyl titanate (Ti (OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, used as TiO<sub>2</sub> source) was added to acetyl acetone at a molar ratio of 1:4 and the solution was stirred and until reached the situation of homogenization. Then, the two solutions were mixed, which has a molar ratio of 80GLYMO-20TiO<sub>2</sub>, and the final mixture was stirred for 4 hours at room temperature. Followed that commercial DR13 azodye compound was added to the TiO<sub>2</sub>/GLYMO sol-gel hybrid matrix solution with different weight ratios of the hybrid solution, which includes 2%, 1%, 0.02% and none. The final mixture solutions added with DR13 azodye were stirred for about one to two days at room temperature again. The bulk samples doped with different DR13 contents were obtained by drying them in air at room temperature for about two weeks and the bulk samples should be polished before being used for measurement of the optical nonlinearity. While for the fabrication of the hybrid film samples, silicon and silica-on-silicon glass were used as substrates and they were ultrasonically cleaned in acetone and ethanol, respectively, rinsed with the de-ionized water and dried by gas. The sols doped with 2% and 1% DR13 molecules were used for the deposition of the hybrid films. Following is the common practice for spin-coating; a 0.22-micron-pore filter was attached to a syringe to remove foreign particles before the resultant solution was spin-coated onto a substrate. One layer of the sol-gel film was spun onto the substrate at 3500 rpm for 35 seconds and then the film-coated samples were directly baked at different temperatures for 10 min in air.

In the measurement of nonlinearity and ultrafast response of the samples, as Figure 1 shows that a Ti: sapphire laser, emitting 30-fs and 800 nm laser pulses with a repetition rate of 1 kHz, was employed and split into two beams, which one of the output of the laser is used as the probe beam and the other is the pump beam. The power of the probe beam is 10.6 mW, and the pump power is varied at about 41.5 mW. The distance between the sample and the lens is 22.5 cm. The OKE signals were detected by photomultiplier tube. The data were displayed and recorded by a computer that was also used to control the time delay between the pump and probe pulses by a stepping motor. The solution of the time-solved OKS signal was 10.4 fs. In addition, the refractive index, the thickness, and the propagation mode of the planar waveguide films were measured by an m-line apparatus (Metricon 2010) based on the prism coupling technique for both transverse electric (TE) and transverse magnetic (TM) polarization. The absorbance spectra of the hybrid films deposited on glasses were measured by UV-Vis spectroscopy in the wavelength range from 200 to 800 nm. And the microstructural properties of the hybrid films were also characterized

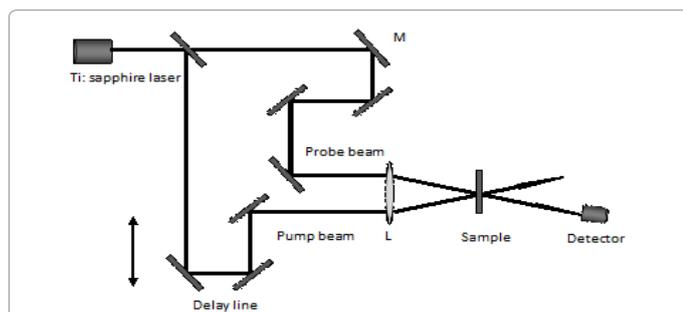


Figure 1: Experimental setup for OKS using femtosecond laser at 800 nm. BS, beam splitter; L, lens; and M, mirror.

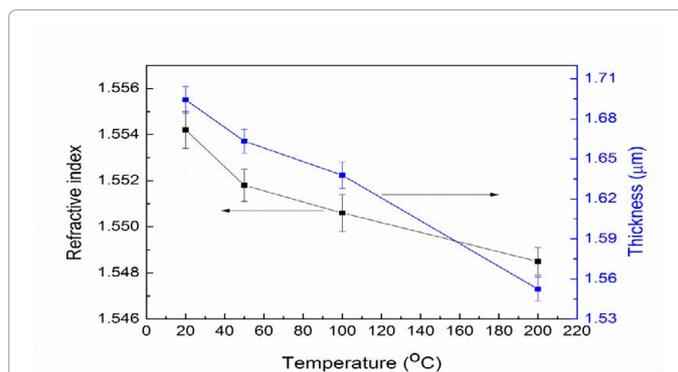


Figure 2: Dependence of the thickness and the refractive index of the hybrid films on the baking temperature.

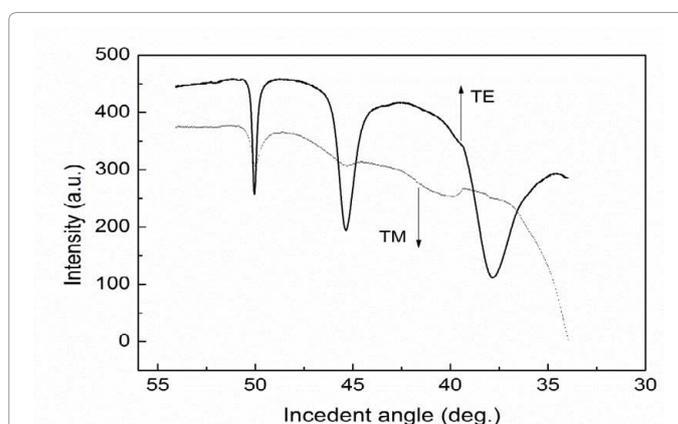


Figure 3: Modes of the hybrid planar waveguide film doped with DR13 of 0.5% and baked at 100°C at the wavelength of 1312 nm for both of TE and TM modes.

by atomic force microscopy (AFM), thermal gravimetric analysis (TGA), and Fourier-transform infrared spectroscopy (FTIR).

## Results and Discussion

Figure 2 shows the dependence of the thickness and the refractive index of the hybrid films on the baking temperature. The hybrid films were spun on the silicon substrates and baked at room temperature, 50, 100, and 200°C for 10 min, respectively. It can be observed that with an increasing of baking temperature, both of the thickness and the refractive index present to decrease. Such phenomenon should be related to the combination of organic and inorganic system. As the baking temperature rises, the thermal decomposition of the organic solvents leads to a decrease of the film thickness. In our previous work, the refractive index of the hybrid films based on TiO<sub>2</sub>/organically modified silane matrix without dopant shows an increase as the baking temperature rises [15]. Here, we reported on the hybrid films added with DR13 molecules, which is a member of azobenzenes. Therefore, the decrease of the refractive index is probably related to a possible structural change of the hybrid film due to a thermal initiated orientation of the DR13 small molecules. As one knows, azobenzenes have a trans-cis photo isomerization process, which can be induced not only by the light but also by the thermal treatment. Such photo isomerization may cause the structural change of the hybrid film during the heat treatment, thus resulting in the refractive index of the hybrid film decreases.

Figure 3 shows the propagation modes of the hybrid film deposited on the substrate of silica-on-silicon with the size of 1 cm×5 cm, doped with 1% DR13 and baked at the temperature of 100°C based on the prism coupling technique at the wavelength of 1312 nm. Considering only when the refractive index of the hybrid film is higher than that of the substrate, the hybrid film can be used for optical propagation. Therefore, silica-on silicon is selected as substrate since its refractive index is 1.46, which is lower than that of the hybrid film. It can be observed from Figure 3 that the hybrid film obtained under present conditions only can support two TE modes and one TM mode at the wavelength of 1312 nm. For the TE mode, the two modes can be used to determine the effective refractive index and the thickness of the hybrid film, and the obtained values are 1.5184 and 1.5491 nm, respectively. While for the TM mode, the other dips observed in the intensity spectrum are attributed to the substrate modes due to their index smaller than the value of the substrate refractive index. The propagation loss at the wavelength of 1312 nm was also measured for both TE and TM modes, respectively. Optical propagation loss value of the sample is 0.78dB/cm for TE mode, and 0.8 dB/cm for TM mode, respectively. Such value of the propagation loss is in acceptable range for optical application. Typically, the main reasons for the propagation loss have two aspects, one is the deviations from a perfect plane geometry at the waveguide-cladding boundaries and the other is the no uniform hydrolysis and condensation of the silicon alkoxides and titanium alkoxides.

Figure 4 shows the UV-visible absorption spectrum of the bulk sample doped with 0.1% DR13 molecules. The absorption spectrum of the sample indicates that the absorption band of the material locates around 514 nm and is almost no absorption after the wavelength of 650 nm. Figure 5 shows the time-resolved OKS signals of the reference sample quartz glass and the as-prepared hybrid bulk samples doped with different content of DR13 molecules of 0.1%, 0.05% and 0.01%, for the reason of choosing such lower content than that using above is in order to reduce scattering in nonlinear measurement. In addition, film samples are not fit to use in OKS measurement for the reason that the substrate of glass may influence the authenticity of the results. Samples were measured by using an OKS setup with the pump and probe beams of equal wavelength. The full-width at half-maximum of time-resolved optical Kerr signal for the hybrid bulk samples and the quartz glass are estimated about 208 fs, 146 fs, 135fs, and 115 fs, respectively. It can be observed from Figure 5 that the four curves are symmetric correlation

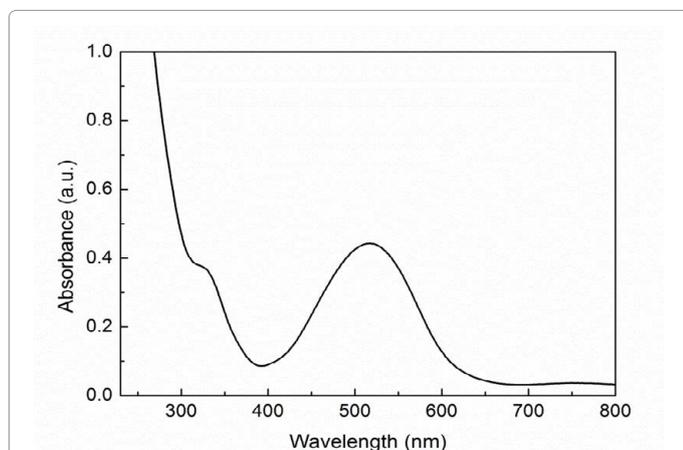


Figure 4: UV-Vis absorption spectrum of the hybrid films doped with DR13 of 2% and baked at the temperature of 100°C.

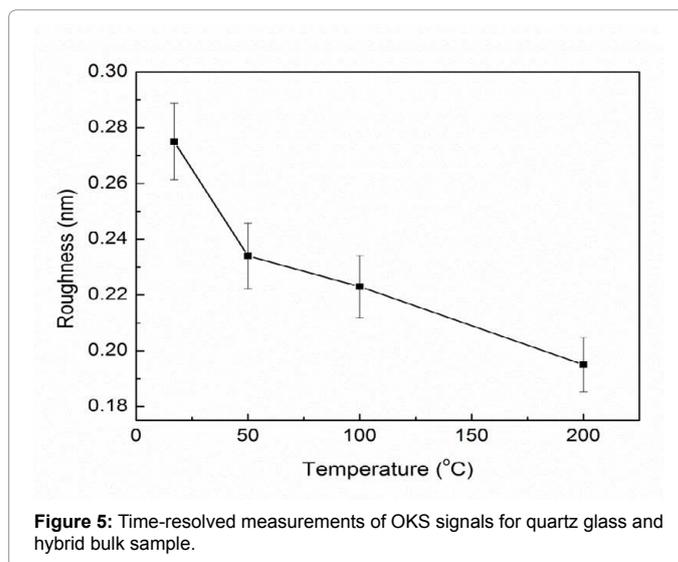


Figure 5: Time-resolved measurements of OKS signals for quartz glass and hybrid bulk sample.

lines and have no obvious slow component in the decay process. Therefore, the response curves of the hybrid bulk samples doped with different content of DR13 molecules was determined by the pulse-width and the recovery time were faster than the value of the full-width at half-maximum of time-resolved optical Kerr signal. That means, for example, the recovery time of the sample doped with 0.1% content of DR13 was faster than 208 fs. The equation of calculating for the third-order nonlinear susceptibility  $\chi^{(3)}$  of the samples is as following [16]:

$$\chi_S^{(3)} = \chi_R^{(3)} (I_S / I_R)^{1/2} (n_S / n_R)^2$$

The subscripts of the S and R indicate for the measured sample and the reference sample, which are the hybrid material and the quartz glass at present work, respectively. I am intensity of the OKS signal while the polarization angle between the pump beam and the probe beam is fixed and the delay time between the two pulses is 0, n is the linear refractive-index of the sample. According to the above equation, since it is can be easily observed from Figure 5, that with increasing of the DR13 content, the signal intensity is increases, the value of  $\chi^{(3)}$  of the samples are related to the content of DR13, for higher content sample can obtain higher  $\chi^{(3)}$ . As reported in Ref [17], the third-order nonlinear refractive index of quartz glass is  $2.7 \times 10^{-16} \text{ cm}^2/\text{W}$ . According to the equation above, the third-order nonlinear refractive of the hybrid bulk sample doped with different content of DR13 molecule are estimated and their value are about  $1.141 \times 10^{-15} \text{ cm}^2/\text{W}$ ,  $8.752 \times 10^{-16} \text{ cm}^2/\text{W}$ , and  $4.215 \times 10^{-16} \text{ cm}^2/\text{W}$ , respectively. To discuss the origin of the optical Kerr nonlinearity in the DR13 doped material, there are three principal mechanisms: electronic nonlinearities, trans-cis photo isomerization, and thermal effects. In our case, the third-order nonlinearity was generated by an ultrafast laser pulsed at 800nm, which is between fundamental absorption and two-photon absorption resonance of DR13 molecules. In this range of wavelength, the main mechanism of optical nonlinearity is from the electronic nonlinearity, which arises from either population redistribution or distortion of electronic clouds. So that it can be observed that the curves are almost symmetric correlation lines and have no obvious slow component in the decay process. According to above result, the origin of the nonlinear response of the organic-inorganic hybrid material doped with DR13 molecules should be attributed to electronic process and the characteristic time of the samples are much faster than 208 fs, 146 fs, and 135 fs, respectively. Such a rapid response time and a relative high nonlinear refractive

index indicate that the as-prepared materials are a promising candidate for ultrafast optical applications.

The value of the root mean square (RMS) surface roughness of the hybrid films deposited on the silica-on-silicon substrate was also examined over a 2 μm×2 μm area for several times and then got an average value by an atomic force microscopy (AFM). Figure 6 shows the dependence of the RMS of the hybrid films doped with DR13 of 1% on the baking temperature. It is obvious that the surface roughness of the hybrid film obtained at room temperature is relatively big. With increasing the baking temperature, the RMS roughness of the hybrid films reduces gradually and the hybrid films become smoother due to the volatilization and the thermal decomposition of the organic solvents. Therefore, it recommends that in order to obtain smoother surface, the heat treatment should be done at an appropriate high temperature. To get better understanding above results, TGA was further employed to examine the thermal properties of the hybrid material during heating process.

Figure 7 shows the TGA curves of the gel obtained by drying the solution at room temperature for about two weeks. The sample of the gel was crushed into powers for about 22 mg, and then put them into Al<sub>2</sub>O<sub>3</sub> crucible for TGA measurement. During the analysis, the heating rate was controlled at 20 K/min in a flowing nitrogen gas, while the recorded temperature range is from room temperature to 800°C. Figure 7 shows the TGA curves of the samples. Curve (a) is the sample

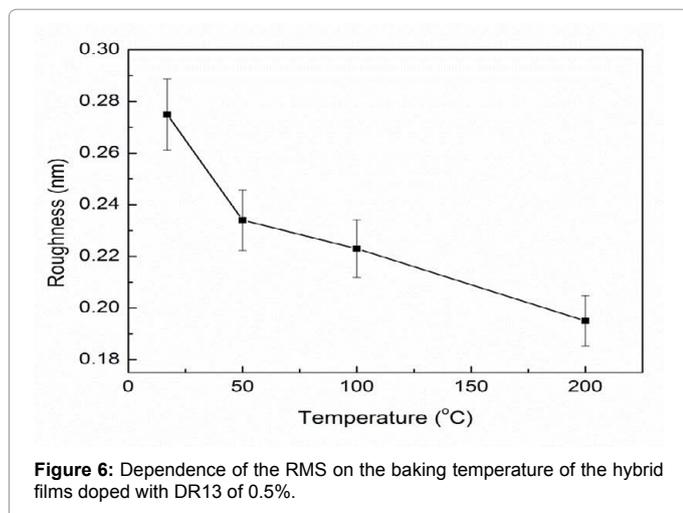


Figure 6: Dependence of the RMS on the baking temperature of the hybrid films doped with DR13 of 0.5%.

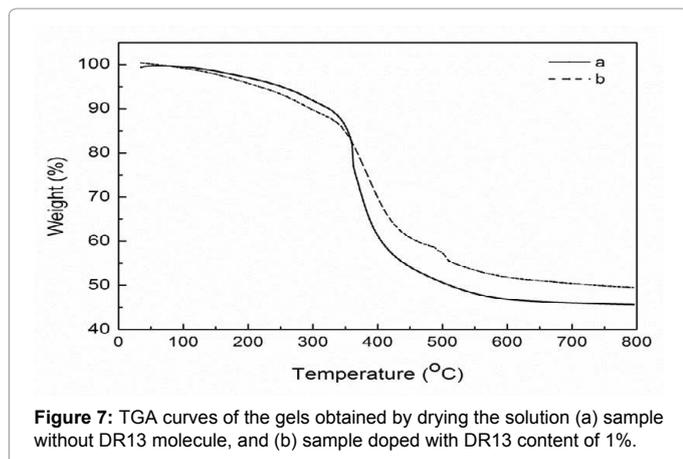


Figure 7: TGA curves of the gels obtained by drying the solution (a) sample without DR13 molecule, and (b) sample doped with DR13 content of 1%.

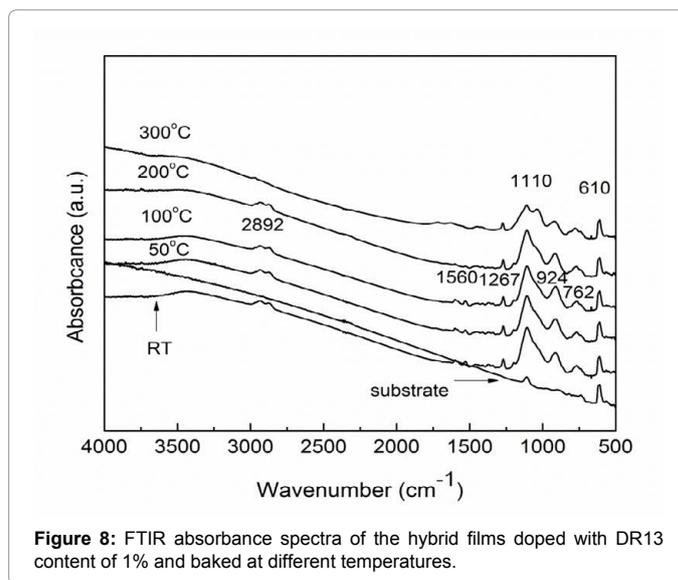


Figure 8: FTIR absorbance spectra of the hybrid films doped with DR13 content of 1% and baked at different temperatures.

un-doped with DR13 molecule and curve (b) is the sample doped with DR13 content of 1%. It is noted that there exists some clear differences between the two curves. Firstly, a peak between 450°C and 510°C can be observed from the sample doped with DR13 molecule, which is not observed from another. Secondly, both TGA curves show a stage which weight loss is obviously and quickly decreased, and the weight loss range of both samples is between 85% and 55%, but the change range of the temperature is obviously different; that is, the slope for this range of the weight loss is quite different. It can be observed that in the curve (a), the change range of the temperature is from 350°C to 520°C, while the other one is from 352°C to 441°C. Clearly, these differences between the two curves as mentioned above should be related to the DR13 molecules. It should be pointed out that the mechanism of the combination of the DR13 molecules and the ormosil matrix is not a simple dissolution process, but a chemical bonding. So that, such bonding could affect the combustion of the sample and thus leads to a difference in TGA measurement as a whole. It can be seen from the curve (b) in Figure 7 that below 350°C, there is no obvious weight loss, indicating that our hybrid films obtained at present condition has a good thermal stability. Actually, above results and discussion are helpful to get better understanding for the results of the refractive index, the film thickness, and the RMS. For instance, the baking temperature of the hybrid film is below 200°C, the film thickness and the refractive index are not very sensitive to the increasing of the baking temperature. Although, there exists a little fluctuation with the increasing of the baking temperature, the fluctuation change is not so obvious. However, while the baking temperature increases, the RMS roughness of the hybrid films reduces obviously due to the volatilization and thermal decomposition of the organic solvents or the combustion of the organic compounds, thus the hybrid film becomes smooth relatively.

In order to further identify the bond properties of the hybrid film, Figure 8 shows the FTIR absorption spectra of the hybrid films deposited on silicon wafers and baked at different temperatures from room temperature to 300°C in the range of 400-4000 cm<sup>-1</sup>. The main band around 1000-1200 cm<sup>-1</sup> (the main peak at 1110 cm<sup>-1</sup>) is attributed to the Si-O-R stretching vibration of the ethoxy groups directly bonded to silicon [18], and the band in intensity reduces with increasing the baking temperature gradually. Actually, a similar behavior can be also seen from the band centered at 2892 cm<sup>-1</sup> which corresponds to -CH<sub>2</sub>-

symmetric stretching and another broad band around 3100 cm<sup>-1</sup>- 3500 cm<sup>-1</sup> which is attributed to OH stretching vibration. With further increasing the baking temperature, these bands in intensity decrease gradually and even vanish at a higher baking temperature, which is probably due to a combustion reaction in the densification process [19]. The peak at 1267 cm<sup>-1</sup> is due to a symmetric deformation of the Si-CH<sub>3</sub> bond [20], the peak at 924 cm<sup>-1</sup> is attributed to the stretching vibration of Si-O-OH or SiO- groups superimposed onto that by Si-O-Ti stretching [21], and the band centered at 762 cm<sup>-1</sup> is attributed to the symmetric stretching motions of the oxygen atoms along the bisector of the Si-O-Si bridging angle. Obviously, these peaks are not sensitive to the change of the baking temperature. As compared to our previous work [22], one additional peak at 1560 cm<sup>-1</sup> can be clearly observed, which should be attributed to the DR13 molecule. It is noted that as the baking temperature increases, this additional peak in intensity becomes weak and even vanishes when the baking temperature is increased up to 300°C. Therefore, it can be concluded that in order to get the hybrid films with the properties of the nonlinearity and photo isomerization, the baking temperature should be controlled below 300°C to obtain the hybrid films doped with DR13 molecules. It should be pointed out that as compared to the FTIR absorption spectrum of silicon substrate, the peak at 610 cm<sup>-1</sup> is from the silicon substrate and not related to the hybrid film.

## Conclusions

In summary, a TiO<sub>2</sub>/GLYMO organic-inorganic hybrid material doped with DR13 molecules has been successfully prepared by the sol-gel technique at a low temperature process for ultrafast photonic applications. The ultrafast nonlinear optical (NLO) response of the as-prepared hybrid material has been investigated by the femtosecond OKS setup, and the results show that the as-prepared hybrid material doped with 0.1% content of DR13 molecules has an ultrafast response time less than 208 fs. With the increasing of DR13 content, the value of  $\chi^{(3)}$  increases, and also the response time. By a prism coupling technique, results indicate that the as-prepared hybrid films can guide optical signal on both TE and TM modes at the wavelength of 1312 nm meanwhile with a low propagation loss. It has been also demonstrated that the DR13 molecules has been successfully incorporated into silicon oxide matrices by the sol-gel technique by investigating the chemical bonding. All the results indicate that the easy to be prepared materials, with tunable optical properties by controlling preparation details and content of dopant, are expected to be potential candidate in ultrafast optical applications.

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