

Synthesis of Hybrid Polymer and Its Application as Distributed Feedback Laser (Sintesis Polimer Hibrid dan Aplikasinya Sebagai Laser Suap Balik Tertabur)

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ABSTRACT

The hybrid inorganic-organic polymer was synthesized by sol-gel method from TMSPMA. Organic dye laser of DCM was added into hybrid polymer host matrices by means of solution method at room temperature. The distributed feedback (DFB) laser was fabricated from hybrid polymer-DCM film using Lloyd Mirror interference technique. The surface profile of device was observed using AFM. From the AFM image, we obtained that the grating period was about 385 nm and the depth of corrugation was about 60 nm. The characteristics of DFB laser was investigated by optical pumping using SHG Nd-YAG ($\lambda=532$ nm). The laser emission has been demonstrated at 582 nm with the spectral width (FWHM) less than 2 nm at pumping power of 14.00 mJ/pulse cm^2 . The experimental results have been confirmed by the theoretical model using coupled mode theory. The confirmation of experimental works by the theoretical model has a good result.

Keywords: Coupled mode theory; DFB laser; hybrid polymer; sol-gel method

ABSTRAK

Polimer hibrid telah disintesis dengan kaedah sol-gel daripada TMSPMA. Laser dai organik DCM telah ditambahkan ke dalam matriks polimer hibrid dengan menggunakan kaedah larutan pada suhu bilik. Laser Suap Balik Tertabur (DFB) telah difabrikasi daripada filem polimer hibrid-DCM menggunakan teknik pembelauan Lloyd Mirror. Profil pada permukaan daripada peranti laser diamati menggunakan AFM. Daripada imej AFM, kita boleh mengukur kala parutan ~385 nm dan kedalaman kerut ~60 nm. Ciri laser DFB telah dikaji dengan pam optik menggunakan SHG Nd-YAG ($\lambda = 532$ nm). Pemancaran laser telah ditunjukkan pada 582 nm dengan lebar spektrum (FWHM) kurang daripada 2 nm untuk daya pam 1400 mJ/denjut cm^2 . Hasil eksperimen telah disahkan oleh model teori menggunakan teori mod terganggu. Pengesahan hasil kerja eksperimen dengan model teori mempunyai hasil yang baik.

Kata kunci: Kaedah sol-gel; laser DFB; polimer hibrid; teori mod terganggu

INTRODUCTION

In the last decades, the miniaturization technologies of devices has attracted much attention in many fields, such as optics, electronics, materials sciences and biomedical engineering (Cheng et al. 2012; Vyawahare et al. 2010). Besides, there is also a market demand for a low processing cost for fabrication such devices. Both factors have encouraged many scientists to continue their research for new materials. Hybrid inorganic-organic polymers are good candidate for application in micro-size devices since the hybrid polymer can be fabricated as micro-planar devices with a simple fabrication method, such as spin-coating followed by Ultra Violet (UV) patterning (Darracq et al. 1998; Hidayat et al. 2010).

Polymers are widely used for optical devices, such as a host matrix for dye laser in lasing application (Hidayat et al. 2010). Yurista et al. (2001) have reported fabrication of DFB grating using photoresist with UV holographic method. The gain medium consists of disperse-red-one chromophore side chain polymethyl methacrylate (DR1-MMA) deposited on Si substrate. The lasing emission can be tuned in various wavelengths from gain medium layer up-covered with photoresist grating (Yurista et

al. 2001). Although offering advantage of simplicity in processing, but the polymer based optical system faced many problems due to its low thermal stability (Paquet & Kumacheva 2008). That has encouraged scientists to used hybrid inorganic-organic polymer instead of conventional organic polymer.

In recent years, there have been many reports on application of hybrid inorganic-organic polymer materials for optical devices (Hidayat et al. 2010), that is related to excellent optical properties and a high thermal stability of hybrid inorganic-organic polymer in comparison with conventional polymers. Moreover, hybrid polymers exhibit a good transparency in optical region, can be customized by adding some functional material and have several advantages such as easy in synthesizing and patterning process (Soppera et al. 2002).

In this paper, we synthesized hybrid inorganic-organic polymer of poly(3-(trimethoxysilyl) propyl methacrylate) (TMSPMA), modified the material using organic dye laser of 4-dicyanomethylene-2-methyl-6-p-dimethylamino-styryl-4H-pyran (DCM) and further using the material we fabricate 1D grating as laser resonator using Lloyd mirror interference technique. The DFB grating was characterized

by optical pumping using second harmonic generation (SHG) of Nd-YAG ($\lambda=532$ nm).

MATERIALS AND METHODS

Materials used in our experiment consist of TMSPMA , Aldrich), DCM (Aldrich), 2-Benzyl-2 dimethylamino-1-(4-morpholinophenyl)- butanone-1 (IRGACURE 369, Ciba), chloroform (p.a. Merck), ethanol (p.a. Merck), toluene (p.a. Merck), hydrochloride acid (p.a. Merck) and distilled water.

The precursor of hybrid inorganic-organic polymer was synthesis by sol-gel method based on the process described previously by Soppera et al. (2002) using different monomer. The synthesis procedure of hybrid polymer precursor was done as the following steps. First, monomer of TMSPMA was dissolved in ethanol while stirred for 1 h at room temperature. Then, distilled water was added gradually and followed by addition of HCl solution (0.1 M). The mixed solution was stirred while being heated and kept at 50°C until the gel was formed. The gel formed was referred as a hybrid polymer precursor. The final step was purification for removing remaining catalyst by extraction process using water-chloroform mixture. It formed biphasic mixture which remaining catalyst dissolved in water and gel dissolved in chloroform. After purification process, the gel dissolved in chloroform was separated from the mixture and then heated at 60°C to evaporate the chloroform.

In order to prepare the DCM doped DFB grating, the DCM (0.1% w/w) was incorporated into hybrid polymers precursor by solution method beforehand. Prior to photopolymerization, the photoinitiator of IRGACURE 369 (0.5% w/w) was added into the gel solution. For grating fabrication, the precursor was previously diluted by addition of chloroform. Then, thin film of precursor hybrid polymer was fabricated using spin coating method on the

glass substrate. The film was then pre-baked for 15 min at 60°C to evaporate the remaining solvent. The grating structure was formed by laser interference technique using Lloyd Mirror configuration as schematically shown in Figure 1. In this experiment, the third harmonic generation (THG) of Nd:YAG ($\lambda=355$ nm) was used as UV curing source. After the formation of grating, the sample then post-baked at 60°C for 1 h.

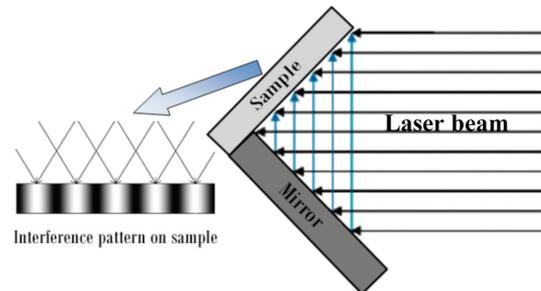


FIGURE 1. Schematic diagram of laser interference setup based on Lloyd Mirror configuration for grating fabrication

The interference pattern on the sample depends on the incident angle and it corresponds with the grating period (Λ), that is proportional to the curing wavelength, as shown by:

$$\Lambda = \frac{\lambda_c}{2 \sin \theta}, \quad (1)$$

where λ_c is the curing wavelength and θ is the angle between the incident beam axis and mirror surface.

The lasing characteristics of the DFB gratings obtained in this experiment were investigated by optical pumping using SHG Nd:YAG ($\lambda= 352$ nm) with pulse wide 2 nm. The schematic diagram of apparatus for lasing characterization is shown in Figure 2.

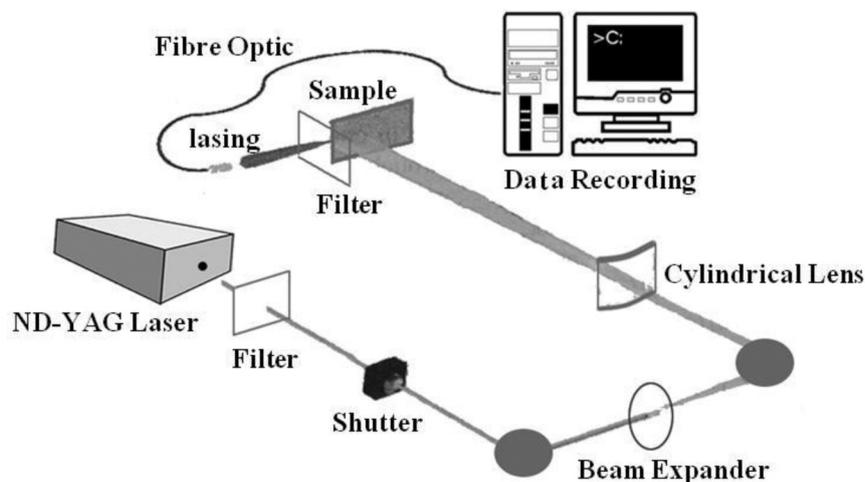


FIGURE 2. The schematic diagram of set-up for photo-pumped lasing experiment

RESULTS AND DISCUSSION

We have synthesized a precursor gel of hybrid polymer using TMSPMA monomer by sol-gel process, with a reaction yield around 80%. The reaction yield of sol-gel process was estimated from the weight ratio of the resulted precursor gel to a monomer. Figure 3 shows the typical Fourier transform infra-red (FTIR) spectra of the synthesized precursor film before and after irradiation with UV light. We observed an absorption band at $\nu = 1115 \text{ cm}^{-1}$ which is associated with Si-O-Si vibration, at $\nu = 1710 \text{ cm}^{-1}$ and at $\nu = 1633 \text{ cm}^{-1}$ that correspond, respectively, with C=O and C=C stretching. There is a broad band around 3423 cm^{-1} which is related to OH vibration. We need to clarify the origin of the OH vibration.

The sol-gel process was used to synthesis the hybrid polymer precursor. Figure 4 shows the TMSPMA monomer consist of silicon with three alkyls (R) chains and methacrylate (M) chain. In general, the sol-gel method is based on hydrolysis of the metal alkoxide, followed by condensation reactions of hydrolyzed alkoxides. During hydrolysis, the alkoxide group in the metal alkoxide is replaced by the hydroxo ligand as shown in Figure 4. There are three probabilities product resulted in hydrolysis reaction, i.e. metal hydroxide (fully hydrolysis), hydroxo metal alkoxide (partially hydrolysis), or metal alkoxide (un-hydrolyzed) as shown in Figure 5.

The hydroxo metal alkoxide resulted from hydrolysis reaction tends to react with other hydroxo or alkoxo groups

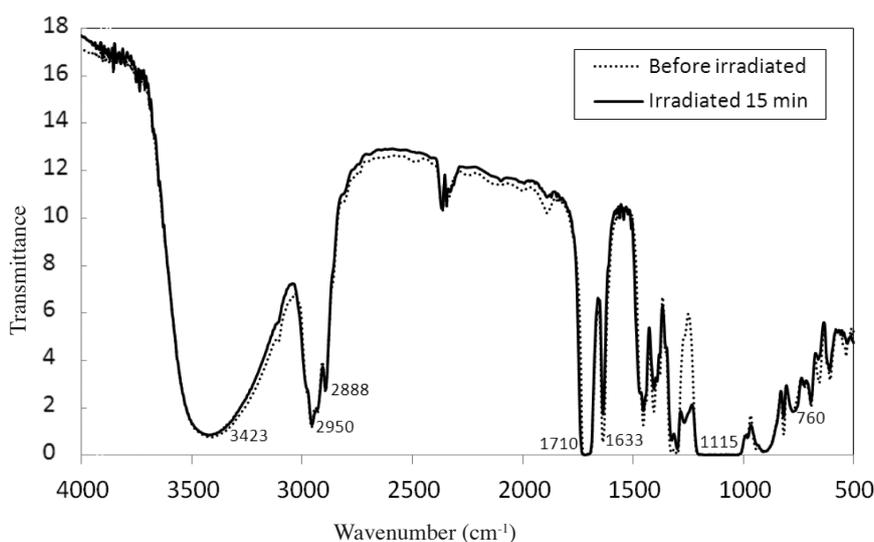


FIGURE 3. The FTIR spectra of hybrid polymer precursor before (dashed line) and after irradiation for 15 min (solid line)

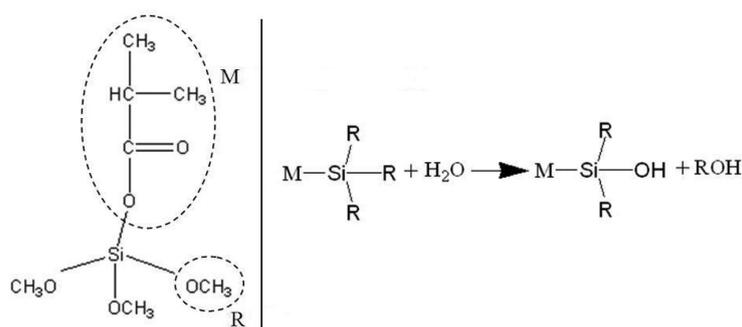


FIGURE 4. Hydrolysis reaction of TMSPMA molecule

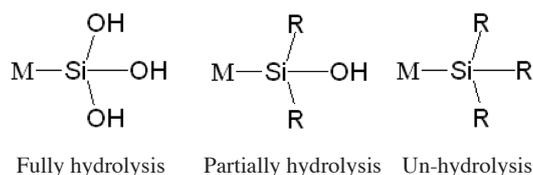


FIGURE 5. Three probabilities of hydrolysis-reaction product

in the polycondensation reaction. There are two types of polycondensation reaction, i.e. the hydroxo metal alkoxide react with other hydroxo or alkoxide groups in the hydroxo metal alkoxide or metal alkoxide as shown in Houbertz et al. (2003). During the sol-gel process, the condensation reactions proceed further, leading to the formation of a three dimensional network. These processes will convert the liquid sol into a solid gel. From our FTIR spectra, the OH stretching may have its origin from hydrolyzed siloxanes that failed to proceed into polycondensation.

Furthermore, the photo polymerization process resulted to cross linking in organic side chains. After photo-polymerization process, the infra red band at 1633 cm^{-1} was significantly decreased as the result of conversion from double (C=C) bond into single (C-C) bond (Hidayat et al. 2011). The process followed by alteration of hybrid polymer phase from gel into solid phase.

The photo-polymerization process was used to fabricate grating by means of irradiation sample using light pattern. In this experiment, light pattern was generated from Lloyd Mirror interference system using THG Nd:YAG Laser as shown on Figure 1. Various grating periods have been prepared by changing incident angle θ of the two interfering laser beams. The dependence of grating periodicity on the incident angle of the interfering beam was described in (1). Figure 6 shows an example of AFM image of surface grating structures obtained in our experiments. The thickness of the slab above the substrate is about $2\ \mu\text{m}$ and a periodicity of the grating is about 385 nm with the depth of about 60 nm .

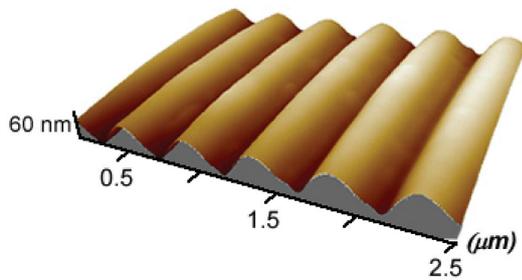


FIGURE 6. The AFM image of 1D surface grating obtained in this work

The characteristics of fabricated grating as DFB laser was examined by optical pumping using the SHG Nd:YAG laser (532 nm). Figure 7 shows the emission spectrum measured from 1D grating contained DCM at various pumping power. Without grating structure, we only found an amplified spontaneous emission (ASE), although the pumping power was high. With a grating structure, we obtained that when the pumping power was less than 3.4 mJ/pulse cm^2 , we still obtained a broad ASE with a low intensity. Then, when the pumping power was increased above 4.8 mJ/pulse cm^2 , we observed lasing action at 582 nm . Increasing of pumping power narrowed the width

of spectrum and increased the emission intensity. The lasing wavelength was remained at 582 nm when the pumping power was increased. At pumping power of 14 mJ/pulse cm^2 , the intensity increased remarkably along with decreasing a width of the spectral. The full width half maximum (FWHM) of the emission spectrum is about 2 nm , which is in the limit of the spectrometer resolution used in our experiment.

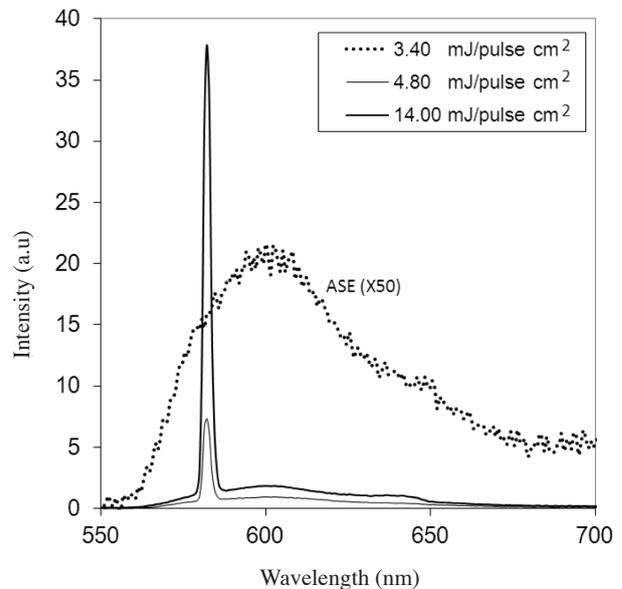


FIGURE 7. Lasing action observed at DCM-doped hybrid polymer at various pumping power, which the ASE was multiplied 50 times

The correlation between the pumping power with the intensity and FWHM of laser is shown in Figure 8. The curve in Figure 8 indicates the pumping threshold is around 4 mJ/pulse cm^2 . The increasing of pumping power above the threshold will produce the higher laser intensity and more narrow spectral width. The pumping threshold seems not too low, because the lasing action occurred by the second-order Bragg reflection. Theoretically, the second-order Bragg reflection commonly requires higher pumping threshold in comparison with the first-order Bragg reflection.

In order to confirm the experimental results, we have performed a theoretical study of DFB laser using the obtained experimental data. Since the thickness of the slab was about $2\ \mu\text{m}$, the waveguide has a multimode. Applying a coupled mode theory, the TE transmittance is expressed as (Yariv & Yeh 2007):

$$T = \left| \frac{S}{-(\Delta\beta + ig) \sinh(SL) + iS \cosh(SL)} \right|^2, \quad (2)$$

where

$$S = \sqrt{|k|^2 - (\Delta\beta + ig)^2}, \quad (3)$$

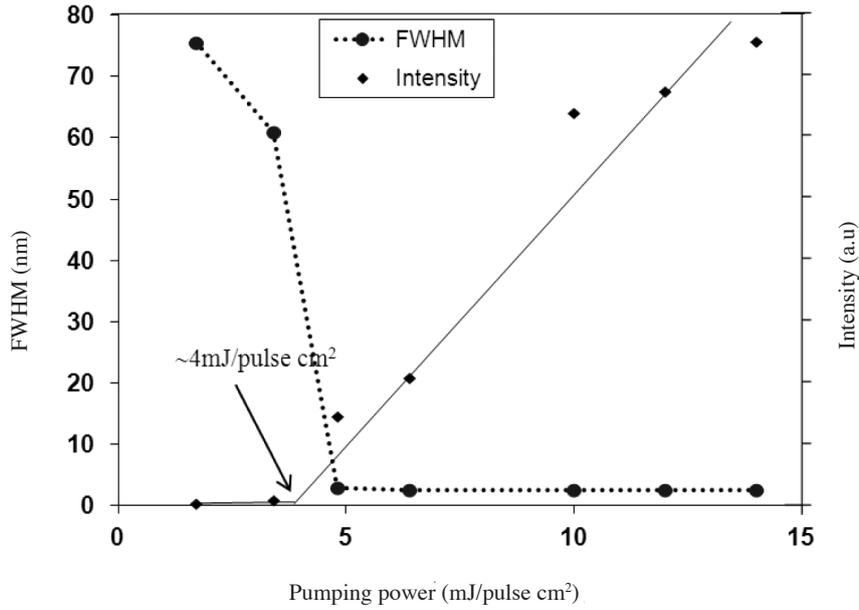


FIGURE 8. Lasing intensity and FWHM at various pumping power

L is the length of the structure, g is the gain of dye laser, κ is the coupling constant caused by the periodic dielectric perturbation due to the surface corrugation, and $\Delta\beta$ is expressed as (4).

$$\Delta\beta = n_{\text{eff}} \frac{\omega}{c} - \ell \frac{\pi}{\Lambda}, \quad (4)$$

n_{eff} is the effective refractive index, Λ is periodicity of the corrugation and ℓ is the mode number.

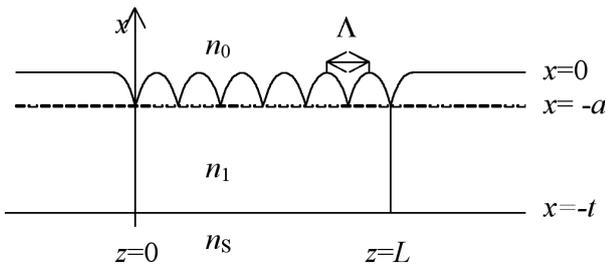


FIGURE 9. Planar waveguide with rectified full-wave surface corrugation

Grating structure in Figure 6 that is considered as a surface corrugation, is approximated as a rectified full-wave as shown in Figure 9. The dielectric perturbation caused by the corrugation is expressed as (Yariv & Yeh 2007):

$$\Delta\epsilon = \begin{cases} 0 & x > 0 \\ \epsilon_0 (n_1^2 - n_0^2) F(z), & -a < x < 0, \\ 0 & x < -a \end{cases} \quad (5)$$

where $F(z)$ in that equation is written as:

$$F(z) = \sum_{m=-\infty}^{\infty} b_m \exp(-im2\pi z / \Lambda), \quad (6)$$

and Λ is the period of the corrugated structure and the coefficients b_m is:

$$b_m = \frac{1}{(2m-1)\pi} \sin(2m-1)\frac{\pi}{2} + \frac{1}{(2m+1)\pi} \sin(2m+1)\frac{\pi}{2}. \quad (7)$$

Using (4)-(6), the coupling constant due to the m^{th} component of the periodic dielectric perturbation is thus:

$$\begin{aligned} \kappa &= \frac{\omega}{4} \int_{-a}^0 E_y^*(x) \Delta\epsilon_m(x) E_y(x) dx \\ dx &= \frac{\omega}{4} \epsilon_0 (n_1^2 - n_0^2) b_m \int_{-a}^0 E_y^*(x) E_y(x) dx, \end{aligned} \quad (8)$$

where a is the depth of the corrugation. For planar waveguide, the mode function $E_y(x)$ of the electric field is:

$$E_y(x) = \begin{cases} C \exp(-\gamma_0 x), & x \geq 0 \\ C [\cos(\gamma_1 x) - (\gamma_0 / \gamma_1) \sin(\gamma_1 x)], & -t \leq x \leq 0, \\ C [\cos(\gamma_1 t) - (\gamma_0 / \gamma_1) \sin(\gamma_1 t)] \exp[\gamma_s (x+1)], & x \leq -t \end{cases} \quad (9)$$

where

$$C^2 = \frac{4\gamma_1^2 \omega \mu_0}{\beta (t+1/\gamma_0 + 1/\gamma_s) (\gamma_1^2 + \gamma_0^2)}, \quad (10)$$

$$\gamma_0 = \sqrt{\beta^2 - (n_0 \omega / c)^2},$$

$$\gamma_1 = \sqrt{(n_1 \omega / c)^2 - \beta^2},$$

$$\gamma_s = \sqrt{\beta^2 - (n_s \omega / c)^2}. \quad (11)$$

Using (9)-(11), (8) then becomes:

$$\kappa = \left(\frac{\omega}{c}\right)^2 (n_1^2 - n_0^2) b_m \frac{\gamma_1^2}{\beta (t + 1/\gamma_0 + 1/\gamma_s)(\gamma_1^2 + \gamma_0^2)} I, \quad (12)$$

where:

$$I = \left\{ \frac{1}{4\gamma_1} \left[1 - \left(\frac{\gamma_0}{\gamma_1}\right)^2 \right] \sin(2ha) + \frac{a}{2} \left[1 + \left(\frac{\gamma_0}{\gamma_1}\right)^2 \right] + \frac{\gamma_0}{\gamma_1} \sin^2(\gamma_1 a) \right\}. \quad (13)$$

By using experimental data: $t = 2 \mu\text{m}$, $A = 0.2 \mu\text{m}$, $a = 0.05 \mu\text{m}$, $n_0 = 1$, $n_s = 1.4$ and $n_1 = 1.55$, we calculated the transmittance with $L = 100 \mu\text{m}$ and gain $= 0.02/\mu\text{m}$ (Leonetti et al. 2009). Figure 10 is the theoretical transmittance of corrugated waveguide obtained by calculation using mode number $l = 2$ (4) and $m = 1$ (7). There is a bandgap about 15 nm centered at $\lambda = 568 \text{ nm}$. At the edges of the gap, there are two high peaks at $\lambda = 548 \text{ nm}$ and $\lambda = 580 \text{ nm}$. The last peak is agreed with the experimental result as shown in Figure 7. But, the first peak did not appear in the experiment, probably it is reabsorbed by the material.

CONCLUSION

We have synthesized hybrid polymer precursor using monomer of TMSPMA and modified the precursor with DCM dye for obtaining luminescent material. We further have fabricated 1D DFB grating structure using DCM contained hybrid polymer precursor by Lloyd mirror interference method. From the AFM image we found the grating periodicity is about 385 nm and the depth is about 60 nm. We observed photopumped lasing action in the 1D DFB

grating structure with a threshold power around 4 mJ/pulse cm^2 and emission wavelength at $\lambda = 582 \text{ nm}$. Using coupled mode theory and experimental data of the corrugated waveguide and material gain of $0.02/\mu\text{m}$, the theoretical calculation is agreed with the experimental result.

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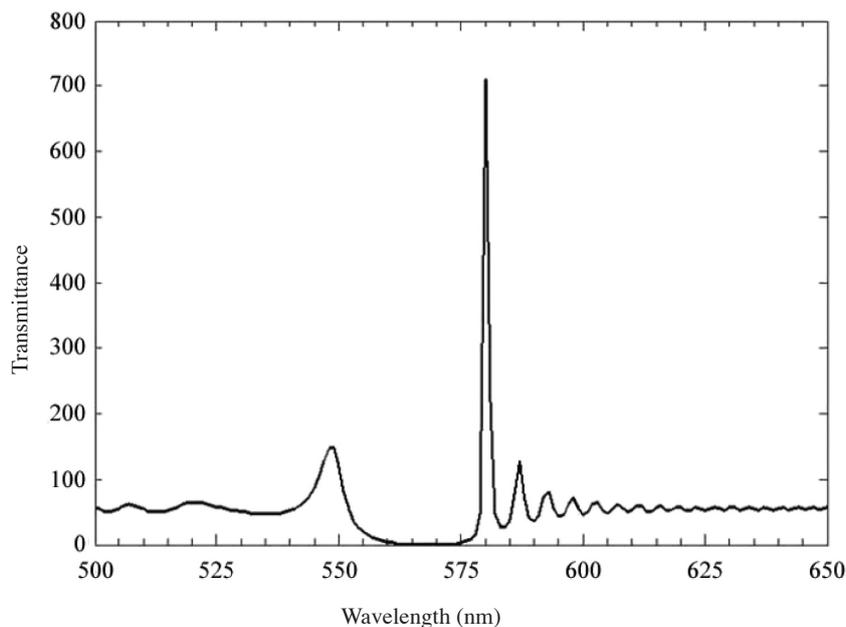


FIGURE 10. Theoretical calculation of transmittance of the corrugated waveguide

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