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

SAHRUL HIDAYAT*, R. HIDAYAT, FITRILAWATI, A. BAHTIAR & R.E. SIREGAR

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 (∆=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 cm². 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


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

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 (Darraqq 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-styril-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 (λ=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 laser (λ=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](image1)

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:

\[ Λ = \frac{λ_c}{2\sinθ} \]  

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 (λ= 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](image2)
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 infrared 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 $\theta$ 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 $\mu$m and a periodicity of the grating is about 385 nm with the depth of about 60 nm.

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 lasing 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.

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 $\mu$m, the waveguide has a multimode. Applying a coupled mode theory, the TE transmittance is expressed as (Yariv & Yeh 2007):

$$T = \frac{S}{-(\delta \beta + ig)\sinh (SL) + iS \cosh (SL)}$$

where

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

![Figure 6. The AFM image of 1D surface grating obtained in this work](image)
$L$ is the length of the structure, $g$ is the gain of dye laser, $\kappa$ is the coupling constant caused by the periodic dielectric perturbation due to the surface corrugation, and $\Delta \beta$ is expressed as (4).

$$\Delta \beta = \frac{n_{ef} \omega_0}{c} - \frac{x}{\Lambda},$$  \hspace{1cm} (4)

$n_{ef}$ is the effective refractive index, $\Lambda$ is periodicity of the corrugation and $t$ is the mode number.

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

$$\kappa = \frac{\omega_0}{4} \int_{-\infty}^{\infty} E'_x(x) \Delta \varepsilon_a(x) E_x(x) \, dx,$$

$$\kappa = \frac{1}{(2m-1)\pi} \sin\left(\frac{(2m-1)\pi}{2}\right) + \frac{1}{(2m+1)\pi} \sin\left(\frac{(2m+1)\pi}{2}\right).$$  \hspace{1cm} (7)

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

$$E_y(x) = \begin{cases} C \exp(-y_0 x), & x \neq 0 \\ C \left[ \cos\left(\gamma_s x\right) - \frac{\gamma_s}{\gamma_t} \sin\left(\gamma_s x\right) \right], & -t \leq x \leq 0, \\ C \left[ \cos\left(\gamma_t x\right) - \frac{\gamma_t}{\gamma_s} \sin\left(\gamma_t x\right) \right] \exp\left[\gamma_s (x+1)\right], & x \approx -t \end{cases}$$  \hspace{1cm} (9)

where

$$C^2 = \frac{4\gamma_s^2 \gamma_t^2}{\beta (r+1/\gamma_0 + 1/\gamma_s)(\gamma_t^2 + \gamma_s^2)},$$  \hspace{1cm} (10)

$\gamma_0 = \sqrt{\beta^2 - \left(n_{g0}/c\right)^2},$

$\gamma_1 = \sqrt{\left(n_{g0}/c\right)^2 - \beta^2},$

$\gamma_s = \sqrt{\beta^2 - \left(n_{g0}/c\right)^2}.$  \hspace{1cm} (11)
Using (9)-(11), (8) then becomes:

\[
\kappa = \left( \frac{\omega}{c} \right)^2 \left( n_2^2 - n_0^2 \right) \beta \left( \frac{1}{\gamma_0} + \frac{1}{\gamma_f} \right) \left( \gamma_f^2 + \gamma_0^2 \right), \tag{12}
\]

where:

\[
I = \left( \frac{1}{4 \gamma_0} \right) \left[ 1 - \left( \frac{\gamma_0}{\gamma_f} \right)^2 \right] \sin^2 \left( 2 \pi a \right) + \frac{a}{2} \left[ 1 + \left( \frac{\gamma_0}{\gamma_f} \right)^2 \right] \frac{\gamma_0}{\gamma_f} \sin^2 \left( \gamma_f a \right). \tag{13}
\]

By using experimental data: \( t = 2 \ \mu m, \ \Lambda = 0.2 \ \mu m, \ a = 0.05 \ \mu m, \ n_0 = 1, \ n_1 = 1.4 \) and \( n_2 = 1.55 \), we calculated the transmittance with \( L = 100 \ \mu m \) and gain = 0.02/\( \mu m \) (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 cm² 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/\( \mu m \), the theoretical calculation is agreed with the experimental result.

ACKNOWLEDGEMENTS

This research has been financially supported by the Hibah STRANAS from Directorate General of Higher Education, Ministry of National Education Indonesia, contract no: 395/SP2H/PL/Dit Litabmas/IV/2011. We would like to thank Prof. Dr. Masanori Ozaki for AFM measurements and laser facilities.

REFERENCES


