Photocuring by Infrared Irradiation Using Upconversion Emission

Kohei Soga, Aya Okada and Masayoshi Yamada

*Department of Materials Science and Technology
Tokyo University of Science*

2641 Yamazaki, Noda, Chiba 278-8510, Japan (e-mail: mail@ksoga.com)

Infrared-to-visible upconversion emission was used for photocuring of a pentaerythritol tetraacrylate (PETA) by infrared laser irradiation to achieve local polymerization on an upconversion phosphor. Submillimeter-sized, cone-shaped and solid poly (PETA) was successfully formed on a Y_2O_3 compact doped with 5 mol%Er under 985 nm diode laser irradiation with about 900 mW power. By changing the irradiation time, it was found that the formation of the cone starts in seconds and takes minutes to form a millimeter-sized cone. The correlation between the irradiation time and the cone volume was linear in the seconds-to-minutes time region with 800-900 mW irradiation powers.

Keywords: upconversion, photocuring, rare-earth, infrared, coating

1. Introduction

Infrared (IR)- to- visible (VIS) upconversion (UPC) is a known phenomenon for rare-earth ions in inorganic hosts with low phonon energies [1-5]. The UPC emits VIS or ultraviolet light by multi-step excitation in discrete energy levels of rare-earth ions by the IR excitation with lower photon energy than the emitted photon. To achieve the UPC, an important requirement for the host material is low phonon energies to avoid the quick vibrational relaxation of the intermediate excited state. Generally, the low phonon energy requires weak bonding or heavy mass of the consistent atoms. Hence the selection of host materials for high UPC efficiency causes the poor chemical durability of the materials due to the weak bonding [6].

The UPC is a phenomenon useful for general wavelength converters, full color three dimensional displays, bio-imagers, etc[7-9]. For these applications, polymer coating to on the UPC phosphor is an important technology to give the chemical

durability as a functional material. Especially, recent importance of the coating is the coating on UPC nano-particles for forming transparent UPC- phosphor- polymer composites for displays and bio-imagers.

Photocuring is a method to control the polymerization filed for forming a shape for a polymer solid. For forming a polymer coating on the above nano-particles, spatial control of the polymerization is required since the polymerization should occur only on the surface of the particles. The polymerization in any other space should be avoided.

In the present study, the authors propose a novel photocuring route for achieving local polymerization only nearby the UPC phosphor surface. The photon field of the VIS light from the surface of the phosphor diminishes quickly by the distance from the surface. The locally dense photon field can achieve the local polymerization in a limited space. Y_2O_3 compact doped with Er was used as the UPC emissive material under IR laser diode irradiation. As monomers, methyl-

methacrylate (MMA) and pentaerythritol tetraacrylate (PETA) were used to compare the polymerization types[10, 11].

2. Experimental

2.1. UPC emissive material

As an UPC emissive material, Y_2O_3 sintered compact doped with 5 mol%Er ($\text{Y}_2\text{O}_3:\text{Er}$) was prepared by conventional sintering method.

Upconversion emission spectrum of the sample was measured by using spectrofluorometer (RF-5000, Shimadzu) under the excitation by IR diode laser at 980 nm with about a 100 mW power.

2.2. Starting materials for photocuring

Two sets of starting materials were prepared for the photocuring experiments.

One is reagent grade MMA (Tokyo Kasei) with 2.6 wt% Irgacure 784 (Chiba Specialty Chemicals Inc.) as a photosensitive initiator.

The other is PETA (Beamset 710; Arakawa Kagaku Kogyo) with 0.5 wt% Irgacure 784.

2.3. Photocuring configuration

Photocuring experiment was carried out at first directly on the $\text{Y}_2\text{O}_3:\text{Er}$ compact dipped in the starting materials. To examine the growth rate of the solid polymer, a glass slide was inserted between the starting materials and the $\text{Y}_2\text{O}_3:\text{Er}$ compact. The schematic of the experiment is shown in Fig. 1. For the UPC excitation, a laser diode at 985 nm with about 850-900 mW power was used.

3. Results and Discussion

3.1. UPC emission

The UPC spectrum of the $\text{Y}_2\text{O}_3:\text{Er}$ compact was measured and shown in Fig. 2. Green (530 and 550 nm) and Red (660 nm) emissions are observed by 980 nm excitation. The emission spectrum corresponds to the ones in the previously reported studies on the upconversion of Er^{3+} in the Y_2O_3 host [5], where the color balance of the green and red emissions are reported to be controllable by changing the Er concentration. Fig. 3 illustrates the scheme of the UPC process. Two steps excitation by 980-nm IR light through the $^4\text{I}_{13/2}$ level results in the excitation into $^4\text{F}_{7/2}$. After relaxing down to the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{I}_{11/2}$ levels, VIS light at

Fig. 1 Schematic of IR photocuring experiments by using upconversion process.

Fig. 2 Upconversion emission spectrum of Y_2O_3 compact doped with 5 mol%Er under 980 nm excitation.

Fig. 3 Schematic of upconversion process of Er^{3+} in Y_2O_3 under 980 nm excitation.

530, 550 and 660 nm, respectively, are emitted. The photosensitive initiator used in this study, Irgacure 784, does not have absorption at the excitation wavelength, 980 nm, but have absorption band tails to 560 nm, which can absorb the above green UPC emission. Thus the starting materials with Irgacure 784 are expected to be photocured only by the green UPC emission.

3.2. Photocuring by UPC emission

At first we examined the UPC photocuring by irradiating the IR excitation light on $\text{Y}_2\text{O}_3\text{:Er}$ compact, above which the MMA starting material was located. The material solidified in a few days. The polymerization did not occur locally around the UPC emission point. Whole of the materials solidified all at once. The reason for the through solidification is the chain polymerization of MMA into poly (MMA). The reason of the solidification is increase of the melting point due to the increase of the poly (MMA) molecule. Our purpose of the solidification is not the through one but local one for forming a coating on the UPC phosphor. Thus, we had to seek for another route for solidification by using other starting material.

To achieve a local photocuring, the solidification process should be mass polymerization, where originally chain polymer molecule will be bridged to form a solid three dimensional network of the polymer. To have an efficient bridging, we looked for a starting polymer with many hands for shaking around.

The PETA is a molecule that has the above structure as shown in Fig. 4. We next examined the UPC photocuring with the PETA starting material. The local solidification was successful with the PETA starting material by irradiating the IR laser for several minutes. A cone-shaped piece of the solid polymer with submillimeter size was formed on the $\text{Y}_2\text{O}_3\text{:Er}$ compact as shown in Fig. 5. The cone shape is formed by the power distribution in the beam spot of the irradiated laser. Since the UPC is a two photon process, the UPC emission intensity corresponds to the square of the excitation power [1]. Therefore the power distribution in the beam spot tends to be enhanced in the intensity distribution of

Fig. 4 Molecular structure of pentaerythritol tetraacrylate (PETA).

Fig. 5 Poly (PETA) formed on a Y_2O_3 compact doped with 5 mol%Er. An IR laser at 985 nm with 600 mW power was irradiated for 60 sec.

Fig. 6 Correlation of the volume of formed poly (PETA) against laser irradiation time. Open triangles and squares correspond to the condition A and B in the text. Solid lines are the results or least square fitting on the data assuming linear correlation.

the UPC emission.

The size of the solid polymer is much larger than the one we expect to form a film on UPC phosphors. The useful size of the

phosphors as composite material is expected to be submicrometer. Accordingly, the thickness of the film should also be submicrometer. For forming submicrometer object by the present method, we estimated the dependence of the solidified volume on the irradiation time. For the efficiency of the experiments, a glass slide was inserted between the starting materials and the $\text{Y}_2\text{O}_3\text{:Er}$ compact as shown in Fig. 1. The cones were grown on the glass slide on behalf of the direct growth on the compact. Fig. 6 shows the two series of the experiments. Essentially, these two series were not intentionally given different condition. The diode laser beam is designed to focus at a certain distance. The experiment was planned to emit have the focus point at the surface of the $\text{Y}_2\text{O}_3\text{:Er}$ compact. Since the focus length is not so long, a slight difference of the position of the compact changes the photon density. Furthermore, the difference of the power will be magnified by the reason discussed above. Thus, the difference of the size for the two series is not essential. As shown in Fig. 6, the volume of the formed solid polymer linearly corresponds to the irradiation time. The volume formed by 100 sec irradiation is roughly in the order from 0.1 to 1 mm^3 .

The condition to form a 1 μm thickness coating film can roughly be the one for forming 1 $(\mu\text{m})^3 = 10^{-9} \text{ mm}^3$ volume object. Thus, the corresponding irradiation time for the 1 μm thickness coating film is estimated to be as a product of 100 sec and 10^{-9} , i.e. $10^{-7} \text{ sec} = 0.1 \mu\text{sec}$, which corresponds to the duration time of a pulsed or quasipulsed laser. Another important factor to be encountered is the irradiation laser power. To give a variety

for the irradiation time, experiments under varied laser power is the next coming issue.

4. Conclusion

The UPC photocuring using a combination of a $\text{Y}_2\text{O}_3\text{:Er}$ compact phosphor, PETA precursor and Irgacure 784 initiator successfully formed a cone-shaped submillimeter sized solid object, which means the occurrence of the local polymerization around upconversion emission spot. The volume of the cone object increased linearly by increasing the irradiation time. Under laser irradiation for 100 sec with 900 mW power at 980 nm, the size of the object was about 0.1-1.0 mm^3 .

References

1. K. Soga et al., *J. Non-Cryst. Solids*, **222** (1997) 272-281.
2. M. Tsuda et al., *J. Appl. Phys.*, **85** (1999) 29-37.
3. M. Tsuda et al., *J. Appl. Phys.*, **86** (1999) 6143-6149.
4. M. Tsuda et al., *J. Appl. Phys.*, **88** (2000) 1900-1906.
5. D. Matsuura et al., *J. Electrochem. Soc.*, **152** (2005) H39-H42.
6. K. Soga et al., *J. Appl. Phys.*, **93** (2003) 2946-2951.
7. K. Soga et al., *J. Photopolym. Sci. Tech.*, **18** (2005) 73-74.
8. R. Koizumi et al., *J. Photopolym. Sci. Tech.*, **18** (2005) 51-54.
9. E. Downing et al., *Science*, **273** (1996) 1185-1189.
10. M. Doytcheva et al., *Macromol. Mater. Eng.*, **286** (2001) 30-33.
11. J. Pavlinec et al., *Macromol. Chem. Phys.*, **202** (2001) 2387-2393.