# Australian – Japanese Students workshop on Nanophtonics

## (Student Exchange Support Program by Shizuoka University)

Professor Saulius Juodkazis's group Center for Micro Photonics Swinburne University of Technology, Melbourne, Australia

> Professor Atsushi Sugita's group Department of Materials Science Shizuoka University, Japan.

> > November 16-23, 2012

Swinburne University of Technology, Melbourne, Australia

#### Preface

On behalf of the members of Shizuoka University, I would like to thank Professor Saulius Juodkazis to give us the opportunity to visit the laboratory and to organizing the symposiums. And we are grateful for all the members of Center for Micro Photonics in Swinburne University of technology for sharing the special times with us. We also appreciate Professor Vygantas Mizeikis and Dr. Atsushi Ono for their help of arranging the program.

I begin by introducing the SSSV program organized by our institute and the backgrounds. The aim of the program stimulates our undergraduate and graduate students by exchanging the discussions with the young researches of the same generations. The program has two options; in first options, we visit the institute in the foreign countries and hold the symposium for discussions about their researches. In the second, we invite the students in the foreign countries and hold the symposium. This is the second year of the program and ten groups participate in the programs.

As you know, Japan is surrounded by the ocean. Most of the Japanese people do not have any experiences of interactions with the foreign countries and foreign peoples. It is a big adventure for them to visit the foreign countries and make conversations with non-native languages. Until about 20 years ago, the Japanese economy was booming, because of the good cycles between the domestic consumptions and productions. Most of the Japanese people do not have to contact directly with the foreign peoples. At the edge of the 21<sup>st</sup> century, the Japanese economy is turndown and most of production companies are expanding their production base worldwide. It is unavoidable for most of the Japanese engineers to do their business with the engineer in the foreign countries, especially Asia. Off course, even if our students visit Australia for one week, it is not sufficient to learn what looks like the foreign countries and the foreign people. Their experiences in Melbourne are the great step for them to grow up the independent engineer in the future.

Off course, the symposium is one of the most important events in the program. Our group makes a lot of effort for producing thin film optical materials, especially thin film nonlinear optical materials. These materials are not always our original ones, but we may create new technologies by assembling them with other optics or optronics technologies. We give great attentions to their applications to the fields of the nanotechonologies and nanosciences. Professor Juodkazis's group is the one of the most prominent laboratories in the field of the nanophotonics. We believe that new technologies such as nonlinear optics for nanophotonics will be born by combining the knowledge and skills accumulated by the two groups.

Finally, we are grateful if the program are fruitful for all the participants of the two groups.

Professor Atsushi Sugita

## Shizuoka-Swinburne Workshop on fast & small (fs)

Swinburne University of Technology 19 November 2012

## Room ATC 205 (Advanced Technologies Centre)

Time	Presenter	Title
10.00 - 10.15	Coffee/tea	Welcome
10.15 - 10.30	Prof. Atsushi Sugita	Research activity about nonlinear optics and femtosecond
	Shizuoka University, Japan	spectroscopy
10.30 - 10.45	Mr. Yasuaki Sato	Second order Nonlinear optics of on electrically poled
	Shizuoka University, Japan	host-guest type polymers
10.45 - 11.00	Mr. Kazuma Ito	Development of new nonlinear optical chromophores for
	Shizuoka University, Japan	near-infrared frequency regions
11.00 - 11.15	Mr. Yoshihiro Ono	Second harmonic generations of Nonlinear optical
	Shizuoka University, Japan	polymers pumped by surface plasmons excited by
		Kretchmann configurations.
11.15 - 11.30	Mr. Masashi Kamiya	Development of luminescence thin films for
	Shizuoka University, Japan	Electron-excitation assisted optical microscopes
11.30 - 11.45	Coffee/tea	
11.45 - 12.00	Ms. Jennifer Hartley	Optical fiber SERS probe for biochemical sensing
	Swinburne University	
12.00 - 12.15	Ms. Zubaidah Ningsih	The Temporal Co-stimulation of NGF and EGF Effect
	Swinburne University	Toward the Kinetics of Cell Signal Transduction Pathways
12.15 - 12.30	Mr. Jonathan Tollerud	Ultrafast Multidimensional Spectroscopy to Reveal
	Swinburne University	Many-Body Effects in Semiconductor Nanostructures
		Coherent Dynamics in Photosynthetic Light-Harvesting
12.30 - 13.30		Lunch at ATC 205
13.30 - 13.40	Mr. Ričardas Buividas	Lab tour: femto-laser microfabrication
13.40 - 13.50	Mr. Alireza Lajevardipour	Lab tour: fluorescence lifetime imaging microscopy
13.50 - 14.00	Mr. Gethin Richards	Lab tour: ultra-fast spectroscopy
14.00 - 14.30	Mr. Gediminas Gervinskas	Lab tour: nano-lab
	Mr. Gediminas Seniutinas	
14.30 - 15.00	End	

#### About Shizuoka University and Shizuoka prefecture

Here, we introduce Shizuoka University and Shizuoka prefecture. The Japan has 47 local governments and at least one national university is established in each prefecture. Our Shizuoka University is located in Shizuoka prefecture. The population of Shizuoka prefecture is approximately 3,700,000 in 2012 and it is the tenth most populated in 47 prefectures. The most important industry is the production of transportation machineries, such as automobiles and motor cycles. Yamaha Motor Company and Suzuki Motor Corporations, famous for their motor cycles, have their headquarters in Shizuoka. The founders of Toyota Motor Corporation and Honda Motor Company were born and began their businesses in Shizuoka. Before World War II, cotton textile industry used to be one of the major industries in Japan. Toyota, Yamaha, and Suzuki started from supplying weaving machines. Hamamatsu Photonics K. K., famous for their Photomultiplier tubes, has the headquarter in Hamamatsu city. The origin of the name is clearly the name of the city, the second biggest city in Shizuoka Prefectures.

Now, Shizuoka University has 6 faculties, and approximately 8,800 undergraduate students and 1,500 graduate students study their academics under the instructions of 1,100 university staffs. There are two campuses at Shizuoka cities and Hamamatsu cities. Our team belongs to Faculty of Engineering in Hamamatsu campus.

Shizuoka University was inaugurated on June 1, 1949, following approval on May 31 of the same year for the university's establishment through the unification of five educational institutions: the former Shizuoka High School, Shizuoka Normal School and Shizuoka 2nd Normal School, Shizuoka Normal School for Youth and Hamamatsu College of Technology.

Subsequently, the university absorbed Shizuoka Prefectural College of Agriculture, moved to its present Shizuoka and Hamamatsu Campuses, and by undertaking the reorganization and enlargement of its faculties and other educational departments, assumed its present form. In the years to come, the university will continue to make efforts to upgrade and enrich its structure.

The roots of the Faculty of Engineering date back to 1922 and the founding of Hamamatsu Technical High School. With the ideal of "Freedom and Enlightenment, Creation for the Future," the Faculty has trained numerous pioneering researchers and technologists. Hamamatsu City, where the campus is located, has a rich tradition of innovation and was a gathering place for technologists from throughout Japan during the Edo era. Today, the city retains a spirit of craftsmanship, with many enterprises possessing unique technologies and products. In tune with this environment, the Faculty of Engineering hosts a variety of enterprise-supported courses. Through such efforts as Creative Educational Training, in which students gain experience in robot construction from their first year, the Faculty conveys the pleasure of hands-on fabrication, and many go on to the Graduate School of Engineering's Doctoral Program.

### Introductions of Dr. Sugita laboratory in Shizuoka University Educational Background of Professor Atsushi Sugita

Professor Atsushi Sugita received B.A. degree in 1994, Master degree in 1996 and Ph. D degree in 1999 from Tokyo University. He studied ultrafast dynamics of solid-state semiconducting materials with femtosecond time-resolved spectroscopies. He also tried building the optical parametric amplifier systems covering the near-IR and mid-IR wavelengths. He joined the department of Materials Sciences in Shizuoka University as a research associated in 2001. He joined the attosecond science team in Max-Plank Institute for Quantum Optics in Germany as a visiting researcher for a year in 2005. Professor Ferencz Krausz, the coordinator of the team, is a pioneer of the attosecond sciences and he is also famous as one of the founders of the Femtolasers GmbH. Professor Sugita built high power mode-locked oscillator based on Yb:YAG thin disk laser. He established his independent laboratory in 2007. In 2012, ten members, five undergraduate students and five Master course students join his laboratory. 24 alumni have graduated from his laboratory.

#### **Current Research Projects**

Our group joins the divisions of the polymer science and engineering. We play a part of examining surface and interface properties of polymeric materials using spectroscopic techniques. The surface properties of the polymers have been studied for long decades. The phenomena are closely associated with the adhesion phenomena between the two materials. However, we do not fully understand the phenomena, even though a lot of efforts have been made. It is probably because the polymer can take several conformations and they exhibit complex structures depending on their surrounding environments.

Professor Sugita has a lot of experiences of operating femtosecond lasers. Taking advantage of the novel light sources, we study vigorously about surface alignment effects and the subsequent nonlinear optics. The researches include not only examining the physical properties of the polymer surface but also preparing the materials exhibiting excellent optical behaviors in the surface. Recently, we try building the new technologies by combining the surface nonlinear optics with surface plasmonics.

#### **Research Topics**

#### Surface Nonlinear Optics of Polymer Materials

In the project, we examine the methods nonelectrically poling polymer nonlinear optical materials for second order nonlinear optical susceptibilities. The polymer optical materials have attracted great interests because of their unique properties such as light weightiness, low production cost and easiness in fabrications. The investigation about the nonlinear optical (NLO) polymers is one of the most important issues in the fields, and a lot of unique NLO polymers have been ever designed and developed until now.

When we operate the NLO polymers for the second order nonlinear optics, we have to conduct so-called poling procedures. The procedure includes the process of applying electric fields as high as a few kV/mm in the materials. Dielectric break down occurs frequently and it is difficult to prepare the materials with wide areas and large volumes. We have developed a series of polar polymers which unique behaviors of self-organizing polar conformations. Taking advantage of the polarization self-organization effects, we successfully obtained second order nonlinear susceptibilities without conventional poling procedures. We continue to seek the optimized conditions for obtaining larger nonlinearities with nonelectrical methods.

#### **Nonlinear Optics for Plasmonics**

In the project, we make investigations about nonlinear optical interactions between surface plasmon and nonlinear polymers. As you know, nonlinear optics is one of the most fundamental element technologies in the fields of current optics and optronics. The challenge of developing nonlinear optical devices for nanophotonics and plasmonice is one of the most important issues for further progress of these fields. The nonlinearities of the metallic materials, where the surface plasmon are created, are generally small because of their conductivities. In order to overcome the problems, we propose to enhance the nonlinearities of the metal surface by fabricating the nonlinear optical polymers developed in our previous studies.

As a first step, we succeeded in observing the intense second harmonic signals from the NLO polymers excited by surface plasmon enhanced optical fields induced with attenuated total reflection methods. We are now making examinations about the nonlinear optical interactions between the polymers and localized surface plasmons in metal nanoparticles.

#### Synthesis of Nonlinear Optical Chromophores for Near-IR Operations.

Fundamental structures of nonlinear optical polymers consist of host – guest complex structures. The guest chromophores play a role of nonlinear light-matter interactions, while the host polymers fix the positions of the guest chromophores. Depending on the molecular designs, we can control the nonlinearities and resonance frequencies of the chromophores. Recently, the synthesis of chromophores for near-infrared operations has advanced considerably. These novel chromophores are attractive for applications to fast optical telecommunication systems. These materials are also useful for improving our thin film nonlinear optical polymer technologies and developing the nonlinear optical devices for the plasmonics. We are now preparing the novel chromophores systematically with different resonance wavelengths from 400 and 800nm.

#### Developing Inorganic nonlinear optical thin films

Our institute has long traditions of crystal growth technologies for semiconducting materials. With the aids of these groups, we begin developing the nonlinear optical inorganic thin films. In general, the inorganic nonlinear optical materials are robust and their damage thresholds and nonlinearities are much higher than the NLO polymers. We begin by preparing thin films of AgGaS<sub>2</sub>, the materials known as the novel NLO materials for mid-IR operations. In the future, we would like to build the NLO photonic crystals or waveguides based on these materials.

# Second-Order Nonlinear Optical Susceptibility of host-guest type polymers containing TCF-based guest chromophore

Shizuoka University, Department of Material Science

Kazuma Ito, Yasuaki Sato, Wataru Inami, Nobuyuki Mase, Kawata Yoshimasa, Atsushi Sugita.

#### Introduction

Nonlinear optics (NLO) has been studied for almost half a century since P. A. Franken first succeeded in observing second harmonic generation (SHG) in 1961. Recent progress of stable and high power light emitting diode technologies promoted solid-state laser and fiber laser technologies in near-infrared regions. Furthermore, the LED pumped ultrafast oscillators and amplifiers are also reported. A lot of researchers propose and examine the applications of these advanced light sources especially in the fields of high density and fast telecommunication systems, biomedical imaging and mechanical machining. The nonlinear optics and their applications are one of the most fundamental technologies that are made up of the current optics and optronics. Hence, it is important to develop NLO materials operating in the near-infrared regions so as to satisfy the demands.

The NLO materials are typically classified into three groups, that is, inorganic crystalline materials, organic crystalline materials and polymeric materials. Even though the first two classes are in practical use, the NLO polymers still attract great interests because of their flexibility, easiness in fabrication and low production cost. The fundamental structures of the NLO polymers are typically consisted of host-guest complex materials. The guest chromophores play a role of nonlinear light-matter interactions, while the host materials fix the positions of the chromophores. Until now, a lot of host polymer materials, such as poly (methyl methacrylate), poly carbonate and poly styrene have been developed. Most of the efforts seem to be mode to develop the guest chromophore with large molecular hyperpolarizabilities.

As for molecular designs of the guest chromophore, most of the popular NLO chromophores consist of  $\pi$ -conjugated system sandwiched between electron donoting and electron accepting moieties. By combining the moieties with appropriated design, we may prepare the chromophores at specific operating light frequencies. Recently, there are several reports about the novel NLO chromophores for near-IR operations2, 3. These chromophores are mostly used for the applications to the 3rd order nonlinear optics. However, supposed that we manage to orderly orient these chromophores in host materials, the materials will be useful for the 2nd order nonlinear optics.

In the present, among several NLO chromophores for near-IR frequencies, 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydroofuran (TCF), one of most promising NLO chromophore for the near-IR operations were synthesized and studied as the guest materials for the 2nd order nonlinear optics. The TCF chromophores are unique in that they have TCF acceptors with highly electron withdrawing abilities.

First, the synthesis of the TCF chromophores is reported. Second, the 2nd order nonlinear

optical susceptibility of the polymers with the TCF chromophores as the guest is addressed. In the last part of the presentation, we will report the strategy of developing the chromophore with longer conjugation lengths and the progress of synthesis.

#### Experiments



The TCF chromophore (5) was synthesized with the two steps shown in Scheme 1. At First step, TCF acceptor (3) was carried out with 5-hydroxy-3-trimethyl-butan-2-one (1) and malononitrile (2). At the second step, the material (4) with the electron donoting moieties was added to TCF acceptor (3), which results in the productions of the molecule (5).

The samples for measuring several optical properties were the host-guest materials consisting of the molecule 5 as the guest and polymethyl methacrylate (PMMA) as the host. The thin film of the

host-guest polymers were fabricated on the glass substrate with the spin coating method. The film thickness of the films was 100 nm. The linear and nonlinear optical properties were characterized with a UV-VIS absorption spectroscopy and a second harmonic spectroscopy.



**Figure 1.** Structure and hyperpolarizability of TCF cromophore and DR1.

The materials should have noncentro-symmetric structures for the second-order NLO susceptibilities. In as prepared conditions, the host-guest polymers have the centro-symmetric structures because the guest chromophores are randomly oriented in the host polymers. In general, so called poling procedure is conducted to align the chromophores in polar order. In the present, we tried aligning the NLO chromophores in the polar order with nonelectrical poling method proposed in our previous study. In the methods, the driving forces of alignments are the surface orientation effects and the orientation polarization effects with the internal field due to the surface energy difference between the electrodes sandwiching the polymers. As a reference, the materials with Disperse Red 1(Figure 1), one of the most popular NLO chromophores was measured under the

same conditions. The excitation light sources for the second harmonic method is femtosecond optical pulses from the Ti:sapphire regenerative amplifier. The center wavelength, the pulse energy and the pulse width were 800 nm, 1mJ and 150 fs, respectively.

#### **Results and Discussion**

Figure 2 shows the linear absorption spectrum of the PMMA doped with the TCF and DR1chromophores. The absorption peak and edge of the materials with the TCF chromophore were 588 nm, and 660 nm, respectively, while those of the materials with DR1 were 506 nm and 595 nm, respectively. Both of the absorption peak and edge wavelengths of the former were much longer than of the latter. Hence, the former materials are more suitable than the latter materials as the guest

chromophore for near-IR operations in term of the resonance conditions. Figure 3 show the SH signal intensities as a function of the polarization angles yp of the excitation lights. Here, the p-polarized components of the SH lights was recorded. The similar pump light polarization dependence were reported in the case of the the poled polymer and self-assembled monolayer in the previous studies. Assuming that the



Figure 2. Absorption spectram of DR1 and TCF



orientation of NLO chromophores belong to  $C_{\infty v}$  Figure 3. SHG intensity of the dependence of the symmetry, there are only three nonzero second-order nonlinear optical susceptibilities components,  $\chi_{zzz}$ ,  $\chi_{zii}$ , and  $\chi_{izi}$ . Using these nonzero tensor components, the SH light intensity is expressed as.

$$I_{SH}(\gamma_p) = K \cdot \left| \cos^2 \gamma_p \cdot \left( A \cdot \chi_{zzz} - B \cdot \chi_{izi} \right) + \left( C \cdot \cos^2 \gamma_p + D \cdot \sin^2 \gamma_p \right) \cdot \chi_{zii} \right|^2$$
(1)

A, B, C, D and K are the parameters related to the refractive index, frequencies at the fundamental and SH lights. The details are seen in Ref. 4.

The present pump beam polarization dependence results in this study were well reproduced with Eq. (1). In Table 1, orientation order parameter  $P_2$  as well as the nonlinear coefficients is summarized. The absolute value of the nonlinear coefficient was determined by comparing the SHG signals from the z-cut quartz

Table 1. Various parameters of DR1 and TCF			
	Nonlinear	Onden neuemeten	
	coefficient	Order parameter	
	<i>d</i> [pm/V]	$P_2[-]$	
DR1	0.71	0.82	
TCF	1.42	0.84	

substrates studied with the same geometries. The order parameter  $P_2$  was related to the ratio  $\chi_{zzz}/\chi_{zii}$  as shown in Ref. 4. The nonlinear coefficient of TCF chromophore doped PMMA was almost

as twice as that of the DR1 doped PMMA. Since the order parameter  $P_2$  of the former is almost the same as that of the latter, the difference in the nonlinear coefficients is attributed to the difference in the molecular hyperpolarizabilities between these two NLO chromophores.

#### **Future Scope**

The peak absorption wavwlength of the chromophores is approximately 800 nm. The wavelength is important in the field of the femtosecond technologies, because it matches to the oscillation wavelengths of mode locked Ti: sapphire lasers, one of the most popular femtosecond optical light sources.



Figure 4 dvanced NLO chromophore design

We start developing the new NLO chromophore 23 with larger nonlinearities in the near-IR reagions (Scheme 2). The following two points are taken into accounts to meet the demands. First, the NLO chromophore 23 has TCF-CF3 moiety as the electron acceptors with higher electron-withdrawing abilities than the TCF moiety. Second, the  $\pi$ -conjugation length is much longer than that of TCF chromophore 5 for red-shifting the resonance wavelengths.

It should be noticed that the  $\pi$ -conjugated moiety and the acceptor moiety are linked with a thiophene so as to extend  $\pi$ -conjugation length. It is because of improving the stabilities. In order to



Scheme 2. Synthesis of advanced NLO chromophore.

inducing noncentro-symmetric structures with the poling procedures, the annealing procedures at the high temperatures are unavoidable. Hence, it is ideal for the chromophores to have high thermal decomposition temperatures. So the NLO chromophores having a maximum absorption wavelength in the vicinity of the near infrared have been developed by extending the  $\pi$ -conjugation length while maintaining high thermal stability by introducing a thiophene at the site of  $\pi$ -conjugation. The solubility of the chromophore is poor because they have polar structure. In order to improve the solubility of the chromophores, the long alkyl side chains are introduced



(

Figure 4).

The synthesis proceeds by dividing into three routes. The first route is the production of II-conjugated system bondedwith electron donating moieties 10. The second route is the synthesis of due thiophene linker 14. The third route is the production of TCF-CF3 acceptors. In the present stage, the products 8, 12, 19 are successfully obtained. We will build to the products 10, 14, and 19 and combine them to build the final product 23 in the near future.

#### References

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## Second-order nonlinear optical susceptibility of nonelectrically poled host-guest type polymers Shizuoka University. Department of Material Science

Yasuaki Sato, Yasuaki Tamaki, Kenta Murakami, Kazuma Ito, Wataru Inami, Nobuyuki Mase, Yoshimasa Kawata, Atsushi Sugita.

#### Introduction

Nonlinear optical (NLO) polymers have been studied for long decades, because of their unique properties such as lightweightness, low production costs and easiness in fabrications. Taking advantage of those unique properties, these materials are indispensable for building all plastic optics or optronics. The fundamental structures of NLO polymers consist of complexes between the host and guest materials. The nonlinear light-matter interactions occur in the guest chromophores, while the host polymers fix the position of the guest materials. Basic configuration of guest chromophores often have so-called push-pull structures, in which  $\pi$ -conjugated systems are sandwiched between electron-donating and electron-accepting moieties. These materials exhibit large nonlinearity, when they are operated by the light waves with near-resonance frequencies. Even though a lot of novel NLO chromophores have been developed, a lot of efforts still have been made to design and synthesize new chromophores.

Recently, several NLO chromophores were developed suitable for the operation in the near-IR regions. These new chromophores seem to meet demand for the applications in fast telecommunication systems. Especially, the NLO chromophores with tricyano furan moieties attract great interests because of its large nonlinearity in the near-infrared regions. Most of the previous studies paid attentions to their third order nonlinearity for fast optical modulator and optical switching systems. Supposed that they were oriented in the polar configurations, the polymers with the TCF chromophores are promising as second order nonlinear optical materials for the operations in the near-infrared regions.

In as-prepared conditions, the NLO polymers do not exhibit second-order nonlinear optical susceptibility for the wavelength conversions. It is because the NLO choromophores are distributed randomly and the materials have symmetric structure. In order to break the centro-symmetry,

so-called polling procedures are conducted. In the conventional poling procedure, the DC electric fields as high as 100 kV/mm are applied inside the materials at the temperature above the glass transition points (Tg). During the poling procedure, the dielectric breakdown occurs frequently and it is quite difficult to prepare the second-order NLO susceptibilities in large volume and wide areas. In our previous study, noncentro-symmetric structures were successfully induced in NLO polymers with nonelectrical poling method. All we had to do was to



Figure 1. Triciano furan (TCF) chromophore was investigated in present study.

sandwich the polymeric materials between the electrodes with different surface energies and to anneal at the temperatures higher than the glass transition points. We demonstrated the nonelectrical poling effects in the materials with the Disperse Red 1 (DR1), one of the most popular NLO chromophores. The nonelectrical poling method is universally applicable for the materials other than the systems with the DR1.

In present study, we will report the second-order nonlinear optical properties of host-guest polymers with TCF chromophores as a guest. The polar ordering of the chromophores were obtained with the nonelectrical poling effects proposed in our previous study. Our experimental results proved the second harmonic conversion efficiency was approximately two times higher than that with DR1 at 800 nm.

#### Experiment

The TCF chromophore was synthesized with the method reported in previous studies. Poly (methyl methacrylate) (PMMA), one of the most popular host materials for the NLO polymers was selected. The concentration of the chromophores in the nonlinear optical material was 10 wt%. The NLO polymers were coated on the glass substrates with spin coating methods. The films with the thickness between 100 nm and 2 µm were prepared. The DR1 doped PMMA was also prepared as a reference. The nonelectrical poling procedure reported in our previous study was conducted to induce the non-centrosymmetry in the materials.



Figure 2 Linear absorption spectrum of TCF chromophores and DR1 doped PMMA

The second order nonlinear optical susceptibility was characterized with the second harmonic methods. The light source was optical pulses emitted from a Ti: sapphire regenerative amplifier. The wavelength, the pulse energy, and the pulse width were 800 nm, 1 mJ, and 150 fs, respectively at 1 kHz-repetition frequencies. The polarization of the excitation light is controlled with a half wave plate, and the polarization of the SH lights was resolved by Glan-Tellar prism. The SH lights was detected by a photomultiplier tube after separating from unconverted fundamental components with color glass filters.

#### Result and discussion

Figure 2 shows linear absorption spectrum of the TCF chromophores doped films as well as the DR1 doped PMMA films. The absorption peak of the TCF chromophores doped PMMA was  $\lambda max = 558$  nm, while that of the DR1 doped PMMA was  $\lambda max = 494$  nm. The former was 60 nm longer than the latter. Since the conjugation lengths of those two chromophores were almost comparable, the difference in the resonance conditions is likely due to the difference in the degree of the electron

acceptances between these two materials.

Figure 3 shows the SH signals intensity from the TCF chromophores doped PMMA's. The measurements were conducted during a heating subsequent cooling procedure and atthe temperatures between 40 and 150  $^\circ C$ . The temperature changing rate was  $3^{\circ}$ C/ min. In the as-prepared conditions, the sample did not exhibit almost any SH signals. In the heating steps, the samples emitted the SHsignals  $\mathbf{at}$ the temperature higher than  $100 \,^{\circ}\mathrm{C}$ . The glass transition point of the PMMA was approximately 100  $^{\circ}$ C. It is concluded that the re-distributional



Figure 3. Temperature dependence of the emits SHG intensity of the TCF chromophores doped in PMMA

motions of the polymer chain segments promoted forming the non centro-symmetric structures in the host materials. The polar order of the NLO chromophores are likely accompanied by the polarization formations of the host polymers. Once the non centro-symmetric structures in the NLO

polymers are formed, they existed stably. Once the noncentrosymmetric structures in the NLO polymers are formed, they existed stably and remained even after cooling the materials below  $T_{g}$ . The present experimental results indicated that nonelectrical poling procedures are suitable for the NLO polymer systems with new TCF chromophores as a guest.

Figure 4 shows the p<sup>-</sup> and s<sup>-</sup>polarized SH signal intensities as a function of the polarization angles yp of the excitation lights. Here, the thickness of the sample was 700 nm,



Figure 4. Excitation light polarization dependence of the SH signal intensities emitted from the TCF chromophores doped PMMA.

and it was annealed at 140 °C. The curves were quite similar to those of poled polymer and self-assembled monolayers (SAM) in the Langmuir-Blodgett films. In the poled polymer and the SAM, the orientational order of the NLO chromophores is expressed with C $\infty$ v symmetry (Figure 5). The chromophores are slightly tilted against the normal of the substrate, while they are distributed randomly in the plane of the substrate surface. In the symmetry, there are only three non-zero macroscopic nonlinear optical susceptibility components as  $\chi_{zzz}$ ,  $\chi_{zii}$ , and  $\chi_{izi}$  (*i*=*x* or *y*). Assuming that  $\beta_{\zeta\zeta\zeta}$  is the predominant tensor component the molecular hyperpolarizability, the macroscopic nonlinear optical susceptibility components are expressed as Eq. (1) - (3).

$$\chi_{zzz} = N_s \cdot L_z(2\omega) \cdot L_z^2(\omega) \cdot \left\langle \cos^3 \Theta \right\rangle \cdot \beta_{\xi\xi\xi}$$
(1)

$$\chi_{zii} = \frac{1}{2} N_s \cdot L_z(2\omega) \cdot L_i^2(\omega) \cdot \left\langle \cos \Theta \cdot \sin^2 \Theta \right\rangle \cdot \beta_{\xi\xi\xi}$$
(2)

$$\chi_{izi} = \frac{1}{2} N_s \cdot L_i(2\omega) \cdot L_z(\omega) \cdot L_i(\omega) \Big\langle \cos \Theta \cdot \sin^2 \Theta \Big\rangle \cdot \beta_{\xi\xi\xi}$$
(3)

Here,  $\zeta$  is the molecular long axis and  $\Theta$  is the average molecular tilt angle. Ns is the density of the chromophores, and  $L_i(\omega)$  represents the local field factor in the direction at the *i* frequency  $\omega$ . Using these tensor components, the p- and s-polarized SH are expressed with Eq. (4) and (5).

$$I_{SH}(\gamma_{p}, \gamma_{a} = 0) = K \cdot \left| \cos^{2} \gamma_{p} \cdot (A \cdot \chi_{zzz} - B \cdot \chi_{izi}) + (C \cdot \cos^{2} \gamma_{p} + D \cdot \sin^{2} \gamma_{p}) \cdot \chi_{zii} \right|^{2}$$
(4)  
$$I_{SH}(\gamma_{p}, \gamma_{a} = \frac{\pi}{2}) = K \cdot \left| E \cdot \sin \gamma_{p} \cos \gamma_{p} \cdot \chi_{yzy} \right|^{2}$$
(5)

Here, *A*, *B*, *C*, *D*, *E*, and *K* is the parameter related to the incident angle of the pump beam, and the refractive index of the fundamental and SH light waves. The present experimental results were reproduced well with the model expressed with Eq. (4) and (5). The average molecular tilt angle  $\Theta$  is related to the ratio of the nonlinear susceptibility tensor components as  $\chi_{zzz}/\chi_{zii}$  as Eq. (6) and (7).

$$\tan^{2} \Theta = \frac{2}{\chi_{zzz} / \chi_{zii}}$$

$$P_{2}(\Theta) = \frac{3\langle \cos^{2} \Theta \rangle - 1}{2}$$
(6)
(7)

Using the fitted values of  $\chi_{zzz}/\chi_{zii}$ , the average molecular tilt angle and order parameter are determined as  $\Theta = 17.7^{\circ}$  and  $P_2(\Theta) = 0.862$ .

Figure 6 shows the film thickness dependence of nonlinear coefficient of TCF chromophores and DR1 doped PMMA. The absolute value of the nonlinear coefficient deff was determined by comparing with the data of the z-cut quartz plate measured at the same spectroscopic geometry. The nonlinear coefficients of the both the materials decrease monotonously as the film thickness becomes thicker. The nonlinearity of the materials with the TCF chromopores is greater than that of DR1 doped PMMA. On the other hand, the order parameter of the TCF chromophores doped thin film was almost the same as that of DR1 doped the thin film. This result would indicate that TCF choromophores have resonance condition is closer to the excitation light and nonlinearity of chromophores itself is large.



Figure 6. Nonlinear coefficients (a) and order parameter (b) of the TCF chromophores doped and DR1 doped PMMA as a function of film thickness.

#### Conclusion

In the study, the second-order nonlinear optical susceptibility of the TCF chromophores doped in the PMMA was reported. The material exhibited the second-order nonlinear optical susceptibility simply by annealing at a temperature higher than Tg. The nonlinearity of the materials was twice as large as that of the DR1 doped PMMA at the operating wavelength of 800 nm. The materials are promising as the second-order nonlinear optical materials for all-plastic optronics in the near-infrared operations.

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#### Nonlinear optics polymers excited by surface plasmon enhanced field in Kretchmann configuration

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#### Introduction

Optical properties of meal thin films or metal nanostructures related to surface plasmon resonance, have attracted great interests. Upon the photo excitations of the surface plasmons the intense optical fields appear in the vicinity of the metal surface and the field intensities are two or three magnitudes higher than that of the incident light waves. Taking advantage of the intense optical fields, due to the surface plasmon, a lot of novel optics and optronics for nanotechnologies and nanosciences are proposed. Especially, a lot of researchers pay attentions for their applications of the drives for high energy quantum beams. The intensity of the surface plasmon enhanced optical fields pumped by a few nJ femtosecond optical pulses is high enough to generate higher order harmonics or to accelerate electrons with keV kinetic energies.

On the other hand, there are not so many reports dealing with their applications to the lower order nonlinear optics such as second order or third order nonlinear optics. It is probably because the small nonlinearities of the metals were quite small because of their conductivities. It seems to be effective to fabricate materials with large nonlinearity on the metal surface to enhance the nonlinearity of the metal surface where the surface plasmon-enhanced optical field is created.

In the present study, we will report the second-order nonlinear optical interactions between the nonlinear polymers and the surface plasmon enhanced optical fields. Our experimental result indicated that second-order nonlinearity of the metal surface was efficiently enhanced by coating the polymer materials.

#### Theory

First, the surface plasmon resonance conditions for the silver thin films coated with the NLO polymer films were examined theoretically with a multiple wave interference model. The model system consisted of four layers, that is, a BK7 glass, the silver thin films, the NLO polymer thin films and the air. In the calculations, the refractive indexes of the BK7, the silver, the NLO polymer and the air were 1.51078, 0.148431 and 1.0, at 800 nm respectively. The thickness of the silver film was fixed at  $d_{Ag}$ =40 nm while determined by changing  $d_{polymer}$  the thickness of the NLO polymers were changed between 0 and 100 nm.

Figure 1 (b) shows the reflectivity of the systems against the incidence angles of the excitation light. The dip structures, corresponding to the surface plasmon resonance, are seen in the curves. The position of the dip is dependent on the thickness of the NLO polymer layers and it becomes wider as the film thickness is thicker. Fig. 2 (a) shows the field intensity inside the polymer layers. The field intensity is represented by the values at the deepest positions of the dip. Assuming that the extinction coefficient of the NLO polymers is negligible, the field intensity of the optical field is not attenuated inside entire the polymer layers. The field intensity becomes lower as the polymer



Figure 1 (a) Schematics of model system for determining the surface plasmon resonance conditions. (b) Incidence angle dependence of the reflectivity of the polymer coated Ag films

film thickness is wider.

The second harmonic (SH) intensities are expressed with an Equation (1).

$$I_{SHG} = \eta^4 E_{tn}{}^4 l^2 d_{NLO}{}^2 \cdots (1)$$

Here,  $\eta$ , l, and  $d_{NLO}$ , are the enhancement factor of the incident optical field  $E_{in}$ , the polymer thickness and the nonlinearity of the nonlinear coefficient polymers, respectively. Assuming that the nonlinearity  $d_{NLO}$  is independent of the polymer layer thickness, the SH intensity  $I_{SH}$  is dependent on the polymer film thickness as shown in Fig. 2(b). The curve indicates that SH conversion efficiency is the highest at the polymer thickness of d=50 nm. The SH conversion efficiencies were determined by the balance between the enhancement factor of the electric fields and the light – matter interaction lengths.



Figure 2(a) Increase the intensity of the optical field in the portion of each polymer film thickness. (b) A secondary non-linear optical polarization is excited in the polymer of various thicknesses.

#### Experimental

The surface plasmons were excited with the attenuated total reflection method using a prism. The samples for nonlinear optical spectroscopy consisted of three-layers. The silver layers, were deposited on the flat surface of the BK7 glass prism, above which the NLO polymer films were deposited.The silver thin film was deposited by a vacuum evaporation method.The thickness of the silver films was 40 nm. On the other hand, the polymer films was prepared by a spin coating method. By controlling the concentrations and rotational speeds, the thickness of the polymers were controlled between 10 and 100 nm .The NLO polymers consisted of host –guest complex structures. The guest chromophores for nonlinear light-matter interactions, was Disperse Red 1, play, while the host materials for fixing the positions of the guest clomophores was poly (methyl methacrylate). In general, the materials for second order nonlinear optical susceptibilities should be lack of inversion symmetry. In the present study, the non-centro symmetric structures were induced with nonelectrical poling effects proposed in our previous studies. The polar ordering of the NLO

chromaphores was induced by taking advantage of the surface alignment effects and polarization orientations of the host polymers.

Fig. 3 shows the experimental apparatus for measuring the second harmonic generations under the surface plasmon resonance conditions. The excitation light source is femtosecond optical pulses from Ti:sapphire regenerative amplifiers . The center wavelength, the pulse width and the pulse energies were 800 nm, 150 fs, 1 mJ, respectively. The beam diameter on the sample surface was approximately  $\varphi$ 5mm. The pulse energies of the excitation lights were attenuated with natural



Figure 3 An experimental apparatus system for observing the second harmonic generation in a nonlinear optical polymer optical field excited by surface plasmon enhanced optical fields.

densities filters and it was 20 µJ on the samples .The SH signals were detected with a photo multiplier tube after separating the fundamental lights with a color glass filter. The pump beam polarization angle dependence of the SH signal was studied, while their polarization angle dependence was also resolved.

#### **Results and Discussion**

Figure 4 (a) shows the SH signal intensity as a function of the incidence angles of the excitation lights. The polarization of the excitation beams was p-polarized and the p-polarization components of the SH signals were recorded. Here, the data correspond to the samples with the polymer film thickness of 15 and 40 nm. As a reference, the data of the polymer uncoated silver films uncoated with the polymer films is also shown. Both of the polymer–coated and uncoated silver films exhibit a dip structure at the critical angles  $\theta_{sp}$ , where the surface plasmon resonance conditions are satisfied. The polymer uncoated silver film exhibit the dip at  $\theta_{sp} = 41.2$ °. The position of  $\theta_{sp}$  depends on the polymer film thickness and it is wider as the polymer film thickness is thicker. The width of the dips was wider as the polymer film thickness is thicker. These observations are consistent with the expectation indicated with the theory based on the multiple wave interference models. On the other hand, the samples emitted the SH signals and the intensities of the signal were the highest at

the critical angles  $\theta_{sp}$ .

Figure 4 (b) is plotted as a function of the intensity of the excitation light intensity  $I_{pump}$  SHG. Hence, it is concluded that the SH signal was excited by the surface plasmon enhanced optical fields. The SH signal intensities were plotted as a function of the excitation



Figure 4(a) The reflectivity and SHG from the polymer coated Ag films as a function of the incidence angles. (b) Excitation pump power dependence of the SHG signals.

light  $I_{pump}$  was proportional to the square of the excitation light intensities  $I_{pump}$ . The SH signal intensities from the polymer – coated Ag films were much higher than those from the polymer – uncoated Ag films. The second order NLO susceptibilities of the polymer – uncoated Ag films were related to the nonlinear polarizations excited by the surface plasmon enhanced optical fields in the polymers.

Fig. 5 shows the SH signal intensities of the polymer coated Ag films as a function of the polymer film thickness. The data is represented by the value at the critical incidence angle  $\theta_{sp}$ . The SH conversion efficiency was the highest from the sample with the 40 nm polymer film thickness. The present experimental results were quantitatively consistent with the expectations presented by the models using



Figure 5 SHG intensities as a function of the polymer of various thicknesses

the multi wave interference. However, the curve can not be reproduced well with the theoretical results shown in Fig. 2(b). The discrepancy between the experimented and theoretical results is probably not substantial. As one of the probable reason, the polymer films are not uniform and the

roughness may stimulate unexpected enhancement of the optical fields.

Figure 6 shows the dependence of the polarization angle of the excitation light  $\gamma_p$ . Here, the thickness of the polymer film was 15nm. The experimental results are well reproduced with function  $\cos^4\gamma_p$ . The result indicates that the non-linear optical polarizations were excited only by the *p*-polarized pump beams. The polarization of the SH signal was resolved with the polarizer



Figure 6 (a) Polarization dependence of the excitation light polarization dependence of second harmonic light intensity (b) the second harmonic light.

and it is shown in Fig. 6(b). The data is well reproduced by  $\cos^2\gamma_a$  function. This result indicates that the SHG signal is *p*-polarized.

In general, second-order nonlinear susceptibility of the NLO host - guest polymers is expressed with a linear combination, three independent tensor components of  $d_{33}$ ,  $d_{31}$  (= $d_{32}$ ),  $d_{24}$  (= $d_{13}$ ). The present  $\gamma_p$  and  $\gamma_a$  dependence means that the nonlinearity is only related to the  $d_{33}$  components. The *p*-polarized components of the pump beams excite the surface plasmon enhanced optical fields in the direction normal to the surface of the Ag films. The nonlinear polarization occurred in the direction normal to the Ag film surface in the NLO polymer.

#### Conclusions

In this study, we have examined the second-order nonlinear optical susceptibility of surface plasmon resonance conditions in the silver thin film coated with polymer. The second order nonlinear optical susceptibilities of the polymer can be excited with the surface plasmon enhanced optical fields in the Ag films. The SH conversion efficiency the highest SH conversion efficiency was obtained from the sample with the 40 nm polymer films. The optimized conditions for the SH conversion were determined by the balance between the polymer – optical field interaction lengths and the enhancement factor of the optical fields.

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# Development of rare earth doped $Y_2O_3$ fluorescent thin film for electron beam assisted optical microscope

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#### Abstract

Here we report the development of luminescence thin film for Electron-beam eXitation Assisted (EXA) optical microscope system as new novel super-imaging microscope. The luminescence thin films consisting of  $Eu^{3+}$  doped Y<sub>2</sub>O<sub>3</sub> were prepared with an electron beam evaporation method. The films with the thickness between 80 nm and 200 nm were prepared and they were annealed at the temperatures between 500°C and 1000°C. The intensity of the cathode luminescence signals were recorded as functions of the film thickness and the electron acceleration voltages. The optimized conditions for fabricating the luminescence films will be reported in terms of the film thickness and the accelerating voltage and the annealing temperatures.

#### Introduction

Several super-imaging microscopy techniques, which enable us to records the images with the spatial resolutions smaller than diffraction limit, have been studied extensively. Two-photon excitation fluorescence microscope <sup>[1]</sup>, second and third harmonic optical microscopes <sup>[2]</sup>, Coherent Anti-Stokes Raman Scattering (CARS) microscope <sup>[3]</sup> are some of the most promising ones. Since we can operate the microscopes in the air atmosphere, they are suitable for observing biomedical samples, such as living cells and tissues. However, the in spatial resolution is at most few hundred nanometers.

Recently, we proposed  $\underline{E}$  lectron-beam  $\underline{eX}$  aitation Assisted (EXA) optical microscope <sup>[4]</sup> as new super imaging microscope. The light sources of the EXA microscope cathode luminescence light emitted by inelastic scattering of the high energy electron beam. Since de Broglie wavelengths of the electrons with ~keV kinetic energies is much smaller than angstrom. In principle they can be focused in the area smaller than nanometer scales. Hence, the luminescence light waves should spread in the area much smaller than the diffraction limit just after they are emitted from the materials. In our previous study, we made an examination about the spread of the luminescence in the thin films excited by electron beams with sever keV kinetic energies with Monte Carlo simulation methods.



Figure1 Schematics of EXA microscope

When the film thickness was thinner than 50 nm the spread of the luminescence was smaller than 50 nm.

It should be noticed that EXA microscope enables us to measure the images in the air atmospheres. The substrates separate the vacuum atmosphere for air atmosphere. The specimens are put on the front side of the luminescent films, while the electron beams are irradiated from the back in the vacuum. Supposed that the film thickness is narrower than the penetration depth of the electron beams, the luminescence light waves penetrate to the front side of the substrate. In our previous study, we chose  $Si_3N_4$  substrate as a luminescent films. The  $Si_3N_4$  is famous as the constitutional materials. The  $Si_3N_4$  substrates with the thickness as narrow as 50 nm is stiff enough to separate the vacuum atmosphere from the air atmosphere.

In our previous studies, we succeeded in imaging the polystyrene latex beads with  $\sim 50$  nm diameter with the sufficient spatial resolutions. The lights were due to the luminescent from the Si<sub>3</sub>N<sub>4</sub> substrate was the near-ultraviolet. If the EXA microscopes are operated with visible luminescence lights their applications will covers much fields.

Some of the rare-earth doped materials seem to satisfy the demands for the visible luminescent wider for the EXA microscope films. There materials have been used as the visible light emitters for the florescent light tube. In the present study, Eu - doped  $Y_2O_3$  was chosen as the visible



Figure 2 Schematics of luminescent thin films for EXA microscope.

luminescent emitters for the EXA microscope. The films were fabricated on the  $Si_3N_4$  substrates as shown in Fig. 2. We will also optimized conditions for the demonstrations of the EXA microscope with the  $Y_2O_3$  luminescent films. The fabricating the thin films will be reported.

#### Experimental

The Y<sub>2</sub>O<sub>3</sub>: Eu thin films were fabricated on Si<sub>3</sub>N<sub>4</sub> substrates with electron beam evaporation method. First, the powders of Y<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub> were mixed and pressed into pellet forms. The pellets were sintered at 1000°C. The concentration of the Eu<sup>3+</sup> ion in the material was 2 mol %. The evaporation was done in the vacuum chamber in which the pressure was set to approximately 10<sup>-6</sup> Torr. The electron beams were accelerated under the conditions of 4kV and 50 mA current. The film thickness was monitored by a quartz crystal microbalance method. The degree of crystallinity of luminescent thin films was low because the oxygen vacancies. The films were annealed at the temperatures between 500 and 1000°C under the flow of the oxygen gas for 3 hours in order to fill the vacancies and improve the crystallinities.

The structural properties of the films were characterized with X-ray diffraction patterns (XRD) and Atomic Force Microscope (AFM). The optical properties of the films were studied with a cathode luminescence spectroscopy. Finally, the imaging the polystyrene (PS) latex beads with  $\varphi \sim 100$  nm was conducted with the Y<sub>2</sub>O<sub>3</sub>: Eu luminescence thin films.

#### **Results and Discussion**



Fig. 3 CL measurement (a)CL intensity dependence of the acceleration voltage which is emitted from the phosphor thin film by electron beam irradiation. (b) Luminescence image of the thin film emitters. (c)the dependence of the emission intensity for the thickness of the thin film emitters.

Fig. 3 (a) shows the acceleration voltage dependence of the CL intensity from  $Y_2O_3$ : Eu luminescence thin films on the  $Si_3N_4$  substrates. Fig. 3 (b) shows the images of the luminescence films irradiated by the electron beams accelerated with the different voltages. Here, the thickness of the films was 200 nm. The films emitted the luminescence signals at the acceleration voltage higher than 2 kV. The electron beams with the kinetic energies smaller than 2kV could not penetrate the  $Si_3N_4$  substrates and could not excite the Eu<sup>3+</sup> ions in the luminescent thin films.

Fig. 3 (c) shows the CL intensities against the film thickness the  $Y_2O_3$ : Eu film thickness. The accelerating voltage was 5kV. Only the films with the thickness thicker than 85 nm emitted the CL signals.

Fig. 4 (a) shows the picture of  $Y_2O_3$ : Eu thin films annealed at the different temperatures between 500 and 1000 °C. The thickness of the  $Y_2O_3$ : Eu films were 200 nm. The films were irradiated by the ultraviolet lights with 254 nm from a high pressure Hg lumps. Film emitting stronger photoluminescence has a tendency of brighter cathode luminescence. The films annealed at higher temperatures emitted brighter photo luminescence.

Fig.4 (b) shows the X - ray diffraction patterns of the  $Y_2O_3$ : Eu thin films annealed at different



Figure4 (a) XRD pattern of Y2O3:Eu thin film annealed at different temperatures. Image of Y2O3:Eu thin films irradiated by the black lights. The samples annealed at different temperatures are shown

temperatures. The as-deposited films were also shown as a reference. After the annealing procedures, all the diffraction peak intensities increased. The peak positions of the thin films were almost the same as those of the powder samples. Hence, the crystal structures of the thin films were cubic one like that of the powder samples <sup>[5]</sup>. It should be remarkable that was shifted during the annealing procedure. The result indicated that the crystallinity of the thin films were improved fill by the oxygen atoms in the vacancies in the crystals. Furthermore, the peak positions of the (222) diffraction was different from that of powder samples. Using Bragg equation, the lattice spacing due to the (222) diffraction were determined to be d = 6.13 nm for the powder sample and d = 6.08 nm for the film sample.

The Y<sub>2</sub>O<sub>3</sub> crystal belongs to the cubic groups with a unit length a = 10.60 Å. The lattice spacing along (222) plane is 15.00 Å. On the other hand, the Si<sub>3</sub>N<sub>4</sub> crystal belongs to the hexagonal groups with unit lengths a = 7.61 Å, and c = 2.90 Å. The lattice spacing of the (222) plane of Y<sub>2</sub>O<sub>3</sub> is d is almost as twice as the unit length a = 7.61 Å of the Si<sub>3</sub>N<sub>4</sub> crystal. It is natural to conclude that the (222) plane of the Y<sub>2</sub>O<sub>3</sub> crystal is jointed on the (001) plane of Si<sub>3</sub>N<sub>4</sub> crystals. In the junction, the lattice mismatch between two crystals is 1.40%. In general, when the degree of the mismatch is

larger than 1%, the lattice distortion is significant at the boundaries. In the present case, the lattice mismatch is larger enough to make significant distortions in the boundary area.

Fig. 5 shows the AFM images of thin films annealed the at 500and temperatures between  $1000 \ ^{\circ}\mathrm{C}$ . The images of the as deposited films are also shown as a reference. The measurements were conducted in the square area 500  $\times$ 500The surface nm. of the as-deposited films consisted of the aggregates of the small particles



Fig. 5 AFM (a) As-deposited samples and (b) the samples annealed at 500, (c) 700, (d) 900, and (e) 1000 °C.

with after the annealing procedures, the particle size became larger as the annealing temperatures were higher. During the annealing procedures, the atoms diffused so as to grow the grain size of the particles.

Finally, the EXA microscope image of the polystyrene latex was shown in Fig. 6 (a). Here, the polystyrene latexes with average diameter of 100 nm were scattered on the  $Y_2O_3$ : Eu thin films. The SEM image of the same sample is also shown in Fig. 6 (b). The accelerating voltage of the electron beams was 5 kV and the electron current was 270 pA. In both of the pictures, the white spots due to

the PS latexes can be seen at the same corresponds positions. Hence, it was concluded that the spatial resolution of the EXA microscope with  $Y_2O_3$ : Eu thin films was at least 200 nm, and the microscope could record the image with the sub diffraction resolution on the present stage.

#### Conclusions

In this presentation, we report the fabrications of  $Y_2O_3$ : Eu thin films as the luminescent emitters



Fig. 6 Spatial resolution evaluation when putthe latex beads on a substrate (a) SEM image(b) EXA image

for the EXA microscope. Our experimented result indicates that the cathode luminescence from the  $Y_2O_3$ : Eu thin films are suitable for the light sources for the EXA microscope. The optimized fabrication conditions were determined in terms of the film thickness and the annealing temperatures. The conversion efficiency of the cathode luminescence was higher at the higher annealing temperatures. The oxygen vacancies were filled and the crystallinity improved more effectively at the higher annealing temperatures. The intensity of the CL signals is also dependent on the accelerating voltage, and the luminescence occurred only at the accelerating voltage higher the 5 kV. The intensity of the CL was also dependent on the accelerating voltage and the most optimized conditions in the present stage has not yet to be determined, and we will report the further progress in the presentation.

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