

JAERI-Review

95-015



ANNUAL REPORT OF THE OSAKA LABORATORY  
FOR RADIATION CHEMISTRY  
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE  
(No. 28)  
(April 1, 1994 – March 31, 1995)

October 1995

Osaka Laboratory for Radiation Chemistry

日本原子力研究所  
Japan Atomic Energy Research Institute

本レポートは、日本原子力研究所が不定期に公刊している研究報告書です。

入手の問い合わせは、日本原子力研究所技術情報部情報資料課（〒319-11 茨城県那珂郡東海村）あて、お申し込みください。なお、このほかに財団法人原子力弘済会資料センター（〒319-11 茨城県那珂郡東海村日本原子力研究所内）で複写による実費領布をおこなっております。

This reports are issued irregularly.

Inquiries about availability of the reports should be addressed to Information Division Department of Technical Information, Japan Atomic Energy Research Institute, Tokaimura, Naka-gun, Ibaraki-ken 319-11, Japan.

© Japan Atomic Energy Research Institute, 1995

編集兼発行 日本原子力研究所  
印 刷 ニッセイエプロ株式会社

JAERI-Review 95-015

Annual Report of the Osaka Laboratory for Radiation Chemistry  
Japan Atomic Energy Research Institute  
(No.28)

April 1, 1994-March 31, 1995

Osaka Laboratory for Radiation Chemistry

Takasaki Radiation Chemistry Research Establishment  
Japan Atomic Energy Research Institute  
Mii-minami-machi, Neyagawa-shi, Osaka-fu

(Received August 30, 1995)

The annual research activities of Osaka Laboratory for Radiation Chemistry, JAERI during the fiscal year of 1994(April 1, 1994-March 31, 1995) are described.

The research activities were conducted under two research programs: the study on laser-induced organic chemical reactions and the study on basic radiation technology for functional materials. Detailed descriptions of the activities are presented as reviews on the following subjects: laser-induced chemical transformation, laser-induced reaction of polymer surface, microprocessing by radiation-induced polymerization, preparation of fine metal particles by gamma ray irradiation, and electron beam dosimetry. The operation report of the irradiation facilities is also included.

Keywords : Excimer Laser, Electron Beam,  $\gamma$ -ray, Photochemical Reaction,  
Polymer Modification, Polymerization, Dosimetry.

平成6年度大阪支所年報 (No. 28)  
1994年4月1日～1995年3月31日

日本原子力研究所高崎研究所  
大 阪 支 所

(1995年8月30日受理)

本報告書は、大阪支所において、平成6年度に行われた研究活動をまとめたものである。主な研究題目は、レーザー有機化学反応の研究と放射線加工技術の基礎研究であり、本報告書では以下の研究活動について詳細に述べる。レーザー光による物質変換、レーザー光による高分子の表面化学反応、放射線重合による微細加工、放射線による金属微粒子の合成、線量測定および照射施設の運転・管理。

## Contents

|     |                                                                                                                                                                                                                                                                            |    |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| I   | Introduction.....                                                                                                                                                                                                                                                          | 1  |
| II  | Current Research Activities .....                                                                                                                                                                                                                                          | 3  |
| 1.  | Irradiation of Tartaric Acid with Circularly Polarized Laser Beam<br><i>Y.Shimizu and S.Kawanishi</i> .....                                                                                                                                                                | 3  |
| 2.  | Excimer Laser-induced Surface Photochemical Reactions of Fluoropolymer<br><i>N.Ichinose, M.Maruo, A.Okada and S.Kawanishi</i> .....                                                                                                                                        | 6  |
| 3.  | Surface Treatment of Tetrafluoroethylene-perfluoroalkyl Vinyl Ether<br>Copolymer(PFA) by Excimer Laser Irradiation in Contact with Aqueous<br>Ammonia Solution<br><i>A.Okada, N.Ichinose and S.Kawanishi</i> .....                                                         | 15 |
| 4.  | Excitation Wavelength Effect on Laser-induced Dehydrochlorination<br>of poly(vinyl chloride)(PVC)Film<br><i>Y.Izumi, M.Maruo, S.Kawanishi, N.Ichinose and T.Yamamoto</i> .....                                                                                             | 19 |
| 5.  | Improvement of Wettability of PTFE Membrane by Excimer Laser Irradiation<br>with an Aqueous Solution of Hydrogen Peroxide:Effect of Impregnating<br>Temperature and Laser Fluence<br><i>T.Tanaka, H.Mishima, T.Nishino, M.Nishii, S.Sugimoto<br/>and S.Kawanishi</i> ..... | 22 |
| 6.  | Excimer Laser Irradiation of Fluoropolymer Films Coated with Sodium<br>Anthraquinone-2-sulfonate as an Ultraviolet Absorbent for Improvement<br>of Adhesive Property<br><i>T.Nagase, M.Endo, Y.Koshino, M.Nishii, S.Sugimoto<br/>and S.Kawanishi</i> .....                 | 25 |
| 7.  | Separation of Silicon Isotopes by Infrared Multiple-photon Decomposition<br><i>S.Sugimoto, A.Isomura, S.Arai and S.Kawanishi</i> .....                                                                                                                                     | 28 |
| 8.  | Excimer Laser-assisted Fluorination of Tooth Enamel Affording<br>Acid-resistance<br><i>C.Miyazawa, M.Kokubun, M.Amano, S.Hamada, T.Shimizu,<br/>S.Sugimoto and S.Kawanishi</i> .....                                                                                       | 32 |
| 9.  | The Effect of Excimer Laser Irradiation on Growth of Oral Bacteria<br><i>S.Hamada, Y.Akiyama, M.Kokubun, C.Miyazawa, M.Amano,<br/>T.Shimizu, S.Sugimoto and S.Kawanishi</i> .....                                                                                          | 35 |
| 10. | Radiation-induced Polymerization of Thin Epoxyacrylate Films<br><i>Y.Nakase, A.Nakamune and I.Kaetsu</i> .....                                                                                                                                                             | 37 |

|     |                                                                                                                                                          |    |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 11. | Formation of Fine Particles from Aqueous Solution of Silver Ion by $\gamma$ -ray Irradiation<br><i>Y.Nakase, K.Ushiroda, I.Kaetsu and M.Hatada</i> ..... | 41 |
| 12. | A Study on Defects in Electron-irradiated Silicon<br><i>L.Liu, Y.Nakase, T.Mitamura and M.Terasawa</i> .....                                             | 45 |
| 13. | Charge Accumulation of Open-cell Type Polyethylene Foam by Electron Beams<br><i>N.Kotani and Y.Nakase</i> .....                                          | 50 |
| 14. | Simulation of the Absorbed Dose in Thin Films Irradiated by 300-keV Electrons<br><i>T.Kijima, Y.Nakase and K.Nakato</i> .....                            | 54 |
| 15. | Operation and Maintenance of Irradiation Facilities<br><i>K.Nakato</i> .....                                                                             | 59 |
| III | List of Publications .....                                                                                                                               | 60 |
| 1.  | Published Papers .....                                                                                                                                   | 60 |
| 2.  | Oral Presentations .....                                                                                                                                 | 61 |
| 3.  | Patent Applications .....                                                                                                                                | 63 |
| IV  | List of Cooperative Studies .....                                                                                                                        | 65 |
| V   | List of Personnel .....                                                                                                                                  | 66 |

## I. Introduction

The annual research activities of Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, during the period of April 1994 - March 1995, are presented in this report.

The research activities were conducted under the following two research programs: i) The Study on Laser-Induced Organic Chemical Reactions and ii) The Study on Basic Radiation Technology for Functional Materials, with the support of Operation and Maintenance Group of the irradiation facilities. The total number of people working in the laboratory was 25 including visiting research collaborators from industrial companies and student research assistants from universities. JAERI funded expenditures during the period amounted to ca. 64 million yen, excluding personnel expenses.

The study on laser-induced organic chemical reactions was initiated in 1988 as an advanced frontier subject to utilize lasers to chemistry. Under this program, three research subjects were studied in this fiscal year: (1) laser-induced chemical transformation, (2) laser-induced surface photoreaction of polymers, and (3) photochemical separation of stable isotopes. In the subject of (1), a multiphotonic process was examined for optical resolution of organic compounds by the use of circularly polarized laser light. Surface modification of fluoropolymers is a topic of the subject (2), where improvement of the surface properties such as adhesivity or wettability as well as mechanistic feature involved therein was studied. The subject (3) has been started with multiphotonic photodecomposition of a fluorinated silicon compound by the use of IR laser, which aims at performing in a preparative scale.

Concerning the research program of the basic study on radiation technology for functional materials, three research subjects were studied: (1) microprocessing by radiation-induced polymerization, (2) preparation of fine metal particles by gamma ray irradiation, and (3) electron beam dosimetry. Polymerization properties of spin-coated epoxy oligomer film was studied for application to microelectronics in the subject of (1). Growth of metal particles was studied for solutions containing silver and paradium ions and silver ion alone in the subject of (2). Some physical properties of materials induced by electron beam including low energy electron beam dosimetry were examined through experimental and computational approaches. Cooperative research programs with universities (7 groups) and joint research programs with industrial companies (4 groups) were conducted under our research subjects.

In the operation and maintenance of the irradiation facilities, the cobalt gamma ray source and two electron accelerators of 800 keV and 2 MeV were operated without any serious trouble for irradiation besides renewal of a device for handling of the cobalt

source and a power supply of the Van de Graaff accelerator. Irradiation service has been extended to request from researchers outside of the laboratory since April 1991. In this fiscal year, ca. 10% of the beam time was used for this purpose.

A training program which is offered for researchers from universities, governmental institutions, and industries has been held once a year since 1968. This seven-day program includes lectures and instruction on radiation chemistry of polymers, to which laser chemistry has been added as a subject in this year. We accepted 14 trainees this year. A seminar is also offered to local citizens give basic knowledge of radiation and nuclear energy. About 80 citizens joined this one-day seminar.

Detailed description of each activity is given in Chapter 2. A list of publications including patent applications is given in Chapter 3. Cooperative and joint research programs are summarized in Chapter 4.

Dr. Masafumi Nakano, Director  
Osaka Laboratory for Radiation Chemistry



## II. Current Research Activities

### 1. Irradiation of Tartaric Acid with Circularly Polarized Laser Beam

*Y. Shimizu and S. Kawanishi*

Optical resolution of racemic mixtures is very important in preparation of optically active compounds. Procedures by preferential crystallization, diastereomeric salt formation, and enzymatic degradation are commonly used at present for this purpose.<sup>1)</sup> On the other hand, it is known that the resolution is also possible by a photochemical procedure using a circularly polarized light (CPL) via preferential photodecomposition of one enantiomer of a racemic mixture.<sup>2)</sup> However, enantiomeric enrichment in the reported studies has been limited to a few classes of compounds such as camphor.<sup>3)</sup> Recently, the possibility of the efficient optical resolution by laser irradiation has been proposed on the assumption that multiphotonic absorption with a CPL of high intensity laser leads to an enantioselective excitation to a high-lying electronic level of a molecule.<sup>4)</sup> We, therefore, have attempted the efficient optical resolution of racemic tartaric acid (DL-TA), which was chosen as a model compound because of the absence of its absorption band in the wavelength range of  $>300$  nm, via a multiphotonic excitation process using a CPL of high intensity XeF excimer laser (351 nm).

The laser irradiation was carried out in a cylindrical Pyrex vessel (volume: 59 mL, diameter: 35.5 mm, length: 50 mm) with a Suprasil window (diameter: 45 mm, thickness: 3 mm) for the incidence of laser beams. As shown in Fig. 1, XeF laser beam (Lumonics Hyper EX-460, initial energy: 1.5W, frequency: 16 Hz, pulse duration: 12-15ns, beam size:  $9 \times 34$  mm<sup>2</sup>) was converted to a CPL by passing through a polarizer and a quarter-wave plate, and focussed at the center of the vessel with a condenser lens (focal length: 120 cm). The initial energy of the CPL was about 1.31W at 16 Hz. An aqueous solution of DL-TA (0.6667 M) was placed in the vessel and bubbled with N<sub>2</sub> to remove O<sub>2</sub>. The N<sub>2</sub>-saturated solution being stirred magnetically was irradiated with focussed right (r)-CPL at room temperature. The sample was analyzed by HPLC (Shimadzu LC-6A, column: SUMICHIRAL OA-5000, column length: 5 cm, column temperature: 55 °C, UV detector: 280 nm). Gaseous products were analyzed by GC (Shimadzu GC-3BT, column: Molecular sieve 5A).

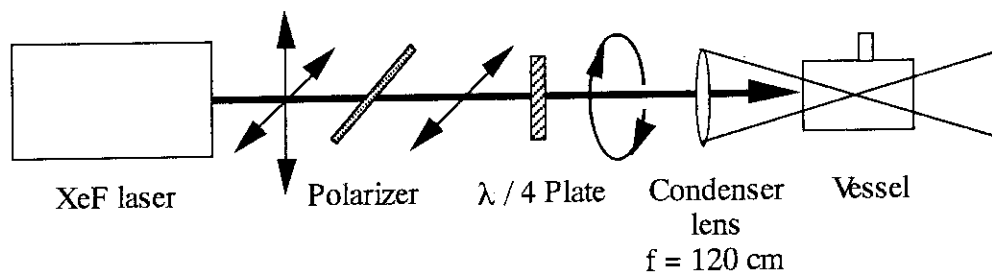
Figure 2 shows the L-TA concentration in the sample irradiated with a focussed r-CPL (the fluence at the center is much larger than  $6.3$  J cm<sup>-2</sup> pulse<sup>-1</sup>). Though L-TA was consumed by the irradiation, consumption of D-TA was much smaller than that of L-TA. Furthermore, meso-TA was not produced. GC analysis of a gas within the vessel

revealed that CO, CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, and CH<sub>4</sub> were formed. On the other hand, neither consumption nor decomposition of L-TA observed upon irradiation with a nonfocussed r-CPL (fluence: 274 mJ cm<sup>-2</sup> pulse<sup>-1</sup>).

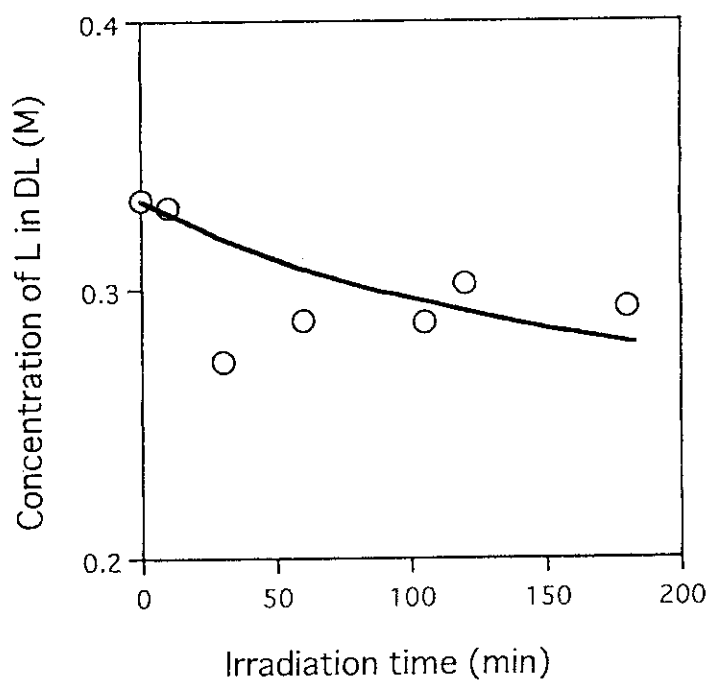
From these results, it was demonstrated that DL-TA can be resolved optically by the irradiation with a focussed r-CPL from XeF laser through the selective decomposition of L-TA. Since TA scarcely has absorption at a wavelength of >300 nm, the resolution with the focussed CPL from XeF laser would proceed via a multiphotonic absorption. Related works are now in progress for quantitative analysis of the laser-induced optical resolution.

### References

- 1) M. Nohira, "Kogaku Kasseitai," ed. by H. Nohira, Asakura Shoten, 1989, Chapter 3.
- 2) Y. Inoue, *Chem. Rev.*, **92**, 741 (1992).
- 3) G. Belavoine, A. Moradpour, and H. B. Kagan, *J. Am. Chem. Soc.*, **96**, 5152 (1974).
- 4) D. N. Nikogosyan, Yu. A. Repeyev, and E. V. Khoroshilova, *Chem. Phys.*, **147**, 437 (1990).



**Fig. 1** Generation of a focussed CPL from XeF laser.



**Fig. 2** The change in L-TA concentration in the course of the irradiation with a focussed r-CPL.

## 2. Excimer Laser-Induced Surface Photochemical Reactions of Fluoropolymer

*N. Ichinose, M. Maruo,\* A. Okada,\*\* and S. Kawanishi*

Surface treatment of fluoropolymers is of general interest from practical point of view such as adhesion, printing, or plating. Recently surface treatment of fluoropolymers by excimer laser irradiation, which induces chemical<sup>1)</sup> and/or physical<sup>2,3)</sup> change in various surface properties, has been focussed instead of classical chemical treatment or plasma discharge because of its potential advantages in spatial control and operation time. Though several surface modification methods of fluoropolymers using excimer lasers have been studied by several research groups including us to improve adhesivity and hydrophilicity, their mechanistic feature has little been clarified. In this review, we describe laser-induced photoreactions of fluoropolymer surface in contact with liquid phase which proceed via photoionization of reactants by intense laser irradiation.

### **Laser-induced surface photoreaction of fluoropolymers with water:<sup>4)</sup>**

Several authors including our laboratory have reported surface modification to improve hydrophilicity by ArF or KrF laser irradiation of fluoropolymers such as poly(tetrafluoroethylene) (PTFE) and poly(tetrafluoroethylene-co-perfluoroalkylvinylether) (PFA) in contact with water.<sup>5)</sup> However, no one has described surface functionality responsible for wettability and mechanism involved therein. We have examined surface properties of poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) irradiated with ArF or KrF laser in contact with water and also studied reactivity of several fluoropolymers with water upon irradiation with various light sources.

An FEP film (50- $\mu\text{m}$  thickness) was fixed in contact with a nitrogen-purged water in a cell sealed with quartz windows. The film was irradiated with ArF (10-40  $\text{mJ cm}^{-2}$  pulse<sup>-1</sup>) or KrF laser (40-100  $\text{mJ cm}^{-2}$  pulse<sup>-1</sup>) for 2-12 min at a repetition rate of 10 Hz. The contact angle of the film with water droplet was 107° before irradiation, which decreased with shot number of laser pulse up to 40-50° (Fig. 1.). Since the irradiated surface remained smooth to rule out roughening induced by laser ablation, some chemical change like as formation of polar functionality can be responsible for the wettability. The surface functionality was assigned to carboxylic group by the following observations: 1) X-ray photoelectron spectroscopy (XPS) indicated appearance of a broad peak at 286-290 eV in the C<sub>1s</sub> region and loss of fluorine (2.3 to 0.6-1.2) and increase of oxygen (0.02 to 0.10-

---

\*Osaka University.

\*\*Shiga Laboratory, Gunze Ltd.

0.20) in atomic ratios F/C and O/C. 2) Basic or cationic dyes such as rhodamine 6G adsorbed selectively on the irradiated area and not anionic ones such as eosin Y. 3) The contact angle showed pH-dependence, where lower values were obtained with alkaline buffer droplets as compared to those with acidic ones. Surface concentration of carboxylic group was semiquantitatively estimated from surface coverage of adsorbed dye (S)  $S = A/1000\epsilon$ , where A is the absorbance of a film due to the dye adsorption and  $\epsilon$  is the molar extinction coefficient of the dye used. For instance,  $A = 0.017$  was obtained with rhodamine 6G after irradiation of 5000 pulses of ArF laser ( $22 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ ), which corresponds to  $1.7 \times 10^{-10} \text{ mol cm}^{-2}$  ( $1.0 \text{ molecule nm}^{-2}$ ).

In a similar manner, thin films of various fluoropolymers were irradiated at 185, 193, 248, and 254 nm to examine the effect of fluorine contents. The results were summarized in Table 1. For perfluorinated polymers, irradiation at 185 nm with a 30-W super low-pressure mercury lamp gave essentially the same effect as that with ArF laser. Irradiation at 254 nm with a 100-W low-pressure mercury lamp, however, gave no effect while that with KrF laser effectively afforded surface wettability. For less fluorinated polymers such as poly(ethylene-co-tetrafluoroethylene) (ETFE) and poly(vinylidene fluoride) (PVDF), irradiation at all wavelength was less effective as compared with the results obtained for perfluorinated polymers. These results suggested that the present reaction proceeds in an electrophilic mechanism. Liquid water ionizes to give hydrated electron and hydroxyl radical upon photoirradiation at  $< 190\text{-}200 \text{ nm}$  in a one-photon mechanism and two-photon ionization occurs with intense laser pulses at  $> 200 \text{ nm}$ . The difference between the results obtained for 254 and 248 nm can be explained by two-photon ionization of liquid water if it initiates the photoreaction of fluoropolymer. It is strongly suggested that the photoionization of water is the primary process of the reaction: 1) neither decrease in contact angle with water nor dye adsorption was observed upon irradiation of an FEP film in contact with oxygen-saturated water with ArF laser, where oxygen must play a role of an electron scavenger. 2) Amount of adsorbed dye per laser pulse corresponding to that of carboxylic group formed was proportional to  $[1.4 \pm 0.2 \text{ and } 3.2 \pm 0.5 \text{ for ArF and KrF lasers, respectively, where } I \text{ is the laser intensity (Fig. 2). These values are slightly larger than those expected for hydrated electron ejection by photoionization of water, which may be due to presence of a secondary photoreaction. 3) Simple attack of hydroxyl radical can be ruled out by the similar irradiation with an aqueous solution of } H_2O_2 \text{ which gave no effect on the surface properties. As a conclusion at present, electron transfer from water to fluoropolymer via photoionization must be involved as a key step for activation of fluoropolymer surface by excimer laser irradiation (Scheme 1).}$

**Laser-induced surface photoreaction of fluoropolymers with organic molecules:** On the basis of electrophilic nature in the reactivity of fluoropolymers, we

can design some reactions for their surface modification as depicted in Scheme 2, where fluoropolymer is activated via electron transfer from reactant molecule. With proper choice of an electron-donating organic molecule, various functionalities would be introduced to fluoropolymer surface. In addition, incorporation of quasi-free electron via photoionization of reactant or photoinduced single electron transfer from the lowest excited state of reactant in the primary process is an important problem from mechanistic and also practical points of view. In this section, surface photoreactions with alkylcarboxylic acids and aliphatic amines are described.

Thin films of fluoropolymer were irradiated with KrF or XeCl laser in contact with solutions of alkylcarboxylic acids or aliphatic amines in various solvents in a similar manner to the reaction with water. In the case of alkylcarboxylic acids such as octanoic acid, fluoropolymer surface became oleophilic after irradiation of low energy KrF pulses ( $22 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ ) with its alkaline aqueous solution. The contact angle with hexadecane droplet was lowered from  $42$  to  $0^\circ$  for PFA. The XPS analysis indicated considerable loss of fluorine and growth of a peak at  $285 \text{ eV}$  in  $\text{C}_{1s}$  region. These results strongly suggest surface alkylation to form a thin layer consisted of alkyl group.<sup>6)</sup> Aromatic chromophore was introduced to the surface of FEP by the photoreaction with an alkaline aqueous solution of 1-naphthylacetic acid (NA), which was detected by absorption and fluorescence spectroscopy. The photoreaction proceeded in water or in acetonitrile only with intense laser irradiation ( $> 50 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ ) but not in cyclohexane. This strongly suggests a role of electron transfer in the photoreaction. Laser flash photolysis of an aqueous solution of NA revealed that two-photon ionization of NA to give hydrated electron and radical cation of NA ( $\text{NA}\cdot^+$ ) took place under the reaction condition (Fig. 3), but no transient species were observed in acetonitrile and cyclohexane.<sup>7)</sup> The radical cation  $\text{NA}\cdot^+$  rapidly decomposed by decarboxylation to give 1-naphthylmethyl radical. Photoionization of alkylcarboxylic acid followed by Kolbe-type decomposition and electron transfer to fluoropolymer giving alkyl and polymer radicals will be a plausible mechanism of surface alkylation (Scheme 3). The surface alkylation method will be applied to alkylcarboxylic acids bearing various functional groups such as poly acids,<sup>8)</sup> hydroxy acids, amino acids.

Photoionization of aliphatic and aromatic amines has been studied well by fluorescence spectroscopy, transient photocurrent, and time-resolved absorption spectroscopy. KrF laser irradiation ( $35 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ ) of an FEP film in contact with an acetonitrile solution of triethylamine (TEA) induced both hydrophilicity and oleophilicity to the surface.<sup>9)</sup> The irradiated surface showed pH-dependence of the contact angle characteristic to basic functionality such as amine, which indicated introduction of aminoalkyl group as observed in the photoinduced electron transfer reactions of cyano-

and haloaromatics with aliphatic amines. Though various side reactions accompanied with aminoalkylation were indicated by UV and XPS spectroscopic analyses, the surface will satisfy practical properties such as adhesivity. The photoreaction also showed a similar solvent effect as observed for 1-NAA to suggest the electron transfer mechanism. The photoreaction was also induced by irradiation at 254 nm with a Hg lamp to suggest incorporation of photoinduced electron transfer as a primary process as well as photoionization of TEA by irradiation with KrF laser.

**Conclusion:** We have shown some excimer laser-induced photoreactions of fluoropolymers which seem to proceed via mono- or multi-photon ionization of reactant and capture of quasi-free electron by the polymers. The activation by electron transfer is a key to introduction of various functionalities onto the polymer surface, whose application is now in progress.

### References

- 1) M. Ookoshi and M. Murahara, K. Toyoda, *J. Mater. Res.*, **7**, 1912(1992); H. Niino and A. Yabe, *Appl. Phys. Lett.*, **63**, 3527(1993).
- 2) S. Küper and M. Stuke, *Appl. Phys. Lett.*, **54**, 4(1988); S. Wada, H. Tashiro, K. Toyoda, H. Niino, and A. Yabe, *Appl. Phys. Lett.*, **62**, 211(1993).
- 3) M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, T. Nagase, M. Endo, and Y. Eguchi, *Chem. Lett.*, **1992**, 2089; M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, T. Nagase, M. Endo, and Y. Eguchi, *Chem. Lett.*, **1993**, 1063; G. C. D' Couto, S. V. Babu, F. D. Egitto, and C. R. Davis, *J. Appl. Phys.*, **74**, 5972(1993).
- 4) N. Ichinose and S. Kawanishi, submitted to *Macromolecules*.
- 5) A. Okada, Y. Negishi, Y. Shimizu, S. Sugimoto, M. Nishii, and S. Kawanishi, *Chem. Lett.*, **1993**, 1637; S. Yamamoto and U. Kubo, *Trans. IEE Jpn*, **14A**, 487(1994).
- 6) N. Ichinose and S. Kawanishi, in preparation.
- 7) N. Ichinose and S. Kawanishi, in preparation.
- 8) A. Okada, N. Ichinose, and S. Kawanishi, *Polymer*, in press.
- 9) N. Ichinose, M. Maruo, S. Kawanishi, Y. Izumi, and T. Yamamoto, *Chem. Lett.*, in press.

**Table 1** Surface wettability of fluoropolymers irradiated through a 100- $\mu\text{m}$  water film by the use of various light source.

| Polymer                                                                                                                                    | Wavelength (nm)  | Surface wettability |
|--------------------------------------------------------------------------------------------------------------------------------------------|------------------|---------------------|
| $\left(\text{CF}_2-\text{CF}_2\right)_n \left(\text{CF}_2-\overset{\text{CF}_3}{\underset{ }{\text{CF}}}\right)_m$ FEP                     | 185 <sup>a</sup> | yes                 |
|                                                                                                                                            | 193 <sup>b</sup> | yes                 |
|                                                                                                                                            | 248 <sup>c</sup> | yes                 |
|                                                                                                                                            | 254 <sup>d</sup> | no                  |
| $\left(\text{CF}_2-\text{CF}_2\right)_n$ PTFE                                                                                              | 185 <sup>a</sup> | yes                 |
|                                                                                                                                            | 193 <sup>b</sup> | yes                 |
|                                                                                                                                            | 248 <sup>c</sup> | yes                 |
|                                                                                                                                            | 254 <sup>d</sup> | no                  |
| $\left(\text{CF}_2-\text{CF}_2\right)_n \left(\text{CF}_2-\overset{\text{O}(\text{CF}_2)_k\text{F}}{\underset{ }{\text{CF}}}\right)_m$ PFA | 185 <sup>a</sup> | yes                 |
|                                                                                                                                            | 193 <sup>b</sup> | yes                 |
|                                                                                                                                            | 248 <sup>c</sup> | yes                 |
|                                                                                                                                            | 254 <sup>d</sup> | no                  |
| $\left(\text{CF}_2-\text{CF}_2\right)_n \left(\text{CH}_2-\text{CH}_2\right)_m$ ETFE                                                       | 185 <sup>a</sup> | no                  |
|                                                                                                                                            | 193 <sup>b</sup> | no                  |
|                                                                                                                                            | 248 <sup>c</sup> | no                  |
|                                                                                                                                            | 254 <sup>d</sup> | no                  |
| $\left(\text{CF}_2-\text{CH}_2\right)_n$ PVDF                                                                                              | 185 <sup>a</sup> | no                  |
|                                                                                                                                            | 193 <sup>b</sup> | no                  |
|                                                                                                                                            | 248 <sup>c</sup> | no                  |
|                                                                                                                                            | 254 <sup>d</sup> | no                  |

<sup>a</sup> 30-W super low-pressure Hg lamp, 60 min. <sup>b</sup> ArF laser (22 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, 3000 shots). <sup>c</sup> KrF laser (68 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, 3000 shots). <sup>d</sup> 60-W low-pressure Hg lamp, 4 h.



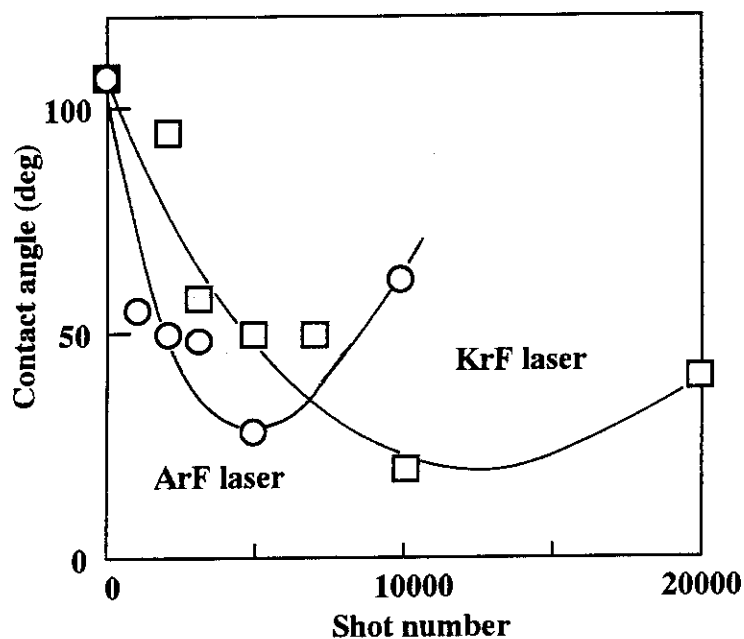


Fig. 1 Plot for contact angle of water droplet on FEP films irradiated with water vs. laser shot number.

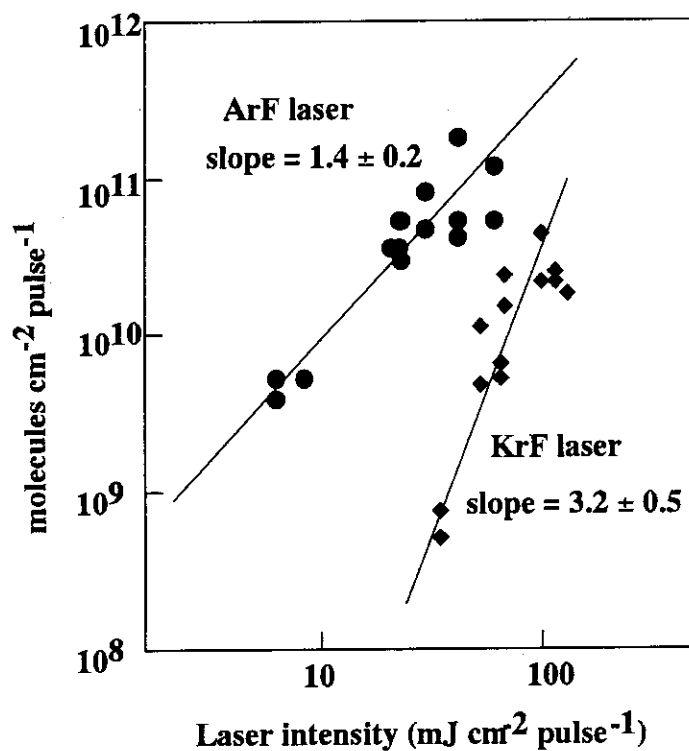
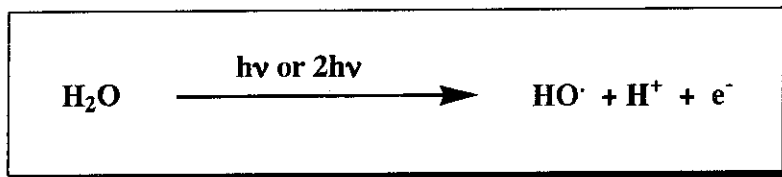
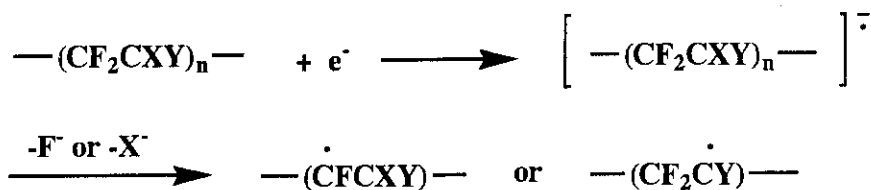


Fig. 2 Laser power dependence of carboxylic group formation estimated by rhodamine 6G adsorption onto the films irradiated with nitrogen-purged water.

**Photoionization of water**

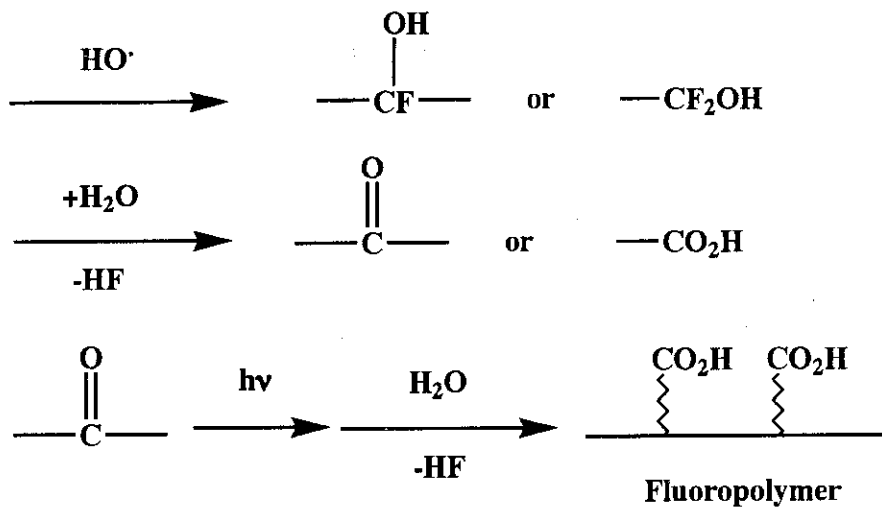


**Interfacial electron transfer**

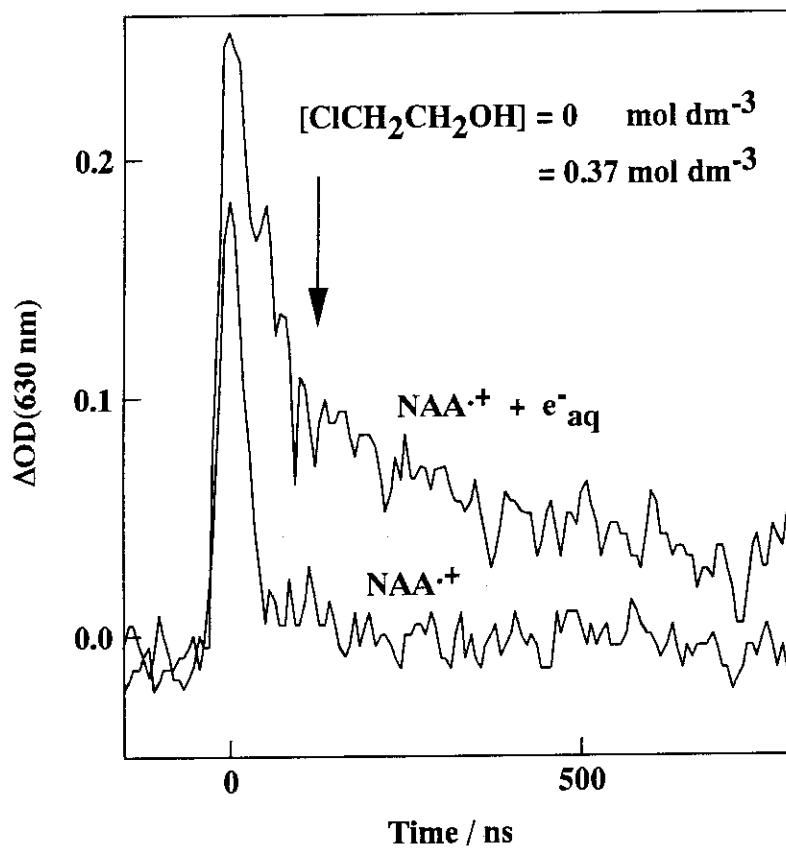


(X, Y) = (F, F); (F, CF<sub>3</sub>); (Cl, F); (F, OC<sub>m</sub>F<sub>2m+1</sub>); not (H, H)

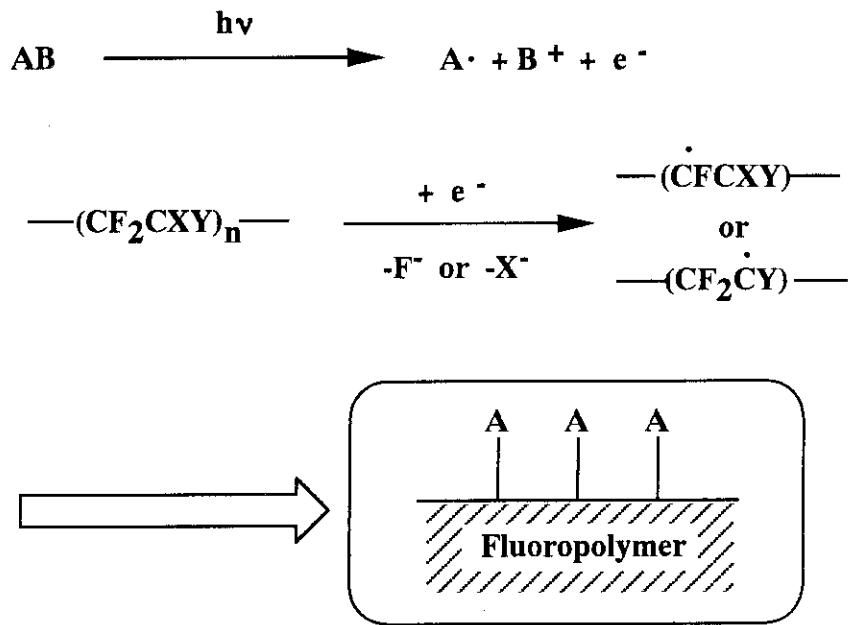
**Attack of hydroxyl radical (formation of carboxylic group)**



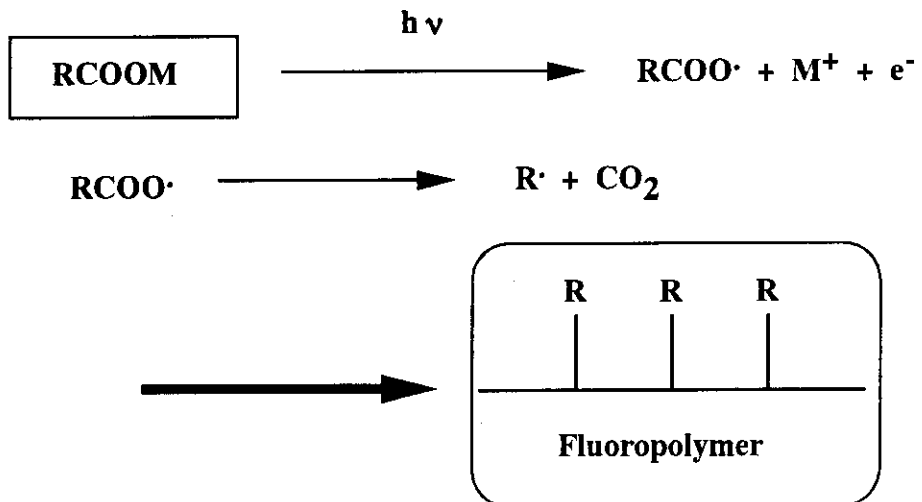
**Scheme 1**



**Fig. 3** Decay curves of transient absorption at 630 nm obtained by laser flash photolysis of an aqueous solution of 1-NAA in the absence and presence of an electron scavenger, 2-chloroethanol:  $[1\text{-NAA}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ; XeCl laser(308 nm), 30 mJ pulse<sup>-1</sup>.



Scheme 2



Scheme 3

### 3. Surface Treatment of Tetrafluoroethylene-Perfluoroalkyl Vinyl Ether Copolymer (PFA) by Excimer Laser Irradiation in Contact with Aqueous Ammonia Solution

*A. Okada,\* N. Ichinose, and S. Kawanishi*

In the previous report,<sup>1,2)</sup> we have demonstrated surface modification of tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) by excimer laser irradiation with aqueous solutions of various gasses such as carbon monoxide, argon, and so forth. In this report, we described the surface treatment of PFA by KrF laser irradiation in aqueous ammonia solution, and enter the chemistry involved within the laser treatment through surface analyses<sup>3)</sup>.

Sample PFA films (0.1-mm thickness) were prepared from the extrusion processing of PFA resin (Mitsui-Dupont, Teflon<sup>®</sup>-PFA 350J). Pieces of the film (5 cm x 5 cm) were washed in EtOH with a supersonic wave and air-dried at room temperature before laser irradiation. An aqueous ammonia solution (Wako Pure Chemical, 28% conc.) was diluted with distilled water into 0.01%. A PFA film contacted with the aqueous ammonia solution was irradiated with excimer laser (Lumonics Hyper EX-884) at a wavelength of 193 (ArF) or 248 nm (KrF) (frequency: 50 Hz, fluence: 13-94 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, number of pulses: 10-16000 pulse). The wettability of the PFA film was estimated by the contact angle with water droplet at 25 °C. The chemical property of the PFA film was analyzed by X-ray photoelectron spectroscopy (XPS). In order to obtain some information on the surface of the PFA film, the angular dependence of the atomic ratios (F/C, O/C, and N/C), and morphology by scanning electron microscopy (SEM) (Topcon DS-130S) were also examined.

Figure 1 shows the contact angle of the PFA films as a function of the total laser energy. It is obvious that the contact angle decreased with the energy for both ArF and KrF lasers. In the case of ArF laser, the irradiation reduced the contact angle from 106° (unirradiated) to 30° more effectively than that with KrF with respect to the total energy. The contact angle was leveled off in the range of the irradiation energy of > 100 J cm<sup>-2</sup>. Change in the chemical composition of the PFA surface was studied by XPS to indicate that the atomic ratio O/C and N/C were increased, whereas that of F/C was decreased by laser irradiation. Figure 2 shows that the changes in atomic ratios were closely related to the decrease of the contact angles.

While PFA has no absorbance at 193 nm and 248 nm, ammonia in aqueous solution

---

\*Shiga Laboratory, Gunze Ltd.

shows an absorbance at 193 nm, but little at 248 nm. Therefore, the photoreaction proceeded by one-photon excitation of ammonia with ArF laser. On the other hand, the reaction will be induced by multi-photon excitation with KrF laser. As shown in Fig. 1, the changes in the contact angles were dependent on the total energy of ArF laser, not on the fluence in the early stage of the reaction. On the other hand, the course of the reaction depended on the fluence of KrF laser. It was suggested that the introduction of nitrogen atom proceeded through a photoreaction of ammonia.

Figure 3 shows an angle dependence of XPS atomic ratios (depth profiling). A sampling depth is described as a function of an escape depth of photoelectron:

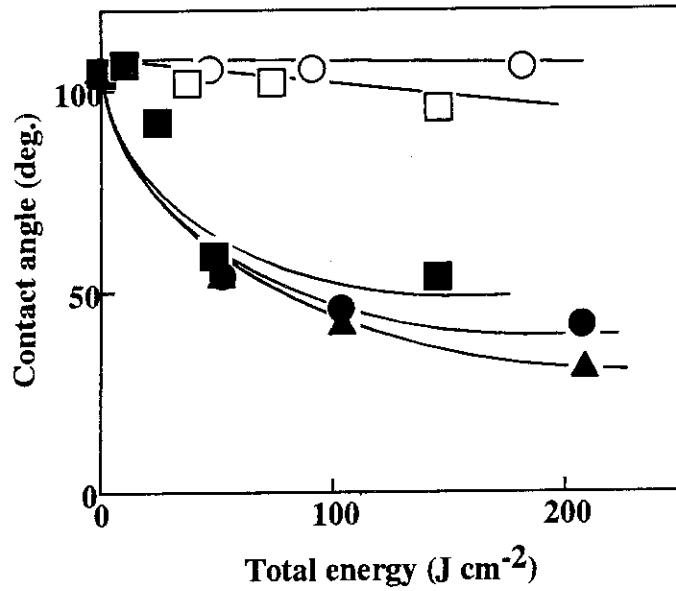
$$d' = d \cdot \sin\theta$$

where  $d'$ , the effective sampling depth,  $d$ , the escape depth, and  $\theta$ , grazing exit angle to the plane of the sample. Since the F/C atomic ratio showed a considerable change around the  $\sin\theta = 0.7$ , it can be attributed to the border between the bulk and the reaction layer. With a reported value for the depth of a photoelectron ( $d = 2-10$  nm),<sup>4)</sup> the thickness of the reaction layer was estimated to be 1.5-7.0 nm. In fact, no morphological change was observed by SEM before and after laser irradiation to support the thinness of the modification layer.

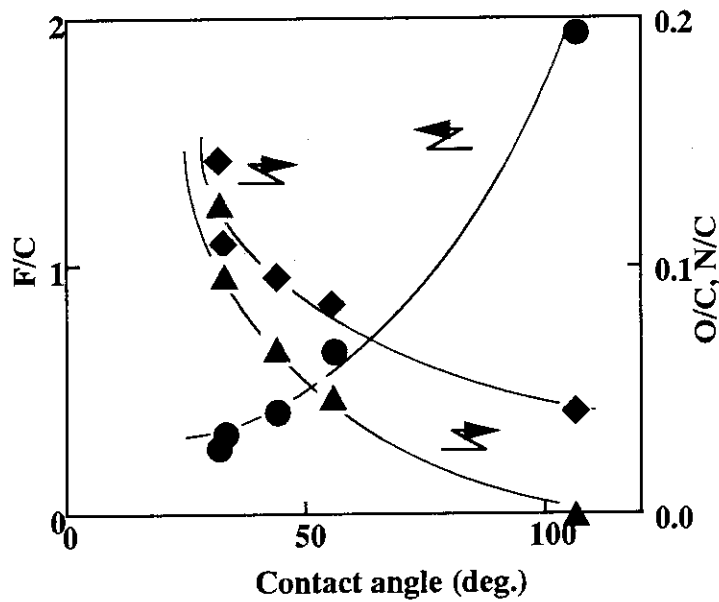
As a conclusion, the present reaction induced by excimer laser may offer a useful method for functionalization of fluoropolymer surface for adhesion, printing, and other industrial use.

## References

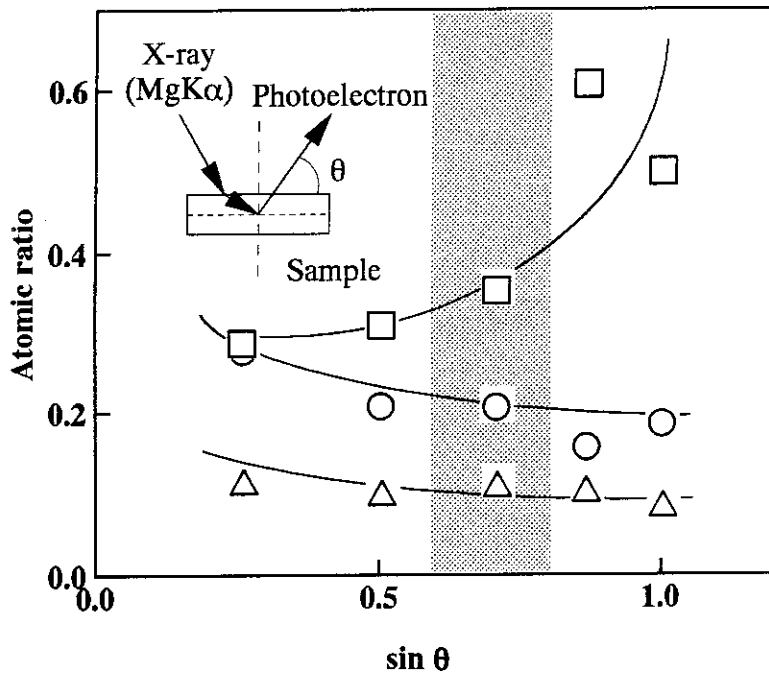
- 1) A. Okada, Y. Negishi, Y. Shimizu, S. Sugimoto, N. Nishii, and S. Kawanishi, *Chem. Lett.*, 1637 (1993).
- 2) A. Okada, Y. Negishi, Y. Shimizu, S. Sugimoto, and S. Kawanishi, *JAERI-Review*, **95-002**, 15 (1995).
- 3) A. Okada, N. Ichinose, and S. Kawanishi, *Kobunshi Ronbunshu*, **52**, 66 (1995).
- 4) S. C. Yoon and B. D. Ratner, *Macromolecules*, **19**, 1068 (1986).



**Figure 1** Changes in the contact angle with total laser energy: (○), KrF 23 mJ cm<sup>-2</sup> pulse<sup>-1</sup>; (□), KrF 90 mJ cm<sup>-2</sup> pulse<sup>-1</sup>; (■), ArF 13 mJ cm<sup>-2</sup> pulse<sup>-1</sup>; (●), ArF 23 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, and (▲), ArF 94 mJ cm<sup>-2</sup> pulse<sup>-1</sup>.



**Figure 2** Relationship between the contact angle and the atomic ratios: (●), F/C; (◆), O/C, and (▲), N/C.



**Figure 3** Depth profiling of the atomic ratios of a PFA film surface irradiated with ArF laser as a function of  $\cos \theta$ , where  $\theta$  is the grazing angle of photoelectron: (□), F/C; (○), O/C, and (△), N/C. Total laser energy,  $190 \text{ J cm}^{-2}$ .



#### 4. Excitation Wavelength Effect on Laser-Induced Dehydrochlorination of Poly(vinyl chloride) (PVC) Film

*Y. Izumi,\* M. Maruo,\* S. Kawanishi, N. Ichinose, and T. Yamamoto\**

Poly(vinyl chloride) (PVC) is one of the most versatile commercial polymers often used under exposure to sunlight.<sup>1)</sup> However, PVC is quite unstable against sunlight like heat and high energy radiation, which leads to considerable changes in the polymer structure. Though there are a large number of papers and reviews on the mechanism and kinetics of photodegradation of PVC,<sup>2)</sup> the primary process, however, concerning absorption site and transient excited states has not been clear. In addition, photochemical, photothermal and thermal reactions may have been observed in the earlier works where various mercury lamps were usually used as irradiation sources, for mercury lamp emits a lot number of lines in the region of deep UV to IR to which PVC will be sensitive. It is, therefore, important to use monochromatic light sources like excimer laser to clarify the effect of excitation wavelength. Since pure PVC has an absorption at  $< 210$  nm, different behaviors will be expected for irradiation with ArF (193 nm) and KrF (248 nm) lasers.

Cast films of PVC (10-30  $\mu\text{m}$ ) were prepared from a cyclohexanone solution and were washed thoroughly with  $\text{CS}_2$  and methanol. Then the film was evacuated in 1 Pa for more than 2 days to remove the solvents. The film was irradiated with ArF (193 nm,  $83 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ ) or KrF (248 nm,  $100 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ ) excimer laser at a reduced pressure ( $< 10^{-3}$  Pa). Pulse durations of the lasers were 10-20 ns and pulse repetition rate was 1 Hz. The course of reaction was monitored by UV-vis absorption spectroscopy in the wavelengths ranging from 700 nm to 190 nm.

Figures 1 and 2 shows the UV-vis absorption spectra of PVC films irradiated with ArF and KrF excimer lasers, respectively. The irradiation with XeCl laser (308 nm) induced no considerable reactions. The spectrum of non-irradiated film shows the presence of unsaturated bonds to some extent and absence of any solvents in the film. The absence of solvents was confirmed by FT-IR measurement. While the growth of a broad band at around 500 nm was reported,<sup>4)</sup> such a band was not observed in the present study. Our results seem to be different in absorption spectra from those of chlorinated PVC irradiated with KrF laser.<sup>3)</sup> The absorption bands at 196, 238, 288, 326 and 367 nm are assigned to double bond, diene, triene, tetraene and pentaene, respectively.<sup>5)</sup> Disappearance of these peaks after bromination also support the polyene

---

\*Department of Nuclear Engineering, Osaka University.

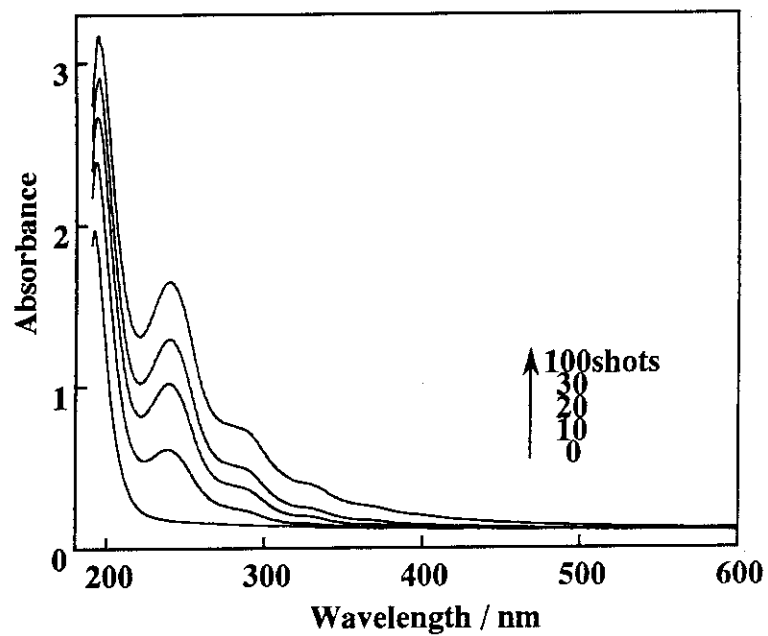
structures. As shown in these figures, the ArF and KrF laser irradiation caused mainly formation of diene and triene, respectively.

The ArF laser light will be absorbed effectively by olefin or diene site in polymer chain to give rise its excited state, whereas KrF laser can excite diene only. Chlorine atoms surrounding these sites will facilitate the intersystem crossing of their singlet to the lowest excited triplet states. These olefinic sites have allylic Cl atom which undergoes homolytic photochemical dissociation via triplet states. Hydrogen abstraction by Cl atom produces diene in the polymer chain. Some of absorbed energy may be transferred as a thermal energy to form isolated double bond which plays a roll of reaction initiator. Excitation of diene, however, will not lead to the bond dissociation from its excited triplet state. Typical triplet energies of aliphatic olefin and diene are  $\approx 330$  and  $\approx 250$  kJ mol<sup>-1</sup>, and dissociation energy of allylic C-Cl bond lies between the two triplet energies ( $\approx 290$  kJ mol<sup>-1</sup>, supposing similar to that of benzylic C-Cl bond).<sup>6)</sup> On consideration of the relationship between triplet energies and dissociation energies of allylic Cl atom for diene and triene, photochemical dehydrochlorination will be limited to diene formation. The polyene formation in the case of KrF and other stationary state light source therefore can be attributed to photothermal effect. Less selective dehydrochlorination was reported for thermolysis of PVC giving polyene structure, through a "zipper-like" radical chain mechanism.<sup>7)</sup>

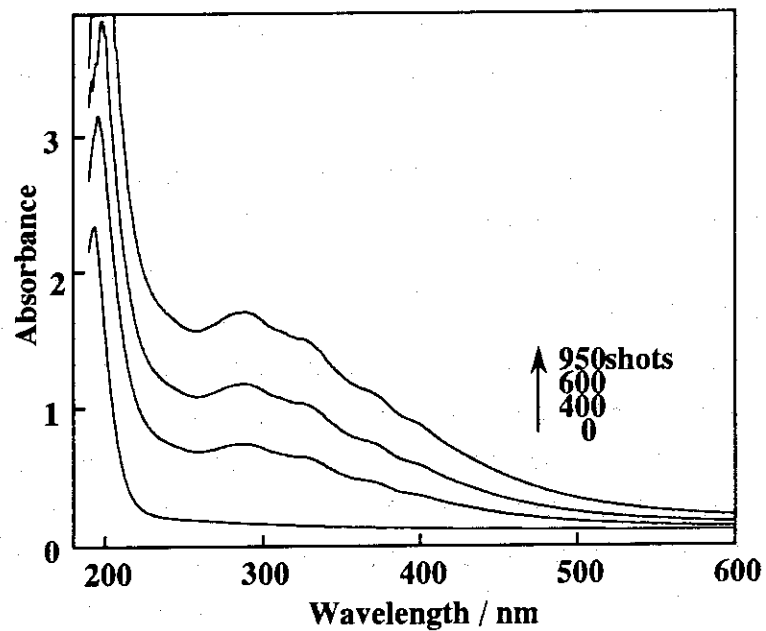
It can be concluded from these results and consideration about the photochemistry of PVC that laser-induced dehydrochlorination of PVC proceeds via photochemical pathway upon irradiation at 193 nm and via photothermal pathway at 248 nm.

## References

- 1) A. Torikai, H. Tsuruta, and K. Fueki, *Polym. Photochem.*, **2**, 227(1982).
- 2) For example: D. Braun, "*Degradation and Stabilization of Polymers*," ed. by G. Geuskens, Appl. Sci., London (1975) p. 23; J. F. Rabeck, G. Canbäck, J. Lucky, and B. Rånby, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1447 (1976).
- 3) M. Shimoyama, H. Niino, and A. Yabe, *Makromol. Chem.*, **193**, 569(1992).
- 4) For example: J. F. Rabeck, G. Canbäck, and B. Rånby, *J. Appl. Polym. Sci.*, **21**, 2211 (1977); G. J. Atchison, *J. Appl. Polym. Sci.*, **7**, 1471 (1963).
- 5) G. J. Atchison, *J. Appl. Polym. Sci.*, **7**, 1471 (1963); P. Nayer and M. C. Whiting, *J. Chem. Soc.*, **1955**, 3037.
- 6) S. L. Murov, I. Carmichael, and G. L. Hug, "*Handbook of Photochemistry 2nd Ed.*," Marcel Dekker, New York (1992).
- 7) D. Braun, "*Degradation and Stabilization of Polymers*," ed. by G. Geuskens, Appl. Sci., London (1975).



**Fig. 1** UV-vis absorption spectra of PVC films irradiated with ArF laser at a fluence of  $83 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ .



**Fig. 2** UV-vis absorption spectra of PVC films irradiated with KrF laser at a fluence of  $100 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ .

## 5. Improvement of Wettability of PTFE Membrane by Excimer Laser Irradiation with an Aqueous Solution of Hydrogen Peroxide: Effect of Impregnating Temperature and Laser Fluence

*T. Tanaka,\* H. Mishima,\* T. Nishino,\* M. Nishii, S. Sugimoto,\*\* and S. Kawanishi*

Since poly(tetrafluoroethylene) (PTFE) membrane has the advantages with respect to resistance to heat and chemicals as compared with other membranes, it has been utilized mainly in microfiltration in electronic industries which require low-elution and high-performance conditions. However, high hydrophobicity of PTFE makes it difficult to filter chemicals with high surface tension or aqueous solutions directly with the membrane. We have tried to give wettability to the surface of a porous PTFE membrane for improvement of filtration efficiency and found an effectiveness of a treatment: impregnation in a hydrogen peroxide aqueous solution followed by KrF laser irradiation. In this report, the effect of impregnation temperature and laser fluence during the treatment on the wettability of the PTFE membrane are described.

The PTFE membrane purchased from Japan Gore-Tex has a pore size and a thickness of 0.1  $\mu\text{m}$  and 45  $\mu\text{m}$ , respectively. The PTFE membrane washed with ethanol was immersed in an aqueous solution of 0.3 wt% hydrogen peroxide at 20 or 40 °C. After 20h, it was irradiated in air with a KrF excimer laser at room temperature (fluence: 200  $\text{mJ cm}^{-2}$  pulse<sup>-1</sup>). The treated membrane was repeatedly washed with pure water and was dried in air. Wettability index of the membrane was evaluated by the use of standard wettability-index solutions prepared according to a JIS K-6768 specification. The standard solutions were dropped on the membrane in an ascending order of surface tension. The wettability index of the membrane was determined as a maximum surface tension of the standard solution which penetrates the membrane. The wettability index of a raw membrane determined by this method was less than 31  $\text{dyn cm}^{-1}$ .

Figure 1 shows a relationship between the total irradiation energy of laser and the wettability index of the PTFE membrane. Enhancement of the wetting property of the membrane, which can be due to formation of carboxylic group,<sup>1)</sup> was more effective for the impregnation at 40 °C than for that at 20 °C. It is possibly caused by sufficient penetration of the solution into the micropores of the PTFE membrane at a high temperature, because lower surface tension and viscosity of solution are expected. From

---

\*Technical Research Laboratory, Kurabo Industries, Ltd.

\*\*Radiation Application Development Association.

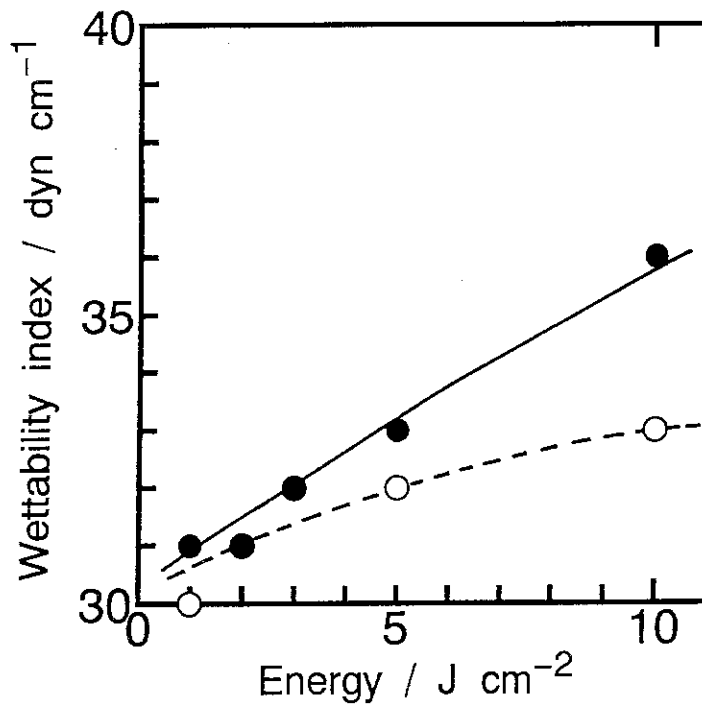
a practical viewpoint, it is desirable that pretreatment time can be reduced simply by the elevation of the temperature.

Figure 2 shows a relationship between the laser fluence and the wettability index of the membrane irradiated at a constant total energy of  $10 \text{ J cm}^{-2}$ . It does not show a clear threshold energy, and therefore improvement of wettability can be achieved even with lower laser fluences. The wettability index of the irradiated membrane was increased with the laser fluence and showed a maximum of  $37 \text{ dyn cm}^{-1}$  at  $300 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ . Since the present modification is due to a chemical reaction and not due to the morphological change such as laser ablation which is highly sensitive to laser intensity in the case of PTFE, uniformity of laser beam will be not necessarily important for this application. The laser fluence over the range of 200 to  $400 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  will be effective for the present purpose.

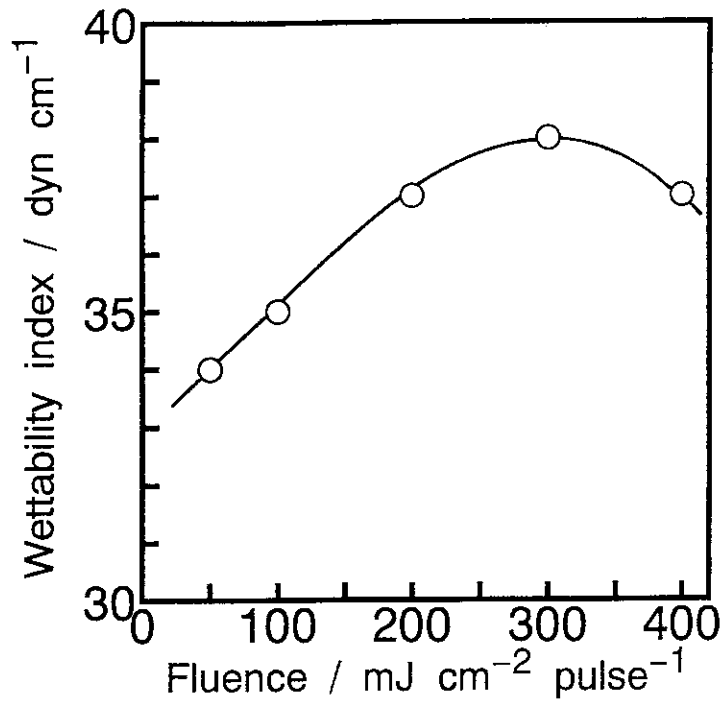
The treatment of the treated membrane made it easier to filter various solutions with high surface tension and a cartridge equipped with this membrane was also suitable to filter solutions which readily bubbles. Since the present modification method can afford hydrophilicity at any part of the porous PTFE membrane, further applications not only to electronic industry such as medical use can be expected.

#### Reference

- 1) T. Tanaka, M. Sano, M. Nishii, S. Sugimoto, and S. Kawanishi, *JAERI-Review*, **95-002**, 12(1995).



**Fig. 1** The wettability indices of the PTFE membranes irradiated with KrF laser at a fluence of 200 mJ cm<sup>-2</sup> pulse<sup>-1</sup> after impregnation in the 0.3 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution at 20 (open circle) and 40 °C (closed circle).



**Fig. 2** The fluence dependence of the wettability indices of the PTFE membranes irradiated with KrF laser at total energy of 10 J cm<sup>-2</sup>.

## 6. Excimer Laser Irradiation of Fluoropolymer Films Coated with Sodium Anthraquinone-2-sulfonate as an Ultraviolet Absorbent for Improvement of Adhesive Property

*T. Nagase,\* M. Endo\*, Y. Koshino,\* M. Nishii, S. Sugimoto,\*\* and S. Kawanishi*

Though fluoropolymer is an organic material with excellent properties such as thermal stability and chemical inertness, there is a difficulty in adhesion without chemical/physical treatment because of its extremely low surface energy. Several groups including us have recently attempted to improve adhesive property of fluoropolymers by excimer laser irradiation.<sup>1-4)</sup> Since fluoropolymers have no absorption band in ultraviolet region, we have studied the use of aromatic ultraviolet absorbents of polymers and small molecules such as Ekonol<sup>1)</sup> and sodium benzoate<sup>4)</sup> in forms of blend and coating, respectively. Here we report the effect of sodium anthraquinone-2-sulfonate (SAQS) as an ultraviolet absorbent.

Tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) films (100- $\mu\text{m}$  thickness) were used as sample. A surfactant containing perfluoroalkyl group was added to an aqueous solution of 1 wt% SAQS in order to obtain a good coating on the PFA film by reducing surface tension. The solution was coated uniformly by an applicator (thickness: 25  $\mu\text{m}$ ). After air-drying, the film was irradiated with KrF laser (wavelength: 248 nm, fluence: 50-500  $\text{mJ cm}^{-2} \text{ pulse}^{-1}$ , frequency: 40Hz, number of pulses: 2-10) in an ambient condition. The adhesivity of the irradiated film was evaluated as a 180°-peel strength of the sample adhered on a stainless steel plate with an epoxy resin adhesive. The surface of the irradiated film was analyzed by SEM and XPS to obtain morphological and chemical information.

The adhesive strength of a PFA film coated with SAQS was remarkably increased from 0.1 to 1.0  $\text{kgf cm}^{-1}$  by the irradiation (fluence: 300  $\text{mJ cm}^{-2} \text{ pulse}^{-1}$ , irradiation energy: 3.0  $\text{J cm}^{-2}$ ), whereas the similar irradiation of the film without the coating gave almost no effect. Though a similar results was obtained for sodium benzoate at a fluence of > 200  $\text{mJ cm}^{-2} \text{ pulse}^{-1}$ , the fluence was reduced to  $\approx 50 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  by the use of SAQS. The difference in the action of two absorbents may be attributed to that of molar extinction coefficient ( $\epsilon$ ) at 248 nm (1200  $\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$  for sodium benzoate and 35000  $\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$  for SAQS). Figure 1 shows the 180°-peel strength of PFA irradiated with SAQS at a fluences of 50 and 100  $\text{mJ cm}^{-2} \text{ pulse}^{-1}$  as a function of total

---

\*Technical research Laboratory, Kurabo Industries, Ltd.

\*\*Radiation Application Development Association.

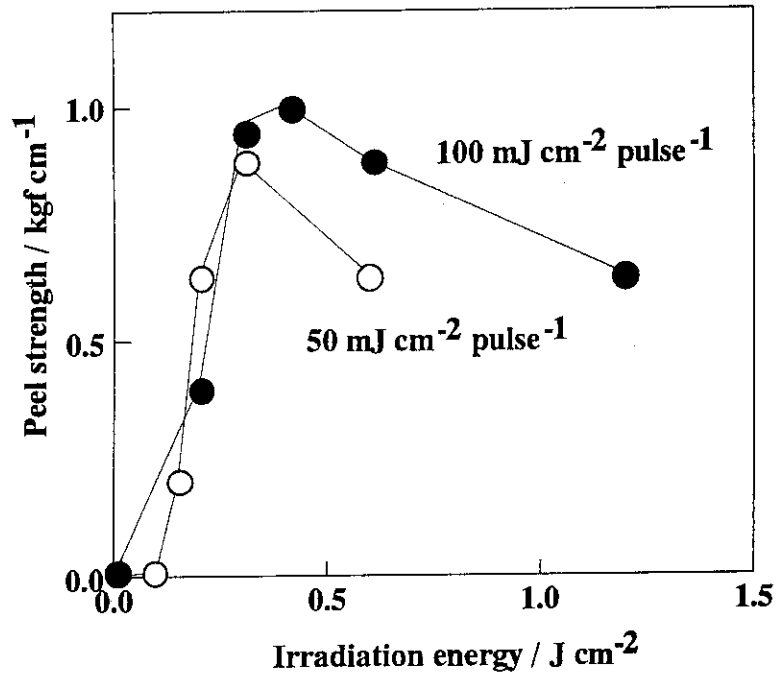
laser energy. The 180°-peel strength reached  $1.0 \text{ kgf cm}^{-1}$  at a total energy of  $0.4 \text{ J cm}^{-2}$  from  $< 0.01 \text{ kgf cm}^{-1}$  for an untreated film. The peel strength increased with the irradiation energy, and showed a maximum between  $0.3$  and  $0.4 \text{ J cm}^{-2}$ .

Elemental analysis of the irradiated PFA films by XPS indicated a decrease of fluorine and an increase of oxygen as compared to carbon. The atomic ratios of F/C and O/C were changed by irradiation at  $0.4 \text{ J cm}^{-2}$  to 1.02 and 0.14 from 2.10 and 0.01, respectively. Figure 2 shows a relationship between the peel strength and the O/C ratio of PFA. Since the plots of the peel strength for the irradiation at fluences of 50 and  $100 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$  increased with the O/C ratio in the same manner and no morphological change was observed by SEM before and after the laser irradiation of the film, it is concluded that formation of polar functionalities containing oxygen should play an important role in the enhancement of adhesive property. The reduction of the peel strength observed at an irradiated energy of  $> 0.4 \text{ J cm}^{-2}$  is presumably due to decomposition of the polar groups. The intensive excitation of SAQS by laser irradiation, therefore, induces some changes in chemical structure of the PFA surface, which enhances an interaction between the polymer and adhesive, rather than changes in the surface morphology as seen in the laser ablation.

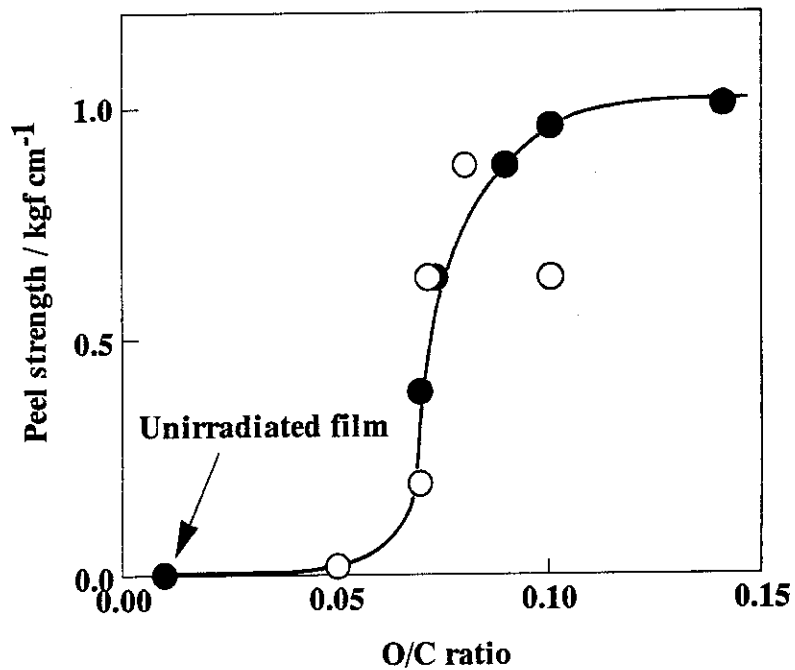
#### References

- 1) M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, T. Nagase, M. Endo, and Y. Eguchi, *Chem. Lett.*, **1992**, 2089.
- 2) M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, T. Nagase, M. Endo, and Y. Eguchi, *Chem. Lett.*, **1993**, 1063
- 3) M. Okoshi, T. Abe, and M. Murahara, *The 14th Annual Meeting of the Laser Society of Japan*, Chiba, Technical Paper, 188(1994).
- 4) T. Nagase, M. Endo, M. Nishii, S. Sugimoto, and S. Kawanishi, *JAERI-Review*, **95-002**, 9(1995)





**Fig. 1** A plot of the peel strength in the course of the KrF laser irradiation of the PFA films coated with sodium anthraquinone-2-sulfonate (SAQS) vs. total irradiation energy at a fluences of (open circle) 50 and (closed circle) 100 mJ cm<sup>-2</sup> pulse<sup>-1</sup>.



**Fig. 2** A relationship between the peel strength and the O/C ratio of the PFA films (see text) irradiated at a fluence of (open circle) 50 and (closed circle) 100 mJ cm<sup>-2</sup> pulse<sup>-1</sup>.

## 7. Separation of Silicon Isotopes by Infrared Multiple-Photon Decomposition

*S. Sugimoto,\* A. Isomura,\*\* S. Arai,\*\* and S. Kawanishi*

Silicon is one of the fundamental element which consists of the crust of the earth. Natural silicon contains three stable isotopes in a ratio (natural abundance ratio) of  $^{28}\text{Si} : ^{29}\text{Si} : ^{30}\text{Si} = 92.23 : 4.67 : 3.10$ . Small amounts of silicon isotopes can be separated by the use of large-sized mass spectrometer-type analyzer. On the other hand, Arai et.al. have studied the separation of the silicon isotopes from a fluorinated silicon compound by means of the infrared multiple-photon decomposition (IRMPD) method using TEA  $\text{CO}_2$  laser.<sup>1)</sup> However, physical properties of the silicon isotopes separated have not been examined. The aims of the present study are: firstly to establish an efficient IRMPD system of for isolation of the silicon isotopes in a preparative scale and secondly to determine various properties of each isotope.

Hexafluorodisilane ( $\text{Si}_2\text{F}_6$ ) purified by trap to trap distillation using liquid nitrogen was cooled at Dry Ice-ethanol mixture and tetrafluorosilane ( $\text{SiF}_4$ ) contained as an impurity was removed by evacuation. The purified  $\text{Si}_2\text{F}_6$  was introduced at a pressure of 2 Torr into a cylindrical irradiation vessel (100 mm $\phi$  x 950 mm, 5.1 L) made of Pyrex glass with NaCl windows (50 mm $\phi$  x 5mm thickness) at the both ends. Infrared laser beam (wavelength: 10.513  $\mu\text{m}$ ) from a  $\text{CO}_2$  laser (Ushio Electric UGL-TEA-3A) was introduced through the window to irradiate  $\text{Si}_2\text{F}_6$  at 1Hz. After the irradiation, the reaction mixture was collected in a bottle (65mL) cooled with liquid nitrogen. The temperature of the mixture was adjusted to that of the Dry Ice-ethanol mixture to separate into two parts A and B. The fraction A was a gaseous component at the Dry Ice-ethanol temperature and fraction B was a condensed component at that temperature. Each sample was analyzed by GC-MS (Shimadzu corporation. QP-5000). Mass spectrum of a main component of the fraction A showed peaks corresponding to  $^{28}\text{SiF}_3^+$ ,  $^{29}\text{SiF}_3^+$ , and  $^{30}\text{SiF}_3^+$  ions and parent ion ( $\text{SiF}_4^+$ ) was observed only as a small signal. On the other hand, that of fraction B indicated  $\text{Si}_2\text{F}_5^+$  ion but no parent ion ( $\text{Si}_2\text{F}_6^+$ ). Therefore, the main components of the fractions A and B were assigned to  $\text{SiF}_4$  and  $\text{Si}_2\text{F}_6$ , respectively.

A relationship between selectivity of  $^{29}\text{Si}$  and  $^{30}\text{Si}$  isotopes and the  $\text{CO}_2$  laser fluence is shown in Fig. 1. The separation ratio of  $^{30}\text{Si}$  isotope increased with the laser

\* Radiation Application Development Association.

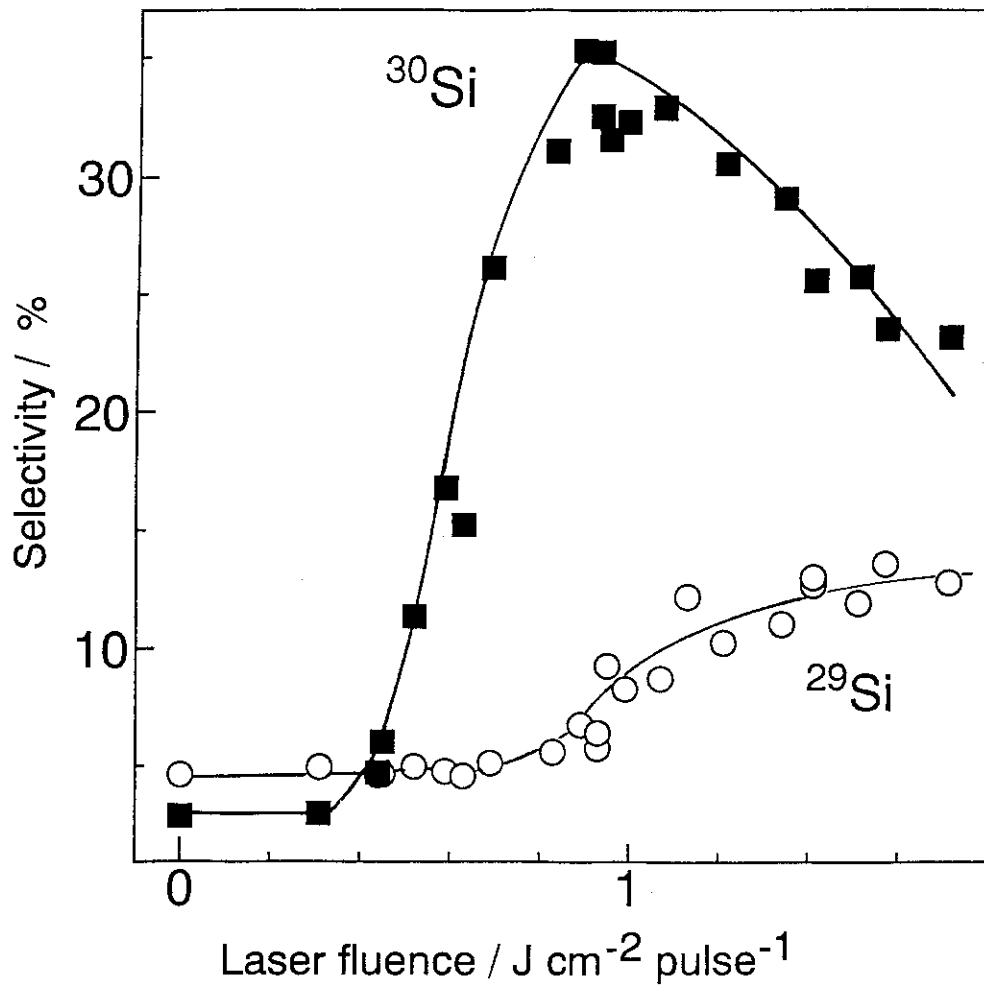
\*\* Material Science and Technology, Kyoto Institute of Technology.

fluence and reached a maximum (about 35%) at  $0.95 \text{ J cm}^{-2} \text{ pulse}^{-1}$  and then decreased. On the other hand, the separation ratio of  $^{29}\text{Si}$  isotope was constant at 5% up to  $1 \text{ J cm}^{-2} \text{ pulse}^{-1}$  and then increased with the laser fluence. The decomposition ratio of  $^{30}\text{Si}$  isotope in the reaction mixture reached about 100% at a laser fluence of  $1.6 \text{ J cm}^{-2} \text{ pulse}^{-1}$ . Figure 2 shows the selectivity of  $^{29}\text{Si}$  and  $^{30}\text{Si}$  isotopes as a function of laser shot number at  $0.9 \text{ J cm}^{-2} \text{ pulse}^{-1}$ . The separation ratio of  $^{30}\text{Si}$  increased with the shot number up to 3000 shot and became constant to further irradiation, whereas that of  $^{29}\text{Si}$  showed slight increase with the laser shot number.

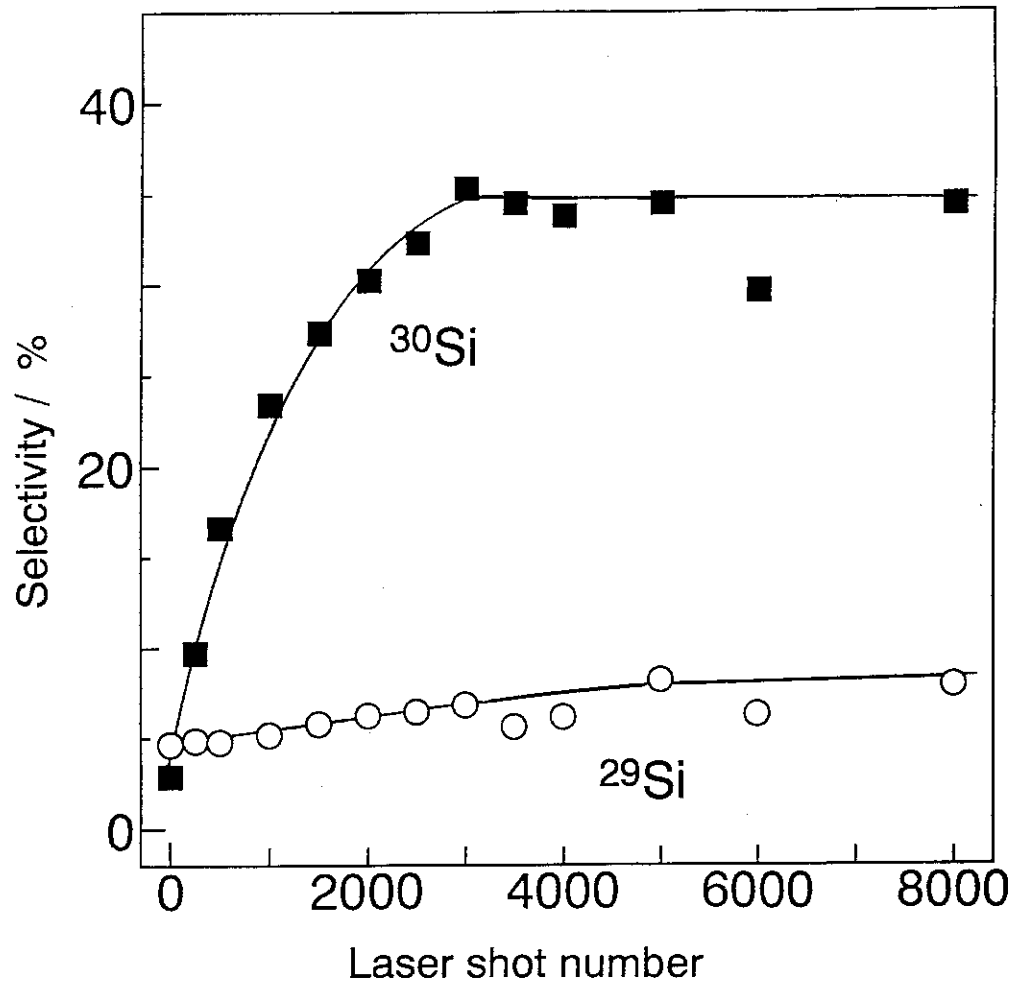
Separation of silicon isotopes has been studied by the IRMPD method. The separation ratio of  $^{30}\text{Si}$  isotope reached a maximum of 35% at a fluence of  $\approx 1 \text{ J cm}^{-2} \text{ pulse}^{-1}$  and decreased with fluence. On the other hand, the decomposition of  $\text{Si}_2\text{F}_6$  containing  $^{29}\text{Si}$  isotope became considerable at a high fluence. The present study is now in progress to optimize the reaction parameters for isolation of silicon isotopes in a large scale.

#### Reference

- 1) M. Kamioka, S. Arai, Y. Ishikawa, S. Isomura, and N. Tanaka, *Chem. Phys. Lett.*, **119**, 357(1985).



**Fig. 1** Selectivity of <sup>30</sup>Si and <sup>29</sup>Si isotopes in the IRMPD of Si<sub>2</sub>F<sub>6</sub> with a 10.513- $\mu$ m CO<sub>2</sub> laser as a function of the laser fluence: initial pressure of Si<sub>2</sub>F<sub>6</sub>, 2 Torr; total energy  $2.8 \times 10^3$  J cm<sup>-2</sup>.



**Fig. 2** Selectivity of  $^{30}\text{Si}$  and  $^{29}\text{Si}$  isotopes as a function of the laser shot number in the IRMPD of  $\text{Si}_2\text{F}_6$  with a  $10.513\text{-}\mu\text{m}$   $\text{CO}_2$  laser at a laser fluence of  $0.9\text{ J cm}^{-2}\text{ pulse}^{-1}$  (initial pressure of  $\text{Si}_2\text{F}_6$  was 2 Torr).

## 8. Excimer Laser-Assisted Fluorination of Tooth Enamel Affording Acid-Resistance

*C. Miyazawa,\* M. Kokubun,\* M. Amano,\* S. Hamada,\* T. Shimizu,\*  
S. Sugimoto,\*\* and S. Kawanishi*

We previously reported that carbonate ion ( $\text{CO}_3^{2-}$ ) is photochemically released from apatite crystals in tooth enamel by excimer laser irradiation,<sup>1,2)</sup> which accelerated uptake of fluoride ion ( $\text{F}^-$ ) into crystals in the preirradiated enamel upon reaction with a alkali fluoride solution.<sup>3)</sup> From a viewpoint of acid-resistance of the fluorinated enamel surface for preventive dentistry, we examined the photochemical reaction and the following fluorination, which lead to formation of fluoroapatite (FAp).

Enamel powder was pressed to prepare smooth disks (Enamel Disk; 13-mm diameter, 0.7-mm thickness). The Enamel Disk was coated with a 2 wt% NaF solution (40  $\mu\text{L}$ ), and was irradiated at 248nm with a KrF excimer laser (Lumonics, EX-884). The irradiation was performed under conditions of: A (50  $\text{mJ cm}^{-2}$  pulse<sup>-1</sup>, 1400 shot), B (70  $\text{mJ cm}^{-2}$  pulse<sup>-1</sup>, 1430 shot), C (70  $\text{mJ cm}^{-2}$  pulse<sup>-1</sup>, 2000 shot), and D (70  $\text{mJ cm}^{-2}$  pulse<sup>-1</sup>, 3000 shot). The Enamel Disks were washed with an aqueous solution of KOH (1M) for one day before analysis. The surface was analyzed by scanning electron microscopy (SEM), X-ray small angle diffraction, and X-ray photoelectron spectroscopy (XPS). The acid-resistance was estimated by measuring calcium ion concentration dissolved into a 0.4M-acetate buffer solution (pH 4.0).

Though the irradiation of the Enamel Disk under the condition B gave a rough surface owing likely to ablation, a markedly smooth surface was obtained besides a slight roughness by the irradiation in the NaF solution. The FAp concentration at the Enamel Disk surface was estimated by X-ray small angle diffraction with an incidental angle of 8° to the sample surface, where signal intensities derived from a plane of FAp of the Miller index of (213) was converted into the FAp concentration by the use of a calibration curve previously obtained for the samples of various FAp concentration. While no FAp was formed on the surface by immersing in the NaF solution, FAp was markedly formed by the irradiation in the solution (Fig. 1). Apparently, there must be a considerable effect of laser irradiation on the formation of FAp, which was also supported by a marked increase of an atomic ratio F/Ca obtained by XPS elemental analysis of the samples.<sup>2,3)</sup>

The acid-resistance of the Enamel Disks was more desirable for the irradiated samples

---

\*Department of Preventive Dentistry, Ohu University

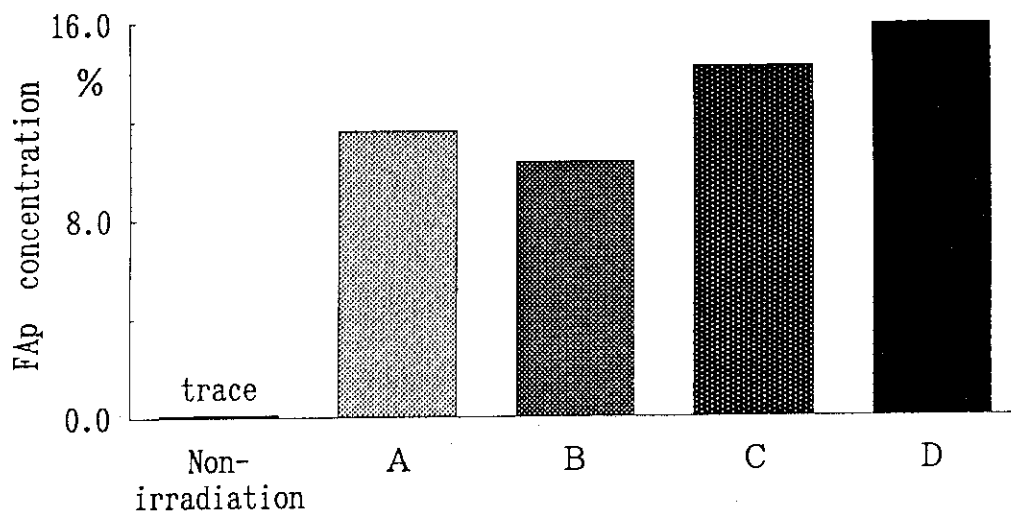
\*\*Radiation Application Development Association

than the non-irradiated one as shown in Fig. 2.<sup>1,2)</sup> The laser irradiation seemed to be the most effective under the condition C as judged by the one-way analysis of variance. The present results demonstrate that KrF laser irradiation of teeth enamel in an aqueous solution of NaF enhances acid-resistance through formation of fluoroapatite (FAp), which will be favorable with respect to prophylaxis of caries of the teeth by the use of KrF laser.

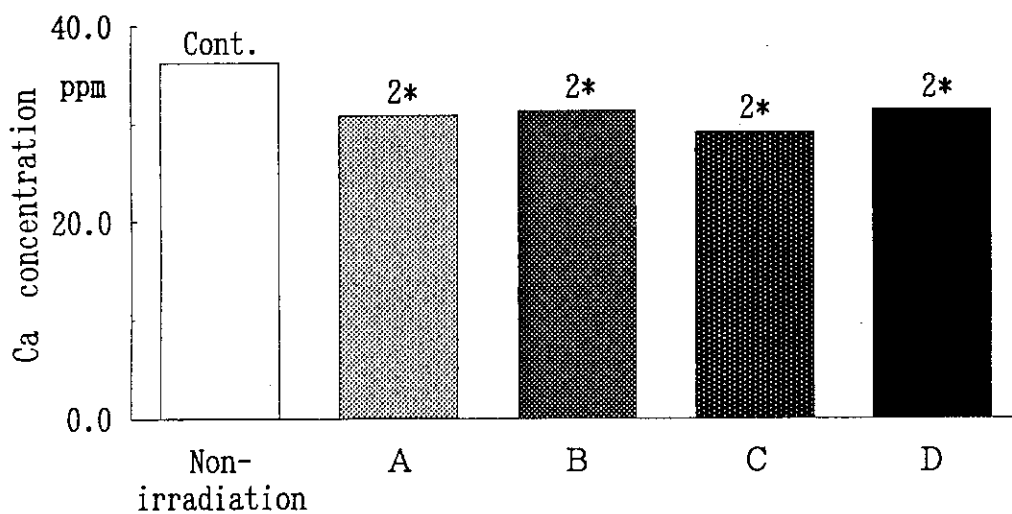
The present work was supported in part by a Grant-in-Aid for Scientific Research No. 06672065 (received in 1994) from the Japanese Ministry of Education, Science, and Culture.

### References

- 1) C. Miyazawa, M. Kokubun, M. Yuki, and T. Shimizu, *Dent. Jpn*, **30**, 99(1993).
- 2) C. Miyazawa, M. Kokubun, S. Hamada, T. Shimizu, S. Sugimoto, Y. Shimizu, M. Nishii, S. Kawanishi, and N. Suzuki, *JAERI-M*, **94-017**, 22(1994).
- 3) C. Miyazawa, S. Hamada, M. Kokubun, M. Amano, T. Shimizu, S. Sugimoto, Y. Shimizu, and S. Kawanishi, *JAERI-Review*, **95-002**, 24(1995).



**Fig. 1** The formation of fluoroapatite (FAp) in the Enamel Disk after the irradiation in the 2 wt% NaF aqueous solution: for A-D, see text. Irradiation A-D:  $p < 0.01$  (one-way ANOVA).



**Fig. 2** The acid-resistance of the Enamel Disks before and after the irradiation in the 2 wt% NaF aqueous solution: for A-D, see text. 2\*:  $p < 0.01$  (t-test).



## 9. The Effect of Excimer Laser Irradiation on Growth of Oral Bacteria

*S. Hamada,\* Y. Akiyama,\* M. Kokubun,\* C. Miyazawa,\* M. Amano,\*  
T. Shimizu,\* S. Sugimoto,\*\* and S. Kawanishi*

It has been reported that KrF excimer laser beam has a sterilizing power for unicellular organisms which in part inhibits DNA synthesis,<sup>1,2)</sup> though the precise mechanism, however, is not clear. While KrF excimer laser has been utilized in order to strengthen tooth enamel in dental treatment and prophylactic dentistry,<sup>3,4)</sup> the sterilization will be also a possible application. The influence of excimer laser irradiation on the growth of causative bacteria<sup>5,6)</sup> of caries teeth was examined from these fundamental and practical points of view.

An excimer laser (Lumonics hyper EX-884) was used for irradiation. The 4 types of sample stocks of oral bacteria were used, which were isolated from human saliva: *Streptococcus mutans* PS-14 (*Str. mutans*), *Streptococcus sobrinus* (*Str. sobrinus*), *Lactobacillus casei* ATCC 4646 (*Lact. casei*), and *Streptococcus salivarius* ATCC 9759 (*Str. salivarius*). These samples were supplied from the Department of Dental Pharmacology, School of Dentistry, Ohu University. Each bacterial suspension 0.1 mL adjusted to transmissivity of 30% ( $1.8 \times 10^8$  CFU/mL) at 660 nm was applied to a solidified agar medium (Brain Heart Infusion agar, Difco) in a sterilized Petri dish. The Petri dish was wrapped with polyethylene film to prevent contamination by sundry germs or dust, and was irradiated at 248 nm with laser beam through the film. The KrF laser irradiation was performed with laser shots of 200, 400, and 600 at fluences of 0.4, 4, and  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ , respectively. The area of the irradiation was 12 mm length x 12 mm width. The sample was incubated in an anaerobic condition at a temperature 37 °C for several days to grow bacteria.

Figure 1 shows the growth of *Str. sobrinus* with application of 200, 400, and 600 laser shots at  $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ . This indicates that the irradiation at each shot number obstructed the growth of the bacteria and the bacteria growth zone had a tendency to decrease with the energy of KrF excimer laser. While similar results were observed for *Lact. casei* and *Str. mutans*, it seemed that *Str. salivarius* was less affected by KrF laser irradiation. The correlation between the laser energy and the growth zone of oral bacteria as a correlative coefficient ( $r$ ) was calculated from these results to be,  $r = 0.73$  ( $p < 0.01$ ) for *Str. sobrinus*,  $r = 0.52$  ( $p < 0.05$ ) for *Lact. casei*, and  $r = 0.49$  ( $p < 0.05$ ) for *Str.*

---

\*School of Dentistry, Ohu University .

\*\*Radiation Application Association.

mutans.

This study demonstrates that some oral bacteria are susceptible to laser irradiation and the others are not. While it should be cleared that the influence of excimer laser beam on the obstruction of the growth of oral bacteria is based on a similar effect of ultraviolet irradiation<sup>1,2)</sup> as seen with a sterilizing light of a wavelength of 254 nm, the present results strongly suggest a validity of KrF laser for prophylaxis of dental caries.

### Reference

- 1) J. C. Sherris et al., "*Medical Microbiology*," ed. by J. C. Sherris, Elsevier, New York, 1984, p. 37.
- 2) K. Yokota and R. Kawana et al., "*Standard Textbook of Microbiology 4th Ed.*," ed. by K. Yokota and R. Kawana, Igakushoin, Tokyo, 1990, p. 79-80.
- 3) C. Miyazawa, M. Kokubun, S. Hamada, T. Shimizu, S. Sugimoto, Y. Shimizu, M. Nishii, S. Kawanishi, and N. Suzuki, *JAERI-M*, **94-017**, 22(1994).
- 4) C. Miyazawa, S. Hamada, M. Kokubun, M. Amano, T. Shimizu, S. Sugimoto, Y. Shimizu, and S. Kawanishi, *JAERI-Review*, **95-002**, 24(1995).
- 5) J. Nishikata, Y. Hirano, K. Ito, O. Takada, S. Narukawa, and S. Murai, *J. Jpn Soc. Periodont.*, **34**, 410(1992).
- 6) T. Iwase, H. Okamoto, T. Saito, M. Murakami, and T. Morimoto, *J. Jpn Soc. Laser Med.*, **13**, 27 (1992).

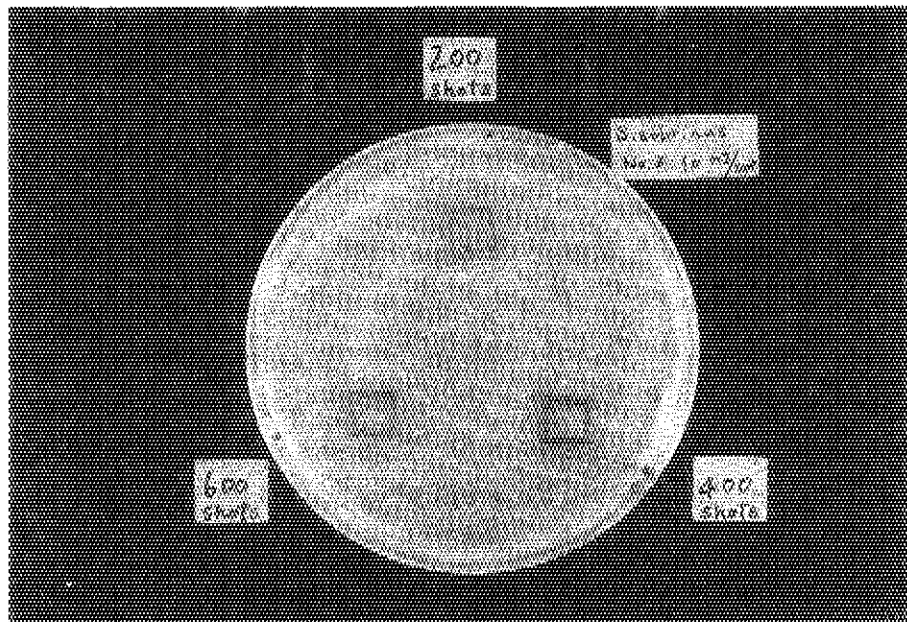


Fig. 1 The growth zone of *Str. sobrinus* with application of KrF excimer laser beam: ( $10 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$ ; 200, 400, and 600 shots).

## 10. Radiation-Induced Polymerization of Thin Epoxyacrylate Films

*Y. Nakase, A. Nakamune,\* and I. Kaetsu\**

Recently, various functional polymers have been developed to satisfy the requirements of microelectronic devices. There is a strong demand for stable and adhesive organic materials for microlithography, microsensing and so on. Several studies were reported on ultraviolet- (UV-) or electron beam- (EB-) induced polymerization of bisphenol A epoxy resins containing an initiator in spin-casted films with thicknesses of several tens of micrometers to 1 mm.<sup>1-3)</sup> In this paper, we report a novel behavior of EB-induced polymerization of an epoxyacrylate oligomer in spin-casted thin films without an initiator under nitrogen stream.

An epoxyacrylate resin (Arakawa Kagaku Kogyo) was used as received and was dissolved in acetone for thickness control if necessary. Spin-casted films of the resin placed on a conveyer, which traveled back and forth at a speed of 90 mm/s during irradiation, were irradiated under nitrogen stream with a Van de Graaff accelerator with an accelerating voltage of 1.5 MeV. The energy deposited in the film was estimated by CTA-film dosimeter. The thickness of the films was determined from the absorbance of a band of =CH<sub>2</sub> group at 2940 cm<sup>-1</sup>. The polymerization rates are estimated from the decreasing rate of absorbance of a band of vinylic =CH<sub>2</sub> group at 1636 cm<sup>-1</sup>. No polymerization took place when the sample was irradiated in air, or without nitrogen stream.

Figure 1 shows changes in the IR spectra of the films by irradiation. The absorbance at 1636 cm<sup>-1</sup> decreased with the absorbed dose, while that at 2940 cm<sup>-1</sup> remained almost unchanged. This indicates that the decrease of =CH<sub>2</sub> group corresponds to the polymerization of the resin. Figure 2 shows a relationship between the dose rate and the conversion in the polymerization obtained for the samples of 1.8- $\mu$ m thickness irradiated up to 200Gy. The dose rate and the polymerization rate are functions of absorbed doses per pass (Gy/pass) and conversion of the vinylic =CH<sub>2</sub> group per pass (%/pass) at a constant conveyer speed, respectively. The polymerization rate increased linearly with the dose rate. This is characteristic of a unimolecular termination reaction. These results suggest that growing chain ends of polymer cannot move freely in the matrix. Such a hindered molecular motion can be attributed to an orientational geometry of the oligomer molecules in thin films. The orientation of the oligomer molecules was observed by the X-ray diffraction method. Figure 3 shows a wide-angle X-ray scattering

---

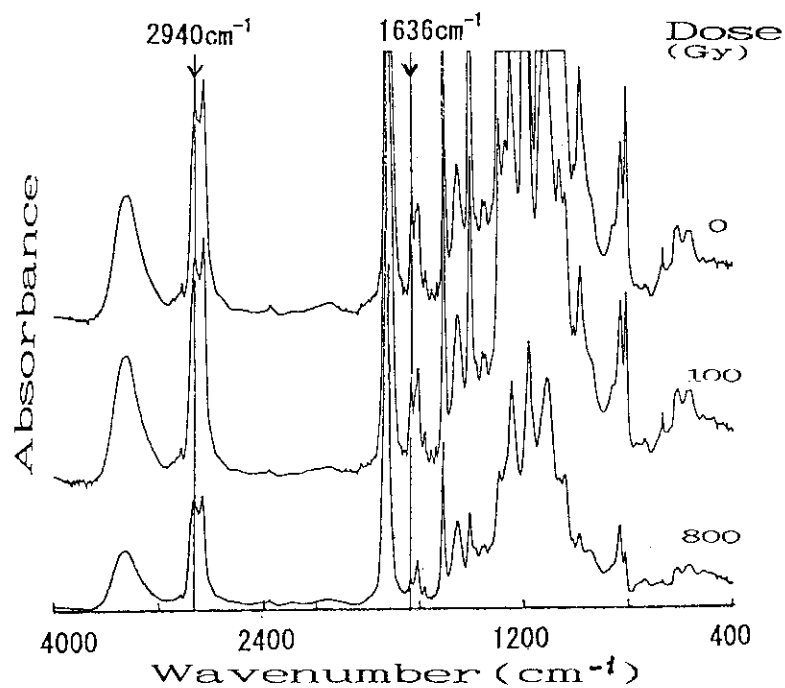
\*Kinki University.

profile of the irradiated film of 10- $\mu\text{m}$  thickness. There is a peak at an angle of ca.  $29^\circ$  of  $2\theta$  on the amorphous halo diffraction curve beside a sharp peak at  $30^\circ$  due to Si wafer. The peak at  $29^\circ$  indicates a molecular orientation of the oligomer approximately parallel to Si wafer surface, which must be caused by the spin-casting process.

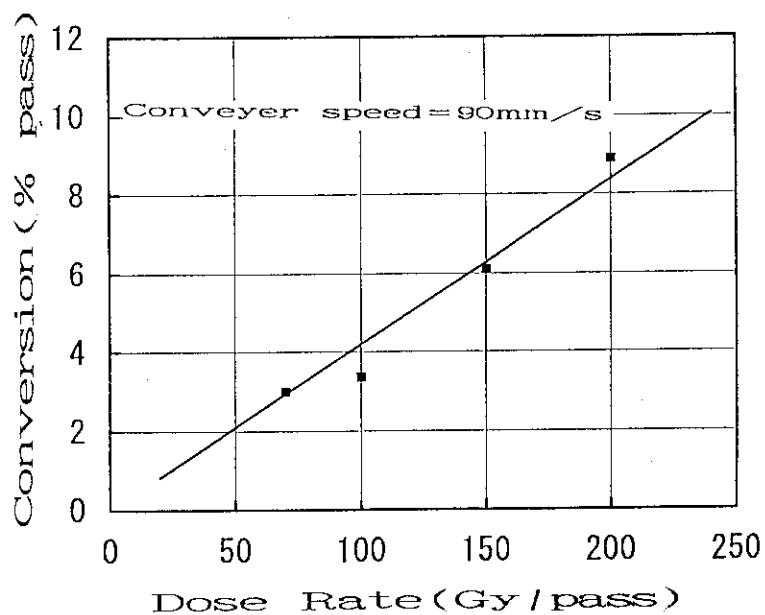
The effects of the sample thickness on the polymerization rate have been examined. Figure 4 shows a relationship between the thickness of the sample and the polymerization rate obtained for the initial stage of the irradiation. The initial polymerization rate is dependent on the thickness of the films up to 4  $\mu\text{m}$ . The rate increased with the thickness to become almost constant for the films of  $> 4 \mu\text{m}$ . This indicates that the molecular motion in the polymerization is hindered considerably in a thin matrix. This motion can be released from the hinderance by heating. When a thin sample films at a conversion of ca. 50% was heated at  $160^\circ\text{C}$  for a few minute, the absorbance at  $1636 \text{ cm}^{-1}$  was decreased to indicate the polymerization induced by the increase of molecular motion. The present results strongly suggest that molecular or segmental motion of polymer chain is hindered in general in thin film matrices such as spin-casted films.

### References

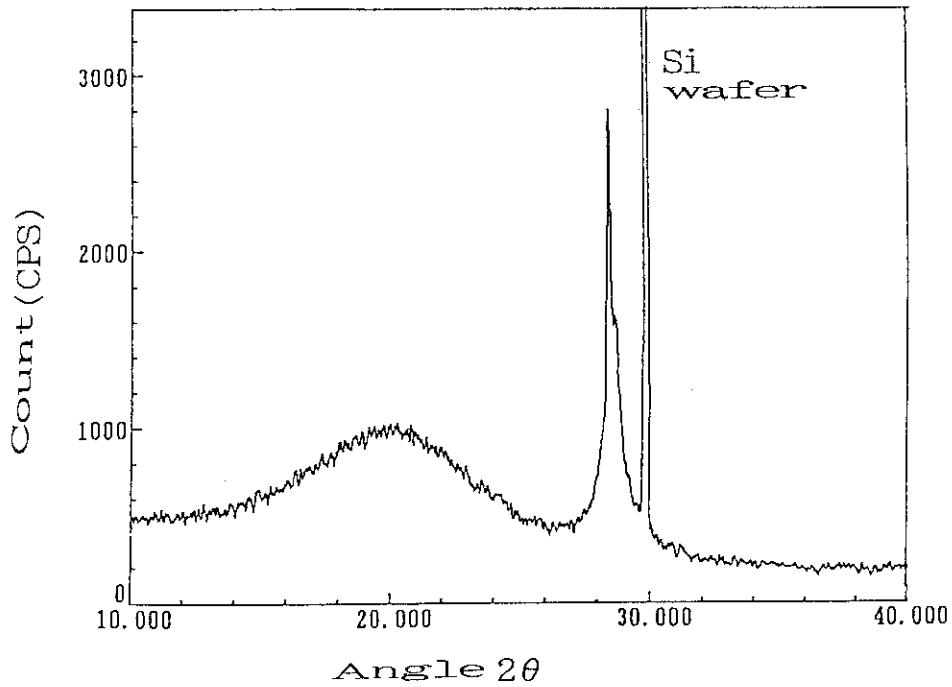
- 1) T. Okada, T. Asano, M. Hatada, J. Takezaki, and K. Ochi, *Kobunshi Ronbunshu*, **44**, 761 (1987).
- 2) I. Fijita, Y. Tanaka, and J. Takezaki, *Radiat. Phys. Chem.*, **40**, 161(1992).
- 3) Y. Nakase, H. Doi, and I. Fujita, *JAERI-Review*, **95-002**, 31(1995).



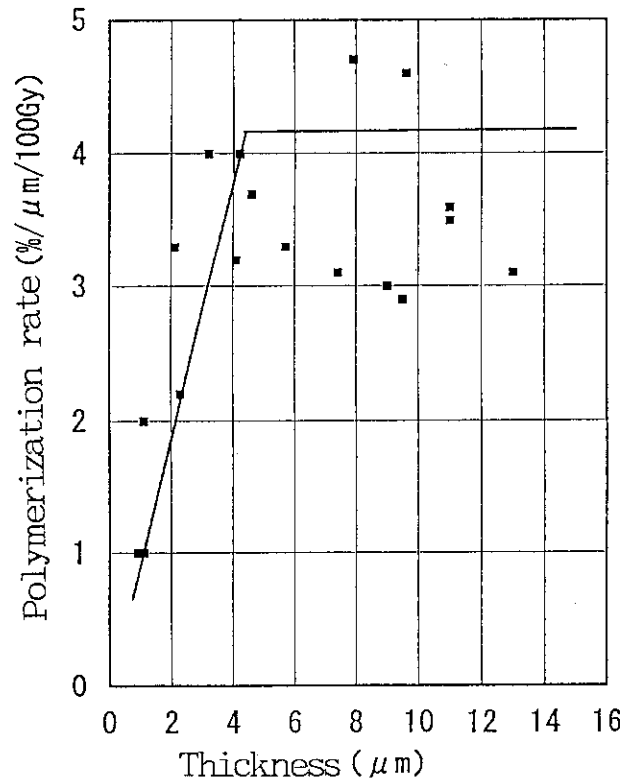
**Fig. 1** Changes in the infrared spectra of the epoxyacrylate oligomer film by EB-irradiation. Doses are indicated in the figure.



**Fig. 2** A relationship between dose rate and conversion in the polymerization by EB-irradiation (1.5 MeV). The sample thickness is ca.  $1.8\ \mu\text{m}$ .



**Fig. 3** A wide-angle X-ray scattering profile of the sample irradiated with an electron beam (1.5 MeV, 1 k Gy) at room temperature; X-ray source: Cu-K $\alpha$ , 50 kV, 400 mA, scanning rate: 4°/min (2 $\theta$ ).



**Fig. 4** A relationship between the sample thickness and the initial polymerization rates of the epoxyacrylate in the course of irradiation at 100 Gy.

## 11. Formation of Fine Particles from Aqueous Solution of Silver Ion by $\gamma$ -Ray Irradiation

*Y. Nakase, K. Ushiroda,\* I. Kaetsu,\* and M. Hatada\*\**

Many studies have been conducted on the radiation-induced formation of metal clusters from aqueous solution of metal ions, mostly noble metals. Their efforts were concentrated on reaction mechanisms of cluster formation,<sup>1,2)</sup> where surface active reagents were used to stabilize metal cluster formed. We are intending to prepare functional materials having catalytic activities for solid-gas heterogeneous reactions. In the previous papers,<sup>3,4)</sup> we have reported that palladium particles were formed in deaerated aqueous solutions of palladium sulfate by  $\gamma$ -ray irradiation and the particles grew during and even after irradiation as well. Silver ion was reduced to form fine metal particles by the irradiation of solutions at a pH of 1.43 in the presence of palladium ion, while no reduction was observed for silver sulfate solutions at pH < 4 in the absence of palladium ion. The present study has been carried out in order to obtain some information on the mechanisms of the radiation-induced formation of silver metal particles in solutions of silver ion containing palladium ion at pH 0.43 and those without palladium ion at pH 7.

Deaerated solutions containing silver ion were irradiated by  $^{60}\text{Co}$   $\gamma$ -rays and was transferred to a cuvette for UV measurement or to a quartz tubing for dynamic light scattering within 3 min after the irradiation as described elsewhere.<sup>3)</sup> Figure 1 shows turbidity of a solution containing silver sulfate and palladium sulfate (0.5 mM + 0.5 mM) as a function of time during and after the irradiation with 2.5, 5, and 10 kGy. The turbidity of the samples increases with dose to indicate that the amount of particles formed by irradiation increases with dose. The increase of the turbidity at the earlier period after the irradiations at 2.5 and 5 kGy indicates coagulation of particles or clusters formed. The turbidity after maxima decreased fast in an order of the dose to indicate that a fast coagulation of aggregates is induced by high dose to form larger particles which precipitate rapidly.

Figure 2 shows average diameter of particles as a function of time during and after irradiation. It is obvious that the particle size increased monotonically with time up to 5 h, and leveled off after that where larger final particle size was observed at higher dose.

An electrochemical relationship between silver and palladium in consideration of

---

\*Kinki University.

\*\*Guest Researcher of JAERI (1993-1994).

cluster size suggests that the particle formed in palladium-silver sulfate solutions has a morphology that is composed of a palladium core covered with silver surroundings. Even noble metal cluster or aggregate  $M_n^0$  undergoes reoxidation into ions  $M^{m+}$  by  $H^+$ ,  $H\cdot$ , or  $OH\cdot$ , which is formed by the irradiation of water, when its aggregation number  $n$  is small.<sup>1)</sup> Since standard electrochemical potential ( $E_0(Pd^{2+}/Pd^0) = 0.915$  V) is larger than those of hydrogen ( $E_0(H^+/H_2) = 0.00$  V) and silver ( $E_0(Ag^+/Ag^0) = 0.799$  V), the reoxidation is unfavorable even when  $n$  is small. In the case of silver, small clusters will be oxidized more readily than palladium clusters. Reduction of palladium, therefore, will proceed faster than that of silver ion by irradiation. Then silver atoms will deposit readily on the surface of the palladium clusters.

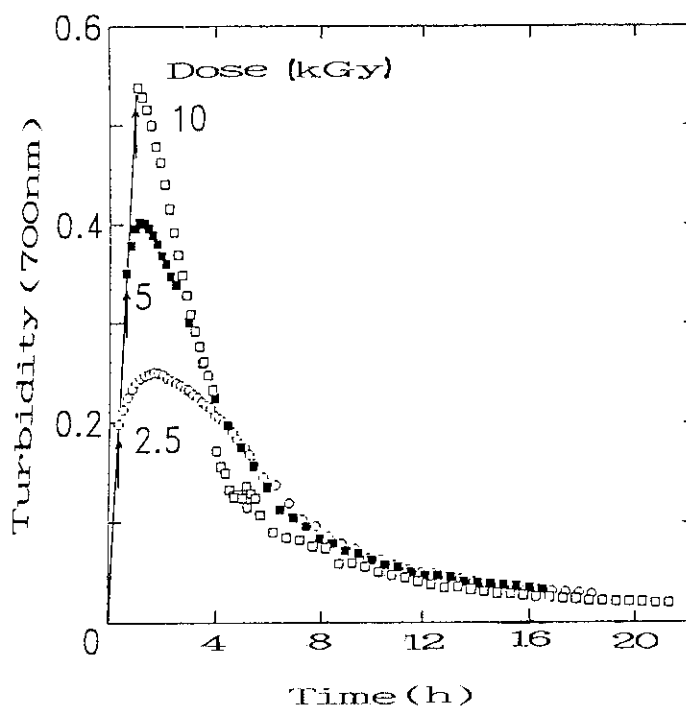
Figure 3 shows turbidity of a solution of silver perchlorate (2.0 mM) as a function of time during and after the irradiation at doses of 90, 180, and 350 Gy, which are about 1/30 of that applied to the palladium-silver mixture. Though the turbidity of the samples which is about half of that seen in Fig. 1, it increases with dose to indicate that the amount of particles increase with dose. The increase of the turbidity at an earlier period after irradiation was observed only at 90 Gy, but not at higher doses. The decrease of turbidity with time indicates that the aggregates coagulate further to form larger particles, though the coagulation rate is not so fast. Figure 4 shows average diameter of particles as a function of time during and after irradiation. It should be noticed that the diameters are 1/10 to 1/5 of those observed for the mixed solutions, and increase continuously with time though some of larger aggregates precipitate. The small size may be explained by the reoxidation which prevents the growth of the particles with small  $n$ .

The  $\gamma$ -ray irradiation of the  $Pd^{2+}$ - $Ag^+$  and  $Ag^+$  solutions yielded fine silver-palladium bimetallic and, in particular, silver particles of a few micrometers to hundreds nanometers. The difference between the two cases of the solutions of  $Pd^{2+}$ - $Ag^+$  and  $Ag^+$  alone can be attributed mainly to the reoxidation which affects the initial size of particles formed during irradiation.

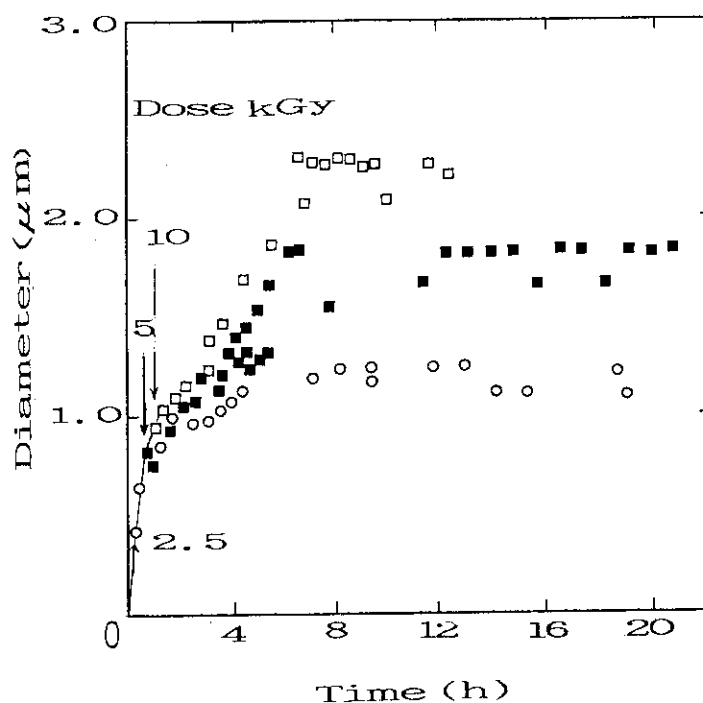
## References

- 1) J. L. Marignier, J. Belloni, M. O. Delcourt, and J. P. Chevalier, *Nature*, **317**, 344(1985).
- 2) A. Henglein, *J. Phys. Chem.*, **97**, 5457(1993).
- 3) M. Hatada, *JAERI-M*, **93-232**, (1993).
- 4) M. Hatada and C. D. Jonah, *JAERI-Research*, **94-019**, (1994).

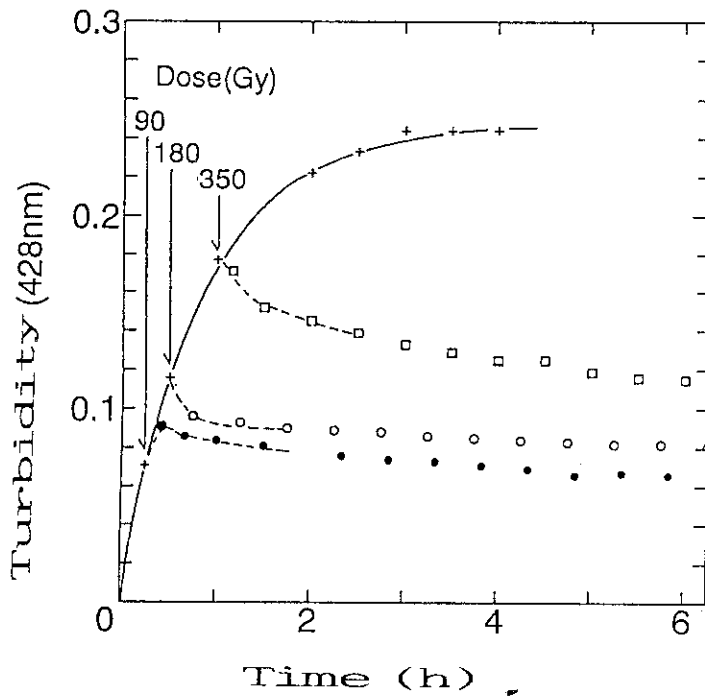




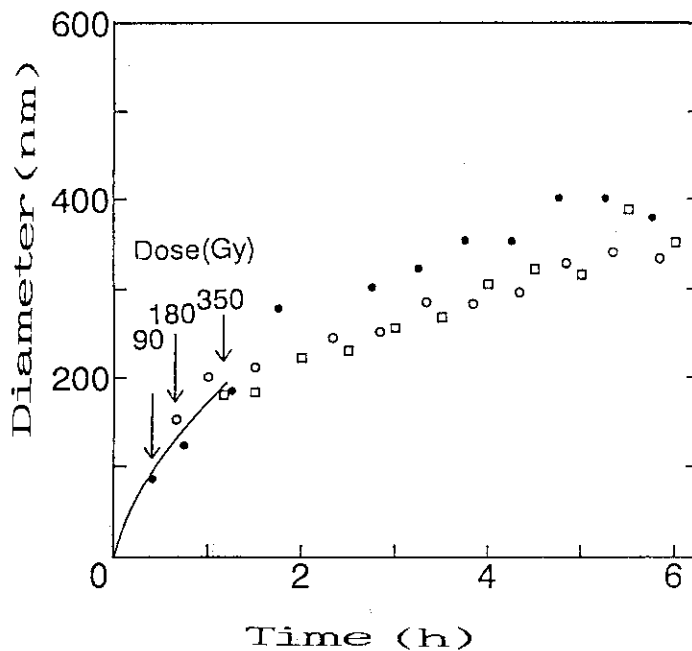
**Fig. 1** Turbidity (O.D. at 700nm) as a function of time after the irradiation of a palladium sulfate-silver sulfate solution:  $[\text{Pd}^{2+}] = [\text{Ag}^+] = 0.5 \text{ mM}$ , pH 0.43, and at doses of 2.5 kGy (open circle), 5 kGy (closed square), and 10 kGy (open square).



**Fig. 2** Average diameter of particles as a function of time during and after the irradiation for a palladium sulfate-silver sulfate solution:  $[\text{Pd}^{2+}] = [\text{Ag}^+] = 0.5 \text{ mM}$ , pH 0.43, and at doses of 2.5 kGy (open circle), 5 kGy (closed square), and 10 kGy (open square).



**Fig. 3** Turbidity (O.D. at 428nm) as a function of time during and after the irradiation of a silver perchlorate solution:  $[Ag^+] = 2 \text{ mM}$ , pH 7, at doses of 90 Gy (closed circle), 180 Gy (open circle), and 350 Gy (open square).



**Fig. 4** Average diameter of particles as a function of time during and after the irradiation of a silver perchlorate solution:  $[Ag^+] = 2 \text{ mM}$ , pH 7, and at dose of 90 Gy (closed circle), 180 Gy (open circle), and 350 Gy (open square).

## 12. A Study on Defects in Electron-Irradiated Silicon

*L. Liu,\* Y. Nakase, T. Mitamura,\* M. Terasawa\**

Radiation-induced defects in matter have been investigated in connection with applications to processing of semiconductor devices and preparation of new materials for nuclear field. The resistivity of semiconductors increases exponentially with electron fluence at low fluence level. In order to investigate the damage production process, the measurement of changes in a resistivity of silicon with electron irradiation must be useful. For n-type and p-type silicon irradiated by high-energy electron (2-9 MeV), the relations between resistivity and electron fluence and between defect production rate of each complex defect and electron energies were investigated by Wada et al.<sup>1,2)</sup> It was suggested from the resistivity-electron fluence curves that the same kinds of defects were introduced at any electron energy. The relative rate of defect production in their experiment was reported to be in good agreement with the curve calculated by Cahn's theory.<sup>3)</sup> On the other hand, Corbett and Watkins<sup>4)</sup> have reported that the energy dependence for the introduction of both divacancies and oxygen-vacancy pairs are significantly different in the electron energy range of  $0.5 < E < 1.5$  MeV and that the introduction of the oxygen-vacancy pair slightly depends on the amount of oxygen present in silicon, while the introduction rate of other deep traps is usually greater when the oxygen concentration is smaller. Recently, some authors<sup>5)</sup> discussed defect types about the newly observed peaks in infrared (IR) absorption spectra in p-type silicon irradiated by 2-MeV electron beam, for example, peaks at  $830\text{ cm}^{-1}$  (V-O),  $1225$ ,  $1175$ ,  $1080\text{ cm}^{-1}$  (V-O<sub>2</sub>) and  $904$ ,  $969$ ,  $986\text{ cm}^{-1}$  (V-O<sub>3</sub>).

We are intending to show that resistivity measurements are valuable for studying radiation effects in silicon together with other methods such as electron paramagnetic resonance (EPR) and infrared (IR) measurements. In the present work, preliminary experiments were carried out in order to study the production and evolution process of radiation defects by electron irradiations in silicon single crystal, using the electrical resistivity measurement as well as EPR and IR spectroscopic measurements. The electron-energy dependences of the resistivity change and the defect production rate were deduced. The EPR and IR spectra of the irradiated silicon by 800-keV electron beam were also compared to the result of resistivity measurement.

The specimen was an undoped type silicon wafer, which had dimensions of  $40 \times 10 \times 0.38\text{ mm}^3$ . The surface of the specimen is parallel to the (111) plane. The specimens

---

\*Himeji Institute of Technology.

were mounted on a copper plate which was cooled with running water and were irradiated by electron beam. The both sides of the specimen were covered with Pb plates to prevent 2 electro-probe connecting wires from electron irradiation. After the irradiation, the specimens were left at room temperature about 30 minutes enough for reaching a stable state, and then the resistivities were measured by means of the two-point probes method. EPR and IR measurements were performed to study defect types and their annealing behaviors.

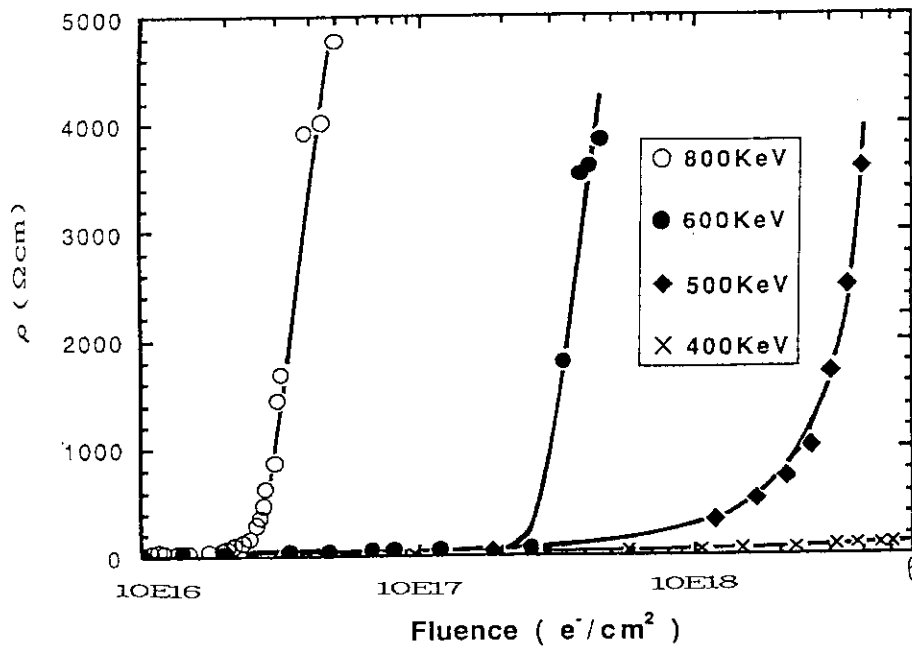
Variation of the resistivity  $\rho$  are shown in Fig. 1 as a function of electron fluence, in the cases of 0.4, 0.5, 0.6, and 0.8 MeV electrons. All the  $\rho$  curves have similar tendencies; namely, they increase slowly at first with electron fluence, show rapid increase next. Figure 2 shows the EPR spectra for both specimens unirradiated and irradiated by 800-keV electron with respect to the applied magnetic field B (a) parallel ( $B_{\parallel}$ ) and (b) perpendicular  $B_{\perp}$  to the  $\langle 111 \rangle$  plane. For irradiated specimen, a new EPR signal having the g factor of 2.006 was observed beside that of 2.001 which did not shift at  $B_{\perp}$ . We also observed that the EPR signal having g of 2.001 changed to that of 2.009 as  $B_{\parallel}$  changed to  $B_{\perp}$ . It is concluded that the defects corresponding to the EPR signal having g of 2.006 are produced in the bulk of Si wafer by irradiation. Figure 3 shows the IR absorption spectra of Si irradiated by 800 keV electron. The bands appearing at 607 and 1115  $\text{cm}^{-1}$  are independent on irradiation and annealing. The peaks at 825, 926, and 1225  $\text{cm}^{-1}$  showed a sharp rise when the annealing time reached to 60 min, and then decreased with the annealing time. From Fig. 3, the peak appearing at 825  $\text{cm}^{-1}$  induced by electron irradiation represents the defect V-O which should be contributed to the vibration of the oxygen atoms in the V-O complex, and the peak at 1225  $\text{cm}^{-1}$  to V-O<sub>2</sub> complex.<sup>5)</sup> In the present experiment, the defect V-O<sub>3</sub> at band position 926  $\text{cm}^{-1}$  by electron irradiation was also found which is in agreement with the result derived from neutron irradiation.<sup>6)</sup>

The resistivity measurements are useful to obtain preliminary data on the defects formation. These data can be analyzed with other results obtained by EPR, IR, and Hall effects methods.

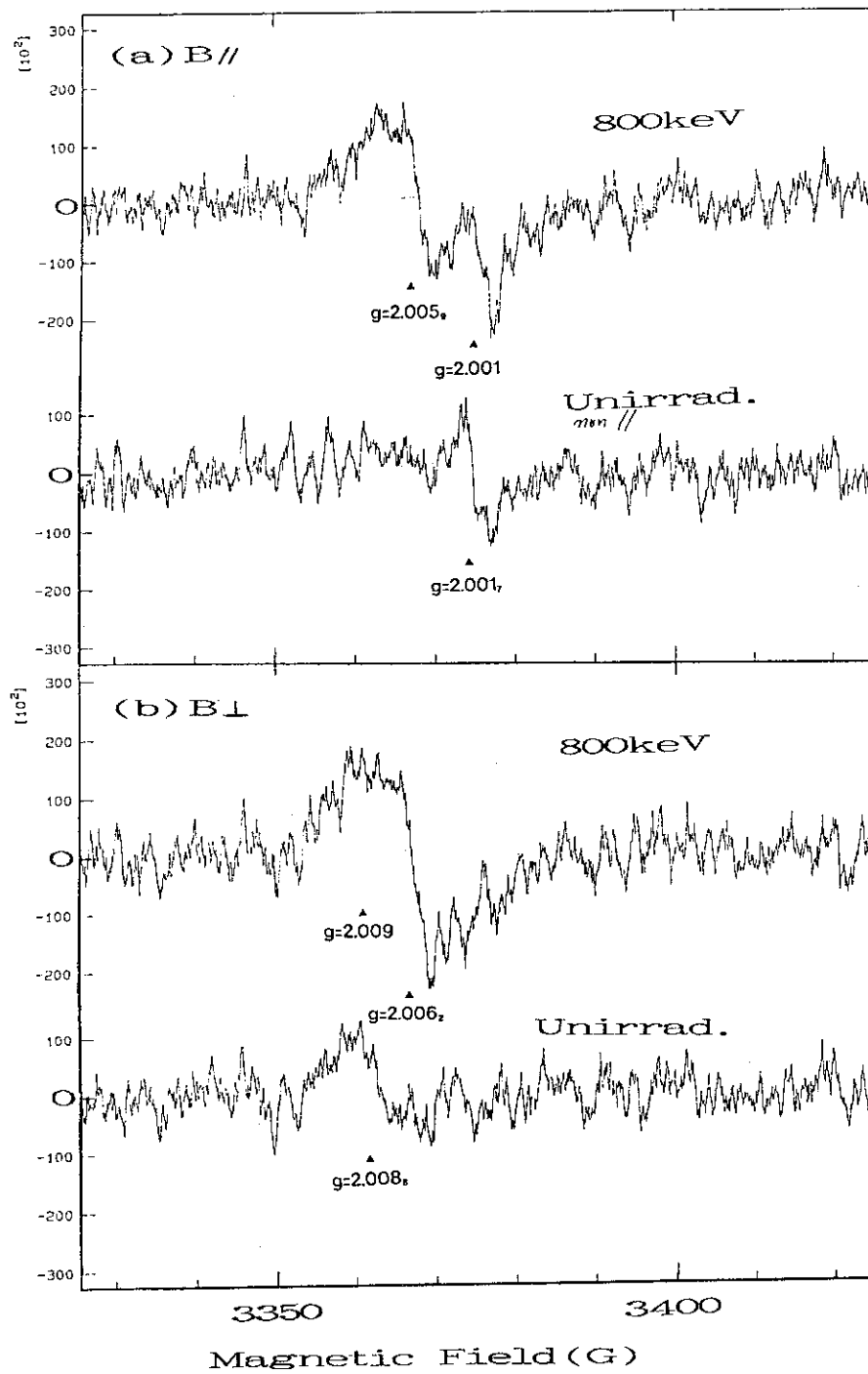
## References

- 1) T. Wada, K. Yasuda, S. Ikuta, M. Takeda, and H. Masuta, *J. Appl. Phys.*, **48**, 2145(1977).
- 2) K. Yasuta, T. Wada, H. Masuta, M. Takeda, and S. Ikuta, *Phys. Stat. Sol.*, (a)**88**, 543(1985).
- 3) J. H. Cahn, *J. Appl. Phys.*, **30**, 1310(1959).

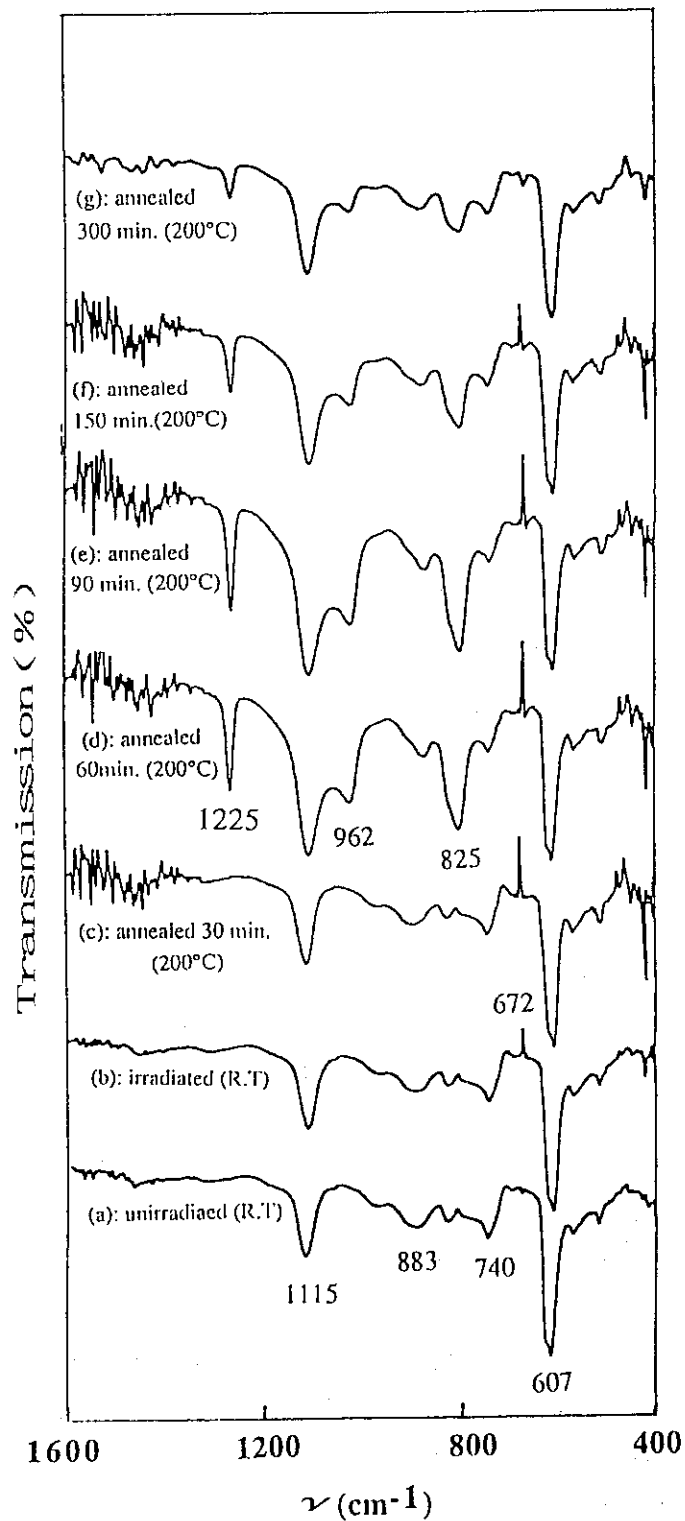
- 4) J. W. Corbett and G. D. Watkins, *Phys. Rev.*, **138**, A555(1965).
- 5) T. L. Hallberg and J. L. Lindstroem, *J. Appl. Phys.*, **72**, 5130(1992).
- 6) C. A. Londos, G. I. Georgion, L. G. Fytros, and K. Papastergion, *Phys. Rev. B.*, **50**, 11531 (1994).



**Fig. 1** Variation of the resistivity as a function of irradiation fluence at different electron energies for the irradiated single crystal silicon specimen.



**Fig. 2** EPR spectra for the specimens unirradiated and irradiated by 800 keV electron with  $7.8 \times 10^{16} \text{ e/cm}^2$  with magnetic field B, parallel to the incident  $\langle 111 \rangle$  beam direction (B//) and perpendicular to the incident  $\langle 111 \rangle$  beam direction (B⊥).



**Fig. 3** IR absorption spectra of the electron-irradiated silicon (800 keV,  $9.4 \times 10^{16}$  e/cm<sup>2</sup>). Every curve is characterized by the annealing temperature (200 °C) and the annealing time (min).

### 13. Charge Accumulation of Open-Cell Type Polyethylene Foam by Electron Beams

*N. Kotani\* and Y. Nakase*

Positive or negative charging-up takes place within dielectric solids, when they are bombarded by electron beams. Charged dielectrics (electrets) are widely used in industry such as microphone, electric recording devices, filters and so on. The charging-up can be controlled by applying bias through an external electrode. Though electron injection produce a negative charge in general, samples can be charged positively by electron irradiation by hole generations, which are occurred in the sample whose metallized rear electrode is negatively biased during irradiation.<sup>1)</sup> It is, however, difficult to understand the mechanism of charge build up and decay, since the number of electrons emitted from a bombarded surface (secondary electrons) is influenced by several factors such as an incident beam current, energy distribution of elastically and inelastically back-scattered electrons. In addition, the number of emitted electrons is larger than that of primarily injected electrons in some cases. We have studied the charging and decay behavior of open-cell type polyethylene foam irradiated by electron beams for its new applications.

The open-cell type polyethylene foam (OPCELL) has apparent density of 0.029 g/cm<sup>3</sup>, and contains cells of 0.5 mm of average radius. Irradiation was carried out in air with an electron beam from a Van de Graaff through a window of Ti foil. Samples of OPCELL sheet of (4-10)<sup>2</sup> cm<sup>2</sup> x 5 mm were placed on a conveyer which traveled back and forth during the irradiation. The irradiation conditions were as follows: accelerator voltage 300-1500 keV, beam current 5-50  $\mu$ A, and conveyer speed 8-32 mm/s. The dosimetry was performed with a 125- $\mu$ m thick cellulose triacetate film (CTA) dosimeter. Surface voltage of the irradiated sample was measured on an aluminum plate with a Shishido Type S-5109 electrostatic voltmeter. Charges retained in the foam were measured by a Faraday cup under an ambient condition.

Figure 1 shows that negative initial surface voltage is induced by the absorbed dose at every accelerating voltages by applying the bias of 5 kV. It was reported that the surface charge density on poly(ethylene terephthalate) (PET) films measured by an induction type electrometer increased linearly with dose in a range of 10 to 300 Gy, and decreased in a range of 300 to 4000 Gy.<sup>2)</sup> On the other hand, the initial surface charge density on polyethylene film increased almost linearly with dose in a range 100 to 4000 Gy.<sup>3)</sup>

---

\*Sanwa Kako, Ltd.



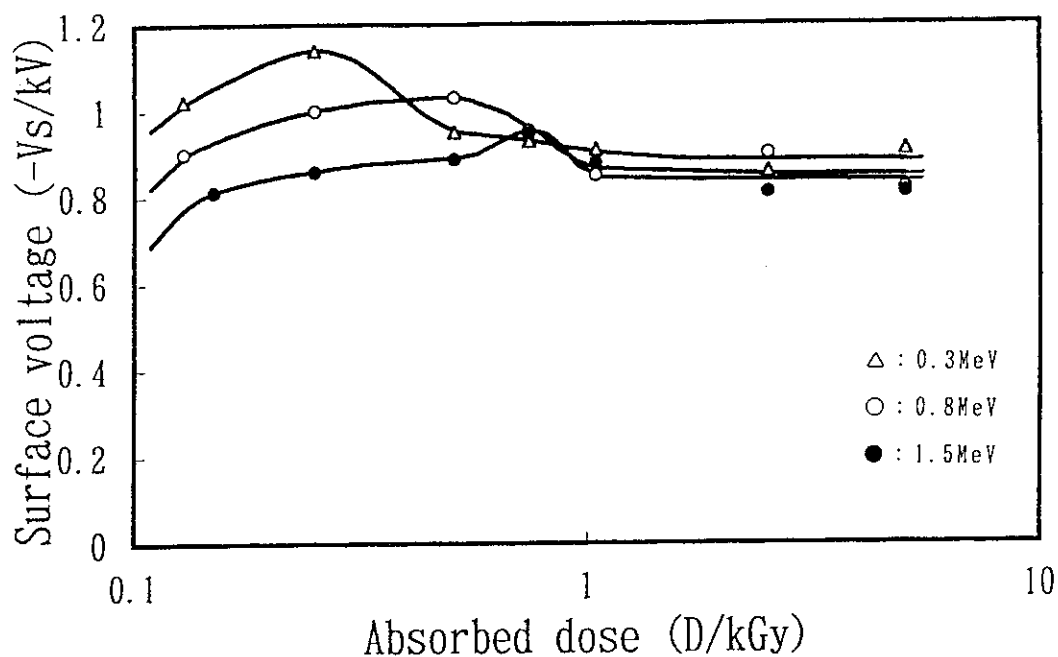
Therefore, the charging-up behavior in our case of polyethylene foam by the electron beam irradiation is similar to that observed for PET.

Figure 2 shows the relationship between the applied voltage ( $V_a$ ) on an aluminum plate electrode under the sample and the initial surface voltage ( $V_s$ ) of a sample. When a positive voltage was applied on the electrode, a negative surface voltage ( $-V_s$ ) was observed, and vice versa. The positive  $V_s$  increases linearly with the negative  $V_a$ . As shown in Fig. 3, a relationship between  $V_s$  and the charge density ( $\rho$ ) of the sample was obtained as  $\rho = -1.3V_s \times 10^{-15}$  (C cm<sup>-3</sup>), where  $V_s$  is in an unit of V. Then the charging up behavior on the sample can be discussed with  $V_s$ . In order to explain the appearance of the most probable absorbed dose seen in Fig. 1, we have considered the distribution of absorbed doses in the sample. Figure 4 shows the depth-dose distribution curves for electrons of 0.3, 0.8 and 1.5 MeV.<sup>4)</sup> Ratios of absorbed doses of electrons for 0.8 and 1.5 MeV to that for 0.3 MeV in the sample as denoted as  $c$  on the abscissa are 0.5 and 0.4, respectively. These values are in fairly good agreement with the reciprocal ratios of 0.5 and 0.3 of the most probable absorbed doses, which were obtained for 0.8 and 1.5 MeV to that of 0.3 MeV, respectively, by taking into account of the back-scattering of electrons from the Al electrode in the OPCELL case. It was concluded that higher deposition of electrons on the sample is obtained by applying lower electron energies.

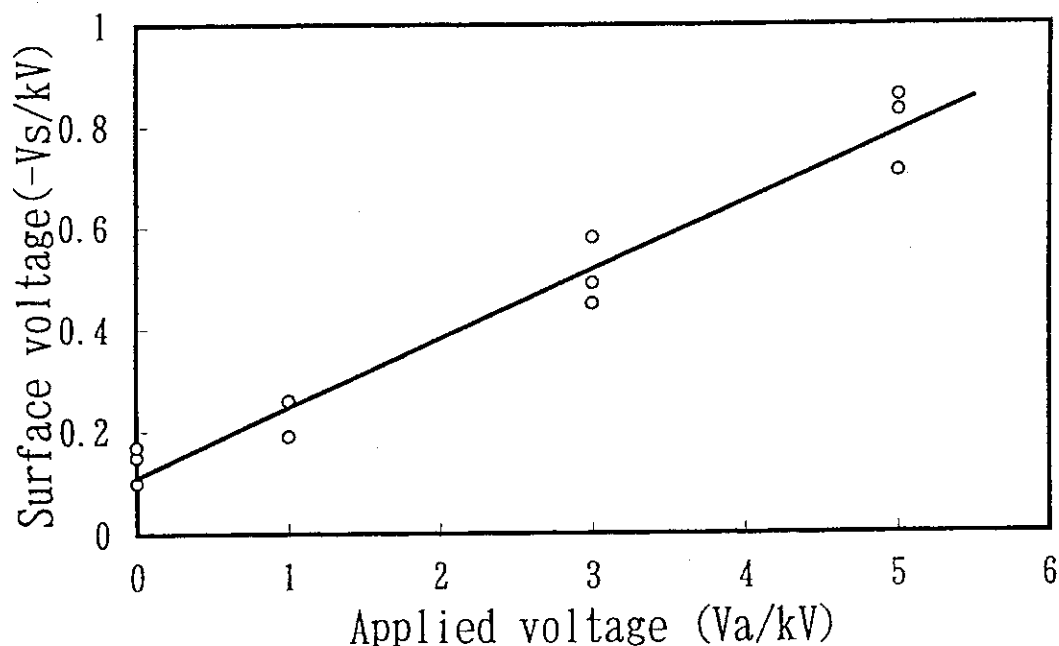
The stability of the restored charge in the polyethylene foam is now in progress.

### References

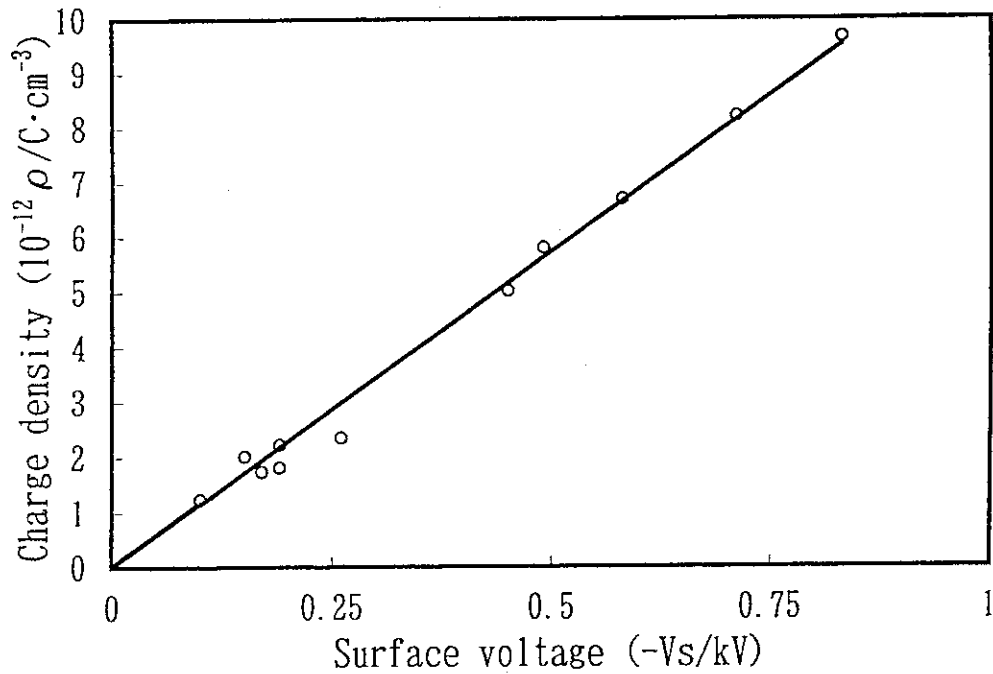
- 1) B. Gross, H. von Seggern, and J. E. West, *J. Appl. Phys.*, **56**, 2333(1984).
- 2) M. Kajimaki, T. Takagaki, and K. Matsuda, *JAERI-M*, **8569**, 138(1979).
- 3) M. Kajimaki and T. Okada, *JAERI-M*, **7355**, 52(1977).
- 4) K. Kijima and K. Matsuda, *Appl. Radiat. Isot.*, **42**, 235(1991).



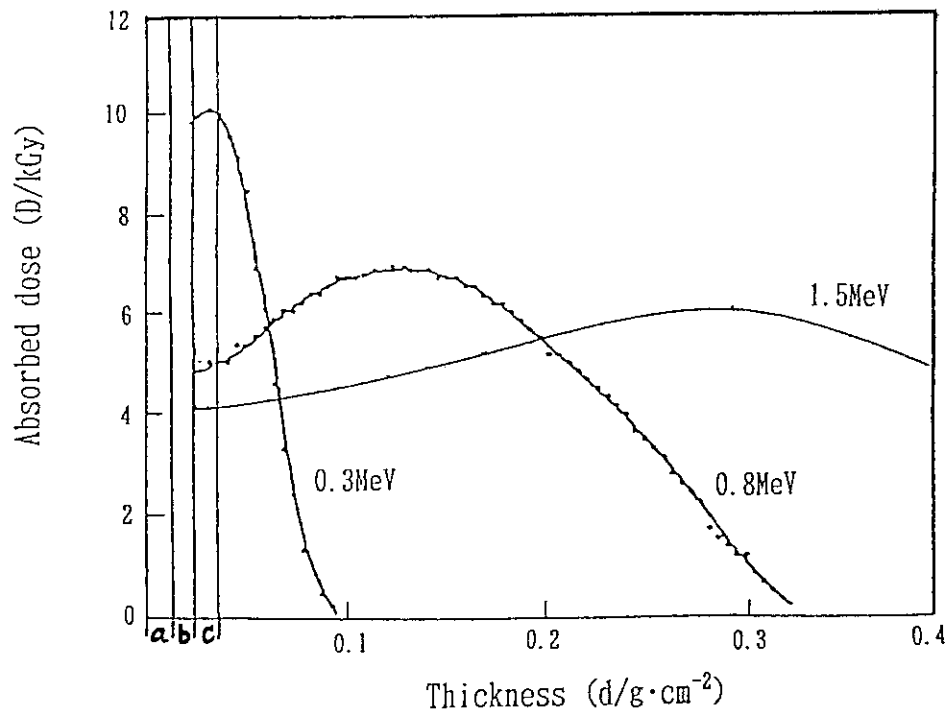
**Fig. 1** Effect of absorbed dose on initial surface voltage of polyethylene foam by applying bias of 5 kV. Accelerating voltages are indicated in the figure, and other parameters are: beam current 5  $\mu$ A, conveyer speed 8 mm/s.



**Fig. 2** A relationship between the applied voltage on an electrode and initial surface voltage of the polyethylene foam. Data of three samples obtained simultaneously under the irradiation conditions of accelerating voltage 1.5 MeV, beam current 5  $\mu$ A, conveyer speed 8 mm/s, absorbed dose 0.5 kGy.



**Fig. 3** A relationship between the initial surface voltage and the charge density measured by a Faraday cup. Irradiation conditions: accelerating voltage 1.5 MeV, beam current 5  $\mu$ A, conveyer speed 8 mm/s, absorbed dose 0.2-1.0 kGy.



**Fig. 4** Depth-dose distribution curves for electrons of 0.3, 0.8, and 1.5 MeV under the same irradiation condition. The notes a, b, and c on the abscissa correspond to the thickness of Ti foil of the accelerator window, that of air gap and that of the sample polyethylene foam, respectively.

## 14. Simulation of the Absorbed Dose in Thin Films Irradiated by 300-keV Electrons

*T. Kijima, Y. Nakase, and K. Nakato*

An electron beam of energies below 300 keV is commonly used to improve surface properties of industrial polymeric materials. Electron beam dosimetry for low-energy electrons is difficult owing to their short range in material and to the self-shielding structure of some accelerators. In order to overcome these problems, a semi-empirical computational method (EDMULT),<sup>1)</sup> and Monte Carlo method (ETRAN, ITS)<sup>2)</sup> have been developed. These codes are so large that a computer with large memory must be used. We have developed a Monte Carlo code<sup>3)</sup> to calculate absorbed dose with the simple model based on the algorithm of Murata et al.<sup>4)</sup> developed for the limited energy region of a 10-50 keV. We describe an outline of our code, which can be adapted easily to an arbitrary number of target layers, and the results obtained for energy spectra and angular distributions of electrons on the sample surface and those for absorbed doses in a sample irradiated by 300-keV electrons. The computed absorbed doses are compared with the experimental results obtained with a cellulose triacetate (CTA) film dosimeter.

The single scattering cross section of an electron due to elastic collision with atoms is calculated from the screened Rutherford-type expression. The relativistic momentum and velocity of the electron are introduced. An electron trajectory is expressed stepwise, where the step length equals the elastic-scattering mean free path, assuming that the collision is a Poisson process. Energy losses of incident electrons are mainly caused by collisions and radiative process, and the energy loss per unit path length due to the former effect can be calculated from the relativistic Bethe formula.<sup>5)</sup> It is well known that radiative losses are significant only for absorber materials of high atomic number and the primary energy above a few MeV. In the present case of organic absorber material (CTA) and a low energy of 300 keV, therefore, radiative losses can be neglected. Trajectory of an electron normally follows until its energy decreased below 1 keV (cut-off energy). This value is less than 0.5 % of the incident energy of 300 keV and small enough compared with the cut-off energy of 5 % of the incident energy used in ITS calculation. The number of trajectories calculated was 30000, and a smoothing routine was performed.

The scanning electron accelerator used is of a rectified transformer type. The irradiation conditions were as follows: accelerator voltage 300 kV, beam current 0.02 mA, and conveyer speed 8 mm/s when used. The scanning width of the electron beam is set at 30 cm at the Ti windows. The accelerated electrons pass first through the Ti

window ( $30 \mu\text{m}$  thick ;  $0.0136 \text{ g cm}^{-2}$ ), then travel through a 5-20 cm air gap ( $0.00603\text{-}0.0241 \text{ g cm}^{-2}$ ), and finally traverse a stack of thin films of the CTA dosimeter placed on a conveyer travels back and forth under the irradiation window perpendicularly to the direction of the scanning beam.

In Fig. 1, simulated trajectories of 200 incident electrons in the Ti window and those of 1500 electrons in a 10 cm air gap are plotted. The 300-keV electrons of a pencil beam are scattered and diffused to a width of about 0.1mm in the window, and to a width larger than 40 cm in the air layer. After scattering about 450 times in the Ti and air layers, the electrons enter the CTA layer, and then are scattered about 1700 times. The average trajectory length of electrons (0.47 mm) in CTA is quite close to the extrapolated projected penetration depth (0.46 mm), while the extrapolated trajectory length (0.65 mm) is quite large to indicate the strong effect of scattering on 300-keV electrons. The effects of backing materials on the energy spectra of electrons on the front and back surface of the CTA layer of  $114\text{-}\mu\text{m}$  thickness were calculated and are shown in Fig. 2. The electron energy spectra are considerably influenced by the backscattered electrons in the region of  $< 200 \text{ keV}$ , where the higher the atomic number of the backing material, the greater the influence.

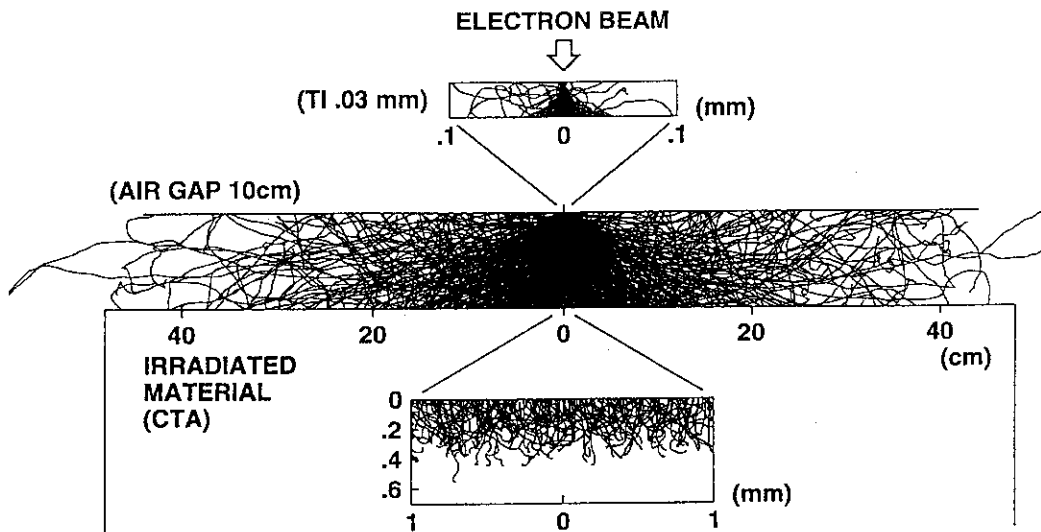
The validity of our calculation code was investigated using the experimental data on the absorbed dose in CTA. Figure 3 shows the calculated and experimental depth-dose distributions in thin CTA stacks placed at distances of 5, 10, 15, and 20 cm from the Ti window. The depth-dose distribution calculated by our code shows good agreement with the experimental data in each case. Figure 4 shows the energy spectra of electrons on the surface of the CTA layer placed at distances of 0, 5, 10, 15, and 20 cm from the Ti window. The most probable energies of electrons at the CTA surface obtained from these energy spectra are plotted as a function of the distance from the Ti window in Fig. 5 and compared with the experimental data obtained by Okabe et al.<sup>6)</sup> with a semiconductor detector and a 400-channel pulse-height analyzer. The calculated and the experimental results show fairly good agreement.

We are now improving our model so that it can be used for wider ranges of electron energy and can precisely simulate absorbed dose under various conditions.

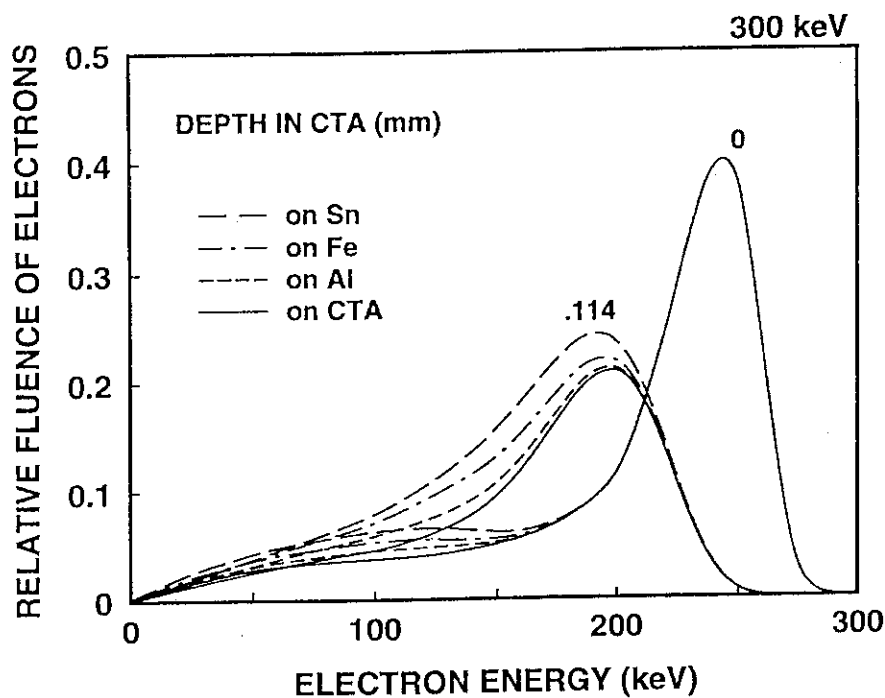
## References

- 1) P. Andreo, R. Ito, and T. Tabata, *Technical Report of Research Institute for Advanced Science and Technology, University of Osaka Prefecture*, No. 1, (1992).
- 2) J. A. Halbeib, R. P. Kensek, G. Valdeg, S. M. Seltzer, and M. J. Berger, *IEEE Trans. Nucl. Sci.*, **NS-39**, 1025(1992).

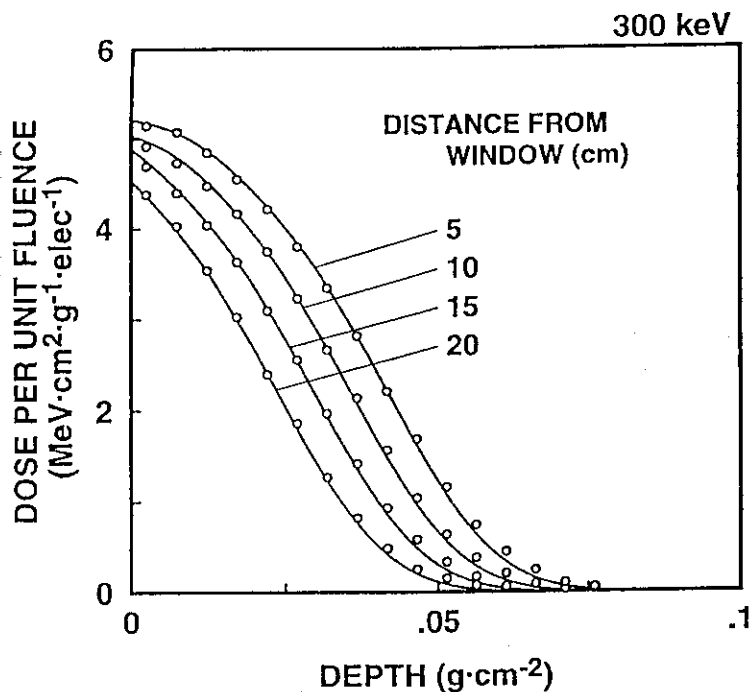
- 3) T. Kijima, M. Kotera, H. Suga, and Y. Nakase, *IEICE Trans. Electron.*, **E78-C**, 5(1995).
- 4) K. Murata, T. Matsukawa, and R. Shimizu, *Jpn. J. Appl. Phys.*, **10**, 678(1971).
- 5) *ICRU Report*, **37**, Bethesda, Maryland, U.S.A.(1984).
- 6) S. Okabe, K. Tsumori, T. Tabata, T. Yoshida, A. Nagai, S. Hiro, K. Ishida, I. Sakamoto, T. Kawai, K. Arakawa, T. Inoue, and T. Murakami, *Oyo Buturi*, **43**, 909(1974).



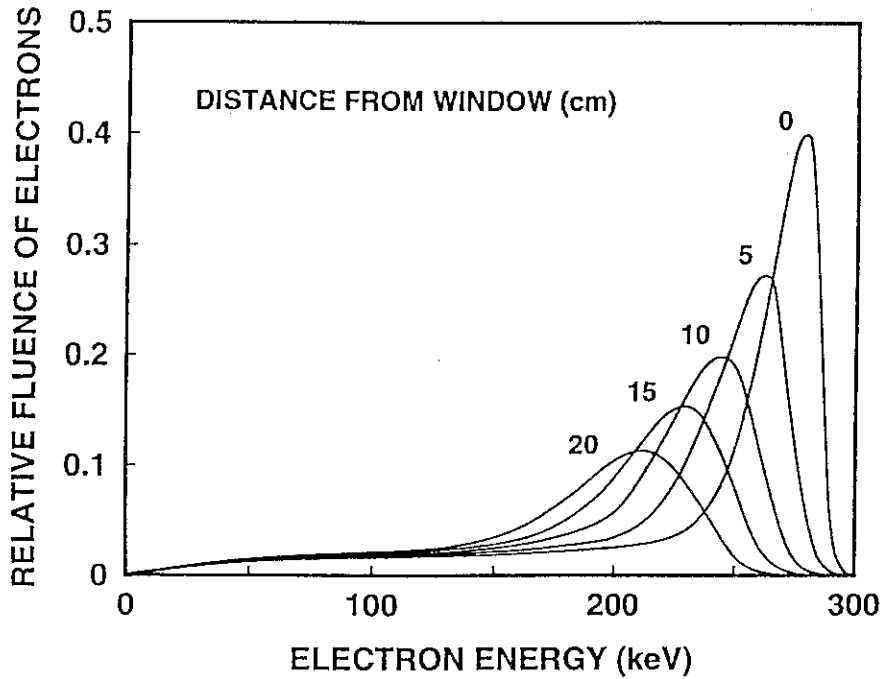
**Fig. 1** Simulated electron trajectories in Ti window (30  $\mu\text{m}$ ), air (10 cm) and semi-infinite CTA.



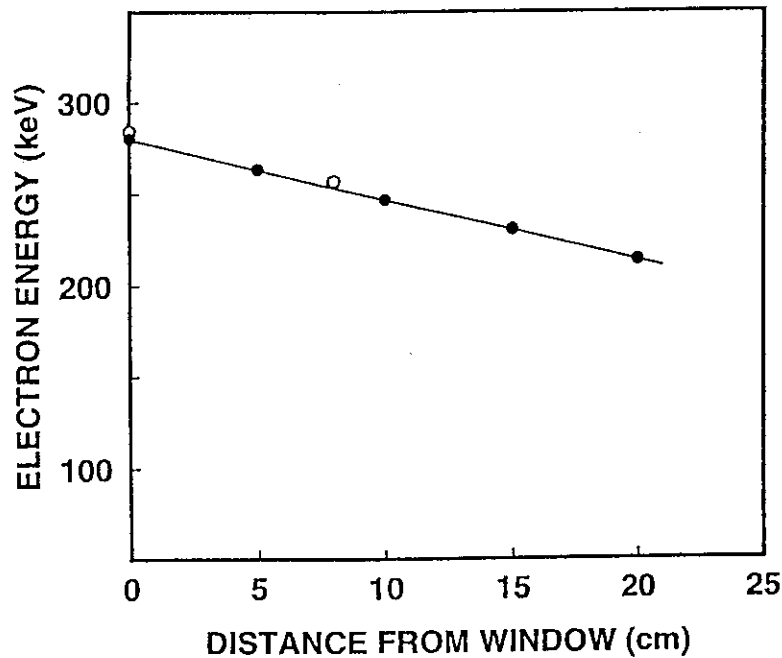
**Fig. 2** Calculated energy spectra of electrons after passing through the Ti window of 30- $\mu\text{m}$  thickness and the air layer of 10-cm thickness, on the front and back surfaces of CTA films of 114- $\mu\text{m}$  thickness placed on various backing materials.



**Fig. 3** Comparison of calculated (solid lines) and experimental (open circles) depth-dose distribution in the effectively semi-infinite CTA film stacks placed on the conveyer at distances of 5, 10, 15, and 20 cm from the Ti window.



**Fig. 4** Calculated energy spectra of electrons on the surface of an effectively semi-infinite CTA layer at distances of 0, 5, 10, 15, and 20 cm from the Ti window.



**Fig. 5** Comparison of calculated most probable energies (closed circles) obtained from Fig. 4 and the experimental data (open circles) reported by Okabe et al.<sup>6)</sup>



## 15. Operation and Maintenance of Irradiation Facilities

*K. Nakato*

The irradiation facilities in our laboratory are operated for research performed in the laboratory and for that in cooperation with universities or industries. The facilities are also operated for irradiation service to industrial companies. Operation of the Van de Graff accelerator (No. 1 accelerator), the accelerator of a transformer type (No. 2 accelerator), and the cobalt-60 irradiation equipment were carried out without any major trouble throughout the current year.

In addition to the routine maintenance works including the annual overhaul of the accelerators, a power supply for electron beam scan of the Van de Graff accelerator and a handling device for the radiation source of the cobalt-60 irradiation equipment were renewed this year. They became superannuated, for they had been used since were set in 1958. By the replacement, stability in the beam scan with the Van de Graff accelerator has been restored, and handling of the cobalt-60 source has been much improved.

The annual operation of the facilities is listed in Table 1.

Table 1 Utilization and operation of the facilities during fiscal 1994

|                        | Van de Graff<br>accelerator<br>(Accelerator No.1) | Accelerator of rectified<br>transformer type<br>(Accelerator No.2) | Cobalt 60 gamma-<br>ray apparatus |
|------------------------|---------------------------------------------------|--------------------------------------------------------------------|-----------------------------------|
| Operation time         | (hour:min)<br>79:15                               | (hour:min)<br>43:16                                                | (hour:min)<br>3085:12             |
| Number of experiments  |                                                   |                                                                    |                                   |
| JAERI                  | 127                                               | 77                                                                 | 211                               |
| Universities           | 0                                                 | 0                                                                  | 0                                 |
| Industries             | 9                                                 | 2                                                                  | 18                                |
| Research organizations | 0                                                 | 0                                                                  | 0                                 |
| Total                  | 136                                               | 79                                                                 | 229                               |

### III. List of Publications

#### 1. Published Papers

"Wavelength Dependence of Excimer Laser Irradiation Effects on Ethylene-Tetrafluoroethylene Copolymer"

Y. Hamada, S. Kawanishi, M. Nishii, S. Sugimoto, and T. Yamamoto, *Jpn. J. Appl. Phys.*, **33**, 4764 (1994).

"Decarbonylation of Adamantan-2-one by Two-Photonic Excitation with XeCl Laser"

N. Ichinose and S. Kawanishi, *J. Chem. Soc., Chem. Commun.*, **1994**, 2017.

"Application of Excimer Lasers for the Chemistry on Polymer Surface"

S. Kawanishi, *EMC*, **78**, 27 (1994).

"Surface Modification of Tetrafluoroethylene-Perfluoroalkyl Vinyl Ether Copolymer by Excimer Laser Irradiation"

A. Okada, N. Ichinose, and S. Kawanishi, *Kobunshi Ronbunshu*, **52**, 66-8 (1995).

"Surface Modification of Fluoropolymer by Excimer Laser Irradiation"

S. Kawanishi, CRC Press, *The Polymeric Material Encyclopedia*.

"Laser-Induced Photochemical Reaction of Aqueous Maleic Acid Solutions Containing H<sub>2</sub>O<sub>2</sub>"

Y. Shimizu, S. Kawanishi, and N. Suzuki, *Proceedings of 6th International Symposium on Advanced Nuclear Energy Research*, pp.418-423.

"Surface Modification of Polymer Materials by Excimer-Laser Irradiation"

S. Kawanishi, M. Nishii, Y. Shimizu, and S. Sugimoto, *Proceedings of 6th International Symposium on Advanced Nuclear Energy Research*, pp.246-253.

"Depth-Dose Distributions in a Thin-Layer Absorber Irradiated by 300-keV Electrons"

T. Kijima, H. Suga, and Y. Nakase, *Appl. Radiat. Isot.*, **45**, 759 (1994).

"Formation of Solid Particles from Aqueous Solutions of Palladium Sulfate -Silver Sulfate by Gamma Ray Irradiation"

M. Hatada, *KURRI-TR-394*, 36 (1993).

"Growth and Sedimentation of Fine Particles Produced in Aqueous Solutions of Palladium Sulfate and Palladium Sulfate-Silver Sulfate Induced by Gamma Ray Irradiation"

M. Hatada and C. D. Jonah, *JAERI-Research*, **94-019**, (1994)

"Formation of fine Solid Particles from Aqueous Solutions of Solid Chloropalladate by Gamma-ray Irradiation"

M. Hatada, I. Fujita, and K. Korekawa, *JAERI-Research*, **94-024**, (1994).

"Irradiation Effects on Properties of Reverse Osmosis Membrane based on Crosslinked Aromatic Polyamide"

Y. Nakase, T. Yanagi, and T. Uemura, *J. Nucl. Sci. Technol.*, **31**, 1214(1994).

"The Survey of the Nuclear Sciences in the Curricula of Senior High Schools"

Y. Ujeno, M. Inaoka, Y. Nakase and S. Okamura, *Radioisotopes*, **43**, 365(1994).

## 2. Oral Presentations

"Photochemical Reactions of Fluoropolymer Surface with Water and Alkyl Carboxylic Acids"

N. Ichinose and S. Kawanishi, *14th International Symposium on Fluorine Chemistry* (Yokohama).

"Excimer-Laser Irradiation Effect on F<sup>-</sup> Uptake of Enamel"

S. Kawanishi, Y. Shimizu, S. Sugimoto, C. Miyazawa, M. Kokubun, and T. Shimizu, *55th Spring Meeting of Japan. Society of Applied Physics* (Nagoya).

"Wavelength Dependence of Photochemical Reaction of Aqueous Maleic Acid Solution by High Intence UV Laser Light"

Y. Shimizu and S. Kawanishi, *37th Symposim on Radiation Chemistry* (Sapporo).

"The Effect of Excitation Wavelength on Polyene Formation of Poly (Vinyl Chloride) by Irradiation of Excimer Laser Lights"

Y. Izumi, M. Maruo, and S. Kawanishi, and N. Ichinose, *68th Annual Meeting of the Chemical Society of Japan*. (Nagoya).

"Photochemical Surface Modification of Fluoropolymers: Photoreaction with Water and Alkylcarboxylic Acids"

N. Ichinose and S. Kawanishi, *43rd Symposium on Polymer Science Japan*. (Hukuoka).

"Application of Excimer Laser to Chemical Field"

S. Kawanishi, Y. Shimizu, M. Nishii, N. Ichinose, and S. Sugimoto, *Symposium on Ion & Laser Processing for Advanced Materials* (Hirakata).

"Surface Photoreaction of Fluoropolymers with Water and Alkyl Carboxylic Acids"

N. Ichinose and S. Kawanishi, *Symposium on Photochemistry 1994* (Suita).

"Photochemical C-C Bond Cleavage Reaction of 1,2-Diarylethanes Bearing Acetylphenyl Group"

N. Ichinose, S. Kawanishi, K. Mizuno, Y. Otsuji, and H. Tachikawa, *3rd Japan-Sino Binational Symposium on Photochemistry* (Suita).

"Laser-Induced Two-Photonic Reaction of 2-Adamantanone"

N. Ichinose and S. Kawanishi, *Symposium on Photochemistry 1994* (Suita).

"Wavelength Dependence on Chemical Reaction of Ethylene-Tetrafluoroethylene Copolymer Induced by Excimer Laser"

Y. Hamada, S. Kawanishi, S. Sugimoto, M. Nishii, and T. Yamamoto, *Symposium on Photochemistry 1994* (Suita).

"Effect of Excimer Laser Irradiation on Fluoridization of Enamel"

M. Amano, C. Miyazawa, M. Kokubun, T. Shimizu, S. Kawanishi, Y. Shimizu, and S. Sugimoto, *42nd Meeting of Japan. Association for Dental Research* (Suita).

"Photoreaction of Fluoropolymer Surface with Aliphatic Amines"

M. Maruo, N. Ichinose, and S. Kawanishi, *69th Annual Meeting of the Chemical Society of Japan* (Kyoto).

"Photoreaction of Fluoropolymer Surface with Aliphatic Carboxylic Acids"

N. Ichinose and S. Kawanishi, *69th Annual Meeting of the Chemical Society of Japan* (Kyoto).

"Surface Reaction of Fluoropolymers through the Photoionization and Electron Transfer of Water"

N. Ichinose and S. Kawanishi, *55th Autumn Meeting of Japan. Society of Applied Physics* (Hiratuka).

"Depth-Dose Distributions in a Thin Layer of Organic Absorber Irradiated by Low Energy Electrons"

T. Kijima, H. Suga, and Y. Nakase, *37th Symposium on Radiation Chemistry* (Sapporo).

"Growth and Sedimentation of Fine Particles Produced in Aqueous Solutions of Palladium Sulfate Induced by Gamma Ray Irradiation"

M. Hatada and C. D. Jonah, *37th Symposium on Radiation Chemistry* (Sapporo).

"Formation of Fine Solid Particles from Aqueous Solutions of Chloropalladate by Gamma Ray Irradiation"

M. Hatada, I. Fujita, and K. Korekawa, *37th Symposium on Radiation Chemistry* (Sapporo).

"Dose Distributions in a Thin Layer for 300 keV Electrons From an EB System"

T. Kijima, H. Suga, and Y. Nakase, *1994 Autumn Meeting of the Institute of Electronic Information and Communication Engineers* (Sendai).

"Dose Distributions in a Thin-Layer Absorber for 300 keV Electrons From an EB System"

T. Kijima, H. Suga and Y. Nakase, *1995 Spring Meeting of the Institute of Electronic Information and Communication Engineers* (Fukuoka).

### **3. Patent Applications**

"Surface-Hydrophilize Fluororesin Moldings and Method of Producing Same"

A. Okada, Y. Shimizu, S. Kawanishi, M. Nishii, and S. Sugumito,  
*US Patent*, application, 08/192, 285.

"Surface Modification of Fluorine Resin with Laser Light"

M. Nishi, N. Suzuki, S. Sugimoto, Y. Hirajima, M. Endo, and T. Nagase,  
*US Patent*, 5, 320, 789.

"Surface Modification of Fluorine Resin"

M. Nishi, Y. Shimizu, S. Kawanishi, S. Sugimoto, M. Endo, and T. Nagase,  
*Jpn. Kokai Tokkyo Koho*, 06-248097 (940906).

"Surface Modification of Fluoropolymers by UV Excimer Lasers"

M. Nishi, Y. Shimizu, S. Kawanishi, S. Sugimoto, T. Tanaka, and Y. Eguchi,  
*Jpn. Kokai Tokkyo Koho*, 06-172560 (940621).

#### IV. List of Cooperative Studies

"Effect of Laser Beam Irradiation on Polymer Materials (II)"

*Faculty of Engineering, Osaka University*

"Infrared Multiphoton Decomposition of Fluoroorganic Compounds (II)"

*Material Science and Technology, Kyoto Institute of Technology*

"Effects of Irradiation on Oral-Related Materials"

*Department of Preventive Dentistry, Ohu University*

"Surface Modification of Fluoropolymers by Laser Irradiation"

*Kurabo Industries, Ltd.*

"Improvement of Vital Affinity on Fluoropolymers"

*Gunze Ltd.*

"Distribution of Trapped Electrons in Thin Plastic Layer Absorbers"

*Osaka Institute of Technology*

"Studies on Radiation-Induced Crosslinking of Biopolymers"

*Institute of Biomedical Engineering, Kyoto University*

"Studies on Lattice-Defects Formation Induced by Electron Irradiation"

*Faculty of Engineering, Himeji Institute of Technology*

"Studies on Functions of Fine Particles"

*Faculty of Science and Technology, Kinki University*

"Mechanism of Electron-Trapping in Thin Layers"

*Sanwa Kakou Co. Ltd.*

"Radiation-Induced Curing of Fine Particles"

*Kaginushi Kogyo Co. Ltd.*

## V. List of Personnel

Dr. Masafumi Nakano, Director

Prof. Hiroshi Masuhara, Invited Researcher from Osaka University

Dr. Motoyoshi Hatada, Scientific Consultant

### OFFICE OF ADMINISTRATION

Mr. Teruo Yagi, Administrative Manager

Ms. Junko Kobayashi

Ms. Atsuko Hayashi

Ms. Harumi Ogata [1]

### STUDY ON LASER-INDUCED ORGANIC CHEMICAL REACTIONS

Dr. Shunichi Kawanishi, Group Leader, Principal Scientist

Mr. Yuichi Shimizu, Senior Scientist

Dr. Masanobu Nishii, Research Scientist

Dr. Nobuyuki Ichinose, Research Scientist

Mr. Shun'ichi Sugimoto [2]

Mr. Tomohiro Nagase [3]

Mr. Tadaharu Tanaka [3]

Mr. Atsushi Okada [4]

Mr. Akihiro Isomura [5]

Mr. Masaharu Maruo [6]

### STUDY ON BASIC RADIATION TECHNOLOGY FOR FUNCTIONAL MATERIALS

Dr. Yoshiaki Nakase, Group Leader, Senior Scientist

Mr. Nobuyoshi Kotani [7]

Mr. Tetsu Kaginushi [8]

Ms. Liu Li [9]

Mr. Atsushi Nakamune [10]

Mr. Kazushi Ushiroda [10]

### OPERATION AND MAINTENANCE OF IRRADIATION FACILITIES

Mr. Kiyori Nakato, General Manager

Mr. Toshiyuki Kijima [11]



- [1] Office Assistant
- [2] Cooperative Staff from Radiation Application Development Association
- [3] Research Collaborator from Kurabo Industries, Ltd.
- [4] Research Collaborator from Gunze Industries, Ltd.
- [5] Fellow of Advanced Science from Kyoto Institute of Technology
- [6] Fellow of Advanced Science from Osaka University
- [7] Research Collaborator from Sanwa Kako, Ltd.
- [8] Research Collaborator from Kaginushi Kogyo, Ltd.
- [9] Fellow of Advanced Science from Himeji Institute of Technology
- [10] Student Research Assistant from Kinki University
- [11] Technical and Research Assistant