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Taniike, Akira
Iwaoka, Kyohei
Fujita, Naoki
Furuyama, Yuichi

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INTRODUCTION OF CONDUCTIVITY TO A POLYMER WITH A HEAVY ION BEAM IRRADIATION FOR PRODUCTION OF A FUNCTIONAL POLYMER SUBSTRATE

Akira. TANIIKE*

Kyohei. IWAOKA**

Naoki. FUJITA***

Yuichi FURUYAMA****

ABSTRACT

Recently, many products made of functional polymers have been developed and used in many fields. Radiation induced graft polymerization is one of the production methods for a functional polymer; it is applied to make industrial products. The method can be conducted with ion beams, and we have studied the ion beam induced graft polymerization method. If a polycarbonate substrate is irradiated by a heavy ion beam, a conductivity part is introduced in the substrate. We apply these methods using ion beams to produce a functional polymer. This study investigates the introduction of conductivity to the polycarbonate substrate irradiated by heavy ion beams.

A tandem accelerator at Kobe University was used for the ion beam irradiation in this study. Polycarbonate plate was set on the sample holder, and was irradiated by heavy ion beams, such as Cu^+ , Ag^+ , and Au^+ . The energy was from 200 keV to 1000 keV. The resistance of the sample was measured by an in-line four-point probe. For example, the conductivity was 2.7 S/m for 500 keV Cu^+ ion beam irradiation at the fluence of $5 \times 10^{16} \text{ cm}^{-2}$. The dependence of the conductivity on the ion energy and the fluence was measured, and the dependence was discussed.

Depth profile of the heavy metals in the sample after irradiation was measured by

* Associate Professor, Graduate School of Maritime Sciences, Kobe University. 5-1-1 Fukaeminamimachi, Higashinada, Kobe, Hyogo, 658-0022, Japan. taniike@maritime.kobe-u.ac.jp

** MRc Student, Graduate School of Maritime Sciences, Kobe University. 5-1-1 Fukaeminamimachi, Higashinada, Kobe, Hyogo, 658-0022, Japan. Email : 153w505w@stu.kobe-u.ac.jp

*** MRc Student, Graduate School of Maritime Sciences, Kobe University. 5-1-1 Fukaeminamimachi, Higashinada, Kobe, Hyogo, 658-0022, Japan. Email : 173w320w@stu.kobe-u.ac.jp

**** Professor, Graduate School of Maritime Sciences, Kobe University. 5-1-1 Fukaeminamimachi, Higashinada, Kobe, Hyogo, 658-0022, Japan. Email : furuyama@maritime.kobe-u.ac.jp

Rutherford back scattering spectroscopy analysis. The heavy metals did not exist from the surface to the ion range. Oxygen lost was investigated at the surface of polycarbonate sample. Molecular orbital calculations with GAMESS code, an ab initio quantum chemistry package, was conducted, and the relation between conductivity and the structure of the polymer was discussed. Overlap of the electron clouds was confirmed for the oxygen lost polycarbonate sample.

Keywords: heavy ion, irradiation, polycarbonate, graft polymerization

1. INTRODUCTION

Recently, many products made of functional polymers have been developed and used in many fields. To produce those polymer materials, radiation such as electron beams, ion beams, gamma rays, UV radiation, and neutrons can be used. Radiation induced graft polymerization is one of the methods used to make a functional polymer, and is applied to make industrial products. Generally electron beams are utilized for this method, and ion beams can be also used for this applications (Betz 1995). In our laboratory, we have conducted the radiation graft polymerization method with ion beams (Taniike 2011, Taniike 2014), as ions have large LET (short range) compared with electrons with the same energy. When a substrate is irradiated with an ion beam, many radicals are generated from the surface to the range. After graft polymerization, the graft chains are produced at the surface to the range. The ion beam graft polymerization method can produce some kinds of graft chains with a functional base. In our laboratory, an application to thin film diagnostics was studied (Taniike 2015).

Much research has been devoted to polymer irradiation and dope with heavy ion (Deka 2013, Yue 2016, Bougharraf 2016, Himanshu 2011, Asad Ali 2010, Abdelrahman 2016). The substrates are various solid polymer electrolytes, a dielectric devise, and the radiation are also various. The characteristics of the polymers in these studies were analyzed with the methods such as FTIR, UV-Vis. spectroscopy, photoluminescence measurement, XRD, electrical conductivity, dielectric constant measurement, etc. In these studies of ion beam irradiation, a various kind of ions are used. For example, the substrates are poly(ethylene oxide) / montmorillonite irradiated by 90 MeV O^{7+} (Deka 2013), polyimide irradiated by 60-110 keV proton (Yue 2016), polyvinylalcohol films doped by 4-dimethylaminobenzonitrile irradiated by UV (Bougharraf 2016), conducting polymer PANI-PVA irradiated by 150 keV Ar^{9+} (Himanshu 2011), Lexan polycarbonate irradiated by 95 MeV O^{6+} (Asad Ali 2010), and polyvinyl alcohol irradiated by low energy electron

and nitrogen (Abdelrahman 2016).

An introduction of conductivity into polycarbonate (PC) substrate irradiated by Cu ions was studied by V. Resta et.al (2013). The energy is 1 MeV. The fluence of Cu ions were up to 10^{17} cm^{-2} , and was much larger than experiments in earlier references (Deka 2013, Yue 2016, Bougharraf 2016, Himanshu 2011, Asad Ali 2010, Abdelrahman 2016). If a PC substrate is irradiated by a narrow ion beam, a narrow conductivity part can be introduced in the substrate. When we produce the functional polymer with ion beam technics, the region is applicable for conduction between two functional parts. In this study, PC samples were irradiated by heavy ion beams, such as Cu, Ag, and Au. The energy was up to 1 MeV, and the fluence was up to 10^{18} cm^{-2} . The depth profile of ions in the irradiated sample were analyzed by RBS. The conductivity of the irradiated samples were measured by four-point probe, and the dependence on the incident ion energy and the fluence are discussed. The oxygen density near the sample surface decreased, and the decrease (loss) is regarded as a cause of the electrical conduction.

2. EXPERIMENTAL

A PC plate, $30 \times 50 \times 1 \text{ mm}$, was irradiated with Cu^+ , Ag^+ , and Au^+ ion beams generated by the 1.7 MV tandem Pelletron accelerator at Kobe University (model 5SDH-2, NEC). The energy was ranging from 200 keV to 1000 keV. The irradiation was conducted in two chambers installed in the P15 beam line and M15 beam line. Because heavy ions are heavy, there is a 15 degrees bending limitation by a magnet. For example, an irradiation with Au ion up to 300 keV can be conducted. PC was set on the rotatable holder at M15 chamber, as shown in Fig. 1 (a). An irradiation section on the PC was restricted by an aperture whose diameter was 5 mm. The holder can rotate, and the beam spot observed a luminescence of polyethylene film with a camera. The ion beam current could not be measured correctly in this experiment. The current was measured at an aluminum part. Integrating the current over the irradiation time, the fluence was obtained. The current was ranging from 10 to 300 nA and the fluence rate was $2 - 7 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$. In the experiments at P15 chamber, the ion beam was focused in 1 mm diameter by Q lens system. The target holder can move in x, y direction in $\square\text{m}$ step as shown in Fig. 1 (b). A line section, $1 \times 5 \text{ mm}$, was irradiated by moving the target. The current could be measured in this system.

RBS experiment was also conducted in the P15 chamber. The probing beam was 2 MeV He^{2+} and the diameter was 1 mm. RBS spectrum was measured by SSD, and the solid angle was 0.684 msr. A copper sheet, a polyethylene film, and a gold plate were set on the holder, and these were used for the energy calibration in RBS analysis.

The resistance of the samples was measured by an in-line four-point probe. Because the irradiated section is too small, a commercial probe cannot be used. We manufactured a probe according to the JIS standard. A conductivity, σ , is calculated by the next equation.

$$\sigma = \frac{1}{R \cdot r_{CF} \cdot t} , \quad (1)$$

where R is measured resistance, r_{CF} is correction factor for the shape of the conducting region, and t is depth of conducting area. The range calculated by SRIM code (Ziegler 1985) is used as the conduction depth, t , and r_{CF} is, for example, 4.5 for 500 keV Cu^+ . Some resistances are measured, and the average is used as R .

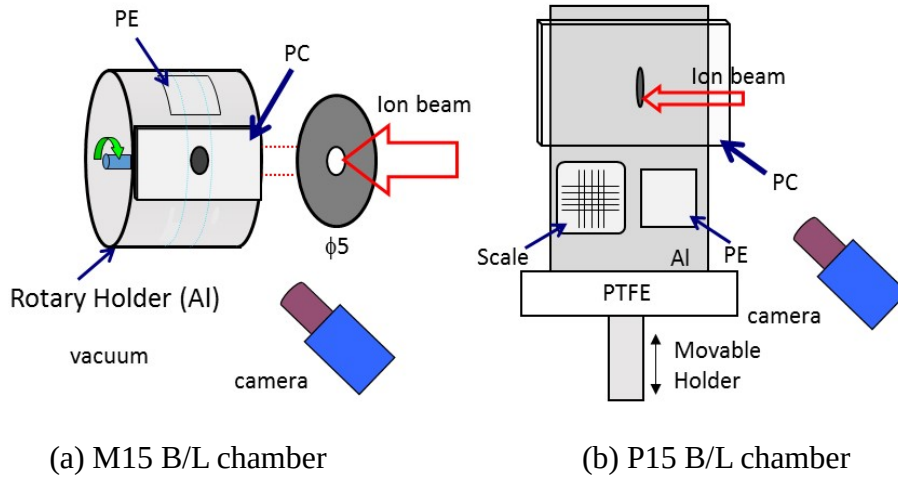


Fig. 1. Irradiation set up for polycarbonate plate at M15 beam line (a) and P15 beam line (b).

3. Results and Discussions

3.1. RBS analysis of the irradiated PC and ion ranges

PC samples were irradiated by heavy ions, and the depth profile of heavy ions was measured by RBS analysis. Assuming the substrate as PC, the density profile was calculated from the RBS spectrum. The density profiles for 300 keV Au^+ , 500 keV Cu^+ , and 1000 keV Cu^+ are shown in Fig. 2. The incident ion fluence are 4.9×10^{16} , 7.4×10^{16} , and $1.3 \times 10^{17} \text{ cm}^{-2}$, respectively. For comparison, the range was calculated by SRIM code. The number of the incident ions is 20000. The ion distribution of the experimental results are smaller than that of the calculations. Because heavy ions contained in the substrate and the stopping power in the substrate was different against pristine PC, the depth was calculated in a deeper region than the real depth. It is shown that the peak density of the heavy ions are about 1/10 of carbon density, and the heavy ion does not exist near the surface part. From this, it is considered that a metallic bond does not bring conductivity.

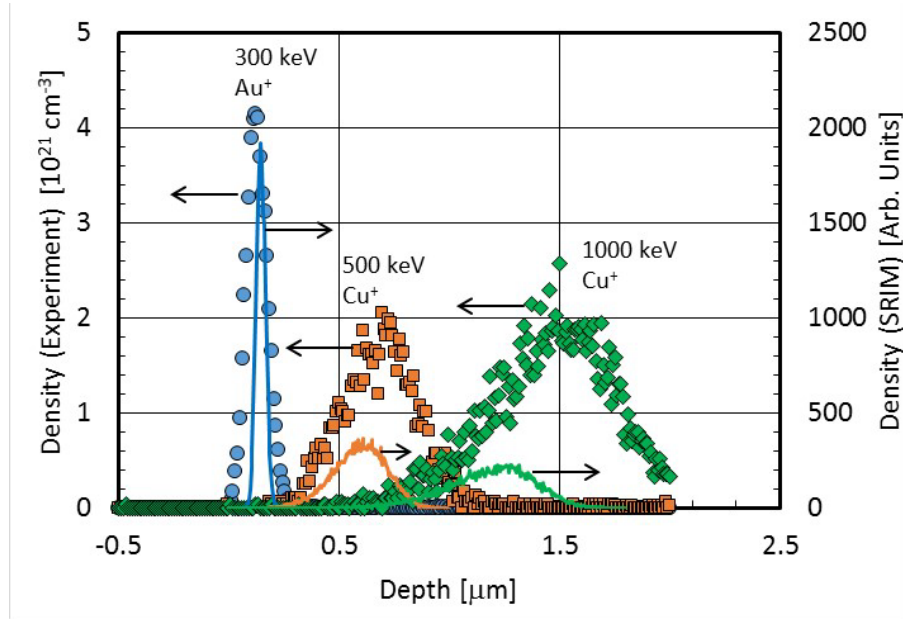


Fig. 2. Density profiles in PC substrates obtained from the experiments and SRIM simulations. The incident ions are 300 keV Au⁺, 500 keV Cu⁺, and 1000 keV Cu⁺.

3.2. Conductivity of irradiated PC

The resistance of the samples was measured by an in-line four-point probe, and the conductivity was obtained by Eq. (1). The energy dependence of the conductivity is shown in Fig. 3. The value for large section irradiation (at M15 B/L) is smaller in one order of magnitude than for small section irradiation (at P15 B/L). It is considered that the irradiation is not uniform enough for the large section case and the correction factor is not precise enough for both cases. If conduction is caused by damage to PC, there is small energy dependence. This is because the stopping power for the same ion is almost equivalent. The result shows that the conductivity is large for small energy ions. In the case of Au and Ag ions, the conductivity is large. The large conductivity may be caused by the existence of heavy ions near the surface.

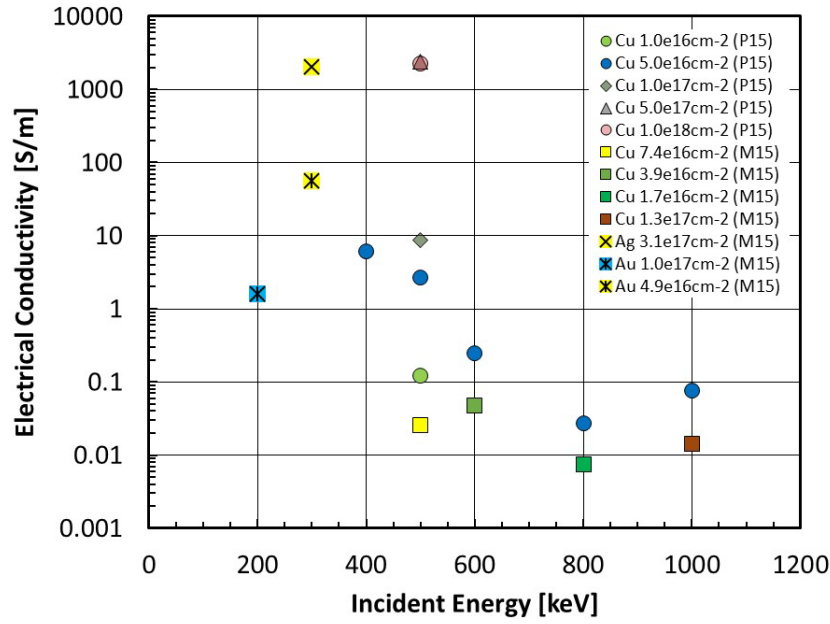


Fig. 3. Electrical conductivity dependence on the incident ion energy.

Fig. 4 shows the dependence of conductivity on the ion fluence. The conductivity increases as the fluence increases, and the conductivity increases in orders above 10^{17} cm^{-2} . This tendency is consistent with the result in Ref. (Resta 2013). The conductivity gain occurred in smaller fluence as heavier ion irradiation. The reason can be explained by the difference of the stopping power, or a damage in the polymer. If one wants to obtain a sufficiently large conductivity part in PC, it seems that an irradiation of the fluence larger than 10^{17} cm^{-2} is needed.

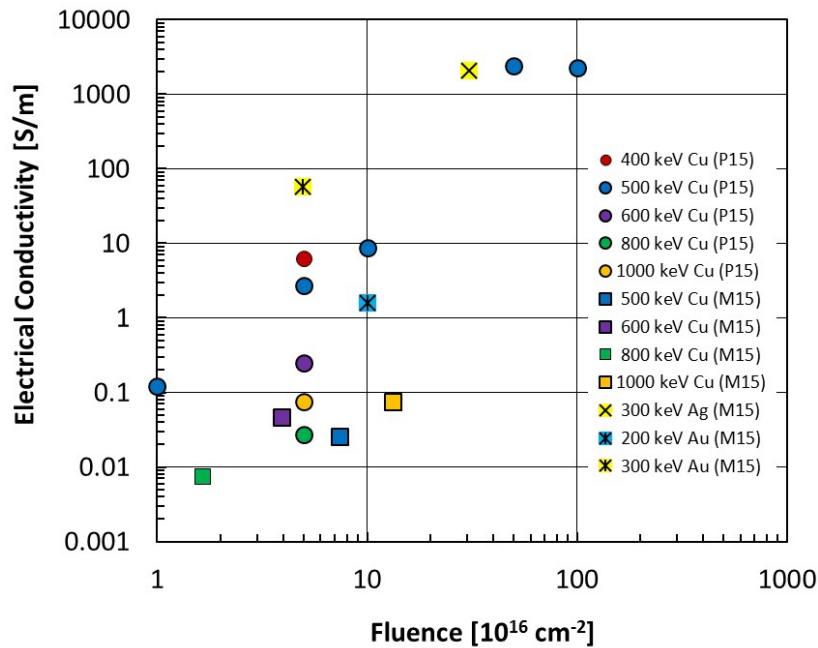
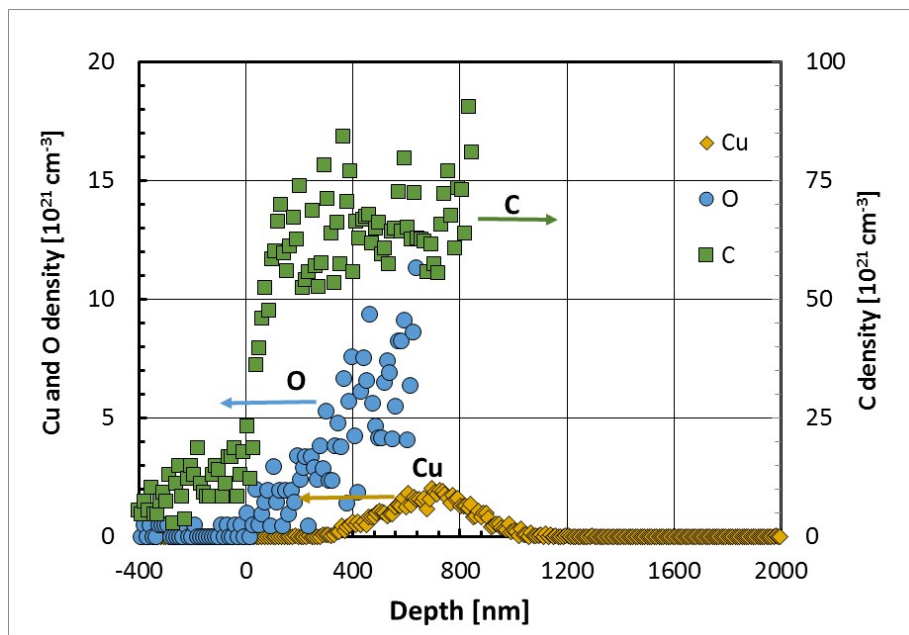


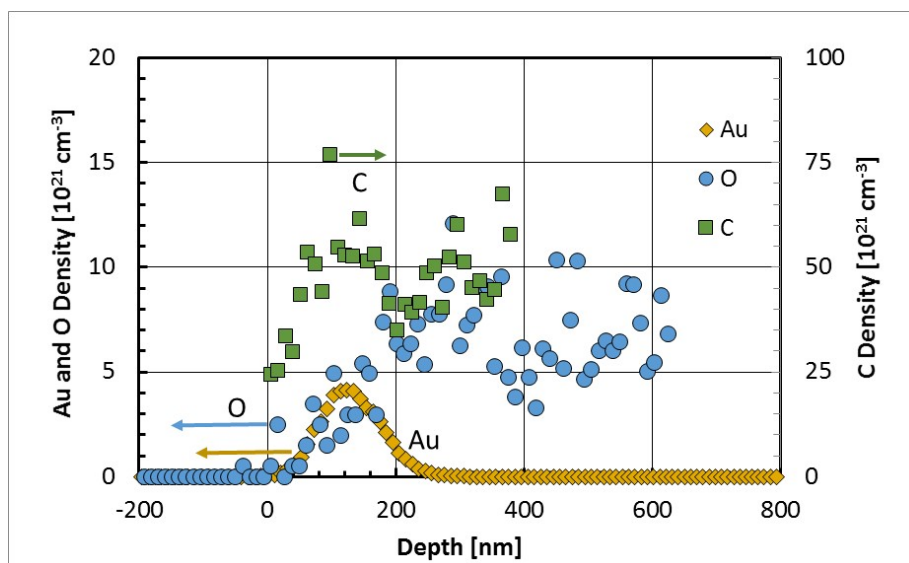
Fig. 4. Electrical conductivity dependence on the incident ion fluence.

3.3. Oxygen profile in PC

Density profiles of heavy metal, C and O are shown in Fig. 5. Fig (a) shows the profiles for 500 keV Cu irradiation and (b) shows for 300 keV Au irradiations. A decrease of oxygen atom was observed from the surface to the ion range in the case of (b). In the case of Cu irradiation (a), the decrease was difficult to recognize in the depth more than 200 nm, because O profile was overlapped with Cu and C profiles. This is the same for higher energy irradiations. Because the profiles were calculated as a pristine PC substrate, the density and the depth are a little different from true values. The oxygen density decrease in the depth from 0 to 200 nm compared with a pristine PC for Cu⁺ irradiation was plotted as a function of the fluence, as is shown in Fig. 6. The data suggests that the conductivity increases with a decrease in oxygen density except for 600 keV irradiation. The chemical structure of PC is shown in Fig. 7. A bond cleavage can occur at a weak bond caused by irradiation damage. The phenomena of a hydrogen loss in a polymer is well known (Taniike 2001). Phenyl ring or C-C bond has a large binding energy; those bonds have harder bonding than C-H or -O(C=O)O- bonds. Cleavage of C-O bond is described in Ref. (Asad 2010).



(a) 500 keV Cu^+ irradiation



(b) 300 keV Au^+ irradiation

Fig. 5. Density profiles for heavy ions, O and C for 500 keV Cu^+ irradiation (a) and 300 keV Au^+ (b).

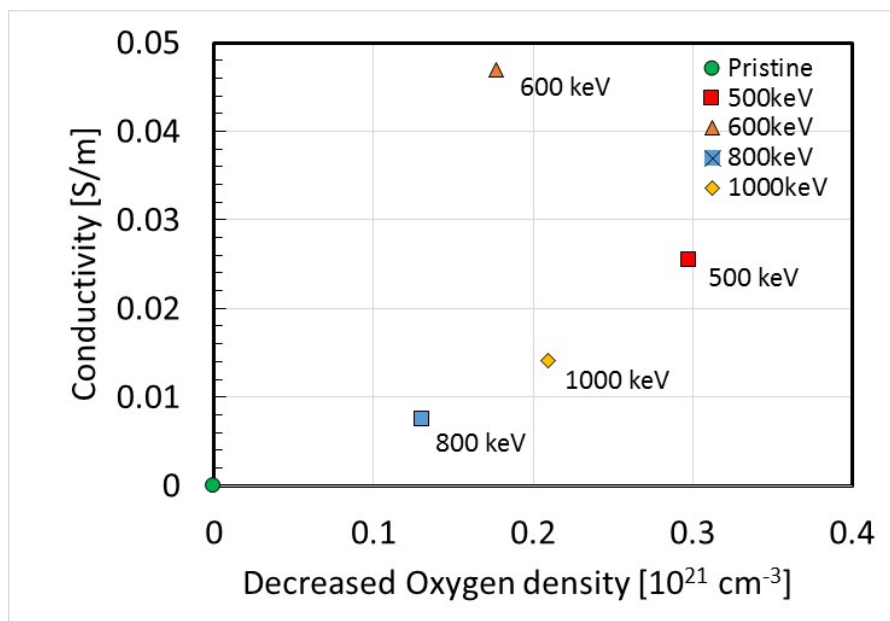


Fig. 6. Electrical conductivity of PC as a function of decreased oxygen density.

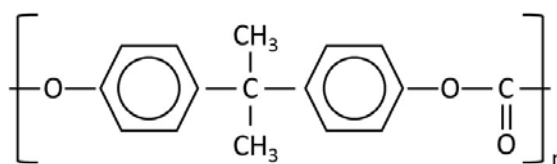


Fig. 7. Chemical structure of PC.

3-4 MO calculations

Molecular orbital was calculated by a GAMESS simulation code, which is an ab initio quantum chemistry package. To visualize the results, the application ChemBio 3D Ultra (perkin Elmer) was used. Electron clouds of a PC (some molecule units) were calculated. Overlap of the electron cloud which indicates conductivity is not seen between the atoms. PC without the carbonate part, $-\text{O}(\text{C}=\text{O})\text{O}-$, was supposed. One of the calculation orbitals on two molecule units are shown in Fig. 8. The electron clouds expand broader, suggesting conductivity. In the case of a benzene chain, some electron clouds are broader. Because the electron contributes to electrical conduction, it can be supposed that the loss of carbonate part by irradiation causes the electrical conduction in PC.

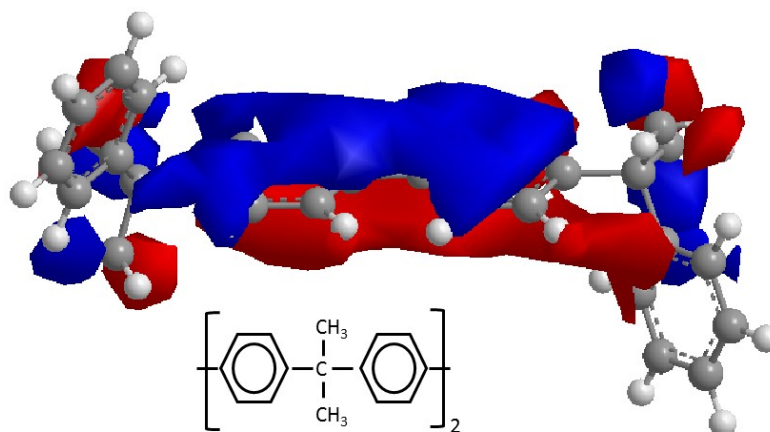


Fig. 8. A result of MO calculation for two PC molecules without carbonate part.

4. Summary

PC samples were irradiated by heavy ion beams such as Cu, Ag, and Au. The energy was up to 1 MeV, and the fluence was up to 10^{18} cm^{-2} . The depth profile of ions in the irradiated sample were analyzed by RBS. The ranges were almost the same as the results of SRIM calculations. The electrical conductivity of the irradiated samples was measured by four-point probe, and the dependences on the incident energy fluence were discussed. The oxygen density near the sample surface decreased, and the decrease (loss) is regarded as a cause of the electrical conduction. The introduction of the conduction can be applicable to produce a functional polymer.

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References

- N. Betz (1995) *Ion track grafting*, Nucl. Instrum. Methods B, 105, 1-4, 55-62, DOI: 10.1016/0168-583X(95)00911-6.
- A. Taniie, Y. Kida, Y. Furuyama, and A. Kitamura (2011) *Fabrication of polymer with the three-dimensional structure by ion beam graft polymerization method*, Nucl. Instrum. Methods B, 269, 24, 3237-3241, DOI: 10.1016/j.nimb.2011.04.094.
- A. Taniie, Y. Hirooka, N. Nakanishi, R. Nakamura, Y. Furuyama (2014) *High fluence irradiation effect on the ion beam graft polymerization method*, Nucl. Instrum. Methods. B, 331, 191-195, DOI: 10.1016/j.nimb.2014.01.026
- A. Taniie, R. Nakamura, S. Kusaka, Y. Hirooka, N. Nakanishi, Y. Furuyama (2015)

- Application of the ion beam graft polymerization method to the thin film diagnosis*, Phys. Procedia 80, 151-154, DOI: 10.1016/j.phpro.2015.11.095
- M. Deka, and A. Kumar (2013) *Dielectric and conductivity studies of 90 MeV O^{7+} ion irradiated poly(ethylene oxide)/montmorillonite based ion conductor*, J. Solid State Electrochem., 17:977-986, DOI: 10.1007/s10008-01201951-9
- L. Yue, Y. Wu, C. Sun, Y. Shi, and Y. Zhang (2016) *Effects of proton pre-irradiation on radiation induced conductivity of polyimide*, Rad. Phys. Chem. 119, 130-135, DOI: 10.1016/j.radphyschem.2015.09.019.
- H. Bougharraf, R. Benallal, T. Sahdane, B. Kabouchi (2016) *Study of electrical conduction of polyvinylalcohol films doped by 4-dimethylaminobenzonitrile molecule*, Opt. Quant. Electron., 48:91, DOI: 10.1007/s 11082-016-0389-1.
- A. K. Himanshu, S. K. Bandyopadhyay, Pintu Sen, Nagendra Nath Mondal, A. Talpatra, G. S. Taki, and T. P. Sinha (2011) *Electrical studies of low energy Ar^{9+} irradiated conducting polymer PANI-PVA*, Rad. Phys. Chem. 80, 414-419, DOI: 10.1016/j.radphyschem.2010.09.007.
- S. Asad Ali, Rajesh Kumar, F. Singh, P. K. Kulriya, Rajendra Prasad (2010) *Study of modifications in Lexan polycarbonate induced by swift O^{6+} ion irradiation*, Nucl. Instrum. Methods B 268, 1813-1817, DOI: 10.1016/j.nimb.2010.02.081.
- M.M. Abdelrahman, M. Osman, and A. Hashhash (2016) *Electrical properties of irradiated PVA film by using ion/electron beam*, Prog. Theor. Exp. Phys., 023G01, DOI: 10.1093/ptep/ptv 178.
- V. Resta, L. Calcagnile, G. Quarta, L. Maruccio, A. Cola, I. Farella, G. Giancane, L. Valli (2013) *Optical and electrical properties of polycarbonate matrices implanted by high energy Cu ions*, Nucl. Instrum. Methods B, 312, 42-47, DOI: 10.1016/j.nimb.2013.07.004.
- J. F. Ziegler, J. P. Biersack, U. Littmark, *The stopping and Range of Ions in Solids*, Pergamon Press, 1985, <http://www.srim.org/>.
- A. Taniie, N. Kubota, M. Takeuchi, Y. Furuyama, A. Kitamura (2002) *Ion-irradiation induced hydrogen loss from polyethylene film*, J. Appl. Phys., 92,11, 6489-6494, DOI 10.1063/1.1516251.