Change in Spectrum of Ionic Liquids Exposed to 2.45 GHz Surface Wave Plasmas

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Spectrum of three ionic liquids (ILs), those of which are 1-hexyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, and trioctylmethylammonium bis(trifluoromethanesulfonyl)imide, are measured with an ultra violet-visible-near infrared (UV-VIS-NIR) spectrophotometer and a Raman spectroscopy. After being exposed to surface wave plasmas (SWP) for 10 min., apparent broad spectrum appear in the wide range of longer wavelength for all cases of the three ILs. Data strongly suggest that due to the SWP irradiation, the ILs are altered considerably and some materials of wide conjugated carbons are produced in the ILs.

Keywords: plasma-liquid interaction, ionic liquid, UV-VIS-NIR spectroscopy, Raman spectroscopy, surface wave discharge, plasma processing, wide conjugated carbon material, diamond-like carbon

1. Introduction

While studies on plasma-surface (or plasma-wall) interaction have been performed intensively for a couple of decades in various areas of plasma processing and fusion technology, plasma-liquid interaction has just been investigated [1] as a new field of plasma material processing. In most experiments, water [2] or oil are mainly tested as a target, where plasmas with low temperature T have been used to either modify the characteristics of the liquid [3] or perhaps create a completely different materials in it [4]. As the method of producing the low-T plasmas, rf discharge has been applied [5], which actually can alleviate technical difficulties to generate the low-T plasmas. However, this technique would be inadequate if we intend to apply low-T plasmas to biological fluids, because those properties can be easily-altered. In fact, careful treatments must be applied to the fluids for the medical purposes. Obviously this calls some low-T plasmas which are produced with an exactly-controlled procedure and those behaviour in the imposed electric field $\vec{E}$ (also magnetic field $\vec{B}$, if it is forced.) must be completely understandable.

There exists the surface wave discharge [6] that can generate high-density plasmas with diameters as large as 15 cm. In the discharge, no imposed $\vec{B}$ is required. Electromagnetic waves propagate along the surface of the plasmas and be absorbed by them, sustaining the surface wave plasmas (SWP). Thus, the surface waves have strong $\vec{E}$ only near the plasma surface. The absorption lengths of the electromagnetic wave surface modes are very long in comparison with the ECR microwave discharge [7]. Both space and time evolutions of $\vec{E}$ on the plasma surface can be obtained also in numerically from two-dimensional computation using the FDTD method [8]. These properties, therefore, could provide controlled-plasmas more adequate to meet the needs for research on plasma-liquid interactions.

As the first target of the SWP, we have tested ionic liquids (IL) [9, 10]. IL is classified in a class of Coulombic fluids, which has actually attracted lots of interests in the past decade [11] due to its remarkable properties applicable to those in industrial developments. In fact, in the field of chemistry, IL has acted as a useful catalyst to enhance or trigger chemical reactions. Usually, IL is produced by means of precise synthesized techniques [12]. Although several different ways using less synthetic steps have been established recently, those processes still take long time due to the heating period that is more than an hour. A new method which shortens the length of the time has thus been required.

Clearly, for the above demand, low-T controlled-plasmas may be the candidate, although the density of plasmas is smaller than liquid. In order to experimentally test the possibility of that, SWP has been irradiated to three different ILs for 10 min. Remarkably, apparent change in spectrum of IL is appeared in the broad range of longer wavelength after the SWP irradiation, indicating alteration of IL. And, from the aspects of spectrum observed, materials of wide conjugated carbons are considered to be produced in the IL. In Sec. 2, the experimental setup for this research is described. Argon (Ar) gas is discharged using 2.45

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Table 1. Nominal characteristics of three different ionic liquids employed.

	Chemical name	Viscosity (mPa·s)	Melting point (˚C)	Decomposition point (˚C)
(1)	1-hexyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide	97	12	476
(2)	1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	88.1	-8	482.9
(3)	trioctylmethylammonium bis(trifluoromethanesulfonyl)imide	634.9	N/A	484.6

GHz microwave. Pictures of ILs taken before and after the SWP irradiation are presented in Sec. 3. Spectrum analyses for all ILs are explained in Sec. 4. Finally, a summary is given in Sec. 5.

2. Experimental Setup

Figure 1 shows a schematic diagram of the experimental apparatus. The vacuum chamber made of SUS304 is a cylindrical tank of 13 cm in radius and 25 cm in height and can be pumped down to 6.0×10^{-7} Torr by a diffusion pump. An electromagnetic wave traveling to the left-hand direction reaches at the single slot (1 cm in width and 5 cm in depth) on the waveguide and launches from there. The frequency of the electromagnetic is 2.45 GHz and can be powered up to 2 kW. However, the output power is fixed to be 0.2 kW for the presented experiments.

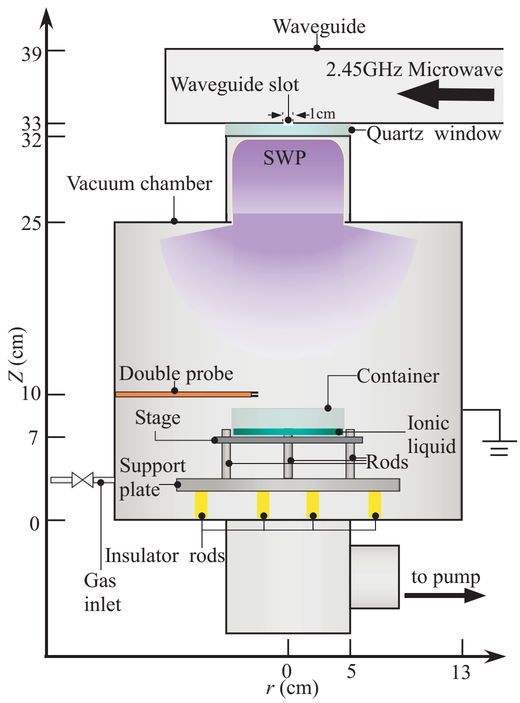

Fig. 1 A schematic drawing of the experimental apparatus. With a controlled procedure, surface wave plasmas are produced using 2.45 GHz microwave and diffused towards the stage on which a container with an ionic liquid is placed.

The launched microwave can propagate in the vacuum vessel through the quartz window and SWP are produced just below it (at $z = 32$ cm). The produced SWP then diffuses downward so that the plasma density n decreases gradually. In experiments, values of n have been measured with a double probe. The typical value of n at $z = 10$ cm is about 5×10^{9} cm^{-3} and it is almost constant in radial direction except near the inner wall of the chamber. Finally, a diffused plasma falls down the stainless stage at $z = 7$ cm on which a container is placed. The container is cylindrical, which is made of plate glass. The diameter and depth are 9 and 2 cm, respectively. In the container, we have put 10 ml of an ionic liquid before every discharge.

As for the stage, it is electrically isolated from the ground (0 V) so that the potential becomes the floating potential of Ar plasmas during the discharge. The vertical position of the stage is adjustable, however during the presented experiments it has been fixed to be at $z = 7$ cm, which is 26 cm apart from the waveguide slot. On the surface of the stage, thirty perforations are made and each of which has 1.2 cm in diameter. Through those holes, pictures and movies of IL can be taken from the bottom of the chamber.

With regard to ILs, we have employed three different ILs: (1) 1-hexyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide of the *'pyridinium'* family, (2) 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide of the *'pyrrolidinium'* family, and (3) trioctylmethylammonium bis(trifluoromethanesulfonyl)imide of the *'ammonium'* family. Nominal characteristics of them are summarized in Table 1. As recognized, all ILs used here are at liquid state at room temperature.

3. Ionic Liquids Exposed to SWP

Experiments have been conducted on all ILs. Typical parameters are listed in Table 2. The procedure of the experiment is the following. After placing the container having one of ILs on the stage, we start to pump down the chamber to 4.0×10^{-6} Torr. Argon gas with higher pressure of 0.2 Torr is initially installed in the chamber through the gas inlet to eas-

Table 2 Typical parameters of SWP-IL experiments.

Gaseous species	Ar
Background pressure	4×10^{-6} Torr
Fuel gas pressure	$(6-7) \times 10^{-3}$ Torr
Electron density	$\sim 5 \times 10^{9}$ cm^{-3}
Electron density at the stage	$< 5 \times 10^{9}$ cm^{-3}
Electron temperature	~ 1.5 eV
Microwave power	0.2 kW
Irradiation time	10 min.
Quantity of ionic liquid	10 ml

ily succeed in discharge with the 2.45 GHz microwave having a power of 0.2 kW. Once a dense SWP is generated, the amount of the fuel gas is quickly reduced to $\sim 7 \times 10^{-3}$ Torr. This gas pressure has been kept to be constant for the period of 10 min. During the discharge, the picture of the IL has been always recorded by a video camera. Finally, the IL is taken out from the container.

Figure 2 shows changes in colors of the three different ILs (see also Table 1) before and after the irradiation of SWP. As recognized from Fig. 2, all ILs are completely pigmentized, though they are usually transparent and colorless. Thus, these changes clearly mean that characteristics of ILs are altered considerably by the SWP irradiation. Also, as seen from movies recorded, the change in color has seemed to proceed gradually from the top surface. This result strongly suggests that the SWP causes some chemical reactions only on the surface of ILs or near there, not the deep inside of ILs.

Regarding the colours of ILs, each has a different colour (not clearly seen in Fig. 2, because of black and white); in fact, the IL of (1) turns to be brown, while ILs of (2) and (3) do to be yellow. Such a yellowish-IL has been reported in another experiment using 13.56 MHz electromagnetic wave [13]. These obtained results also suggest that due to the SWP irradiation, inherent properties of each IL are changed significantly. Three parameters, which are the exposed time, the plasma density and the temperature of SWP, have been changed in the presented experiments. Among those, the plasma density seems to the most one to affect the change in color of ionic liquids.

4. Spectroscopic Analyses

After the SWP irradiation for 10 min., all ILs have been altered considerably. In order to investigate what have been produced in ILs, we have performed ultra violet- visible-near infrared (UV-VIS-NIR) spectroscopic measurements on those.

Figure 3 shows spectrum outputted from the three different ILs before and after the SWP irradiation. Comparing the two spectrum taken from each IL, apparent change is recognized on the side of '*longer*' wavelength where a broad spectrum appears considerably. One notes that all ILs employed here belong to the organic family. For such materials, it has been well examined in the research field of chemical spectroscopy that the observed broad spectrum in the wide range of the longer wavelengths reflects some materials of wide conjugated carbons. If this knowledge held for the current SWP-IL experiments as well, those kinds of wide conjugated carbons are considered to be produced in the ILs exposed to the SWP.

The above may be supported by the fact that different intensities of the new spectrum have been outputted from different ILs; in fact, the strongest intensity is obtained from the IL of (1) and the color of it has turned to be most darkish, on the other hand (see also Figs. 2 and 3).

Since ILs are pigmentized, the question may be asked on whether those still possess their characteristics as ILs or not. We have not measured any physical quantities such as viscosity after the SWP irradiation. Thus the answer will be provided in the next paper where dependences on the power of SWP (equivalently, plasma parameters) and plasma species will also be reported.

Finally, we describe about depositions that have been found on the internal surface of the container (not presented in this paper). Regardless of the kind of ILs used here, lots of small deposition spots have been always spread uniformly on the inner wall of container about 3 mm up from the surface of IL. Although the

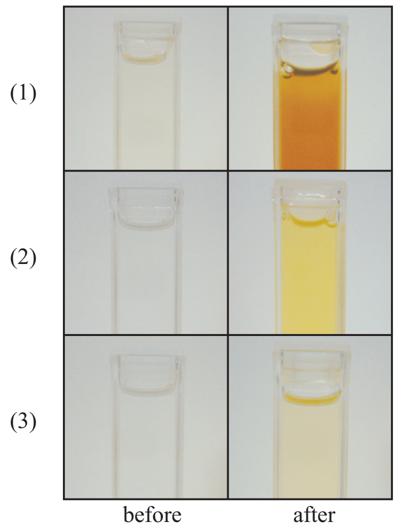

Fig. 2 Changes in colors of three different ILs before and after the SWP irradiation. The irradiation time is fixed to be 10 minutes for all ILs. The three index numbers of ILs correspond to those in Table 1: (1), (2), and (3).

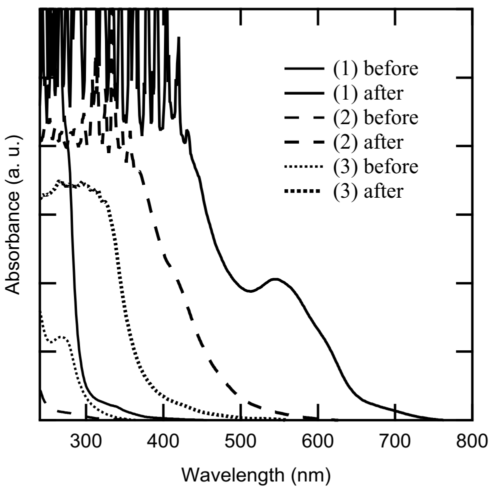

Fig. 3 Spectrum of ILs measured by the UV-VIS-NIR spectrometry. For each IL, those are diagnosed before and after the SWP irradiation. Clearly, spectrum having *'longer'* wavelengths newly appears.

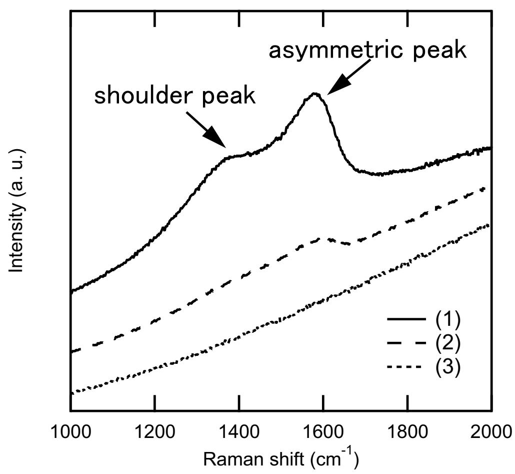

Fig. 4 The Raman spectroscopy on the deposition produced for the case of (1), (2), (3). The measured profile is similar to the spectrum obtained from diamond-like carbons.

detail of the deposition process is still unclear, it is more likely that some materials are blown up from the surface of IL during the SWP irradiation and then fall onto there. In order to examine the depositions, we have applied the Raman spectroscopy.

Figure 4 shows typical spectrum of the depositions. As seen from the data for the case of (1), the intensity of the spectrum increases gradually with increasing the Raman shift (wave number), due to the luminescent influences. The spectrum is broad and has an asymmetric peak at 1580 cm^{-1}. Besides, a small shoulder peak can be recognized at 1390 cm^{-1}. These aspects of the spectrum are quite similar to those obtained from diamond-like carbons (DLC) [14]. Since ILs contain lots of carbons, the observed depositions are possibly diamond-like carbons produced as byproducts during the SWP irradiation. It may be asked on what forms the observed DLC. Within the limit of Te 1.5 eV, the plasma density seems to be the most effective parameter to make the DLC. This can be inferred from the result of the Raman spectroscopy on the deposition of DLC. In fact, the outputted spectrum has shifted apparently, as the plasma density changes. With regard to the thickness of the deposition of DLC, on the other hand, it clearly increases with increasing the exposed time.

5. Summary

In order to investigate the possibility of exactly altering ionic liquids (ILs), experiments on ILs exposed to controlled surface wave plasmas (SWP) with low temperature have been conducted. Regardless the kind of ILs, apparent changes in colors of ILs are observed after the SWP are irradiated for 10 min. The change gradually proceeds during the SWP irradiation from the top surface of ILs, which thus indicates that the ILs could be altered under control by the SWP. Moreover, both an ultra violet- visible-near infrared (UV-VIS-NIR) and Raman spectroscopic measurements are applied to ILs. Data show that due to the SWP irradiation apparent spectrum appears in the wide range of longer wavelengths, strongly suggesting that some materials of wide conjugated carbons are produced in the ILs. Also, the depositions found on the inner wall of the container are possibly diamond-like carbons, which could be originally produced on the surface on ILs and then blown up from there.

[1] M. Tezuka and M. Iwasaki, Plasmas & Ions **2**, Issue 1, 23-26 (1999).
[2] A. A. Ivannikov *et al.*, High Energy Chem. **37**, No.2, 115-118 (2003).
[3] S. Roychowdhry *et al.*, Plasma Chemistry and Plasma Processing **2**, No.2, 265 (1982).
[4] S. Nomura *et al.*, Appl. Phys. Lett. **88**, 265 (2006).
[5] K. Köhler *et al.*, J. Appl. Phys. **57**, 59 (1985).
[6] F Werner *et al.*, Plasma Sources Sci. Technol. **3**, 473-481 (1994).
[7] M. A. Lieberman and A. J. Lichtenberg, *Principle of Discharges and Materials processing* (John Willey & Sons, 1994).
[8] K. S. Kunz, *et al.*, *The Finite Difference Time Domain Method for Electromagnetics* (CRC Press, Boca Raton, FL, 1993).
[9] R. D. Rogers and K. R. Seddon, Science **302**, 792-793 (2003).
[10] W. Xu and C. A. Angell, Science **302**, 422-425 (2003).
[11] K. R. Seddon, Nat. Mater. **2**, 363-365 (2003).
[12] P. Wasserscheid and T. Welton, *Eds. Ionic Liquids in Synthesis* (WILEY-VCH, Weinheim, 2003).
[13] K. Baba *et al.*, Appl. Phys. Lett. **90**, 201501 (2007).
[14] J. Robertson, Surf. Coatings Technol. **50**, 185-203 (1992).