Plasma Irradiation to Ionic Liquids using 2.45 GHz Microwave Discharges

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Experiments on plasma irradiation to ionic liquids (ILs) have been initiated. Despite lower density and kinetic energy of ions, discoloration of ILs is still observed. Spectrometric and calorimetric measurements show that once the visible change in color of ILs happens, spectra of both the crystallization temperature and the melting point completely disappear, suggesting decompositions of a part of components of ILs by plasma irradiation.

Key words: Plasma chemistry, Ionic liquids, Argon plasma treatment, Plasma-liquid interaction, Surface wave plasmas

1. INTRODUCTION

During a couple of past decades, irradiation of plasmas or especially ions to materials has been widely applied to many manufacturing processes [1] such as plasma etching for removing one type of material from surfaces while leaving other materials unaffected, plasma-assisted deposition for producing a solid product on the surface, and ion implantation for changing the atomic composition and structure of the near surface of the target material, that is, modifying its property of the material surface. Those are indeed important and key techniques born out of the need to access a parameter space in the material processing unattainable by strictly chemical reactions. Consequently, a variety of high technology devices has been produced from the irradiated materials.

While much of the target materials irradiated by plasmas are at solid state, experimental tests for liquid matter has been just initiated [2, 3] in order to investigate if the plasma irradiation changes properties of even the fluid as well. In fact, using plasma with precisely controlled particle flux $\Gamma$ and temperature $T$, plasma irradiation may offer a new way to synthesis a nanoparticle [2] and even hydroxyfluoride nanofibers through an ionic liquid [4] instead of the conventional chemical process. In order to explore a new research field of the plasma-assisted chemistry, the effect of the plasma irradiation to liquids must be investigated. This means that chemical properties of the liquid need to be measured after plasma irradiation, because the synthesis process strongly depends on the components of the fluid. In fact, those seem to play a key role to produce nanoparticles [2]. However, in past preliminary studies, most attention was paid to plasma parameters of the irradiated plasma and the resultant product by the gas-liquid interfacial plasmas [2, 5]. Regarding the property of the liquid itself, on the other hand, only the change in color was reported. Detailed chemical analyses of the liquid irradiated by plasmas are thus called for.

In this paper, we report the analyses of chemical properties of ionic liquids (ILs) irradiated by Argon surface wave plasmas [6]. It is revealed that once the visible change in color of ionic liquids (ILs) occurs, both spectra of the crystallization temperature $T_c$ and the melting point $T_m$ completely disappear. In the colored ILs, no visible impurities can be observed after plasma irradiation. These results strongly suggest that a part of chemical structure of ILs is decomposed by plasma irradiation. In Sec. II, the experimental setup is briefly explained. High density argon (henceforth, Ar) plasmas are produced by the surface wave discharge using 2.45 GHz microwave. Three different ILs are irradiated by the surface wave plasmas (SWP). The crystallization temperature and the melting point of the ILs are measured before and after plasma irradiation. Obtained data are presented in Sec. III. Finally, discoloration of ILs and related phenomena are discussed in Sec. 4.

2. EXPERIMENTAL SETUP

2.1 Apparatus

Figure 1 shows a schematic diagram of the experimental apparatus. The vacuum chamber made of stainless (SUS304) is a cylindrical tank of 13 cm in radius and 25 cm in height. The machine can be pumped down to $4 \times 10^{-6}$ Torr by a diffusion pump. The filling gas pressure is $(6 - 7) \times 10^{-3}$ Torr. 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 towards the vacuum chamber. The frequency of the wave is 2.45 GHz and can be powered up to 2 kW. However, the output power is set to be between 0.3 and 0.7 kW for the presented experiments. The launched microwave can propagate in the vacuum chamber through the quartz window and
Surface wave plasmas (SWP) having the electron density $n_e$ of $\sim 6 \times 10^{11}$ cm$^{-3}$ are produced just below the quartz window, that is, at $z = 32$ cm. The produced SWP then diffuses downward so that $n_e$ decreases gradually. As seen in Fig. 1, the value of $n_e$ just above the cross-section where ILs are placed is measured with an electrostatic (double) probe [3]. The typical value of $n_e$ at $z = 10$ cm is about $5 \times 10^6$ cm$^{-3}$ and it has been almost constant in radial direction except near the inner wall of the chamber. Using the double probe, the electron temperature $T_e$ is also measured and the value of $T_e$ is typically about 6 eV. Details of SWP of this experiment will be published elsewhere.

Fig. 1 Schematic diagram of the experimental setup. The surface wave discharge with 2.45 GHz microwave is employed to produce surface wave plasmas.

As for the stage on which the glass container is placed, it is electrically isolated from the ground (0 V). Thus, the electric potential of the stage becomes to equal so called the floating potential of Ar plasmas during the SWP irradiation. The vertical position of the stage is adjustable in the chamber. However, for 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 holes are made and each of which has 1.2 cm in diameter. Through those holes, pictures and movies of ILs can be taken from the bottom side of the chamber. Above the container, on the other hand, a set of four metal mesh grids, which are made of SUS304, are employed. By applying potentials to them, we can reduce the number of ions and/or electrons, and furthermore prevent charged particles with energy lower than the potential value of the grid from injecting into ILs.

### Table I: Nominal characteristics of three different ionic liquids employed.

<table>
<thead>
<tr>
<th></th>
<th>viscosity (mPa s)</th>
<th>melting point (°C)</th>
<th>decomp. point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>97</td>
<td>12</td>
<td>476</td>
</tr>
<tr>
<td>(b)</td>
<td>88</td>
<td>-8</td>
<td>483</td>
</tr>
<tr>
<td>(c)</td>
<td>635</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

(a) 1-hexyl-4-methylpyridinium bis imide  
(b) 1-butyl-1-methylpyrrolidinium bis imide  
(c) trioctylmethylammonium bis imide

2.2 Ionic Liquids

Regarding ILs, we have employed three different ILs: (a) 1-hexyl-4-methylpyridinium bis imide of the pyridinium family, (b) 1-butyl-1-methylpyrrolidinium bis imide of the pyrrolidinium, and (c) trioctylmethylammonium bis imide of the ammonium. Nominal characteristics of them are summarized in Table I. As recognized from Table I, all of those ILs are at liquid state at room temperature. Also, those are usually transparent and colorless. It should be noted that the names of the three ILs will be abbreviated as their above index letters (a) through (c) hereafter.

### Table II: Typical plasma parameters of SWP.

<table>
<thead>
<tr>
<th>gaseous species</th>
<th>argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>background pressure</td>
<td>$&lt; 4 \times 10^6$ Torr</td>
</tr>
<tr>
<td>filling gas pressure</td>
<td>$7 \times 10^3$ Torr</td>
</tr>
<tr>
<td>electron density</td>
<td>$10^{17}$ m$^{-3}$</td>
</tr>
<tr>
<td>electron density at the stage</td>
<td>$10^{16}$ m$^{-3}$</td>
</tr>
<tr>
<td>electron temperature</td>
<td>$&lt; 6$ eV</td>
</tr>
</tbody>
</table>
3.1 Dependence of change in color of ILs on density and kinetic energy of injected ions

As mentioned in Sec. 1, it has been reported that the color of ILs is considerably changed after plasma irradiation [2, 3]. And, high-energy ions accelerated by the sheath electric field in the liquid-gas interfacial region were supposed to cause the observed discoloration [2]. Obviously, one of methods to examine the above speculation is to reduce both the density \( n_i \) and the kinetic energy of ions. These can be brought by the use of metal grids with finite transmittance and electrostatic potential applied to those.

Figure 2 shows changes in colors of all ILs before and after plasma irradiation with \( n_i \sim 10^9 \) cm\(^{-3}\). This value of \( n_i \) is two orders of magnitude smaller than those of the past experiments [2, 3]. Regarding other experimental parameters, the microwave power is 680 W and the irradiation time \( t_{ir} \) is 5 min. The value of bias potential applied to the first grid \( V_{g} \) is continuously variable, but for the presented research, it is fixed to either 0 or \( \pm 9 \) V, larger than \( T_e/k \) where \( k \) is Boltzmann’s constant. As recognized, regardless of \( V_g \), little discoloration can be observed except for the case of (a). In fact, these results show a striking contrast to those observed in the past experiments [3] in which all ILs have been completely colored. In fact, even for the case of (a), the color turns to be yellow for \( n_i \sim 10^8 \) cm\(^{-3}\), while completely brown for \( n_i \sim 10^{11} \) cm\(^{-3}\) [3]. In experiments, two other parameters of \( t_{ir} \) and \( T_e \) have been also varied. Among those, \( n_i \) seems to be the most one to affect the change in color of ILs.

The above result of change in color clearly reflects the spectra outputted from an ultra violet-visible-near infrared (UV-VIS-NIR) spectrometry shown in Fig. 3 (a). As seen from the curves at \( \lambda \sim 310 \) nm, all values of transmittance decrease considerably after plasma irradiation, regardless of \( V_g \). This means that apparent change occurs on the side of longer wavelength. In other words, the slope of the spectrum becomes so broad in the visible range that the discoloration is observed with our eyes. On the other hand, no such alteration can be recognized in the measured spectra depicted in Fig. 3 (b) and (c) and in that case, no discoloration has been happened (see also Fig. 2).

3.2 Differential scanning calorimetric (DSC) measurements

As described in the above, the IL of type (1) is still colored slightly with lower \( n_i \) of SWP. On the other hand, no visible discoloration can be recognized for cases of type (b) and (c). As mentioned in Sec. 2, ILs are transparent and colorless. Thus, the question is asked on whether those ILs after plasma irradiation with lower \( n_i \) still possess their characteristics as ILs or not. To answer it, for the first time, we perform the differential scanning calorimetric (DSC) measurements by which the crystallization temperature \( T_c \) and the melting point \( T_m \) of ILs can be examined. Figure 4 shows the set of data...
irradiation only for the case of type (a). Actually, both sharp peaks seem to almost disappear after the SWP irradiation, regardless of \( V_g \). As for the values of \( T_c \), the peak seems to shift slightly to a lower temperature after the SWP irradiation, which is from \( T_c \approx -17 \, ^\circ C \) to \( \approx -19 \, ^\circ C \). Similar shift is also recognized for \( T_m \), which is actually larger from \( \approx 12 \, ^\circ C \) to \( \approx -10 \, ^\circ C \). On the other hand, for cases of types (b) and (c), no significant change in the measured spectra is occurred.

4. DISCUSSION

First of all, the correspondence between the observed pigmentation and inherent thermal properties of ILs is considered. When even little discoloration of ILs occurs by plasma irradiation (see also Fig. 2), the profile of the transmittance is necessarily changed simultaneously (see also Fig. 3). Moreover, both spectra and values of \( T_c \) and \( T_m \) are also completely altered, in other words, the chemical property becomes a different one. Contrary to those, nothing is changed in any measured spectra as long as ILs are transparent and colorless. Accordingly, these results mean that once the discoloration happens, the irradiated IL is no longer pure. From a chemical point of view, some impurity is produced by plasma irradiation although it has not been identified yet.

Regarding the source of the impurity involved in the irradiated IL, three possibilities could be thought, which are (1) the dissolving of a part of the container in IL (see also Fig. 2), (2) the solution of Ar gas in IL, and (3) the decomposition of ILs. But, the first one is not the case. As already explained, during all the experiments, both the microwave power (680 W) and the irradiation time (5 min.) have been kept constant. Hence, if a part of the container had dissolved in IL, the impurity should have been involved also in both types of (b) and (c) of ILs and as a result, some discoloration or change in measured spectra would have been observed. No such signals, however, have been seen for cases of type (b) and (c). Next, as for the second possibility, gas solubility in ILs are hot theme and intensively studied in the research field of physical chemistry in order to develop environmentally benign green chemical processes \cite{7,8}. In general, the gas solubility in liquids depends on its gas pressure and the liquid temperature macroscopically, while microscopically being governed by the interactions between the gas molecules and the solvent molecules. Thus, Ar gas can be solved in [bmin][PF_6] that is one of the most common ILs used in reaction studies \cite{7}. In fact, the solubility of Ar gas is fairly higher than those of other gases. However, those have been measured under quite higher pressure (\( p \gg 760 \) Torr). Looking at the data plotted at \( p < 760 \) Torr, little amount of Ar gas seems to be solved, although [bmin][PF_6] used in their experiments \cite{7} is completely different from those in our experiments. Besides, no studies have been so far found out yet on the
change in color of ILs saturated with Ar gas, unfortunately. So, the second possibility is still an open question. Lastly, about the third possibility, it seems to be more likely to cause the observed discoloration. In other experiments with higher $n_i$, the Raman spectroscopy has clearly detected the existence of some diamond-like carbons (DLC) on the inner surface of the container [3]. Although no such DLC has been observed on the container for the presented research possibly due to lower $n_i$, those may be still involved in IL. Details of this will be published elsewhere.

Finally, since $n_i$ and the kinetic energy of plasmas have been reduced by the use of potential grids, we should mention on how the decomposition of ILs could take place by the plasma irradiation. As explained, the lower $n_i$, the lighter discoloration. Intuitively, this result can be understood. However, the dependence of $V_g$ on the discoloration has not been observed, on the other hand. In fact, when $V_g$ is -9 V (approximately double of $T_e$), most of ions are expected to be retarded. In other words, there would exist little fast ions with kinetic energy larger than binding energies of components of ILs. Nevertheless, the discoloration has happened (see also Fig. 3) although only for the case of (a). These results suggest that some effect of radiation emitted from plasmas plays a key role in decomposing ILs rather than the plasma particle flux. This will be examined in the next experiments.

REFERENCES

(Received September 14, 2009; Accepted February 22, 2011)