1 Introduction

Development of a molecular device requires techniques to deposit molecules on a substrate. The deposition techniques conventionally used for organic molecules include wet processes such as the Langmuir-Blodgett technique, the self-assembling technique, and the spin-casting technique, as well as dry processes such as the conventional evaporation technique, and the organic molecular-beam epitaxy technique. Dry processes use thermally stable molecules that can be volatilized by heat. On the other hand, wet processes use a solution, and can be applied to many types of molecules, though these processes are difficult to combine with dry processes.

Many molecules can be dissolved into solutions. Therefore we adopt an approach that starts from a solution. Currently we are conducting studies to establish a technique to generate a molecular beam of non-volatile neutral molecules in vacuum from solution mists (the spray-jet technique) in order to deposit molecules on a substrate. Enabling vacuum handling of molecules unsuitable for ordinary dry processes leads to expansion of the range of molecular materials that can be used in vacuum. Observation of non-volatile molecules will also be possible under ultra-high vacuum by combining this technique with microscopic observation techniques such as those involving the ultra-high-vacuum scanning tunneling microscope (UHV-STM).

The above discusses the characteristics of the spray-jet technique in terms of molecular deposition. Spectroscopic analysis of non-volatile molecules in the molecular beam generated with this technique is also of particular interest. The spectroscopic information obtained with this technique differs from information obtained using other analysis techniques such as the supersonic jet technique[1], the electrospray ionization (ESI) technique[2], and the matrix assisted laser desorption ionization (MALDI) technique [3]-[5]. When we developed the spray-jet molecular beam apparatus, we simultaneously constructed a system for spectroscopic analysis of the electronic states of the molecules in the molecular beam or of the conditions of solvent.
adsorption to the molecule (this system includes a laser, and TOF-MS). We designed this system to provide information on the basic properties of the non-volatile molecules in the molecular beam, and also to provide feedback data to assist in improving the equipment, and determining optimal conditions of use.

In this paper, we first explain the molecular beam apparatus that uses the spray-jet technique we developed, and how it is different from other analysis techniques. We then report on the results of spectroscopic experiments performed on non-volatile molecules in the generated molecular beam. Finally, we report on the apparatus currently under development for application of the spray-jet technique to molecular beam deposition.

2 Spray-jet technique

Figure 1 shows a schematic diagram of the molecular beam apparatus with the spray-jet technique that we developed, and Fig. 2 shows its external appearance. This molecular beam apparatus consists of (1) a new inlet system including an ultrasonic nebulizer, an inlet chamber, and a pulsed nozzle, (2) a multiple differential pumping vacuum system with a double skimmer structure, (3) a high-vacuum chamber equipped with a time-of-flight mass spectrometer. First, the ultrasonic nebulizer generates a thick mist of the sample solution. The mist is then stored in the inlet chamber, where the solvent is removed to the full extent possible. The mist then passes through the pulsed nozzle, and the double skimmer structure, and is subject to adiabatic expansion to form a pulsed molecular beam of non-volatile molecules. The background vacuum level in the main chamber is approximately $1.3 \times 10^4$ Pa, and the vacuum level as the molecular beam is introduced is $1.3 \times 10^3$ Pa. For spectroscopic analysis, we irradiate a one- or two-color tunable nano-second laser to the pulsed molecular beam, and measure the spectra, including the resonantly enhanced multiphoton ionization time-of-flight mass spectrum (REMPI-TOFMS spectrum), and the resonantly enhanced multiphoton ionization excitation spectrum (REMPI excitation spectrum). These measurements provide information on the electronic, and vibrational states of the non-volatile molecules in vacuum.

REMPI is a phenomenon in which multiphoton ionization efficiency increases due to the resonance that takes place when the transition energy to the excited electronic states (including the vibrational states) of the neutral molecules coincides with the photon energy of the incident laser beam. The REMPI-TOFMS spectrum is obtained as follows: the neutral molecules are excited using a laser beam with a certain photon energy, radical cations are generated through resonantly enhanced multiphoton ionization, and the ions are measured with a time-of-flight mass spectrometer. The REMPI excitation spectrum is obtained by scanning the photon energy of the excitation laser beam while monitoring a radical cation with a certain mass. In general, the REMPI excitation spectrum reflects the absorption spectrum of the neutral molecule in vacuum.

Here we will discuss the difference between the spectroscopic analysis of non-volatile molecules using the spray-jet technique, and using other analysis techniques (specifically, the supersonic jet, ESI, and MALDI-TOFMS techniques).

Figure 3a shows a schematic diagram of the supersonic jet technique. In this technique, the sample molecules are heated so as to have sufficient vapor pressure, and are then introduced along with the carrier gas through the pulsed nozzle, and the skimmer into the vacuum; a cold molecular beam is then generated by adiabatic expansion. However, while this technique can be applied to spectroscopic analysis, and molecular deposition of volatile neutral molecules, it cannot be applied to non-volatile neutral molecules.

Figure 3b shows a schematic diagram of the ESI technique, which involves the spraying of ionic solutions. High voltage applied to the capillary continuously draws the ionic mist into the vacuum. After removal of the solvent
molecules, the ionic molecules pass through the skimmers, and octapoles. They are then mass-filtered by the ion trap, and subsequently detected. This technique is extremely effective for mass analysis of ionic non-volatile molecules but cannot be applied to non-volatile neutral molecules.

Figure 3c shows a schematic diagram of the MALDI-TOFMS technique. This technique involves proton transfer to the sample molecules through photo-excitation, and/or photo-ionization of the matrix molecules by laser irradiation. The generated sample molecule ions are measured with a time-of-flight mass spectrometer. This technique is extremely effective in measuring the mass spectra of non-volatile neutral molecules but cannot be applied to spectroscopic analysis of the sample molecules themselves, as this technique involves an indirect ionization relying on the photo-excitation, and/or photo-ionization of the matrix molecules.

Thus the molecular beam apparatus using the spray-jet technique that we developed can provide information not available using existing analysis techniques.

3 Spectroscopic experiments for non-volatile neutral molecules

Figure 4 shows the samples, and the sample solutions used in this experiment. The spray-jet technique was applied to various
molecular systems including liquid crystal (4′-n-pentyl-4-cyanobiphenyl: 5CB), naphthalene derivative (1,5-dihydroxy naphthalene: DHNA), fluorochrome (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran, DCM), and dendrimer (poly (propylene imine) dendrimer) molecules. The REMPI-TOFMS spectra, and REMPI excitation spectra for these molecular systems were measured. The 5CB/acetone solution was used for spectroscopic studies on the excited states of non-volatile neutral molecules (solute molecules) in vacuum. The DHNA/methanol solution was used for studies on the interactions between solute, and solvent molecules. DCM/acetone solution, dendrimer/acetone solution, and mixed DCM/dendrimer/acetone solution were used for studies on the interactions between different solute molecules.

The following are the experimental results with 5CB/acetone solution. Figure 5a shows the REMPI-TOFMS spectrum obtained by excitation of a 270-nm laser beam. Although no signal was observed with the ordinary supersonic jet technique even when the sample was heated to 125°C, the spray-jet technique enabled us to detect 5CB parent radical cations (m/z=249), and 5CB fragment ions (m/z=192). DFT calculation confirmed that the fragment ion forms with minimum energy as a result of the cleavage of the parent radical cation. Figure 5b shows the REMPI excitation spectrum monitored at the 5CB parent radical cation. The REMPI excitation spectrum generally reflects the absorption spectrum of the target molecule in vacuum. Compared to the spectrum for 5CB absorption spectra in a cyclohexane solution shown in Fig. 5c, the peak position is slightly shifted toward the higher energy. The REMPI excitation spectrum also has some structures arising due to the (relatively weak) coupling with the vibrational levels.

Next we discuss the results of experiments using the DHNA/methanol solution. Although
DHNA has a low molecular weight, its melting point is above 250°C, and it is non-volatile. These characteristics are considered to be due to intermolecular hydrogen bonding. Figure 6 shows the REMPI-TOFMS spectrum obtained by excitation of a 300-nm laser beam. The clusters of the solvent, and solute molecules ([DHNA - (methanol)]·⁺(m/z = 192), [DHNA - (methanol)]₂·⁺ (m/z=224)), and the dimers of the solute molecules ([DHNA₂]·⁺ (m/z = 320)) are observed as well as the parent radical cations ([DHNA]·⁺ (m/z=160)). This is considered to be due to hydrogen bonding between the solvent molecule, and the solute molecule or to hydrogen bonding between the solute molecules. Such clusters are not observed in the 5CB/acetone solution.

Next we discuss experimental results for solute-solute interactions in the dendrimer, and DCM solutions. Figure 7a shows the REMPI-TOFMS spectrum for the acetone solution of the dendrimer. Signals were not observed with excitation at 455 nm. Figure 7b shows the REMPI-TOFMS spectrum for the acetone solution of DCM. In this spectrum, the DCM parent radical cations (m/z=303) were observed with 475-nm excitation. Figure 7c shows the REMPI-TOFMS spectrum for the dendrimer/DCM/acetone mixed solution. While peaks 1 to 4 (probably attributable to the dendrimer fragments) were observed with excitation at 455 nm, interestingly, almost no parent radical cations of DCM were observed. These results indicate that DCM, and dendrimer molecules are extremely close to each other within the molecular beam generated from the DCM/dendrimer/acetone solution,
and that the resonantly enhanced multiphoton ionization of the DCM molecule interacting with a dendrimer molecule caused the reaction between these two molecules. Figure 7c also shows the attribution of peaks 1 to 4. We then performed DFT calculations, the details of which are indicated in reference [8], and confirmed that it is possible to observe the dendrimer fragment ions, as shown in Fig. 7c.

Figure 8a shows the REMPI excitation spectrum for the DCM/acetone solution. Figure 8b shows the REMPI excitation spectrum for the dendrimer/DCM/acetone solution, monitored at the dendrimer fragment ions. The REMPI-TOFMS spectra indicate that the dendrimer fragment ions are observed as a result of the reaction between the dendrimer, and DCM molecules induced by the resonantly enhanced multiphoton ionization of the DCM molecule interacting with the dendrimer molecule. Therefore, Fig. 8b is considered to reflect some of the features of the absorption spectrum in vacuum of the DCM interacting with the dendrimer. Comparing Figs. 8a with 8b, the peak position in Fig. 8b is shifted toward the higher energy. This tendency is confirmed to be consistent with that observed in the absorption spectra for these two solutions.
4 Application to molecular beam deposition

We have recently developed the apparatus shown in Fig. 9, designed to observe the molecules deposited on a clean substrate surface by the spray-jet technique, using an ultra-high-vacuum scanning tunneling microscope (UHV-STM). This apparatus has the same spray-jet inlet source as shown in Fig. 1. However, the current apparatus has an ultra-high-vacuum chamber equipped with a unit for transferring the sample plate to the UHV-STM, instead of the time-of-flight mass spectrometer. The background vacuum level of the ultra-high-vacuum chamber is approximately $8 \times 10^{-8}$ Pa. First, a clean substrate is prepared in the ultra-high-vacuum chamber (Position $\alpha$). The substrate is transferred to Position $\beta$ for molecular beam deposition, and transferred back to the ultra-high-vacuum chamber (Position $\alpha$) after molecular deposition. The substrate is then transferred to the UHV-STM using the unit for transferring sample plate while maintaining vacuum, to enable observation of the morphology of the molecular beam deposition film. Using this apparatus, we have recently succeeded in observing single-molecule images of non-volatile molecules.

5 Conclusion

This paper reported on the characteristics of a molecular beam apparatus that uses the spray-jet technique we developed. We also presented the results of the spectroscopic experiments for molecular beams of non-volatile molecules obtained by the spray-jet technique, and mentioned recent advances related to the application of the spray-jet technique to molecular beam deposition. We intend to improve the performance of this technique, to apply it to functional molecules with large molecular weights such as polymers, and bio-molecules, and to perform spectroscopic analysis, molecular deposition, and surface analyses. We also plan to apply the spray-jet technique in the production of molecular devices based on functional molecules.

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References