e-J. Surf. Sci. Nanotech. Vol. 12 (2014) 414-417 Regular Paper

Optical Sum Frequency Generation Spectra of Water Molecules on a Polycarbonate Film Exposed to O_2 Plasma

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(Received 22 August 2014; Accepted 8 September 2014; Published 27 September 2014)

We have performed sum frequency generation (SFG) spectroscopy of water molecules on a polycarbonate (PC) film with and without 1 minute O_2 plasma exposure. The intensity of SFG signal corresponding to the O–H stretch vibrations of water at a water/PC film interface was ∼1000 times as low as that of signal from a water/quartz interface. In the SFG spectrum of water facing a pristine PC film, peaks at 3270 and 3440 cm^{-1}, and a shoulder at 3620 cm^{-1} were observed. In the SFG spectrum of water on the film exposed to O_2 plasma, peaks were observed at 3200 and 3450 cm^{-1}. The peak at 3270 cm^{-1} red-shifted to 3200 cm^{-1} by the O_2 plasma exposure. The intensity of the peak at 3200 cm^{-1} was higher than that at 3450 cm^{-1}. The shoulder at 3620 cm^{-1} disappeared after the O_2 plasma exposure. The modulations of these peaks represent that the packing structure of water molecules was more ordered on the film after the O_2 plasma exposure. [DOI: 10.1380/ejssnt.2014.414]

Keywords: Sum frequency generation; Water; Polycarbonate; O_2 plasma

I. INTRODUCTION

Recently, control of wettability by nano texturing become important, and it is expected to be related to industrial applications such as self-cleaning [1,2], anti-reflection [3,4], and omniphobicity [5]. On the other hand, new dynamics of water droplets on a super-hydrophobic interface have been reported [6,7], and the science of the wettability has achieved remarkable development.

Polycarbonate (PC) is one of the engineering plastic materials. It has high transparency in visible light region and high heat resistance. The film also can be made with low cost. Thus, it is commonly used as a hardened glass material [6]. In recent years, nano texturing has been made on the surface of the PC film by O_2 plasma exposure, and thus it is expected as a functional plastic glass having a superhydrophilic surface [6].

In spite of the success of some models of the wettability of a solid film with nano texturing [7,8], the control of the wettability is still difficult. The most important issue in the case of O_2 plasma treated films is that the plasma exposure gives rise to volatile species e. g. C=O bonds on the surface of the PC film [6], and then the chemical composition changes, and the change influences the surface tension γ_{SL}. Moreover, the wettability of the PC film also deteriorates with time. For instance, according to Palumbo et al., the forward contact angle of the PC surfaces was 9 degree soon after 5 minutes O_2 plasma exposure with 100 mW, but it became 63 degree after 21 days [6].

The behavior of superhydrophilic and superhydrophobic interfaces due to nano-texturing can be described by Wenzel or Cassie-Baxter model [7,8]. For instance, in Wenzel model, when one has a contact angle on a flat solid surface θ_E, a cast contact angle θ^* of the surface having small asperity is written as

$$\cos\theta^* = r\cos\theta_E. \quad (1)$$

Here r represents the degree of asperity. In this model, the change of cast contact angle due to the mesoscopic asperity is related to a macroscopic phenomenon of water, and it is assumed that the water structure on the interface and the θ_E itself is invariant.

Surface tension reflects also the arrangement of water molecules on a solid surface. Generally, if the wa-

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ter molecules are well packed by hydrogen bonding, surface tension defined by the surface energy per area should decrease. Thus, in order to control the wettability of the film, one must study a packing condition of water molecules on the PC film. However, there has been no study on the change of the packing condition on the film due to O_2 plasma exposure.

In this study, we have investigated the water arrangement on the plasma-exposed and pristine PC films by using visible-IR sum frequency generation (SFG) spectroscopy. The SFG method was established as a unique tool for analyzing the water structure at water/solid interfaces, and in some cases, the solid surfaces were modified by an organic thin monolayers [9-13]. However, the SFG signals corresponding to O–H stretching modes of water molecules at a water/polymer interface were generally weak [14], and thus there were few related papers [15]. Especially, there was no report about SFG signals of the O–H vibrational modes of water molecules on an engineering plastic material. Thus, in this paper, we demonstrated that SFG spectroscopy could be useful for investigation of the water alignment on a membrane of engineering plastic material.

By using the SFG spectroscopy, we found that the water arrangement on the PC film improved by the O_2 plasma exposure. Here, the asperity of the nano texturing with a few nm order is unlikely to influence the water structure with a few atomic layers at the interface. SFG is a macroscopic probe, but it can selectively monitor the water structure within a few layers from the interface, and thus, the spectrum is not influenced by the asperity.

II. EXPERIMENTAL

Optical-transparent polycarbonate films of thickness 100 μm (Sumitomo Bakelite Co., Ltd.) were treated with oxygen plasma generated with a high-frequency oxygen plasma generator (PC-300; SAMCO, Kyoto, Japan). Briefly, we explain the SFG system, since it was already reported elsewhere [13,16]. In the SFG spectroscopic system used in this study, we used doubled frequency output from a mode-locked Nd^{3+}:YAG laser [EKSPLA PL2143] as the visible light at wavelength 532 nm, and output ($\sim$4.8μm) from an optical parametric generator and amplifier system (OPG/OPA) [EKSPLA PG401] as the wavelength-tunable infrared light. The SFG light pulses passed through high pass filters, a monochromator, and then was detected by a photomultiplier. The pulse energies of the IR probe and visible light beams in front of the sample were $\sim$25 μJ/pulse and $\sim$300 μJ/pulse, respectively. The incident angles of the visible and IR probe light beams were $\sim$84° and $\sim$53°, respectively. The polarizations of the SFG, visible, and IR light were s, s, and p, respectively. These polarization combination is the most sensitive to the orientation of water molecules at the interface [9]. The peaks attributed to the O–H stretching vibration in the SFG spectra were fitted using the equation

$$\chi^{\mathrm{SFG}} = \chi^{\mathrm{NR}} e^{i\psi} + \frac{\chi_\nu}{\omega - \omega_\nu + i\gamma}. \qquad (2)$$

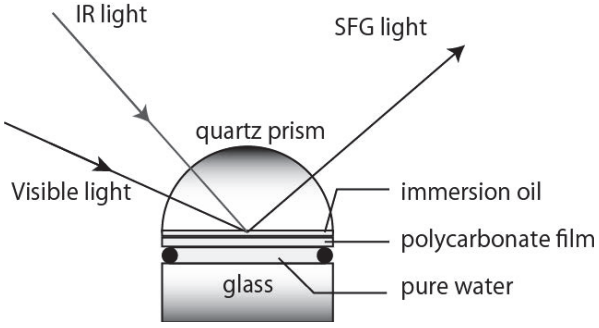

FIG. 1. Schematic diagram of the sample holder.

Here χ^{NR}, χ_ν, ψ, ω_ν, and γ are nonlinear susceptibility, total hyperpolarizability of the water molecules, phase difference between the resonant and non-resonant terms, the resonant frequency, and the damping constant of the resonant mode, respectively [10].

Figure 1 shows a schematic diagram of the sample holder for SFG spectroscopy. We built up the holder as follows. In order to remove impurities of quartz surface, we exposed the quartz prism with a semicircular column shape to UV light in two hours. Immediately after the exposure, we dropped a small amount of immersion oil (Olympus UVFL, n=1.404) on a flat face of the quartz prism, and put the PC film on the quartz plate. Then, we put a circular elastic ring on the film, and poured ultra pure water inside the ring, and finally sealed it with a cover glass. In order to prevent IR light absorption in bulk water, the incident light beams irradiated the film from the prism side, and the reflected SFG light was observed as shown in Fig. 1.

The signal intensity at a water/PC film interface was $\sim$1000 times as low as that at a water/quartz interface. Moreover, if strong incident visible light was exposed to the sample, the light beam gave rise to avulsion of PC film in the sample holder. At the avulsed area, the visible light strongly scattered, and became dominant noise source. The noise intensity is comparable to the weak signal intensity, and the intensity data was unreliable. Thus, the intensity of visible light had to be under 25 μJ/pulse for preventing the avulsion.

The IR light absorption of air/PC film/immersion oil/quartz interfaces is negligible in our SFG measurements, since 80% of the IR light is transmitted in the spectral region from 3150 to 3800 cm^{-1}. Strong IR light absorption was observed in a region from 2900 to 3150 cm^{-1}. However, O–H stretching vibration was seen mainly above 3150 cm^{-1} and can be analyzed by using our sample holder. We also confirmed few SFG signals corresponding to O–H vibrational modes generated at air/PC film/immersion oil/quartz interfaces. By using the sample holder, we observed clear SFG signals attributed to O–H vibrational modes only at the water/ PC film interface.

Topographic images of the films were taken by using an atomic force microscope (AFM, Keyence VN-8000) in the dynamic force mode. We took SFG spectra and AFM images, and measured contact angles of the films four weeks after the O_2 plasma exposure in ambient conditions.

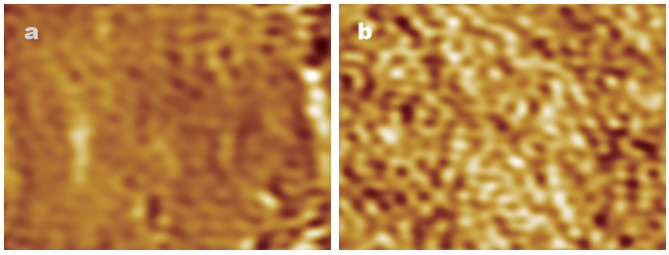

FIG. 2. AFM images of polycarbonate film (a) without and (b) with 1-minute O_2 plasma exposure (1×0.75 μm^2).

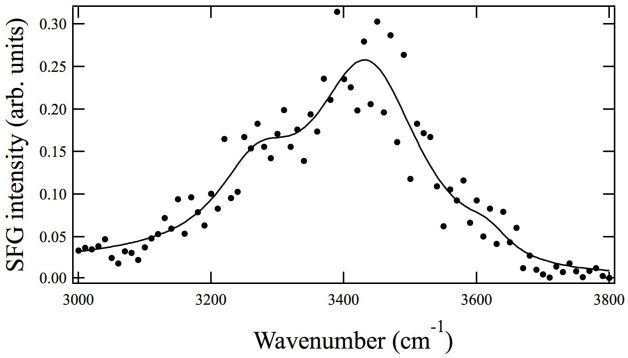

FIG. 3. SFG spectrum of water molecules on a polycarbonate film without O_2 plasma exposure.

III. RESULTS AND DISCUSSION

First, in order to investigate the change of morphology on the PC film due to O_2 plasma exposure, we observed AFM images of the films. Figures 2(a) and (b) show the AFM images of the PC film without and with O_2 plasma exposure, respectively. On the pristine PC film, there were several defects, but the roughness of most area was estimated to be smaller than 1 nm. Thus, the asperity of the film is negligible. On the other hand, as shown in Fig. 2(b), all area on the film treated by the plasma had asperity with amplitude 1∼4 nm and the lateral sizes ∼40 nm. The morphology was basically consistent with that of the PC film exposed to O_2 plasma for three minutes observed by Palumbo and his coworkers [6].

Next, in order to evaluate the wettability, we put drops of 5 μl pure water on the PC films, and measured the contact angles. As the results, the contact angles without and with plasma exposure were 80.7°± 1.3° and 52.3°± 0.1°, respectively. The result indicates that the PC film with O_2 plasma treatment is more hydrophilic. The result may appear to be explained by the Wenzel model. As shown in eq. 1, one could consider that the cast angle θ^* of the exposed film was reduced due to the nano-texturing. However, one must remind himself that the small asperity (<∼1.2) as seen in Fig. 2(b) can hardly induce such big hydrophilicity [8].

Here, one must also consider how the wettability was influenced by the change of chemical components due to plasma exposure and variation with time. According to XPS spectra taken by Palumbo *et al.*, the ratio of oxidized species increased to 15% after 5 min O_2 plasma exposure. We also measured XPS spectra of our films in order to investigate the chemical compositions, but we could not observe the spectrum of the fabricated film due to strong inelastic scattering of the probe electrons. In this study, we can also think that the oxygen species might increase by one-minute exposure. The change of chemical components influences water structure on the surface and thus the surface tension γ_{SL}. For instance, species such as C=O bonds should be bound to water molecules via hydrogen bonding, so that these new bonds may modify the water structure at the interface.

Thus in order to understand the change of water structure, we observed SFG spectra of the water on the PC films. Figure 3 shows the SFG spectrum of water on a pristine PC film. We see peaks at 3270 and 3440 cm^{-1} and a shoulder at 3620 cm^{-1}. According to an ab initio calculation, the peak at ∼3200 cm^{-1} is attributed to O–H symmetric stretching vibration delocalized by hydrogen bonding [17]. The peak at ∼3400 cm^{-1} corresponds to some mixture of symmetric and asymmetric stretching of the O–H bonds [17]. It should be noted that the peak at 3270 cm^{-1} is obviously blue shifted compared with the peaks at 3200 cm^{-1} at typical interfaces e. g. water/air or water/quartz interfaces [9]. We would note that the blue shift of the peak due to the disorder of water molecules was also observed at an air/fatty acids/water interfaces [18]. This indicates that the hydrogen-bonding network size is not large due to the disorder of the water packing arrangement. The shoulder at 3620 cm^{-1} is attributed to inhomogeneous mixture of symmetric and asymmetric stretching vibration of O–H bonds. This peak was classified as a localized mode due to embryotic hydrogen bonding network [17]. For instance, this SFG peak appeared at water/quartz interface with pH=3.8∼5.6 due to the disorder of the water molecular arrangement [9]. The SFG intensity at 3440 cm^{-1} is higher than that at 3270 cm^{-1} in Fig. 3. These results also suggest disordered water arrangement on the pristine PC film [9].

Figure 4 shows a SFG spectrum of water on a PC film treated by O_2 plasma exposure for one minute. We note that the absolute intensities of SFG signals from water on the fabricated film were not dramatically changed from those on the pristine film. Peaks at 3200 and 3450 cm^{-1} are seen in Fig. 4. Obviously, the spectral shapes of the SFG peaks are different from those on the pristine PC film in Fig. 3. First, the left peak was red-shifted to 3200 cm^{-1}. This represents that hydrogen network was well developed on the interface of the O_2 plasma treated PC film. The shoulder at 3620 cm^{-1} also disappeared. This also represents that the packing of water molecular arrangement was improved. The height of the peak at 3200 cm^{-1} is higher than that at 3450 cm^{-1}, and this result also indicates the improvement of the packing [13]. As the origin of the dramatic change of the SFG spectra, we suggest that oxygen radicals on the exposed PC film, like the film observed by Palumbo *et al.* [6], influenced the microscopic water structure.

In this study, we demonstrated that SFG spectroscopy is a useful tool for investigation of the water alignment on PC films, especially exposed to O_2 plasma. We also found clearly that the change of the water arrangement at a water/solid interfaces influences the surface tension γ_{SL}

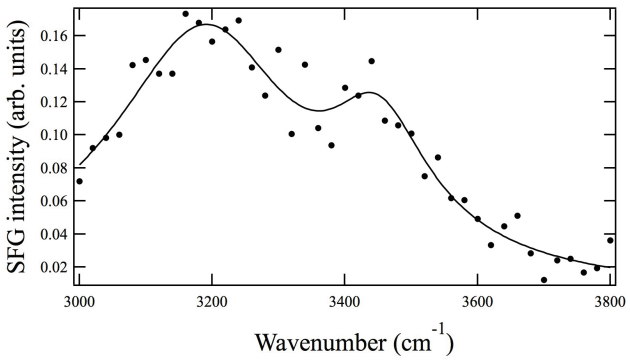

FIG. 4. SFG spectrum of water molecules on a polycarbonate film exposed to O_2 plasma for one minute.

on the PC film so that it is a key factor for understanding the wettability. As a further study, one should investigate water arrangement at the interface of the films with change of chemical components and the time-dependent change.

IV. CONCLUSION

We have performed SFG spectroscopy of water on PC films with and without O_2 plasma treatment in order to study the packing order of water molecules. As the result, in the SFG spectrum of water on a pristine PC film, the peaks at 3270 and 3450 cm^{-1} and a shoulder at 3600 cm^{-1} were observed. The relative intensity of the peak at 3270 cm^{-1} was lower than that of 3450 cm^{-1}. On the other hand, in the SFG spectrum of the plasma exposed film, the peak at 3200 cm^{-1} red shifted from 3270 cm^{-1}, and the peak at 3600 cm^{-1} was absent. The relative intensity of 3200 cm^{-1} was higher than that of 3450 cm^{-1} for this film. This represents that the packing of water arrangement on the PC film was improved at least by one minute O_2 plasma exposure.

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