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A Study on the Plasma-Treated Surfaces of MgO(100) and Quartz Substrates by Infrared Multiple-Angle Incidence Resolution Spectrometry

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In this study, contact angle measurements and an infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique were performed on MgO(100) and quartz substrates. The contact angle and IR spectra of the in-plane and out-of-plane vibration modes depended on the cleaning methods. The surface of the as-received substrates was contaminated in MgO(100) and quartz substrates. As determined by contact angle and p-MAIR spectra analysis, plasma treatment resulted in a relatively clean and superhydrophilic surface under atmospheric conditions. [DOI: 10.1380/ejssnt.2012.229]

Keywords: Plasma processing; Amorphous surfaces; Coatings; Wetting; Infrared absorption spectroscopy

I. INTRODUCTION

Technologies and scientific studies that employ thin films are attracting significant attention. Recently, many functional thin films have been investigated and developed [1–19]. Atoms or molecules at the surface of a material experience a different environment from those in the bulk of the material, and thus have different free energies, electronic states, reactivities, mobilities, and structures [17]. Most thin films require a clean substrate and a clean substrate surface. Therefore, an understanding of the surface state is important in experiments that employ substrates. There are many methods available for cleaning surface of the substrates. Often surfactants are applied leading to negative effects on the environment of the substrate surface [20]. Small particles on the surface are harder to be removed. For example, submicron particles often adhere to surfaces via Van der Waals and capillary forces, which are proportional to their diameters d [21]. The importance of cleaning the substrate for fabricating electroluminescent devices was highligted by So *et al.* [22]. Recently a plasma treatment was used as pretreatment to fabricate a self-assembled monolayer (SAM) on the substrate in the field of micro electro mechanical systems (MEMS).

Recently an infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique was developed by Hasegawa [23–26]. Infrared p-MAIRS can provide the in-plane (IP) and out-of-plane (OP) molecular vibration data simultaneously from an identical substrate. This technique is recognized as a powerful spectroscopic tool for revealing molecular orientation in thin films (even if the sample is amorphous). In this paper, the surface wettability and p-MAIR spectra were investigated in order to determine the surface state of the MgO(100) and quartz substrates. As reflection-absorption spectrometry could not be performed, it was difficult to characterize the surface cleanness of the infrared transparent substrate. Only IP molecular vibration modes were obtained by measuring infrared transparent spectra. The aim of this study is to investigate the contaminants on the surface by using p-MAIR spectra.

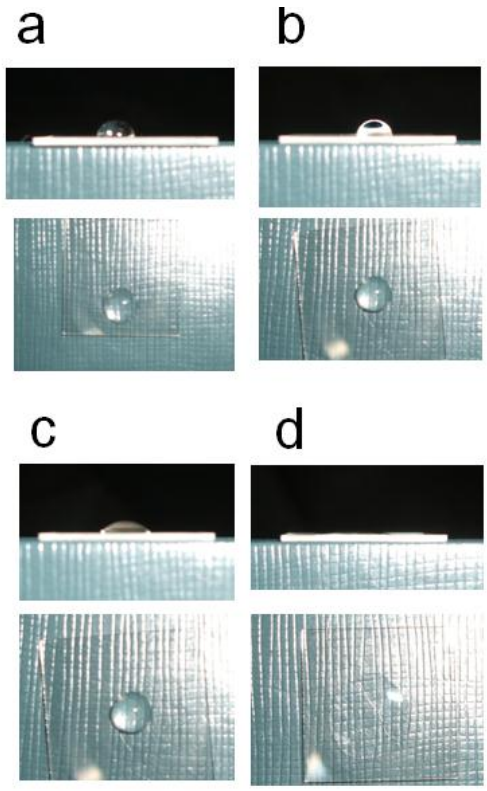

FIG. 1: Photographs of the top and side views of water droplets on the surface of MgO(100) substrate. These images show the contact angles of a water sample for the as-received substrate (a), after washing with wet acetone (b), and after washing with dry acetone (c), after cleaning by plasma treatment (d).

II. EXPERIMENTAL

The commercially available substrates investigated in this paper were MgO(100) and quartz substrates. The sizes of MgO(100) and quartz substrates used were 15×15×0.5 mm and 17 mmϕ×1 mm, respectively. Two substrates were mirror polished. Wet acetone and dry ace-

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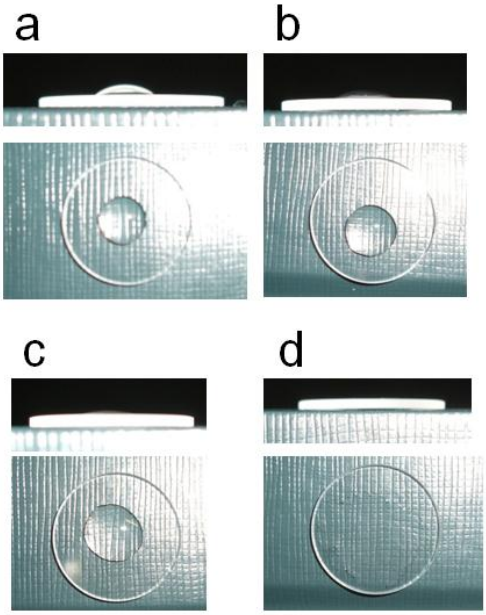

FIG. 2: Photographs of the top and side views of water droplets on the surface of quartz substrate. These images show the contact angles of a water sample for the as-received substrate (a), after washing with wet acetone (b), and after washing with dry acetone (c), after cleaning by plasma treatment (d).

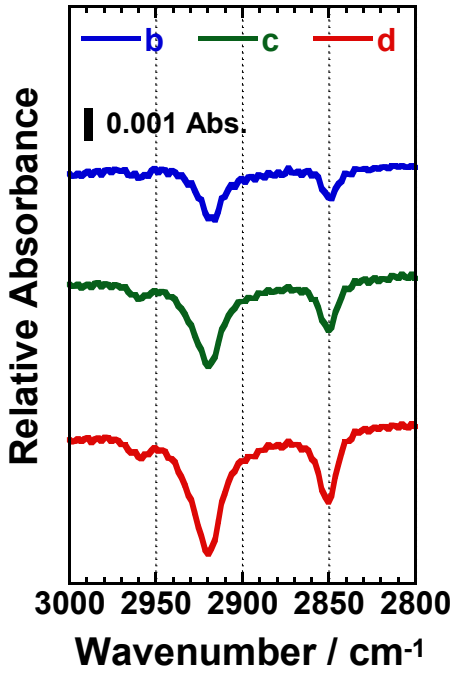

FIG. 3: Infrared p-MAIR spectra of the IP vibration mode in the MgO(100) substrate after acquiring the single-beam spectra measured from 38° to 8° at 6° steps. The single-beam spectrum of the as-received MgO(100) substrate was used as a background spectrum. The spectra shown were obtained after washing with wet acetone (b), after washing with dry acetone (c), and after cleaning by plasma treatment (d). For clarity, the curves were offset along the Y-axis.

tone were used to wash these substrates. In this paper, the term "wet acetone" is used to describe an already opened bottle of acetone, which includes a little atmospheric water vapor. As a result, few small water droplets remained on the surface when the substrate was washed with wet acetone. In contrast, when the substrate was washed with dry acetone, no droplets were observed on the surface. Each substrate was washed for 15 min using an ultrasonic cleaner and dried completely with an air gun in a clean booth. To check the surface hydrophilicity of each substrate including the as-received substrates, the contact angles were measured using water droplets. The measurements were performed in the following order. The contact angle of the substrate was measured, first, in as-received condition (Figs. 1(a) and 2(a)), second, after washing with wet acetone for 15 min (Figs. 1(b) and 2(b)), third, after washing with dry acetone for 15 min (Figs. 1(c) and 2(c)), and finally after cleaning the substrate by plasma treatment (Figs. 1(d) and 2(d)). The plasma treatment was performed using a vacuum plasma system (CUTE-MP, FEMTO SCIENCE). Air was used as the inlet gas, and the power supply was operated at 50 kHz. The substrate was activated at the optimum conditions (70 W, 75 mTorr, 10 sec).

To investigate the contamination on the surface of the substrates after every washing or cleaning, infrared p-MAIRS was performed. The p-MAIRS measurements were performed on a Thermo Fisher Scientific Nicolet 6700 FT-IR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. Single-beam spectra were collected from 38° to 8° at 6° steps in the range of the angle of incidence. The aperture was fully opened (size of 150) and a metal plate with small pores was placed in the light path of the incident beam to prevent saturation. To obtain the p-polarized light, a ZnSe polarizer was used. The p-MAIRS analysis of the collected spectra was automatically performed by p-MAIRS analyzer software (Thermo Fisher Scientific). The as-received substrate was used as the reference data.

III. RESULTS AND DISCUSSIONS

Figure 1 shows photographs of the top and side views of water droplets on the surface of the MgO(100) substrate. The contact angle on the as-received substrate was 82°, as shown in Fig. 1(a). Therefore the surface of the as-received MgO(100) was in a hydrophobic state. On the other hand, the contact angles on the substrates washed with wet acetone (Fig. 1(b)), dry acetone (Fig. 1(c)), and plasma treatment (Fig. 1(d)) were 46°, 28°, and less than 10°, respectively. Therefore, the contact angle strongly depended on the cleaning method. The surface cleaned by the plasma treatment was found to be superhydrophilic under atmospheric conditions. From these results, it was assumed that some contaminants (wax or aliphatic oil etc.) remained on the surface after mirror polishing of the substrate. When the as-received MgO(100) substrate was cleaned only by plasma treatment without washing with dry acetone, the surface was found to be superhydrophilic under these conditions as well.

Figure 2 shows photographs of the top and side views

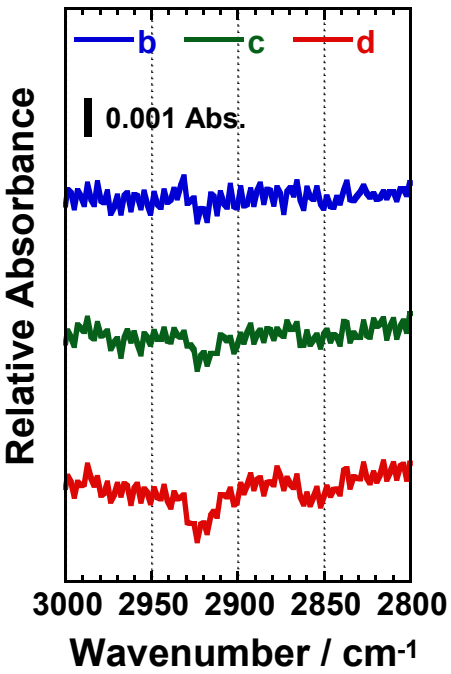

FIG. 4: Infrared p-MAIR spectra of the OP vibration mode in the MgO(100) substrate after acquiring the single-beam spectra measured from 38° to 8° at 6° steps. The single-beam spectrum of the as-received MgO(100) substrate was used as a background spectrum. The spectra shown were obtained after washing with wet acetone (b), after washing with dry acetone (c), and after cleaning by plasma treatment (d). For clarity, the curves were offset along the Y-axis.

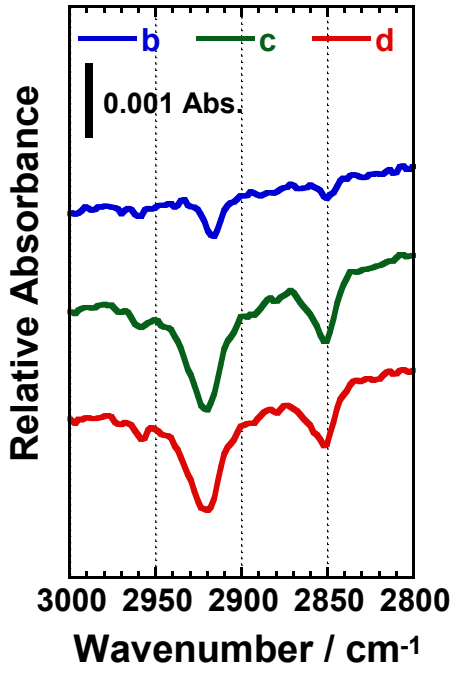

FIG. 5: Infrared p-MAIR spectra of the IP vibration mode in the quartz substrate after acquiring the single-beam spectra measured from 38° to 8° at 6° steps. The single-beam spectrum of the as-received quartz substrate was used as a background spectrum. The spectra shown were obtained after washing with wet acetone (b), after washing with dry acetone (c), and after cleaning by plasma treatment (d). For clarity, the curves were offset along the Y-axis.

of water droplets on the surface of the quartz substrate. The contact angle on the as-received substrate was 39° as shown in Fig. 2(a). This contact angle was less than that of the MgO(100) substrate. The contact angle depended on the state of the as-received substrate. The contact angles on the quartz substrates washed with wet acetone (Fig. 2(b)), dry acetone (Fig. 2(c)), and plasma treatment (Fig. 2(d)) were 34°, 11°, and less than 10°, respectively. The contact angle also strongly depended on the cleaning method. It was assumed that the difference between contact angles is due to varying degrees of hydrocarbon contamination on the surface. When the as-received quartz substrate was cleaned only by plasma treatment without washing it with dry acetone, the surface was found to be superhydrophilic under these atmospheric conditions. From the view point of wettability of two substrates, plasma treatment is a more useful cleaning procedure.

To investigate the contaminants on the surface of MgO(100) substrate, measurements of the p-MAIR spectra were carried out. Figure 3 shows the IP mode spectra of MgO(100) substrate after each treatment. The single-beam spectrum of the as received MgO(100) substrate was used as a background spectrum. For clarity, curves were offset along the Y-axis. The CH_2 vibration modes were observed in the wavenumber range of 2800-3000 cm^{-1}. The absorbances at 2919 and 2850 cm^{-1} were due to the typical asymmetric (v_a) and symmetric (v_s) vibrations of CH_2 groups of the hydrocarbon, respectively. The absorbance of the CH_2 vibration modes decreased to a greater degree by washing with wet acetone, dry acetone, and cleaning by the plasma treatment. These results suggest that some hydrocarbons on the surface of the MgO(100) substrate were removed by cleaning the surface. The largest decrease in the absorbance was observed in the MgO(100) substrate at 2919 cm^{-1} after cleaning by plasma treatment. Therefore, the plasma treatment can remove the hydrocarbon contaminant from the surface.

Figure 4 shows the OP mode spectra of MgO(100) after each treatment. It was observed that the absorbance due to CH_2 vibration modes decreased to a greater degree by washing and cleaning. The largest decrease in absorbance was observed at 2921 cm^{-1} after cleaning by plasma treatment. Therefore, it was confirmed that plasma treatment of the MgO(100) substrate was useful for cleaning the surface. Infrared p-MAIRS reveals the information of the IP and OP molecular vibrations in an identical substrate. Hence, the molecular orientation could be calculated by the following equation [23].

$$\phi = \tan^{-1}\left(\sqrt{\frac{2I_{IP}}{I_{OP}}}\right). \quad (1)$$

Here ϕ is the orientation angle from the surface normal and $2I_{IP}$ and I_{OP} are the decreased band intensities of IP and OP spectra, respectively. The factor of 2 in I_{IP} has been explained in Ref. [23]. From Fig. 4, the orientation angles of the transition dipoles for the modes (v_a and v_s) for the CH_2 group were calculated to be 54° and 58°, respectively, from the surface normal. Since the hydrocar-

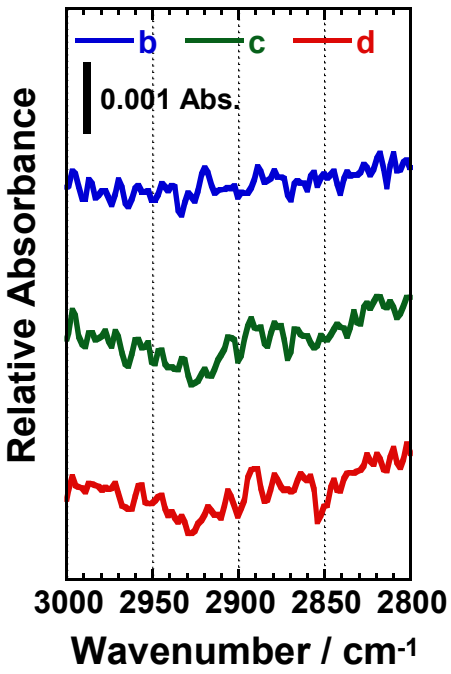

FIG. 6: Infrared p-MAIR spectra of the OP vibration mode in the quartz substrate after acquiring the single-beam spectra measured from 38° to 8° at 6° steps. The single-beam spectrum of the as-received quartz substrate was used as a background spectrum. The spectra shown were obtained after washing with wet acetone (b), after washing with dry acetone (c), and after cleaning by plasma treatment (d). For clarity, the curves were offset along the Y-axis.

bon chain comprised of all-trans-zigzag conformers due to the band locations, the tilt angle of the hydrocarbon chain was evaluated by using the following equation [27].

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1. \quad (2)$$

Here α and β are the orientation angles of the transition dipole moment of the respective modes v_a and v_s for the CH_2 group. The tilt angle of the molecular axis of the hydrocarbon chain from the surface normal (γ) was 52°. This tilt angle suggested that the structure of the contaminant was in a completely disordered state [28].

Figure 5 shows the IP mode spectra of the quartz substrate after each treatment. The decrease in the absorbance due to the CH_2 vibration modes were observed in the wavenumber range of 2800-3000 cm^{-1}, which implied the elimination of the contaminants. The contact angle on the quartz substrate washed with dry acetone (Fig. 2(c)) decreased (11°). This result was consistent with the observed IP mode spectrum. The degree of the decreasing absorbance after the plasma treatment was comparable to that of dry acetone washing. These results inferred that the contaminants could be almost completely removed by using dry acetone. This result was different from that of the MgO(100) substrate, where the hydrophilic state on the surface was more improved and became superhydrophilic when plasma treatment was performed. Therefore, in case of the quartz substrate, the results of the p-MAIRS inferred that the contaminants could be removed with dry acetone.

Figure 6 shows the OP mode spectra of the quartz substrate after each treatment. The absorbance of the CH_2 vibration modes decreased, and the width of the decreasing band broadened compared to that of the MgO(100) substrate. This result suggested that the hydrocarbon chain did not comprise all-trans-zigzag conformers. The hydrocarbon contaminant exhibited different structures on the surface of the MgO(100) compared to the quartz substrate. The decrease of relative absorbance in the quartz substrate was found to be small compared to that in the MgO(100) substrate. The degree of contamination was relatively small in this quartz substrate and it strongly depended on the supplier of the substrates. (The supplier was not shown here.) When wet acetone was used for cleaning the substrates, an additional effort was required to remove contaminants from the surface for both MgO(100) and quartz substrates.

IV. CONCLUSION

To investigate the surface state of MgO(100) and quartz substrates, the contact angle measurements and infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique were performed on the substrates. I found that the contact angle and IR spectra of the in-plane and out-of-plane vibration modes depended on the cleaning methods. The surface of the as-received substrates was contaminated by hydrocarbons on both MgO(100) and quartz substrates. A plasma treatment resulted in a relatively clean and superhydrophilic surface under atmospheric conditions for the two substrates. Although, dry acetone was useful for cleaning the surface, wet acetone required additional steps to remove the contaminants from the surfaces of both MgO(100) and quartz substrates.

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