Preparation of Water-Repellent Thin Film with Inductive Plasma using $C_2H_2F_2$ /Ar gases and Investigation of Its Adhesion by Positively Pulse-Biasing

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We have prepared water-repellent thin films on polycarbonate substrates by inductively coupled $C_2H_2F_2$ /Ar plasma CVD method for hydrophobic nature of automobile plastic window. The adhesion of water-repellent film is investigated by an ion-assist effect. Main plasma was produced by inductive discharge. $C_2H_2F_2$ and Ar mixture gases were introduced into the vacuum chamber at a fixed each other pressure of 20Pa. As the source gas includes fluorine atoms, negative ions are formed in the deposition area. Thus, in order to achieve the ion assist effect to the deposition due to the negative ions, the substrates was biased by positively pulsed voltage. The adhesion of a deposition film was estimated by the hardness of the pencil. It is obtained that the hardness pencil of the prepared film at substrate bias frequency of 500 Hz and pulsed bias voltage of 300V is the highest in various conditions. A water contact angle of the prepared film is attained at about 100 degree.

Key words: water repellency, plastic plate, adhesion, low-electron-temperature plasma

1. INTRODUCTION

Water-repellency is required for surfaces of all sorts of products in various industrial fields [1]. For instance, the windshield must ensure a clear vision of the road under any meteorological conditions. That is, water-repellent glass enables safe driving by reduction of glare in the rain, especially at night, because the water-repellency brings beads up and rolls off raindrops [2]. Recently, automobile companies are being investigated to use a plastic window for reductions of its weight and carbon oxides.

Many techniques have been developed to get good water-repellent as follows. Soga *et al.* reported on the preparation of chemically adsorbed monolayers on glass substrates from solutions of fluoro-alkyl silanes (FASs)[3]. Takai *et al.* have proposed a novel preparation method using plasma chemical vapor deposition (PCVD), referred to the surface of a lotus leaf with many biological microstructures [1]. They have performed the ultra-water-repellency by PCVD mixing FASs and trimethylmetoxysilane (TMMOS)[1].

On the other hand, fluorinated polymers are well known as low surface energy materials, which have oil- and water-repellent surfaces and have been proposed for coating of substrates such as textiles, paper, leather, wood etc [4]. 1-1 difluoroethylene ($C_2H_2F_2$) gas including fluorine has been widely used as a source material for fluorinated rubber sheet (Poly (vinylidene fluoride) (PVDF)) and fluorinated resin [5].

Recently, the ultra water-repellent thin films have been prepared with $C_2H_2F_2$ capacitively coupled plasma CVD operated by conventional radio frequency (RF: 13.56 MHz) power [6]. The high visible transparency with more than 90 % of the prepared films was attained with pulse-modulation technique [7].

However, the sticking to the prepared films on the substrate was very weak. For practical use of the repellent films, it has to advance the adhesion of the films. The cause that the adhesion has been feeble is due to the deposition of high-density radicals dissociated by high electron temperature plasma without strong bonding to the substrate. In order to improve the adhesion, it is effective to apply a low-electron-temperature plasma and a biasing to the substrate.

In this paper, the adhesion of the water-repellent films on plastic plate has been investigated with positively biasing to substrate in low temperature plasma of an inductively coupled discharge of $C_2H_2F_2$ and Ar mixture gases. The low-electron-temperature plasma was produced by grid biasing method [8]. The adhesion was measured with pencil- hardness method based on Japanese Industrial Standards (JIS-K-5600-5-4) and water contact angle was also discussed.

2. EXPERIMENTAL SETUP

Figure 1 shows a schematic diagram of low electron temperature plasma CVD apparatus with inductively coupled plasma and grid biasing

Fig. 1 Schematic diagram of low electron temperature plasma CVD apparatus.

method [8]. This consists from a plasma source chamber with 160 mm diameter and 100 mm length and a processing chamber with 160 mm diameter and 300 mm length. The grid electrode which is biased by radio frequency voltage of 1 MHz separates between the plasma source and the processing chamber. The voltage V_G of the grid electrode (stainless steel, 16 mesh / inch²) is fixed at -50 V. Three turn spiral antenna is mounted on the glass plate of 190 mm diameter which covers the top of the plasma source chamber. The RF power of 100 W is input to the spiral antenna through the matching box and then high density inductively coupled plasma is produced. According to the grid biasing method [8], the high energy electrons only can move the processing region through the grid electrode so that the low-electron-temperature plasma is generated after these electrons collide with neutral gases. The electron temperature of Ar plasma measured with Langmuir probe was about 2.3 eV at the processing region, whereas at the plasma source region was 4 eV. In the region of the processing chamber, low electron temperature plasma was accomplished.

In the preparation of the repellent films, $C_2H_2F_2$ and Ar mixture gases were introduced into the chamber at total pressure of 40 Pa at fixed $C_2H_2F_2$ gas concentration of 50 %. A process time was 40 min. The substrates of polycarbonate plate and silicon wafer were set on the substrate holder. The substrate holder is positioned at distance of 50 mm away from the grid electrode. Figures 2 (a) and (b) show voltage waveforms of the substrate holder applied by radio frequency voltage 300 V_{pp} (peak to peak value) of 13.56 MHz at (a) Ar plasma and (b)

Fig.2 Substrate voltage waveforms at (a) Ar plasma and (b) Ar/ $C_2H_2F_2$ mixture plasma.

Ar/ $C_2H_2F_2$ mixture plasma, respectively. As shown in Figs. 2 (a) and (b), a negatively self-biased voltage [9] is detected on the voltage waveforms. The self-biased voltage at Ar plasma and Ar/ $C_2H_2F_2$ mixture plasma are -70V and -27 V, respectively. That is, absolute value of the self-biased voltage for Ar plasma is higher than that for Ar/ $C_2H_2F_2$ mixture plasma. This indicates that there is the presence of negative ions for Ar/ $C_2H_2F_2$ mixture plasma. Thus, the substrate is biased by positive pulse power supply. The reason is that the positive pulse voltage attracts the negative ions to the substrate. In order to enhance the deposition of these ions to the substrate and these assistances to the films due to the ion bombardment, the biasing of the positive pulse voltage has been investigated. The substrate bias frequency of the positive pulse voltage was changing from 0.5 to 10 kHz. Here, an on-time T_{on} was fixed at 50 μ s. The pulse voltage V_b was ranged from 100 to 300 V.

The adhesion of the prepared films to the substrate was measured with pencil-hardness method based on Japanese Industrial Standards (JIS-K-5600-5-4). In pre-treatment of the substrate, the substrates of polycarbonate and

Fig.3 Water contact angles of the prepared films on polycarbonate plate as a function of pulse bias voltage at various substrate bias frequencies.

Fig.5 Pencil-hardness of the prepared films on the substrate as a function of substrate bias frequency. Here, the pulse voltage was ranged from 100 to 300 V.

Fig.4 Pencil-hardness of the prepared films on the substrate as a function of pulse bias voltage. Here, the modulated frequency was ranged from 0.5 to 10 kHz.

silicon wafer were ultrasonicated in ethanol for 5 min and then cleaned on these surfaces by Ar ion sputtering for 30min. After the pre-treatment, the hardness with pencil of polycarbonate plate changed from HB to 3B, whereas silicon wafer was not affected.

The contact angle of water droplet on the prepared films was measured with an optical contact angle meter for hydrophobic nature. The volume of the water droplet was fixed at about 20 μ l. The water droplet was placed on the deposited film by the tip of a micro syringe.

The deposition thickness measured by surface roughness measuring machines ranged from 400 to 500 nm in all experimental conditions.

3. RESULTS AND DISCUSSION

Figure 3 shows water contact angles θ of the prepared films on polycarbonate plate as a function of positively pulse bias voltage V_b at various substrate bias frequencies f . It is found that the water contact angle keeps being more than 90 deg and conventional water hydrophobic nature. As our previous work [6] had reported, it is considered that the chemical components of films prepared in this experiment include C-H and C-F bonds. Since the water contact angle is about 90 deg, the surface of the prepared films might be almost flat. This is because ultra repellent nature is performed if there is a roughness on the film [6]. It is seen that the contact angle decreases with increasing pulsed bias voltage at all substrate bias frequencies. This indicates that the incident energy of negative ions to the substrate become higher with increasing the pulsed bias voltage positively. Thus, the surface of the prepared film is changed to be uniform by the higher incident energy. It is found that the prepared films have a water-repellent nature with the contact angle of 90-100 degree which is effective for the hydrophobic property of the automobile window. Next, the adhesion of the prepared films with the substrate is discussed by applying the ion-assistance.

The influences of the substrate bias frequency f and the voltage V_b of the positive pulse biasing on the adhesion of the prepared films have been examined in low electron temperature plasma using $C_2H_2F_2$ and Ar mixture gases. Figure 4 shows pencil-hardness of the prepared films as a function of pulse bias voltage. Here, the substrate bias frequency was changed from 0.5 to 10 kHz. The pencil-hardness of the polycarbonate was 3B before plasma treatment. It is found that the pencil-hardness increases with increasing pulsed

bias voltage at all conditions. This reason is considered as follows. With increasing the pulsed bias voltage, the incident energy of negative ions raises so that the ions removes the weaken films from the substrate. Thus, the pencil-hardness is enhanced by the positively pulsed bias voltage. This phenomenon is self-consistent with the influence of the pulsed bias voltage on water contact angle as mentioned above.

Figure 5 shows pencil hardness of prepared films on polycarbonate plate as a function of substrate bias frequencies f at various pulse bias voltages V_b . It is seen that the pencil hardness increases with increasing V_b at all substrate bias frequencies. It is found that the pencil-hardness keeps being 2B at substrate bias frequency region of 1 – 10 kHz at $V_b = 200V$ and $300V$, whereas the pencil hardness at $V_b = 100V$ is 3B. The maximum value is B at $f = 500$ Hz and $V_b = 300V$. It is seen that $f = 500$ Hz is best to improve the adhesion between prepared films and substrate. The higher substrate bias frequency can produce the additional discharge around the substrate so as to generate radicals dissociated from reactive gas. These radicals are deposited on the substrate and then their adhesion becomes weak.

4. CONCLUSION

We have investigated the influences of positive pulse biasing to the substrate on the adhesion of the prepared water repellent films to the substrate in low electron temperature plasma. The low electron temperature plasma was produced by inductively coupled discharge and grid biasing method. Positive pulse biasing to the substrate has been applied to enhance the deposition and

the assistance of negative ions. The pencil-hardness of the prepared films was improved with increasing the positive pulse voltage. The best condition that the good adhesion of the prepared films to the substrate was satisfied in this experiment was at $f = 500$ Hz and $V_b = 300V$. In future, the advanced improvement will make the adhesion of the prepared films strong.

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