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# Reduction of Pinhole Defects in DLC Film Prepared with Plasma-based Ion Implantation and Deposition

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Diamond-like carbon (DLC) films were prepared on the SUS304 substrate with a hybrid process of plasma-based ion implantation and deposition using toluene plasma. The pinhole defects in DLC films reached to the substrate deteriorate corrosion resistance. The area ratio of pinhole defects to the bare substrate was evaluated by the critical passivation current density (CPCD) method. The CPCD measurement indicated that the area ratio of pinhole defects in the DLC film was decreased with increasing film thickness and reached to about $1 \times 10^{-3}$ % at more than 6 μm in thickness. The apparent area ratio of pinhole defects were also reduced by the interfacial treatment before DLC deposition such as the production of an interfacial mixing layer by carbon ion implantation to the substrate or the formation of $SiC_x$ nanolayer in front of substrate in the thinner film thickness. The ultrasonic cleaning in the acetone during the deposition reduced the area ratio of pinhole defects to $6 \times 10^{-4}$ % at the DLC film thickness of 1 μm.

Key words: diamond-like carbon (DLC), pinhole defect, plasma-based ion implantation and deposition (PBIID), critical passivation current density (CPCD), corrosion resistance

## 1. INTRODUCTION

Diamond-like carbon (DLC) has extremely high corrosion resistance because it is stable in acid and alkali environments. However, there are many micro defects in DLC films, so that these defects deteriorate corrosion resistance. A pinhole defect reached to the substrate is the most serious one because the corrosion starts from the substrate surface at the bottom of the pinhole. It is important to minimize the number of the pinhole defects in the DLC film for corrosion-resistant coatings. Thick film, multi-layer film, and surface cleaning before or during the deposition should be useful methods for reducing pinhole defects. It was found that the area ratio of pinhole defects in the DLC film on the SUS304 substrate was decreased with increasing DLC film thickness [1].

In this paper, we study on the reduction of pinhole defects by the formation of an interfacial mixing layer between the DLC film and the substrate and also by surface cleaning during the deposition. DLC films with the interfacial mixing layer are prepared by a hybrid process of plasma-based ion implantation and deposition (PBIID) process [2] using methane, acetylene and toluene plasmas. Pinhole defects in DLC films are evaluated by the critical passivation current density (CPCD) method [3].

## 2. EXPERIMENTAL

DLC films were prepared by the PBIID system using superimposed RF and negative high-voltage pulses. In this system, RF pulse (frequency 13.56 MHz, peak power 300 W, pulse duration 50 μs) for plasma generation was supplied to the substrate together with the negative high-voltage pulse (voltage -5 ~ -20 kV, pulse width 5 μs) for ion implantation. As the substrate itself worked as an RF antenna, the uniform initial plasma was generated around the substrate. When the negative high-voltage pulse with the same repetition rate of 1 kHz as RF pulse was applied to the substrate at the time of 50 μs later after each RF pulse, RF plasma ions were accelerated by the sheath potential formed around the substrate and implanted into the substrate. Then, the secondary electrons due to ion impact were emitted and accelerated by the sheath potential to ionize or dissociate gas atoms and molecules, generating lots of additional ions and radicals very close to the substrate. As a result, rapid deposition rate of uniform DLC film was realized on three-dimensional substrates [4].

Three kinds of DLC films with/without interface treatment were prepared on SUS304 substrate (15 mm in diameter and 1 mm thick) with following processes. In the condition (a), DLC film was prepared with the toluene plasma without high-energy ion implantation, indicating no interfacial mixing layer. In the condition (b), an interfacial mixing layer between the DLC film and the substrate material was produced by carbon ion implantation using -20 kV negative pulsed voltage from the methane and acetylene plasmas before DLC film deposition with the toluene plasma. In the condition (c), mixed ions of carbon and silicon extracted from HMDSO (hexamethyldisiloxane, $C_6H_{18}OSi_2$) plasma were used to produce the interfacial mixing layer. The surface of substrate was polished for mirror finish and cleaned by argon plasma sputtering before DLC deposition. The gas pressure was 0.5 Pa and the deposition rate of DLC film was approximately 0.5 μm/h.

The area ratio of pinhole defects in DLC-coated specimen was evaluated by the potentiodynamic anodic polarization measurement in a deaerated 0.5 kmol/m$^3$ $H_2SO_4$ + 0.05 kmol/m$^3$ KSCN (potassium thiocyanate) solution at 298 K. Figure 1 shows a schematic diagram of potentiodynamic anodic polarization device. After the specimen was immersed in the test solution, the potential was set at −0.5 V (*vs*. Ag/AgCl) immediately, and then swept to +1.5 V at the rate of 20 mV/min. At this time, the current between the specimen and the counter electrode to the potential was measured, and the anode polarization curve was obtained. Figure 2 shows a typical anode polarization curve of SUS304 specimen. In the anode polarization curve, the less passive current density indicates the higher corrosion resistance of specimen and the CPCD is proportional to the area of metal exposed to the chemical solution. Therefore, assuming the hemispherical pit geometry at the bottom of pinhole defect, the 'true' area ratio of pinhole defects, $R$, to the bare substrate is defined as follows [4]:

$$R = \frac{i_{crit}\,(DLC\,/SUS304)}{2i_{crit}\,(SUS304)} \times 100\ \% \qquad (1)$$

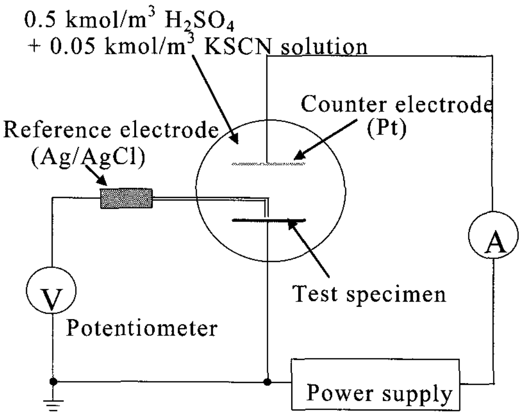


Fig. 1. Schematic diagram of potentiodynamic anodic polarization device.

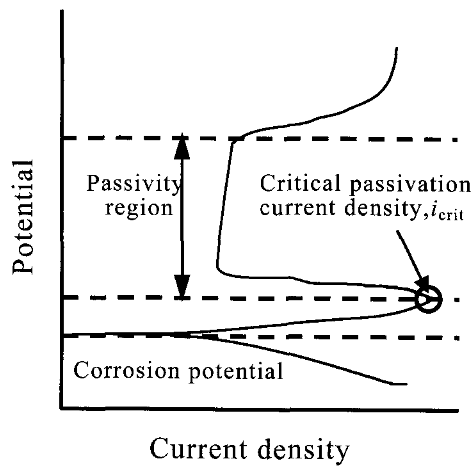


Fig. 2. Example of anodic polarization curve of SUS304 stainless steel.

where $i_{crit}(SUS304)$ refers to the critical passivation current density of the bare substrate and $i_{crit}(DLC/SUS304)$ is the DLC-coated one.

## 3. RESULTS AND DISCUSSION

### 3.1 Area ratio of pinhole defects

The anodic polarization curves for DLC-coated specimens prepared with the different process condition (a), (b), and (c) are shown for various thicknesses together with the anodic polarization

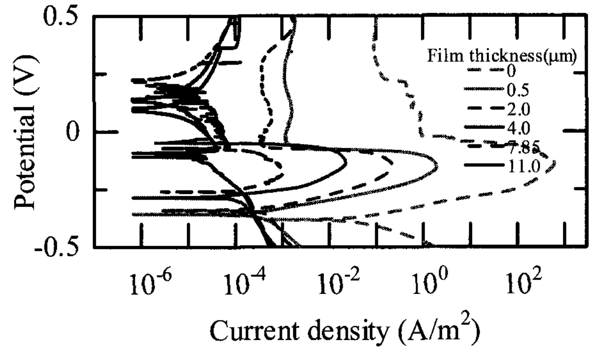


Fig. 3. Anodic polarization curve for the bare SUS304 substrate (the right-hand side) and the DLC-coated specimens with no interfacial treatment (condition (a)).

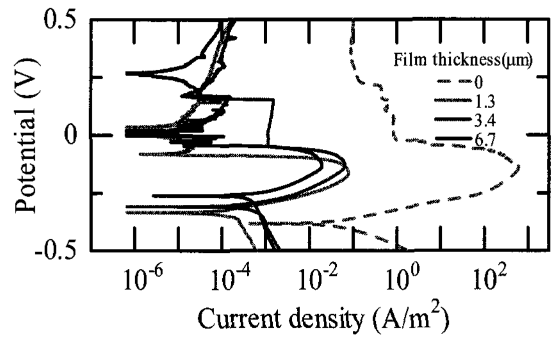


Fig. 4. Anodic polarization curve for the DLC-coated specimens with the interfacial treatment by C ion implantation to the substrate (condition (b)).

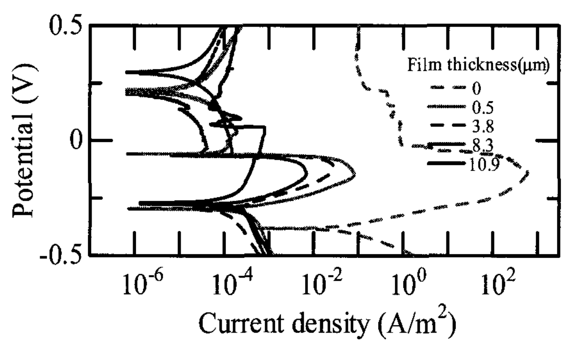


Fig. 5. Anodic polarization curve for the DLC-coated specimens with the interfacial treatment by ion implantation of mixed C and Si (condition (c)).

curve of the bare substrate in Figs. 3-5, respectively. As can be seen in Figs. 3–5, the CPCD of bare substrate is about $8\times10^2$ A/m$^2$, while those of DLC-coated ones decrease more than almost three orders of magnitude. Moreover, the CPCD of DLC-coated specimen decreases with increasing film thickness *d*, indicating the reduction of pinhole defects. Figure 6 shows the pinhole area ratio *R* determined from eq. (1) using the results in Figs. 3-5, where ○ corresponds to no interface mixing layer (condition (a)), □ carbon ion implantation (condition (b)), and ▲ implantation of mixed ions of carbon and silicon (condition (c)). It is known that if the CPCD is too small, such an evaluation as the CPCD method is invalid [4]. As there is no clear peak of CPCD for $d$=11 μm in Fig. 3 and $d$=10.9 μm in Fig. 5, these data were excluded in Fig. 6. As seen in Fig. 6, the pinhole area ratio is decreased with increasing thickness of DLC film and reaches to about $R = 1\times10^{-3}$ %. The production of interfacial mixing layer by carbon ion implantation to the substrate surface before the DLC deposition also serves to reduce the area ratio of pinhole defects for the lower film thickness less than about 4 μm. However, there is little effect of interfacial mixing layer on suppression of pinhole defects for the larger film thickness more than 4 μm. The optical microscope observation of pinhole defects after an anodic polarization test indicated that the number of pinhole defects was independent on the interfacial treatment by ion implantation before the DLC deposition [5]. The TEM observation indicated that the substrate structure of the carbon-ion-implanted region was transformed into the amorphous-like phase [6], suggesting the improvement the corrosion resistance of substrate surface. From these considerations, it is found that the interfacial treatment before the deposition serves to decrease the 'apparent' area ratio of pinhole defects by the improvement of the corrosion resistance of substrate surface.

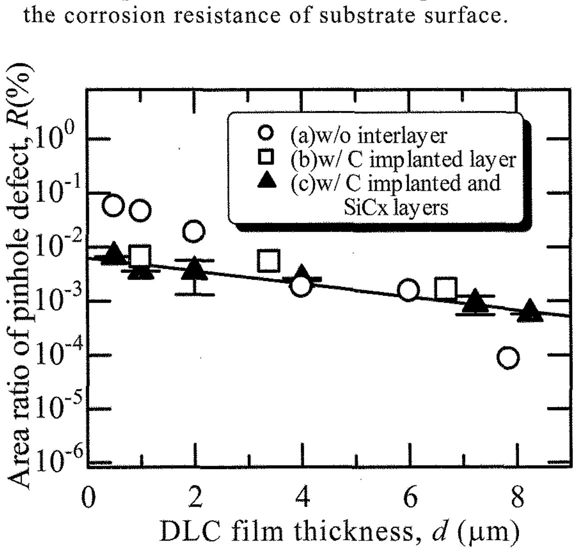


Fig. 6. Area ratio of pinhole defects in DLC films prepared with/without interfacial treatments as a function of film thickness.

Suppression of pinhole generation in DLC films is studied on the surface cleaning of DLC film during the deposition and its procedure is summarized in Table 1. One of the surface cleaning methods was the ultrasonic cleaning in the acetone and another was the Ar plasma sputtering during the DLC deposition. As shown in Table 1, first of all, the DLC films of 0.75 μm in thickness were prepared on the SUS304 substrate with the process conditions (a), (b), and (c) mentioned in Chap. 2. Then, the DLC deposition was stopped temporarily for the cleaning of DLC surface by the ultrasonic cleaning in the acetone or the Ar plasma sputtering, which were followed by the DLC deposition with the process condition (a). The total film thickness of all specimens was 1 μm. Figure 7 shows the area ratios of pinhole defect in the DLC-coated specimens with various

Table 1. DLC coating processes with various surface cleanings during the deposition.

| | Stage | $1^{st}$ | $2^{nd}$ | $3^{rd}$ |
|---|---|---|---|---|
| | | Deposition | | Deposition |
| (a-a) | Condition | (a) | Surface cleaning by Ultrasonic in acetone or Ar plasma sputtering | (a) |
| | Process time (min) | 120 | | 60 |
| (b-a) | Condition | (b) | | (a) |
| | Process time (min) | 120 | | 60 |
| (c-a) | Condition | (c) | | (a) |
| | Process time (min) | 120 | | 60 |

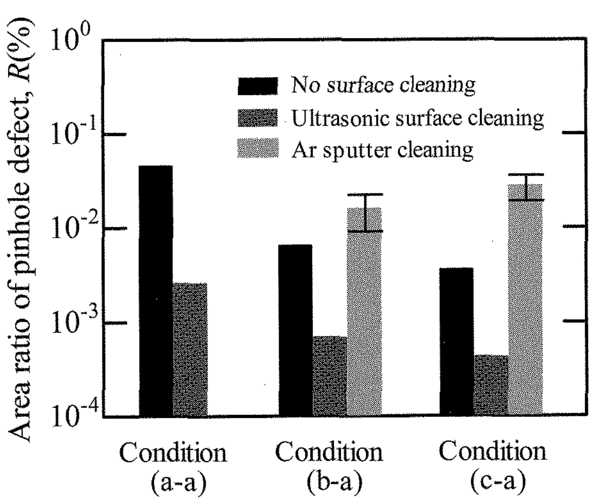


Fig. 7. Area ratio of pinhole defects in DLC films prepared with various surface cleanings during the DLC deposition. DLC coating conditions is shown in Table 1.

process conditions. As seen in Fig. 7, those prepared with the conditions (a), (b), and (c) are $R = 4.5 \times 10^{-2}$, $6.4 \times 10^{-3}$ , and $3.6 \times 10^{-3}$ %, respectively, indicating that the production of interfacial mixing layer serves to suppress pinhole formation. The interfacial mixing layer with mixed ions of carbon and silicon is useful for suppression of pinhole generation. Besides, the surface ultrasonic cleaning during the deposition reduces dramatically the pinhole defects and using the process condition (c-a) the area ratio of pinhole defect decreases to $6 \times 10^{-4}$ % which is two orders in magnitude smaller than the pinhole area ratios of TiN films prepared with various dry processes [3]. On the contrary, Ar plasma sputtering during the deposition increases pinhole defects. It should be ascribed to the deposition of sputtered particles generated by Ar plasma sputtering. It can be used practically for the corrosion-resistive films, if the area ratio of pinhole defects is less than $10^{-3}$ %. It is found that the ultrasonic cleaning during the deposition could be useful method to prevent from the generation of pinhole defects in the DLC film.

3.2 Observation of pinhole defects

It was hard to observe pinhole defects in DLC films by SEM before an anodic polarization test, so we observed pinhole defects after the anodic polarization test. The concentration profile of elements in the vicinity of pinhole after anodic polarization test was studied with EPMA. Figure 8 shows the distribution of carbon (upper, right), iron (lower, left) and chromium (lower, right) in the DLC film prepared with the process condition (a). As seen in Fig. 8, carbon is not observed around the center of pinhole. On the other hand, iron and chromium, which are constituent elements of SUS304 substrate, are observed inside the pinhole, indicating that the pinhole is penetrating into the DLC film.

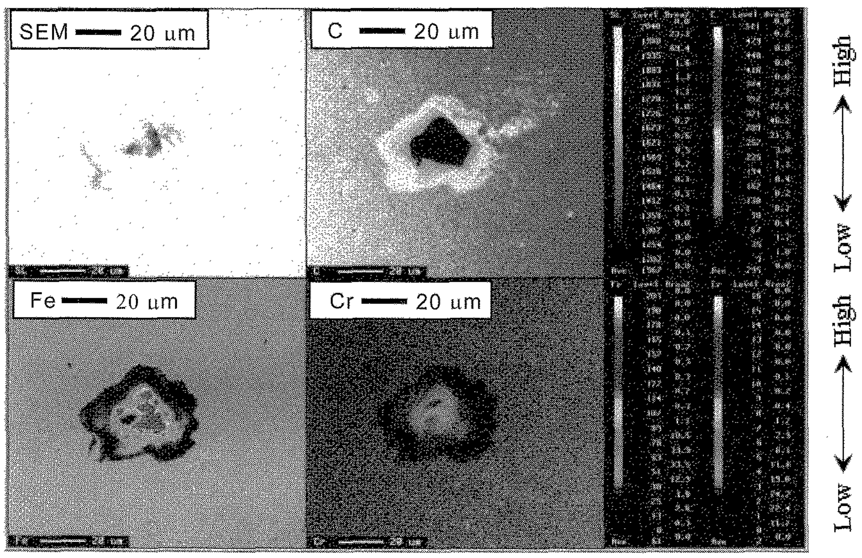


Fig. 8. Distribution of C (upper, right), Fe (lower, left), and Cr (lower, right) in the vicinity of pinhole, showing little C and much Fe and Cr inside the pinhole area, where Fe and Cr are the constituent elements of SUS304 substrate.

4. CONCLUSION

The DLC films of various thicknesses from 0.5 to 11 μm were prepared on the SUS304 substrate with the hybrid process of plasma-based ion implantation and deposition using toluene plasma. The pinhole defects in DLC films were evaluated by the CPCD method. The area ratio of pinhole defects was decreased with increasing film thickness and reaches less than $1\times10^{-3}$ % above approximately 6 μm in thickness. An interfacial mixing layer produced by ion implantation of carbon or a mixed of carbon and silicon prior to DLC deposition served to reduce pinhole defects in DLC films. The surface ultrasonic cleaning in the acetone during the deposition was most effective for the suppression of pinhole formation in DLC films and then the area ratio of pinhole defects reduced to $6\times10^{-4}$ %.

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