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Hardness of DLC film prepared using toluene plasma and hybrid process of plasma-based ion implantation and deposition

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A few μm diamond-like carbon (DLC) film on a trench substrate of aluminum alloy (A-5052) was prepared by the hybrid process of plasma-based ion implantation and deposition (PBIID) using combined RF and high-voltage pulses. The thickness of DLC film was typically 5 μm for the preparation time of 5 hours using a toluene plasma, indicating the deposition speed of 1 μm/h. The hardness of DLC film measured by a nano-indentation method was approximately 12 GPa at the center on the top surface of trench, while the hardness on the sidewall and the bottom were 9.9 GPa and 11 GPa, respectively.

Keywords: DLC, hardness, nano-indentation, trench, PBIID,

1. Introduction

Diamond-like carbons (DLCs) attract attention since it has many outstanding features such as high hardness, low friction coefficient, and chemical inertness [1]. The DLC films deposited using discharge plasmas of hydrocarbon gases have hardness value ranging from 5 to greater than 20 GPa depending on the deposition conditions [2]. Generally, lower hydrogen content and lower gas pressure increase the hardness of DLC. Authors have prepared thick good-adhesive DLC coatings on the three-dimensional substrates by the hybrid process of plasma-based ion implantation and deposition (PBIID) using combined RF and high voltage pulses and toluene plasma [3-6]. In this process, the RF pulse for plasma production was supplied to the substrate together with the high voltage pulse for ion implantation, resulting in the plasma generation around the substrate and the uniform coating on the three-dimensional substrates [3-6]. The toluene ($C_6H_5CH_3$) plasma was useful for high rate of DLC deposition. However, the hardness value of DLC prepared with the toluene plasma has not yet measured. For industrial applications, it is important to know the hardness of DLC film on each surface of complex substrate geometries.

In this work, we present the preparation of thick DLC film of more than a few μm in thickness on trench substrate using the PBIID process and the $C_6H_5CH_3$ plasma. The hardness of DLC film on each surface of a trench substrate of aluminum-alloy (A5052) was measured by a nano-indentation tester.

2. Experimental

The DLC films were prepared by the PBIID system, which has been fully described previously [3].

Figure 1 shows a schematic diagram of the trench substrate with the aspect ratio of 1, the trench width of 10 mm and the length of 40 mm. The substrate surface was polished to a mirror finish before DLC coating and set at the center of vacuum chamber.

The precursor gases used in the present experiment were methane (CH_4) and acetylene (C_2H_2) for production of interface and $C_6H_5CH_3$ for DLC deposition. The procedure of DLC film preparation was the four-steps as follows: The first step was the sputter-cleaning process using the plasma of mixed gases of Ar and CH_4 (50:50%) with the negative high-voltage pulse (voltage V_b = -10 kV, duration τ = 2 μs, repetition rate f =1 kHz). In the second step, the carbon ion implantation with the negative high-voltage pulse (V_b = -20 kV, τ = 1~2 μs, f =1 kHz) was performed with the CH_4 plasma to make carbon anchors inside the substrate and in the third step the C_2H_2 plasma was used to produce a graded mixing layer between the coating film and the substrate using the negative high-voltage pulse (V_b = -20 kV, τ = 1~2 μs, f = 1 kHz). When skipping the second and the third steps, it was hard to obtain good adhesion of DLC film. The last forth step was the rapid deposition process for production of thick film using the $C_6H_5CH_3$ plasma and the negative high-voltage pulse of medium voltage (V_b = -10 kV, τ = 2 μs) and a high repetition rate (f = 4 kHz). The gas pressure was p = 0.3 to 0.5 Pa in the second and third steps and p = 1.0 Pa during deposition of the forth step. The RF pulse had the maximum power of 3 kW, the pulse duration of 20 μs, and the frequency of 13.56 MHz. In the present experimental conditions, at the forth step, the glow discharge was generated by the negative high-voltage pulse around the substrate. The typical deposition rate was approximately 1 μm/h using the $C_6H_5CH_3$ plasma for deposition.

The film thickness was measured with the cross-sectional SEM observation. The hardness was measured with a nano-indentation tester (ENT1100, ELIONIX).

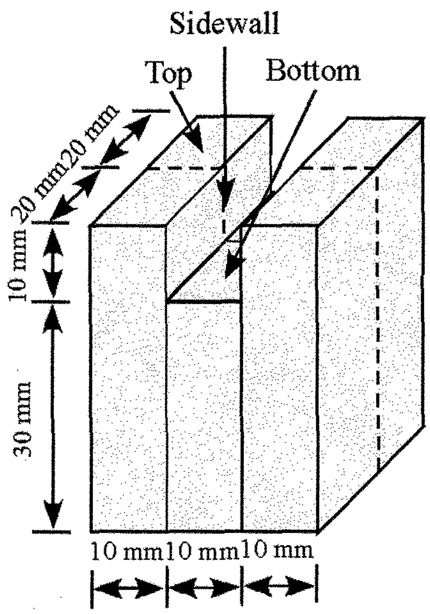

Fig. 1. A Schematic diagram of trench substrate of aluminum alloy (A-5052) with aspect ratio of 1.

3. Results and discussion

Figure 2 shows the typical cross-sectional SEM micrograph of DLC film on the center of top surface of a trench, where the preparation time was 5 h. As seen in Fig. 2, the film thickness is approximately 5.0 μm, indicating the deposition speed of about 1.0 μm/h. From the similar results of thickness measurement, the thickness profiles on the trench substrate were obtained.

Figure 3 shows the thickness profile of DLC film on the trench with the aspect ratio of 1 at the center of trench length. As seen in Fig. 3, the film thickness at the top surface is about 2.3 times of that at the sidewall and about 1.4 times of bottom. The reason why the DLC thickness of sidewall is less than the top and bottom ones might be ascribed to little ion implantation to the sidewall.

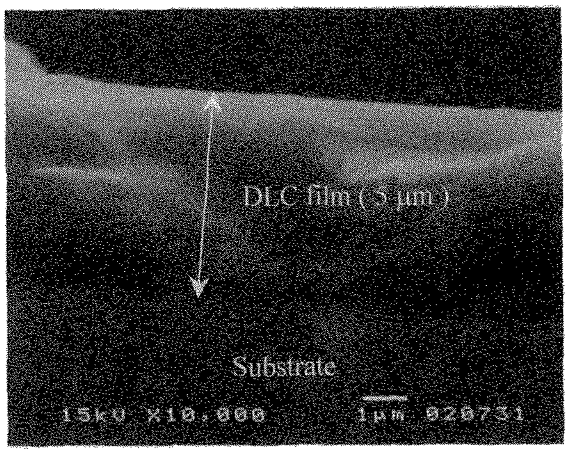

Fig. 2. Cross-sectional SEM micrograph of DLC film on the center of top surface of trench, where the preparation time was 5 h.

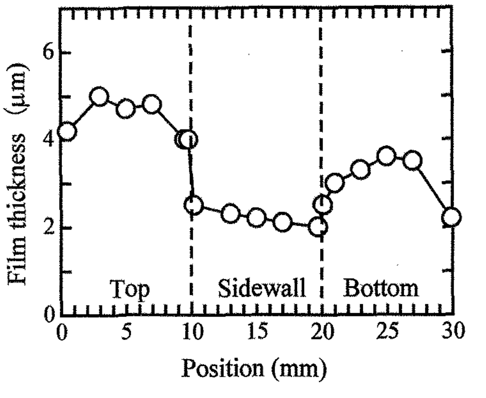

Fig. 3. Thickness profile of DLC film on the center of trench length.

Figure 4 shows the typical load displacement curve of DLC-coated substrate surface on the center of top of the trench, where the thickness of DLC film was approximately 5.0 μm, the maximum load of diamond pyramidal intender was 1 g, the loading time was 5 s, the holding time was 1 s, and the unloading time was 5 s. The hardness in each surface was determined from the maximum load and the maximum displacement of the load-displacement curve using geometric calculation. From Fig. 4, the hardness is found to be about 11 GPa. As the maximum displacement is approximately 0.18 μm corresponding to about 1/28, the evaluation follows the Bueckle rule (maximum indentation depth is 1/10 of film thickness) [7]. However, the aluminum substrate is much more soft than the DLC, so that the hardness value obtained above might not indicate the exact hardness of DLC. Then, the hardness values of the DLC-coated substrate were measured with various maximum loads of diamond pyramidal intender to clarify the effect of aluminum substrate on hardness measurement.

Figure 5 shows the hardness of DLC-coated top surface of trench and the maximum displacement of diamond pyramidal indenter as a function of maximum load of diamond pyramidal indenter, where the DLC film thickness was 5 μm. As seen in Fig. 5, the hardness of specimen decreases with increasing the maximum load, while the maximum displacement increases with increasing the maximum load. When the maximum load is 100 g, the maximum displacement is about 7.5 μm which is larger than the film thickness. Then the observed value at the load of 100 g indicates the hardness of aluminum alloy substrate. Although we expect that the hardness value approaches to a constant one in the region of lower loads, the measured hardness increases with decreasing the load in Fig. 5. In lower load region less than 0.1 g, the hardness measurement is difficult because the indenter displacement is too shallow compared with surface roughness. Here we determined the DLC hardness with the measured value at the load at which the maximum displacement of indenter becomes less than 1/30 of film thickness.

It is found in Fig. 5 that the hardness is 12 GPa at the maximum load of 0.5 g. The observed hardness shows the hardness of DLC itself with little effect of substrate materials since the maximum displacement of indenter is 0.12 μm corresponding to about 1/40 of film thickness.

Figure 6 shows the hardness of DLC-coated trench (DLC thickness in 2.2 μm) and the maximum displacement of diamond pyramidal indenter as a function of maximum load of diamond pyramidal indenter. It is found in Fig. 6 that the hardness is 9.9 GPa at the maximum load of 0.1 g, where the maximum displacement of indenter is 0.076 μm corresponding to about 1/30 of film thickness.

Figure 7 shows the hardness of DLC-coated bottom (DLC thickness in 3.6 μm) and the maximum displacement, showing the hardness of 11 GPa at the maximum load of 0.5 g, where the maximum displacement is 0.13 μm corresponding to about 1/28 of film thickness. The hardness of DLC film at the top surface is about 1.2 times of that at the sidewall and about 1.1 times of bottom. It is found that the hardness of DLC film is little difference in each surface.

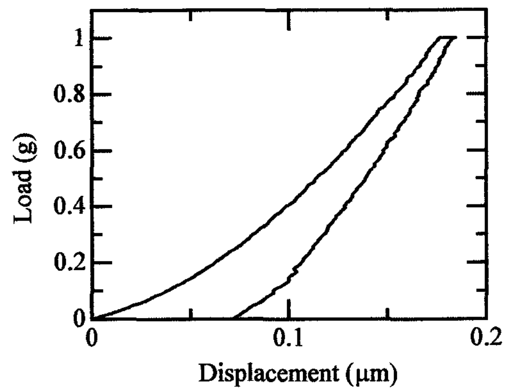

Fig. 4. Load versus indenter displacement of DLC film on the center of top surface of a trench, where the maximum load was 1 g and the thickness of DLC film was approximately 5.0 μm.

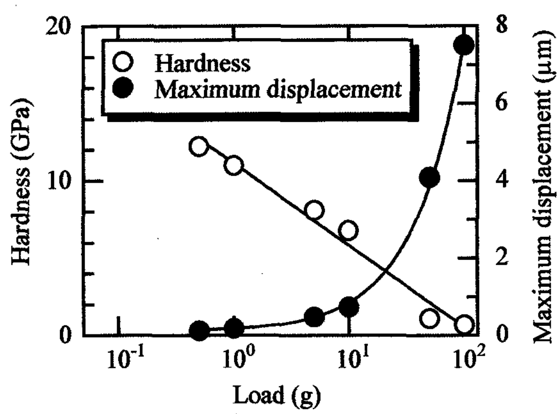

Fig. 5. Hardness and maximum displacement of DLC film with the thickness in 5 μm on the top surface of trench as a function of maximum load of diamond pyramidal indenter.

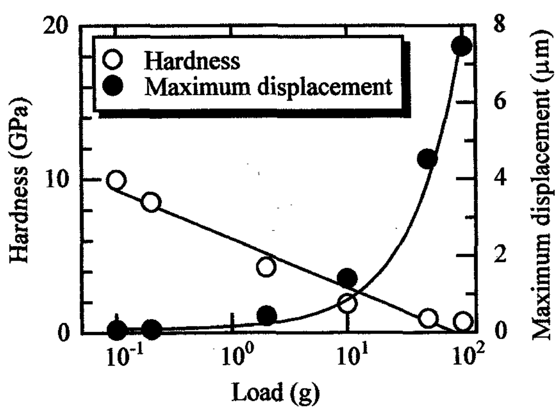

Fig. 6. Hardness and maximum displacement of DLC film with the thickness in 2.2 μm on the sidewall surface of trench as a function of maximum load of diamond pyramidal indenter.

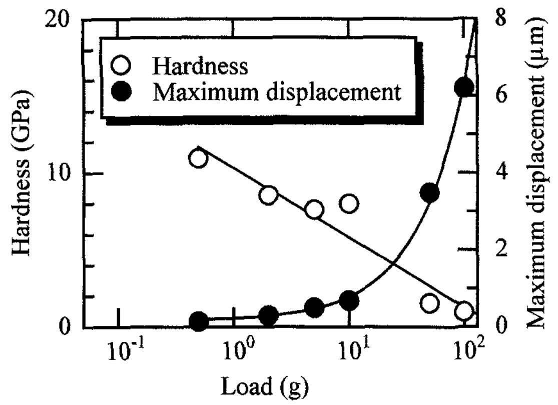

Fig. 7. Hardness and maximum displacement of DLC film with the thickness in 3.6 μm on the bottom surface of trench as a function of maximum load of diamond pyramidal indenter.

4. Conclusion

A few μm diamond-like carbon (DLC) film on a trench substrate of aluminum alloy (A-5052) was prepared by the hybrid process of plasma-based ion implantation and deposition (PBIID) using combined RF and high-voltage pulses and the toluene plasma. The hardness of DLC film with a thickness of 5 μm on the top surface of trench was 12 GPa, where the maximum displacement of diamond pyramidal intender into surface was 0.12 μm corresponding to about 1/40 of film thickness. The hardness of DLC film on the top surface is about 1.2 times of that on the sidewall and about 1.1 times of bottom.

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