

The stability of diamond-like carbon films during thermal annealing in air

T. M. Wang, W. J. Wang, Z. Y. Chen and J. J. Wu

Department of Materials Science, Lanzhou University
Lanzhou, 730001, China

Diamond-like carbon films, deposited by dual-ion beam sputtering on glass substrates, were annealed in air at 300°C. The annealing time was 1.5hrs and 3.0hrs, respectively. Property measurement and structural characterization showed that the annealing caused a reduction of the film layer and increases of both film resistivity and infra-red transmittance of the specimens. The influence of the annealing process depended only on annealing temperature, not on annealing time. The annealing at 300°C could not lead to breaking of the C-H bonds in films. The aging effect of the annealed films in air was also observed. The transformation mechanism of diamond-like carbon films under this condition is briefly discussed.

1. INTRODUCTION

Diamond-like carbon (DLC) films have received considerable attention in the past few years because of their unique physical, chemical and mechanical properties [1]. It is believed that the films have potential applications in the fields of protective coatings or anti-reflective coatings for optics, heat sinks in electrical devices, as well as protective coatings of some devices used in space and nuclear reactions [1,2]. However, compared with preparation investigations [3,4], only a few studies have been done on the stability behavior of the films under different post-treatment conditions [5-7].

We have studied the stability behavior of DLC films under high energy hydrogen ion (H^+) and carbon ion (C^+) irradiations [8-10]. As a continuation of this work, we have recently annealed the films in air. In the present paper, we report some preliminary experimental results and briefly discuss the transformation mechanism of DLC films.

2. EXPERIMENT

The DLC films were deposited by the dual-ion beam sputtering method on glass substrates of size of 70 × 20 × 1.0 mm. The details of the deposition process can be found

elsewhere [11]. The film thickness was about 2000 Å. The as-deposited substrates were cut into small specimens with a size of 20 × 10 mm and were then isothermally annealed in flowing air for 1.5 and 3.0 hrs, respectively. The annealing processes for both specimens are shown in Fig. 1. During the annealings, the square resistivity R_{\square} of the films [11] were measured *in situ*. Before and after annealing, the square resistivities, the Raman spectra and the infra-red (IR) transmittances of specimens were used to characterize the films. The aging effects of film resistivities after annealing were also studied in air.

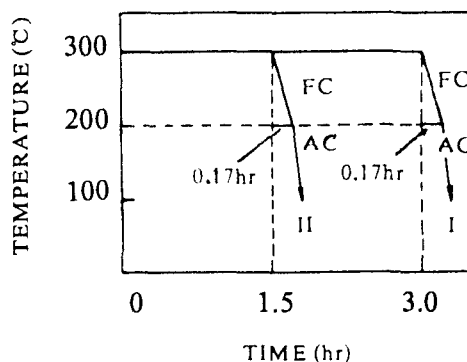


Figure 1. The two isothermal annealing processes at 300°C (FC—furnace cooling, AC—air cooling).

3. RESULTS AND DISCUSSIONS

The square resistivity R_{\square} of the DLC films vs. annealing time at 300°C and subsequent furnace cooling and air cooling time curves are illustrated in Fig. 2 (I-3.0hrs, II-1.5hrs). The aging effects of R_{\square} at room temperature after isothermal annealing are shown in Fig. 3. It is clear that the variations of R_{\square} for both films are similar although their annealing times were different, that is: (1). The R_{\square} reduced about one order of magnitude quickly when the specimens were put into the furnace at 300°C; (2). With the increase of annealed time, the R_{\square} increased gradually and exceeded the original value. One hour later, the R_{\square} of both specimens tended to stable values. Both values are nearly the same; (3). During the furnace cooling from 300°C down to 200°C, the R_{\square} increased again; while during the air cooling from 200°C down to room temperature, the R_{\square} increased about 2.5 orders of magnitude rapidly and then decreased about 2 orders of magnitude sharply. After then, the R_{\square} of the two specimens increased again with the increase of time at room temperature and, in the end, reached approximately the same stable values. The stable value is about 10^4 times the as-deposited value.

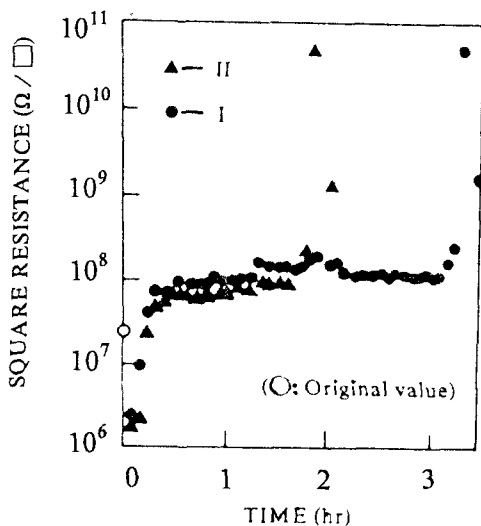


Figure 2. R_{\square} vs. time curves

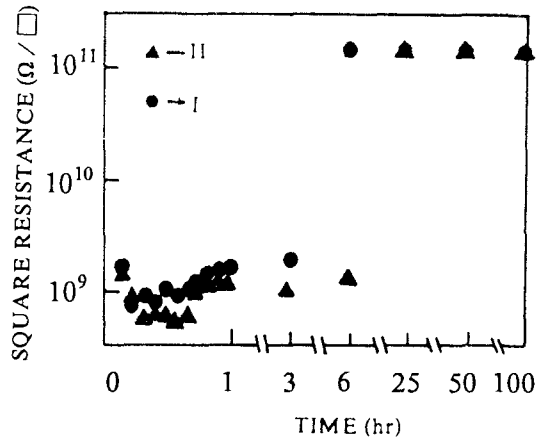


Figure 3. The aging effects of R_{\square} at room temperature.

The IR transmittances of specimens before and after annealing are shown in Fig. 4. In order to eliminate the influence of the glass substrate, the relative IR transmittances of the film layers were obtained by using a computer, as shown in Fig. 5. It can be seen that: (1). In comparison with the as-deposited value, the IR transmittances of the annealed specimens were increased; (2). The annealed films displayed apparent sp^3C-H absorption peaks at about $2920cm^{-1}$ and $2850cm^{-1}$.

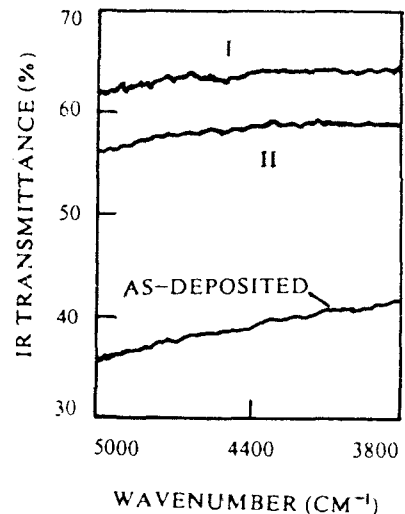


Figure 4. The IR transmittances of specimens.

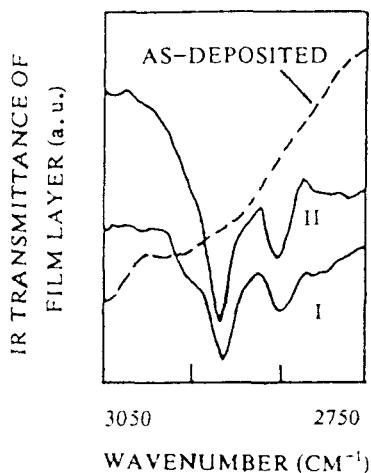


Figure 5. The relative IR transmittances of film layers.

It was reported that the DLC films annealed in vacuum displayed graphite-like properties, such as the decrease of the resistivity and the IR transmittance, as well as the reduction of the sp^3C-H peak intensities [7]. But the present results are not in agreement. This implies that the thermal annealing effect of DLC films in air is different from that in vacuum.

We know that the bond energy of C-H is higher than that of C-C, and the bond energy of O-H is larger than that of C-O. Therefore we can deduce that, compared with C-H bonds, the C-C bonds (including sp^3C-C bonds) in films could be broken more easily at $300^\circ C$ annealing in air; the broken carbon atoms would combine with the active oxide atoms in air (forming CO_2 or CO , for example) and then released into the air. As a result, the R_{\square} of both films was increased at the initial stage of annealing. On the other hand, the amount of C-C bonds which would be broken was constant at a given temperature, thus, the R_{\square} of both specimens tended to stable values after nearly the same annealing time. In other words, the influence of the annealing on the DLC films in air depended only on the annealing temperature and not on the annealing time.

Based on the explanations above, it can

be concluded that the breaking of C-C bonds and the release of C-O components from film layers should lead to the reduction of film layers and both specimens (I and II) should have almost the same thickness. This is in agreement with our IR transmittance results, as shown in Fig. 4. This figure indicates that the IR transmittances of the annealed specimens are much higher than those of as-deposited ones and the annealing time had hardly any influence on the transmittance. This phenomenon implies that both films have nearly the same thickness and structures. In addition, the sp^3C-H absorption peaks in Fig. 5 mean that the C-H bonds had not yet been broken at $300^\circ C$ and there were still relatively more C-H bonds in the films after annealing.

The breaking of C-C bonds and the reduction of film layers could also be observed in the Raman spectra, as shown in Fig. 6. It can be seen that the as-deposited film displays a single line at about 1530 cm^{-1} (the G line) and another line at about 1350 cm^{-1} (the D line) [12], but the annealed films has no such lines. This means that the annealed films contained none of or very few C-C bonds. On the contrary, an apparent scattering peak of the glass substrate at about 1100 cm^{-1} can be observed in annealed specimens. This gives further evidence for the reduction of film layers.

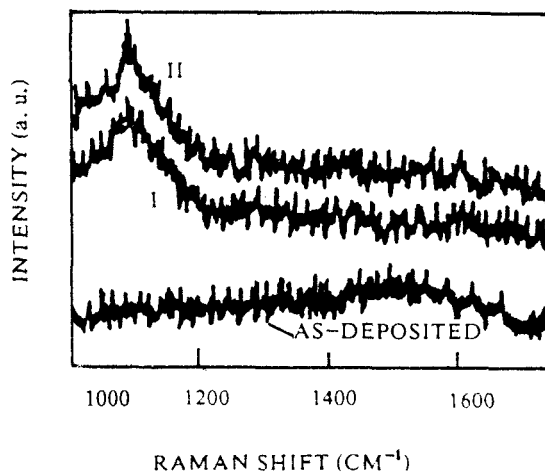


Fig. 6. The Raman spectra of film layers.

As to the decreases of the R_{\square} of two specimens during the period in the furnace and their increase on cooling, we believe that they were caused by the negative temperature coefficient of resistivity of the film layer. We find that the R_{\square} decreased again after being taken out of the furnace. This might be caused by the absorbed impurities (such as H_2O) on the surface of the film layers. However, the further increase of the R_{\square} with aging might be induced by new bonds formed in air[13] or the cracking of film layers. The direct evidence for this should be investigated further.

4. CONCLUSIONS

(1). The isothermal annealing of DLC films in air at $300^{\circ}C$ caused the breaking of C-C bonds, and the oxidation and the release of carbon atoms. However, the degree of breaking depended only on annealing temperature and not on annealing time.

(2). The annealing at $300^{\circ}C$ could not lead to the breaking of C-H bonds in DLC films.

(3). The bond changes and the film thickness reductions caused by annealing led to the increases of both R_{\square} and IR transmittance of specimens.

(4). The aging effect of film resistivity occurred at room temperature after annealing.

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