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The Thermal Annealing Effect on The Residual Stress And Mechanical Property in The Compressive Stressed DLC Film.

H. W. Choi[1,a], M.-W. Moon[1,b], T.-Y. Kim[1,2,c], K.-R. Lee[2,d] and K. H. Oh[1,e]

[1]School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

[2]Future Technology Research Center, Korea Institute of Science and Technology, P.O.Box 131, Cheongryang, Seoul 136-791, Korea

[a]joiner03 @ snu.ac.kr, [b]mwmoom @ snu.ac.kr, [c]assun @ kist.re.kr, [d]krlee @ kist.re.kr, [e]kyuhwan@snu.ac.kr,

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Abstract. The thermal annealing effect on the compressive residual stress has been presented in thin diamond-like carbon (DLC) film on Si substrate. Annealing experiments were carried out with Rapid Thermal Procedure system at from 200 to 600 °C, and the variation of residual stress with annealing temperature was investigated by in-situ stress measurement system. The stress reduction occurs as annealing temperature increases, while the change of chemical structure of DLC film is not significantly changed with observation by Raman spectrometer. The elastic modulus and hardness are not deteriorated when annealing temperature is controlled at less than 400 degree of Celsius, where the residual stress is apparently reduced.

Introduction

Diamond-like carbon (DLC) film has been a candidate for various applications due to its excellent tribological and mechanical properties. However, since a highly compressive stress up to 10GPa in DLC film has been induced from deposition process, researches suggested that multilayer, incorporating metals, silicon, would be practical method to reduce residual stress of DLC film [1-3]. But, metal incorporation has drawbacks such as removing the optical transparency of film. The case of incorporating Ni, W and Ti during DLC deposition has been reported to degrade the quality in coating wear resistance [4, 5]. The annealing treatment has been suggested for the reduction method of compressively stressed film, while no mechanical properties of elastic modulus and hardness of film is affected [2]. This work studied on the annealing effect on stress reduction and on mechanical properties of elastic modulus and hardness of thin Diamond-Like Carbon (DLC) film, especially hydrogenated amorphous carbon (a-C:H), under compressively stress state. Chemical bonding structures of DLC film has been considered by comparison of as deposited film and annealed film. Details of observation methods have been addressed below.

Experimental method

Diamond-Like Carbon film deposited on Silicon has been deposited with hydrogenated amorphous carbon (a-c:H) film by using a radio frequency plasma-assisted chemical vapor deposition (R.F-PACVD) technique[6]. The chamber was evacuated to 10^{-5}Torr by a turbo molecular pump. The base pressure of the reaction chamber was less than 10^{-3}Pa. Before deposition, the substrates have been cleaned by Ar Plasma generated by rf power at the self bias voltage of -400V for 1 minute. For

DLC film deposition, a glow discharge of C_6H_6 at a pressure of 1.33Pa was supplied with negative self-bias voltage controlled between –500Vb and -600Vb by adjusting the r.f. power. With respect to the deposition time, the resulting film thickness has been measured about 140nm. After film deposition, the original residual stress of about 1.2GPa (Fig.1b) and chemical bonding structure (Fig. 3a) of as-deposited film were measured. Then annealing procedure was carried out in Rapid Thermal Procedure (RTP) system to consider the influence on residual stress. The pressure of furnace of RTP was fixed at 5m Torr pressure in vacuum during annealing processing and heated for 10 min at the annealing temperatures of from 200 to 600 °C. Second sets of annealing experiment were carried out with cyclic annealing temperatures: 10minutes cycle and 60minutes (1hr) cycle.

A micro-Raman spectroscope with a Spectra Physics Ar-ion laser (Jobin- Yvon 64000) was used to characterize the chemical bonding structure of DLC film at both of as deposited and as-annealed films. Using curvature method with Stoney's equation, the relative variations of the stress were traced for each annealing procedures. The mechanical properties of annealed films such as Young's modulus and hardness were measured by using a Nano-indenter. By using in-situ heating stage built in Environment SEM (ESEM, FEI XL-30/PHILIPS) with a set up condition of increasing temperature at 500°C, the adhesion deterioration, interface delamination, has been observed in compressively stressed DLC film on glass substrate.

Result and Discussion

The stress reduction with annealing temperature has been compared with as deposited film as shown in Fig.1. As annealing temperature increases, the residual stress in annealed film at 300°C has been measured to be 20 percent lower than that at as deposited one. When as deposited film was annealed with thermal cycles at 200°C and 300°C, where each temperature was held for 10 minutes and 60minutes as shown in Fig. 1b. It is found that the stress relief has been shown during first cycle and maintained as constant through last cycles. For the case of 300°C, a short cycle annealing time of 10 minute reduced the stress more effectively than a long cycle annealing time of 1hour.

Annealing effect on hardness and Young's modulus has been presented with annealed a-c:H film at 200, 300, 400, 500 and 600 °C given in Fig.2a. Both of hardness and Young's modulus are not significantly reduced until 500°C, while abruptly decreased at 600 °C.

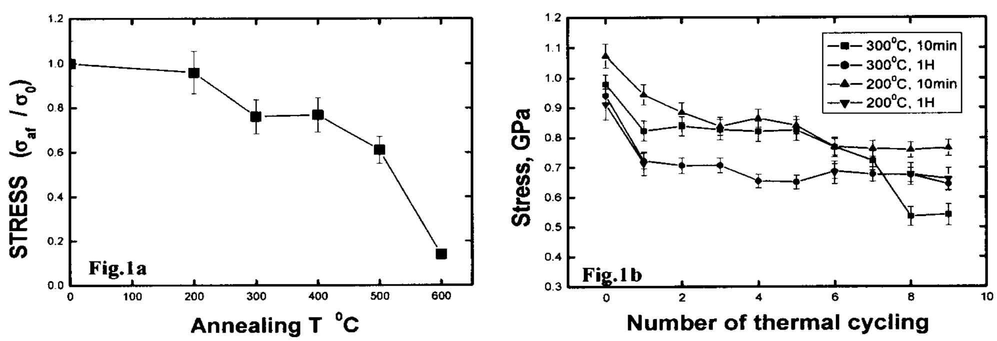

Fig. 1 (a) The stress reduction ratio as a function of annealing temperature (σ_0: stress of before annealing, σ_{af}: stress of after annealing). (b) The stress reduction by thermal cycle annealing from 200°C to 300°C with holding temperature for 10 min or 60min.

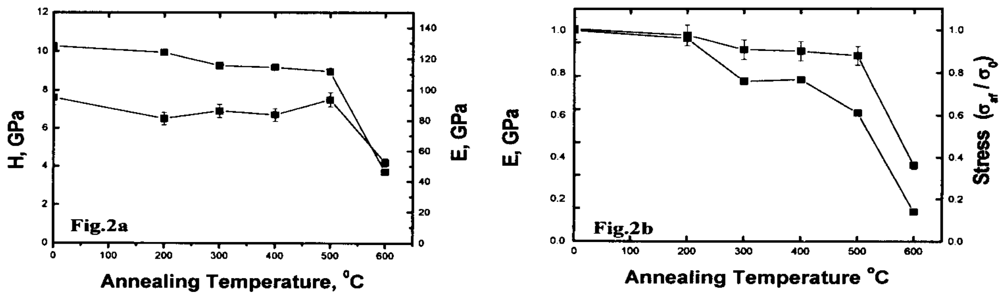

Fig. 2 (a) Hardness and Elastic modulus of annealed a-c:H films (B) Elastic modulus and stress change vs annealing temperature.

In order to find the stable condition in elastic modulus with significant stress reduction, the variation of stress and elastic modulus has been measured during annealing procedure and compared with each other in fig. 2b. Stress reduction apparently started at above 300 °C, while the value of elastic modulus is not changed at below 500°C. This comparison in fig. 2b implies that, during annealing procedure, a stable condition for elastic modulus of compressed film could lay between 300 to 500°C, where significant stress reduction occurred.

The behavior of chemical bonding structure has been investigated with Raman spectra for annealed DLC films. D peak for a film as-deposited appears in the 1350 cm^{-1} region due to disordering of ordered graphite structure [7]. G peak appears in the 1580 cm^{-1} region of Raman shift owing to graphite [7]. The shape of peak decomposition was not significantly changed until annealing at 400°C. However, the observable separation of the D and G peaks appeared at 500 °C as compared with that as-deposited in fig. 3a and 3b. Fig.3c shows the intensity ratio of the D and G peaks (ID / IG) in Gaussian analysis with the data of Raman spectra. The ID / IG ratio in the DLC films started to increase significantly at 300°C with a rapidly stress reduction. Such an increase of ID / IG ratio in the DLC films means the increase of sp2 –bonded clusters in the films, indicating the increase of graphite micro crystallites in its volume.

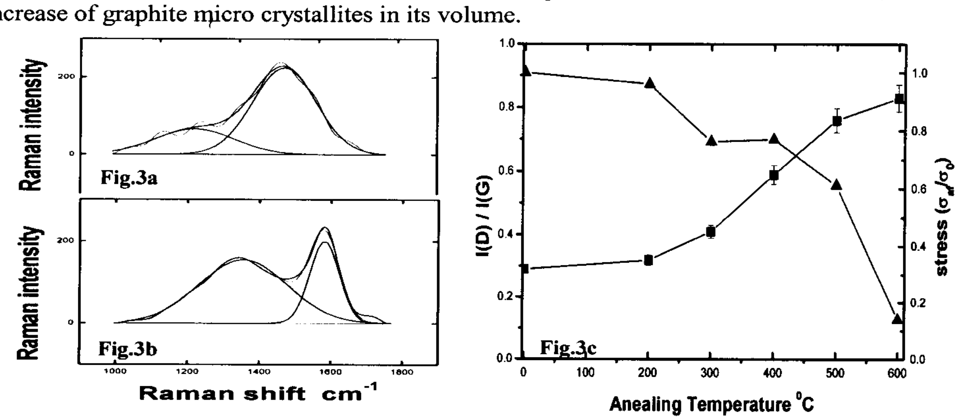

Fig. 3 The Raman Intensity of annealed film (a) as-deposited (b) at 600°C (c) the Raman spectrum intensity of I(D)/ I(G) ratio as a function of stress reduction.

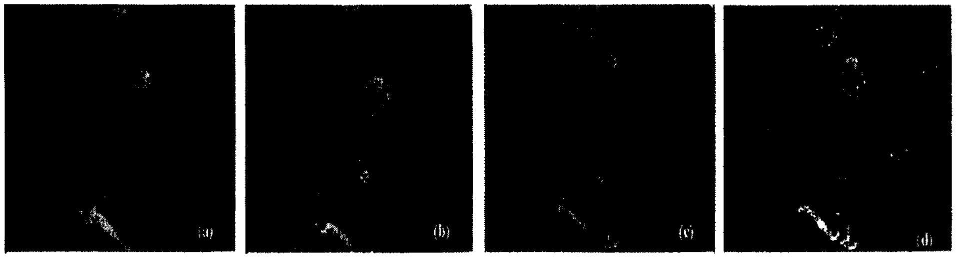

Fig. 4 The observation of delamination between the substrate and the film during annealing under in-situ. (a) at 400°C (b) at 406°C (c) at 409°C (d) at 410°C

Delamination buckle phenomenon under in-situ annealing processing has been shown on glass substrate for temperatures at higher than just 400 °C. The circular type of buckling on annealing DLC surface is shown to develop at 400°C and then it gradually developed its growth as a telephone-cord type of buckling from 401 to 412 °C [8]. This indicates that adhesion of annealed film were became deteriorated from 400 °C in spite of stress reduction as shown in fig. 4. Although the delamination of a compressive film at higher temperature is consistent with the previous report [9], which gave the unclear conclusion for this mechanism. The further work is required

Summary

The stress reduction has been observed for a-c:H film with increasing annealing temperature by thermal annealing. The stress reduction of annealed a-c:H films was observed from 300°C to 600°C. While its mechanical properties such an Elastic modulus and hardness is kept almost constant until 500°C. The I_D / I_G ratio in the DLC films increases significantly from 300°C to 500°C which indicates the increasing of sp^2-bonded clusters in the films. A stress relief of a-c:H films can be achieved by thermal annealing at 500°C. Over 500°C, we observed a graphitic property in the annealed a-c:H films. We also observed that short cycle annealing time is effective than long cycle annealing time at same annealing temperature.

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