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The Annealing Effect of Diamond-like Carbon Films for RF MEMS Switch

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ABSTRACT

Stiction in microelectromechanical systems (MEMS) has been a major failure mechanism. Especially, in RF MEMS switches, moving parts often suffered in-use and release related stiction problems. Some materials and methods have been used to prevent this problem. Diamond-like carbon (DLC) has not only been used as a protective material owing to its good mechanical properties but also has been used as a hydrophobic material. Its properties could be controlled by post annealing treatment in various conditions. We synthesized DLC films using a radio frequency plasma enhanced chemical vapor deposition (RF PECVD) method on silicon substrates using methane (CH_4) and hydrogen (H_2) gas. Then, the change of the hydrophobic property of the films was investigated undervarious annealing temperatures in nitrogen and in oxygen ambient. The films, that were annealed above 700°C in nitrogen ambient, showed a high contact angle of water (>90°) even though their mechanical property was sacrificed to some degree. The structural variation and the changes of the hydrophobic and mechanical properties of the DLC films were analyzed by Raman spectrum, contact angle measurement, surface profiler, and a nanoindentation test.

Key Words : Diamond-like carbon (DLC), RF MEMS switch, stiction, annealing, hydrophobic

Ⅰ. Introduction

In microelectromechcanical systems (MEMS) technology, the stiction problem is still a challenging issue in spite of innovative advances. Especially in RF MEMS switches, moving parts often suffered stiction problem. The stiction of a microstructure to an adjacent surface can occur either during the final steps of the micromachining process (release related stiction) or after packaging of the device, due to over-range input signals or electromechanical instability (in-use stiction). The cause of strong adhesion can be traced to the interfacial forces existing at the dimensions of the microstructures. These include capillary, electrostatic, van der Waals, and chemical forces[1,2]. Release related stiction is caused at the sacrificial layer removing step, which includes etching, rinsing, and drying. When the rinsing liquid is dried, surface tension pulls down the suspended microstructure to the substrate. The structure may adhere permanently. In order to reduce this release related stiction problem, several processes are used for instance: supercritical drying with CO_2[3], freeze-drying sublimation[4], and employing posts[5]. On the other hand, in-use stiction usually occurs upon exposure of successfully released microstructures to a humid environment. Hydrated surfaces may increasingly stick to one another as the exposure time is extended. It is closely related to the reliability of the MEMS devices. An anti-stiction layer coating and surface treatment for stiction reduction methods have been reported solutions for both stiction problems which include self assembled mono layers (SAM) coating[7,8], diamond-like carbon (DLC) coating[9,10,24], and surface treatment with ammonium fluoride

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(NH_4F) [6], etc.

DLC has recently emerged as one promising class of materials for MEMS because it is hydrophobic and has excellent mechanical properties[9,10]. DLC is also of interest as a biocompatible coating[11].

Various physical and chemical methods such as sputtering[12,13], plasma enhanced chemical vapor deposition[10], and vacuum arc deposition[14,15] have been employed to synthesize DLC film. Among these methods, a radio frequency plasma enhanced chemical vapor deposition (RF PECVD) method has been widely used to synthesize DLC films[16-18], because this method uses standard plasma processing which is simple, relatively inexpensive, and operates at low temperatures. Some methods including surface modification[22], incorporation of elements such as F, N, O, or Si into the film[15,17,19,23], and post annealing[12,13,16,20] have been reported to improve the hydrophobic and mechanical properties of the film.

In this paper, DLC films with the hydrophobic property were synthesized by the RF PECVD method[18]. We investigated the change of the hydrophobic property of the DLC films under various rapid thermal annealing (RTA) temperatures in nitrogen and in oxygen ambient.

Ⅱ. Experimental Details

DLC films were deposited on p-type (100) silicon substrates using a RF PECVD method. The substrates were cleaned in D. I. water, acetone, and methanol for 10 min in each solution, respectively. Also, they were cleaned in a solution of sulphuric acid (H_2O_2:H_2SO_4=1:5) at 80°C for 10 min and then etched in a hydrofluoric acid solution to strip off native oxide, followed by a 5 min in-situ H_2 plasma cleaning operation at a gas pressure of 1 Torr and a RF power of 150 W in order to remove any contamination on the surface and to activate the surface. Then, methane and hydrogen gas were introduced into the reaction chamber for the film growth. We summarize the deposition condition in Table 1. The thickness, the interface between the film and substrate, and the hydrophobic property of the as-deposited films were observed by field emission scanning electron microscopy (FESEM), high resolution transmission electron spectroscopy (HRTEM), a surface profiler, and contact angle measurement. We carried out the contact angle measurement by dropping D. I. water on the surface at room temperature.

Table 1. Optimized deposition condition of the DLC thin films

Deposition gas	CH_4: 20 sccm H_2: 80 sccm
Working pressure	1 Torr
RF power	150 W
Electrode to substrate distance	7 cm
Deposition time	5 min 30 sec
Substrate temperature	Room Temperature

After the DLC films' deposition, they were annealed at temperatures ranging from 500 to 900°C in steps of 100°C using RTA equipment in N_2 and in O_2 ambient for 1 min. Nakazawa et al. reported that the properties of the DLC film were changed by the post annealing process due to rearrangement of carbon from a diamond to a graphite structure[12,13,16,20]. Therefore the film was expected to be more hydrophobic. To investigate the change of the hydrophobic property of DLC films under various post annealing conditions, contact angle and surface roughness measurements were carried out. Also, to analyze structural variations and the variation of hardness of the films, we carried out analyses by using Raman spectra and a nano-indentation test.

Ⅲ. Results and Discussion

The thickness, the interface between film and substrate, surface roughness, and contact angle of the as-deposited DLC film are illustrated in Fig. 1. The thickness of the DLC film was 120 nm. Amorphous DLC film was well deposited on the silicon substrate. The film showed a smooth rms surface roughness of 0.16 nm and a relatively high

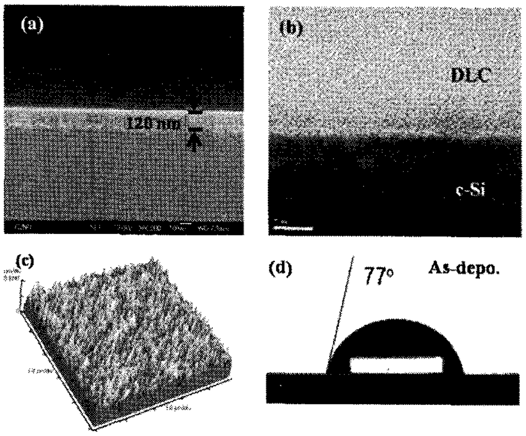


Fig. 1. Images of the as-deposited DLC film: (a) the cross-sectional SEM image, (b) the cross-sectional TEM image, (c) an AFM surface image, and (d) the surface contact angle

contact angle of 77°. The contact angle of water on the surface gives a good indication of its hydrophilic/hydrophobic properties. Usually, a hydrophilic surface has a contact angle of less than 70° while a hydrophobic surface has a contact angle of more than 70°. Therefore, the as-deposited film has a hydrophobic property in itself.

Fig. 2. illustrates the variation of contact angles of the DLC films under various annealing conditions. The values of the contact angles increased with increasing annealing temperature in N_2 ambient, but decreased in O_2 ambient. The films showed a good hydrophobic property (>90°) which were annealed above 700°C in N_2 ambient. With increasing annealing temperatures, the bonded hydrogen effused from the films and the films subsequently reordered themselves into a more graphitic structure. A graphite surface is known to be much more hydrophobic than diamond[22]. In O_2 ambient, however, surface oxidation of DLC film occurred simultaneously[13,23]. Therefore, oxidation was mainly affected decreasing the contact angle. In N_2 ambient, the contact angle was continually increased and then abruptly increased from 800°C to 900°C. This increase was due to improved surface roughness[21] as well as prevention of surface oxidation of the films. The surface roughness variation under various annealing conditions is illustrated in Fig. 3.

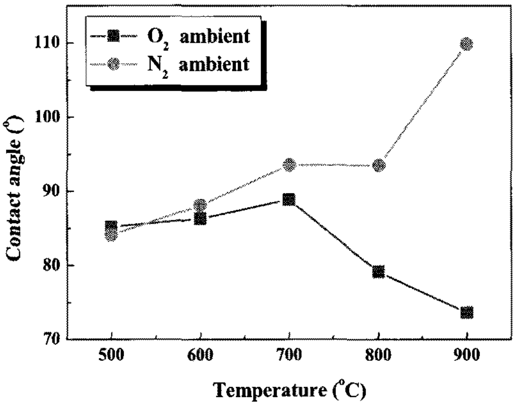


Fig. 2. Contact angle of DLC films under various annealing conditions

To analyze the structural variation of the films, we carried out Raman analysis. The result is illustrated in Fig. 4. The Raman mapping method has been widely used for the characterization of the structure of DLC films because of this method's ability to distinguish the sp3 and sp2 bonding types[9,10]. The Raman spectrum could be deconvoluted into two peaks using a Gaussian line shape, usually denoted as the G (graphite) and D (disordered) band, respectively. The ID/IG ratio increased with increasing annealing temperatures irrespective of ambient and is illustrated in Fig. 5. The results indicated that the as-deposited DLC films were graphited[9].

The variation of mechanical properties of DLC films according to annealing temperature was also

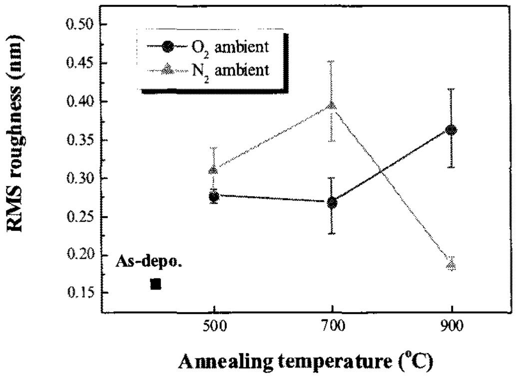
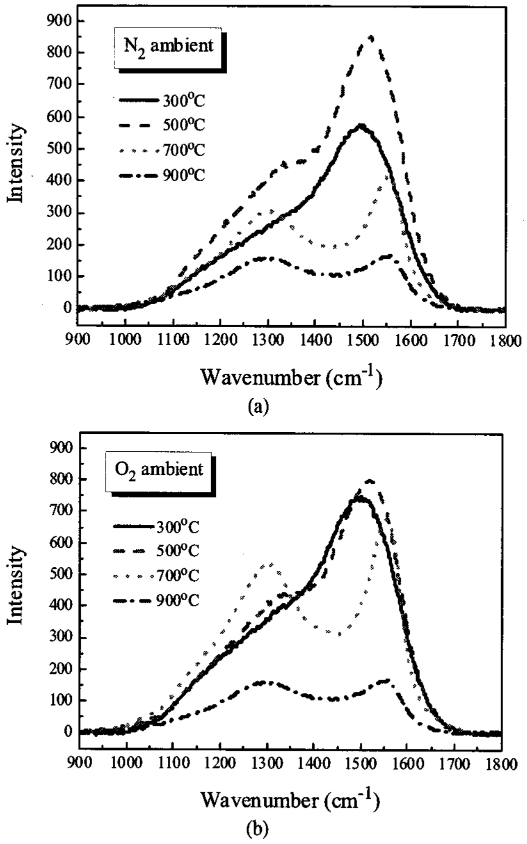


Fig. 3. Surface roughness of DLC films under various annealing conditions



(a)

(b)

Fig. 4. Raman analysis of DLC films as a function of the annealing temperature: (a) in N2 ambient and (b) in O2 ambient

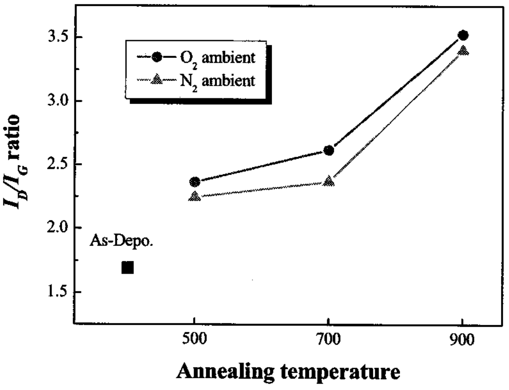


Fig. 5. The ID/IG ratio of DLC films as a function of the annealing temperature

investigated using a nano-indenter. The nanoindentation test is useful method to measure hardness[9,10]. Fig. 6. illustrates the hardness of as-deposited and annealed DLC films under Fig. 6. The hardness of DLC films as a function of the annealing temperature various annealing conditions. These values decreased abruptly between 500 and 700°C. The annealing treatment resulted in the increase of the graphitic fraction in the film and clustering of the sp2 bonded carbon[12,13,16,20]. However the DLC film which was annealed in N_2 ambient still had a strong advantage in its mechanical property.

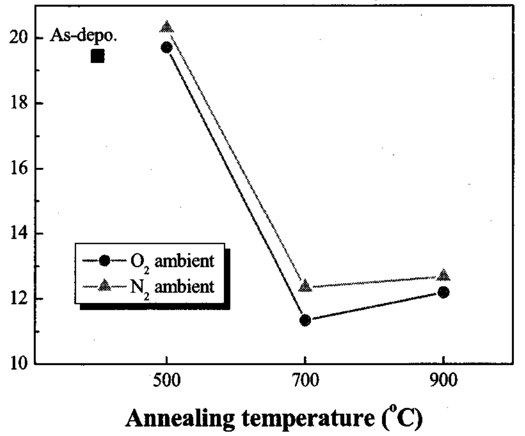


Fig. 6. The hardness of DLC films as a function of the annealing temperature

Ⅳ. Conclusions

In this study, DLC thin films were investigated as an anti-stiction layer for MEMS. The change of the films' hydrophobic property was examined under various post annealing conditions. The DLC films were synthesized by a RF PECVD method on silicon substrates using CH_4 and H_2 gas. The as-deposited films had a relatively high contact angle and good mechanical properties in themselves. We performed a contact angle measurement, surface profiler measurements, and a Raman analysis to analyze the films' surface properties. We also performed a nanoindentation test for measuring hardness. The films showed a high contact angle of water (>90°) which was annealed above 700°C in N_2 ambient. The films still had the strong advantage of hardness in spite of decreasing the values. The cause was that the post annealing treatment in N_2 ambient resulted in the increase of the graphitic fraction in the film and clustering of sp2 bonded carbon, the prevention of the surface oxidation, and the improvement of the surface roughness.

References

〔1〕 R. Maboudian, R. T. Howe, “Adhesion in surface micro-mechanical sturctures”, *J. Vac. Sci. Technol.*, B15, pp.1-20, 1997.

〔2〕 C. H. Mastrangelo, C. H. Hsu, “Mechanical Stability and Adhesion Micorstructure under Capillary Forces”, *J. Microelectromech. S.*, 2, pp.33-43, 1993.

〔3〕 S. M. Ali, J. M. Jennings, L. M. Phinney, “”Temperature dependence for in-use stiction of polycrystalline silicon MEMS cantilevers”, *Sens. Actuators A*, 113, pp.60-70, 2004.

〔4〕 N. Takeshimo, K. J. Gabriel, M. Ozaki, J. Takashashi, H. Horiguchi, H. Fujita, “Electrostatic parallelogram actuators”, *Transducers’ 91. International Conference*, pp.63-66, 1991.

〔5〕 H. S. Hwang, J. T. Song, “An effective method to prevent stiction problems using a photoresist sacrificial layer” *J. Micromech. Microeng.*, 17, pp.245-259, 2007.

〔6〕 M. R. Houston, R. Maboudian, R. T. Howe, “Ultra hydrophobic wetting behavior of amorphous carbon films”, *Transducers’ 95. International Conference*, pp.210-213, 1995.

〔7〕 Pornsin-Sirirak T N, Tai Y C, Nassef H and Ho C M, “Flexible parylene actuator for micro adaptive flow control”, *Proc. IEEE MEMS 2001*, pp.511-514, 2001.

〔8〕 B. H. Kim , T. D. Chung, C. H. Oh, K. Chun, “A new organic modifier for anti-stiction”, *J. Microelectromech. S.*, 10, pp.33-40, 2001.

〔9〕 J. Robertson, “Diamond-like amorphous carbon”, *Mat. Sci. Eng. R.*, 37, pp.129-281, 2002.

〔10〕 A. Grill, “Diamond-like carbon: state of the art”, *Diam. Relat. Mater.*, 8, pp.428-434, 1999.

〔11〕 T. I. T. Okpalugo, A. A. Ogwu, P. D. Maguire, J. A. D. McLaughlin, “Platelet adhesion on silicon modified hydrogenated amorphous carbon films”, *Biomaterials*, 25, pp.239-245, 2004.

〔12〕 H. Nakazawa, T. Kawabata, M. Kudo, M. Mashita, “Structural changes of diamond-like carbon films due to atomic hydrogen exposure during annealing”, *Appl. Surf. Sci.*, 253, pp.4188-4196, 2007.

〔13〕 I. A. Faizrakhmanov, V. V. Bazarov, N. Y. Kurbatova, I. B. Khaibullin, A. L. Stepanov, “Synthesis of New Carbon-Nitrogen Nanoclusters by Annealing Diamond-Like Carbon Films in Nitrogen”, *Semiconductors*, 37, pp.230-234, 2003.

〔14〕 D. H. C. Chua, W. I. Milne, Tay, B. K. P. Zhang, X. Z. Ding, “Microstructural and surface properties of cobalt containing amorphous carbon thin film deposited by a filtered cathodic vacuum arc”, *J. Vac. Sci. Technol.*, A21, pp.353-358, 2003.

〔15〕 H. Schulz, M. Leonhardt, H. J. Scheibe, B. Schultrich, “Ultra hydrophobic wetting behavior of amorphous carbon films”, *Surf. Coat. Tech.*, 200, pp.1123-1126, 2005

〔16〕 R. Wachter, A. Cordery, “Effects of post-deposition annealing on different DLC films”, *Diamond Relat. Mater.*, 8, pp.504-509, 1999.

〔17〕 G. Q. Yu, B. K. Tay, Z. Sun, L. K. Pan, “Properties of fluorinated amorphous diamond like carbon films by PECVD“, *Appl. Surf. Sci.*, 219, pp.228-237, 2003.

〔18〕 W. S. Choi, J. Heo, I. Chung, B. Hong, “The effect of RF power on tribological properties of the diamond-like carbon films”, *Thin Solid Films*, 475, pp.287-290, 2005.

〔19〕 M. Grischke, K. Bewilogua, K. Trojan, H. Dimigen, “Application-oriented modifications of deposition processes for diamond-like-carbon-based coatings”, *Surf. Coat. Tech.*, 74-75, pp.739, 1995.

〔20〕 N. M. J. Conway, A. C. Ferrari, A. J. Flewitt, J. Robertson, W. I. Milne, A. Tagilaferro, W. Beyer, “Defect and disorder reduction by annealing in hydrogenated tetrahedral amorphous carbon”, *Diamond Relat. Mater.*, 9, pp.765-770, 2000.

〔21〕 T. S. Chow, "Wetting of rough surfaces", *J. Phys: Condens. Matter*, 10, pp.3007-3018, 1998.

〔22〕 L. Y. Ostrovskaya, A. P. Dementiev, I. I. Kulakova, V. G. Ralchenko, "Chemical state and wettability of ion-irradiated diamond surfaces", *Diamond Relat. Mater.*, 14, pp.486-490, 2005.

〔23〕 Meshinis S, Kopustinskas V, Slapikas K, Tamulevicius S, Guobiene A, Gudaitis R and Grigaliunas V, "Ion beam synthesis of the diamond like carbon films for nanoimprint lithography applications", *Thin Solid Films*, 515, pp.636-639, 2006.

〔24〕 J. K. Luo, Y. Q. Fu, H. R. Le, J. A. Williams, S. M. Spearing, W. I. Milne, "Diamond and diamond-like carbon MEMS, *J. Micromech. Microeng.*, 17, S147-163, 2007.

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