Electrochemical Behaviour of Sputtering Deposited DLC Films*

LIU Erjia, ZENG A, LIU L X
(*School of Mechanical and Production Engineering, Nanyang Technological University*, 50 *Nanyang Avenue*, *Singapore* 639798)

Abstract: Diamondlike carbon (DLC) films were deposited via magnetron sputtering process. The energetic ion bombardment on the surface of growing film is one of the major parameters that control the atom mobility on the film surface and further the physical and chemical characteristics of the films. In this study, the energy of carbon ions was monitored by changing sputtering power density, and its effect on the electrochemical performance of the films was investigated. For the deposition at a higher sputtering power density, a higher sp^3 content in the DLC films was achieved with denser structure and increased film-substrate adhesion. The impedance at the interface of Si substrate/sulfuric acid solution was significantly enhanced, and at the same time higher film resistance, lower capacitance, higher breakdown potential and longer breakdown time were observed, which were related to the significant sp^3 content of the DLC films.

Key words: diamondlike carbon; magnetron sputtering; electrochemistry

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1 Introduction

Diamond-like carbon (DLC) is a metastable form of carbon materials covering a spectrum between diamond and graphite with hybridized carbon atoms. The structure of DLC films, which varies with deposition conditions, determines the film physical and chemical characteristics. DLC with a high sp^3 content possesses properties similar to those of diamond rather than graphite. DLC films can be deposited at ambient temperature over a large area, and therefore are promising as electrode and corrosion protection materials[1-4].

Magnetron sputtering has been widely used to deposit DLC films. The energetic ion bombardment on the surface of growing films is a key parameter that controls the atom mobility on the film surface and therefore their structure. It has been reported that the self-bias of plasma changes with the sputtering power density on the target[5], so changing sputtering power density is an appropriate way to control the quality of DLC films.

2 Experimental details

The DLC films were produced via dc magnetron sputtering with a graphite target ($w(C) = 99.995\%$) on highly conductive (111) Si wafers ($1.6 \times 10^{-3}\ \Omega \cdot cm$). The deposition conditions are given in Tab.1.

The film structure was characterized using micro-Raman spectroscope (Renishaw S2000). The film roughness was measured with atomic force microscope (AFM) (Digital Instruments, S3000), and the film thickness was measured with surface profiler (Dektak^{3}st).

Tab.1 Deposition conditions of DLC films

Vacuum prior to deposition/Torr	10^{-7}
Vacuum during deposition (with Ar as working gas)/Torr	$2 \times 10^{-3} \sim 7 \times 10^{-3}$
Sputtering power density/($W \cdot mm^{-2}$)	0.111 ~ 0.20
Target-substrate distance/mm	140
Deposition time/min	30

The film sheet resistivity was measured with four-point probe. Electrochemical impedance spectroscopy (EIS) according to the Randle cell equivalent circuit gave out the information of the double layer capacitance.

All electrochemical measurements were carried out using electrochemical corrosion tester (ACM Instruments) in a N_2 aerated and quiescent 0.5 mol/L H_2SO_4 aqueous solution contained in a single-compartment cell at room temperature (23 ± 2)℃. A 1000 mV potential was applied onto the bare or DLC film coated silicons to test the chemical durability of the films. The DLC samples were prepared as a work electrode in a way as described in the literature[6,7], which potential was measured with respect to a saturated calomel reference electrode (SCE), and a platinum plate was employed as a counter electrode.

* Received 10 December 2002; Accepted 18 April 2003
Corresponding author: mejliu@ntu.edu.sg(LIU Erjia)

3 Results and discussion

With increase of the sputtering power density, both D and G peak positions of the Raman spectra decrease, the bandwidth (FWHM) of D and G bands increases while the intensity ratio of D band to G band decreases. However, the change of the Raman features in the range of 0.111 ~ 0.167 W/mm^2 is very small while the change in the range of 0.177 ~ 0.20 W/mm^2 is significant. It shows that a high sp^3 content, high bond-angle disorder, and a small sp^2 cluster size are in accordance to a high sputtering power density when the power density is over 0.167 W.

AFM images of the DLC films deposited on the silicon wafers at different sputtering power density shows that the DLC films have ball-like surface features, as shown in Fig.1. The comparatively large particles can be localized sp^2[8]. The sample surface roughness (RMS) is shown in Fig.2. At a lower power density, such as 0.111 W/mm^2, a relatively rougher surface was obtained compared to that of the films obtained at a higher power density, such as 0.20 W.

Fig.2 also shows that the sheet resistivity of the DLC films increases with the power density. The increase of sheet resistivity with the increasing sputtering power density shows the increase of sp^3/sp^2 bond ratio, because the diamondlike phase has a higher resistivity than that of graphite like phase, which further confirms that more diamondlike the films appear to be with the increase of the sputtering power density.

EIS generally provides the data on electrode capacitance and charge-transfer-kinetics. An electrode interface resembles an electronic circuit consisting of a specific combination of impedance. Impedance can be expressed as a combined number, where the resistance is a real component and the combined capacitance and inductance is an imaginary component. One of the simplest circuits representing an electrode/solution interface is a Randle cell[9]. The equivalent circuit, as shown in Fig.3, can be used to simulate the reaction of an insulating layer coated conductive substrate, where (C_1R_1) is the capacitance and ohm resistance of the film, respectively, (C_2R_2) is the double layer capacitance and charge resistance of the film, respectively, and R_4 is the bulk resistance of the solution. The circuits of (C_1R_1) and (C_2R_2) can be simplified as (C_3R_3), where C_3 is the combined capacitance and R_3 is the combined polarization resistance. The whole circuit ((C_3R_3)R_4) is similar to that of the Randle cell.

The Nyquist plots of EIS spectra of a bare silicon substrate and silicons coated with DLC films clearly show that the DLC films have significantly enhanced the impedance amplitude of the silicon substrate, which indicates the protective characteristic of these films.

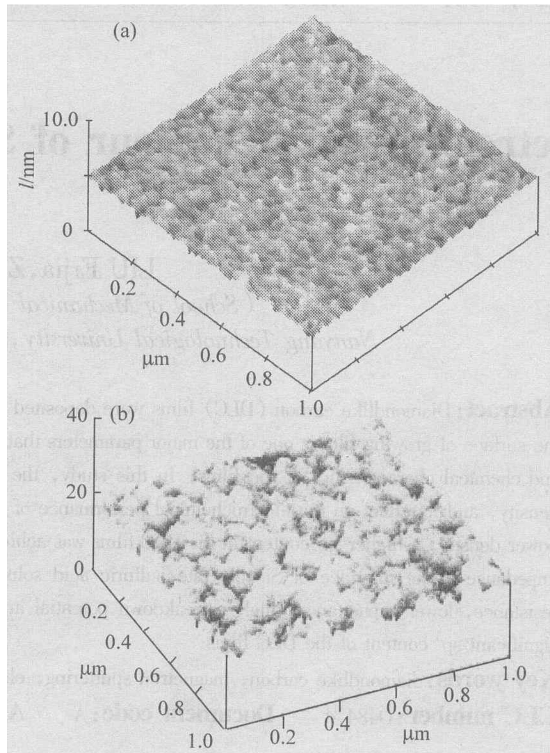

Fig.1 Surface morphology of (a) bare silicon and (b) DLC film deposited at 0.155 W/mm^2

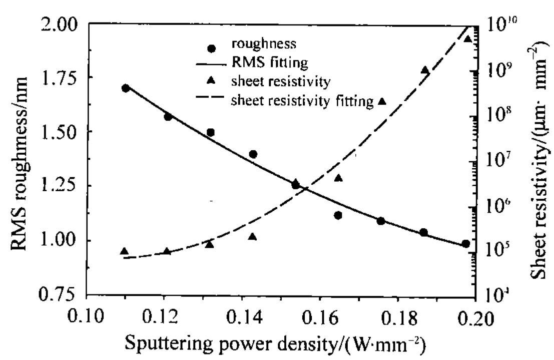

Fig.2 Surface roughness and sheet resistivity of the DLC films

The results illustrate that the sputtered DLC films without pores could be a dense anti-corrosion coating in acid. The values of these parameters obtained by curve fitting using the two equivalent circuits proposed are given in Tab.2.

From Tab.2, it is found that at high frequencies the impedance of the electrode/solution interface is mainly due to the ohmic contribution of the electrolyte solution, and the values are expected to be less than 10 Ω·cm^2.

The relatively higher values measured in the range of 93 to 130 $\Omega \cdot cm^2$ are attributed to the systematic errors at high frequencies. The combined polarization resistance and capacitance of native SiO_2 film were 3.7×10^{-3} $F \cdot cm^{-2}$ and 2.3×10^2 $\Omega \cdot cm^2$, respectively. It is found that the combined polarization resistance R_3 increases significantly while the combined capacitance C_3 decreases dramatically for the silicons coated with DLC films. It demonstrates that the DLC films are good insulating materials and can significantly enhance the corrosion resistance of silicon substrates.

Furthermore, the combined polarization resistance increases with the increase of sputtering power density, and the combined capacitance decreases correspondingly, to which a larger thickness of the films with a more diamondlike structure obtained at higher power densities may also contribute.

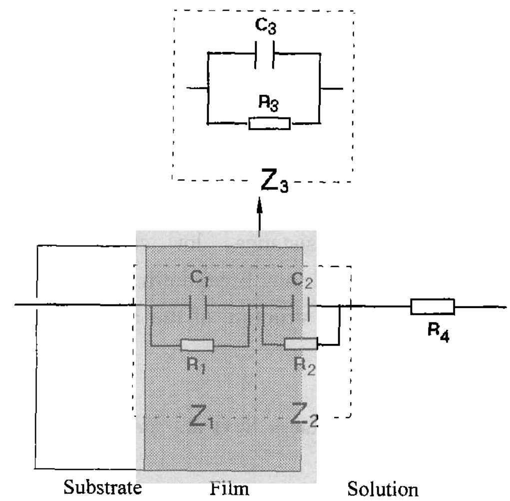

Fig.3 Equivalent circuits of chemical reactions on an insulating DLC film coated conductive Si substrate

Tab.2 Electrochemical parameters of bare and DLC coated silicons

Sample	R_4 $(\Omega \cdot cm^2)$	C_3 $(F \cdot cm^{-2})$	R_3 $(\Omega \cdot cm^2)$	C_2 $(F \cdot cm^{-2})$
Si	93	3.7×10^{-3}	2.3×10^2	–
DLC(0.20) W/mm^2	116	3.4×10^{-8}	3.01×10^8	5.71×10^{-7}
DLC(0.175) W/mm^2	102	2.01×10^{-7}	8.13×10^7	9.10×10^{-7}
DLC(0.167) W/mm^2	130	8.12×10^{-7}	7.12×10^7	9.80×10^{-7}
DLC(0.154) W/mm^2	106	8.13×10^{-7}	7.85×10^7	1.11×10^{-6}
DLC(0.132) W/mm^2	107	9.03×10^{-7}	5.30×10^6	2.71×10^{-6}
DLC(0.111) W/mm^2	110	9.12×10^{-7}	1.83×10^6	3.91×10^{-6}

The polarization curves of bare silicon and silicons with DLC films show that the corrosion potential increases when the DLC films are coated on the silicon substrates. The potential of DLC coated silicons increases sharply with the increase of current, even when the current density is as small as about 10^{-6} mA/cm^2, which depicts that the DLC films are a good passive coating for silicon.

As shown in Fig.4 the breakdown potential increases with the increased power density, which is in agreement with the trend of the sheet resistivity.

A 1000 mV potential was applied onto the bare and DLC film coated silicons in a 0.5 mol/L H_2SO_4 solution to test the chemical durability of the films. The DLC coated samples have lower currents compared to that of the uncoated ones. The current remains unchanged for a certain period before its abrupt rise that implies the peeling of the DLC films off the Si substrates. The breakdown time also increases with sputtering power density as shown in Fig.4.

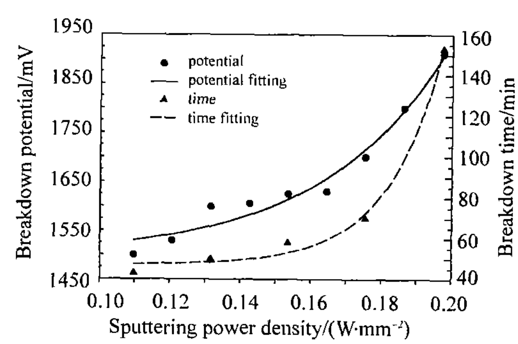

Fig.4 Breakdown potential and time at different sputtering power density

4 Conclusion

With magnetron sputtering deposition, a high sp^3 content in the DLC films could be achieved at a high sputtering power density. A significantly enhanced impedance at the interface of Si substrate/chemical solution, high film resistance, low capacitance, high breakdown potential and long breakdown time were related to a more diamond like structure of the DLC films.

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