PT/C COMPOSITE THIN FILMS FOR USE AS MICROELECTRODES

Howard Lee and Jyh-Ming Ting[e]
Department of Materials Science and Engineering
National Cheng Kung University
Tainan, Taiwan
e: jting@mail.mcku.edu.tw

Introduction

This paper reports a new composite thin film base on carbon for used as microelectrode for electrochemical analysis. Common thin film electrode materials include platinum, gold, silver, iridium, carbon, etc. These materials share a common drawback of relatively narrow potential windows, especially on the negative side of the potential window. [1] This severely limits many reduction reactions for several important electrochemical analysis, for example, trace analysis for many heavy metals. However, carbon materials have a greater potential of providing a wider potential window. [2] When making into diamond and amorphous carbon, potential windows of 3.55 V and 2.50 V were obtained. [3,4] However, amorphous carbon suffers a drawback of low electrical conductivity. To overcome this problem, we have investigated the growth and characterization of a series of C-based thin films with or without the addition of Pt. Growth of boron-doped diamond was also performed for comparison.

Experimental

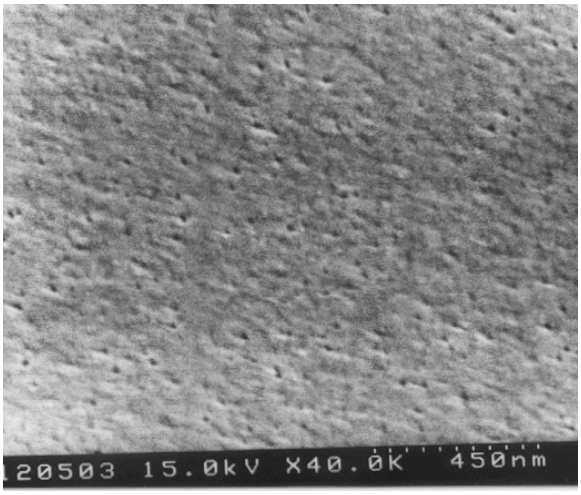
An RF magnetron sputter deposition technique was used for the deposition of Pt/C thin films. The target used was either a 99.99% pure graphite with coupons of platinum on the surface or 99.99% pure platinum. In the former, Ar was used as the sputter gas, while mixtures of methane and Ar were used in the latter case. The base pressure was less than 5×10^{-5} torr. Various working pressures of 5 mtorr, 10 mtorr, 50 mtorr were used.

Thin film thickness was measured on micrographs of cross sections obtained using scanning electron microscopy (SEM). Electrical resistivity was determined using a four-point probe technique. Raman analysis was performed to characterize the microstructure of composite thin films. Electron probe microanalyzer (EPMA) was used to determined concentrations of platinum and carbon in the thin films. Microstructure was also examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Cyclic voltammetry was used to determine the potential window.

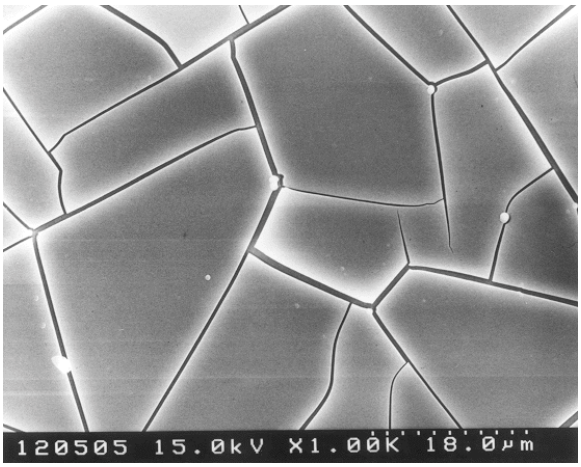
Results and Discussion

Various amorphous carbon (a-C) and Pt/a-C thin films were obtained. The integrity was found to depend on the pressure, compositions of the sputter gas and the composition of target. Lower pressures lead to cracking of a-C film, as shown in Fig. 1, which compares a-C films obtained at different pressures of 1×10^{-2} Torr and 5×10^{-3} Torr. Cracking of film can be improved by the introduction of hydrogen into argon or pasting Pt coupons on the graphite target, as shown in Figs. 1A and 2. Figure

2a shows an SEM micrograph of a-C thin film obtained using a pure graphite target and 1%H_2/Ar sputter gas. Figure 2b shows an SEM micrograph of a Pt/a-C film obtained using a Pt/C target and pure argon sputter gas.



(A)

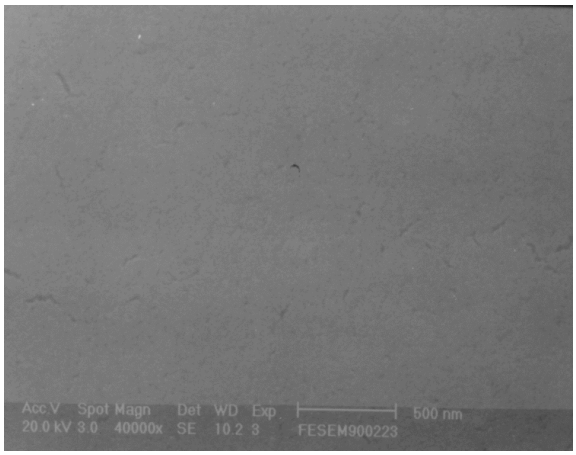


(B)

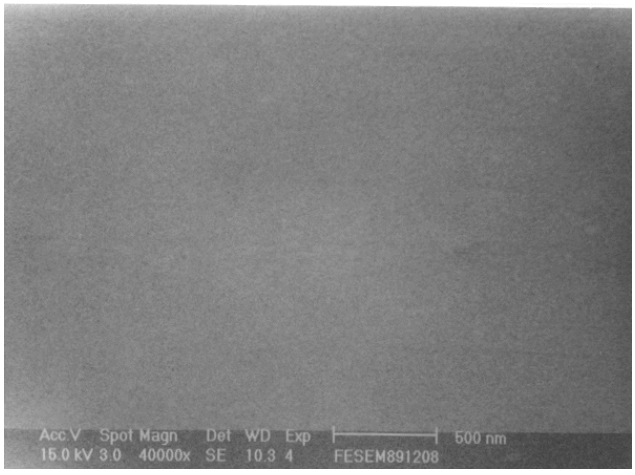
Fig. 1. SEM micrographs of a-C obtained at different pressures of (A) $1x10^{-2}$ Torr and (B) $5x10^{-3}$ Torr.

Raman analysis was performed to examine thin film structure. Raman spectra show signatures of both G-band and D-band, regardless of the film types. However, the I_d/I_g ratio depends on the deposition condition. Figure3 shows I_d/I_g ratio as a function of Ar pressure. The films were obtained at a power of 75 W and a temperature of 100

using a Pt/C target. It is clear that the ratio increases and then decreases with the pressure. Similar trends were also found for films obtained at different power wattages and temperature. The structure was alos examined using TEM. In Pt/a-C composite thin films, Pt was found in all cases to appear as nanoparticles. This is shown in Fig. 4



for a Pt-a-C thin film obtained at $1x10^{-2}$ Torr and 75 W.



(A)

(B)

Fig. 2. SEM micrographs of (A) a-C thin film obtained using a pure graphite target and 1%H_2/Ar sputter gas and (B) a Pt/a-C film obtained using a Pt/C target and pure argon sputter gas.

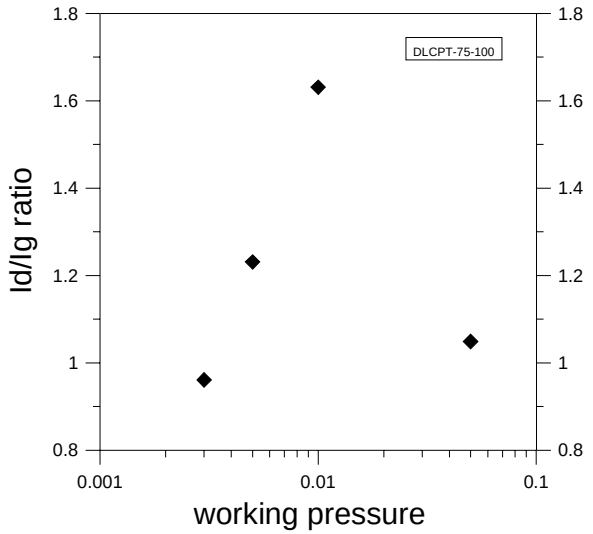


Fig. 3. I_d/I_g ratio as a function of Ar pressure.

Electrochemical analysis was also performed on B-doped diamond. An excellent potential window of 3.5 V was observed in an 1M H_2SO_4 solution, as shown in Fig. 5.

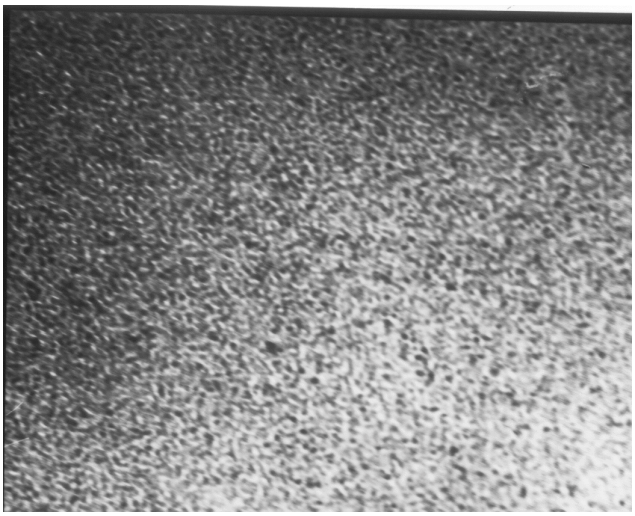


Fig. 4. TEM image of a Pt-a-C thin film obtained at $1x10^{-2}$ Torr and 75 W. The dots are Pt with an average diameter of 3.3 nm.

Conclusion

Various Pt/a-C composite thin films were obtained using a sputter deposition technique. The characteristics of the resulting thin films were examined. Raman signatures suggest an optimum pressure for I_d/I_g ratio wnd TEM analysis indicate the presence of nano-sized Pt in a-C thin films.

Acknowledgement

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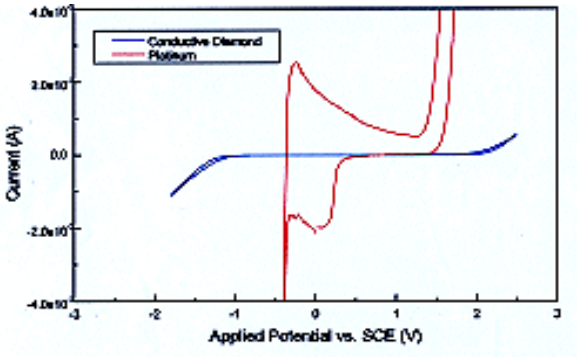

Fig. 5. Potential window of B-doped diamond and platinum.

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