

## DETECTION OF LEAD AND COPPER WITH NITROGEN DOPED DIAMOND-LIKE CARBON THIN FILMS

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### ABSTRACT

Nitrogen doped diamond-like carbon (N-DLC) thin films were prepared on n-Si substrates using a filtered cathodic vacuum arc deposition method. Square wave anodic stripping voltammetry (SWASV) was used to trace Pb and Cu in a neutral KCl solution with pH 7. Stripping voltammograms of Pb and Cu were analyzed in terms of metal concentration, deposition time and deposition potential. The SWASV results showed that the N-DLC film electrodes were promising electrodes to detect Pb and Cu in the neutral solution at about  $\mu\text{M}$  level.

**Keyword:** DLC thin films; N doping; SWASV; Neutral KCl solution

### 1. INTRODUCTION

Pb is of great concern because of the high toxicity of its compounds and accumulation in various organisms [1]. It was reported that a Pb concentration  $\geq 4 \text{ Mm}$  in drinking water is detrimental to fetuses and children with possible development of neurological problems [1]. Although Cu has been found to have relatively low toxicity to human being, prolonged consumption of a large dose can result in some health complications [1]. For Cu, a concentration  $\geq 8 \times 10^{-5} \text{ M}$  can adverse chronic effects [1]. Therefore, fast detection and determination of trace heavy metals are a tough challenge for analysts.

Recently, Khun et al. [2, 3], Liu et al. [4] and Zeng et al. [5, 6] reported that nitrogen doped diamond-like carbon (N-DLC) films had wide electrochemical potential windows in different aqueous solutions and high signals to single and multiple elements at about  $\mu\text{M}$  level. However, such heavy metal tracing was carried out only in the aqueous solution with low pH value. It is known that conducting of electrochemical analysis in corrosive medium (an acidic solution) can cause the corrosion of the electrodes. In addition, an introduction of nitrogen itself into DLC films reduces the corrosion resistance of the film by promoting  $\text{sp}^2$  bonds that degrade  $\text{sp}^3$ -bonded cross-linking structure [7]. The poor corrosion resistance of the films can strongly affect the sensitivity, repeatability, long-term response stability and robustness of the films. Therefore, it becomes tough to improve the sensitivity of N-

DLC films to detect trace heavy metals in neutral solutions at very small concentration.

In this study, nitrogen doped diamond-like carbon (N-DLC) thin films were prepared on n-Si substrates using a filtered cathodic vacuum arc deposition method. Detection of Pb and Cu with the N-DLC film electrodes in a neutral KCl solution with pH 7 was conducted using square wave anodic stripping voltammetry in terms of metal concentration, deposition time and deposition potential.

## 2. EXPERIMENTAL DETAILS

Nitrogen doped diamond-like carbon (N-DLC) thin films were deposited on n-Si (100) substrates ( $0.001 - 0.0035 \Omega \text{ cm}$ ) for 250 sec using a filtered cathodic vacuum arc (FCVA) deposition method. During the room temperature film depositions, a pulsed DC bias of 800 V was used and a nitrogen flow rate of 40 sccm was introduced into the deposition chamber. The thickness of the N-DLC films used was about 100 nm.

The bonding structure of the N-DLC films was characterized using a confocal micro-Raman spectroscope (Renishaw RM1000) having a He-Ne laser (632 nm) over the range of  $800-2000 \text{ cm}^{-1}$ . The Raman instrument had a spectral resolution of  $1 \text{ cm}^{-1}$  and a spatial resolution of  $1 \mu\text{m}$ .

Atomic force microscopy (AFM, Digital Instruments, S-3000) was used to measure  $R_a$  values of the N-DLC films in the scan size of  $1 \mu \times 1 \mu\text{m}$ .

Detection of heavy metals such as Pb and Cu was carried out with square wave anodic stripping voltammetric technique (SWASV) using Bionano workstation (Bionano LK6200) that had a potential resolution of 0.1 mV and a current resolution of better than 0.1 pA and was equipped with a three-electrode flat cell kit. The potential increase, frequency, amplitude and quiet time used were 0.15 V, 10 Hz, 0.15 V and 10s, respectively. An unstirred 0.1 M KCl solution with pH 7 was used as a background electrolyte. All the chemicals employed in this study were analytical reagent grades. For the three-electrode flat cell kit, the film coated sample served as the working electrode while the standard silver/silver chloride (Ag/AgCl) in a saturated KCl solution acted as the reference electrode. For the counter electrode, a platinum mesh was used. The testing region on the films was a circular area of 1 cm in diameter.

## 3. RESULTS AND DISCUSSION

The bonding structure of the N-DLC film deposited with 40 sccm  $\text{N}_2$  is characterized using micro-Raman spectroscopy and the resultant Raman spectrum is fitted using Gaussian functions for both G and D peaks. It is found that the G and D peaks are centered at about  $1546$  and  $1384 \text{ cm}^{-1}$ , respectively. Since G peak comes from in-plane stretching vibration of all  $\text{sp}^2$  sites and D peak is due to breathing vibration of aromatic

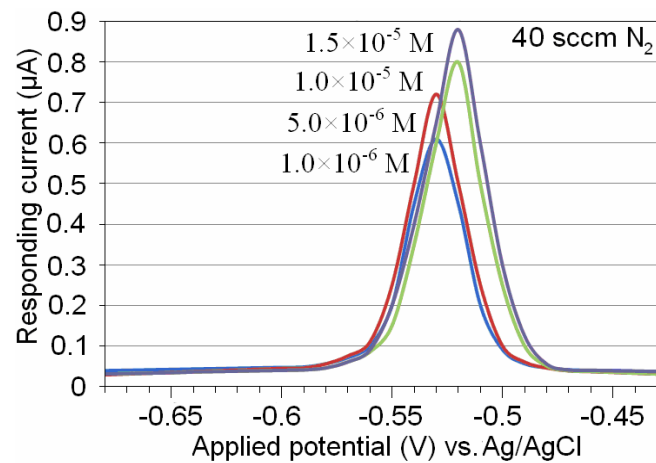
rings, the observed D peak in the N-DLC film indicates the existence of the graphitic phases [7-9]. In addition, intensity ratio between the D and G peaks of the N-DLC film is 0.62 and confirms an occurrence of clustering of the graphitic rings.

The  $R_a$  value of the N-DLC film deposited with 40 sccm  $N_2$  is about 0.19 nm indicating that this film possesses a rather smooth surface.

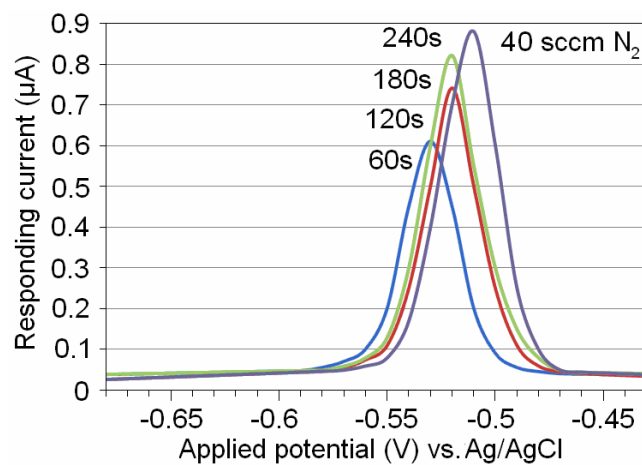
Fig. 1a shows the stripping voltammograms of Pb obtained from the N-DLC film deposited with 40 sccm  $N_2$  as a function of Pb concentration. From Fig. 1a, it is found that an increase in the concentration of Pb in the KCl solution causes the stripping peak intensity to rise. A higher concentration of Pb constitutes to more  $Pb^{2+}$  ions available in the solution which can be deposited on the film electrode surface and therefore more amount of  $Pb^{2+}$  ions being stripped. As a result, there will be a higher stripping peak intensity observed. Thus, the stripping peak intensity increases as a function of Pb concentration in the solution.

The stripping voltammograms of Pb obtained from the N-DLC film (40 sccm  $N_2$ ) as a function of deposition time are reported in Fig. 1b. A longer deposition time results in a higher stripping peak intensity as shown in Fig. 1b. The amount of analytes available on the surface of the film electrode at the stripping stage is dependable on the deposition time. A longer deposition time constitutes to more amount of  $Pb^{2+}$  ions deposited on the film electrode surface, resulting in more  $Pb^{2+}$  ions stripped and hence a higher stripping peak intensity [10]. Thus, a higher stripping peak intensity is found as the deposition time increases.

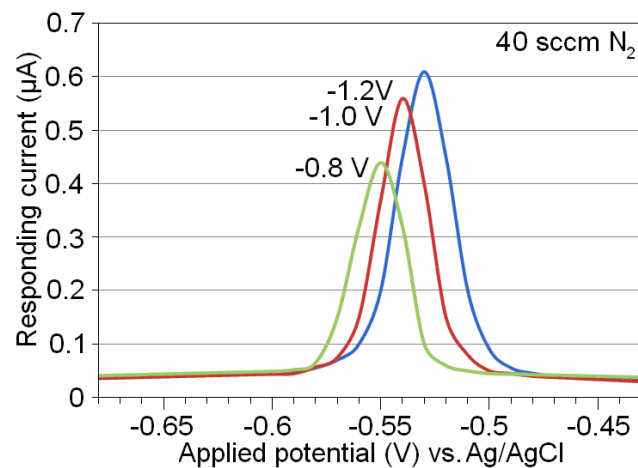
The stripping peaks of Pb obtained from the N-DLC film (40 sccm  $N_2$ ) apparently develops with increased deposition potential as shown in Fig. 1c. A higher negative deposition potential increases the mobility of the  $Pb^{2+}$  ions in the solution, causing the  $Pb^{2+}$  ions to move faster towards the film electrode surface. This results in an increased amount of  $Pb^{2+}$  ions deposited on the surface of the film electrode, eventually leading to a higher stripping peak intensity [3].



(a)



(b)



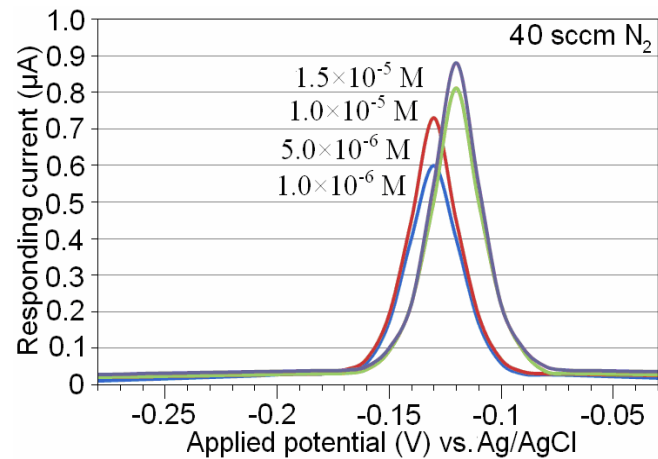
(c)

**Fig. 1: Stripping voltammograms obtained from a N-DLC film electrode (40 sccm  $\text{N}_2$ ) in a 0.1 M KCl (pH 7) solution as functions of (a) Pb concentration, (b) deposition time and (c) deposition potential. For (a), the deposition time and potential are 60 s and -1.2 V, respectively. For (b), the Pb concentration and deposition potential are  $1 \times 10^{-6}$  M and -1.2 V, respectively. For (c), the Pb concentration and deposition time are  $1 \times 10^{-6}$  M and 60 s, respectively.**

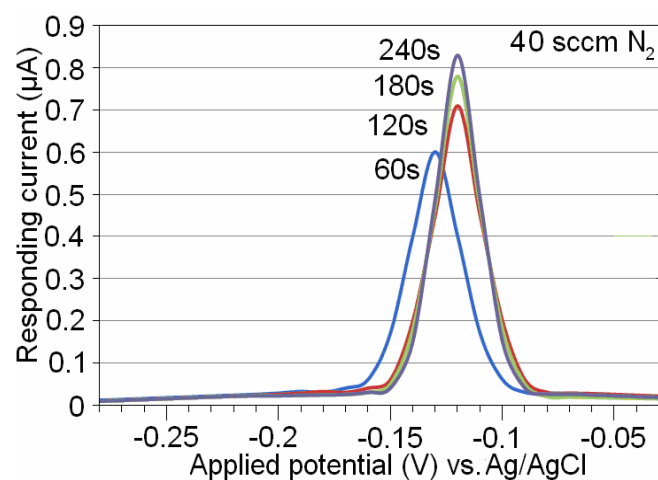
The stripping peaks of Cu obtained from the N-DLC film show the higher stripping peak intensity with higher Cu concentration (Fig. 2a). Under the fixed deposition potential of -1.2 V, the over potential of Cu is higher than that of Pb so the Cu stripping peak intensity coming from the higher deposited Cu atoms on the film electrode surface should be higher than the Pb stripping peak intensity at the same concentration. In addition, the use of the background KCl solution with pH 7 can strongly degrade the deposition of  $\text{Pb}^{2+}$  ions during the accumulation because of the formation of low soluble lead hydroxide in the high pH aqueous solution [11]. However, not much difference between Pb and Cu stripping peak intensities (Fig. 1a and 2a) is found, which may be attributed to the stabilization of  $\text{Cu}^+$  ions with the  $\text{Cl}^-$  ions and the formation of copper oxide at the film electrode surface [3]. It is found that the stripping peak intensities of both Pb and Cu apparently increase with increased metal concentrations (Fig. 1a and 2a), indicating that the transport of the metal ions in the solution remains unrestricted [5]. It is known that the concentration of redox species at the interface region depends on the transport of these species from the bulk solution to the electrode surface. During the accumulation, the deposition of the metal ions as atoms on the film electrode surface consumes the metal ions in the interface region causing concentration gradient that facilitates the transport of the metal ions to the film electrode surface [11]. Therefore, the increased metal concentration pronounces such concentration gradient so that the transport of the metal ions becomes faster with increased metal concentration giving rise to the higher stripping peak intensity.

Usually, an excessive deposition time would result in interference due to formation of intermetallic compounds and should be avoided, unless the concentration of the metal ions is extremely dilute [5]. The significantly increased stripping peak intensities of both Pb and Cu (Fig. 1b and 2b) with increased deposition time point out that the low concentrations of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions at about  $\mu\text{M}$  probably prevent the occurrence of such phenomenon.

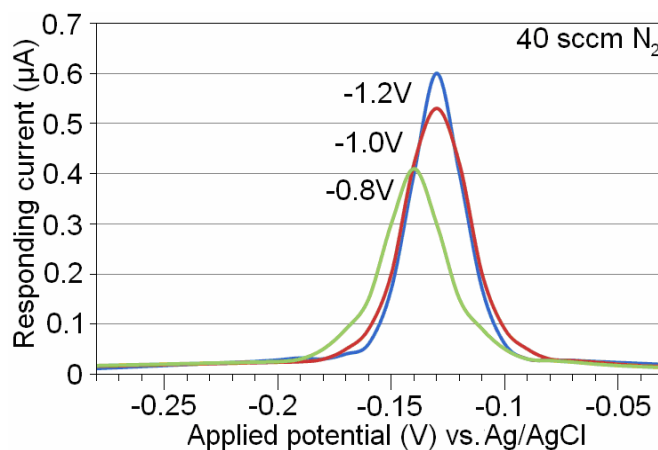
It is known that the increased negative deposition potential can develop the hydrogen evolution that causes disruption of the deposition of the metal ions on the film electrode surface to some extent [5]. The observation of the distinguishable stripping peaks of both Pb and Cu with deposition potential (Fig. 1c and 2c) indicates no significant disturbance of the developed hydrogen evolution with increased negative deposition potential from -0.8 to -1.2 V vs. Ag/AgCl on the deposition of the metal ions onto the film electrode surface.



(a)



(b)



(c)

**Fig. 2:** Stripping voltammograms obtained from a N-DLC film electrode (40 sccm  $\text{N}_2$ ) in a 0.1 M KCl (pH 7) solution as functions of (a) Cu concentration, (b) deposition time and (c) deposition potential. For (a), the deposition time and potential are 60 s and -1.2 V, respectively. For (b), the Cu concentration and deposition potential are  $1 \times 10^{-6}$  M and -1.2 V, respectively. For (c), the Cu concentration and deposition time are  $1 \times 10^{-6}$  M and 60 s, respectively.

At the same time, the stripping potentials of both Pb and Cu shift to more positive values with increased metal concentration, deposition time and deposition potential as shown in Figs. 1 and 2. The shifts of the stripping potentials of both Pb and Cu to more positive values with increased metal ion concentration and deposition time (Figs. 1a and b and 2a and b) can be explained by adopting the propose by Khun et al. [3] in which the increased amount of the stripped metal ions shifts the stripping potential to lower negative value according to the Nernst equation. The amount of the stripped metal ions is directly related to the amount of the deposited metal atoms on the film electrode surface which can be increased by two ways: (i) increasing metal concentration and (ii) increasing deposition time. Therefore, the increased amount of the stripped  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions with increased metal concentration and deposition time lead to the shifts of the Pb and Cu stripping potentials to more positive values, which is in a good agreement with the report made by Khun et al. [3].

When a flux of metal ions to the electrode surface is slower than an electrode reaction, an equilibrium between oxidized and reduced species involved in the electrode reaction is established at the film electrode surface, which indicates a reversible reaction corresponding to a case where the electrode reaction is much faster than the transport of the metal ions. As shown in Figs. 1c and 2c, the shifts of the stripping potentials of Pb and Cu to more positive values with more negative deposition potentials indicate quasi-reversible-reactions of Pb and Cu on the surface of the N-DLC film electrode, implying that the electrode reaction is slower than the transports of the  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions. Therefore, it can be expected that there is a kinetic limit upon the electrode reaction compared to the transports of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions.

#### 4. CONCLUSIONS

Nitrogen doped diamond-like carbon (N-DLC) thin films were prepared on n-Si substrate using a filtered cathodic vacuum arc deposition method. Square wave anodic stripping voltammetric method was used to trace heavy metals of Pb and Cu at about  $\mu\text{M}$  in the neutral KCl solution with pH 7. Tracing analysis of these metals was carried out in terms of metal concentration, deposition time and deposition potential. From the stripping voltammetric results, it was found that N-DLC films provided a significant stripping response for determination of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  in the neutral solution, showing a great promise for the analysis of heavy metals.

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