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Aroused problems in the deposition of diamond-like carbon films by using the liquid phase electrodeposition technique

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Hydrogenated diamond-like carbon (DLC) films were prepared by using liquid phase electrodeposition technique. The effects of the applied potential and the carbon sources on the deposition process and film structures were studied. It has been found that the organic liquids with high dielectric constants, small viscosities and the methyl group bonding to the polar group are appropriate carbon sources. The increasing of potential improves the formation of sp^3 carbon during the deposition process. In a high electric field, organic molecules are polarized and reacted on the surface of the electrode, turning out DLC and other products. It is believed that the reaction follows a polarization-reaction mechanism.

1. Introduction

The deposition of carbon film by using liquid phase electrodeposition technique has attracted great interest in recent years [1–6], as the process is carried out at room temperature or below. In a high electric field, organic molecules react on the surface of the electrode and form carbon and other products. The properties and the microstructure of carbon films mainly depend on the preparation conditions, such as carbon source, deposition parameters, electrode substrates and so on. This paper describes how some carbon sources were chosen to deposit diamond-like carbon (DLC) films and studies the influence of the carbon sources and deposition parameters on the deposition process and the film microstructures. The reaction mechanisms are also discussed.

1.1. The selection rule of carbon sources

Since Namba [1] attempted to deposit carbon films by electrodeposition in alcohol solution, efforts [2–4] have been devoted to synthesize DLC films by the liquid phase deposition techniques. The results obtained were not encouraging: only graphitic or glass carbon materials were deposited while using the ethanol or ethylene glycol solution [2, 3]. Recently, Wang *et al.* [5, 6] and Novikov [7] reported that DLC films with a resistivity of 10^8–10^{10} Ω cm could be obtained in methanol or in a solution of acetylene in liquid ammonia as the starting electrolyte. The results suggested that the properties of the deposited films were affected by the source of carbon.

1.1.1. The dielectric constant of carbon sources

The electrodeposition is a synthesis process by an electrochemical method. Traditional electrochemical reaction takes place in ion solutions or organic solutions containing a conductive medium. The reaction can be carried out under low potentials (several voltages) since the conductive ability of the solution is high. But the deposition reaction of DLC films is carried out in an organic liquid, which is a non-conductor and does not contain any conductive ions. In the deposition process, when the potential is applied to the electrodes, the molecules of the deposited liquid are polarized and react on the surface of the electrodes. The polarization ability of the molecules depends mainly on their properties and structures, which further affects the electrodeposition process in the present reaction.

Hence, we chose some organic liquids with different dielectric constants and measured the current density during electrodeposition process. The experimental setup has been described earlier [6]. The distance between the substrate (Si) and negative electrode (graphite) was 4 mm. The samples were deposited at 60°C by using a pulse-modulated electric source. The modulation duty cycle is 70% and modulation frequency 7 KHz. Fig. 1 shows the relationship between the current density of the substrate and the applied potentials in different organic liquids.

In Fig. 1 the current density increases linearly with the applied potential in all media. However, acetone, 2-propanol and tetrahydrofuran show a poor current density of only a few microamperes per square

TABLE I Physics constants of carbon sources

Carbon sources	Boiling point (°C)	Dielectric constant (ε)	Dipole moment (D)	Viscosity ($\mathrm{mN \cdot s \cdot m^{-2}}$)
Acetonitrile	81.6	37.5	3.92	0.375
DMF	153	36.71[25]	3.86[25]	0.802[25]
Methanol	64.7	32.7[25]	1.70	0.544[25]
Ethanol	78.4	24.55[25]	1.69	1.078[25]
Acetone	56.5	20.70[25]	2.88	0.337[25]
2-propanol	82.5	18.3[25]	1.66	1.765[30]
Tetrahydrofuran	65	7.58[25]	1.75[25]	0.55
Ethylene glycol	197.4	38.66	2.20	21
Glycerin	290	42.5[25]	2.56	945[25]

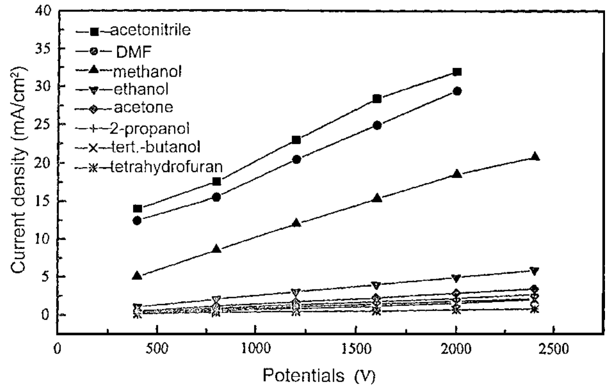

Figure 1 The dependence of current density on voltage.

centimeters. Ethanol shows a current density of about 6 $\mathrm{mA \cdot cm^{-2}}$ under 2400 V, whereas acetonitrile, N, N-dimethyl formamide (DMF) and methanol exceed 15 $\mathrm{mA/cm^{-2}}$ at a low potential of 1600 V. Higher current density indicated that more polarized particles move and react on the surface of the electrode per unit time, which has some effect on the growth rate of the film. In our experiments, no deposits could be seen by the electrochemical reaction of acetone, 2-propanol and tetrahydrofuran. The thickness of film deposited is above 1 μm in acetonitrile, DMF and methanol for 10 h at 1600 V, and the thickness is only 0.6 μm in ethanol.

We know that the properties and the structure of the medium affect the polarization of the molecules, which results in the difference in the deposition rate. Table I shows some physical constant of medium [8]. It is shown in Table I and Fig. 1 that the dielectric constant of a liquid is related to the current density. The dielectric constant decreases gradually from acetonitrile (37.5) to tetrahydrofuran (7.58). The decrease agrees with the order of the decreasing current density.

The deposition reaction of DLC film is carried out between two parallel electrodes, which can be regarded as an ideal parallel-plate capacitor. When the capacitor is full of a medium with a dielectric constant of ε, the medium can be polarized in the electric field. There is induction charge on the surface of the plate, and the density of the induction charge (also called polarization ability) P can be represented by the equation

$$P = \varepsilon_0(\varepsilon - 1)E$$

where ε_0 is a constant, and ε is the dielectric constant of the medium (an organic liquid). E is the electric field, which is proportional to the potentials applied to the two plates ($E = U/d$). Under the same deposition conditions, P is in direct proportion to the dielectric constant ε only. From Table I, the dielectric constants of acetone, 2-propanol and tetrahydrofuran are very low, whereas those of acetonitrile, DMF and methanol are high, which is responsible for the difference in the molecular polarization ability. Hence acetone, 2-propanol and tetrahydrofuran have low current density, and acetonitrile, DMF and methanol high current density.

The above results show that an organic liquid with a high dielectric constant is a suitable carbon source for the liquid phase deposition of carbon films.

1.1.2. The viscosity of carbon sources

Carbon sources with high dielectric constants are suitable for the deposition of carbon films, but though ethylene glycol and glycerin have higher dielectric constants in all selected carbon sources, no carbon film was deposited on the substrates under the same experimental conditions. From Table I, the author attributed the cause to the viscosity factor of the carbon source. During deposition organic molecules are polarized and migrated to the surface of the electrode in the electric field. Then these molecules are absorbed and reacted on the surface of the electrode. In the process, the migration rate of the molecules and the retention time on the surface of the electrode are important factors affecting the reaction rate. Carbon sources with higher viscosities decrease their fluid ability and hinder the migration of the molecules. It will take more time for the molecules to migrate from the liquid to the surface of the electrode and for the products to leave from the electrode to the liquid, which affects further the reaction of the molecules. The above factors lead to the decrease of the deposition rate, so no obvious deposit can be seen on the substrates by using carbon sources with high viscosities. From Table I, we know that although ethylene glycol and glycerin have higher dielectric constants than acetonitrile, DMF and methanol, no obvious deposit can be obtained under the same deposition conditions. Hence, it is necessary that carbon sources for the deposition of a carbon film in the liquid phase must have higher dielectric constants and low viscosities as well.

1.1.3. The molecular structure of carbon sources

Many researches show that carbon sources with a methyl group are suitable for the deposition of DLC or diamond by vapor phase methods. We have compared the deposition results of different carbon sources with or without a methyl group.

Acetonitrile, DMF, methanol and ethanol have been chosen as deposited carbon sources. The deposition condition is the same except for the potential which is fixed at 1000 V. The substrate is conductive glass. The deposited films are measured by XPS spectra, which indicated that the films contain mainly carbon. The IR spectra of films indicated that there is a little hydrogen in it, and the hydrogen is mainly bonded to the $\mathrm{sp^3}$ carbon [9]. The Raman spectra of the films are shown in Fig. 2. From the figure, the Raman lines of films in

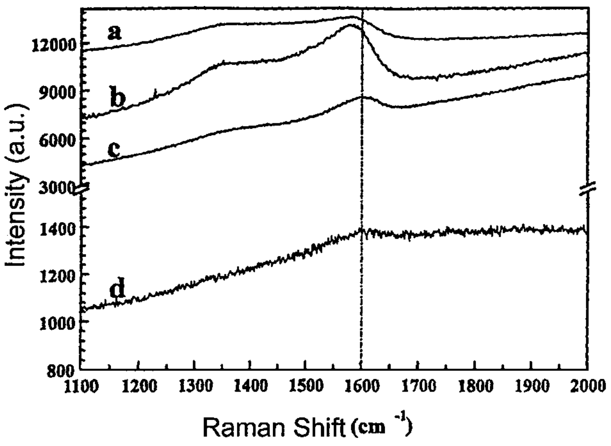

Figure 2 The Raman spectra of films in CH_3CN (a), DMF (b), CH_3OH (c) and CH_3CH_2OH (d).

acetonitrile, DMF and methanol located at 1570 cm^{-1} with a weak tail to low frequency side. The Raman line of films in ethanol consists of only one peak at 1600 cm^{-1}. In general, Raman spectrum of a-C:H film consists of a broad peak at 1570 cm^{-1} (G line) and a shoulder at 1360 cm^{-1} (D line). The low frequency signal (D line) is originated from the distortion structure of sp^2 carbon induced by sp^3 carbon, and the high-frequency signal is characteristic of sp^2 carbon [10–12]. Hence, our results indicate that the films deposited in ethanol contain mainly sp^2 carbon, and the films in the other three liquids are the mixtures of sp^2 carbon and sp^3 carbon, i.e., DLC films.

The results suggested that the structure of the films be related to the molecular structure of the carbon source. Many researchers found that the CH_3 and CH_3^+ are the intermediate states for the deposition of diamond and DLC films in CVD methods. Hence, we infer that the CH_3, CH_3^+ may play important roles in the formation of DLC films by using the liquid phase electrodeposition technique. Under high potentials, organic molecules M–X (M–CH_3 and CH_3CH_2, X = –OH, –CH) can be polarized into $M^{\delta+} \ldots X^{\delta-}$. When the substrates are used as the cathode, the polarized molecules with positive electron $M^{\delta+}$ will turn towards the surface of the substrates. If the energy becomes high enough, the bond between M and X would be broken and the $M^{\delta+}$ particles (CH_3 and CH_3CH_2) react to from carbon films on the substrate surface. According to the reaction mechanism, CH_3 activated state can be obtained directly in acetonitrile ($CH_3 \ldots CN$), DMF ($(CH_3)_2 \ldots NCHO$) and methanol ($CH_3 \ldots OH$). However, with the ethanol liquid, where CH_3 group bonded directly to another carbon atom, when the molecules are polarized, CH_3CH_2 activated state would be broken first. In order to obtain CH_3 activated state, more bonds must be broken in the CH_3CH_2 particles. This may be the major factor in selecting different carbon source.

Based on the above analysis, the author put forward the conditions for selection of appropriate carbon source for the deposition of DLC films by the liquid phase electrodeposition technique. They should have higher dielectric constants, small viscosities, and a methyl group bonded directly to highly negative charged atom.

2. Methods of improving sp^3 carbon in the films by the liquid phase deposition technique

It is also a key problem for deposition of films containing high content of sp^3 carbon. The properties of the films may be improved by choosing a suitable carbon source and enhancing the power applied to the reaction process.

2.1. The comparison among films deposited in acetonitrile, DMF and methanol liquid respectively

The Raman spectra of films in acetonitrile, DMF and methanol liquid are shown in Fig. 2. In order to quantitatively analyze the difference of Raman spectra, commercial non-linear curve fitting software was used to deconvolute the spectra. The results are shown in Table II. From Table II, the position of G line changes with the different carbon sources. The G line downshifts from 1575, 1573 to 1569 cm^{-1} in methanol, DMF and acetonitrile. The intensity ratio I_D/I_G of D and G lines increases in the same order, being 1.67 in methanol, 1.92 in DMF and 2.02 in acetonitrile.

In general, the microstructure and degree of disorder can be analyzed in terms of D and G line position, line width, and I_D/I_G intensity ratio in Raman spectra of carbon films. A report on the density of states (DOS) calculated by Beeman *et al.* [13] has shown that the G line shifts towards lower frequency in Raman spectrum with the increase of the percentage of sp^3 bonding. Richter [14] also found that frequency shifts in the G line are caused by changes in the force constants associated with the change in the sp^3-bonding fraction. The same results have also been reported by Kitabatake [15] and Yoon [16] for DLC films deposited by ion beam sputtering and electron cyclotron resonance, respectively. Hence, the position shift of the G line shows the change fraction of sp^3/sp^2 in the carbon films. The D line is related to the disorder of films, and intensity ratio I_D/I_G determines the degree of disorder in the films [17, 18]. The fitting results indicate that the increase of I_D/I_G ratio suggest the existence of a more intensive disorder in the films from methanol, DMF to acetonitrile. The position shift of the G line indicates that the fraction of sp^3 carbon increases from methanol, DMF to acetonitrile.

From the above results, we may infer that the different dielectric constants of the carbon sources respond to the different I_D/I_G ratios in the present liquid phase method. Increasing the dielectric constant may increase the sp^3 carbon content in the films. From Table I, the dielectric constant of carbon sources increases from

TABLE II The fitting results of Raman spectra

	D line		G line		
Carbon sources	Position (ω)	Half-high width ($\Delta\omega$)	Position (ω)	Half-high width ($\Delta\omega$)	ID/IG
Acetonitrile	1391	221	1569	101	2.02
DMF	1390	220	1573	98	1.92
Methanol	1392	217	1575	92	1.67

methanol, DMF to acetonitrile. Under the condition of applying high potential methyl group can be obtained more easily in acetonitrile than in methanol. Therefore, the sp^3 carbon content in the films is more in acetonitrile than in methanol during deposition process.

2.2. The formation of sp^3 carbon can be increased by increasing the potential

The electrochemical reaction is completed mainly on the surface of the electrodes. As the ability of the electrode surface determines the deposition process and the properties of the deposition film, we may apply high potentials to make the deposition surface have high activity, thus increasing the sp^3 carbon content in the deposition film which at the same time will show good physical–chemical properties, in terms of electric resistance and hardness. The results we obtained conform to what we have expected.

We deposited carbon films in methanol at two applied potentials of 800 and 1600 V and measured its resistivity and hardness. The results indicated that the resistivity and hardness of film increase with the increasing potential applied to the electrode, the resistivity increasing from 10^5 to 10^8 Ω cm, and the hardness from 4500 to 6000 kg/mm^2. The properties of the DLC films can be determined by the ratio of sp^3/sp^2. In general, the resistivity and hardness of DLC films increase with the increase of sp^3 carbon content in the films.

Raman spectrum is a useful and powerful tool for distinguishing sp^2 and sp^3 carbons. The Raman spectra of films deposited under different applied potentials are shown in Fig. 3. From the figure, Raman spectrum of deposit at a high potential consists of an asymmetric broad band (A line). The band is located at about 1575 cm^{-1} with a weak tail shifting to the low frequency side. The spectrum of deposit at a low potential consists of two narrower band centered at 1575 (G) and 1360 (D) cm^{-1}, respectively (B line). Moreover, A line is superposed on the photoluminescence excited by an incident laser beam. For amorphous carbon films, the most conspicuous trend of Raman line is the narrower line width and increased D line intensity, and hence a corresponding increase in the fraction of sp^2 coordinated carbon in the film [19]. The results indicate that the films deposited at a low potential contain more sp^2 carbon content and the high applied potential could improve the formation of sp^3 carbon in the present liquid phase deposition process.

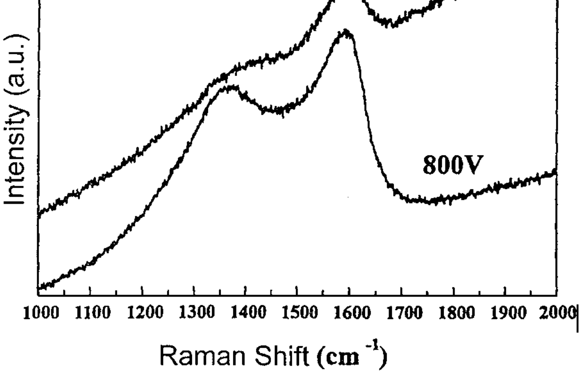

Figure 3 The Raman spectra of films with different applied potentials.

3. Reaction mechanism

The electrochemistry process for liquid phase deposition of DLC films is very complicated. In this paragraph we shall discuss simply the reaction mechanism in terms of the phenomena and results of our test. First, we shall discuss the polarization behavior of the dielectric medium. All molecules from these carbon sources used in deposition of the DLC films are polar molecules. The electron distribution in polar molecules is not symmetric, that is the centers of the positive charge don't coincide with those of the negative charge. When they are exposed to an electric field, the electron distribution becomes more distorted and the distance between the charge centers becomes father apart. The applied electric field distorts the molecular electronic structure and increases the dipole moment of the molecules. This phenomenon is called the polarization.

When the polar molecules are exposed to the electric field, the polarization P of molecule including both the induced and the orientation polarizability, is

$$P = n(\alpha + \mu^2/3\varepsilon_0 kT)E_{\text{eff}}$$

where α is the polarizability of molecule, n is the number of molecules per unit volume, and μ is the dipole moment. E_{eff} is the effective electric field experienced by the medium molecules in the field.

And the polarization of the medium is also written

$$P = 3\varepsilon_0 E_{\text{eff}}(\varepsilon_r - 1)/(\varepsilon_r + 1)$$

where ε_0 is a constant, ε_r is the dielectric constant of the medium, which is a macro parameter describing the polarization of the medium. The dipole moment of the molecules is the micro parameter. And the relationship between ε_r and μ can be expressed:

$$n(\alpha + \mu^2/3\varepsilon_0 kT) = 3(\varepsilon_r - 1)/(\varepsilon_r + 2)$$

which is called the Clausisus–Mosotti equation. From the equation, one can see that ε_r is determined by the value of α and μ. The larger α and μ are, the higher ε_r is, then the polarizability of the medium is enhanced in the same electric field.

When the potential U is applied, the energy of the capacitor is:

$$W = 1/2(CU^2) = \varepsilon_0\varepsilon_r s/2d(U^2)$$

where s is the area of plate plane, d is the distance of between plates. When the potential is increased, the energy of the capacitor will also be increased. Then the polarizable degree of the medium will be enhanced. In the present experiment for the deposition of DLC films, the ability depends mainly on the polarization of the medium in these organic liquids. Under high dielectric constant and high-applied potentials, the polarization of medium is enhanced and then the reaction current density increases. The results can be observed in Fig. 1.

Table III has listed the chemical bond energy and bond length of correlated molecules. From the table,

TABLE III The intensity or length of relative chemical bonds

Chemical bonds	CH_3—OH	CH_3O—H	$(CH_3)_2$—NCOH	$(CH_3)_2N$—COH	CH_3—CN	C≡N
Bond energy (Kcal/mol)	91	104	—	—	119	204
Bond length (nm)	0.143	0.097	0.147	0.132	0.149	0.116

we can see that the chemical bond between the CH_3 group and polar group is the weakest. In a chemical reaction, these weak bonds are always broken first.

According to the above analysis, we infer that the deposition reaction of DLC films follows a polarization-reaction mechanism. And the detailed reaction process is as follows:

1. The centers of the negative and the positive charge aren't coincident in these polar carbon source molecules, and the electron distribution is partial to the polar group.
2. Under high potentials, polar molecules are induced to polarize, the electron structure would change further, the distance of the centers becomes greater, and the molecules turn into energized molecules:

$$CH_3X \xrightarrow{\text{high potential}} CH_3 \cdots X$$

(energized molecules)

3. When a high potential is applied to the surface of the electrode, the surface is activated and becomes the reaction-activated site.
4. Energized molecules CH_3X^* move to the surface of the electrode and are absorbed on the activated sites, turning into activated molecules.

$$CH_3X^* \xrightarrow{\text{absorbed on the activited sites}} CH_3X^{\neq}$$

(activited molecules)

5. Activated molecules brough about the oxidation–reduction reaction on the electrode turn to carbon and other products.

$$CH_3X^{\neq} \xrightarrow{\text{electrochemical reaction}} C + \text{other products}$$

6. Forming continuous carbon films.

The mechanism is only described simply in terms of the experimental and measurement results in our research. However, up to now there are still many problems that need to be studied. Such as the nucleation and growth process of the methyl group absorbed on the surface of the electrode, and methyl group decomposed to the formation of sp^2 or sp^3 carbons in the growth process, etc. These problems must be studied further in order to deposit perfectly DLC or diamond films in the liquid phase.

4. Conclusion

We have mainly studied some problems in the formation process of DLC films by using the liquid phase electrodeposition technique with the following conclusions:

1. The selecting of carbon sources show that some organic liquids, which have higher dielectric constants, small viscosities, and with a methyl group bonded directly to the polar groups, are appropriate carbon sources for the deposition of DLC films by the liquid phase electrodeposition technique.
2. The structure of the films is related not only to the carbon sources but also to the applied potential. High potential can improve the formation of sp^3 carbon.
3. The deposition reaction of the carbon films in the liquid phase follows a polarization-reaction mechanism. Under high-applied potentials, the polar carbon source molecules can be polarized into energized molecules, which move to and are absorbed on the surface of the electrode and become activated molecules. These activated molecules react and turn into carbon films.

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