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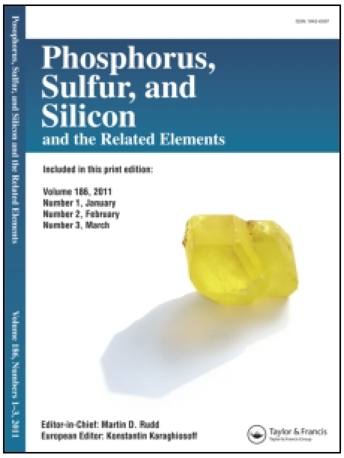

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Structural Characteristics and Electrode Activities of Phosphorus Incorporated Tetrahedral Amorphous Carbon Films

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Studies on structural properties and electrochemical behaviors of conductive phosphorus incorporated tetrahedral amorphous carbon (ta-C:P) films deposited using filtered cathodic vacuum arc technique with PH_3 as the dopant source are presently reported. The structural characteristics of the films are characterized by X-ray photoelectron spectroscopy, Raman spectroscopy and Fourier transform infrared spectroscopy. The electrochemical reactivity of ta-C:P films are evaluated by cyclic voltammetry and differential pulse voltammetry. We find that phosphorus implantation enhances the clustering of sp^2 sites dispersed in sp^3 skeleton, develops the densities of π and π^* states and improves the electrical and electrochemical behaviors of the films. It has been established that the inorganic films with amorphous structure appear excellent electrical conductivity and electrochemical activity similar to boron-doped diamond or nitrogen-doped amorphous carbon electrodes. These characteristics demonstrate greatly potential application of ta-C:P films as electrode materials in terms of its large electrochemical potential window, low background current, and a considerable electrochemical activity towards ferricyanide reduction and metal ions analysis.

Keywords Cyclic voltammetry; filtered cathodic vacuum arc; electrodes; phosphorus incorporated tetrahedral amorphous carbon films

INTRODUCTION

Phosphorus incorporated amorphous carbon (a-C:P) or phosphorus incorporated tetrahedral amorphous carbon (ta-C:P) films are attractive semiconductor materials which can be synthesized via different physical and chemical methods including filtered cathodic vacuum arc (FCVA), ion-beam sputtering, pulsed laser, plasma immersion

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ion implantation and chemical vapor deposition technology.[1–5] Red phosphorus (P_4), trimethylphosphite ($P(OCH_3)_3$) and phosphine (PH_3) are usually workable phosphorus sources.[1–7] In previous reports, for example, Veerasamy prepared ta-C:P films with a low level of phosphorus impurities by using P_4 as a dopant.[1] Pearce adopted CH_4 and PH_3 as the reactive gas and deposited amorphous carbon phosphide with the ratio of phosphorus and carbon atoms up to 3. He also confirmed the existence of C—P bonds in this system by SIMS analysis.[7] However, there is still limited work involved to the studies of the inorganically amorphous carbon and phosphorus compounds. And most of the examinations devoted to investigate the carbon and phosphorus bonding structures are focused on the organic phosphide via the experimental measurement and academic calculation.[8–15] We report here an efficiently synthetic method to elaborate ta-C:P films by using FCVA technique with graphite and PH_3 as the carbon and phosphorus sources, respectively. The structural characteristics and electrode activities of the films are further discussed in detail.

RESULTS AND DISCUSSION

Figure 1 shows a typical overview of X-ray photoelectron spectroscopy (XPS) for ta-C and ta-C:P films. The existence of phosphorus in ta-C:P film is indicated by the two peaks located at 132.4 ± 0.2 eV and 189.5 ± 0.2 eV as P 2p and P 2s spectra, respectively. Due to the unsymmetric lineshape, the P 2p spectrum is fitted with a combination of two

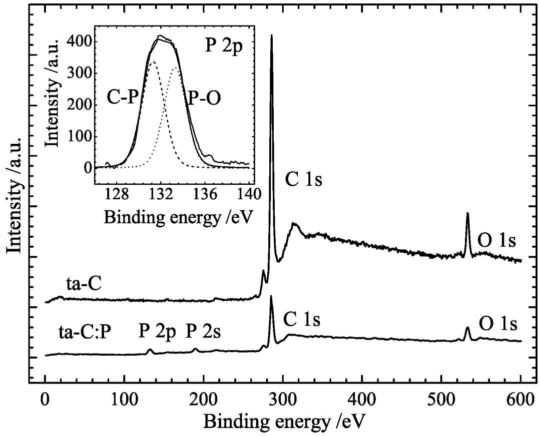

FIGURE 1 XPS spectra of un-doped ta-C and ta-C:P film with 6-sccm PH_3 introduction. Inset is the XPS core level spectrum of P 2p for ta-C:P film.

contributions: a low binding energy component centered at 131.3 ± 0.2 eV and a high binding energy component centered at 133.4 ± 0.2 eV, respectively. We assign the former to the possible function of C-P, while the latter is associated with P—O bonds.[16] The peak centered at 285.4 ± 0.2 eV is caused by the photoelectrons excited from the C 1s spectra. A slight shift of C 1s spectrum towards a lower binding energy is detected by the addition of phosphorus, which indicates the increasing C = C bonding structures. An oxygen signal at 533.2 ± 0.2 eV is the result of air exposure during the experiment and sample transport. The content of phosphorus over the sum of phosphorus and carbon (P/(C+P)) is calculated as 5.8 at.%.

Figure 2 illustrates the Raman spectra of ta-C and ta-C:P films which possess the sensitive and nondestructive features for characterization of the bonding transformation in carbon materials. It appears that the lineshape of two spectra is similar and exhibits a broad band between 1000 and 1800 cm^{-1}determined as the first-order peak of carbon, indicating the amorphous structures of the films. Considering the asymmetry of the band, it depends on D peak centered at about 1370 ± 5 cm^{-1} and G peak centered at 1557 ± 10 cm^{-1}. G peak is attributed to the bond stretching of all sp^2-bonded carbon in rings as well as chains, while D peak is the breathing modes of disordered graphite rings. As seen from the figure, phosphorus incorporation causes the intensity ratio of D and G peaks, $I_{(D)}/I_{(G)}$, increase from 0.31 to 0.34 which is an image of the clustering of sp^2 groups, i.e. an evolution of C=C configurations.[13,17]

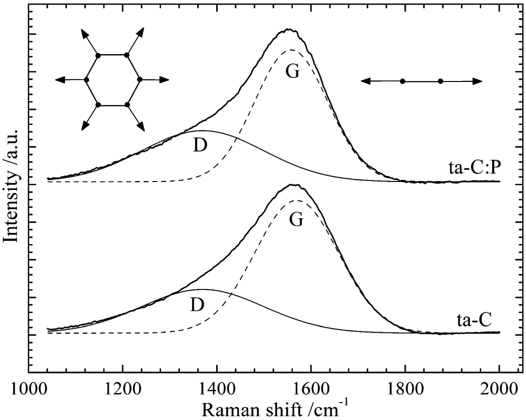

FIGURE 2 Raman spectra of ta-C and ta-C:P films with the eigenvectors of the Raman G and D modes. The broad brushes are the measurements; the dash lines and the thin solid lines are the fitted G and D peaks, respectively.

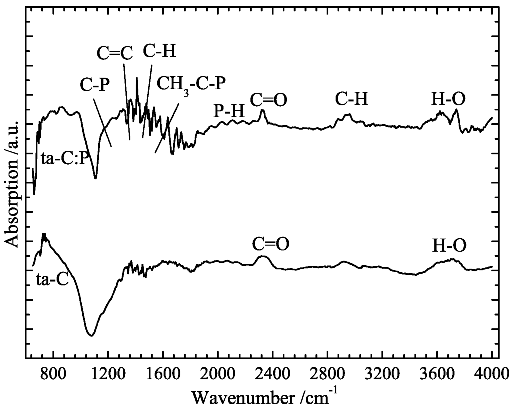

FIGURE 3 IR spectra of ta-C and ta-C:P films.

Figure 3 displays the infrared (IR) spectra of ta-C and ta-C:P films which are widely used nondestructive probes of the bonding in carbon systems. ta-C does not show any significant IR signal because the remaining sp^2 sites in ta-C are localized in isolated π bonds, which gives a much smaller IR activity. In contrast, ta-C:P film demonstrates IR activated. The feature in the 1100–1300 cm^{-1} region is possible due to the C and P stretching mode.[12] The regions at 1375 cm^{-1} and 1460 cm^{-1}contain both C-C skeleton modes and sp^3 $CH_{2,3}$ bending modes.[18] The C—C—P vibration may be located at 1550 cm^{-1} and coupled with CC stretching.[12] The range of 2850–3040 cm^{-1} is attributed to the C-H stretching mode. Additionally, the C=O mode at 2300 $cm^{-1}$is due to oxygen contamination in the sample and the H-O mode at 3600 cm^{-1} is due to water vapor in the air. There is a slight signal of P—H existence at about 2100 cm^{-1}. From above analysis we conclude that the increase in the IR activity after phosphorus implantation originates from the large dynamic charge of the more delocalized π bonding which occurs in more sp^2-bonded networks.[18]

Phosphorus impurities not only change the bonding structures of carbon network, but also improve the conduction behavior of ta-C films, which hints the potential application of ta-C:P as an electrode material. From the viewpoint of fundamentally electrochemical properties as well as that of applications, one of the most important criteria for excellent electrode performance is a wide potential window. Figure 4 shows significant differences in the potential windows of ta-C and ta-C:P electrodes. It appears that ta-C film does not represent evident activity to the redox reaction of water due to its poor conduction, while ta-C:Pelectrode provides a wide potential window, around 1.67 V. In addition, the kinetics

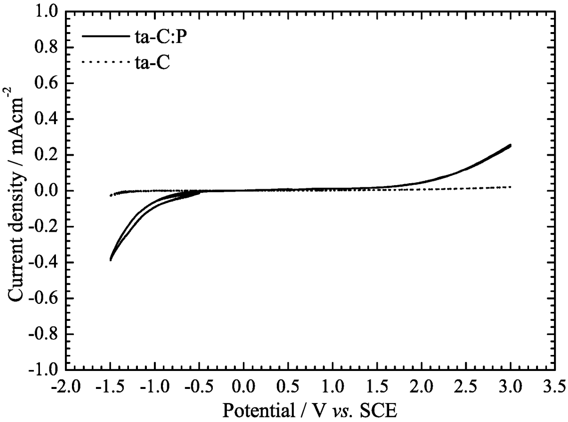

FIGURE 4 Cyclic voltammograms of ta-C and ta-C:P electrodes in 0.5 molL^{-1} H_2SO_4 solution with a scan rate of 0.1 Vs^{-1}.

of $Fe(CN)_6^{3-/4-}$ redox couple is greatly affected by phosphorus impurities in ta-C:P electrode. Ta-C:P exhibits a semi-reversible behavior with a peak potential difference (△ Ep) of 360 mV and a peak current ratio (I_p^{ox}/I_p^{red}) of 0.86 (Figure 5). While ta-C electrode with a high resistivity indicates electrochemically inactive and no remarkable current peak is observed, or the current hardly exceeds the residual current. Based on above experimental phenomena we suggest that the doping agent appears to be of primary importance to enhance the electrical conductivity and electrochemical response of ta-C:P electrode.

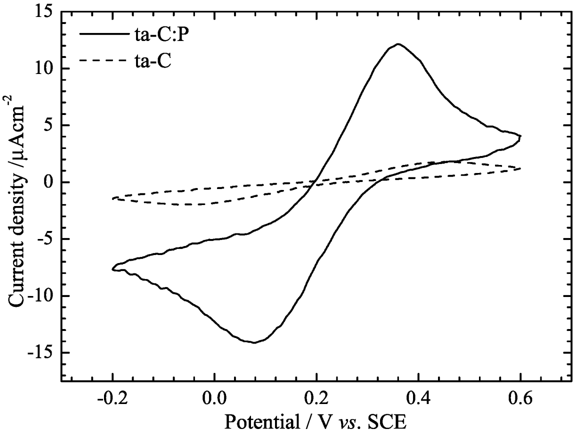

FIGURE 5 Cyclic voltammograms of ta-C and ta-C:P electrodes in 0.01 molL^{-1} $K_3Fe(CN)_6$ and 1 molL^{-1} KCl solution with a scan rate of 0.02 Vs^{-1}.

The procedure described here may be an acceptable method for the preparation of ta-C:P with different phosphorus content by controlling the flow rate of PH_3. Phosphorus impurities favor the rearrangement of carbon skeleton. The one-pot nature of the present film makes it an interesting application as an electrochemical electrode.

EXPERIMENTAL

Preparation of ta-C:P Films

ta-C and ta-C:P films were deposited on highly conductive p-type Si ⟨111⟩ wafers and insulating glass substrates by using FCVA system described elsewhere.[19] Prior to deposition the vacuum chamber was pumped down to 2×10^{-6} Torr and a 100-V negative bias was added to the substrates. The arc current was set to 60 A, and the magnetic field intensity of the filtered duct was 40 mT. Argon ions were used to etch the substrates for approximately 5 min to remove surface contaminants. When 6-sccm PH_3 (purity 99.9999%) gas was introduced into the same vacuum chamber and arrived at the dynamical balance, the arc was ignited by contacting the graphite anode against the graphite cathode, then the mixed plasma formed due to ion collisions passed through a double bend off-plane filter and deposited on the substrates.

Preparation of ta-C:P Electrode

The edges and backsides of ta-C and ta-C:P films were sealed by an O-ring resin with an exposed area of 0.5–0.6 cm^2 on the surface of the films. The resulting samples were used as the working electrodes. Subsequently, fresh ta-C:P film was initially subjected to an electrochemical pre-treatment by cycling it in a 2 $molL^{-1}$ H_2SO_4 solutions for 3 min. Potential limits were defined by a maximum current of ±2 mA at a scan rate of 0.1 Vs^{-1}.

Structural and Electrochemical Measurements

Compositions of ta-C:P film were quantified from the total areas of XPS signals corresponding to P 2p and C 1s core level spectra via a PHI ESCA 5700 spectrometer by using Al K_α line (1486.6 eV) as the x-ray source. C 1s and P 2p spectra were recorded at a step of 0.125 eV with a pass energy of 30 eV. Raman measurement was performed to characterize the structural rearrangement of the films at room temperature on a Jobin Yvon Labram HR 800 spectrometer with 458-nm Ar^+ laser as the excitation source. The transmission spectra of all samples were analyzed by using a Spectrum One Fourier transform infrared spectrometer between 400 and 4000 cm^{-1} with a resolution of 5 cm^{-1}. A four-point probe was used to measure the resistance of the films deposited on glass substrates. The thickness of the films determined by spectroscopic ellipsometry was 70–80 nm.

The electrochemical experiments were monitored in a three-electrode cell configuration by using CHI 660A electrochemical workstation (CHI instruments, Shanghai, China). A saturated calomel electrode (SCE) was used as the reference electrode with respect to which all potentials were measured, and a platinum foil of large size was employed as the auxiliary electrode. Ta-C/ta-C:P films were working electrodes. Furthermore, two electrochemical tests were carried out at 25 ± 2° in the present work. On the one hand, the redox reaction of water on the electrodes underwent in a 0.5 $molL^{-1}$ H_2SO_4 supporting electrolyte at a scan rate of 0.1 Vs^{-1}. On the other hand, the kinetics of $Fe(CN)_6^{3-/4-}$ redox couple on the electrodes was investigated in a 0.01 $molL^{-1}$ $K_3Fe(CN)_6$ and 1 $molL^{-1}$ KCl aqueous solution at a scan rate of 0.02 Vs^{-1}. All solutions were prepared from analytical grade chemicals by using the deionized and twice-distilled water. All current density referred to 1 cm^2 of film surface.

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