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Physical properties of sputtered amorphous carbon coating

M. Yari[a,*], M.M. Larijani[b], A. Afshar[c], M. Eshghabadi[d], A. Shokouhy[d]

[a] Materials Engineering Department, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b] Agricultural Medical and Industrial Research School, Nuclear Science and Technology Research Institute (NSTRI), Karaj, Iran
[c] Materials Engineering Department, Sharif University of Technology, Tehran, Iran
[d] Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

In this study the effect of deposition temperature and thickness on the physical properties of carbon films deposited by magnetron sputtering PVD was investigated. The results of Raman spectra and grazing incidence XRD (GIXRD) patterns show that the graphitization increases by increasing the deposition temperature. There is a change in deposition mechanism at 400 °C from amorphous carbon deposition to nano-structured graphite deposition. Also by increasing substrate temperature the electrical resistance of carbon films reduces significantly up to 300 °C and then remains largely constant. High intrinsic compressive stress in low temperature deposited carbon films causes cracks and delaminating in carbon films.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are one of the most promising candidates as a power sources for automotive applications because of their superior properties such as high energy efficiency (over 40%), little pollution, low temperature operation, rapid start-up, and little noise. However some properties of bipolar plates which are the backbone of the PEMFC stacks must be optimized to allow fuel cells to penetrate the commercial market. Bipolar plates should have high electrical conductivity and good corrosion resistance in the high acidity (pH∼2) and high temperature (<60 °C) environment. Although graphite and graphite composites are considered for this application, they are brittle and permeable to gases relative to metals. In addition metals such as stainless steels and aluminum are not suggested because of high corrosion rate in the aggressive PEMFC environment [1]. Therefore it seems that deposition of carbon films with excellent properties of graphite on the stainless steel could be a good candidate for this application. Several studies have been done in this context [2–5]. Following our previous research [6,7] on the corrosion resistance behavior of stainless steel substrates coated with carbon layer, in this paper the effects of substrate temperature and deposition time on the physical properties of nano-structured carbon thin films deposited by DC magnetron sputtering PVD have been investigated.

2. Experimental

A homemade DC flat unbalanced magnetron sputtering physical vapor deposition (MS-PVD) apparatus was used to coat one side of the stainless steel 316 substrate with carbon. The substrates were placed on a ground electrode in the glassy chamber. A high purity graphite plate target that acts as a carbon source was used. It was located on the magnetron plate with 120 mT magnetic field. The chamber was evacuated to a base pressure of 6×10^{-4} Torr using a combination of rotary and diffusion pumps. The working pressure was kept fixed at 4.3×10^{-3} Torr by introducing a high purity argon gas. The substrate temperature was changed from 100 °C to 300 °C by an electrical heater. Afterward, carbon was coated on the steel substrates with a current fixed at 100 mA. To maintain the current constant, the potential difference between the electrodes is adjusted from 500 V to 900 V during the process. After the deposition the samples were cooled down to room temperature in argon atmosphere.

The carbon film was characterized by the Raman spectroscopy. Raman spectra were collected using the 532 nm line from an Nd-YAG laser with a power of 10 mW.

In order to characterize the carbon-coating structure grazing incidence X-ray diffraction (GIXRD) analysis was used. The work was accomplished with a monochromic Cu Kα X-ray source diffractometer. The incidence angle was fixed at 1° during scanning.

In this work, a four point probe instrument (model Keithley) is applied for measuring the electrical resistivity of carbon films. The voltage and current range were selected from ±1 V and ±100 mA, respectively. Considering R_s which is calculated from I–V characteristic curve, the sheet resistivity (ρ) can be measured from the following equation:

$$\rho = \frac{2\pi t}{ln(2)} \tag{1}$$

where t is the thickness of carbon films. The thickness of the coating was obtained by mechanical thickness profiler model Dektak 3.

The optical stereo microscopy was used to evaluate the morphology of the carbon coatings.

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* Corresponding author. Tel.: +98 2144869790; fax: +98 2144869783.
E-mail address: yari.m@srbiau.ac.ir (M. Yari).

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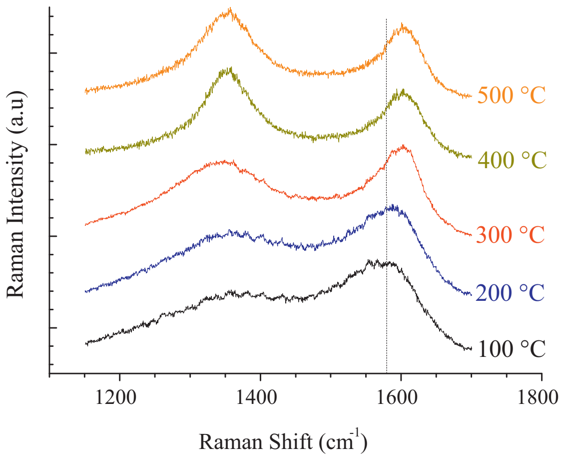

Fig. 1. Raman spectra of carbon films deposited at different substrate temperatures.

3. Results

Raman spectra of the carbon coatings at 8 min are presented in Fig. 1. For other deposition times the same results are achieved. For all spectra there are two peaks in about 1600 cm^{-1} and 1350 cm^{-1}. The former is related to sp^2 bonds and graphite structure (G band) and the later is related to in-planar defects in graphite structure (D band). One of the most predominant defects in the graphite structure is the formation of sp^3 bonds [8–10]. The position and intensity of each band (G or D) will determine the characterization of carbon coating [8]. While these bands overlap, in order to determine the band intensity, the spectra are deconvoluted by Lorentzian method. The intensity of deconvoluted peak extracted from Raman spectra in different substrate temperatures are summarized in Table 1.

According to the results, the structure of carbon coatings deposited at low substrate temperatures (100 and 200 °C) is completely amorphous. By increasing the deposition temperature the G band shifts toward higher wave numbers and crystallization will increase. In fact, in higher substrate temperatures the structure of carbon films becomes glassy and nano-structural. These trends are seen for all deposition times. It is due to increase of atomic and grain boundary mobility at higher temperatures. This behavior can be seen by increasing of the I_D/I_G ratio where I_D and I_G are the intensity of D and G peaks (Fig. 2). Amorphous carbon structure consists of disordered hexagonal aromatic chains. By raising the deposition temperature the formation of ordered rings without distortion will be increased. In this condition the D peak intensity increases due to increasing the number of ordered hexagonal aromatic chains. Therefore, the sp^2 clusters increases and graphite-like structure will be formed by raising the deposition temperature the results provide more evidence for the other studies [6,9,11]. Of course in high deposition temperatures (higher than 400 °C) the I_D/I_G ratio changes are not significant and a saturation mode is happened. It is probably due to change in film growth mechanism. In temperatures higher than 400 °C very fine graphite particles are formed instead of formation of the amorphous carbon structure at lower deposition temperatures. In Fig. 2 the region of different growth modes are separated.

Table 1
Raman parameters extracted from Lorentzian deconvolution of Raman spectra in Fig. 1.

Substrate temperature (°C)	I_D/I_G	FWHM G (cm^{-1})	FWHM D (cm^{-1})
100	1.11	134	420
200	1.34	129	405
300	1.47	86	267
400	1.51	54	91
500	1.43	54	84

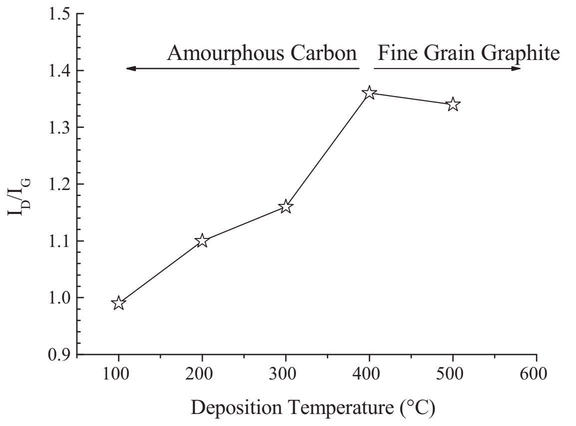

Fig. 2. Dependence of I_D/I_G ratio on deposition temperature for the films prepared during 8 min.

Grazing incidence XRD (GIXRD) patterns of carbon coatings deposited at different deposition temperatures for 8 min are shown in Fig. 3. It is clear that there is any peak in this figure for the temperatures lower than 400 °C. In these conditions the structure of carbon thin films are completely amorphous. However, in higher substrate temperatures three peaks at 43°, 50°, and 75° are revealed which are related to crystalline graphite (Card No. 00-026-1080). This result is in very good agreement with that of Raman spectroscopy.

Ferrari [9] showed that graphite crystallite size (L_a) increases by increasing the I_D/I_G ratio, in-planar ordering range. The following relation is proposed to estimate L_a [9]:

$$\frac{I_D}{I_G} = c \cdot L_a^2 \tag{2}$$

where c is equal to 0.0055 in Angstrom. According to this relation the calculated graphite cluster size vary from 1.3 to 1.7 nm. Cappelli et al. [11] have reported the similar result for deposition of carbon films by Pulsed Laser Deposition (PLD) method. They obtained a L_a of 0.7 nm and 1.7 nm for the coatings deposited at room temperature and 750 °C, respectively. Paulmier et al. [12] also have calculated an approximative value of L_a between 1.5 nm to 1.78 nm for plasma electrolyte carbon coatings.

Fig. 4 shows the effects of deposition time on carbon film thickness at 400 °C. It is obvious that the thickness of carbon coating will be increased by increasing the deposition time due to aggregation

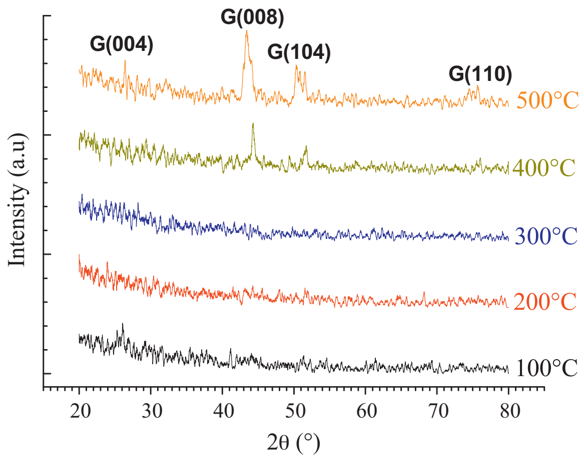

Fig. 3. Grazing incidence X-ray diffraction (GIXRD) patterns of carbon films deposited at various substrate temperatures prepared during 8 min.

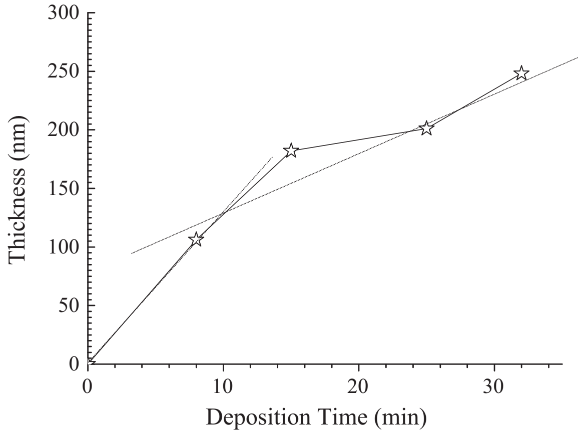

Fig. 4. Variation of carbon coating thickness deposited at 400 °C. Dot lines show the deposition rate extrapolation.

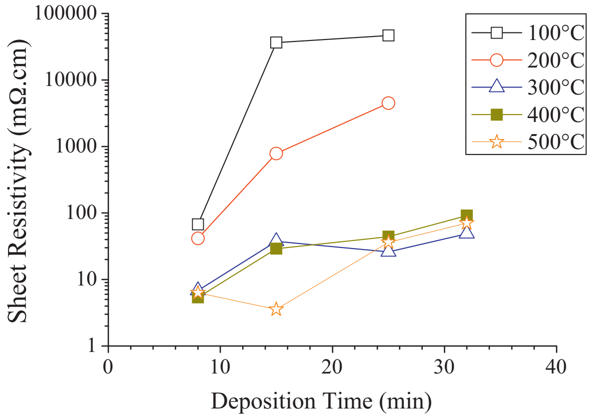

Fig. 6. Dependence of electrical resistance of carbon coatings on deposition time for different temperatures.

of carbon atoms. According to Fig. 4 the thickness growth rate is high in initial steps of deposition and then decreased. Some authors mentioned a reduction of the thickness growth rate after long deposition times [13]. This behavior can be related to the growth mechanism. In initial steps of deposition in which the growth rate is higher, the nucleation, nucleation growth and island coalescence happened. The fast formation and 3D growth of islands result high thickness growth rate. On the other hand, in longer deposition times the growth rate will be reduced due to homogenous growth of carbon coatings. When the islands grow enough to coalesce, the homogenous growth mechanism will occur. The results in Fig. 4 show a change in growth rate for deposition times longer than 8 min. Unfortunately, we cannot estimate time of transition from island growth to homogeneous growth because the thickness of carbon coatings has not been measured at deposition times shorter than 8 min. It has been reported in the literature [13] that this change will occur when the film thickness reaches to about 25 nm. In our case the thickness of coatings reached to ~25 nm after about 2 min. Therefore, we can just estimate that the changing mechanism time is shorter than 8 min.

The variation of sheet electrical resistivity as a function of substrate temperature for different deposition times is shown in Fig. 5. According to this figure for all deposition times the sheet resistivity of carbon coating decreases significantly by raising the temperature up to 300 °C, however in higher temperatures the changes is not considerable. Reducing the electrical resistance with deposition temperature can be related to the augmentation of the sp^2 bond fraction or crystallization of carbon films. According to Raman spectra the graphitization of the deposited carbon films increases with increase of temperature leading to an increase of charge carrier density (electrons) [14]. Some authors explain this phenomenon by formation of C–H bonds at deposition temperatures lower than 300 °C [4,14]. They believe that formation of these bonds can influence significantly the electrical resistivity.

It should be mentioned that at deposition temperatures higher than 300 °C, the electrical resistance of carbon coatings is much closed to that of graphite [15]. It seems that the density of charge carriers in these conditions (>300 °C) is high enough.

Fig. 6 shows the dependence of electrical resistance of carbon coatings with deposition time at different substrate temperatures. As we can see, the electrical resistance of carbon films increases with increase of the thickness (deposition time). It is clear from Fig. 6 that the rate of electrical resistance augmentation is more significant at low temperatures (100 and 200 °C) compared to higher temperatures. It is due to the presence of considerable intrinsic residual compressive stress in amorphous carbon films formed at low temperatures [15,16]. By increasing the deposition temperature the intrinsic stress will reduce [15] resulting in lower rate of electrical resistivity. According to results in the current study it seems that the intrinsic stress in carbon coatings deposited at 100 °C and 200 °C are too high to produce a non-defective coating

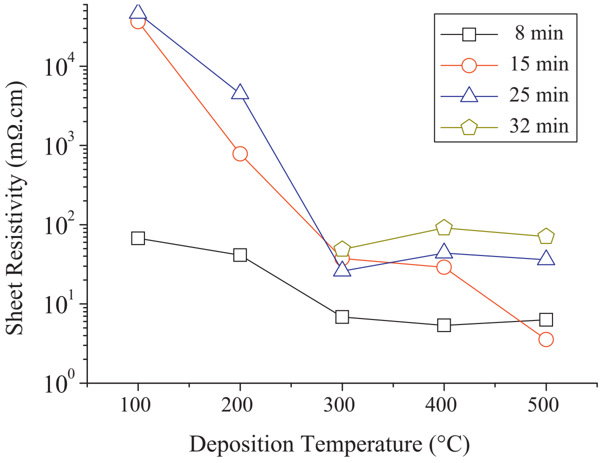

Fig. 5. Dependence of electrical resistance of carbon coatings on deposition temperature for different deposition times.

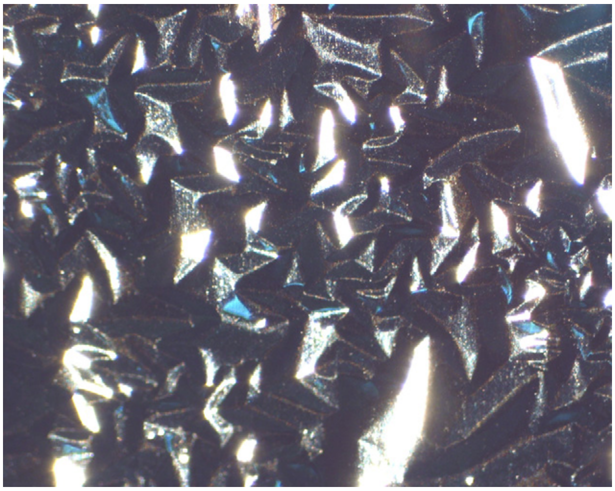

Fig. 7. Optical stereo micrographs of carbon film surface deposited at 200 °C for 32 min (30×).

in long deposition times (longer than 25 min). The carbon coatings that deposited in these conditions cracked and delaminated immediately after deposition. Fig. 7 shows the wrinkle on the surface of a typical carbon coating prepared at 200 °C for 32 min. The nature of cracks illustrate that there is a large compressive stress in carbon coatings deposited at low temperatures. While the compressive stress will reduce by increasing deposition temperature, the electrical resistance does not change by increasing the thickness at the temperatures higher than 300 °C.

4. Conclusion

The carbon thin films were deposited by DC magnetron sputtering physical vapor deposition. The structural and physical properties of carbon coatings depended on the deposition temperature. The structure of carbon coatings varied from amorphous to nano-crystalline. By increasing the deposition temperature the graphitization increased and electrical resistance decreased.

Also the electrical conductivity of carbon films depends on deposition time and substrate temperature. The effect of deposition time on the electrical resistance at low deposition temperatures is more significant than high deposition temperatures because of high intrinsic stress in films deposited at low temperatures.

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