

Fig. 3. Maximum interfacial shear strengths of carbon fibers as a function of Ar⁺ ion beam energy.

Consequently, although slightly different contributions of the fiber/matrix adhesions from fiber surface chemistry and morphology exist, both factors would affect the final composite properties of the interface in a co-operative way [10]. In a similar way, the relation between chemical and

structural modifications plays an important role in the proposed models for the oxidation of carbonaceous surfaces.

References

- [1] Oku T, Kurumada A, Kawamata K, Inagaki M. *J Nucl Mater* 2002;303:242–5.
- [2] Hopfe V, Jäckel R, Schönfeld K. *Appl Surf Sci* 1996;106:60–6.
- [3] Park SJ, Jang YS. *J Colloid Interf Sci* 2001;237:91–7.
- [4] Ramanathan T, Bismarck A, Schulz E, Subramanian K. *Compos Sci Technol* 2001;61:599–605.
- [5] Atkinson KE, Farrow GJ, Jones C. *Composites Part A. Appl Sci Manufact* 1996;27:799–804.
- [6] Park SJ. Interfacial forces and fields. In: Hsu JP, editor, *Theory and application*, New York: Marcel Dekker, 1999, chapter 9.
- [7] Bismarck A, Wuertz C, Springer J. *Carbon* 1999;37:1019–27.
- [8] Greszczuk L.B., ASTM STP 452, Am. Soc. Testing Mater. 1969;42.
- [9] Kim YC, Park SJ. *J Appl Polym Sci* 1999;74:15–21.
- [10] Bismarck A, Kumru ME, Springer J. *J Colloid Interf Sci* 1999;210:60–72.

Temperature-dependence of carbon film growth by electrolysis of a methanol solution

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Amorphous carbon films have attracted much attention for many years due to their special features such as high hardness, low friction coefficient, chemical inertness, biocompatibility and optical transparency. These properties make the film suitable for many practical applications, such as optical window coatings, scratch resistive coatings,

protective coatings for medical implants and field emitters for flat panel displays.

Many studies have been reported on the preparation of carbon films by different types of vapor deposition techniques, including chemical vapor deposition [1], pulsed laser deposition [2] and filtered cathodic vacuum arc [3]. Using these techniques, high quality films and rapid growth rates have been achieved. Liquid phase synthesis of carbon films has received much interest since 1992 [4] due to its merits of low cost, low temperature, simplicity of the experimental set up and possibility of coating on substrates

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with complex shapes. Different kinds of solvents and substrates have been tried and it was confirmed that liquid phase deposition is indeed a feasible method in synthesizing carbon films [5–12]. Although a lot of work has been done, the influence of the temperature of the liquid on the deposition of carbon films has not been studied.

According to previous reports, the potential applied to the substrate during the liquid phase deposition of carbon films is generally between -1200 V and -2000 V. The distance between the substrate and the positive electrode is about 5 – 10 mm and the current density is in the range of 20 – 100 mA/cm². The surface area of the substrate is about 1 cm². Under these experimental conditions, the electrical power delivered between the substrate and the positive electrode is, typically, more than 100 W. The large amount of energy dissipation makes the temperature of the liquid near the substrate very difficult to control, especially when the temperature is below 40 °C. For the work reported in this paper, the electrical power consumed between the substrate and positive electrode was kept below 5 W so that the temperature of the liquid could be controlled accurately. Pure methanol (99.8%) was used as the organic solvent and a silicon (100) wafer polished on both sides was used as the substrate. We found that the temperature of the solution was an important parameter for the liquid phase deposition of a carbon film. There exists a temperature range below which pure carbon films could not be deposited. Instead, a silicon–oxygen–carbon (Si–O–C) surface layer with a porous structure appeared on the silicon substrate.

The deposition system is similar to that reported in [5],

however the electrolytic cell was immersed in a water tank, which was placed on a hot plate. The temperature of the water could be regulated and stabilized at any temperature between room temperature and 65 °C. A magnetic stirrer was placed at the bottom of the electrolytic cell to provide a uniform temperature in the methanol solution. A silicon substrate with a surface area of 5×10 mm² was mounted on the negative electrode. Before deposition the substrate was dipped in a mixture of dilute HNO₃–HF solution for a few minutes and then cleaned by ultrasonic treatment in ethanol and then acetone. The distance between the substrate and the positive carbon plate electrode was set to 15 mm. The deposition time was 5 h and fresh methanol solution was used each time. The dc potential applied to the substrate was kept at -1600 V. The electrical current during the deposition was kept constant at a value between 2.20 mA and 2.50 mA, depending on the temperature of the liquid and the deposition time. As the electrical power was only about 4 W, the effect of heat dissipation on the temperature of the liquid was minimal. Thus the temperature of the organic solution could be accurately controlled. Samples were examined by Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscopy (FESEM).

A series of samples were deposited at different temperatures in the range from 20 °C to 60 °C at 2 – 5 °C intervals. During the 5 h deposition for each sample, the temperature variation was less than ± 1.0 °C. It was surprising to find that the FTIR spectra of samples deposited at temperatures higher than 42 °C were very different from those deposited

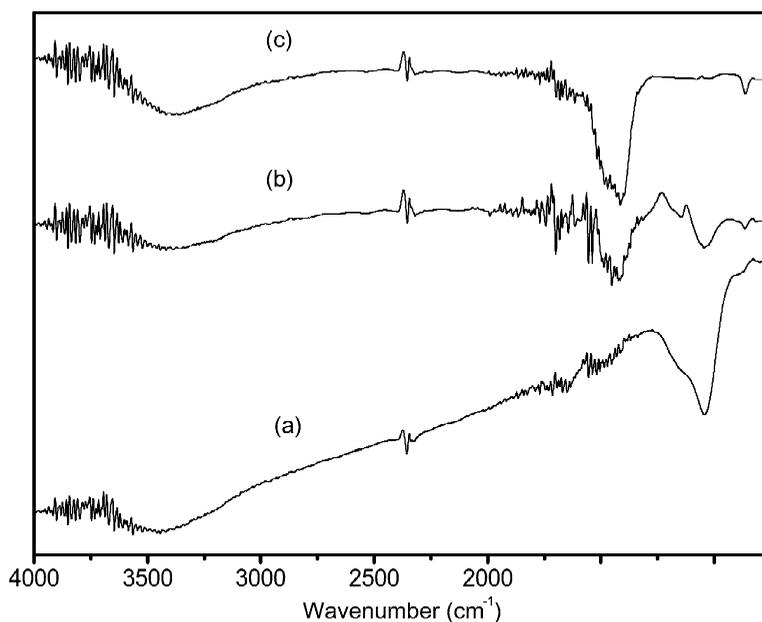


Fig. 1. FTIR spectra of the typical samples deposited (a) below 38 °C, (b) 38 – 42 °C and (c) above 42 °C.

at temperatures below 38 °C. Films deposited at temperatures in between the two showed mixed features. Typical FTIR spectra of samples in these three temperature regions are shown in Fig. 1. Curve (a) shows a typical FTIR spectrum for samples deposited at a temperature below 38 °C. A very strong broad peak centered at 1038 cm^{-1} is observed which is assigned to Si–O–C vibration in the sample [13]. Spectrum (b) is typical for samples deposited at temperatures in the range of 38 °C to 42 °C. In this spectrum, another large band between 1300 and 1650 cm^{-1} is observed and the Si–O–C peak becomes weaker. When the temperature is higher than 42 °C, as shown in spectrum (c), the peak at 1040 cm^{-1} disappears and the unresolved large band between 1300 and 1650 cm^{-1} becomes stronger. The last two peaks are associated with vibrations of the highly connected C skeleton [14,15]. The small peaks at approximately 2330 cm^{-1} are attributed to ambient CO_2 . There is another peak centered at 857 cm^{-1} in spectra (b) and (c), which is attributed to the Si–C bond. We believe that Si–C bonds are formed at the interface between the film and the substrate.

XPS measurements on samples deposited at temperatures above 42 °C were consistent with this argument. Fig. 2 shows typical XPS spectra for these samples. Spectrum (a) is for a sample deposited at a temperature above 42 °C and indicates that the main composition of this film is carbon with no silicon signal detected at the surface of the sample. The peak at 531.5 eV is due to oxygen in C=O and is believed to come from oxygen atoms adsorbed on the film surface. The fact that no C–O vibration peak was observed in the corresponding FTIR spectrum also sug-

gests that most oxygen atoms are not bonded to the carbon network. The surface of the samples deposited below 38 °C is composed of silicon, carbon and oxygen atoms, which can be seen from spectrum (b) and is consistent with the corresponding FTIR results.

Fig. 3 shows FESEM micrographs of samples deposited in the three temperature ranges. From Fig. 3(a) it can be seen that the carbon film deposited above 42 °C is composed of small, compact grains, and seems to be smooth and homogeneous in thickness (about 140 nm as measured by a surface profiler). However, the surface morphology of samples deposited below 38 °C, as shown in Fig. 3(c), exhibits a porous character. Holes with different sizes, ranging from a few nanometers to several micrometers, cover the whole surface. The typical surface morphology of samples deposited between 38 °C and 42 °C is shown in Fig. 3(b). This is mainly composed of two parts, one is a porous structure (shown in the upper-left part in the figure) and another is a smooth carbon film surface (lower-right), and there is a transition region as shown in the middle of the figure. Porous silicon is most commonly prepared by anodic (electrochemical) etching in HF based solutions [16] but this method has environmental consequences because of the use of HF. It is interesting that we can get porous silicon from a pure methanol solution and the processing is carried out under environmental friendly conditions.

The current passing through the two electrodes during deposition exhibits different behaviors, depending on whether the liquid temperature is higher than 42 °C or lower than 38 °C. For $T > 42$ °C the current rose during the

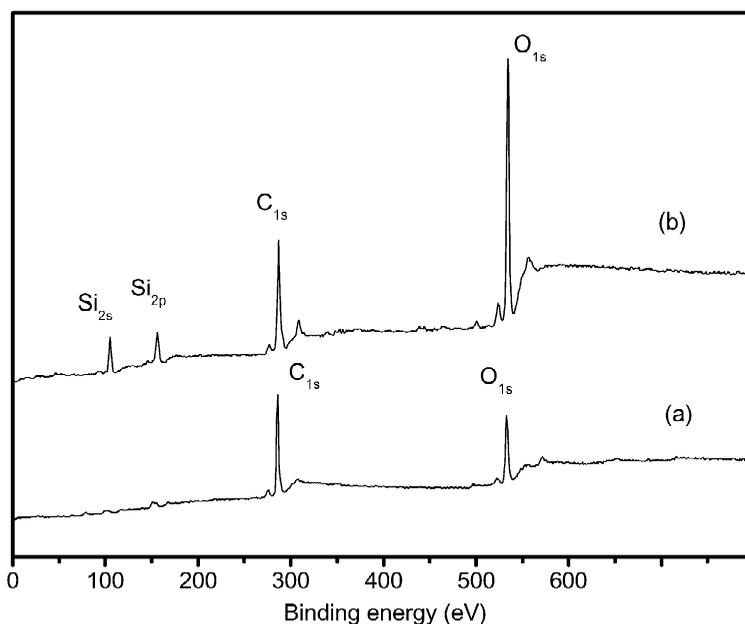


Fig. 2. XPS spectra of the typical samples deposited (a) above 42 °C and (b) below 38 °C.

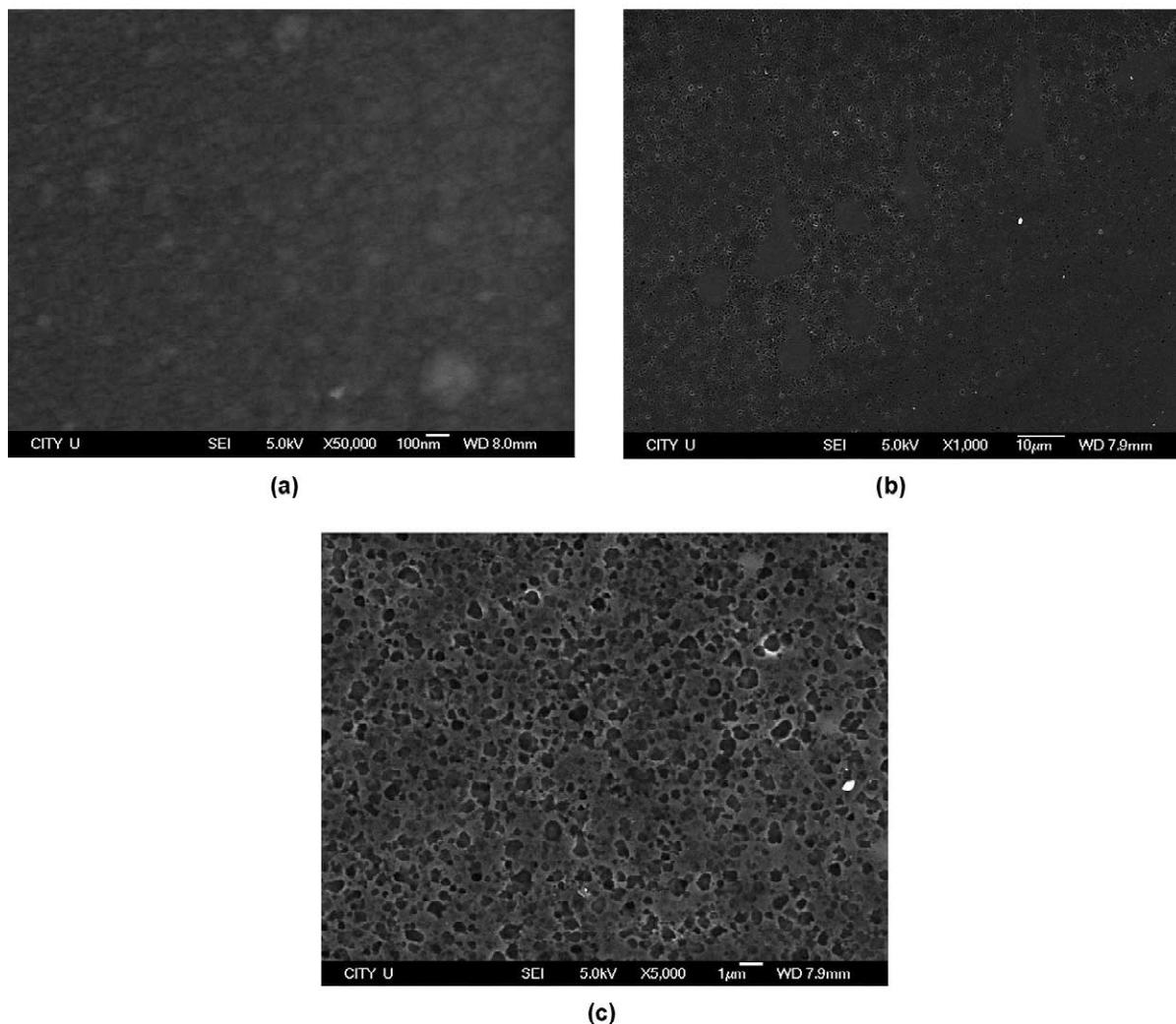


Fig. 3. FESEM images of the typical samples deposited (a) above 42 °C, (b) 42–38 °C and (c) below 38 °C.

first couple of minutes and then decreased slowly with time, while for $T < 38\text{ }^{\circ}\text{C}$ the current remained almost constant with time. It is believed by other authors [12] that a CH_3^+ group produced under a high potential is responsible for the carbon film growth on the negative electrode (substrate). However, from the chemistry point of view, the bond between CH_3O^- and H^+ is the easiest one to break under the high dc potential. We propose that H^+ is the dominant positive ion in the solution when the temperature between the electrodes is lower than 38 °C. The H^+ in the solution will etch the silicon substrate under the high DC potential resulting in the porous structure. When the temperature is higher than 42 °C, in the light of the current change with deposition time, we propose that a certain amount of CH_3^+ will be produced under the high dc

potential and is responsible for the formation of the carbon film on the surface of the silicon substrate. The carbon film in turn prevents the etching of silicon by H^+ .

In conclusion, the temperature of the liquid is a key factor in the liquid phase deposition of carbon films by electrolysis of pure methanol solution. Pure carbon films with compact small grains and a smooth surface on the silicon substrate can only be obtained when the liquid phase temperature is higher than 42 °C. When the temperature is lower than 38 °C, a Si–O–C surface layer with a porous structure is formed. Both pure carbon film and Si–O–C porous structure regions could be found on the substrate surface when the temperature is between 38 °C and 42 °C.

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References

- [1] Amaratunga GAJ, Silva SRP. Nitrogen containing hydrogenated amorphous carbon for thin-film field emission cathodes. *Appl Phys Lett* 1996;68(18):2529–31.
- [2] Missert N, Friedmann TA, Sullivan JP, Copeland RG. Characterization of electron emission from planar amorphous carbon thin films using in situ scanning electron microscopy. *Appl Phys Lett* 1997;70(15):1995–7.
- [3] Satyanarayana BS, Hart A, Milne WI, Robertson J. Field emission from tetrahedral amorphous carbon. *Appl Phys Lett* 1997;71(10):1430–2.
- [4] Namba Y. Attempt to grow diamond phase carbon films from an organic solution. *J Vac Sci Technol A* 1992;10(5):3368–70.
- [5] Wang H, Shen MR, Ning ZY, Ye C, Cao CB, Dang HY, Zhu HS. Deposition of diamond-like carbon films by electrolysis of methanol solution. *Appl Phys Lett* 1996;69(8):1074–6.
- [6] Kwiatek SE, Desai V, Moran PJ, Natishan PM. Characterization of cathodically deposited carbonaceous films on a silicon substrate. *J Mater Sci* 1997;32(12):3123–8.
- [7] Novikov VP, Dymont VP. Synthesis of diamondlike films by an electrochemical method at atmospheric pressure and low temperature. *Appl Phys Lett* 1997;70(2):200.
- [8] Fu Q, Jiu J, Cai K, Wang H, Cao C, Zhu H. Attempt to deposit carbon nitride films by electrodeposition from an organic liquid. *Phys Rev B* 1999;59(3):1693–6.
- [9] Kiyota H, Araki A, Kobayashi H, Shiga T, Kitaguchi K, Iida M, Wang H, Miyo T, Takida T, Kurosu T, Inoue K, Saito I, Nishitani-Gamo M, Sakaguchi I, Ando T. Electron field emission from diamond-like carbon films deposited by electrolysis of methanol liquid. *Appl Phys Lett* 1999;75(15):2331–3.
- [10] Sun Z, Sun Y, Wang X. Investigation of phases in the carbon films deposited by electrolysis of ethanol liquid phase using Raman scattering. *Chem Phys Lett* 2000;318:471–5.
- [11] Wang H, Yoshimura M. Electrodeposition of diamond-like carbon films in organic solvents using a thin wire anode. *Chem Phys Lett* 2001;348:7–10.
- [12] Guo D, Cai K, Li L, Huang Y, Gui Z. Evaluation of carbon films electrodeposited on different substrates from different organic solvents. *Appl Phys A* 2002;74:69–72.
- [13] Kim YH, Hwang MS, Kim HJ, Kim JY, Lee Y. Infrared spectroscopy study of low-dielectric-constant fluorine-incorporated and carbon-incorporated silicon oxide films. *J Appl Phys* 2001;90(7):3367–70.
- [14] Bounouh Y, Theye ML, Dehbi-Alaoui A, Mathews A, Stoquert JP. Influence of annealing on the hydrogen bonding and the microstructure of diamondlike and polymerlike hydrogenated amorphous carbon films. *Phys Rev B* 1995;51(15):9597–605.
- [15] Schwan J, Ulrich S, Roth H, Ehrhardt H, Silva SRP, Robertson J, Samlenski R, Brenn R. Tetrahedral amorphous carbon films prepared by magnetron sputtering and dc ion plating. *J Appl Phys* 1996;79(3):1416–22.
- [16] Chattopadhyay S, Li XL, Bohn PW. In-plane control of morphology and tunable photoluminescence in porous silicon produced by metal-assisted electroless chemical etching. *J Appl Phys* 2002;91(9):6134–40.

Polymerization of short single-walled carbon nanotubes into large strands

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Single-walled carbon nanotubes (SWNTs) have attracted much interest in recent years because of their unique structural, mechanical, and electronic properties, as well as potential applications in nanotube-reinforced materials,

nanoelectronic devices, field emitters, and probe tips for SPM, etc. [1–5]. For most applications a major challenge is how to get nanotubes on a macroscopic scale which have a practical value. Several attempts have been made to do this, such as the formation of SWNT superbundles, and self-assembly of SWNT ribbons using arc plasma or under ambient pressure [6,7]. Important progress was recently achieved by Poulin et al. [8]. They demonstrated that

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