Highly Conducting Graphitic Carbon Films and Nano Patterns from Poly(*p*-phenylenevinylene) Prepared on the Surface of Silicon Wafers by the CVD Method

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Summary: We could prepare highly electrically conducting graphitic carbon films and nano patterns by carbonizing the poly(*p*-phenylenevinylene) (PPV) films and nano patterns prepared on the silicon surface by the chemical vapor deposition polymerization method of α,α'-dichloro-*p*-xylene. When the PPV films on silicon wafers were thermally treated at 850 ^{0}C highly oriented graphitic carbon films were obtained which exhibit an electrical conductivity higher than 0.7 x 10^3 Scm^{-1}. This conductivity value is more than 10 times the value for the carbon films obtained from bulk PPV films or glassy carbons heat treated at the same temperature. Moreover, nano patterns of graphitic carbons were easily obtained on silicon wafers through carbonization of nano patterned PPV obtained by the CVD polymerization method.

Keywords: conductivity; CVD; graphitic carbon; nano pattern; PPV

Introduction

Discovery of fullerenes[1] and carbon nanotubes[2] has aroused an explosive research interest in the structure-property relations[3-5] of carbonaceous materials because of their great promise for numerous applications, especially in nano devices. Moreover, recent advancement in proximal probe techniques[6, 7] and nano fabrication methods[8, 9] are lending additional impetus to develop methods that can tailor the chemical and physical structures of carbonaceous materials at the nanoscale. In spite of many recently developed novel processes for the preparation of carbon materials, nanoscale fabrication[10-12] or nano wiring of carbons on a desired substrate such as silicon wafer is still in its infant stage of development. Utilization of Si wafers is presently playing predominant roles in microelectronics and expected to remain to be so even for nanoelectronics in forthcoming decades.

One[13] of our recent papers is describing the preparation of graphitic carbon tubes and rods in

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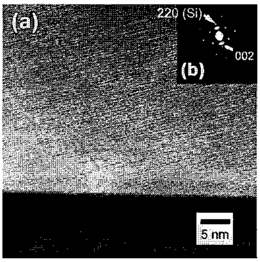


Figure 1. (a) Cross sectional TEM image of carbon film on Si wafer and (b) its electron diffraction pattern.

nano dimensions. They were prepared by carbonizing poly(*p*-phenylenevinylene) formed by chemical vacuum deposition polymerization[14-17] of α,α'-dichloro-*p*-xylene inside the pores of various filter membranes. Alumina and polycarbonate membrane microfilters and mesoporous silica were utilized as substrates, which were removed afterwards by dissolution in proper solvents.

Result and Discussion

In the present investigation we studied preparation of graphitic films directly on the (001) surface of polycrystalline silicon wafers. They were obtained by the carbonization of corresponding PPV films formed by the CVD polymerzation of α,α'-dichloro-*p*-xylene. Detailed preparation methods of PPV films and carbonization of thereof are the same as described in the previous report.[13] α,α'-Dichloro-*p*-xylene was evaporated at 95 °C in a stream of argon at 0.8 torr. The vapor was activated in pyrolysis zone at 625 °C followed by deposition of the precursor polymers on a HF-cleaned silicone wafer[18] at room temperature. The precursor polymer films were thermally treated at 270 °C converting them to PPV. The PPV films were carbonized at 850 °C for 1 hour under argon. When patterns on a silicon wafer were to be obtained, a PMMA lithographed wafer was utilized for CVD. The precursor polymer was then subjected to preliminary thermalysis at 90 °C for 4 hrs. And then PMMA was removed by acetone in a sonicator. Then, the pattern of partially thermolyzed precursor polymer was again heated at 270 °C for 14 hrs followed by carbonization at 850 °C.

Figure 1 shows a transmission electron micrograph (TEM) and an electron diffraction (ED) pattern of a carbon film (60 nm thick) on a Si-wafer. This figure demonstrates that the graphitic

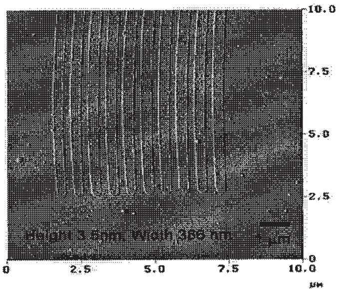


Figure 2. An AFM image of carbon nano patterns (width: 386 nm, height: 3.5 nm) obtained on a silicon wafer.

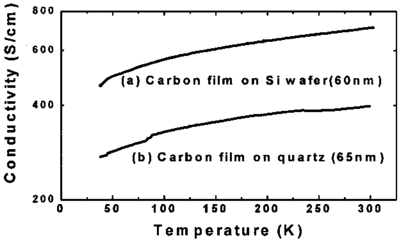


Figure 3. Comparison of electrical conductivities of the graphitic carbon nanofilms.

structures formed are rather well aligned and the formation of a distinctive interface about 0.5 nm thick is clearly discernible. The ED pattern (inset in Figure 1) supports the aligned morphology of the graphitic layers exhibited by the micrograph. An AFM image of the patterned carbon on a Si-wafer is shown in Figure 2. We see that the patterns are of high uniformity. We believe that the present approach is extremely versatile and enables us to easily obtain similar carbon nano patterns in various shapes and dimensions.

We measured electrical conductivities of the graphitic carbon films by the four-probe method[19] and the results are shown in Figure 3. Surprisingly, the room temperature conductivity of the carbonaceous film is very high, $\sigma = 0.7 \times 10^3$ S/cm. The value is about twice the electrical conductivity of the graphitic carbon film obtained under the same condition from PPV deposited on the quartz surface (55 nm thick, $\sigma = 0.4 \times 10^3$ S/cm). In order to understand the reason why the enhanced electrical conductivities of the present carbon films obtained on the surface of Si-wafers are observed, their degree of graphatization was examined by Raman spectroscopy. Figure 4

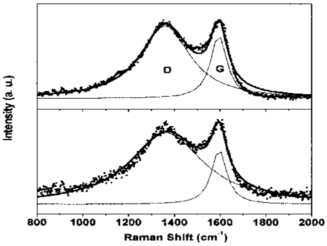


Figure 4. Comparison of Raman spectra of carbon films (850 °C, 1h) prepared on the surface of a (a) Si-wafer and (b) quartz.

compares Raman spectra of carbon films prepared on the surface of a Si-wafer and quartz. They commonly show two peaks: one at 1355 cm^{-1} and the other at 1592 cm^{-1}. The peak at 1355 cm^{-1} is very often called D peak,[20] which is usually assigned to a breathing mode of A_{1g} symmetry involving phonons near the K zone boundary. This mode is not observed in perfect graphite and becomes active only in disordered graphites. The peak at 1592 cm^{-1} is the G mode of E_{2g} symmetry[20] and it involves the in-plane bond-stretching motion of pairs of sp^2 C atoms. When we utilized the double-Lorentzian fit, we obtained the I(D) / I(G) ration values of 3.1 and 6.7, respectively for the graphitic carbon films on a Si-wafer and quartz. According to the following Tuinstra and Koenig equation,[21] the graphitic cluster diameters or in-plane correlation lengths (L_a) of the two films are 1.4 nm and 0.6 nm, respectively.

$$I(D) / I(G) = C(\lambda) / L_a \quad (1)$$

Here the prefactor C (λ) is a constant[22, 23]dependent on the wavelength of the source laser. The wavelength of laser we used was 514.5 nm and C (λ) is 44 Å[22, 23] The fact that the I(D) / I(G) value is about 3 and the G mode occurs at 1594 cm^{-1} tells us that the carbon films we are dealing with are of nanocrystalline graphite.[20] It is known that the G peak moves from 1581 to 1600 cm^{-1} as the perfect graphite becomes disordered to become nanocrystalline graphite. Another important observation to be noted is that I(D) / I(G) value (3.1) of the film on the Si-wafer surface is significantly smaller than that on the quartz, which indicates the significantly higher L_a value for the film on the Si-wafer surface than that (I(D) / I(G) = 6.7) on the quartz, which, in turn, implies that graphatization proceeded to a higher extent in the former than in the latter. This is in accord

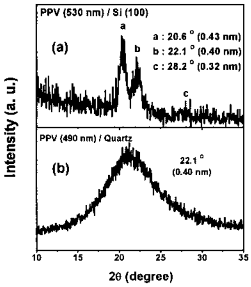
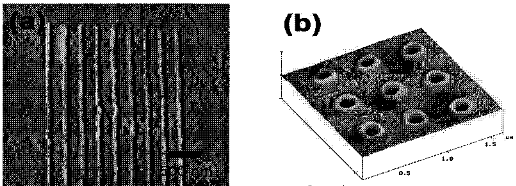


Figure 5. X-ray diffraction of PPV films grown on the (a) Si wafer and (b) quartz.

with the TEM and ED analyses and their electrical conductivities discussed above.

Then, an important question is raised as to why the surfaces of Si-wafer and quartz behave so differently. We hoped that information on the chain orientation of PPV polymers formed by CVD on the two surfaces could provide us with sound scientific answers. Figure 5 compares the wide-angle X-ray diffractograms of the PPV films obtained on the two surfaces. Figure 5(a) clearly exhibits three sharp diffraction peaks at $2\theta = 20.6^{\circ}$ ($d = 0.43$ nm), 22.1° ($d = 0.40$ nm) and 28.2° ($d = 0.32$ nm). This diffraction pattern is very close to that reported by Chen *et al.*[24] who intentionally annealed a PPV sample at 125 – 180 °C to induce crystallization. The crystal structure of PPV revealing this diffraction was earlier proposed to be of herringbone type arrangement (*p2gg* symmetry). On the other hand, the diffractogram (Figure 5(b)) of the PPV film obtained on the quartz surface shows a very broad peak extending from $2\theta \approx 15\ ^{\circ}$ to $30\ ^{\circ}$ implying hat the polymer chains are amorphous. In short, the two surfaces behave completely differently in controlling the PPV chain orientation. It is our present conjecture that there may be chemical reaction between Si atoms on the wafer surface and the reactive intermediates of quinone dimethide or monomethide type formed from the monomer during activation of the monomer. In fact, X-ray photoelectron spectroscopic (XPS) analysis of the PPV deposited Si-wafer surface reveals the formation of Si-C bonds. Recently, Yamamoto and coworkers[25] reported that vacuum deposition of oligomeric poly (*p*-phenylene) on a carbon substrate produce thin films in which the polymer chains are aligned perpendicularly to the surface of the substrate. Evidently, chain orientation direction for a given polymer is highly dependent on the nature of the substrate surface.



Width: 75 nm

Height: 4.5 nm

Width: 230 nm

Height: 16 nm

Wall Thickness: 75nm

Figure 6. An AFM images of patterned PPV nano (a) patterns and (b) wells.

The crystalline nature of PPV chains obtained on the surface of Si-wafer must have played a critical role in carbonization process leading to a higher degree of graphatization and also graphitic order, which, in turn, resulted in higher electrical conductivities.

We examined the possibility of obtaining PPV patterns on silicon wafers by the present CVD method. Figure 6 shows AFM images of a patterned PPV deposited on the silicon wafer surface followed by removal of lithographed PMMA by washing with acetone. Carbonization of the PPV nano patterns lead to carbon nano patterns.

In summary, highly electrical conducting graphitic carbon nano films, patterns, and wells could be readily prepared on the surface of silicon wafers by carbonization of PPV. The PPV formed by CVD of α,α'-dichloro-*p*-xylene is crystalline. The crystalline nature of PPV results in more efficient graphatization at low temperatures. The exact mechanism of surface mediation, however, requires further studies, although there are some indications that direct Si-C bond formation occurs. The present method is expected to provide us with a new tool to process conducting graphitic carbons to desired shapes in nano dimensions.

Experimental

CVD polymerization of PPV film: The CVD apparatus is consisted of vaporization, pyrolysis, and deposition zones equipped with a pressure control system, a tungsten boat, a heating stripe, an electrical furnace, argon gas inlet, vacuum line and a holder of the substrates. α,α'-Dichloro-*p*-xylene (Aldrich Co, Milwaukee, U.S.A.) purchased was purified by recrystallization from benzene. A sample of purified α,α'-dichloro-*p*-xylene placed on a tungsten boat was vaporized at 93 – 95 °C in a steady stream (8 ml/min) of argon at the pressure of 0.7 Torr. The vaporized monomer was allowed to pass through the pyrolysis zone preheated to 625°C. The precursor polymer was collected on the surface of substrate placed in the deposition zone. The precursor polymer were thermally treated at 270 °C for 14 hours converting them into PPV.

Carbonization of PPV film: PPV film was heated until 850 °C with the heating ratio of 5 °C / min and maintained the temperature for 1 hour. Carbonization was achieved under argon atmosphere in a sealed pyrolysis quartz tube.

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