Synthesis of vapor-grown carbon fibers from camphor without catalyst and their characterization

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Vapor-grown carbon fibers and carbon micro-beads were produced in the absence of catalysts from a natural precursor, camphor, by a thermal chemical vapor deposition process, at different temperatures in an argon medium. Scanning and transmission electron microscopy, Raman spectra, and electrical conductivity studies were used to characterize these fibers. It was observed that cylindrical fibers (diameter ~3 μm) were obtained at 1033 K and rippled fibers (diameter ~5 μm) were formed at 1273 K while carbon beads (diameter ~0.5-1 μm) were formed at 1173 K. It is proposed that agglomeration of carbon beads predominate at pyrolysis temperature greater than 1173 K, resulting into rippled type fibers.

I. INTRODUCTION

Carbon fibers of diameter smaller than 10 μm produced by vapor-phase reaction are generally termed vapor-grown carbon fibers (VGCFs).[1] Sometimes they are also called catalytically chemical-vapor grown carbon filaments as they are largely grown in the presence of catalysts. In general, these fibers are short, but long VGCFs have also been synthesized utilizing modified techniques.[2] Currently, the high cost of conventional polyacrylonitrile (PAN) and pitch-based carbon fibers restricts their use from anything other than defense, aerospace, and some sports materials. For domestic purpose, VGCF is only an alternative to PAN and pitch-based carbon fibers with its high mechanical properties to cost ratio.[3] Lower costs of these fibers lie in single-step synthesis and low-cost feeding material. Although they have poorer mechanical behavior than PAN and pitch-based carbon fibers, VGCFs have higher thermal and electrical properties. Therefore, VGCFs have great potential in preparation of composite materials.[4] Significant efforts were made by studying the effect of different precursors, carrier gas, flow rate, and catalysts for the production of these fibers. Numerous precursors, namely acetylene, ethylene, benzene, toluene, n-hexane, and n-butane, have been used for the production of VGCFs. Various catalysts like iron, nickel, cobalt, and their respective salt/compounds have been extensively used for this synthesis. A detailed mechanism of growth has also been elucidated elsewhere.[5,6] These carbon fibers have been applied in areas like secondary lithium batteries,[7,8] electromagnetic interference shielding,[9] electron field emission display,[10,11] etc.

In almost all cases, these vapor-grown carbon fibers have been synthesized in the presence of catalyst particles. Two types of mechanisms, tip and base mode growth, have been proposed.[5,6] However, little effort has been made to understand the growth of VGCFs in the absence of any catalyst particle. In addition, these fibers have been produced from precursors derived from fossil fuels. Hence, for 21st century applications, they should be synthesized from precursors unrelated to fossil fuels. Camphor is one possible alternative precursor for such purpose. Camphor is a natural source extracted from the latex of pine trees or *Cinnamonum Camphora*. Thus, because camphor is a natural product, there is no fear of its depletion and it can be cultivated in large quantities depending upon the requirement. Fullerene,[12] spongy carbon beads,[13] and nanotubes[14] have been synthesized from this precursor. It is therefore interesting to examine whether camphor can be used to synthesize VGCFs without using any catalyst. This paper reports our efforts in this direction. Electrical conductivity and Raman spectra of fibers obtained from camphor have been studied to obtain insight about the nature of fibers.

II. EXPERIMENTAL

Figure 1 shows the experimental setup for the production of vapor-grown carbon fibers. It consists of two electric furnaces (each of length 0.3 m), a 1-m-long quartz tube of inner diameter 1.5 cm kept inside the furnace, an argon cylinder, a flow meter, and a water bubbler. The precursor, camphor (C) and the substrate (D) were kept in their respective furnaces, as shown in

Fig. 1. Then argon gas was purged for 15–20 min to replace air from inside the quartz tube. After 15–20 min of argon gas flow, the second furnace (F2) was heated to the desired pyrolysis temperature. Once the set temperature was reached, the furnace (F1) containing 2–3 g of camphor was heated to 473 K for vaporization. Camphor (2–3 g) vaporized within 10 min and was pyrolyzed and deposited on the substrate kept inside the quartz tube of furnace (F2). The furnace was cooled down to room temperature, maintaining argon medium, and then samples were taken out for study.

III. RESULTS AND DISCUSSION

A. Morphology of as-grown carbon fibers

Figures 2(a)–2(c) show scanning electron micrographs of carbon fibers obtained at 1033 K on alumina substrate in an argon atmosphere. The length and width of these
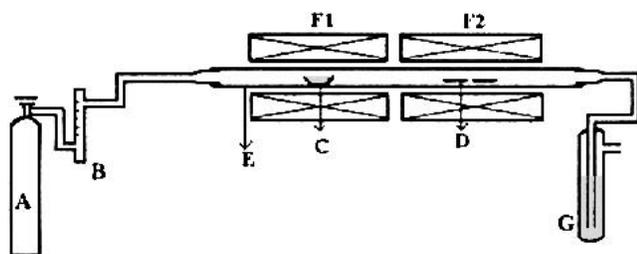

FIG. 1. Schematic diagram of the experimental setup for the synthesis of VGCFs (A, argon gas cylinder; B, flow meter; C, camphor; D, substrate; E, quartz tube; F1, vaporization furnace; F2, pyrolysis furnace; G, water bubbler).

fibers are in the range of 40–50 µm and 2–4 µm, respectively. These VGCFs are straight and nearly flat (plate type) with tapering ends. Along with VGCFs, few carbon beads of diameter in the range of 200–400 nm are also observed on the surface of fibers [Fig. 2(c)]. These fibers are found to be arranged in a specific radial fashion as shown in Fig. 2(b), but the reproducibility of this arrangement is poor. With increase of pyrolysis temperature to 1173 K, only carbon beads of diameter in the range of 0.5–1 µm are obtained. They are spherical in shape and uniformly distributed all over the substrate [Fig. 2(d)]. These carbon beads are interconnected with each other (Fig. 3), in contrast to those formed on the flat fibers at low pyrolysis temperature (1033 K). Figure 3 shows the transmission electron micrograph of interconnected carbon beads formed at 1173 K. With the increase of pyrolysis temperature to 1273 K, growth of rippled fibers was observed [Fig 4(a)]. Further increase of the pyrolysis temperature to 1373 K does not seem to change much in the morphology of these fibers [Fig. 4(d)]. This type of fiber has also been reported by Serp *et al.*[15] The mechanical strength of these rippled fibers is less than that of the quasi and perfect cylinder-type VGCFs.[16] These results suggest that VGCFs can be grown from camphor on alumina without using catalysts.

The role of substrate on the growth of VGCFs was also studied. Figures 5(a) and 5(c) show the scanning electron microscope (SEM) images of carbon structures formed on single crystal silicon (100) and quartz substrates respectively, at 1173 K. It is important to note that single-crystal silicon and quartz pieces were chosen as substrates due to their smooth surface. Carbon fibers are
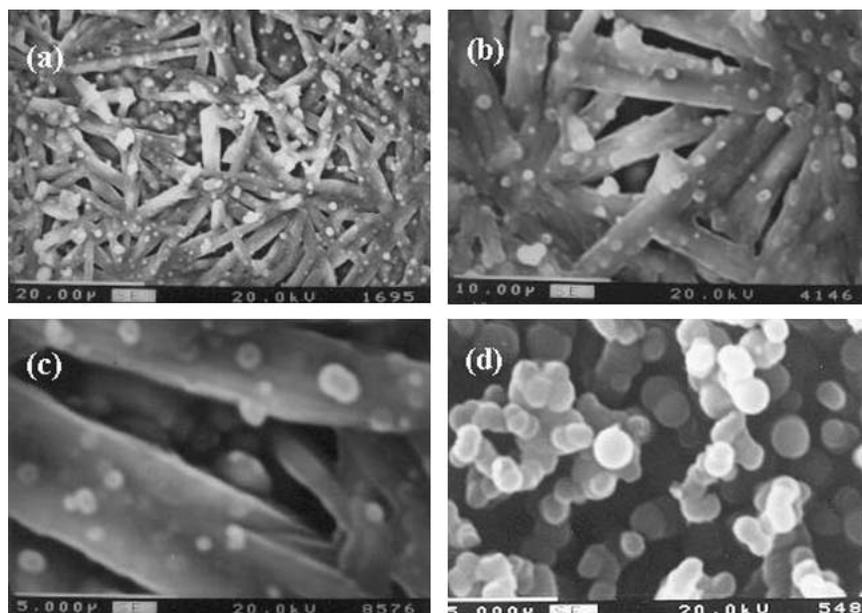

FIG. 2. Scanning electron microscope view of (a–c) as-grown carbon fibers on alumina substrate at 1033 K of different magnifications and (d) spherical carbon beads obtained at 1173 K.

not formed while depositing on these substrates at any temperature. Interestingly, the formation of carbon microbeads (diameter 1.1–1.5 μm) could be seen at the edges of silicon substrate [Fig. 5(b)]. These carbon microbeads are of similar morphology to those obtained on the alumina substrate [Fig. 2(d)].

These results suggest that for the growth of carbon beads, a rough surface like alumina plate or the edges of silicon (or any) substrate is needed. It also appears from these results that during the pyrolysis of camphor (i.e., in the absence of a catalyst), carbon nanobeads and the flat type of fibers are formed simultaneously even at lower temperature on alumina. However, the quantity of
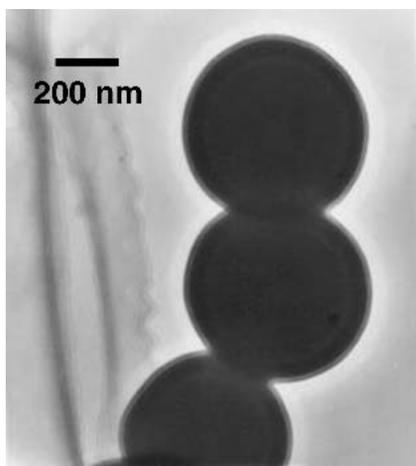
nanobeads is low and their size is small compared to flat type fibers. Moreover, carbon beads seem to be formed on top of the flat fibers. These beads appear as water droplets on a plant leaf. At high temperature (1173 K), spherical carbon bead formation replaces flat fiber formation completely. When the temperature of pyrolysis is further increased, carbon beads formed during the pyrolysis start agglomerating to form rippled-type fibers. It is difficult at this stage to suggest why at lower temperature flat-type fibers are favored over beads. Sharon *et al.*[17] however, have shown that pyrolysis of camphor at 1173 K gives carbon nanobeads. These carbon nanobeads convert into rippled-type fibers on annealing (even at 1173 K).

Although the mechanism of formation of VGCFs in the presence of catalyst particles is well documented,[18] there are no reports available to explain the formation of fibers in the absence of catalysts. It is believed that for the growth of such carbonaceous materials in the absence of any catalyst in a thermal chemical vapor deposition process among other parameters, substrate surface and temperature appear to be prominent. The surface roughness acts as a nucleation center and plays the main role for the formation of beads. Once growth starts from a nucleation center, it grows like bottom catalyst growth mechanism.[18] The mechanism controlling the formation flat type fibers at low temperature (1073 K) and the reason for their poor reproducibility are not very clear yet. However, formation of carbon beads always takes place when the pyrolysis temperature is higher than 1173 K. These carbon beads are spherical in shape, and most

FIG. 3. Transmission electron micrograph of spherically interconnected carbon beads formed at 1173 K.
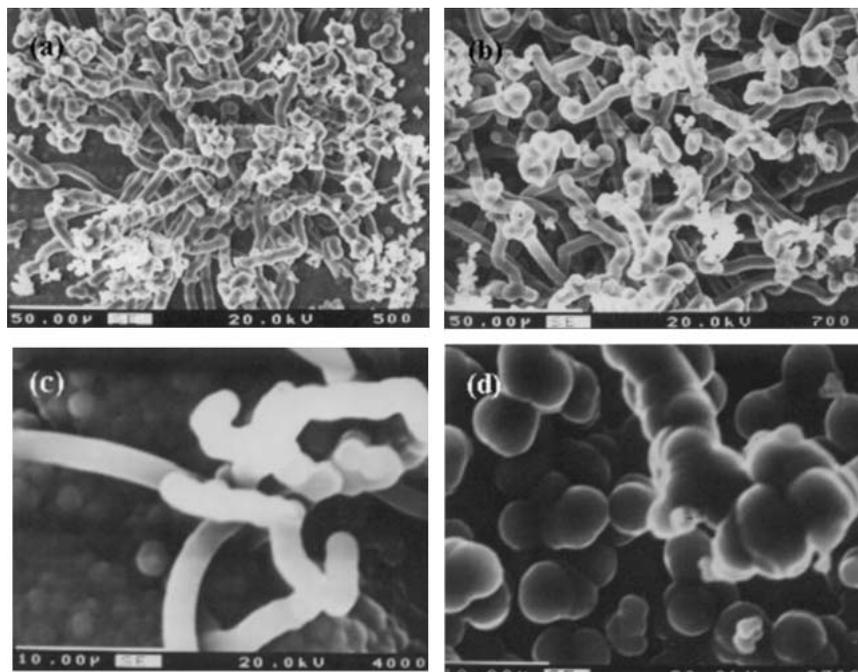

FIG. 4. Scanning electron microscope view of VGCFs formed (a, b) at 1273 K and (c, d) at 1373 K.

of them are interconnected. It is observed that at higher temperatures, pyrolysis leads to formation of rippled carbon fibers due to agglomeration of carbon beads.

B. Raman investigation of VGCFs

Raman spectroscopy is an important technique for the characterization of carbon materials. Here, we studied the Raman scattering from the as-grown carbon fibers. Figures 6(a) and 6(b) show the Raman spectra of carbon fibers and carbon beads formed at 1033 and 1173 K, respectively. Figures 7(a) and 7(b) show Raman spectra of VGCFs formed at 1273 and 1373 K, respectively. These Raman spectra are deconvoluted by Lorentzian distribution function. There are four types of Raman bands found in these spectra. They are at approximately 1180, 1340, 1480, and 1580–1600 cm^{-1}. The broad peaks at approximately 1350 and 1580–1600 cm^{-1} are generally termed as D-band (disorder/defect band) and G-band (graphitic), respectively. It is interesting to observe that a peak at approximately 1180 cm^{-1} is present with films obtained by pyrolysis of camphor at all temperatures

except the one obtained at 1173 K. The SEM image suggests that film obtained at 1173 K contain only carbon beads. Other films contain either flat type fibers or rippled type fibers. The peak at approximately 1180 cm^{-1} may be due to either trans-polyacetylene[19] or sp^3-rich carbon.[20] In addition, the peak at approximately 1480 cm^{-1} comes from either the same trans-polyacetylene or from the semicircular ring stretch vibration in benzene or phonon density of states in finite size crystals of graphite.[21] The analysis of the intensity of the D-peak and the G-peak (Fig. 8) indicates that carbon nanobeads might contain sp^3 disorder carbon or trans-polyacetylene chains. The intensity ratio I_D/I_G versus pyrolysis temperature plot (Fig. 8), exhibits a maximum around 1173 K (i.e., the temperature at which carbon beads are formed). Therefore, it can be concluded that flat-type fibers and rippled-type fibers have more graphitic character, whereas carbon beads have more disorderliness.

C. Electrical properties of VGCFs

Table I summarizes the room-temperature bulk resistivity of the as-grown VGCFs in the absence of any catalyst and their nature of growth. The electrical resistivity of thin films deposited on alumina plate by
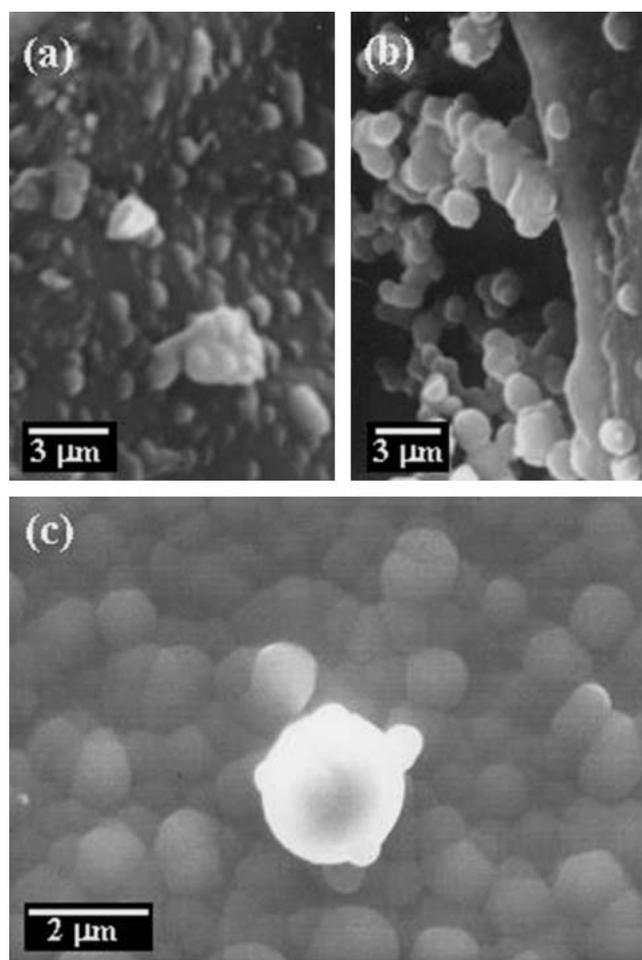

FIG. 5. SEM view of as-grown carbon (a) on the surface of silicon substrate (100), (b) at the edge of silicon substrate, and (c) on quartz substrate at 1173 K.
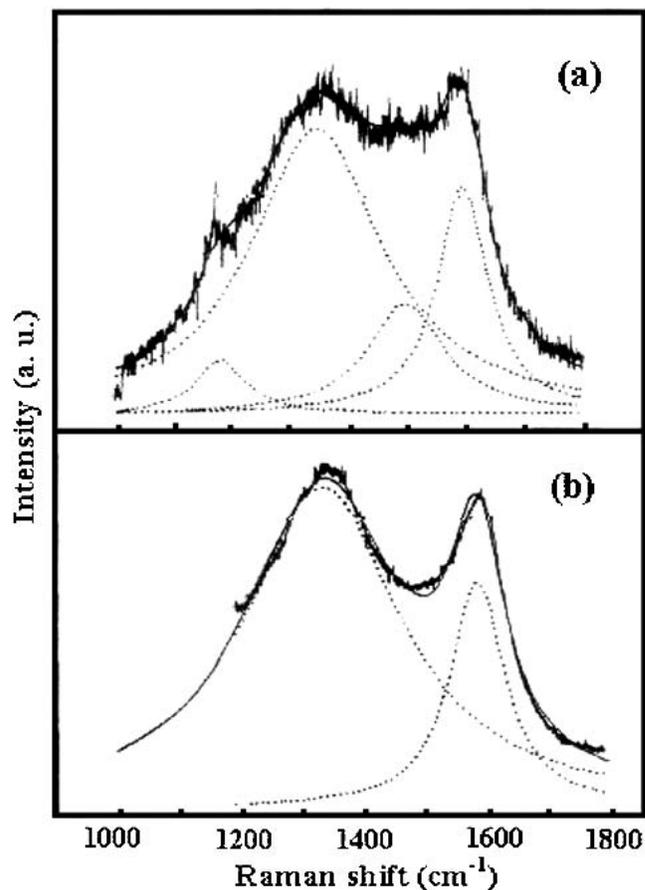

FIG. 6. Raman spectrum of (a) carbon fibers obtained at 1033 K and (b) carbon beads obtained at 1173 K.

pyrolysis of camphor at different temperatures (Fig. 9) shows that flat-type fibers (obtained at 1033 K) have higher resistivity than rippled fibers and nanobeads. Despite their graphitic nature, the flat-type fibers show high resistance because these fibers are disjointed [Fig. 2(b)]. Fi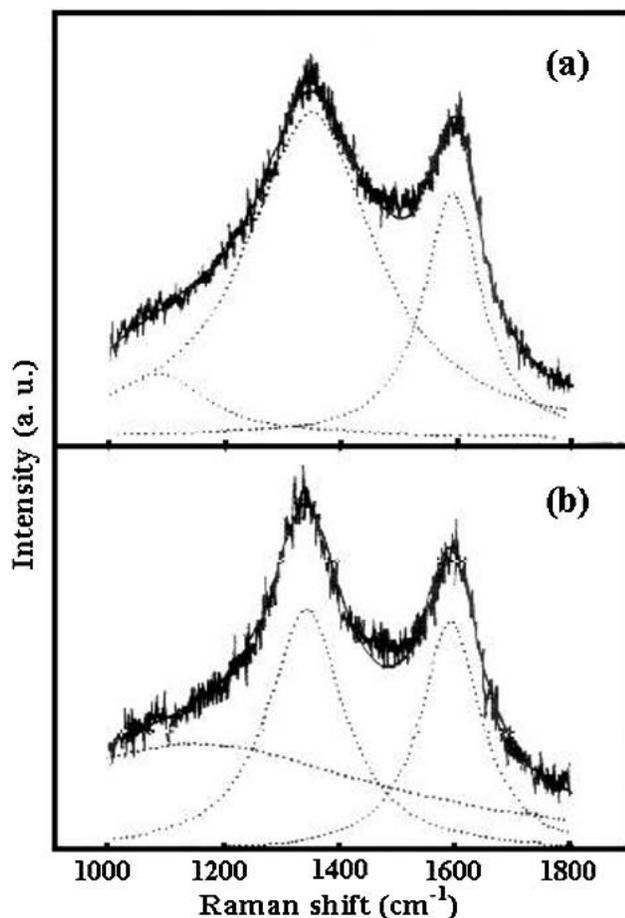lms obtained by pyrolysis at 1173 K and higher temperatures show low resistivity perhaps because of the uniform connection of fibers or beads with each other. In addition, films obtained at 1273 and 1373 K exhibit lower resistivity due to the presence of more graphitic carbon as well. Figure 10 shows the plot of reciprocal of temperature versus natural logarithm of conductance. There is only a minor increase of conductivity with temperature. The variation of ln $(1/R)$ versus $(1/T)$ implies that films grown at 1033 K might be semiconducting. The change in resistivity with temperature is negligible for VGCFs and beads grown at the other temperatures. It is worth noting that these materials may be useful where one requires conductance to be almost independent of temperature. The resistivity of these VGCFs is also in the range reported elsewhere.[22,23]

IV. CONCLUSION

It is observed that camphor (a natural precursor) can also be used to produce VGCFs without using any catalyst on a rough surface. By controlling the pyrolysis temperature, camphor can produce both straight and rippled fibers as well as carbon beads. It is suggested that these fibers or carbon beads can have applications where

FIG. 7. Raman spectrum of (a) carbon fibers obtained at 1273 K and (b) carbon fibers obtained at 1373 K.

TABLE I. Room-temperature resistivity of carbon fibers obtained at different temperatures.

VGCFs	Resistivity	Remark
Carbon fibers grown at 1033 K	1.805×10^{-3} Ω m	Only flat fibers
Carbon beads grown at 1173 K	5.1×10^{-5} Ω m	Only beads
VGCFs grown at 1273 K	1.41×10^{-5} Ω m	Rippled fibers mixed with beads
VGCFs grown at 1373 K	3.41×10^{-5} Ω m	Rippled fibers mixed with beads
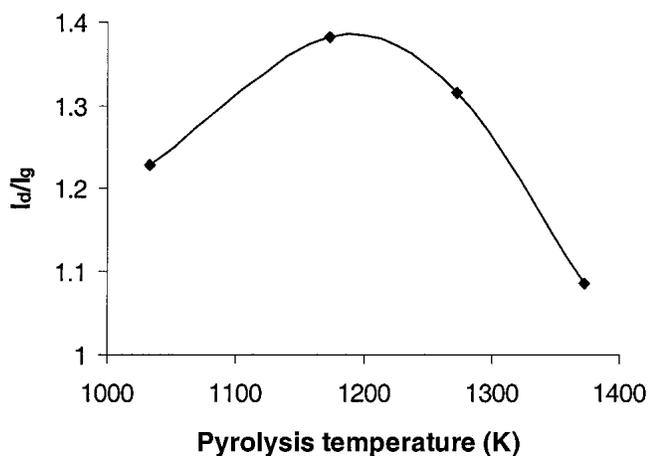
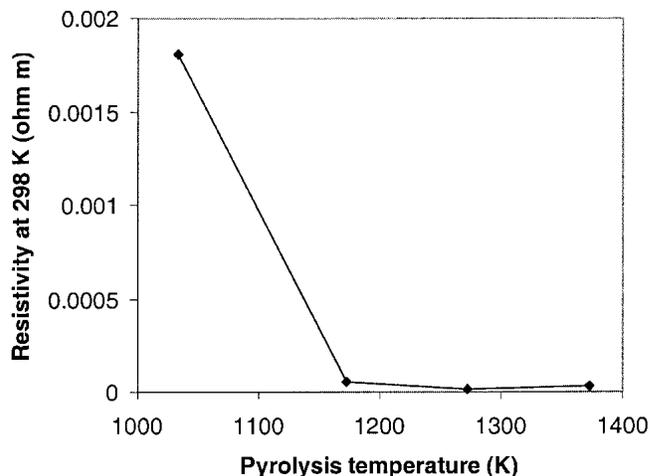FIG. 8. Plot of I_D/I_G ratio versus pyrolysis temperature.

FIG. 9. Resistivity (measured at room temperature) of carbon films versus pyrolysis temperature at which they are obtained.
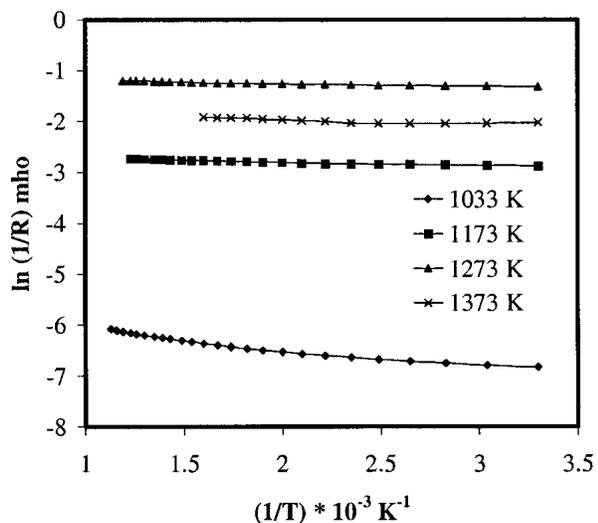
FIG. 10. Plot of reciprocal of temperature versus natural logarithm of conductance for carbon fibers obtained at different pyrolysis temperatures.

a highly conducting material is required. Raman studies were found to be useful in understanding the nature of VGCFs grown at different pyrolysis temperatures.

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