

# EVIDENCE FOR GLIDE AND ROTATION DEFECTS OBSERVED IN WELL-ORDERED GRAPHITE FIBERS (VGCF)

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## INTRODUCTION

Vapor-grown carbon fibers (VGCF's) have a circular cross-section and show a preferred orientation in which carbon planes are arranged like annular rings of a tree. It has been found by X-ray diffraction studies that the VGCF's attain an almost perfect 3D graphite structure when heat-treated at about 3000 °C [1,2]. We report in this paper a new aspect relating to stacking defects of the crystal structure of VGCF's. The glide structure of graphite planes gives rise to a shear effect coexisting with the ideal 3D graphite structure. This glide structure is observed for the first time using transmission electron microscopy (TEM) combined with an image analyzer. Atomic force microscopy (AFM) observations also support the presence of a glide structure coexisting with the 3D graphite and the 2D turbostratic structures.

## EXPERIMENTAL

VGCF samples were heat-treated at 2980°C in Ar for 15 min. Rather thin fibers (several hundred nanometers in diameter) were produced for the TEM measurements by controlling the growth conditions. By TEM and AFM observations, we can obtain the graphene layer structure at the periphery of the fiber using TEM 002 lattice fringe measurements and the atomic arrangement on the top of the fiber using AFM observations, respectively.

We used an image processing system [3] for the analysis of the TEM lattice plane images. Fig. 1(a) shows the original TEM image of the heat-treated VGCF sample. The TEM picture shows a 2D projection containing the 002 direction and a direction in the basal planes perpendicular to the 002 layer planes. A 2D fast Fourier transform (FFT) was carried out on the original TEM image and the power spectrum was calculated.

## RESULTS AND DISCUSSION

The resulting power spectrum is shown in Fig. 1(b). The power spectrum shows full inversion symmetry about the central point O. Thus, it is sufficient to discuss only the right hand side of the power spectrum. As the location spreads from the central point, a high frequency component appears. Each frequency in the FFT corresponds to a periodicity found in the original image.

Two bright spots [positions A and A' in Fig. 1(b)], correspond to 002 lattice planes. Since the VGCF was heat-treated at high temperature, the repeat distances of the 002 lattice planes are found to be 3.36 Å from the

X-ray diffraction pattern [1], which is approximately the distance between the 002 lattice planes of graphite.

The spot (B<sub>1</sub>) at the right thus corresponds to the 100 lattice planes. Using the distance for d<sub>002</sub> (=3.36 Å) and the relation between spot A and spot B<sub>1</sub>, we find the spacing between the 100 lattice planes, d<sub>100</sub>, to be 2.128 Å. Since the spots B<sub>2</sub>-B<sub>7</sub> in the region B are in a row above the 100 spot, we conclude that the corresponding lattice planes are tilted toward the left, while keeping their horizontal distances constant, independent of their tilt angles. The spots in region B thus indicate that the 002 lattice planes glide slightly from their ideal positions in the graphite lattice, as shown in Fig. 2. The angles  $\theta$  for the seven spots B<sub>1</sub>-B<sub>7</sub> were measured directly from the spot locations as shown in Fig. 1(c). Fidelity in the structure could be obtained in some domains. Such domains will show the three dimensional graphite structure upon further graphitization.

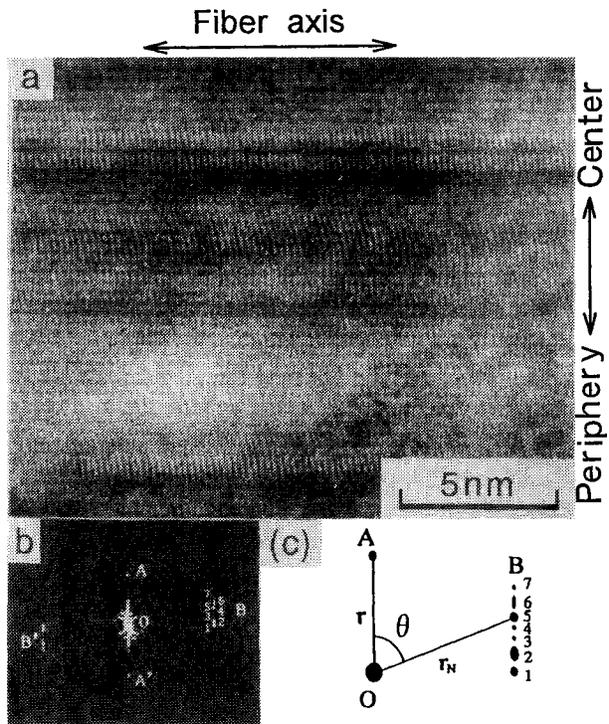


Figure 1 (a) TEM image for a heat-treated VGCF sample. (b) Power spectrum of the TEM image. (c) Schematic diagram showing notation used to analyze (b).

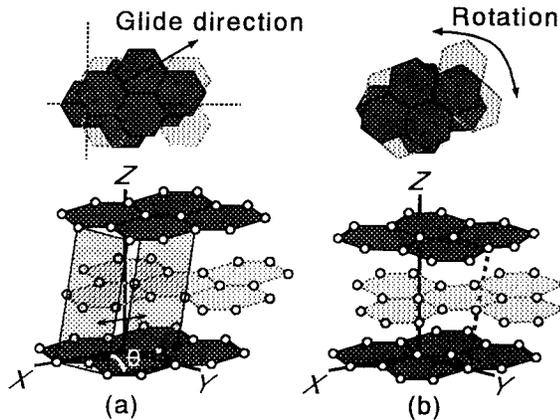


Figure 2 Models for the lattice planes of VGCF. (a) glide plane stacking, (b) rotational stacking.

The areas where no 100 lattice fringes are observed in Fig. 1 may be due to two different reasons, one being out of the diffraction condition, and the other associated with turbostratic stacking. These two cases correspond to a rotational stacking model for adjacent graphene sheets, which is also commonly observed by AFM measurements, as shown below. These glide structures could be mainly associated with shear effects on the lattice planes, since facets are formed from the curved external surface during graphitization.

To interpret these experimental results we propose a model for the structure of VGCF's, as shown in Fig. 2. The structure of VGCF's, heat-treated at high temperature, is almost that of graphite, but with a shift of the 002 lattice planes along a basal plane direction. In the ideal graphite structure the 100 lattice planes are normal ( $\theta = 90^\circ$ ) to the 002 lattice planes, corresponding to the spot  $B_1$ . When the 002 lattice planes are shifted with respect to each other as in Fig. 2(a), the 100 lattice planes make an angle  $\theta < 90^\circ$ , with respect to the 002 lattice planes, and show a corresponding change in interlayer spacing. Thus Fig. 2(a) corresponds to spots  $B_2$ - $B_7$ . The measurements show that the 002 lattice planes can shift over a range of  $\theta$  values, and the spot pattern in Fig. 1(a) indicates that certain shift angles are preferred.

Figure 2(b) shows a rotational turbostratic model, in which the upper 002 lattice planes are rotated with respect to the lower 002 lattice planes. If the two upper 002 lattice planes in Fig. 2(b) have random rotation angles with respect to each other, no diffraction pattern can be observed for the 100 lattice planes. These structures, corresponding to glide and turbostratic regions of the sample are located in Fig. 1(a) in the region where 100 lattice plane images appear and disappear, respectively. These glide structures could be just precursors of the 3D graphite structure, which is formed from a turbostratic structure.

Typical atomic images often observed by AFM on the surface of VGCF heat-treated at 2980 °C are shown in

Fig. 3. It is noteworthy that there are large regions of periodicity as seen in the bright regions of the atomic image shown in Fig. 3(a). We believe that the images of Fig. 3(a) are Moiré patterns due to a rotational misorientation of two adjacent graphene layers near the surface resulting from the turbostratic structure [4]. The periodicity ( $D$ ) of the Moiré patterns observed in Fig. 3(a) is about 2.82 nm.

The periodicity of the graphite lattice of 100 planes is  $d=2.46 \text{ \AA}$ , and the rotation angle  $\theta$  of the misorientation is given by  $\sin \theta / 2 = d / 2D$ . Thus a value for  $\theta$  of about  $\theta = 5 \sim 12^\circ$  is obtained, and the corresponding atomic structure is indicated schematically in Fig. 3(b). In this model, it can be also seen that in some regions hexagons of both layers are nearly superimposed. From the AFM observations, we conclude that VGCF's consist of large graphitic layers which are developed by heat treatment. These AFM results suggest that heat-treated VGCF's also contain residual turbostratic stacking.

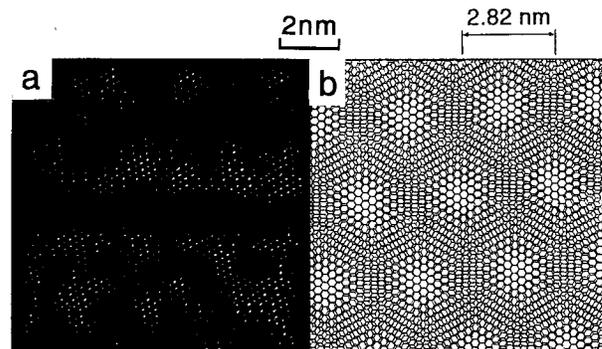


Figure 3 (a) Moiré patterns seen in the AFM image, (b) Diagram of a Moiré pattern with a rotation angle ( $\theta = 5^\circ$ ) between two adjacent layers.

## CONCLUSION

The microstructure of the lattice planes of VGCF's was investigated by TEM observations combined with computer image analysis, as well as AFM observations. It was found that well-ordered graphite fibers contain imperfect crystallites showing graphene glide planes along the basal plane directions and finally turbostratic regions are observed, where the graphene planes on adjacent layers are rotated with respect to each other.

## REFERENCES

1. M. Endo, T. Koyama, and Y. Hishiyama, *Jap. J. Appl. Phys.*, **15**, 2073 (1976).
2. T. C. Chieu, M. S. Dresselhaus, and M. Endo, *Phys. Rev. B*, **26**, 5867 (1982).
3. K. Oshida, M. Endo, T. Nakajima, S. L. di Vittorio, M. S. Dresselhaus, and G. Dresselhaus, *J. Mater. Res.* **8**, 512 (1993).
4. H. Saadaoui, J. C. Roux, and S. Flandrois, *Carbon*, **31**, 481 (1993).