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Ultrafine fibers formed in electric fields*

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Abstract

We describe the preparation of several materials in the form of free-standing ultrafine fibers. The materials are made by evaporating material in an inert gas in the presence of electric fields. Fiber diameters are typically 100–300 Å and irregular. Lengths of fibers or fiber bundles extend up to 10 cm. Materials range from transition metals, non-transition metals, semimetals and semiconductors. In most cases, they appear to be the smallest free-standing microwires of these lengths that have been made from these materials.

1. Introduction

The gas evaporation technique for producing ultrafine particles has been known since at least the 1930s [1, 2]. It has been extensively studied in Japan, beginning in the early 1960s [3, 4], and also elsewhere [5]. Generally the technique involves heating a charge to a temperature where it has a vapor pressure of order 0.01–1 Torr in about 1–100 Torr of inert gas. The evaporated material expands into and is cooled by the inert gas, leading to the condensation of ultrafine particles. Interparticle collisions lead to the growth of larger particles and to multiparticle aggregates. It was later found that the aggregation process and the fractal shapes could be understood on the basis of the diffusion-limited aggregation (DLA) model [6].

For a variety of scientific and technical reasons, it would be useful to be able to prepare large quantities of very small particles having a narrow distribution of sizes. However, under steady state heating with this method, convective flows are set up in the inert gas which tend to confine the particles into a plume where the interparticle density is high. Because the collision rate depends on the square of the local particle density [7] the rate of aggregation is much higher. Thus it appears that eliminating convection might improve the process for small particle production. For this reason we have considered [8] the use of the gas evaporation technique in a microgravity ambient in order to minimize convective effects. However, in microgravity

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a positive means for particle removal would be necessary, so we were led to investigate the use of electric fields for particle removal. In laboratory experiments it was found that, instead of being useful for individual particle removal, electric fields produced large fibers or fiber bundles, with lengths extending up to 10 cm and fiber diameters of 100–300 Å.

Recently [9], it has been reported that carbon fibers form in corona discharges in hydrocarbon gases. These fibers are larger in diameter, of order 10–100 μm, but have the interesting property that they are hollow. Carbon fibers of much smaller diameter form by catalytic processes. These are hollow also [10]. There is another large body of literature on whiskers [11], but these tend to be much larger in diameter than the ultrafine fibers reported here.

Because of their small size and the fact that they are freestanding the fibers have potential scientific and technological applications. Their calculated equilibration time for responding to thermal input on one side is of order 50 ps at room temperature and subpicosecond at cryogenic temperatures. This rapid response time suggests that they may be useful in high frequency bolometers and thermometers. The calculated heat capacities per unit length of the microwires are small: of order 5×10^{-11} J K^{-1} cm^{-1}. At cryogenic temperatures the calculated heat capacities are four orders of magnitude smaller; therefore the materials would be sensitive to very small thermal inputs. These unusual properties suggest that they may be useful as high performance fast response sensors.

This paper describes some of our experimental results on ultrafine fibers and an analysis of the forces involved in their formation. To our knowledge, they are the smallest freestanding fibers of this length that have been made for most of the materials listed below.

2. Experimental details

The experimental apparatus is based on a diffusion-pumped high vacuum system. The system is first evacuated to the low 10^{-6} Torr range and then backfilled with inert gas of purity 99.998%. Most experiments used argon for the inert gas, although helium and xenon were also used. The charge was evaporated from tungsten resistance boat heaters. Heater temperatures were measured by type-K thermocouples below 700 °C and by a pyrometer from 700 to 2000 °C.

Transmission electron microscopy (TEM) was done at 75–100 kV. Electron microscope samples were prepared by touching a grid to a particle deposit and then lightly blowing off excess powder in most cases. This technique seemed to give more reliable results than more standard techniques of sonicating the powder in a liquid to form a slurry, although both techniques were used. Scanning electron microscopy (SEM) was done on uncoated samples adhering to SEM buttons.

Several different electrode geometries were experimented with but most results were obtained using the apparatus shown schematically in Fig. 1.

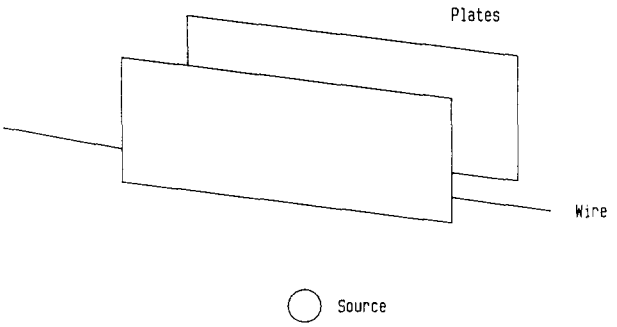


Fig. 1. Schematic diagram of the electrode apparatus. Typical voltages are −200 V on the corona wire, one plate at +200 V, and the other grounded.

The wire labeled "corona wire" had a voltage of several hundred volts applied to it and a voltage difference of several hundred volts was established between the plates.

3. Results

Although it was intended that particles would be charged as they passed through the corona discharge and then accelerated by the electric field between the plates of Fig. 1, no clear sign of charging was observed. Instead it was found that fibers or fiber bundles formed in the inert gas and were attracted to regions of high electric field gradient. Reasons for this are discussed later.

To date ultrafine fibers have been grown of non-transition metals, transition metals, semiconductors, and in one case insulators. The materials investigated are given in Table 1. Control experiments in zero field do not yield any fibers observable to the naked eye, except in the case of iron, cobalt and nickel. The ferromagnetic materials iron, cobalt and nickel are special cases that were grown under the influence of internal magnetic fields alone, in agreement with earlier work, and collect at regions of high magnetic field strength if an externally applied magnetic field is present [12]. Another special case is WO_x which was grown by heating a tungsten heater in the presence of oxygen and electric fields using the apparatus of Fig. 1. The other materials comprise transition metals, non-transition metals, semimetals and semiconductors.

Vanadium is a superconducting transition metal. It was found that vanadium fibers or bundles of fibers up to 1 cm in length grew on the plates and up to 3 cm in length on other charged components, as shown in Fig. 2. Potentials of 200 V were used on the wire and one of the plates. Opening the system caused the fibers to be blown around by air currents. This is a problem with all the materials. A partial solution was found which allows the electrical properties of individual fibers to be measured *in situ* [13]. A further complication is that vanadium and titanium deposits are pyrophoric

TABLE 1

Materials investigated

Material	Length (cm)[a]
Ag	1
Cu	0.3
Pd	5
V	3
Ti	3
Fe	10
Co	ND[b]
Ni	10
WO_x	1
Al	10
Pb	NO[c]
Sn	NO
Mg	NO
Zn	0.2
Bi	1
Ge	5
Si	1

[a]Maximum fiber or fiber bundle length observed.
[b]Not determined.
[c]None observed.

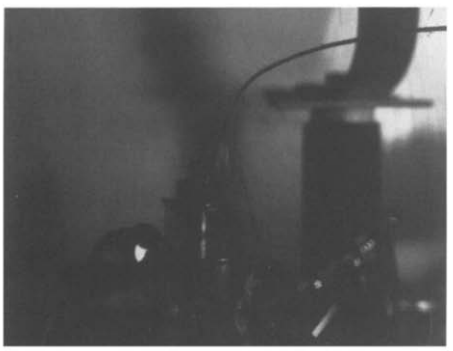


Fig. 2. Photomicrograph of vanadium fiber bundles up to 3 cm long in the apparatus. The wire voltage is on, so the fibers stand out from the wire against gravity.

Fig. 3. Photomicrograph of titanium fiber bundles up to 3 cm long in the apparatus. The wire voltage is turned off, so the fiber bundles are pulled down by gravity.

in air, so that they sometimes ignite when manipulated with metal tweezers. This has not been observed with other materials studied. Electrically grounding the tweezers alleviates the problem.

TEM revealed an average diameter of 250 Å for vanadium fibers. The TEM samples were prepared by the standard technique of sonicating material in water or acetone to disperse it and then putting a drop on a TEM grid.

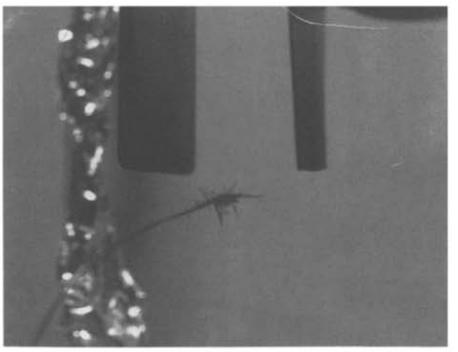
This handling deformed the fibers. It was later found that TEM samples could be prepared without the sonication step.

Titanium fibers are a particularly difficult case. Figure 3 shows an optical micrograph of titanium fiber bundles. Titanium displayed many of the features of vanadium deposits but to an exaggerated degree. Much care had to be taken in handling to avoid ignition in air. For example, dropping material from a few centimeters onto a plastic dish in air would sometimes ignite it. TEM samples show an average particle diameter of 230 Å.

Silicon and germanium were both prepared in fiber form. Figure 4 is a photomicrograph of silicon fibers which grew in the high electric field region around the 0.5 mm corona wire of Fig. 1. Convection in this region causes them to agglomerate into bundles. Figure 5 is an optical photomicrograph of germanium fibers growing in another high electric field region of the apparatus. While the fibers are growing, they agglomerate slowly into bundles as a result of convection currents set up by the hot filament.

Figure 6 is a scanning electron micrograph of germanium fibers which were collected on a microscope slide and then transferred to an SEM button. They were disturbed in this process, as is apparent. In addition, the fibers are too fine to be well resolved in SEM.

An attempt was made to grow fibers of silver directly on a TEM grid using a modified electrode configuration. Conditions similar to other fiber growth experiments were used. Fiber bundles of about 1 cm in length were observed, but it was difficult to collect them onto TEM grids because of convection. However, by scooping up material on TEM grids we observed fiber bundles 5 μm in length and 300–500 Å in diameter, as shown in Fig. 7. The fiber bundles may be collections of long aggregates. It is not known how much damage is done to the material when it is collected for microscopic examination.



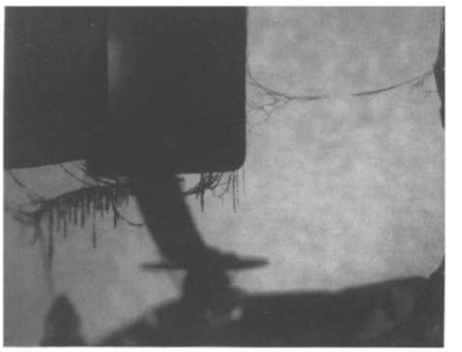


Fig. 4. Photomicrograph of silicon fiber bundles up to 0.3 cm long in the apparatus.

Fig. 5. Photomicrograph of germanium fiber bundles 5 cm long in the apparatus.

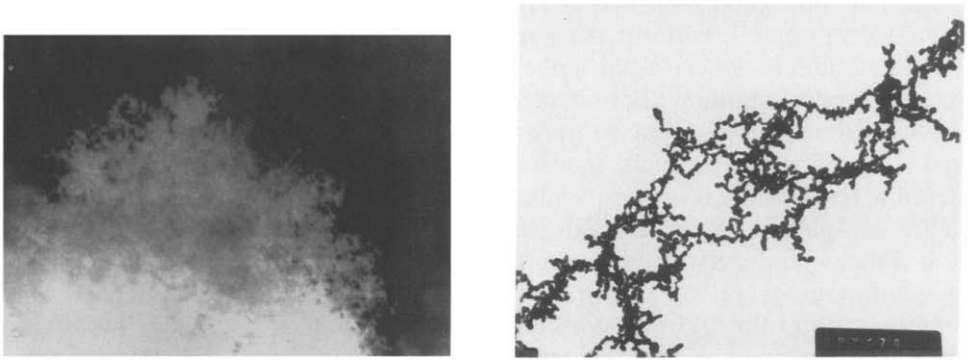


Fig. 6. Scanning electron micrograph of germanium fibers (magnification, 8100 ×). Individual fibers are barely resolved.

Fig. 7. Transmission electron micrograph of a silver fiber bundle (magnification, 24 300 ×).

4. Discussion

As stated above, there was no sign of charging and therefore it was concluded that electric dipole forces dominate the fiber growth process. In an electric field $\boldsymbol{E}$ a dipole of moment $\boldsymbol{p}$ experiences a force $\boldsymbol{F}$ of

$$\boldsymbol{F}=(\boldsymbol{p}\cdot\nabla)\boldsymbol{E} \tag{1}$$

A long thin conducting cylindrical element of length $2l$ and radius a will have an induced dipole moment $\boldsymbol{p}$. If $l/a \gg 1$ then p in a parallel field E is approximately [14]

$$p=\frac{El^3}{3\ln(4l/a)-7} \tag{2}$$

For fibers with $l=1$ cm and $a=100$ Å, typical of those seen here, the first term in the denominator of eqn. (2) is 45.6. For the purpose of discussion we therefore make the further approximation that

$$p\approx\frac{El^3}{3\ln(4l/a)} \tag{3}$$

It is significant that $p\propto l^3/\ln(4l/a)$. In a sphere, for example, p is proportional to the volume but for a long thin conductor p grows much faster with length than does the volume (or mass) at fixed diameter, leading to large forces per unit mass for fibers.

The energy of interaction between an induced dipole and electric field $\boldsymbol{E}$ is

$$U=-\frac{1}{2}\boldsymbol{p}\cdot\boldsymbol{E} \tag{4}$$

From eqns. (3) and (4), the energy of two separate but identical dipoles in a field E is U_s, and if they combine into a dipole twice as long it is U_c,

where

$$U_s = -E^2 l^3/3 \ln(4l/a) \qquad \text{separate} \tag{5}$$

$$U_c = -(1/2)E^2(8l^3)/3 \ln(8l/a) \qquad \text{combined} \tag{6}$$

For large l/a in eqns. (5) and (6)

$$U_s/U_c \approx 1/4 \tag{7}$$

Therefore two induced dipoles lower their potential energy in a field when they combine.

5. Conclusions

For a simplified model of the fiber-forming process, we speculate that the extended structures of order 1 μm in length that are known to form by DLA processes [6] will have a dipole moment induced in them by the electric field. Additionally, from eqns. (1), (3) and (7) it is concluded that the induced dipoles are attracted to the regions of highest field with a force which grows strongly with l and that in high field regions bigger dipoles (longer conductors) form at the expense of shorter ones.

Acknowledgments

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