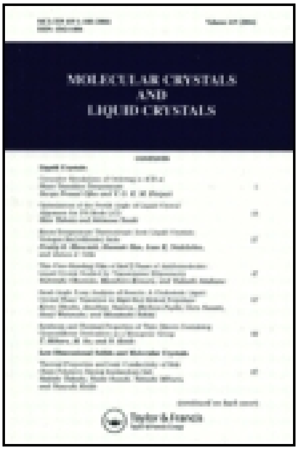

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Super-hard conductive carbon nano-crystallite films

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SUPER-HARD CONDUCTIVE CARBON NANO-CRYSTALLITE FILMS

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Carbon films whose hardness is comparable to diamond's, but whose electrical conductivity is 19 orders of magnitude larger, have been discovered. They were deposited onto silicon substrate by electron cyclotron resonance plasma sputtering. The bonding structure of the film is mainly sp^2. The film consists of sp^2 nano-crystallites having parallel and curved graphene sheets vertically oriented to film surface. The sp^2 nano-crystallites are connected with adjacent crystallites by sp^3 bonding, which gives the film both its high hardness and conductivity. The formation of this sp^2 nano-crystallite film suggests that many applications should be possible.

Keywords: ECR; sputtering; sp^2; sp^3; hardness; conductivity

Carbon films whose hardness is comparable to diamond's, but whose electrical conductivity is 19 orders of magnitude larger, have been discovered. They were deposited onto silicon substrate by electron cyclotron resonance (ECR) plasma sputtering. For the sputtering, argon pressure

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was 5.0×10^{-2} Pa and substrate temperature was room temperature. Irradiation ion current density was 5.8 mA/cm^2 and the ion acceleration voltage ranged from 20 to 130 V. The film thickness was 45 nm.

To evaluate the hardness, we carried out a scratch wear test using an atomic force microscope with a three-sided pyramidal diamond tip [1]. The electrical conductivity was measured by the four-point probe method at room temperature. To evaluate the structure, we used a high resolution transmission electron microscope (HRTEM) and X-ray photo-electron spectroscopy (XPS).

Table 1 shows the electrical conductivity and mean scratch hardness of a typical ECR-sputtered carbon film, diamond (100), and graphite (001). The conductivities of diamond and graphite are from the literature [2]. The electrical conductivity of ECR-sputtered carbon film is 19 orders of magnitude larger than that of diamond and its scratch hardness is comparable to that of diamond. The conductivity of the film is smaller than that of graphite measured along the c plane but larger than that measured perpendicular to the c plane. The film's scratch wear depth is three orders of magnitude smaller than graphite's.

Figure 1 shows bright field images of two films prepared using ion acceleration voltage of 20 (sample A) and 85 V (sample B). The electrical conductivity and mean wear depth are 38 $(\Omega\text{cm})^{-1}$ and 1.1 nm for sample A and 20 $(\Omega\text{cm})^{-1}$ and 0.6 nm for Sample B. Sample A is softer and more conductive than sample B. Sample B is the sample in Table 1. Both bright field images show a fine, intricate lattice. Electron diffraction patterns of the two samples show broad rings corresponding to lattice spacing of 0.34 ± 0.02 nm, which is close to that of graphite (002). Figure 2 shows the cross-sectional image of sample B. Figure 2 shows that the graphene sheets are perpendicularly oriented to the film surface. The bright field image of sample A shows that it consists of 2–5-nm-scale crystallites whose lattice fringes are parallel or curved (region I) and fine closed structures (region II). Sample A mainly consists of the type-I regions. In contrast, sample B contains mostly fine closed type-II regions. Therefore, the ECR-sputtered carbon film consists of sp^2 nano-crystallites having graphene sheets vertically oriented to the film surface.

TABLE 1 Electrical Conductivity and Mean Wear Depth

Substance	σ_{RT} $(\Omega\,\text{cm})^{-1}$	Mean wear depth (nm)
ECR-sputtered carbon film	20	0.6
diamond	10^{-18}	0.5
graphite //c	1.9×10^4	620
graphite ⊥c	1	

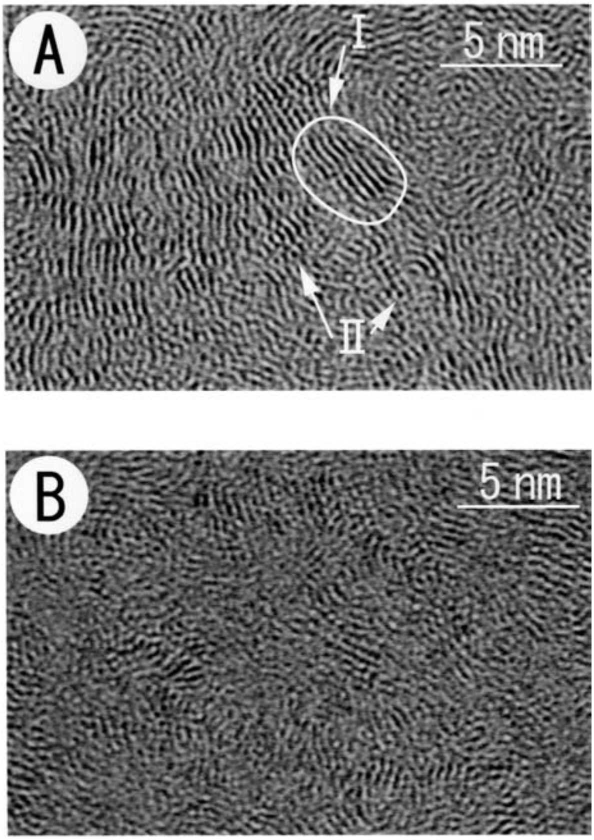

FIGURE 1 HRTEM bright field images of ECR-sputtered carbon films. (A) and (B) are bright filed images of films prepared using ion acceleration voltages of 20 and 85 V respectively.

The XPS spectra revealed that the bond structure of the films is a mixture of sp^2 and sp^3, and the main bond structure is sp^2. The sp^3/sp^2 ratios, which are the ratios of the peak height of sp^3 and sp^2 spectra, are 0.32 and 0.85 for samples A and B, respectively. The sp^3 bonding revealed by XPS connects adjacent crystallites because the graphene sheet itself consists of sp^2 bonds. When the sp^3/sp^2 concentration is large, the volume of the parallel graphene region decreases and the binding force between adjacent crystallites increases. In this case, the film shows high scratch hardness comparable to diamond's. Since this film consists of sp^2 nano-crystallites, the wave functions of the π electrons of each sp^2 crystallite overlap, which provides a current path in the film. It is this current path that gives rise

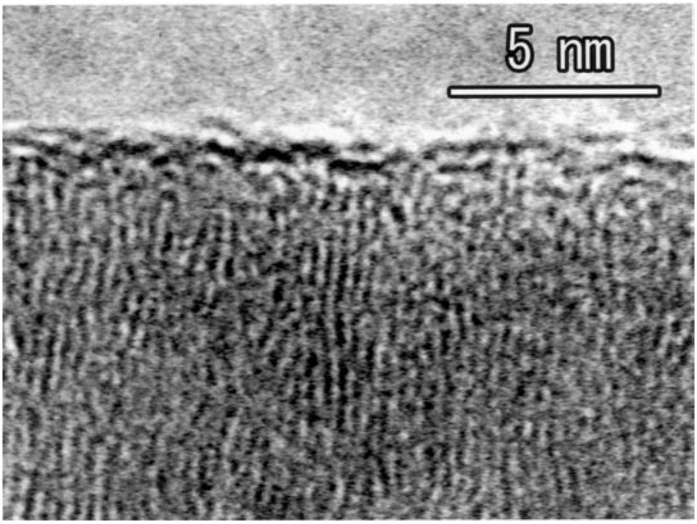

FIGURE 2 The cross-sectional TEM image of ECR-sputtered carbon films formed at the acceleration voltage of 85 V.

to the film's high conductivity. The high hardness of the ECR sputtered carbon film originates in the volume reduction of sp^2 nano-crystallites and the enhanced binding force between adjacent crystallites due to the increase in the sp^3 concentration, which cancels out the effect of the weakness of the van der Waals force.

The ECR-sputtering method can control both the sp^3/sp^2 ratio and the nano-structure of carbon films. The ECR-sputtered carbon film, therefore, is a promising candidate as a new nano-carbon material. This new carbon film will have many applications.

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