Electronic properties of super-hard carbon nanocrystallite film

Ken -i. Matsuda [a,1], Shigeru Hirono [b], Hideaki Takayanagi [a]

[a] *NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi Kanagawa, 243-0198 Japan*
[b] *NTT Afty Corporation, 4-16-30 Shimorennjyaku, Mitaka, Tokyo, 181-0031 Japan*

Abstract

The carbon nanocrystallite(CNC) film is a new type of synthetic carbon material. Recently, it has been found that the film has large electric conductivity ($\sim 10^3$[S cm^{-1}]) at room temperature, while its hardness is comparable to that of diamond. In this paper, we report the temperature dependence of electric conductivity from 1.7 K to 500 K. While a hopping conductance has been observed at low temperature region ($T < 200$ K), conductivity increases with decreasing temperature for $T > 250$ K. Possible mechanism for the electric conductivity in the CNC films is the hopping conductivity in disordered media.

Key words: carbon films; diamond-like carbon; electron cyclotron resonance sputtering ;

Carbon is a unique element in a sense that it has various material forms, including diamond, graphite, C_{60} [1], carbon nano-tube [2] etc. They consist of the same element "carbon" but show different mechanical and electronic properties. The carbon nonocrystallite (CNC) film is a new type of synthetic material and it has been invented by one of the authors (S.H.) [3]. The films consist of vertically oriented graphene sheets but there is no long-range order along the surface direction. It has recently been found that the CNC film has both high wear durability [4] comparable to that of diamond and electric conductivity [3]. In general, σ-bond in sp^3 hybrids in carbon materials contributes to their hardness. Diamond is made up of such chemical structure so that it is known as one of the hardest materials. Since there is a wide energy gap in such a chemical bond structure, it can hardly be expected that such materials are electrically conductive. In this paper, we show the temperature dependence of the DC resistivity of the CNC films. We also discuss the possible mechanism for the electric conductivity of these films.

The CNC films were deposited onto silicon substrates by electron cyclotron resonance(ECR) sputtering method. All samples used in this study were grown under the argon pressure of 5×10^{-2}Pa at room temperature. Five CNC films were prepared for this study with different ion acceleration voltages ($V_{\mathrm{accel.}}$) ranged from 20 to 150 V (see Table1). The typical dimension of the film was 40 nm $\times$ 3 mm $\times$ 2mm. DC resistivities were measured by using four-probe configuration.

Table 1
The parameter of film growth and fitting parameters in eq. (1)

Sample	$V_{\mathrm{accel.}}$ [V]	T_0 [K]	α
A	20	4.81×10^2	0.44
B	50	2.48×10^2	0.35
C	75	1.02×10^2	0.47
D	100	5.82×10^2	0.17
E	150	5.58×10^2	0.15

Figure 1 shows the temperature dependence of the DC resistivity $\rho(T)$ of five different CNC films. Here, all the data show that $\rho(T)$ increases with increasing temperature above 300 K. Typical resistivity at room temperature is 1×10^{-3} Ω·cm. Although $\rho(T)$ is not linear to temperature, these results imply that the electron-phonon interaction is dominant in this temperature region. On the other hand, at a sufficiently low temperature region, $\rho(T)$ increases with decreasing tempera-

[1] E-mail: ken@will.brl.ntt.co.jp

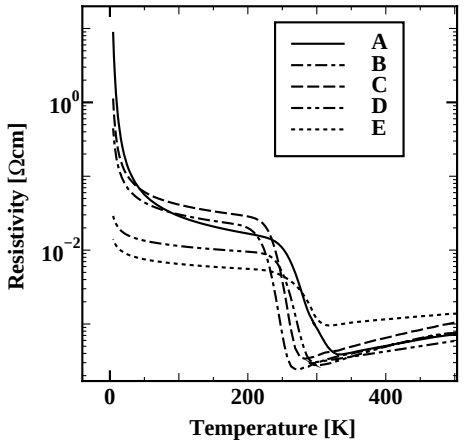

Fig. 1. Temperature dependence of the DC resistivity of CNC films. Solid line: Sample A, dash-dotted line: B, dashed line: C, two-dots-dashed line: D, and dotted line: E.

ture. Hereafter, we would like to focus our attention on the temperature dependence of $\rho(T)$ at this low temperature region.

Figure 2 shows the typical temperature dependence of $\rho(T)$ at low temperature and the solid line represents the following equation:

$$\rho(T) \propto \exp\left[\left(\frac{T_0}{T}\right)^{\alpha}\right]. \quad (1)$$

In a conventional band-insulator or semiconductor, the exponent α is equal to unity and T_0 corresponds to its energy gap. Our experimental results are well fitted by this equation in this temperature region. As shown in Table 1, however, the exponents α obtained from experimental data are quite different from that of conventional insulator.

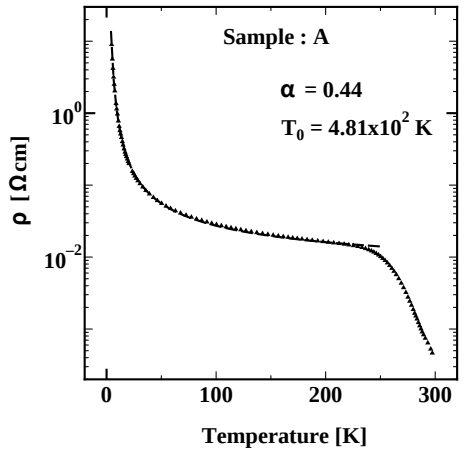

Fig. 2. Temperature dependence of the resistivity of sample A at low temperature region. Solid line represents eq. (1).

The possible explanation for this temperature dependence is the hopping conductivity in disordered media or "*variable-range hopping*"[5]. In the variable-range hopping, the exponent α is related to the spatial dimension d as $\alpha = 1/(d+1)$. It is well known that many isotropic amorphous carbon materials that consist of sp^2 and sp^3 netsowrks show the conventional variable-range hopping behavior[6]. Recent X-ray photoelectron spectroscopy (XPS) measurement has revealed that the bond structure of the film is a mixture of sp^2 and sp^3[3]. If the CNC film is an isotropic two-dimensional conductor, α should be 1/3. However, the exponents obtained from experimental data are different from this simple theoretical prediction. The reason for this disagreement between theoretical prediction and our results may be found in its crystal structure. Since the CNC films consist of vartically oriented graphene sheets, we have to take into acount the effect of anisotropic band structure to explain our experimental results.

In summary, we have studied the temperature dependence of the CNC films. While metallic behavior has been observed above room temperature, the resistivity increases with decreasing temperature at the low temperature region. Possible mechanism for the electric conductivity observed at low temperatures is variable-range hopping in disordered sp^2 network.

Acknowledgements

The authors would like to thank Prof. S. Umemura of Chiba Institute of Technology for valuable discussions. We also thank Ms. T. Miyagi of NTT Afty-engineering for sample preparations.

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