Dimer Formation of Pentacene by Heated Tungsten

Akira Heya, Naoto Matsuo
Univ. of Hyogo, 2167 Shosha, Himeji, Hyogo, 671-2280, Japan
Phone: +81-79-267-4909 E-mail: heyaa@eng.u-hyogo.ac.jp

Abstract
Dimer formation of low weight organic molecules was investigated using Hot Mesh Deposition (HMD) method. In this method, a heated tungsten (W) mesh was set between a pentacene source and a quartz substrate. Pentacene molecules were decomposed by the heated W mesh and the decomposed precursors was deposited on the quartz substrate via vapor phase polymerization. It is found that organic films with a structure close to pentacene dimer were obtained by HMD using two heated catalysts (W mesh and W wire).

1. Introduction
Nonographene is one of the attractive two-dimensional materials which consists of carbon atoms arranged in a hexagonal lattice [1-3]. In general, carbon-based thin films are obtained from CH₄, C₂H₂ [4], or an alcohol source [5-7]. If a thin film can be deposited using a precursor that maintains its structure, a compound with a complicated structure may be formed at a high deposition rate. In addition, the edge shape and ribbon width in graphene nanoribbons could be controlled by adjusting the precursor structure and the number of their polymerization reactions. The high-efficiency generation of pentacene-based precursors from a pentacene source is one of the key technologies for the synthesis of large graphene sheets and graphene nanoribbons with the controlled edge shape and width.

Recently, we proposed a novel method for formation of graphene by vapor phase polymerization of pentacene molecules. The method is named Hot Mesh Deposition (HMD) method [8,9]. In this study, the formation of peripentacene (pentacene dimer) was investigated for development of novel dimer formation technique.

2. Experimental
The HMD apparatus used in this study is illustrated in Fig. 1. A pentacene source (30 or 60 mg) in a Mo boat was placed in a 26 mm diameter quartz tube. A W mesh (85 mm×45 mm) mesh with a wire diameter of 0.03 mm and 50 holes/inch was positioned between a pentacene source and a quartz substrate (0.5×20 mm×20 mm). To enhance the decomposition reaction of pentacene molecules (pentacene dimer formation), a W wire (0.4 mmΦ, 120 mm) was added between the pentacene source and the W mesh. The temperature of W mesh (T_mesh) were varied from 800 to 2000 °C and the temperature of W wire (T_wire) was fixed at 1400 °C. The T_mesh and T_wire were measured by a pyrometer. The flow rate of H₂ gas and base pressure were 400 sccm and 6×10⁻³ Pa, respectively. The gas pressure was fixed at 30 Pa during film formation. The distance between the W mesh and the quartz substrate was 100 mm. The Mo boat was heated to 315 °C by a source heater for vaporization of pentacene. The film properties of the obtained organic thin films were evaluated by UV-vis spectroscopy and Laser Desorption / Ionization Mass Spectrometry (LDI-MS). In LDI-MS, 337 nm line from an N₂ laser was used for desorption.

3. Results and discussion
The UV–vis spectra of the organic thin films deposited at various values of T_mesh are shown in Fig. 2 (a). For a comparison, UV-vis spectrum of amorphous carbon (a-C) prepared by a resistive heating is also shown. The remarkable peak in UV region was not observed in a-C film. Although the W wire was enough high temperature to decompose pentacene molecules, peaks due to pentacene in the range of 500 and 700 nm were observed at the T_wire of 1400 °C and T_mesh of 800 °C. In the UV region, the peaks due to conjugated double bonds were observed. The surface area of W mesh and W wire used in this study were estimated to be 930 and 150 mm², respectively. Therefore, the pentacene decomposition was not occurred on W wire with small surface area in spite of high T_wire. On the other hand, the pentacene decomposition was confirmed above T_mesh of 1100 °C. The T_mesh of 1100 °C was not enough to decompose [8]. It is considered that the pentacene molecules collided with W mesh came into contact with W wire again. A part of the organic film prepared at T_wire of 1400 °C and T_mesh of 1400 °C had anomalous white color region as...
shown in Fig. 2(b).

LDI-MS spectrum of the white color region is shown in Fig. 3. The peaks are observed between 250 and 400, 500 and 800. Since a mass number of pantacene and peripentacene are 278 and 546, it is suggested that an organic film having a structure close to pentacene dimer was deposited by HMD method. Although the yield was not so high, we believe that the yield can be improved by controlling the ratio of pentacene to dihydropentacene which shall be mentioned later.

Finally, we discuss the decomposition mechanism and the effect of additional W wire on pentacene dimer (peripentacene) formation. A part of introduced pentacene molecules came into contact with W wire. The decomposed precursor is dihydropentacene mainly [8]. It is considered that the formation of dihydropentacene was occurred on the heated W surface via dissociative adsorption. The dihydropentacene desorbed from W surface. Northrop et al. had studied the reaction of peripentacene formation computationally with density functional theory as shown in Fig. 4 [10]. Computational and kinetic analyses indicate that dihydropentacene is required to form the peripentacene. It is considered that the dihydropentacene formed on the 1st heated W surface reacted with pentacene not in gas phase but on the 2nd heated W surface. The generated 6,6'-dipentacenyl radicals can dimerize and form 6,6'-dipentacenyl in gas phase. For this speculated reactions, existence of both pentacene and dihydropentacene on a heated W is one of the key points for the formation of pentacene dimer (peripentacene). It implies that this situation was achieved at TWire of 1400 °C and TMesh of 1400 °C.

4. Conclusions
The formation of nanographene (pentacene dimer) was investigated for development of novel dimer formation technique. The decomposition reaction was enhanced by using the two heated catalysts. It is confirmed that the organic film having a structure close to pentacene dimer (peripentacene) can be obtained by HMD using two heated catalysts.

References