Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Synthetic Metals 154 (2005) 177–180
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Metallic electrical conduction in alkaline metal-doped pentacene

Yutaka Kaneko*, Tomoaki Suzuki, Yasumitsu Matsuo, and Seiichiro Ikehata

Department of Applied Physics, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Abstract

We have prepared a cesium-doped pentacene film and a rubidium-doped pentacene film and have investigated their electrical properties in order to obtain a new molecular conductive film based on pentacene. It is found that the electrical conductivity depends strongly on the doping temperature. A high electrical conductivity is obtained by annealing of pentacene film doped with the alkaline metal. As a result, the electrical conductivities equal 74 S/cm and 47 S/cm in the cesium-doped pentacene film and in the rubidium-doped pentacene film, respectively. Moreover, we have observed that these conductivities increase with decreasing temperature and show metallic behavior below room temperature. Furthermore, it is found that the electrical resistivity shows anomalous behavior at around 80 K in the cesium-doped pentacene film and at around 90 K in the rubidium-doped pentacene film.

Keywords : Electrochemical doping ; Single crystalline thin films ; Metallic films

1. Introduction

Conducting molecular and organic materials have attracted considerable attention because of their wide variety of applications in electronic and optical devices. Pentacene ($C_{22}H_{14}$) is one of the well known molecular materials because of its high mobility that is comparable to the mobility of amorphous silicon. Pentacene possesses interesting properties. For example, pentacene film prepared by evaporating pentacene powder on the glass substrate is an insulator and has a layered structure [1-3]. Moreover, the doping of the pentacene film with both acceptors and donors causes the dopant to intercalate into the pentacene molecular layers, and the physical properties of the pentacene film change drastically [4,5]. For example, the doping of pentacene film with iodine (acceptor) makes it to intercalate between the molecular layers of pentacene, and the lattice constant of *c* axis ranges from 15.1 A to 19.1 A [4]. Furthermore, the electrical conductivity increases drastically to approximately 10^{10} times larger than that of the pure pentacene film by the doping with iodine and is characterized by metallic behavior below 240 K [3]. In this manner, pentacene doped with iodine shows interesting phenomena with respect to the structural and electrical properties. On the other hand, despite the fact that the electrical conductivity of pentacene film increases by the doping with the alkaline metal (donor) and attains a value greater than 10^{-5} S/cm [6,7], the metallic behavior for electrical conductivity has not been observed yet. In the present work, we have prepared a cesium-doped pentacene film (Cs-PEN film) and a rubidium-doped pentacene film (Rb-PEN film) by controlling the doping condition and have measured the electrical properties below room temperature.

2. Experimental

Pentacene film used in the electrical resistivity measurement was prepared on a glass substrate in a vacuum of 6×10^{-4} Pa. Pure pentacene was thermally evaporated from a sublimation cell. The film thickness and deposition rate monitored by a quartz oscillator were controlled by the heating temperature of the sublimation cell. Pure pentacene was deposited at a rate of 0.5 nm/s. The substrate temperature was 305 K. The doping of pentacene with the dopant was performed by an ordinary two-bulb method [8] as follows: (1) the pentacene film was mounted in a glass vessel with alkaline metals of approximately 50 mg placed in Ar gas as the source of dopant. (2) the glass vessel, in which both the pentacene film and the alkaline metal were inserted, was sealed in a vacuum of 8×10^{-4} Pa. (3) the

* Yutaka Kaneko. Tel: +81-3-3260-4272-2436; fax: +81-3-3260-4772; E-mail: j1203618@ed.kagu.tus.ac.jp

0379-6779/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.synthmet.2005.07.045

pentacene film and the alkaline metal were heated and alkaline metals were then doped at a doping temperature of 343–353 K. The pentacene film doped with the alkaline metal ("A-PEN" film) was annealed after the doping. In the doping of cesium, the temperature of both the pentacene film and cesium were controlled at 343 K in the first step. Thereafter, the Cs-PEN film was annealed at 403 K. In the doping of Rb, both temperatures of pentacene film and rubidium were controlled at 353 K in the first step, and thereafter, the Rb-PEN film was annealed at 413 K.

The electrical resistivity of the A-PEN film was measured using the DC four-terminal method. Thin gold films were used as electrodes on the A-PEN film, and copper wires were attached to the Au electrodes. The DC electrical resistivity was measured with a low noise multimeter (Keithley: 2010). The specimen used in the electrical resistivity measurement had a thickness of 200 nm. In the conductivity measurement, the A-PEN film was sealed in the glass tube to prevent decomposition due to air and moisture.

3. Results and Discussion

3-1. Electrical Properties of the Cs-PEN Film

Figure 1(a) shows the doping time dependence of DC electrical resistivity for the Cs-PEN film in the *a-b* plane, which is perpendicular to the pentacene molecular layer. As shown in Fig. 1(a), the electrical resistivity drastically decreases with increasing doping time at around 13 min, attains a peak value at around 26 min, and drastically decreases with increasing doping time thereafter. This result indicates that pentacene becomes a good conductor by the doping with cesium. Moreover, we can clearly observe that the decrease in the electrical resistivity is not monotonous but that there is a step-wise decrease when the doping time increases to a value greater than 100 min. The doping time corresponds to the amount of Cs that is doped in pentacene. Therefore, this result indicates that the step-wise decrease of resistivity with increasing doping time is caused by the increase in the number of Cs doped in pentacene. We further note that the characteristic feature, which is that the resistivity reaches a minimum and then a peak, is similar to the feature in the formation of the higher stage structure where resistivity reaches a peak observed in GIC'S (Graphite Intercalation Compounds). In addition, the possibility of the formation of the stage-2 structure has already been shown in the iodine-doped pentacene. Based on these facts, it is suggested that the step-wise decrease in resistivity results from the formation of the stage structure. Figure 1(b) shows the annealing effect for the Cs-PEN film doped at 343 K. It is evident that the electrical resistivity drastically decreases by approximately 10^3 times than that before annealing. Thus, in the Cs-PEN film, annealing effect is an important factor for the determination of electrical resistivity.

Figure 2 shows the temperature dependence of the electrical resistivity of the Cs-PEN film. As shown in Fig. 2, the electrical resistivity reaches a value of $13.5\times10^{-3}\ \Omega\cdot$cm at 300 K. This value corresponds to an electrical conductivity of 74 S/cm and is close to that of the iodine-doped pentacene film. Moreover, we can clearly observe that the electrical resistivity decreases with decreasing temperature. This result indicates that the electrical resistivity of the Cs-PEN film shows a metallic behavior below room temperature. Furthermore, we have observed that the electrical resistivity in the Cs-PEN film rapidly decreases at around 80 K. This result suggests that the Cs-PEN film undergoes some kind of phase transition

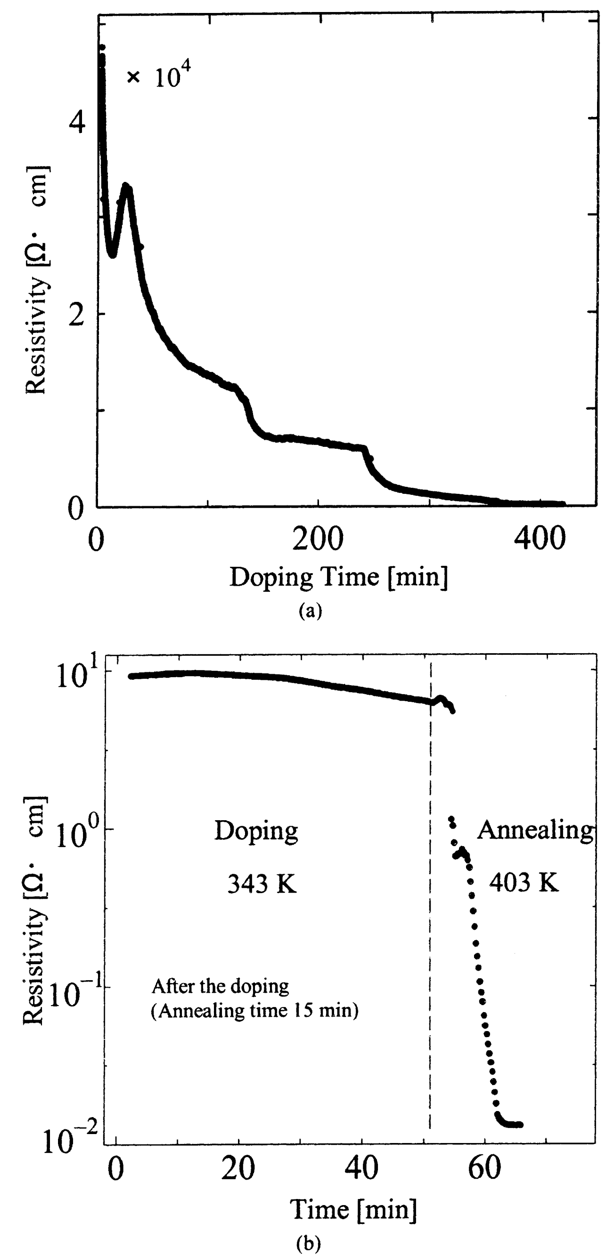

Fig. 1. Doping and annealing time dependence of electrical resistivity in the Cs-PEN film: (a) doping time dependence and (b) annealing time dependence.