

Pressure dependence of phase transition of organic material, 9,10-di(2-naphthyl)anthracene (ADN), under vacuum

Jin-Tae Kim^{*}, Seob Shim^{*,**}, Ju-Young Yun^{*1}, Ohyun Kwon^{***2}

^{*} Vacuum Center, Korea Research Institute of Standards and Science, Daejeon 305-340, Korea

^{**} Department of Nano and Bio Surface Science, University of Science and Technology, Daejeon 305-333, Korea

^{***} Samsung Display Co., Ltd., Yongin 446-711, Korea

ABSTRACT

The phase transition characteristics of 9,10-di(2-naphthyl)anthracene (ADN) used for an organic light emitting diode (OLED) are evaluated under vacuum. The phase transition shows a plateau in the temperature curve of the ADN material when it is heated to its melting or sublimation temperature under pressure in a vacuum chamber. At 1 atmospheric pressure, the ADN has a melting temperature that can be verified by differential scanning calorimetry (DSC). As the vacuum chamber is evacuated from 1 atmospheric pressure, the melting temperature decreases by a few degrees, and it sublimates below 1 Torr. The sublimation temperature decreases slightly as the pressure is lowered as well. This result provides not only the optimal evaporation condition of ADN but also information about the thermal stability of ADN and other types of organic materials for OLEDs under a high vacuum.

Keywords: phase transition, organic material, ADN material, vacuum, OLED

1 INTRODUCTION

Electroluminescence, the emission of light from materials under a strong electric field, was first reported for anthracene single crystals in the 1960s [1, 2]. Despite the high quantum efficiency obtained from such organic materials, it has been hard to develop commercial products, owing to the high driving voltage required as a result of the somewhat large film thickness and poor interface contact quality. Since the first publication of small-molecule organic light-emitting diode (OLED) devices in 1987 by Tang and Van Slyke who reported an efficient and low-voltage OLED from a thin-film heterojunction structure made by vacuum deposition, development of OLED has accelerated [3].

OLED has attracted considerable commercial and academic interest due to its great potential in full-color, flat-panel display and in solid-state lighting applications.

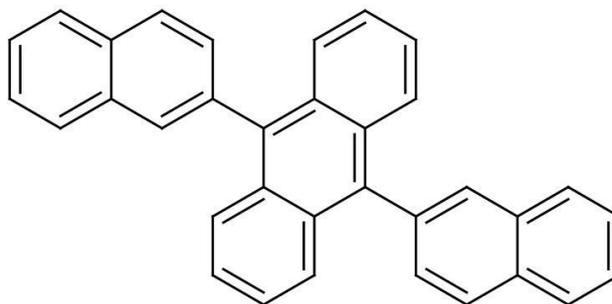


Figure 1: Chemical structure of ADN

For full-color OLED display devices, in particular, many studies have focused on improving the color purity and the efficiency of the primary red, green, blue emitting materials. Among the three primary colors, the performance of blue emitting materials is usually inferior to that of green or red emitting materials. Therefore, blue emitting materials with a wide band gap, high efficiency, and a long lifetime are still of prime importance for application in full-color OLED display, and extensive research has been carried out to develop high-performance blue emitting materials [3, 4].

With specific molecular designs, anthracene derivatives can be excellent blue emitting materials with a wide band gap for full-color OLED display. Among anthracene derivatives, 9,10-di(2-naphthyl)anthracene (ADN) has been used as a high efficient blue emitting material for OLED devices due to its good film and optical properties. The chemical structure of ADN is shown in Fig. 1. Shi et al. demonstrated that ADN with 2,5,8,11-tetra(t-butyl)perylene (TBP) as a dopant produced blue emissions with CIE coordinates(x,y) (0.154, 0.232), luminous efficiency of about 3.5 cd/A, and a half lifetime of 4000 hr with an initial light output 700 cd/m² [5]. However, ADN proved to be morphologically unstable due to crystallization.

Various substitutions to the ADN molecule such as MADN, TBADN, and TTBADN were carried out to improve the luminous efficiency, thermal stability, and life time of OLED [6]. Although recently numerous materials

¹ Corresponding author: Ju-Young Yun, jyun@kriss.re.kr

² Corresponding author: Ohyun Kwon, o.kwon@samsung.com

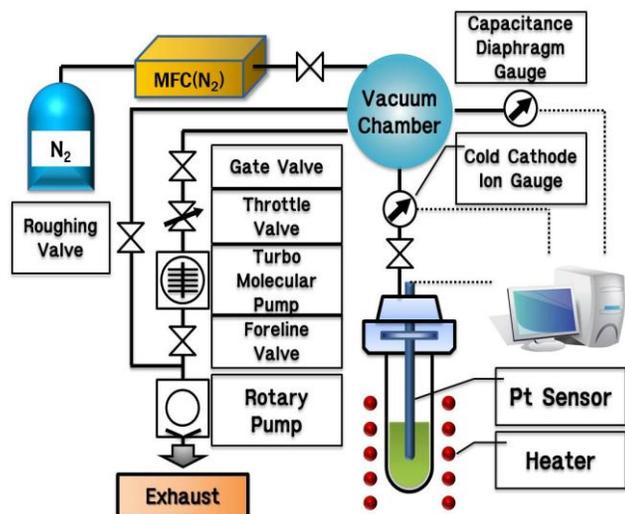


Figure 2: Schematic diagram of phase transition measurement system

are being synthesized and reported to improve the electroluminescent properties of OLED devices, studies on the material phase transition that occurs during the thermal evaporation are rare. In the case of small molecules for OLED, film has been fabricated by thermal evaporation in high vacuum below 10^{-6} Torr [7] and the phase transition that occurs in this process affects film fabrication. Information regarding the phase transition of each material in vacuum plays a key role in optimizing process conditions and significantly contributes to the improvement of the device's quality and yield rate.

In this study, the phase transition characteristics of the ADN under vacuum were evaluated using a vacuum system that is able to control the pressure and temperature.

2 EXPERIMENTAL

Figure 2 shows the schematic diagram of the phase transition measurement system. This system is composed of a pumping system that controls the pressure, a sample container that is connected to the vacuum chamber, a heater that heats the samples, and a platinum resistance thermometer that measures the sample temperature. First, the rotary vane and turbo molecular pumps were used to establish a high vacuum of 10^{-6} Torr in the pumping system. In order to control the pressure (10^{-4} ~ 760 Torr) of the vacuum chamber, N_2 gas, a throttle valve, a mass flow controller (MFC), and a capacitance diaphragm gauge (CDG) were used.

The sample container was made of quartz so that the phase transition of the sample can be easily observed and compared with the sample temperature data. Viton O-rings were used in the upper section of the quartz container for vacuum sealing and water cooling was utilized so that the deformation of the O-ring does not occur due to high temperature. The heater was manufactured to raise the

temperature of the sample container to approximately $500\text{ }^\circ\text{C}$. The temperatures of the samples were measured using the platinum resistance thermometer. In order to equally heat the samples, they were placed in the center of the heater.

The experimental procedure was as follows. First, ADN powder ($\sim 0.5\text{ g}$, purity 99.9 %) samples were placed in the quartz container within a glove box filled with Ar gas and the quartz container was brought and attached to the vacuum chamber. After the vacuum chamber was evacuated to $\sim 10^{-6}$ Torr using the turbo molecular pump, the desired vacuum chamber pressure ($760 \sim 10^{-4}$ Torr) was maintained using the N_2 gas, MFC, and throttle valve. The temperatures of the sample and heater were measured while supplying constant power to the heater. To verify the repeatability of the phase transition measurement system, fresh samples were used for every experiment and repeated 3 times each. Also, to verify the reliability of the phase transition measurement system, the melting temperature measured by the differential scanning calorimeter (DSC) at ambient pressure was compared.

3 RESULTS AND DISCUSSION

Figure 3 shows the graph of ADN temperature versus heater temperature measured at ambient pressure while supplying constant power to the heater. With the increase of the heater temperature, the ADN powder temperature increased and then plateaued at $386\text{ }^\circ\text{C}$. At this point, the melting of ADN was observed with the naked eye. Figure 4 shows the ADN melting temperature measured using the differential scanning calorimetry (DSC) at ambient pressure. The ADN melting point of $387\text{ }^\circ\text{C}$ obtained through the DSC and the phase transition measurement system were almost equivalent. Melting and boiling above 8 Torr and sublimation below 1 Torr were observed through the ADN temperature increase rate change and visual observation.

Figure 5 shows sublimation (upper) and melting (lower) taking place. Figure 6 shows the graph of ADN temperature

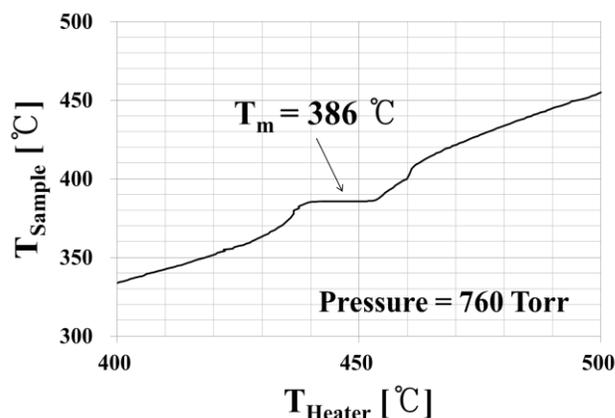


Figure 3: Melting temperature (T_m) of ADN measured by vacuum system at atmospheric pressure

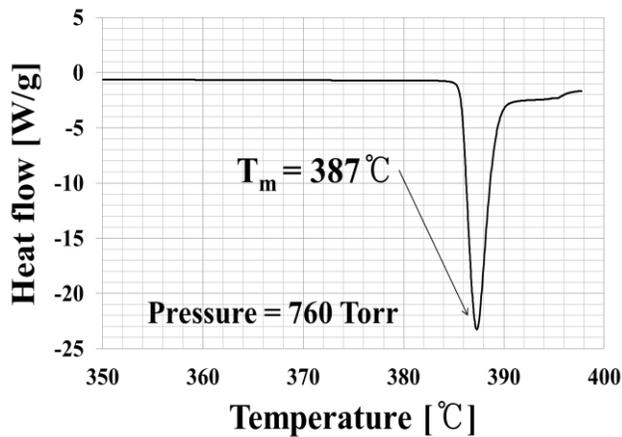
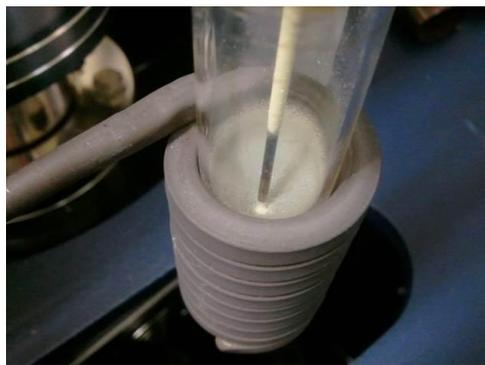


Figure 4 : Melting temperature (T_m) of ADN measured by differential scanning calorimetry (DSC) at atmospheric pressure

measured at pressures below 1 atmosphere (10^{-3} , 10^{-2} , 1, 10 Torr) versus heater temperature. Melting and boiling occurred above 8 Torr. As the heater temperature increased, the ADN temperature rose and this sample temperature increasing trend rapidly decreased and flattened out as melting or boiling occurred. This was also in agreement with the phase transition observed with the naked eye.



(a)



(b)

Figure 5 : Phase transition of ADN ; (a) sublimation at 0.1 Torr and 300 °C, (b) melting at 760 Torr and 385 °C

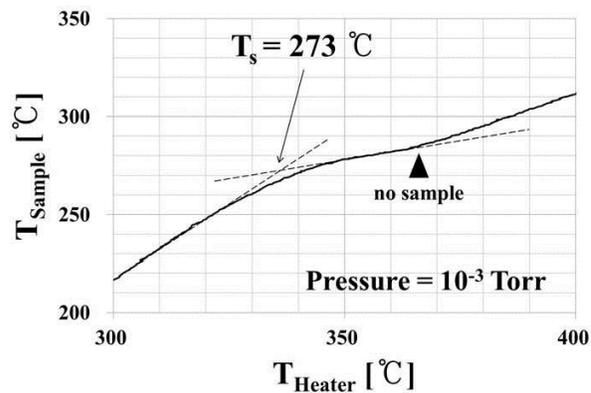
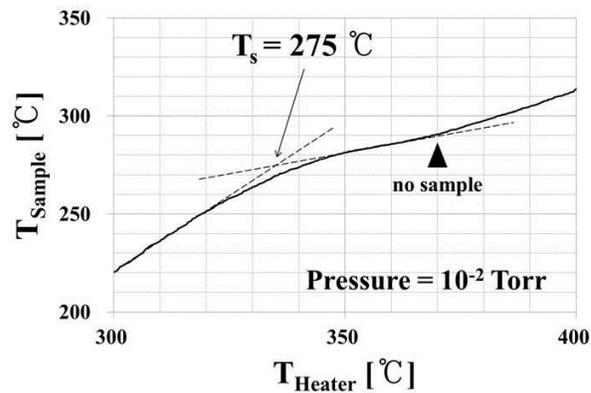
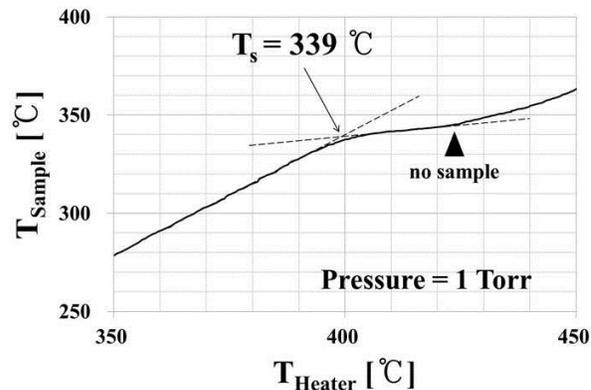
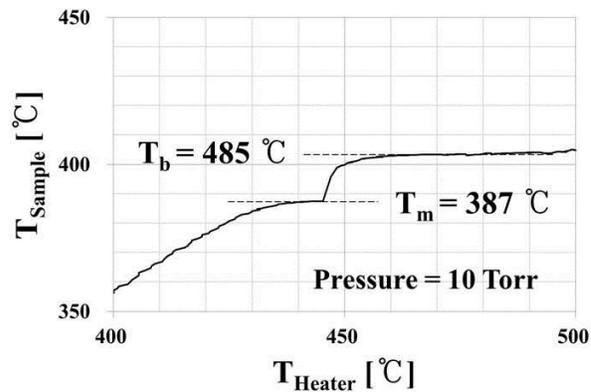


Figure 6 : Phase transition of ADN under vacuum ; melting temperature (T_m), boiling temperature (T_b) and sublimation temperature (T_s)

4 CONCLUSION

Using a vacuum system that is able to control the pressure and temperature, the phase transition of ADN, which is a blue emitting material for OLED, was measured through the variation in sample temperature at vacuum (10^{-4} Torr \sim 100 Torr). This was equivalent to the visual observation results. The melting point obtained at ambient pressure was in good agreement with the result obtained from differential scanning calorimetry (DSC) thermal analysis. The phase diagram of ADN was successfully acquired. These results are expected to contribute greatly to understanding of the behavior of OLED materials under thermal evaporation condition.

REFERENCES

- [1] Helfrich W and Schneider WG, Phys Rev Lett 14, 229, 1965.
- [2] Pope M., Kallmann H. and Magnante P. J, Chem. Phys. 38, 2042, 1963.
- [3] Tang C. W. and Van Slyke S. A, Appl. Phys. Lett. 51, 913, 1987.
- [4] Gong JR, Wan LJ, Lei SB, Bai CL, J Phys Chem B 109, 1675, 2005
- [5] Chan LH, Yeh HC, Chen CT, Adv Mater 13, 1637, 2001
- [6] Shi J and Tang CW, Appl Phys Lett 80, 17, 2002
- [7] S. C. TSE, S. K. SO, M. Y. YEUNG, C. F. LO, S. W. Japanese Journal of Applied Physics 45, 555, 2009
- [8] Franky So, Denis Kondakov, Adv Mater 22, 3762, 2010

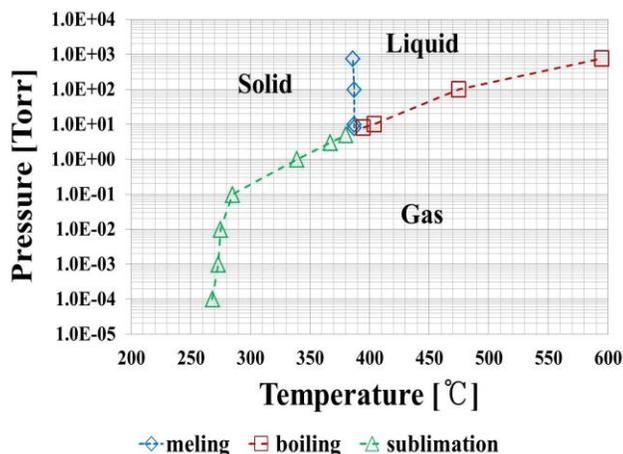


Figure 7: Phase diagram of ADN obtained from melting temperature (T_m), boiling temperature (T_b) and sublimation temperature (T_s) under various pressure condition

Sublimation occurred below 1 Torr where the increasing rate of ADN powder temperature decreased as in melting or boiling. However, unlike when melting or boiling occurred, the sample temperature when sublimation occurs was not constant and rose slightly as shown in Figure 6. This is due to the temperature gradient existing depending on the sample location within the container. In other words, when looking down at the sample from the top of the container, the temperature of ADN powder placed in the center where the temperature sensor is located can be relatively lower than that of the powder near the outside (close to the heater). Sublimation first occurs near the outside of container. As heater temperature is further increased, the powder in the center starts to sublime. During sublimation, the temperature difference can exist because the solid powder has a comparatively less heat transfer compared to the liquid phase. When the powder is completely depleted, the reading of the temperature sensor for the powder starts to increase; no sample denoted in Figure 6.

The sublimation temperature was chosen as the point where two lines drawn at the flat region of the measured sample temperature curve for each pressure meet as shown in Figure 6. The sublimation temperature and pressure data were plotted in logarithmic scale to show the phase diagram of ADN in Figure 7. While the boiling temperature rose as the pressure rose above 8 Torr, the melting temperature did not change. Below 1 Torr, the sublimation temperature decreased as the pressure decreased, but below 10^{-2} Torr, there was almost no change. Between 1 \sim 8 Torr, melting, boiling, and sublimation all occurred at the same time and was visually observed, which was in agreement with the results of Figure 7. From the result of extrapolation from the above three phase transition curves, it is predicted that the triple point of ADN exists in the proximity of 3 \sim 6 Torr, 382 \sim 385 $^{\circ}$ C.