

■ Sublimation Purification of Organic Semiconductor Materials

Materials used in organic semiconductor devices require a purity level necessary for device functionality. Synthetically produced organic compounds contain impurities such as reaction byproducts, unreacted starting materials, catalysts, and solvents. Traditionally, these impurities have been removed in the liquid phase using methods like recrystallization or column chromatography. For organic semiconductor devices, even higher purity is required. When vacuum processes are applicable, sublimation purification is suitable for suppressing gas release from the organic semiconductor material.

Sublimation purification has been used since the 1950s as a method for achieving high purity in molecular crystals, such as polycyclic aromatic compounds, alongside single crystal growth methods

[1].

■ Principle of Sublimation Purification

Organic compounds undergo phase changes based on phase diagrams as shown below (Figure 1). At atmospheric pressure, many organic compounds melt (solid to liquid; blue arrow in figure) as temperature increases, and subsequently boil (liquid to gas; white arrow in figure). It is known that when these organic compounds are heated under reduced pressure (vacuum) some materials undergo sublimation (solid to gas) red arrow in figure. Others vaporize via the liquid phase under reduced pressure, similar to their behavior at atmospheric pressure.

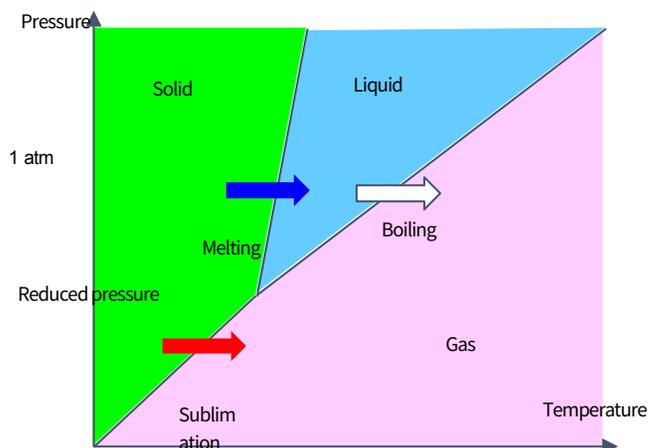


Figure 1. Example of a phase diagram for organic compounds

Vaporized molecules are transported by diffusion from the location of the starting material toward the vacuum exhaust. Nitrogen or argon may be used as carrier gases to assist this mass transport.

Organic molecules transported from the starting point are recovered by undergoing a phase change from gas to solid (opposite direction to the red arrow in Figure 1) at a location set to a predetermined temperature. If volatile components are present as impurities, the temperature is set to ensure sufficient separation between the target substance and the impurities. A conceptual diagram of this sublimation purification process is shown in Figure 2.

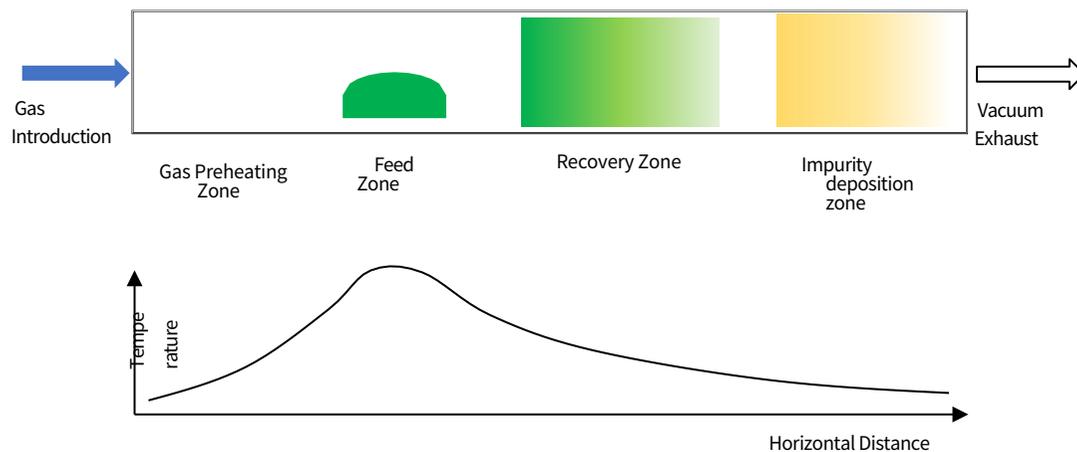


Figure 2. Schematic diagram of sublimation purification

As described above, the method of performing sublimation with a temperature gradient in the recovery zone is called train sublimation and is suitable for purifying metal phthalocyanine compounds [2].

■ Practical Sublimation Purification

Various sublimation purification devices are used depending on the purpose. For research and development purposes, the raw material to be purified ranges from 1 g to 1 kg, and the size of the device is determined according to the purification quantity. Furthermore, depending on the thermal decomposition temperature of the material, some require high vacuum. The number of temperature zones is also set considering separation from impurities.

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Figure 3 shows the configuration of a sublimation purification apparatus. The heating section consists of a quartz glass tube and a quartz recovery tube installed inside it. In the example shown, the heating section where the sample is placed comprises three heaters, while the cooling section on the vacuum exhaust side consists of three temperature measurement zones. A liquid nitrogen trap is installed between the pump and the heating section to prevent solvents, impurities, particles, etc., generated from the sample from entering the exhaust system directly. The type of exhaust pump is determined by the desired vacuum level; in this case, a turbo molecular pump is used to enable sublimation purification at lower temperatures.

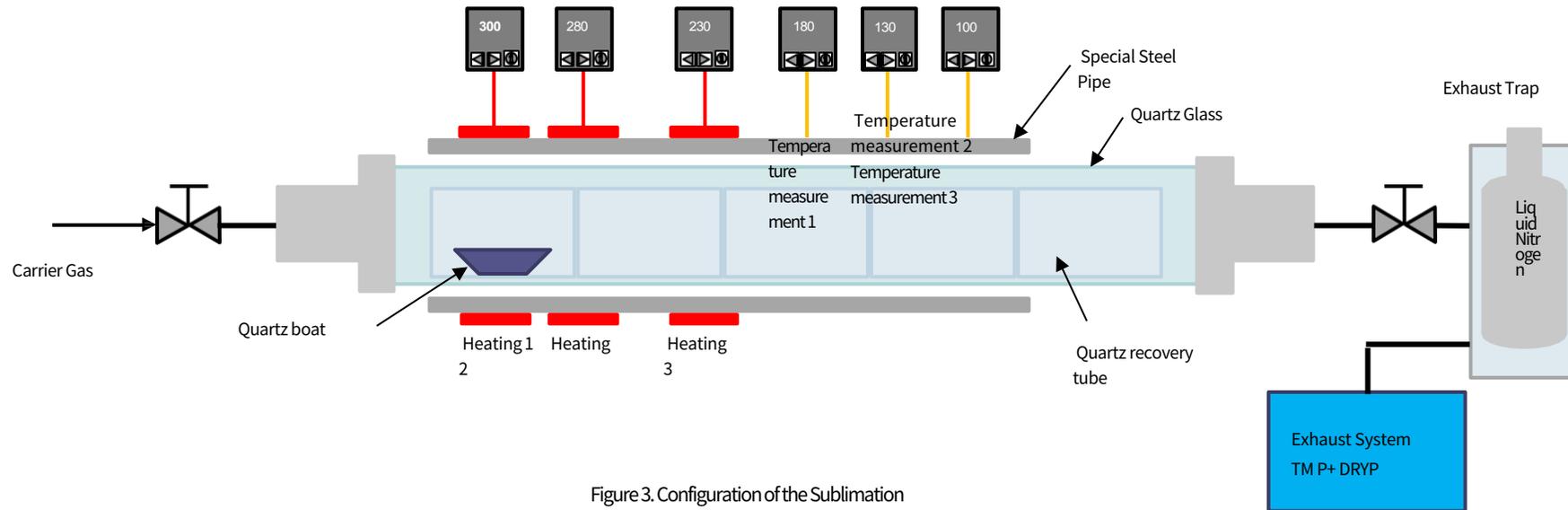


Figure 3. Configuration of the Sublimation Purification System

Sample recovery occurs in a temperature zone lower than where the raw material is placed. However, rapid cooling from the gas phase to the solid phase tends to result in an amorphous state, often forming fine particles. Therefore, the temperature setting in the recovery zone must be determined based on the material's thermal properties.

To further enhance the purity of organic semiconductor materials, sublimation purification using a carrier gas is employed. When sublimation purifying c_{60} materials, using nitrogen as the carrier gas and maintaining the pressure inside the sublimation tube near 1 atm induces convection within the tube, promoting single crystal growth.

and enabling the formation of C_{60} single crystals several millimeters in size [3]. Increasing the crystal size significantly reduces the amount of impurities contained, resulting in materials at the 7N level.

Figure 4 shows an example of a sublimation purification apparatus for research and development. It features an internal observation window to monitor the purification process. Instead of liquid nitrogen, the cold trap can incorporate an immersion heater in the refrigerant to maintain a temperature of -80°C for extended periods.

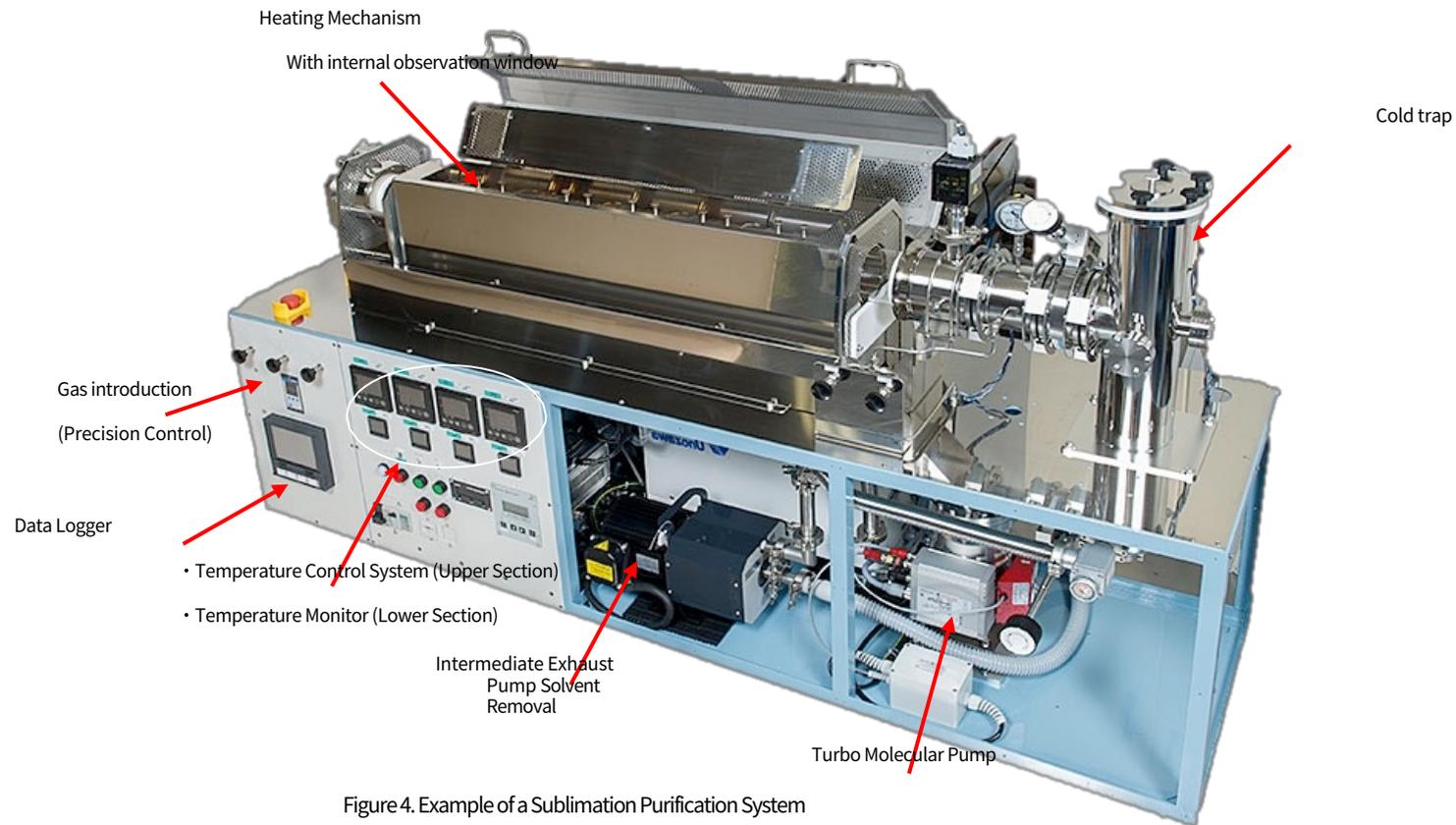


Figure 4. Example of a Sublimation Purification System

Figure 5 shows the typical appearance of a stone-based recovery tube after sublimation purification using the above apparatus.

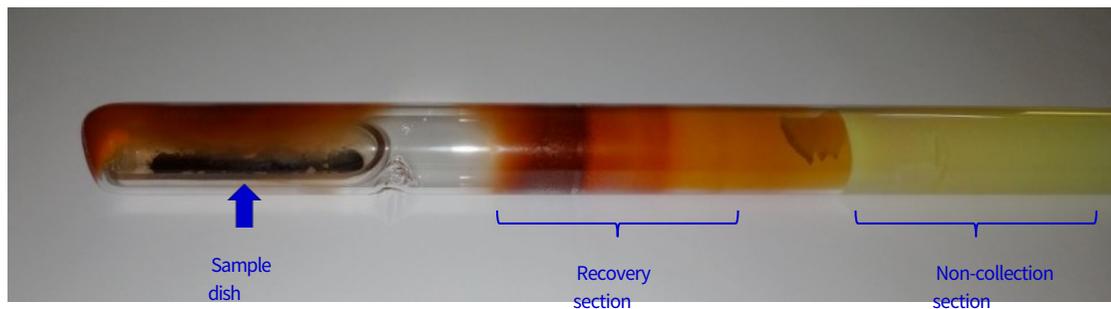


Figure 5. Sample recovery tube after sublimation purification

By repeating the above sublimation purification operations, it is possible to achieve even higher purity. Since physical properties such as the mobility of organic semiconductor materials are significantly affected by the presence of impurities (traps), high-purity purification using the sublimation purification method is an extremely important technology.

□References

- [1] Hiroo Iguchi, Purification of Organic Compounds by Sublimation, **Organic Synthetic Chemistry**, 13 (1955) 486.
- [2] H.J. Wagner, R.O. Loutfy, C-K. Hsiao, *J. Mater. Sci.*, **17** (1982) 2781.
- [3] Masashi Hiramoto, *Applied Physics*, **77** (2008) 539.