

Organic Vapor Phase Deposition for Optoelectronic Devices

The growth of molecular organic thin films by the process of organic vapor phase deposition (OVPD) was initiated by Professor Steve Forrest. OVPD transports organic molecules to a cold substrate by a hot inert carrier gas. It has proven useful for the deposition of organic semiconductors, and is capable of patterned growth with micron resolution. Professors Benziger and Forrest collaborated to engineer the process for a scalable continuous process. Most recently, Profs. Forrest and **Benziger** have demonstrated direct printing of molecular organic materials based on a new method of growth, organic vapor jet printing (OVJP), where molecules are carried to the substrate by a hot carrier gas *jet*. The diameter of the deposit is limited by the gas jet dynamics and nozzle dimensions, and is capable of generating patterns ~500nm.

The context and concept of OVPD: Background and Related Work

Typically, thin (<100nm) film molecular organic electronic devices such as organic light emitting devices (OLEDs), are grown by vacuum thermal evaporation (VTE), permitting the high degree of purity, pattern, and structural control needed for high performance operation. However, control of film thickness uniformity and dopant concentrations over large areas needed for many applications can be difficult when using vacuum evaporation – currently the most commonly used technique for the deposition of organic molecular solids. In addition, a considerable fraction of the evaporant coats the cold walls of the deposition chamber; over time, inefficient materials use results in a thick coating which can flake off, leading to particulate contamination of the system and substrate. The potential throughput for vacuum evaporated organic thin film devices is low, resulting in high production costs. Low pressure organic vapor phase deposition (OVPD) has been demonstrated as an alternative technique that significantly improves control over doping, and is adaptable to rapid, particle-free, uniform deposition of organics on large-area substrates.

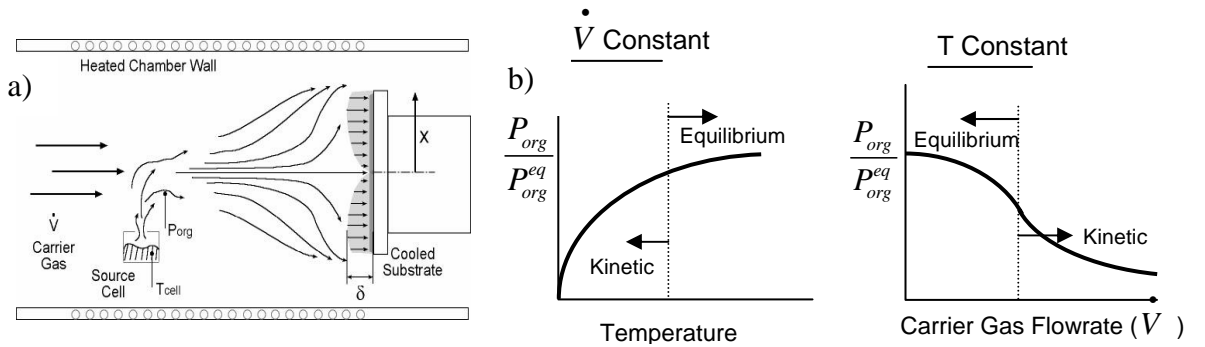


Fig. 1: (a) Schematic of the OVPD process, (b) the regimes of OVPD growth.

In OVPD, the organic compound is thermally evaporated into a diluting, non-reactive gas stream, and then transported in a hot-walled reactor toward a cooled substrate where condensation occurs (see Fig. 1). Flow patterns may be engineered to achieve a substrate-selective, uniform distribution of organic vapors, resulting in a very uniform coating thickness and minimized materials waste. Virtually all of the organic materials used in thin film devices have sufficiently high vapor pressures to be evaporated at temperatures below 400°C, and then be transported in the vapor phase by an inert carrier gas such as nitrogen. This allows for positioning of evaporation sources outside of the reactor tube spatially separating the functions of evaporation and transport, thus leading to precise control over the deposition process. To grow doped films with uniform composition across the entire substrate area, the component streams must be mixed prior to deposition. By carrying out the process at reduced pressure, gas diffusivity is increased, improving rates of mass transfer between component streams and to the substrate, which promotes thickness uniformity of the deposited films.

In vapor phase deposition, organic molecules are carried out of the source cell at a rate, r , proportional to the volumetric flow velocity of the carrier gas, \dot{V} , and the concentration of organic vapors in the evaporation cell, P_{org}/RT_{cell} :

$$r = \dot{V} \cdot \frac{P_{org}}{RT_{cell}} \quad (1)$$

Here, T_{cell} is the evaporation cell temperature, P_{org} is the *actual* vapor pressure of the organic material, and R is the universal gas constant. It can then be shown[7] that the partial pressure of the organic evaporant in the carrier gas stream is given by:

$$\frac{P_{org}}{P_{org}^{eq}} = \frac{k_{evap}}{\dot{V} / RT_{cell} + k_{cond}}, \quad (2)$$

where k_{evap} and k_{cond} are kinetic factors proportional to the rates of evaporation and condensation, respectively, and P_{org}^{eq} is the equilibrium vapor pressure of the organic material. As Eq. (2) and Fig. 1b show, at high evaporation temperatures and sufficiently low gas flow rates, the vapor and solid in the source region equilibrate (i.e. $P_{org} \approx P_{org}^{eq}$), and the concentration of organic exiting the source is constant. The resulting flux of organic species in the “equilibrium” evaporation regime is thus proportional to the vapor pressure and the carrier gas flow rate. At the other extreme of low evaporation temperatures and high gas flows, the carrier gas sweeps the organic out of the source region as quickly as it evaporates, forcing the system away from equilibrium. In this case, the concentration of organics in the gas stream is proportional to r_{evap} and inversely proportional to \dot{V} . In the “kinetic” evaporation regime, therefore, the flux of organic material leaving the source is independent of the carrier gas flow. Figure 1b illustrates how the vapor pressure of organics exiting the source varies with temperature and flow

rate for both the equilibrium and kinetic evaporation regimes. It will become apparent below that the ability to operate OVPD in either of these two regimes provides unprecedented opportunities to control the structure and quality of the thin film.

As in vacuum evaporation, the equilibrium vapor pressure of the organic material depends exponentially on cell temperature, T_{cell} . The partial pressures of the evaporant leaving the source region are:

$$P_{\text{org}}^{\text{eq}} = P_0 \cdot \exp(-\Delta H^{\text{vap}} / RT_{\text{cell}}) \quad (3)$$

$$P_{\text{org}}^{\text{kin}} = \frac{RT_{\text{cell}}}{\dot{V}} k_{\text{evap}} P_0 \exp(-\Delta H^{\text{vap}} / RT_{\text{cell}}), \quad (4)$$

where ΔH^{vap} is the enthalpy of vaporization specific to each compound, and superscripts “eq” and “kin” denote equilibrium and the kinetic evaporation modes, respectively.

Hence, a significant difference between vacuum evaporation and OVPD is that in the latter process, the rate of introduction of the organic species onto the substrate is determined by both source temperature (where the rate is exponential with temperature)

and gas flow rate, \dot{V} (providing linear control of source introduction, c.f. Eq. (5)). Hence, we have shown doping of one or more organic species into a host thin film is far more controllable than using simple temperature control characteristic of vacuum deposition. We have demonstrated very low and controllable doping concentrations of <0.5% of a red lumophore, DCM2, doped into an Alq₃ host.

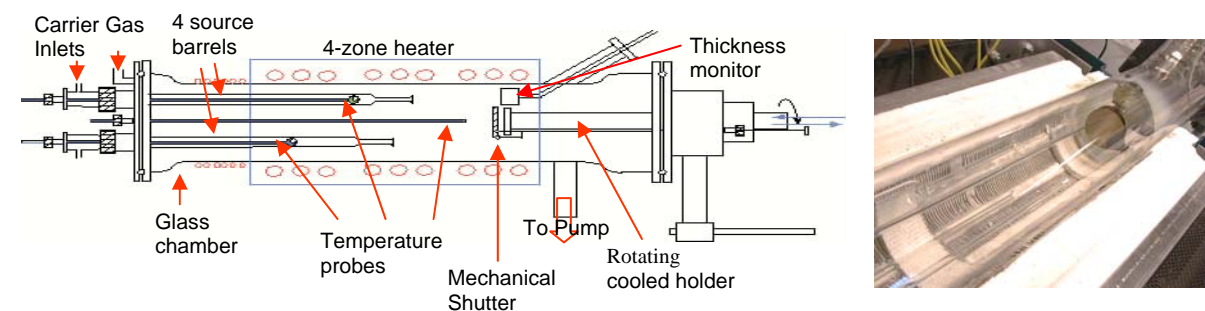
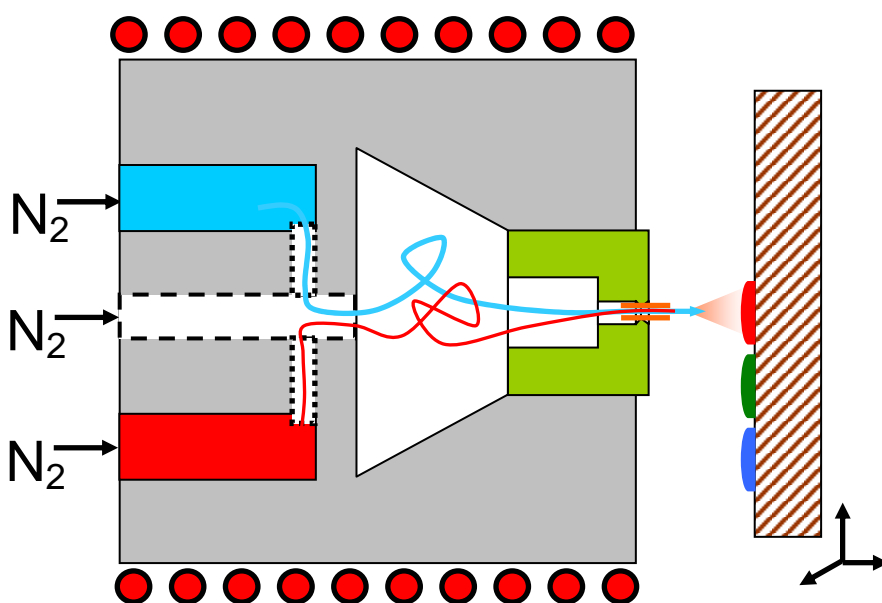


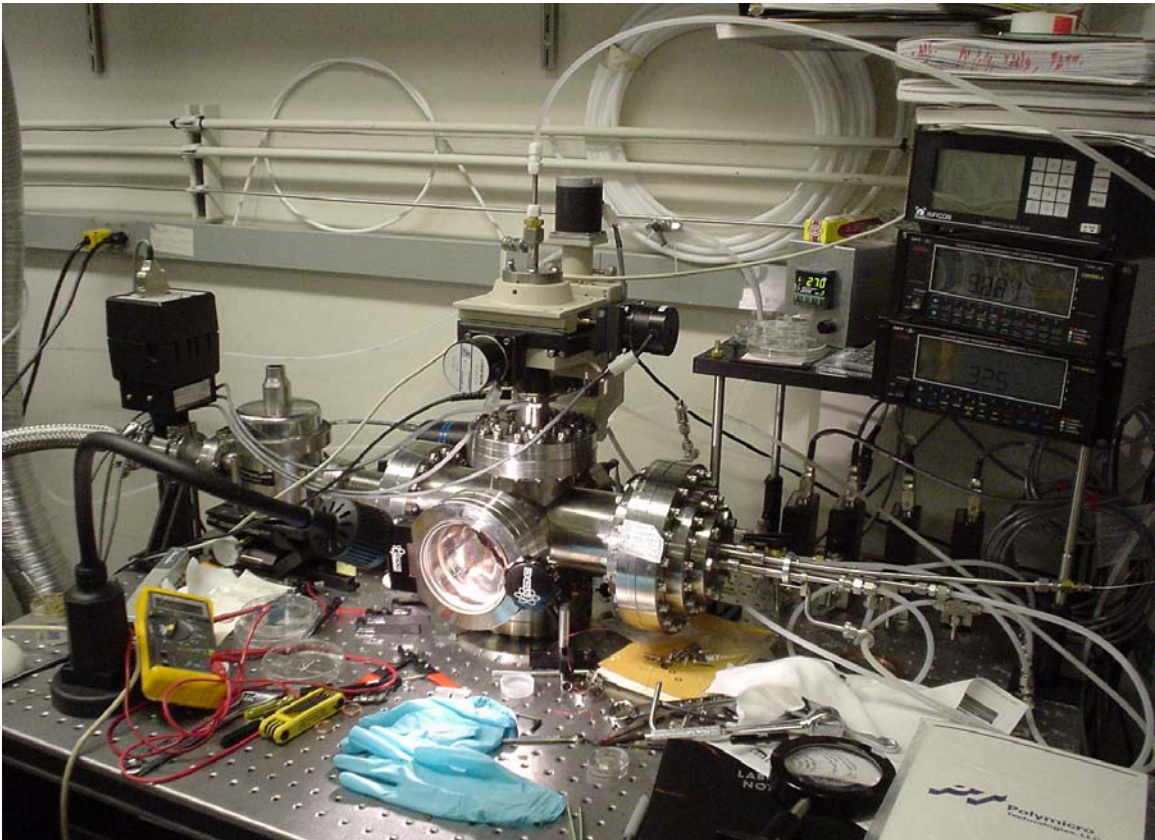
Fig. 2: Schematic of original OVPD system. Photo shows the system with the clam-shell furnace open to show a clean glass tube and substrate holder after >150 growth runs

Organic Vapor Jet Printing (OVJP)

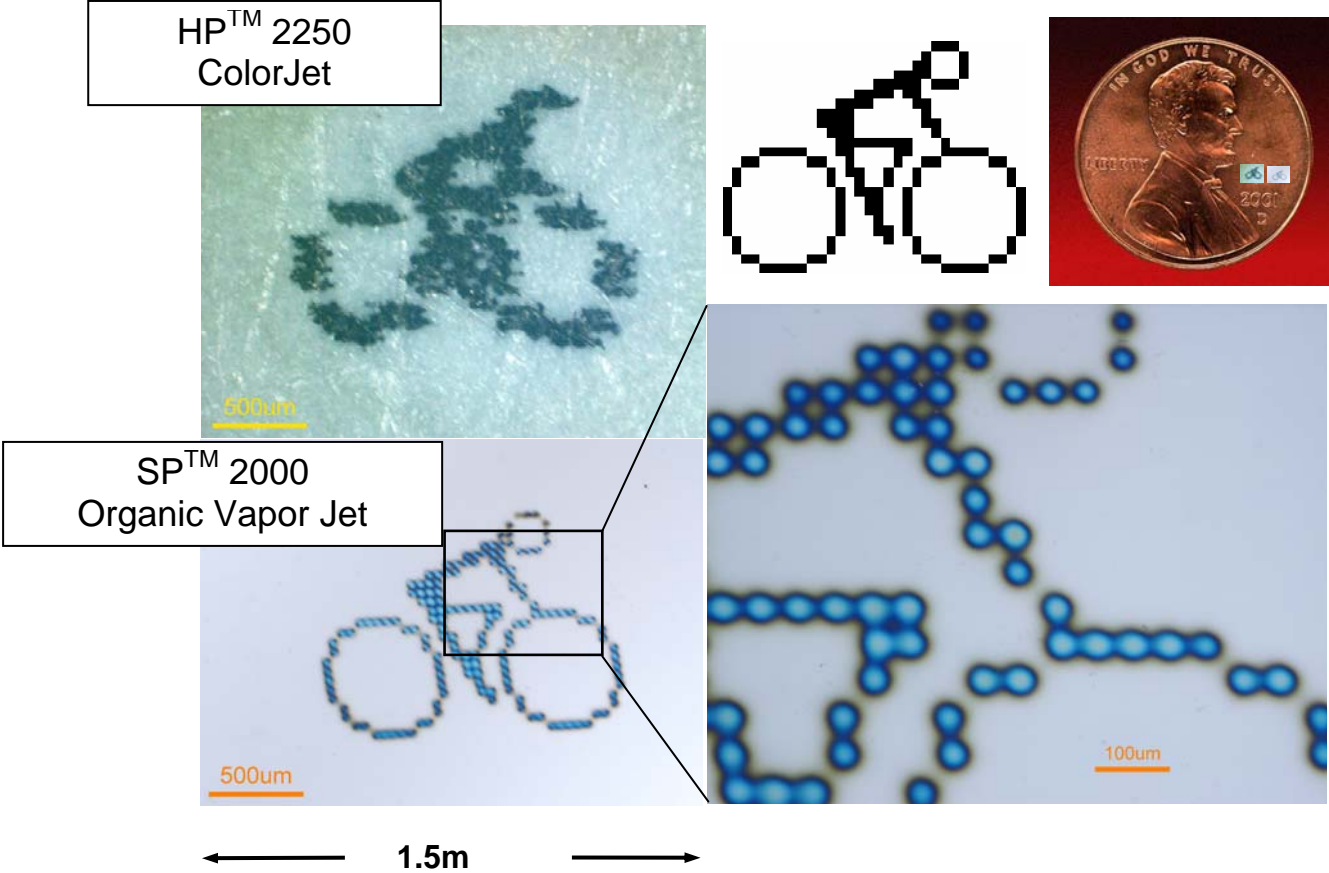
OVJP is a natural extension of OVPD deposition through shadow mask apertures, where organic patterns are individually deposited through a small orifice onto a substrate located directly beneath a nozzle. The nozzle itself is fed by a vapor of organics and a carrier gas, thereby transporting a small amount of material in a spatially confined area. Similar to *ink jet printing*, the deposition of individual pixels on extended plastic substrates continuously deployed in close proximity to the localized jet of gas can be achieved. It differs substantially from solution-based ink jet printing of polymers, however, in that the *solvent in OVJP is a gas*. Hence, it is easily volatilized during growth to leave a uniform film of the desired organic. This process, **invented at Princeton**, has the possibility of revolutionizing the growth of small molecule organic thin films by rapidly and simply depositing ultrasmall (nanometer scale) patterns of organic thin film materials or precursors. Like OVPD, the process works by passing a heated gas through a hot organic source powder or liquid. The gas then entrains the molecular species, carrying it through a valved nozzle to a cooled, horizontally translating substrate where the material deposits. The ultimate deposit resolution achievable by this method is determined by the distance from the nozzle to the substrate, the gas flow velocity, the background pressure, temperature, and the diameters of the orifice and the tip. The practical limits to these dimensions are ~500nm, using an orifice with micropores. Below this diameter, the gas viscosity will limit the transport of material through the orifice.



Schematic of the OVJP process. Carrier gases pick up the organic vapor and direct the organic onto the substrate through a nozzle. The higher mass organic retains its forward momentum towards the substrate and is kept collimated to provide good resolution.

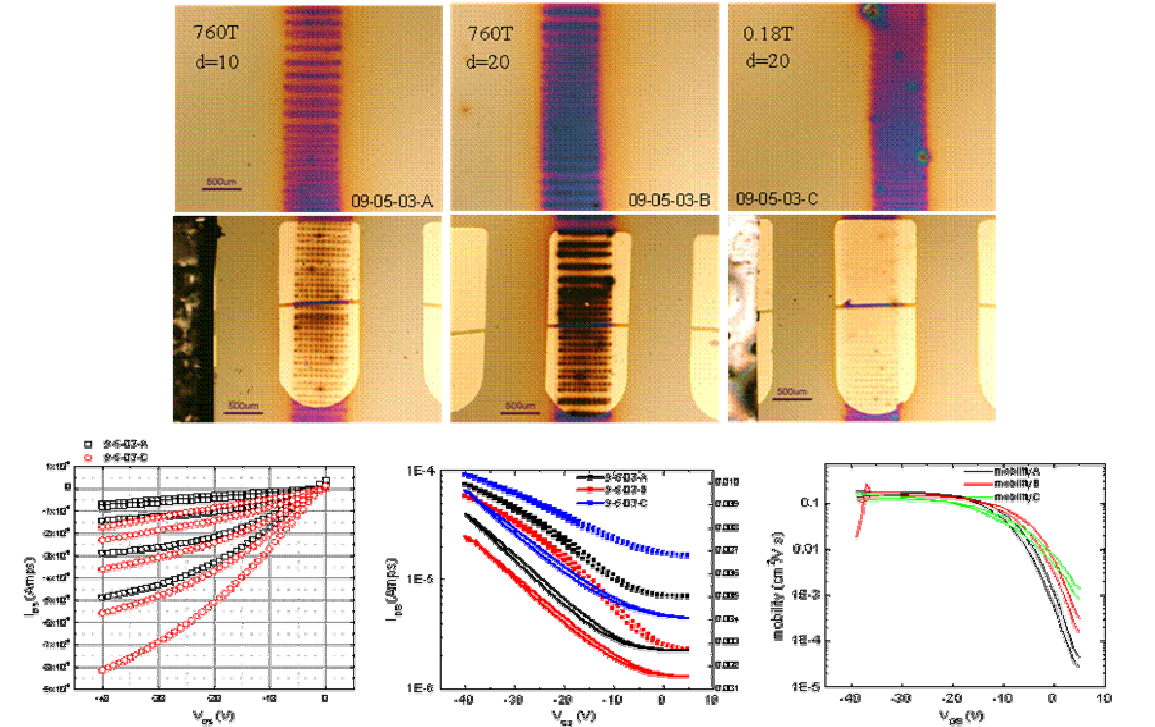


Organic Vapor Jet Printing Apparatus.



Example of the resolution of OVJP. The resolution of the prototype system is ~ 1200 dpi.

Pentacene TFTs printed by OVJP at atmospheric pressure



OVJP can print thin film transistors without the need for a vacuum system.