Physical vapor growth of centimeter-sized crystals of α-hexathiophene

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Abstract

The processes in physical vapor transport: vaporization, transport and crystal growth, the regimes for transport: molecular flow path limited, diffusion-limited, convection-limited and forced-convection-limited are analyzed and the results are used to guide a systematic investigation of physical vapor transport and crystal growth of α-hexathiophene (α6T), a promising thin-film transistor organic material. Successful growth occurred when the gas pressure was such that the regime was convective and when deliberate inert-gas flow (forced convection) improved volatilization. Plate-like growth morphology and thickness differences between the high-temperature and low-temperature polymorphs is explained on the basis of differing atomic structure. Conditions for the reproducible growth of crystals of up to 1 cm in size are reported. We feel that the analyses and procedures reported here can be used to grow crystals of other organic materials.

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1. Introduction

α-6T (α-hexathiophene, α-sexithiophene, α-hexathiienyl, α-sexithienyl) is representative of a class of electronic organic materials with molecular weights between molecular crystals (e.g. napthalene) and polymers. These oligomers have mobilities and on-off currents which have permitted the fabrication of thin-film transistors with interesting device potential. Work on the synthesis, transistor fabrication and properties of α6T has been reported in a series of papers by Garnier et al. [1–3] in France and Dodabalapur and his colleagues [4, 5] at Bell Laboratories.

We became interested in the growth of single crystals of α6T in order to provide material for physical studies. We have reported on the discovery of a new high-temperature phase of α6T (α6T-HT).
its vapor growth [6] and structure [7]. We have also reported on the solubility of α6T in organic solvents and preliminary studies of solution growth [8]. In this paper we report methods for the physical vapor growth of centimeter-sized crystals of the α6T using less than 30 mg of starting material.

Garnier [1–3] pioneered in the growth of the low-temperature (LT) phase of α6T and reported the existence of several other polymorphs, as did Destri et al. [9]. However, no systematic studies of vapor growth seem to have been carried out. In the following, we report methods for closed system growth under controlled conditions and methods for growth in a flowing carrier gas. There have been a numerous reviews [10, 11] and several recent papers [12, 13] on the theoretical basis of physical vapor growth. However, connections to experimental conditions for the practical crystal grower are not always made. Consequently, in addition to reporting reproducible methods for growth, we discuss the processes involved in vaporization, transport and deposition and how to manage them.

2. Experimental procedure

2.1. Starting materials

Starting materials were synthesized by the procedures of Garnier [1–3, 14, 15] as modified by Katz (see Ref. [4, 5]). Commercial synthesis was carried out by Peter Meltzer at Organix, Woburn, MA. Our starting material α6T was sublimed to remove unreacted materials and undesired reaction products [8]. The results presented here do not depend on the exact sublimation conditions.

2.2. Transport systems and furnaces

Two types of experiments were conducted: physical vapor deposition in a closed system at pressures ranging from 10⁻⁴ Torr to 1 atm and transport in an inert flowing gas stream. A typical transport system and furnace is shown in Fig. 1. Systems were designed to present various dynamic characteristics, and to be capable of various temperature profiles. The furnaces were generally of two types: a heated metal block to ensure uniformity of temperature in the volatilization zone (with growth close to the end of the block) or glass tubes (sometimes covered with a thin gold layer to reduce heat loss) wound with resistance wire whose spacing was adjusted to produce the desired temperature profile (Fig. 1). Standard temperature controllers enabled ± 0.5°C temperature control. Temperatures were determined where possible using interior thermocouple probes, otherwise the temperature on the outside of the glass transport tube is reported. The apparatus shown in Fig. 1 requires very little starting material for successful growth experiments – a considerable advantage since for many organics synthesis is difficult, expensive and time consuming. All our experiments were conducted with 20–30 mg of starting material.
3. Results and discussion

A convenient way to organize consideration of vapor-phase crystal growth is to consider the processes required to grow a crystal or a thin film:
- Vaporization.
- Transport.
- Crystal growth.

A series of experiments was performed in which samples were heated at a fixed temperature of 285°C and the weight loss was used to determine volatilization rate as a function of He pressure, (Fig. 2). As can be seen, volatilization was remarkably inhibited by pressures above 10 Torr. Four regimes for the rate-limiting step in volatilization can exist. Three of these regimes and their boundaries are shown in Fig. 2. The fourth, forced convection, depends on inert-gas flow. These boundaries also establish the regimes for transport processes.

3.1. The free molecular flow regime

To first order, the mean free path of a gas is inversely proportional to the pressure ($p$) or density ($\rho$), but it does not depend on the temperature or the mass of the molecule [16, 17]. Under ambient conditions the mean free path of any gas is of the order $10^{-5}$ cm, with slight variations occurring due to differences in the collision cross sections of different gases. These differences are unimportant for the purposes of this discussion. At a pressure of about $10^{-2}$ Torr, the mean free path of argon is about 0.5 cm and helium is about 1.5 cm [16, 17], i.e. dimensions that are comparable to the size of our apparatus. At pressure levels below $\sim 10^{-2}$ Torr (Fig. 2), free molecular flow conditions exist and a significant fraction of the vaporized $\alpha_6T$ molecules move in ballistic trajectories until they encounter either the apparatus wall or a growing crystal surface.

3.2. The diffusion–convection boundary

Table 1 presents the physical properties necessary for our estimates of regime boundaries for argon and helium. Here $\beta$ is the coefficient of thermal expansion, $\mu$ the absolute viscosity, $v$ the kinematic viscosity ($= \mu/\rho$), $\kappa$ the thermal diffusivity, and $Pr$ ($= v/\kappa$) is the Prandtl number. Note that $Pr$ represents the inherent properties of the fluid and is independent of geometry. Under our experimental conditions $Pr \approx 0.7$ for most gases. The quantity $(\beta g/\kappa v)$ is used below in the estimates of the Rayleigh number, $Ra$, which is the ratio of the buoyancy to the viscous and thermal diffusion. For our purposes $Ra$ is defined as

$$Ra = \frac{g \beta \Delta T h^3}{\nu \kappa},$$

(1)

where $\Delta T$ is an appropriate temperature difference and $h$ is an appropriate length scale.
At sufficiently small Rayleigh numbers the fluid motion in tall cavities near the mid-height is parallel to the side walls and heat is transferred across the radius by conduction\(^2\) [20]. When \(Ra\) is of order unity, a balance occurs between buoyancy seeking to generate motion and thermal and viscous diffusive effects that dissipate it. We therefore, postulate that the regime in which diffusive effects are dominant occurs for \(Ra \approx 1\).

Calculations for argon, using the thermosyphon model described below, and the conditions of our apparatus (Fig. 1, \(\Delta T_{\text{vertical}} = 53^\circ\text{C}, h = \frac{1}{2} = 24\text{ cm}\)) suggest that at atmospheric pressure \(Ra \approx 3900\) at ambient conditions. At reduced pressure, since \(v\) and \(K\) are functions of the density

\[
Ra^* = \frac{\rho^*}{\rho_0} Ra_0,
\]

where the stars represent quantities at reduced pressure and the subscript zero indicates ambient condition quantities. Eq. (2) requires that any pressure corrections to the absolute viscosity and thermal conductivity are small [16, 17], which in the present case is true. In order to reduce \(Ra^*\) to unity, it is necessary that \(\rho^* = 0.016 \rho_0\).

From the equation of state for an ideal gas we obtain

\[
p^* = \frac{\rho^* T^*}{\rho_0 T_0} p_0.
\]

Consequently, taking a mean temperature \(T^* = 538\text{ K}\) as typical of our experimental conditions, for argon we estimate the diffusion limited boundary to occur at a reduced pressure \(p^*\) of approximately 30 Torr. The result for helium is not significantly different. In summary, the specific boundaries for vapor transport are delineated as follows:

- molecular flow–diffusion \(\sim 0.01\text{ Torr}\),
- diffusion–convection \(\sim 30\text{ Torr}\),

see Fig. 2. These boundaries are not strongly dependent on the nature of the gas. We realize that the transitions between these regions are not discrete and that we have idealized the system – for example, the temperature distribution within the apparatus is non-uniform. Consequently, these regime boundaries should be regarded as qualitative rather than absolute. Nevertheless, our approximate boundaries provide guidelines for the experimentalist.

3.3. Forced convection and flow patterns

In order to examine the effects of forced convection, i.e., superimposing an external inert gas flow into the system, it is necessary to consider the details of a particular experimental configuration. Several flow patterns are possible in the convective regime, see Fig. 3:

1. Fig. 3a. In a closed system when the walls are hotter than the central region and where the walls are nearly isothermal, gas rises buoyantly near the walls and sinks in the center. This case is probably likely in a closed vertical ampoule where vertical temperature gradients encourage crystal nucleation and growth toward the top of the system.

2. Fig. 3b. However, when a central tube or rod is provided, nucleation and growth can then occur in the colder center of the ampoules even when the vertical gradient is small, provided the radial gradient is sufficient.

3. Fig. 3c. When the central region is colder than the wall at the bottom of the system and hotter than the wall at the top (i.e., the wall is not isothermal) with a region in the middle where the radial gradient is negligible, a flow pattern like Fig. 3c can exist. This is usually referred to as a thermosyphon flow.

4. Fig. 3d. If a central rod or tube is present the flow is similar. Cases (3) and (4) lead to nucleation and crystal growth on the wall in the upper region.

\(^{2}\)"Conduction" of heat in a gas occurs by colliding gas molecules exchanging energy so it is usually termed thermal diffusion, which is not to be confused with mass diffusion where molecules move over macroscopic distances. However, under conditions where thermal diffusion limiting, because stirring is minimal, mass diffusion is, in general, also limiting. When thermal convection is limiting, stirring is effective enough that bulk mass diffusion is not limiting.
(5) Under appropriate conditions, see below, multicellular flow like that shown in Fig. 3e occurs—here again the walls are nearly isothermal with probable temperature drops between cells. Transport from bottom to top will be slower because of stratification. Nucleation will occur in the cooler region at the top or at the central tube if one is present.

(6) Multicellular growth can also occur in connection with thermosyphon patterns when the radial gradient reverses Fig. 3f. Again the pattern is similar when a central tube or rod is present.

Other variants of combining multicellular and thermosyphon circulation are possible.

In vertical containers similar to the apparatus used in these experiments, both radial and axial temperature distributions will exist and each can contribute to the buoyancy-driven motion. However, in examining our geometric configuration, it is evident that while the vertical temperature difference is about 100°C, the vertical temperature gradient is only about 2°C/cm. This result should be contrasted with a larger radial temperature gradients which can occur, for instance, across the annulus width of ~0.85 cm when a central tube is present. Thus, our radial gradients are believed to be at least an order of magnitude greater than the vertical gradients. Therefore, buoyancy-driven convection is dominated by radial gradients and the following discussion is based primarily on these effects.

In a typical case, the flow of argon through the apparatus was 130 ml/min. Using the input tube cross section, this flow rate corresponds to a mean velocity in the delivery tube of about 7.7 cm/s, and a corresponding mean velocity of 0.47 cm/s in the annulus between the inner and the outer tubes. Contrasting with this forced convective motion is the motion induced in the annulus by buoyancy effects due to the imposed external temperature distribution. A measure of this thermal velocity is given by

$$ V = \frac{g\beta \Delta T d^2}{\nu}, $$

see Choi and Korpela [21]. Here $d$ represents the gap between the inner and outer tube radii (i.e., the width of the annulus) and $\Delta T$ is the horizontal temperature difference at a particular vertical location. Using the data in Table 1, yields the result for argon

$$ V = 17.3 \Delta T \quad (cm/s), $$

i.e., each 1°C increment in the differential temperature across the gap of the annulus increases the thermal speed by about 17 cm/s. Thus, the motion within the annulus of the apparatus is dominated by convection induced by buoyancy effects and the external forced convective effects, due to the externally introduced gas flows, are of secondary significance.

As discussed above two buoyancy-driven flows are most likely for the conditions corresponding to our apparatus (i) thermosyphon flow, and (ii) multicellular motion.

For thermosyphon flow to occur a dimensionless measure of the vertical temperature difference $\Delta T$,
given by [22]

\[
\theta_c = \frac{\text{Ra}}{L} = \frac{g \beta d^4 \Delta T}{\nu \kappa L}
\]  \tag{5}

must be less than a critical value of $10^7$. In Eq. (5), \(d\) is the tube diameter and \(L\) is the half-length of the thermosyphon. It should be pointed out that although in our experiments the temperature distribution was measured in an inner thermocouple well (Fig. 1), it is not necessarily a measure of the temperature in the gas. The above expressions can be used to provide estimates that predict the motion in the apparatus even though the outer surface boundary condition, i.e., the temperature distribution, is uncertain and only the temperature near the inner surface has been probed. Using a typical vertical temperature difference associated with Fig. 1 and \(\text{Ra} \approx 3900\), from Eq. (1), the thermosyphon model yields, (Eq. (5) and Table 1),

\[
\theta_c \approx 136
\]

for argon gas flow. This result suggests that the argon flow field is laminar (\(\theta_c\) from Eq. (5), < $10^7\)) and a “figure eight” thermosyphon-like motion occurs as illustrated in Fig. 3d. It can be shown that the result is the same for helium flows where the magnitudes of \(\theta_c\) and \(\text{Ra}\) are much smaller.

Multicellular motion (Fig. 3e) develops when the radial temperature difference between the inner and outer tubes leads to a Grashof number which exceeds a critical value. Under these conditions a multi cellular eddy motion occurs that supports a stably stratified vertical temperature distribution in the bulk of the gas. Motions of this type have been examined by Choi and Korpela [21], who pointed out that the gap of the annulus (expressed in their equations as the radius ratio of the inner/outer tube) influences the magnitude of the critical Grashof number. For an annular gap typical of the apparatus illustrated in Fig. 1, the equivalent radius ratio is 0.32 and the corresponding critical number \(\text{Gr}_c \approx 11400\), where

\[
\text{Gr}_c = \frac{\bar{v} d}{v} = \text{Ra} \text{Pr}^{-1}
\]  \tag{6}

and \(\bar{v}\) is the characteristic thermal speed.

Now, when the apparatus is filled with argon, the data given in Table 1, together with the gap size (0.85 cm) yield a Grashof number

\[\text{Gr} \approx 150 \Delta T,\]

where \(\Delta T\) is the radial temperature difference measured across the annulus. The corresponding value for a helium filled annulus is

\[\text{Gr} \approx 1.9 \Delta T.\]

In these circumstances, a differential temperature \(\Delta T\) between the inner and outer tubes of the apparatus of about 75°C in the argon flow would create multicellular flow (Fig. 3e) conditions. It appears, therefore, that the motion in argon is likely to be multicellular throughout most of the furnace length. Conversely, the helium flow is not expected to become multicellular (it will be an axi-symmetric thermosyphon) since the required temperature differential is impractically large.

In summary, both flow models described above, as illustrated in Fig. 3, can lead to quiescent zones in the gas contained in the apparatus. The thermosyphon flow, which may occur when helium is used, has a quiet zone in the vicinity of the vertical temperature jump introduced by the heater spacing. When argon is used it is more likely that the flow is multicellular and that numerous quiescent zones are present in the gas. Multicellular motions are important since the quiescent regions between the “cells” promote deposition of particular phases in discrete zones of the apparatus. Indeed such deposits are observed and their positions when the flowing gas in Ar are indicated in Fig. 1, where yellow material in the lower temperature region is \(\sim \Delta T\) (LT) and orange material in the higher temperature region is \(\sim \Delta T\) (HT).

An important benefit of forced convection even when the velocities do not exceed buoyancy-driven velocities is that if the gas flow is directed at the volatilization surface, the width of the diffuse layer is reduced and volatilization is enhanced. In addition, gas flow close to the growing surface will affect the width of the diffusion layer at the growing interface reducing the tendency for constitutional supercooling. Thus, in cases where the gas velocity due to forced convection does not exceed the velocity due to natural convection the main effect of
carrier-gas movement is not on bulk transport but is instead on the diffusion zones close to the vaporizing and growing surfaces. An additional benefit is that a flowing gas will remove any decomposition products before their concentration can build up and affect crystal growth or properties.

3.4. Diffusion and partial pressure gradients

Fig. 4a illustrates two cases relative to vapor-phase crystal growth. When there is no mixing or transport due to convection, the partial pressure gradient of $\delta 6T$ between the volatilization surface(s) and growing crystal(s) is approximately linear. This is the case when mass diffusion is limiting and the transport would be expected to be unpractically slow. The $\delta 6T$ partial pressure at A (Fig. 4a) is set by the temperature at A. The $\delta 6T$ partial pressure at D is determined by Fick’s law and the rate of growth. To a first approximation there are no local variations in $\delta 6T$ partial pressure near the volatilization and growth surfaces since diffusion controls end-to-end transport.

In the case of very rapid thermal convection or rapid flow of transport gas (forced convection) the $\delta 6T$ partial pressure gradient across most of the transport region can approach zero, except near the volatilization and growth surfaces.

It is important to point out that in vapor growth, in the presence of an inert gas, volatile dopants or impurities, constitutional supercooling can occur. Consider Fig. 4b and Fig. 4c. Since a growing crystal is a sink for the material being deposited, there will be $\delta 6T$ partial pressure gradient in front of the growing interface. The total pressure in the system would, of course, not exhibit gradients since pressure gradients in $\delta 6T$ are balanced by gradients in the inert carrier gas. Consider two cases, one for a moderate temperature profile ($T_1$, Fig. 4b) and one for a steeper temperature profile ($T_2$, Fig. 4b) close to the growing interface. Consider a region in front of the growing interface (Fig. 4c): For a likely $\delta 6T$ partial pressure profile for a moderate temperature profile ($T_1$) the actual $\delta 6T$ partial pressure exceeds the equilibrium $\delta 6T$ partial pressure over a substantial region (to the right-hand side of (1) in Fig. 4c). It is important to point out that equilibrium partial pressure for deposition exhibits an exponential dependence on temperature (see Fig. 5) and that other more complicated pressure profiles can exist [12]. Where actual partial pressure exceeds equilibrium partial pressure, nucleation and crystal growth can occur (often as dendrites) ahead of the growing interface—the classic behavior for constitutional supercooling in solution growth. In contrast with a steeper temperature gradient ($T_2$) the equilibrium $\delta 6T$ partial pressure is more than the actual $\delta 6T$ partial pressure except very close to the growing interface (to the right-hand side of (2) in Fig. 4c) resulting in controlled growth on initial nucleation sites or seeds. Therefore, if possible, a large temperature gradient close to the growing interface will be advantageous in eliminating
such a plot the enthalpy of vaporization, $\Delta H_{\text{vap}}$, can be calculated. A number of assumptions are made in such a treatment. These assumptions mainly depend upon the $\Delta W$s not being dependent on kinetic phenomena. If this is the case, we calculate $\Delta H_{\text{vap}}$ as 26 kcal/mol. In the earlier work [8] we estimated that $\Delta H_m$, the enthalpy of melting for the liquid–solid transformation as 10 kcal/mol. Now, since the $\Delta H_{\text{sub}}$, the enthalpy of sublimation is related to $\Delta H_{\text{vap}}$ and $\Delta H_m$ by the equation

$$\Delta H_{\text{sub}} = \Delta H_{\text{vap}} + \Delta H_m$$

(7)

we estimate $\Delta H_{\text{sub}}$ the enthalpy of sublimation to be 36 kcal/mol. TGA data below the melting point allowed for an estimate for $\Delta H_{\text{sub}}$ (directly from the log $\Delta W$ vs. $1/T$ plot; Fig. 5b), of $\sim 35.8$ kcal/mol – in excellent agreement with Eq. (7). However, some scattering of $\Delta H_{\text{sub}}$ for different samples was observed.

If we assume our $\Delta H_{\text{sub}}$ is valid we can estimate Jackson's $\alpha$ [23] as

$$\alpha = \frac{\Delta H_{\text{sub}}}{RT}$$

(8)

resulting in $\alpha$'s ranging from $\sim 60$ to 30 over the temperature range from deposition close to room temperature to deposition close to the melting point. Jackson has pointed out that quite high $\alpha$'s are normal for vapor growth of well-formed crystals [23, 24]. The morphology of our crystals was generally rather well-formed plates.

### 3.6. Crystal growth conditions

In our studies of transport and crystal growth we investigated closed systems, open ampoules with dynamic pumping, flowing inert-gas systems, the effect of inert-gas pressure, various flow rates, temperature, temperature gradient, etc. In the molecular flow regime (conditions explored: closed ampoule, $10^{-5}-10^{-3}$ Torr He, source temperature: 230–285°C, deposition temperature: ambient $-225^\circ$C) volatilization and transport can be expected to be efficient. Our estimated transport rates, based on quantity of deposit range from above $10^{-2}-10^{-3}$ g/h comparable with the results of Fig. 2 where direct weight loss of the $\alpha 6T$...
in the hot zone was measured. Lowering the source temperature causes the transport rate to be very low, perhaps due to the fact that the vapor pressures are low. In the thermal diffusion regime (conditions explored: 1–15 Torr He, source temperature: 285°C, deposition temperature: ambient – 240°C) the transport rate is \( \sim 10^{-3} \text{g/h} \), probably slightly less than in the molecular flow regime, as would be expected. The rate at higher pressures is less, because the effective diffusion constant for z6T will decrease as pressure is increased. The nuclei in both molecular flow and diffusion regimes are so numerous that no well-formed crystals are seen. Transport is so rapid that many nuclei are present for growth. At higher pressures (for example, 15 Torr of He in a closed ampoule) transport is slightly slower, nucleation is less and \( \mu \text{m} \) sized crystals are deposited. However, the number of crystals is so large that intergrowth occurs and good growth is prevented.

If inert gas at slightly above 1 atm is used (conditions explored: closed system at 400 Torr He or open system with flowing He or Ar at 1 atm, flow rates: 45–170 ml/min, source temperature: 280–325°C, maximum deposition temperature: 290°C, deposition also occurs down stream at temperatures below 250°C), the transport is in the convection regime. As discussed above, a flow rate of 130 ml/min leads to a velocity in the annulus region of a typical apparatus of only 0.47 cm/s. Even at our maximum inert-gas flow rate (170 ml/min) and even when the flow regime is more confined there are no conditions where flow velocity is likely to be more than \( \sim 2 \text{ cm/s} \). The longitudinal gradient in these experiments ranges from \( \sim 1 \) to \( \sim 10^3 \text{ cm} \). The radial gradient is always larger (mostly because the radius \( \ll \) length) so that it dominates buoyancy-driven convection. Thermally driven (buoyancy) convection produces velocities which are \( \sim 20x \Delta T \) (from Eq. (4)) for Ar, where \( \Delta T \) is the temperature difference across the radius of the apparatus. For He the velocities are higher. Thus, with any reasonable radius the velocity due to buoyancy convection far exceeds the forced convection velocities, i.e., all the experiments in which flowing inert gas at 1 atm was used, are in the buoyancy convection regime. The transport rates measured were generally quite slow (\( \sim 10^{-4}–10^{-5} \text{ g/h} \)) but more than sufficient to provide material for large crystals. Ar, He, and \( \text{H}_2 + \text{N}_2 + \text{H}_2\text{O} \) (provided by passing the gases through a water-containing bubbler) were used as gases.

Because of the differences in properties the detailed convection patterns are dependent on the nature of the temperature distribution. Generally, large vertical temperature gradients are believed to cause thermosyphon patterns. Much smaller temperature gradients would be expected to cause flow patterns consisting of upward vertical motion along the walls and downward motion in the center of the ampoule. If a center tube is present and the gas is Ar, the Grashof numbers would be larger than the critical Grashof number (11 400, see Eq. (6)) so that we expect the flow to be multicellular. Flow results for other gases (\( \text{H}_2 \) and \( \text{N}_2 \)) were not analyzed here but it is worthwhile to notice that traces of \( \text{H}_2\text{O} \), introduced into flowing gas, did not cause any noticeable decomposition.

Millimeter or larger-sized crystals were obtained in all cases in the convective regime. The rates of crystal growth were above 5 mm/day when source was above the melting point. We would expect that growth rate would depend on \( \Delta p_{\text{z6T}} = p_{\text{volatilization}} - p_{\text{deposition}} \). The vapor pressure, \( p_{\text{volatilization}} \) is set by the volatilization temperature which in these experiments was either at \( \sim 280^\circ\text{C} \) or was kept above the melting point (305°C). At the lower-temperature gradients the deposition temperature which determines the deposition equilibrium vapor pressure in the deposition region, \( p_{\text{deposition}} \) was higher. Highest growth rate occurred when the source temperature and hence \( \Delta p_{\text{z6T}} \) was high. HT modification, z6T deposited and grew at temperature above 250°C, LT modification z6T below this temperature. Recent DTA experiments [8] suggest the HFLT transition occurs at \( \sim 287^\circ\text{C} \). Our measured temperature may be low due to thermocouple placement. Thickness was generally not very large when the deposition temperature was lower.

It is important to point out that very little z6T is required to produce the thin plate-like crystals typical of our morphology in vapor growth. For example, since the density is 1.55 g/cm\(^3\) [7] a
crystal 1 cm$^2 \times 1$ µm requires $\sim 0.15$ mg of material. Thus, a transport rate of 1 mg/day would produce more than 6 cm$^2$ of very thin plates. Consequently, not much volatilization is required to produce sufficient surface area even if one grows crystals thick enough to process ($\sim 10$ µm). We frequently observed (under, for example, non-optimum free molecular flow conditions) that many small crystals ($\sim 10$ µm$^2 \times 1$ µm) are produced. Indeed, mass considerations suggest that more than $10^6$ such crystals could be deposited/day at a transport rate of 1 mg/day.

Nucleation control is required so that growth of a smaller number of nuclei into larger crystals without intergrowth and a tendency to dendritic growth due to local depletion of $\alpha$6T is favored. More than enough material can be transported even at high inert-gas pressure. Furthermore, when flowing inert gas is directed at the volatilizing $\alpha$6T surface very rapid transport can be obtained. Even in closed systems at 1 atm He, transport is enough to provide large crystals. We observed that in a flowing system with an Ar or He pressure of 1 atm, a volatilization temperature close to the melting point, and a deposition region encompassing temperatures from just below the melting point to just above room temperature, there was only a very small quantity of a poor-quality deposit overnight. However, when flowing preheated Ar was aimed at the source with a flow rate of, for instance, 20 ml/min and the tube placed within 2 mm of the source, 5 mm crystals were produced overnight. The reason for improvement, as discussed above, is the reduction or elimination of the diffusion regime near the volatilizing surface. Conditions with Ar flowing close to the source were present in our successful growth experiments.

3.7. Morphology

The habit of grown crystals is thin plates with a length or width/thickness ratio of $\sim 10^3$. The anisotropy in growth rates would be comparable. As discussed below, crystallographic structures account for this, since plate edges on the molecular scale provide ready sites for attachment. In addition, molecules sticking to the plate surface can diffuse on the surface to the edge providing a much larger supply of molecules for incorporation on the edge than can be provided by molecular collisions on the edge alone.

Fig. 6 shows the crystallographic structure of the two polymorphs of $\alpha$6T. In our earlier studies [6] we observed that two polymorphs of $\alpha$6T were deposited in vapor growth: HT form ($\alpha$6T) was observed above about 290°C and a LT form ($\alpha$6T) below about 280°C.

The main interactions between molecules of $\alpha$6T are perpendicular to the molecule axis. Interactions in other directions are much less effective. Fig. 6 shows the structures of the low- and high-temperature polymorphs. [7, 25]. Attachment of a molecule in position AB is energetically more favorable than in position BB' so that the growth rate normal to AB is greater than the rate parallel to AB suggesting in a plate-like morphology. This is the morphology observed. Fig. 6a shows the structure of the LT polymorph while Fig. 6b shows the HT polymorph. Note that the molecules are staggered in the HT polymorph with closest intermolecular contacts between the first thiophene ring and the second thiophene ring in adjacent molecules. In contrast to the LT polymorph, the closest contacts occur between the first thiophene rings in each molecule. The surface defined by B B' in Fig. 6a is essentially smooth while that defined by B B' in Fig. 6b is rough with the result that, as is observed, the ease of attachment, growth rate and plate thickness of the HT form tends to be greater than the LT form. To get thick plates of the LT form, it is probably desirable to deposit at as high a temperature as possible to commensurate with 100% yield.

3.8. Best conditions

We found it advantageous to use 1 atm of He or Ar, fairly high temperatures for volatilization (even above 300°C in some cases), and to spread the temperature gradient from volatilization to lowest temperature of interest for deposition over a rather large linear distance $\sim 20$ cm. Providing a local LT gradient near the growing interface and the aiming a flowing gas ($\sim 140$ ml/min in our apparatus of Fig. 1) at the source for volatilizing material.
are advantageous. The reasons for choosing these conditions are:

- 1 atm inert gas to repress nucleation and place the system in the convective regime.
- As high a deposition temperature as practical to produce either HT or for LT to encourage thicker plates. This is limited by the melting point for HT and by the maximum temperature for 100% LT yield for LT.
- Choosing conditions leading to cellular circulation so that isothermal depositions occur over fairly large regions, leading to a separation of LT and HT growth regions.
- Arranging a large temperature gradient in front of the growing interface so as to suppress constitutional supercooling.
- Aiming a flowing gas at the source to reduce local diffusion and aid volatilization.

Fig. 7 shows several of typical crystals where maximum dimension is ~ 1 cm. On several occasion crystals larger than 1 cm were produced.

4. Conclusions

Millimeter-sized crystals of \( \alpha \) hexathiophene with thicknesses exceeding 20 \( \mu \text{m} \) can be grown...
overnight in closed systems with ~1 atm of inert gases or in open systems with flowing inert gas. Under some conditions crystals exceeding 1 cm in size were grown. Key to success was analyzing and understanding the processes occurring in the system: volatilization, transport and crystal growth.

Excessive difficulty in control occurred at low pressures (~10^{-3} Torr) where the mean free path of ~6T was comparable to apparatus dimensions and volatilization and transport were rapid. At intermediate pressures (a few Torr) where transport was diffusion-limited, transport was slow and small crystals formed. At higher pressures and in flowing inert gas (He or Ar at 1 atm) transport, nucleation and crystal growth rate could be controlled. By choosing volatilization temperature (above 250°C), and apparatus geometry (aiming flowing gas at the volatilization region) reasonable control was possible and good crystals could be reproducibly grown. We have recently used similar conditions to grow pentacene single crystals.

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