

Considerations for the physical vapor deposition of high molar mass organic compounds



Jeffrey S. Castrucci^{a, b}, Jeremy D. Dang^a, Brett A. Kamino^a, Andrew Campbell^c, David Pitts^c, Zheng-Hong Lu^b, Timothy P. Bender^{a, b, d, *}

^a Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5, Canada

^b Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario, M5S 3E4, Canada

^c Angstrom Engineering Inc., 91 Trillium Drive, Kitchener, Ontario, N2E 1W8, Canada

^d Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, M5S 3H6 Canada

ARTICLE INFO

Article history:

Received 9 April 2014

Received in revised form

28 May 2014

Accepted 30 May 2014

Available online 16 June 2014

Keywords:

Vapour deposition

Organic semiconductor

Subphthalocyanine

Molar

High

Mass

ABSTRACT

The challenges related to the deposition of high molar mass organic compounds by physical vapor deposition (PVD) are of importance to those developing new organic electronic devices and materials. In this study we report on strategies to maximize film uniformity and mass yield within the context of rapid screening of newly prepared organic semiconductors using small amounts of these highly valuable materials. We propose guidelines for maximizing mass utilization by way of thermal source type and its position selection and tooling factor prediction. As an aside, we also highlight that fluorination of subphthalocyanine (subPc) related compounds increases their vapor pressure, despite a corresponding increase in molar mass.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The last two decades have seen significant increases in the interest in organic semiconductors and a corresponding increase in the variety of novel organic semiconductor compounds that have been synthesized. New candidate organic semiconducting materials are regularly designed and synthesized with targeted applications in organic field effect transistors (OFETs) [1], organic light emitting diodes (OLEDs) [2], and organic photovoltaic (OPV) [3] devices. When small organic molecules are targeted (for example $<700 \text{ g mol}^{-1}$) a common technique for the preparation of the resulting devices is the sublimation of the material from a heated crucible at reduced pressures ($<10^{-6}$ Torr, $<10^{-4}$ Pa) to form nanometer scale thin films on a targeted substrate located above and some distance away from the crucible, a process referred to as physical vapor deposition (PVD) [4].

The successful use of PVD for organic compounds is predicated upon heating an organic electronic material to a point where it is volatile enough to undergo sublimation and be subsequently deposited at an appreciable rate (usually in the range $0.05\text{--}0.2 \text{ nm s}^{-1}$) onto the target substrate without thermal degradation either in the crucible or in the gas phase while in transition between the crucible and the target substrate. Thus the vapor pressure of a compound can have a major impact on its suitability as a PVD depositable organic electronic material. All other things being equal, increasing the molar mass of a material will decrease its vapor pressure, suggesting high molar mass semiconductors may pose a challenge to deposit via traditional PVD techniques.

Chemical engineers have a long history of working with the inorganic semiconductor industry in the development of industrial PVD processes [5–7], and more recent reports on film uniformity exist in the literature [8], but discussion on the unique challenges of organic semiconductors in contrast to existing process knowledge accumulated for inorganic processes is sparse [9]. Such information would be valuable especially during initial screening of new candidate compounds when often only a small amount of the new material will be available for testing due to synthetic limitations in

* Corresponding author. Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5, Canada. Tel.: +1 416 978 6140.

E-mail address: tim.bender@utoronto.ca (T.P. Bender).

early stage development. While such information may be available to those who have practiced in the field, whether in industry or academia, we were unable to find publications in the literature on to how to deal with these challenges, especially once the additional complications of a rotating substrate holder that is not coaxial with the source and non-point sublimation sources are considered.

Additionally, newly conceived and synthesized organic semiconductors are very valuable. Before making devices each new material requires a test deposition to determine the ratio between test material reading on a quartz crystal monitor (QCM) and the actual film thickness to establish a tooling factor is required. The establishment of a tooling factor consumes material without actually producing a functional organic electronic device. If the tooling factor for a new material could be predicted, then the test deposition and the associated use of the valuable organic material could be avoided. Thus there is a desire to identify a universal tooling factor for a given system that would help with the rapid testing of new materials and the maximization of new material usage.

In this paper, we have used a variety of semiconductor materials of proportionally increasing molar mass that can only be made in relatively small quantities to identify how increasing molar mass impacts the physical vapor deposition of films. We have performed the depositions using a small PVD chamber with a rotating substrate holder and four resistive heating sources. We have explored how changes in the source to substrate positioning and the type of thermal source type (including a non-line of sight source, a single aperture source, and a multi-aperture source) influence film yield, mass utilization and film uniformity. We also report helpful relationships for estimating the tooling factor of a new material. Additionally, as an aside and important to our laboratory and others, we also report that axial fluorination of a subphthalocyanine [10,11] can offset an increase in molar mass and increase the resulting vapor pressure.

2. Experimental

The structure of the six compounds explored in this study and their corresponding molecular weights are shown in Fig. 1. Cl-BsubPc [12], F5-BsubPc [10], μ -oxo-(BsubPc)₂ [13], and F5-GBsubPc [14] were synthesized and purified by train sublimation as previously reported. Pentafluorophenoxy boron subnaphthalocyanine (F5-BsubNc) was prepared in a two-step process starting with the cyclotrimerization of 2,3-dicyanonaphthalene with boron trichloride to give chloro boron subnaphthalocyanine (Cl-BsubNc), followed by an axial displacement reaction with pentafluorophenol. Alq3 was purchased from Sigma–Aldrich and used as received.

All films were formed by vacuum depositions conducted in an Angstrom Engineering Covap II vacuum system with a base pressure $<10^{-7}$ Torr ($<10^{-5}$ Pa) and at operating pressure $<5 \times 10^{-6}$ Torr ($<7 \times 10^{-4}$ Pa). Material deposition was monitored by an Inficon quartz crystal microbalance (QCM). Samples were mounted on a circular substrate holder which revolved at 40 rotations per minute. Several types of thermal sources were used to sublime the organic materials, in particular the ME2-.005Ta boat with either the ME2A-.005Ta (single aperture) top baffle or ME2B-.005Ta (multiple aperture) top baffle and the SB-6 with SB-6A top baffle. All thermal sources were purchased from The R.D. Mathis Company and were thoroughly degassed under vacuum while empty before being used for depositions. The width of the thermal source holders on the Covap II mean that the ME2 could be placed at either the inner edge of the holder or the outer edge, as shown in Fig. 2. The SB-6 is wider than the ME2 sources, so it filled the entire thermal source holder and thus no inner edge vs. outer edge alignment distinction was relevant for the SB-6.

Organic films were deposited on two types of substrates which were subjected to two different surface treatments. Clear glass microscope slides were purchased from VWR. ITO patterned glass

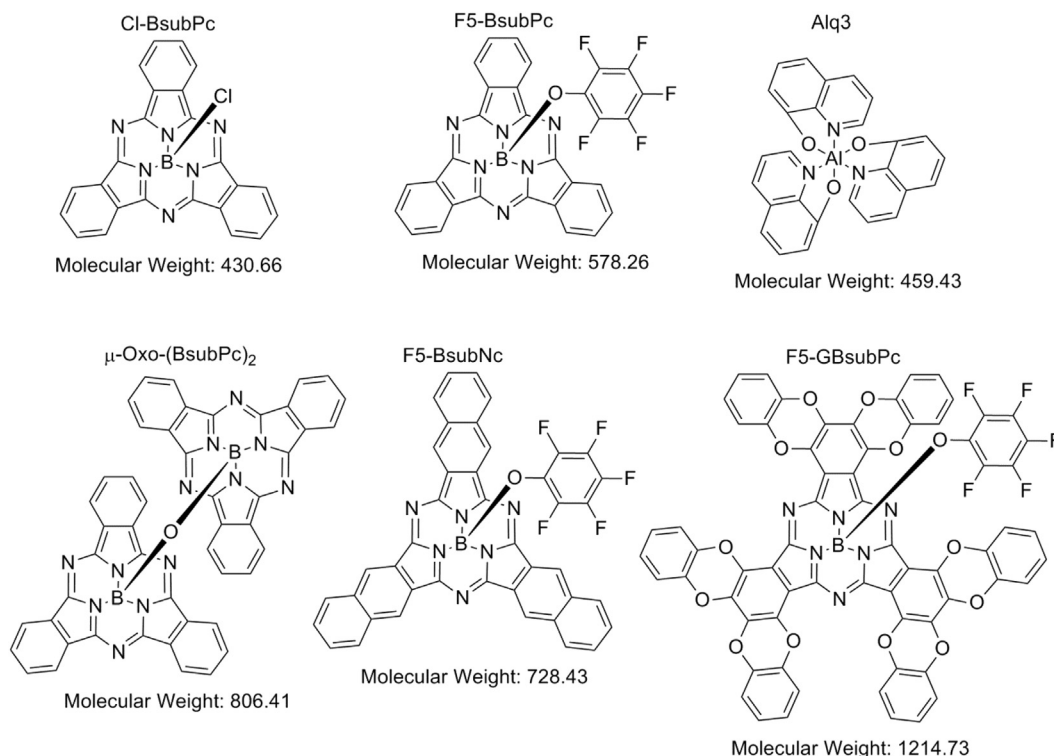


Fig. 1. Compound structures, corresponding abbreviations, and corresponding molecular weights of the compounds used in this study.

Download English Version:

<https://daneshyari.com/en/article/1688473>

Download Persian Version:

<https://daneshyari.com/article/1688473>

[Daneshyari.com](https://daneshyari.com)