Exploiting physical vapor deposition for morphological control in semi-crystalline polymer films

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1 INTRODUCTION

Polymer crystallization, especially in thin film geometry, is an important topic attracting intensive research efforts to unveil its complex nature. The studies are of tremendous importance for functional polymers, which enable a broad range of applications such as solar cells,[1–4] transistors,[5–8] non-volatile memories,[9,10] and sensors.[11–13] Among all the applications, film morphology, arising from the complex semi-crystalline nature of polymers, critically determines performance.[8,14–17] For example, it is generally accepted that a higher extent of crystallinity in the active layer of semiconducting polymer thin films can enhance device efficiency[8,14,15,18] and a longer lateral dimension of defect-free crystalline lamellae can reduce gas permeability through polymer thin films.[11] Despite its significance, ways to drive polymer thin film crystallization into a desired morphology has not been fully understood or mastered, especially since the process is known to deviate from bulk crystallization. During the process of melt-crystallization, the mutually entangled polymer chains are driven by both thermodynamic and kinetic factors into different metastable states comprising both crystalline and amorphous regions.[19] It is strongly influenced by crystallization temperature,[20] molar mass,[21] and additives in the bulk composition.[22] In contrast, in thin films, additional processing parameters such as geometric confinement,[23–25] polymer/substrate interactions,[26–28] and sample history of non-equilibrated films[29] can further influence crystallization, thus impacting the resulting film morphology. Furthermore, the method in which a thin film is processed, including solution processing, physical or chemical vapor deposition (CVD), and melt-crystallization can profoundly impact the film morphology. In this review article, we highlight recent advances in controlling the film morphology of semi-crystalline polymers produced by physical vapor deposition (PVD). We focus on elucidating general processing-structure-property relationships of films formed by this approach. Compared to the more commonly used solution processing techniques, that is, spin casting and solution casting, substrate temperature and
deposition rate can be precisely manipulated during PVD to drive the semi-crystalline morphology of thin films.\textsuperscript{[30–33]} It allows for simultaneous film growth and crystallization, as recently advocated.\textsuperscript{[34]} Furthermore, PVD approaches are amenable for co-depositing polymers that are insoluble in a common solvent or designing multilayered films comprising chemically similar or dissimilar polymers.\textsuperscript{[35,36]}

The critical roles of geometric confinement, polymer/substrate interactions, and crystallization temperature have been reported for polymer thin film crystallization.\textsuperscript{[30,37,38]} To set the context for the continued need of advancements in top-down PVD, Box 1 provides a brief summary of selected studies exploiting solution-based processing methods to manipulate morphology in semi-crystalline polymer films. Challenges still remain to fully understand and control the crystallization mechanism of polymer thin films. For example, many studies have discovered that the orientation of crystalline lamellae atop attractive substrates would preferentially transition to flat-on as film thickness was decreased.\textsuperscript{[39–41]} Researchers have proposed different models to explain such experimental observations.\textsuperscript{[41,42]} Nevertheless, understanding how parameters such as polymer/substrate interfacial energy affect the crystallization process, for example, crystal orientation, still remains a subject of intense debate.\textsuperscript{[38]} Part of the reason arise from the difficulty to tune processing parameters in a systematic manner during the fabrication of polymer thin films. In other words, to better understand how processing affect morphology, it would be useful to exploit a film fabrication technique that has the ability to precisely tune the crystallization conditions at a slow film growth rate. For instance, one potential approach is to characterize the nanoscale crystalline morphology of thin films in a layer-by-layer manner, which would be accessible as a result of top-down film deposition. Such a distinctive approach can be challenging for most processing techniques.

It is, therefore, critical to explore various approaches to processing semi-crystalline polymer thin films. To date, the most frequently reported film production techniques are solution processes such as drop casting, spin casting,\textsuperscript{[43]} and Langmuir-Blodgett deposition.\textsuperscript{[44]} In contrast, dry processes such as vapor deposition, including PVD\textsuperscript{[30]} and CVD,\textsuperscript{[45,46]} can provide new perspectives by altering the processing route to which a thin film is achieved. Without incorporating chemical reactions, PVD is a viable way of exploring the processing-structure-property relationships of crystalline thin films by precisely tuning growth rate, crystallization temperature, and interfacial interactions at distinct stages of film formation. The major drawback of PVD that limits the ability to undertake systematic studies of polymer thin film has been the prospects of polymer degradation during processing due to the high energy input into the target material.\textsuperscript{[47]} Despite this challenge, there are many examples in which PVD has been successfully applied to control the semi-crystalline morphology of polymer films. Furthermore, a recently developed PVD technique termed matrix assisted pulsed laser deposition (MAPLE) has offered a substantial opportunity to bring deeper insights into the field by diminishing material degradation.\textsuperscript{[31]}

The scope of the present article will be specific to the crystallization of polymer thin films via PVD. We start with a description of classical PVD techniques, including a discussion on the uniqueness and challenges for each technique in the context of polymer thin film fabrication. Next, we summarize previous studies related to vapor deposited semi-crystalline films, highlighting how PVD was applied to manipulate film morphology by varying key parameters such as substrate temperature and substrate type. We then highlight recent advances in the field by the utilization of MAPLE, with particular emphasis on work from our group demonstrating, for instance, the ability to control crystal lamellar thickness and extent of crystallinity. Moreover, it has immense potential in the application of polymeric semiconducting devices.\textsuperscript{[48–51]} Future opportunities are discussed at the end of the review.

2 | PVD TECHNIQUES

In this section, we briefly discuss several classical PVD techniques: sputtering, thermal evaporation, and pulsed laser deposition (PLD). We describe the mechanism of film formation and the uniqueness/challenges of each process. Finally, we briefly highlight how each approach has been exploited to deposit semi-crystalline polymer thin films.

2.1 | Sputtering

A typical polymer sputtering process requires a vacuum chamber coupled to a radio frequency generator.\textsuperscript{[56,57]} A target polymer and a substrate are placed on the cathode and the anode, respectively. In most cases, deposition is initiated by the creation of energetic particles in a chemically inert gas via an ionization process. These particles subsequently bombard the solid target with high kinetic energy, thereby ejecting molecules from the target which lead to film formation atop the adjacent substrate.\textsuperscript{[57,58]} Sputtering is, therefore, a dry process that circumvents the use of solvent. It also supports the fine control of deposition rate.\textsuperscript{[59]} Nonetheless, the transfer of kinetic energy from the particles to the target molecules can result in chemical degradation by random polymer chain cleavage.\textsuperscript{[60,61]} This imposes a big constraint to morphological control and characterization of polymer thin film properties.\textsuperscript{[62]} So far, the employment of sputtering has frequently been used to acquire thin film coatings of fluoropolymers, such as poly(tetrafluoroethylene) (PTFE), for enhancing water-repellent\textsuperscript{[63,64]} or gas separation properties\textsuperscript{[65]} where polymer degradation can be tolerated.

2.2 | Thermal evaporation

Thermal evaporation deviates from sputtering in that the energy input into the target polymer is in the form of heat. The thermal energy evaporates the molecules in vacuum. Subsequently, film formation proceeds by the transfer of evaporated molecules that condense atop the substrate. In a typical thermal evaporation process, the substrate temperature is held below the polymer melting temperature to control the degree of supercooling during deposition. Analogous to sputtering, thermal evaporation is a dry process so that the dissolution of polymer is not required. With the control of film thickness spanning from a monolayer to several microns by varying deposition time, this
BOX 1

CONFINED CRYSTALLIZATION OF SOLUTION PROCESSED POLYMER FILMS

Polymer thin film crystallization atop substrates can be markedly different from the bulk process. In thin films, geometric confinement and polymer/substrate interactions can play critical roles. This Box briefly highlights the basic concepts of how confinement/interfaces can influence polymer thin film crystallization. Confinement can be utilized to suppress heterogeneous nucleation of polymer crystals to allow for the attainment of homogeneous nucleation. Massa and co-authors created impurity-free poly(ethylene oxide) (PEO) droplets atop a thin layer of polystyrene by dewetting. They successfully achieved and characterized homogeneous nucleation at large supercooling of micron-sized droplets, as shown in Figure B1A. Homogeneous nucleation was observed to occur randomly for equal-sized droplets because the energy barrier to nucleation is only an intrinsic function of PEO itself. The nucleation kinetics was determined by the volume of the droplet, as a faster rate was found for larger droplets.

Interactions at the polymer/substrate interface can influence the film morphology by changing the crystal orientation. Hu and co-workers applied two substrates, that is, highly oriented pyrolytic graphite (HOPG) and amorphous carbon-coated mica, to spin coat poly(di-n-hexylsilane) (PDHS) films. Ultrathin films of PDHS revealed edge-on lamellae atop HOPG as a result of epitaxial crystal growth at the interface of highly ordered substrates, while flat-on lamellae were found atop substrates coated by amorphous carbon. Mareau and Prud'homme also observed flat-on lamellae for ultrathin poly(ε-caprolactone) (PCL) films atop silicon wafers and carbon-coated substrates, as illustrated in Figure B1B. Additionally, they found a nonlinear reduction of the crystal growth rate as film thickness decreased, as the reduction was more pronounced for films thinner than the lamellar thickness. They attributed this suppression of crystallization kinetics to a slower diffusion of polymer chains to the growth front, imposed by both size confinement and polymer/substrate interactions.

Napolitano and Wübbenhorst applied dielectric spectroscopy for spin coated poly(3-hydroxybutyrate) atop aluminum coated glass slides. They claimed that the slowing down of the crystallization kinetics was related to a reduced mobility layer, that is, irreversibly adsorbed layer, at the interface between polymer and substrate.

Besides the effect of geometric confinement and polymer/substrate interactions, crystallization temperature also influences the crystallization processes and morphology as it determines chain dynamics. Grozev et al. examined the crystallization of mono-lamellar PEO crystals in spin coated poly-2-vinylpyridine-poly(ethylene oxide) films atop silicon wafers. After performing melt-crystallization for the films in a temperature range between 45 °C and 57 °C, they identified that the crystal structure of PEO changed with temperature, as can be compared in Figure B1C. Both lamellar thickness and width of the side branches increased with increasing crystallization temperature. Similarly, Jeon and co-author observed a morphological transition for low-density polyethylene thin films atop silicon wafers when the crystallization temperature changed from 90 °C to 115 °C. As a summary, confinement, polymer/substrate interactions, and crystallization temperature are critical factors in determining the final film morphology of semi-crystalline polymers.

2.3 | Pulsed laser deposition

Pulsed laser deposition is a dry process that utilizes laser pulses at sufficiently high energy density to ablate a solid polymer target. Upon absorption of photons, macromolecules at the target surface rapidly vaporize, creating a plume composed of polymer that is ejected toward the substrate. The most frequently used laser sources include ultraviolet (UV), infrared (IR), F2, F3, and CO2. By sequentially ablating chemically similar materials, PLD can be readily implemented to design multilayered film structures that are challenging for solution processing techniques. Unfortunately, material degradation by thermal dissociation and photochemical reactions are commonly observed with direct laser ablation, making PLD unsuitable for applications that require preservation of bulk chemistry. Consequently, polymers should be kept at low molecular weight for PLD. In order to minimize the destruction of polymers, careful selection of the laser source and the corresponding wavelength should also be considered. For instance, when an ArF laser (λ = 193 nm) was used, the deposition of low-molecular weight (Mw = 1400) polyethylene glycol (PEG) revealed structure modification, as identified by Fourier transform infrared spectroscopy. However, no clear observation of chemical modification was found when the authors switched to a free-electron laser (FEL) with λ = 2.9 or 3.4 μm, wavelengths that are in resonance with specific bond vibrations of PEG.
CRYSTALLIZATION OF POLYMER THIN FILMS BY PVD

Here, we discuss prior work that has employed PVD approaches to probe or control the crystallization of polymer films deposited atop various substrates. By controlling processing parameters such as substrate temperature and substrate type, the change in crystal form, extent of crystallinity, or chain orientation has been achieved for model polymers such as PTFE, PVDF, and PE.

Owing to the slow film growth rate of PVD processes, the crystallization of molecules take place at the substrate. Therefore, one major advantage of PVD is that it can effectively tune the degree of supercooling by simply altering the substrate temperature during film growth. This key parameter enables tunability toward desired polymorphism and crystallinity. For example, the ferroelectric polymer, PVDF is known to adopt distinct crystalline forms based on the method of processing. PVDF crystalline forms are not permanent, as they can be interconverted by applying external heating, electric field, or pressure. Takeno and co-workers produced PVDF films exhibiting α and β forms atop silicon wafers by thermal evaporation at 25°C and -190°C, respectively. Without the need of extra treatment, the β form showed piezoelectricity because of the in situ supercooled crystallization condition provided. The γ form of PVDF was also made using a substrate temperature of 125°C and a much slower deposition rate compared to the previous conditions. The authors further proposed a phase diagram where they claimed the crystal form to be a function of deposition rate and temperature, as illustrated in Figure 1.

Substrate temperature is also known to strongly influence the extent of crystallinity of vapor deposited polymer films. Norton et al. investigated PTFE films atop glass substrates deposited at different temperatures by PLD with a KrF excimer laser. By studying the x-ray diffraction (XRD) pattern, they reported the crystalline fraction scaled with substrate temperature from 200°C to 350°C, while the film remained amorphous below 200°C. Jeong and co-authors also discovered increasing crystallinity of vapor deposited PE crystals with increasing temperatures in the range from -2°C to 100°C. Such trend has been related to higher chain mobility enabled at elevated substrate temperatures for chain disentanglement and reorganization.

FIGURE B1  A, Optical microscopy image of a small section of the sample (1000 μm wide) obtained at a crystallization temperature of -2.6°C. Amorphous droplets appear dark and semi-crystalline droplets appear white under nearly crossed polarizers. The plot shows the fraction of crystallized droplets as a function of temperature upon cooling (0.4°C/min) for homogeneous nucleation. Adapted with permission. Copyright 2004, the American Physical Society. B, Tapping mode atomic force microscopy (AFM) height images of PCL films crystallized at room temperature on carbon-coated substrates at film thicknesses of (1) 15 and (2) 6 nm. Adapted with permission. Copyright 2005, American Chemical Society. C, Typical optical micrographs of crystals in a 40 nm thick film grown at (1) 48°C and (2) 52°C. The average growth rate of the diagonals from center to tip is about 2.9 μm/min for (1) and 0.9 μm/min for (2), respectively. The size of the images is 65 by 65 μm². Adapted with permission.

FIGURE 1  Phase diagram and molecular orientation in poly (vinylidene fluoride) (PVDF) thin films as a function of the deposition rate and the substrate temperature. α, β, and γ denote the crystal forms in PVDF. The symbols ⊥ and || refer to the molecular orientation perpendicular and parallel to the substrate, respectively. Adapted with permission from Ref. Copyright 1994, Elsevier.
Another key parameter that can tune the crystalline film morphology is the interaction between polymer and substrate. The ease of depositing polymers by PVD atop various substrates has been exploited by many researchers to manipulate the molecular orientation by epitaxial crystallization. The concept of epitaxial growth of a polymer crystal is often considered as the matching of crystallographic orientation between the guest polymer and the crystalline substrate.[26,101] Typical substrates used for this purpose are alkali halide or crystalline polymers.[30,70,74] In 1975, Hattori and co-workers reported the epitaxial growth of low-molecular weight PE by performing thermal evaporation atop KCl substrates.[74] At room temperature, rod-like crystals of PE were formed on the cleaved face of a KCl single crystal, with the chains preferentially aligned parallel to the substrate. The crystal structure developed as ellipse-like and disk-like patterns at substrates temperature of 100°C and 150°C, respectively. At approximately the same time, the epitaxial growth of thermally evaporated polymers was also applied to reveal the surface topography of the crystal underlayers, and further be exploited as a means to tune surface functionality.[70,102,103] Wittmann and Lotz deposited a decorating layer of PE crystallized atop a solution processed PE single crystal; the resulting film structure is shown in Figure 2A.[104] The vapor deposited PE aligned as edge-on lamellae atop the crystal substrate, with chains parallel to the direction of the growth face, as illustrated in Figure 2B.[30,104] The crystallization features of the top layer revealed sectorization of the underlying solution processed PE during crystallization. It is worth noting that this type of multiple layered film comprising the same polymeric material can only be achieved by dry processes such as vapor deposition. Applying the same concept but using CNTs as the substrate, Li and co-authors created unique two-dimensional (2D) patterns of PE crystals termed nanohybrid shish kebab (NHSK). Figure 3A is a representative transmission electron microscopy (TEM) micrograph of a PE-coated single-walled carbon nanotube (SWNT).[71] With a schematic illustration in Figure 3B, the formation of the 2D structure, where the rod-like PE crystals stack with their long axes normal to the nanotube, was attributed to a soft epitaxial mechanism due to the extremely small diameter of the nanotubes limiting the strict lattice matching of PE crystal chains.[71,105]

Film morphology after vapor deposition can also be affected by other parameters including target shape and laser source in the case of PLD. For instance, Li et al. deposited PTFE films atop silicon wafers by PLD from two different targets: polished pellets and pressed powder. After ablation by a KrF (λ = 248 nm) excimer laser at a substrate temperature of 300°C, the film made from the pressed powder was
smoother than the one from polished pellets due to rapid depolymerization of the polished pellets.\textsuperscript{[106]} Jiang and co-authors utilized XRD and TEM to characterize the film morphology of PTFE atop glass slides or carbon-coated copper grids by PLD using a KrF ($\lambda = 248$ nm) laser. At a substrate temperature between $200^\circ C$ and $450^\circ C$, the films comprised both amorphous and crystalline regions. The crystalline structure was highly ordered with the long helical molecular chains oriented parallel to the interface plane with the substrate.\textsuperscript{[100]} A similar film structure for PTFE atop silicon wafers at a substrate temperature of $300^\circ C$ was also observed using a femtosecond pulsed Ti: Sapphire ($\lambda = 800$ nm) laser.\textsuperscript{[107]} Nonetheless, when PTFE films atop silicon wafers were made by a synchrotron beam (critical wavelength of 1.5 nm), the chain orientation became perpendicular to the substrate surface at room temperature deposition, compared to parallel chain orientation of the same films made using a Yttrium Aluminium Garnet (YAG) laser ($\lambda = 266$ nm).\textsuperscript{[108]} Zhang et al. reasoned the difference to be the result of a different deposition mechanism. Employing a quadrupole mass spectroscopy, they found saturated fluorocarbons were ejected from the target by a photochemical reaction mechanism when a synchrotron beam was used, as opposed to a normal laser ablation yielding radicals of monomers by thermal unzipping of polymer chains.\textsuperscript{[108]} The larger oligomers from the synchrotron irradiation were more susceptible to form lamellar structures with the molecular axes normal to the interface.\textsuperscript{[108–110]}

The current section has discussed the ability of PVD to control the crystal form, extent of crystallinity, and crystal chain orientation by exploiting the effects of substrate temperature, substrate type and other parameters such as target shape and laser source on film morphology. However, many of these approaches are limited toward fully understanding the processing-structure-property relationships due to polymer degradation. One way of overcoming such challenge is to employ newly developed techniques. Recently, a PVD technique termed MAPLE has been proven to minimize chemical modification of polymers. The gentler deposition approach sets the stage for studying polymer thin film crystallization in greater details. In the next section, we discuss the unique film formation mechanism of MAPLE, followed by highlighting our work in advancing the field by employing MAPLE to enhance the understanding of structure-property relationships of polymer films formed by top-down deposition.

4 | MATRIX ASSISTED PULSED LASER EVAPORATION

Developed nearly two decades ago, MAPLE is a PVD technique that can effectively minimize polymer damage during deposition.\textsuperscript{[111]} While it utilizes a laser sources similar to PLD, such as UV excimer lasers,\textsuperscript{[86,112]} IR lasers,\textsuperscript{[48,113,114]} and FEL lasers,\textsuperscript{[115]} MAPLE uniquely adapts a sacrificial solvent in the target composition to absorb the majority of the laser energy. Such design preserves the target polymers and produces films with identical chemical structure and molecular weight to the starting material.\textsuperscript{[86,116]} A schematic of MAPLE is illustrated in Figure 4. Deposition is initiated by laser ablation on a cryogenically frozen target comprising a dilute polymer solution. Subsequently, phase explosion occurs at the target surface, releasing a vaporized plume containing both polymer and solvent into the vacuum. Film formation proceeds by the addition of polymer molecules, as the volatile solvent gets pumped away.\textsuperscript{[51]} The polymer-friendly technique has been applied to crystalline polymers such as PEO and PE for systematic crystallization studies.\textsuperscript{[34,112,117]} Furthermore, it allows for fabricating electronic and photonic devices with polymers.\textsuperscript{[48–50]} The size of these polymers range from $3$ to $70$ kDa. For example, Ge et al. recently reported a solar-cell performance of over $3\%$ by MAPLE-deposited poly(3-hexylthiophene):[6,6]-phenyl C$_{61}$-butyric acid methyl ester using an Er:YAG laser ($\lambda = 2.94$ $\mu$m).\textsuperscript{[52]} Yet application wise, the major limitation of MAPLE is the unfavorable surface feature. In many cases, MAPLE-deposited films have notable surface roughness with a large size distribution of polymer globules.\textsuperscript{[114]} Molecular dynamics
simulation by Leveugle et al. explained the surface roughness to be a result of the deposition mechanism itself, which involved cluster formation consisting of polymer chains.\cite{118} In order to improve the film quality, researchers have managed different ways such as creating emulsions within the target composition\cite{119} and selecting solvents which have high absorption of the laser source.\cite{120,121}

### 5 | CRystallization OF POLYMER THIN FILMS BY MAPLE

Our investigation on crystallization of polymers thin films by MAPLE has been focused on the governing rules of crystallization kinetics occurring during extremely slow film growth.\cite{34,112,117,122} While MAPLE achieves concurrent film growth and crystallization similar to other PVD technologies, it is distinguished in that (1) the polymer is ejected from the target in the form of a polymer-matrix clusters rather than a gas phase, and (2) the chemical nature and molecular weight of the target polymer can be preserved. This results in some unique features in crystal nucleation-growth mechanism atop the substrate, and more importantly, allows the manifestation of long-chain effects of the molecules in crystallization, that is, chain-folding and adsorption to substrate surface. In the following section we will address our recent work in advancing the understanding of polymer crystallization in thin film geometry by MAPLE.

#### 5.1 | Crystal nucleation and growth mechanism in MAPLE

In MAPLE processing, film fabrication is achieved by the assembly of nano-sized to micron-sized polymer droplets rather than individual molecules. During laser ablation of a target matrix, polymer chains trapped in the matrix are entrained together in the ablation plume.\cite{123} Subsequently, the polymers deposit as confined droplets atop a substrate, as schematically shown in Figure 5A.\cite{112,124,125} The diameter of the droplets typically ranges from tens of nanometers to a few micrometers. Depending on the substrate temperature and droplet size, the droplets either self-nucleate, crystallize from a crystal growth front, or remain in the liquid phase.

The distribution of size in deposited polymer droplets plays a critical role in crystal nucleation due to finite size effects on the rate of nucleation.\cite{24} The nucleation probability is greater in larger liquid droplets.\cite{24}

When polymer droplets are larger than a critical size, they self-nucleate during deposition, while smaller droplets remain in the liquid state.\cite{19,126}

By short time MAPLE deposition with slow film growth rates, we could examine the early stage film morphology composed of confined polymer droplets. Figure 5B shows an atomic force microscopy (AFM) height image of the morphology of a PEO (\(M_n = 4600\) g/mol, \(M_w/M_n = 1.1\)) film deposited onto a silicon (Si) substrate by MAPLE (MAPLE-PEO).\cite{112}

The substrate temperature during deposition (\(T_{dep}\)) was 25°C, which is much lower than the melting temperature of the target PEO (\(T_m = 60°C\)). The film comprised three distinct structures: nucleating droplets, 2D dendritic patterns consisting of mono-lamellar crystals, and the surrounding amorphous phase. Figure 5B illustrates three large droplets denoted N1, N2, and N3, which are nucleating droplets formed by self-nucleation. Once nucleating droplets form, they render the crystallization of small droplets into 2D patterns on the surrounding. The resulting structure is schematically described in the inset of Figure 5B. The liquid layer is formed by small droplets isolated from any crystalline islands and is incapable of self-nucleation and epitaxial nucleation from growth fronts of the crystalline islands.

For strong crystal formers, however, such size-effect on nucleation may not be evident. Figure 5C shows an AFM height image of nanoscale polymer crystals formed by the deposition of low-molecular weight PE (\(M_n = 3000\), \(M_w/M_n = 1.10\)) atop Si at \(T_{dep} = 75°C\) (MAPLE-PE), which...
is more than 50°C below the typical melting temperature of the target PE ($T_m \sim 127^\circ$ C). Most of the isolated PE nuclei were comprised of ~10-nm-thick PE mono-lamellae, as schematically shown in the inset of Figure 5C, which implied that the nucleation capability of PE was sufficient to form single-lamellar nuclei. As a result, the structural formation of PE films formed by MAPLE was highly driven by nucleation of individual droplets, which was in stark contrast to the case of PEO whose self-nucleation event was only limited to micron-sized droplets.

### 5.2 Control of lamellar thickness and melting temperature

The folded-chain structure of polymer crystals has a critical influence on the metastability as well as the mechanical, electrical properties of semi-crystalline polymers. Therefore, controlling the lamellar thickness is of significant interest in polymer processing. Since chain-folding is strongly governed by crystallization temperature, precise tuning of the crystallization temperature ($T_c$) over a wide range is desirable to engineer the lamellar thickness in semi-crystalline polymer films. PVD has a significant advantage in that it enables a facile control of the substrate temperature at which the target material condensates; this prevents the occurrence of crystallization at untargeted temperature on slow cooling from a liquid state. Conventional PVD techniques, however, were not suitable for systematically studying the chain-folding behavior due to the fracture of macromolecules during vaporization. In this sense, the use of MAPLE processing was necessary.

Via MAPLE, a strong correlation between lamellar thickness of the deposited polymers and $T_{dep}$ has been identified with two model polymers, low-molecular weight PE ($M_n = 3000$, $M_w/M_n = 1.10$) and PEO ($M_n = 4600$ g/mol, $M_w/M_n = 1.1$). Figure 6A exhibits the AFM morphology of PE single-lamellar crystals atop silicon wafers, whose height corresponds to the lamellar thickness. The height profiles of PE single crystals formed at four different $T_{dep}$ that is, 75, 80, 100, and 116°C are compared in Figure 6B. While the crystals formed with $T_{dep} = 116^\circ$C exhibited a fully extended chain length of ~27 nm, the lamellar thickness clearly decreased as $T_{dep}$ was lowered.

In addition, by manipulating $T_{dep}$ during MAPLE, crystals with different lamellar thickness can be formed in one film. Figure 6C shows an AFM height image of PEO lamellar crystals, grown using the temperature protocol described in the inset of Figure 6C. The deposition started with $T_{dep} = 25^\circ$C (MAPLE 1st), temporarily ceased to raise the $T_{dep}$ to 35°C and continued again with $T_{dep} = 35^\circ$C (MAPLE 2nd). The rise of $T_{dep}$ from 25°C to 35°C led to a ~3 nm step increase in lamellar thickness of the growing PEO crystals, as shown in Figure 6D that measures the height profiles along P1-P4 in Figure 6C. Such a sudden change of $T_c$ while growing different layers of crystals by top-down approach would not be possible in the case of solution processing and melt-crystallization, where crystals rapidly grow from a consolidated liquid phase. By MAPLE, a delicate control of polymer crystallization could be realizable by extremely slow film growth combined with the capability of tuning $T_c$ by $T_{dep}$.

The control over the film morphology with $T_{dep}$ during MAPLE leads to different thermal properties of the deposited polymer films. Due to the metastability of lamellar crystallites bounded by amorphous surfaces, their $T_m$ strongly varies with lamellar thickness, following the Gibbs-Thomson relationship. The strong correlation between $T_{dep}$ and $T_m$ in MAPLE-deposited PE films was successfully verified using flash-calorimetry (flash-DSC) technology. Flash-DSC can measure heat flow from an infinitesimal amount of a sample (~1 µg) placed on a flash-DSC chip with ultra-high rates of cooling and heating. By MAPLE, PE was directly deposited onto a flash-DSC chip as shown in Figure 7A. The temperature of the chip during deposition ($\sim T_{dep}$) was controlled by a MAPLE substrate heater.

Figure 7B plots the flash-DSC first heating thermograms of MAPLE-PE samples obtained with various $T_{dep}$ where melting peaks were clearly captured. The manipulation of $T_{dep}$ over 118°C (~2-116°C) resulted in a dramatic change in $T_m$ over 20.6°C (105.7-126.3°C). For reference, Figure 7B also illustrates the melting peaks of the same PE obtained by melt-crystallization in bulk (~mg) with two cooling rates; one by 0.5°C/min (dashed line in Figure 7B) and the other by quenching into liquid nitrogen (LN$_2$, dotted line in Figure 7B). Those two
Adsorption of polymers during MAPLE

At the moment of deposition atop a substrate, polymer droplets may physically adsorb to the surface, thereby impeding crystallization. As hinted previously, such adsorption would be evident when the nucleation capability of the deposited polymer droplets is low, that is, when the droplet is smaller than the critical size for nucleation or $T_{dep}$ is higher than the temperature allowed for self-nucleation. While MAPLE of PE does not show a noticeable evidence of adsorption due to the strong nature of PE to crystallize, the effect of droplet size and $T_{dep}$ on adsorption can be clearly observed in MAPLE-deposited PEO. PEO films grown atop Si by MAPLE exhibit an adsorbed layer formed by the deposition of small PEO droplets that failed to nucleate.[112,117] MAPLE of PEO at a temperature slightly below the bulk melting temperature ($\approx 60^\circ C$) can form a film that remains in liquid phase across the deposited area.[112,117]

Adsorption during MAPLE can lead to the loss of the crystallizability of deposited polymer films. In the case of metals and molecular compounds deposited via PVD, any deposited species would eventually crystallize by forming isolated nuclei or incorporating into any nearby growing crystals.[143,144] In MAPLE of PEO, however, adsorbed molecules can stay adsorbed persistently even upon contact with crystal growth fronts.[112,117] Figure 8A presents the evolution of 2D PEO crystals during the total 6 hours of MAPLE at $T_{dep} = 25^\circ C$ atop Si. The deposition was divided into three distinct 2 hours depositions to capture optical images of the same region in the intervals. While the 2D crystals formed in the first MAPLE showed clear evidence of growth during the second MAPLE interval, no detectable growth of the crystals was observed during the third deposition. Figure 8B captures the AFM morphology of a PEO film formed after 6 hours of deposition and the corresponding height profile. Clearly, the growth front of 2D crystals was surrounded by an adsorbed layer with nanometer thickness (nanolayer) without a depletion zone. This suggests that the amorphous PEO in direct contact with the crystalline face is kinetically stable against crystallization.

The kinetic stability of the adsorbed PEO nanolayer against crystallization can depend highly on deposition temperature. In the above study, while adsorbed PEO formed at $T_{dep} = 25^\circ C$ was stable against crystallization, MAPLE at $T_{dep} = 50^\circ C$ rendered strong crystal growth from the nanolayer when the substrate temperature was cooled to $25^\circ C$ after the deposition.[117] The effect of $T_{dep}$ on the stability of nanolayer was investigated by post-deposition aging of the two MAPLE-PEO samples ($T_{dep} = 25, 50^\circ C$) at the same aging temperature.
MAPLE-PEO with $T_{dep} = 25$ °C

MAPLE-PEO with $T_{dep} = 50$ °C

FIGURE 9. A, AFM height images comparing the film morphology of MAPLE-PEO film made with $T_{dep} = 25$ °C right after deposition (left panel) and after 27 days of post-deposition aging at 25 °C under N2 environment (right panel). The yellow dashed lines indicate the position of crystal growth fronts in as-deposited sample, highlighting that there was no growth of the 2D crystals into the nanolayer region during the 27 days of aging. B, Optical microscopy images captured with 405 nm-laser showing 2D crystal growth during post-deposition aging at 25 °C in a MAPLE-PEO film made at $T_{dep} = 50$ °C. The film was quickly transferred onto a 25 °C temperature stage after MAPLE for aging and optical microscopy observation. The upper panel was captured right after crystallization in droplet N1 and the lower panel was captured after 1 hour of aging. C, AFM height image (upper panel) showing 2D crystals grown from a nanolayer during post-deposition aging. Left side of the film was scraped with a razor blade. The measured height of the 2D crystals was ~10 nm as depicted in the lower panel. D, AFM height profile of a residual nanolayer after 20 minutes of toluene washing in MAPLE-PEO film made at $T_{dep} = 25$ °C. E, Graph comparing nanolayer thickness in MAPLE-PEO film made at $T_{dep} = 25$ °C before and after toluene washing. F, AFM height profile of a residual nanolayer in MAPLE-PEO film after 20 min of toluene washing. Original film was made at $T_{dep} = 50$ °C. G, Graph comparing nanolayer thickness in MAPLE-PEO film made at $T_{dep} = 50$ °C before and after toluene washing. All images are adapted with permission from Ref. [117]. Copyright 2016, American Chemical Society.

($T_{deg} = 25$ °C) under N2 environment. In both samples the morphology of a ~5 nm thick nanolayer, formed by 3 hours of MAPLE deposition, was monitored during aging. Figure 9A compares the AFM images when $T_{dep} = 25$ °C captured before (left panel) and after 27 days of aging (right panel), which showed no evidence of the growth of 2D crystals into the nanolayer region. In contrast, when $T_{dep} = 50$ °C crystallization in the nanolayer during aging at 25 °C was observed; see Figure 9B. Figure 9C exhibits the AFM image of film when $T_{dep} = 50$ °C and after crystallization during aging. The ~10 nm height of the 2D crystals (see lower panel of Figure 9C) provides evidence that the crystallization occurred during aging at 25 °C. The stability of adsorbed PEO against crystallization was correlated to the degree of attractions between the PEO and the underlying substrate. The degree of adsorption was conjectured by measuring the residual nanolayer thickness of MAPLE-deposited PEO samples after washing in toluene. Washing the polymer film in a solvent can uncover loosely adsorbed chains, therefore a positive correlation is expected between the degree of adsorption and residual film thickness. Before solvent washing, both $T_{dep} = 25$ °C and $50$ °C samples had an ~5-nm thick uniform nanolayer as a result of MAPLE deposition for 3 hours. Figure 9D shows a representative AFM profile of a residual nanolayer deposited at $T_{dep} = 25$ °C after solvent washing. As compared in Figure 9E, there was no meaningful decrease in the thickness of the nanolayer after washing, which proved the strong adsorption of PEO to the substrate. In comparison, the AFM profile of a residual nanolayer deposited at $T_{dep} = 50$ °C shown in Figure 9F clearly exhibited a noticeable loss of PEO after washing. Figure 9G compares the average nanolayer thickness before and after solvent washing, which showed a noticeable decrease from ~5 to ~1 nm. While the origin of how deposition temperature affects the degree of adsorption is still unclear, the results here imply that the deposition temperature in PVD can critically affect the conformation (or energy state) of the deposited polymer chains. Another intriguing fact from the above results was that the crystallization of long-chain molecules in PVD can exhibit anomalies compared to other crystalline solids due to their ability to strongly interact with underlying substrates.

In this focused section, we have discussed two model polymers deposited by MAPLE and their differences in film morphology and the resulting thermal properties. We first showed that substrate temperature during MAPLE has a critical impact on crystal lamellar thickness and melting temperature. Deposition temperature-lamellar thickness-melting temperature relationships observed in MAPLE of PE agree well with our conventional understanding of polymer crystallization from solution or liquid phase. Due to the rapid cooling effect during the deposition of confined polymer droplets, tuning of lamellar thickness and melting temperature could be achieved over a wide temperature range. In addition, the extremely slow deposition rate of polymers allows for the manipulation of substrate temperature during
deposition, resulting in a non-uniform lamellar thickness of crystals in the same film. Next, we demonstrated that the deposition temperature could affect the stability of the adsorbed polymers formed at the substrate surface. In MAPLE deposition of PEO, the adsorption strongly affects the nucleation of deposited PEO droplets as well as the crystal growth kinetics. Interestingly, the stability of adsorbed layers against crystallization showed a dependence on deposition temperature. We anticipate structure-property relationships observed for these two model polymers can be generally applied to other semicrystalline polymer systems processed via PVD.

6 | FUTURE WORK

Future directions of using PVD to study polymer crystallization in thin film geometry are vast. The development of the technique itself should focus on addressing the limitation of material degradation, unfavorable surface features, and technical concerns in commercial scale-up. Overcoming these challenges will attract more research efforts aiming to understand the crystallization of polymer thin films in greater details, and to expand the use of PVD application wise. Furthermore, the fundamental studies of polymer film crystallization should exploit the film formation mechanism of PVD to design film structures such as multilayered films comprising chemically similar or dissimilar polymers, films made by co-polymers or polymer blends, and polymers atop various substrates. By creating different hard or soft interfaces, the effect of heterointerfaces or confinement on the crystallization kinetics, and the role of irreversible adsorption on the film properties can be further explored. This will inspire ways of engineering film morphologies and material properties to meet various application needs. Last but not least, more parameters can be investigated by utilizing the advantage of additive growth mechanism from PVD techniques such as MAPLE to monitor how they influence the film growth at different stages. For example, the film growth rate, molecular weight of polymers, and side branching.

7 | CONCLUSIONS

In this review, we have discussed the advances in the field of polymer thin film crystallization by PVD. As a top-down deposition method, PVD offers a new route aiming to unveil the processing-structure-property relationships and to control film morphology for various application needs. The key parameters such as substrate temperature and substrate type have been addressed by studies using classical PVD techniques such as thermal evaporation and PLD, as they can control the crystal form, extent of crystallinity, and polymer chain orientation. Furthermore, we have shown that a more recent PVD technique known as MAPLE can expand the research topics by overcoming the limitations caused by polymer degradation. In MAPLE, polymers are confined within separate droplets. The crystallization of these droplets atop a substrate has revealed a dependence of crystal lamellar thickness and melting temperature on the deposition temperature, thereby proving the tunability of film morphology by selection of MAPLE deposition protocols. By changing the substrate temperature, or effectively the crystallization temperature, we showed the tunability of melting temperature by 20.6°C for MAPLE-deposited PE. Additionally, we proposed different kinetic stability of MAPLE-deposited PEO films at various deposition temperatures due to the development of irreversibly adsorbed layers during the deposition. Despite the distinct film formation mechanism of each PVD technique described above, we believe ways to control film morphology and thermal properties by tunable parameters such as substrate temperature and substrate type are generally applicable to other top-down vapor deposition techniques when polymer degradation is prevented.

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