

Stochastic analysis on temperature-dependent roughening of amorphous organic films

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Abstract – We investigate the temperature- and flux-dependent roughening of amorphous organic thin films of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1-1'biphenyl-4,4''diamine (α -NPD) molecules grown by organic vapor phase deposition. We find that organic thin films become unstable at high temperatures and low deposition rates as well as at low temperatures and high deposition rates. Based on a detailed stochastic analysis of the morphology we suggest probable mechanism for the roughening phenomena. Indeed, this result allows us to identify the optimum deposition conditions for relevant technological applications.

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Introduction. – The tremendous potential of organic-based semiconductors in optoelectronic applications has attracted significant attention in recent years [1–4]. Most notably organic light-emitting diodes (OLEDs) based on small conjugated molecules and full-color displays are starting to enter the consumer market. To further improve such devices two areas of development have been identified. In order to enhance the lifetime and conversion efficiency new molecules are synthesized and employed in devices. On the other hand, it is also crucial to deposit organic films with the desired structure and morphology on large-area substrates.

In the last decades an in-depth understanding of the atomic mechanisms governing the growth of inorganic films has been reached [4–8]. Considerable progress has also been made unraveling the governing mechanism of growth for crystalline organic films [9–11]. For applications of organic films as active layers in OLEDs, however, amorphous films are desired. For such amorphous organic films there is still a lack of systematic studies on the growth mechanisms and the resulting morphology. While studies related to the optical and electronic properties of these materials are widespread [3,12–14], studies dedicated

to uncover growth mechanism and to explain observed morphologies of amorphous organic films are rather sparse.

In this work we report on the a systematic study of the temperature and flux-dependent morphology of amorphous organic thin films of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1-1'biphenyl-4,4''diamine (α -NPD) molecules grown by organic vapor phase deposition (OVPD) [15, 16]. The morphology is characterized by atomic force microscopy (AFM) and the height fluctuations are quantified by the root mean square roughness as well as deterministic and random noise coefficients [6,7]. We find that organic thin films become extremely rough both at high temperatures and low deposition rates as well as at low temperatures and high deposition rates.

Based on a tentative identification of the underlying mechanisms that lead to a roughening of the surface, we argue that this behavior may be specific to amorphous organic thin film growth. In addition, since α -NPD is extensively used as a hole injection and transport material in OLEDs, our study, beyond academic interest, also allows us to pin point the optimum deposition conditions for smooth and rapid α -NPD thin film growth, a finding of technological relevance.

In order to characterize the morphological evolution quantitatively and to determine the relevance of

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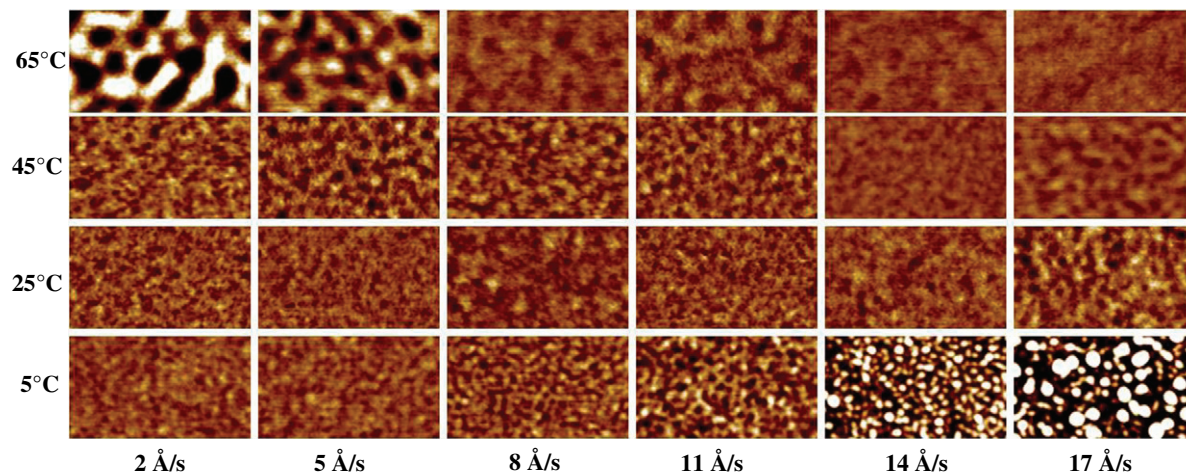


Fig. 1: (Colour on-line) AFM images of 500 Å, thick α -NPD films on Si-substrates deposited by OVPD with rates from 2 Å/s to 17 Å/s, and substrate temperatures from 5 °C to 65 °C. Image size: $1.25 \mu\text{m} \times 0.70 \mu\text{m}$, the colour height scale corresponds to 50 Å.

deterministic and random effects on growth, we rely on a stochastic framework established recently to characterize height fluctuations $h(r)$ by a Langevin equation [6,7,17]. Together with an analysis of the temperature-dependent initial stages of film growth we are able to link the surprising roughening of the film growth front for two distinct sets of growth parameters to specific mechanisms. We will argue that the deflection of the molecular trajectories towards the local surface normal through far-reaching van der Waals interactions between gas phase molecules and thin film molecules induces destabilization and surface roughening at low temperatures and high deposition fluxes. This deflection effect was previously investigated theoretically by Shevchik and Wormeester [18,19] and analyzed experimentally by Raible and van Dijken [20–22] for metals. Moreover, The effect of van der Waals interactions between the organic molecules in the gas phase on the growth of organic thin films has been studied, mainly for the case of crystalline organic films [9–11]. Here, we argue that it may be of special importance in amorphous organic thin film growth.

Experiments. – We have prepared α -NPD thin films at substrate temperatures of 5 °C, 25 °C, 45 °C and 65 °C with deposition rates between 2 Å/s and 17 Å/s. As substrate silicon covered with a thin layer (~ 2 nm) of native SiO_2 is used. The films were grown by OVPD[®] which has been developed for the uniform growth of films on large-area substrates [15,16]¹. In this deposition technique, a hot carrier gas transports organic source materials through a hotwalled reactor to a cooled substrate where the organic molecules are preferentially physisorbed. In OVPD, the film morphology and structure can be modified by the deposition rate, substrate temperature and chamber pressure. The pressure during

film deposition was fixed at 0.9 mbar in this study. The film thickness is around 50 nm for all samples and has been measured by spectroscopic ellipsometry and X-ray reflectometry (XRR). The amorphous state of the samples has been proved through X-ray diffraction (XRD) measurements. AFM has been employed to measure their surface morphology which is the interest of this paper.

Morphology investigation and statistical analysis. – Figure 1 shows representative AFM images for all samples at different substrate temperatures and deposition rates. Extraordinary roughness behavior is observed at the two opposite ends of the main diagonal of our morphology matrix. At the low temperature of 5 °C the roughness is large for the high deposition rates of 14 Å/s and 17 Å/s. At the high temperature of 65 °C the roughness is large for the low deposition rates of 2 Å/s and 4 Å/s. Explaining this surprising double set of roughening conditions is the challenge we are dealing with in this paper. At the two moderate substrate temperatures (25 °C and 45 °C) the roughness remains low. Specifically, at 45 °C not only the roughness is low but also it shows no tendency for an increase with deposition rate. This temperature may thus be considered as optimal for production of smooth films in industrial applications. These qualitative observations are backed up by our quantitative roughness analysis displayed in fig. 2. The roughness values given in fig. 2 are saturation values of vertical rms-roughness and do not depend on the lateral length scale. Also noticeable from the AFM topographs (fig. 1) is the considerably increased typical structure size (mound separation) for 65 °C, best visible for low deposition rate.

For additional characterization of the surface morphology, the stochastic approach based on the Langevin equation is employed. To this end, the height fluctuations, $h(r)$, are considered as a set of data which contain a degree of stochasticity. If the fluctuations are due to a Markov process (a process without memory) they can be

¹OVPD[®] technology has been exclusively licensed to AIXTRON from Universal Display Corporation (UDC), Ewing, NJ, USA, for equipment manufacture.

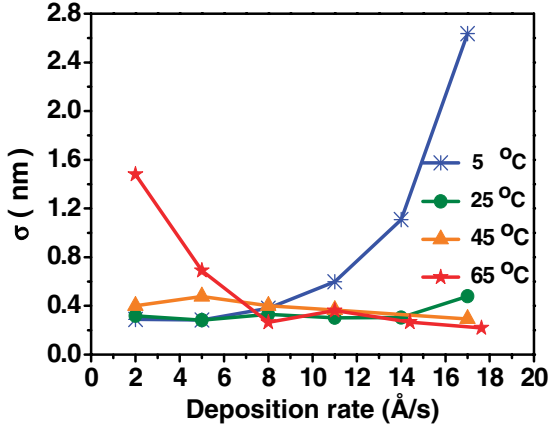


Fig. 2: (Colour on-line) Rms-roughness σ as a function of deposition rate at different substrate temperatures. Colours are differentiating between different temperatures.

successfully modeled by a Langevin equation of the form [6,7,17]:

$$\frac{d}{dr}h(r) = D^{(1)}(h, r) + \sqrt{D^{(2)}(h, r)} f(r). \quad (1)$$

Here, $f(r)$ is a Gaussian δ -correlated white-noise process. The coefficient $D^{(1)}$ describes the deterministic effects on the surface morphology which are, in this case, the diffusion and drift forces caused by the substrate temperature. Next, the coefficient $D^{(2)}$ determines the strength of the random noise fluctuations. These so-called Kramers-Moyal coefficients, $D^{(n)}$, can be directly calculated from the experimental data using the conditional moments of the height fluctuation:

$$D^{(k)}(h, r) = \frac{1}{k!} \lim_{\Delta r \rightarrow 0} \frac{1}{\Delta r} \langle [h(r+\Delta r)h(r)]^k \rangle |_{h(r)=h}. \quad (2)$$

The deterministic and random terms, $D^{(1)}$ and $D^{(2)}$ have been calculated from the AFM topographs of each sample. We have checked the Markov nature of height fluctuations and find a Markov length scale in the range of 30–90 nm for different samples. The Markov length scale is the minimum length interval above which the data can be considered as due to a Markov process. We find that the resulting deterministic and random terms are linear and quadratic functions of h , respectively (as shown in the insets of fig. 3) and are well-presented as approximations, $D^{(1)}(h) = -a^{(1)}h$, $D^{(2)}(h) = a^{(2)} - b^{(2)}h + c^{(2)}h^2$. Hence, in order to estimate the coefficients $a^{(1)}$, $a^{(2)}$, $b^{(2)}$, $c^{(2)}$, functions of $D^{(1)}$ and $D^{(2)}$ vs. h have been fitted with a linear and quadratic functions of h , respectively. The plot of the coefficient $a^{(1)}$ vs. substrate temperature (fig. 3(a)) shows a clear decrease with increasing temperature. Considering the differential form of eq. (1), it can be analytically shown that the coefficient $D^{(1)}$ (and consequently $a^{(1)}$) is proportional to the inverse of the lateral structure size which is quantified as the correlation length, λ . Our independent calculations for the correlation length, λ , from the height-height correlation function ($\langle h(0)h(r) \rangle$) shows that it decays as $\exp(-a^{(1)}r)$ which is consistent

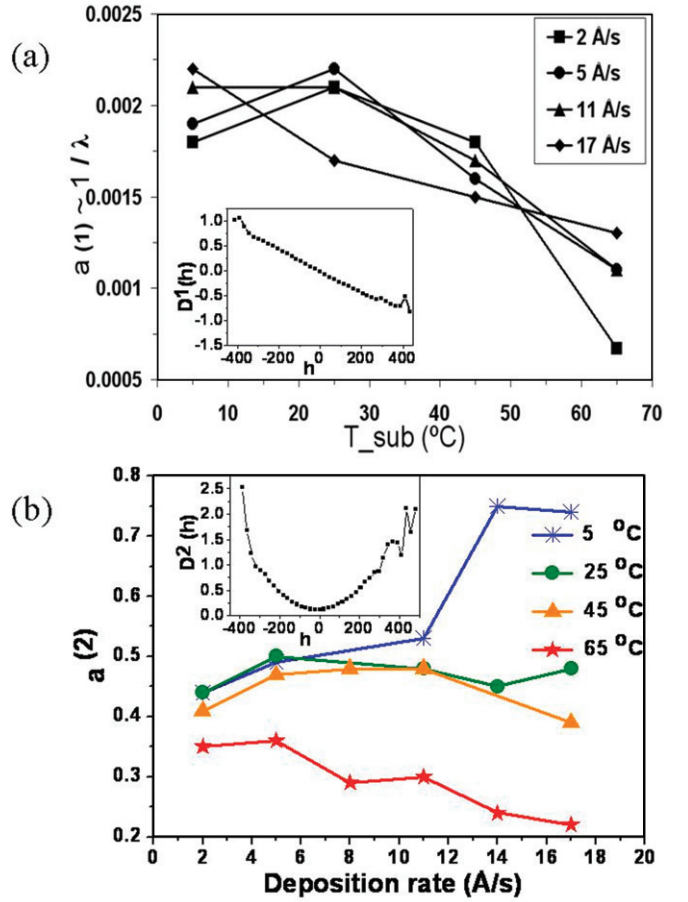


Fig. 3: (Colour on-line) (a) Deterministic coefficient ($a^{(1)}$) as a function of substrate temperature. (b) Random noise coefficient ($a^{(2)}$) as a function of deposition rate for different temperatures. The two insets show an example of the linear and quadratic functions of $D^{(1)}$, $D^{(2)}$ for the sample at 5 °C and a deposition rate of 10 Å/s. Colours are differentiating between different temperatures.

with the above results. We thus conclude that the lateral structure size has a slight tendency to increase with substrate temperature for all fluxes but for 17 Å/s this effect is rather strong. This fact can be also seen directly in the AFM matrix of fig. 1. The second term in the eq. (1) is the random noise term $D^{(2)}$ for which our calculations show the dominance of the constant term $a^{(2)}$, while $b^{(2)}$ and $c^{(2)}$ are of the order 10^{-6} and 10^{-3} , respectively. Figure 3(b) displays $a^{(2)}$ as a function of deposition rate at different substrate temperatures. This figure depicts a significant dependence for the trend of the noise coefficient, $a^{(2)}$, vs. rate with the substrate temperature. At 5 °C, increasing the deposition rate yields a strong increase of the random fluctuation coefficient, $a^{(2)}$. It is this increase of the random noise fluctuation coefficient, which causes the large increase of the roughness (fig. 2).

Roughening by initial dewetting. – We now first discuss the extreme rise of vertical roughness and lateral

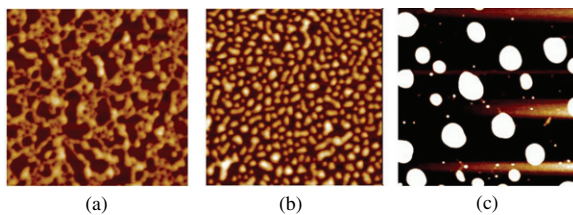


Fig. 4: (Colour on-line) AFM images of low thickness films (3–4 nm). (a) With the deposition rate of 4 Å/s at the lowest substrate temperature 5 °C, (b) with the deposition rate of 2 Å/s at the highest substrate temperature 65 °C. (c) Sample (b) after annealing at 100 °C for 600 s. The colour height scale is 20 nm for all three images. The image size is 2.5 $\mu\text{m} \times 2.5 \mu\text{m}$.

structure sizes of the growth front at high temperatures and low deposition rates. For this case, our stochastic analysis indicated that $a^{(1)}$, the deterministic coefficient, is small. Deterministic coefficient, $a^{(1)}$, is proportional to the inverse of surface diffusion and drift, hence one can conclude that surface diffusion for the case of high substrate temperature and low rate is high. This is also directly visualized through the large length scale of the structures. The assumption that surface diffusion is decisive for this destabilization is backed up by the fact that it dies out by decreasing the available diffusion time, *i.e.* by increasing the deposition rate. In order to understand more directly the effects of diffusion on the growth of α -NPD films, the morphology at the initial stage of growth has been investigated. For this purpose, two thinner samples (thicknesses around 3–4 nm) were prepared at both the highest and the lowest substrate temperature, *i.e.* 65 °C and 5 °C. The AFM images of these samples displayed in fig. 4 show that at the lowest substrate temperature of 5 °C (fig. 4(a)), molecules spread over the substrate and form a connected molecular network. However, for the molecules deposited at 65 °C (fig. 4(b)) molecules dewet from the substrate and agglomerate to islands. This observation is underlined by an annealing experiment where the sample of fig. 4(b) was heated to 100 °C for 600 s. The AFM topograph of the annealed sample is displayed in fig. 4(c). Upon annealing large, high and well-separated islands are formed. Taking into account the dewetting of the film to islands at 65 °C and the low deposition rate, we tentatively attribute the observed roughening and the increase of structure sizes to this effect. Dewetting causes a considerably larger initial roughness being amplified during subsequent growth. Due to surface diffusion the islands formed initially coarsen during film growth, giving rise to both larger roughness and larger lateral length scale as observed for the thicker films depicted in fig. 1. This mechanism is very similar to the non-wetting model for growth of metal on metal or the cases of epitaxial growth [8,23]. We note that the enhanced initial roughness may trigger also a second roughening mechanism described below, which may contribute to the final roughness observed in the thicker films.

Roughening due to steering. – We next turn to the analysis of destabilization and surface roughening at low temperature and high deposition rate. Our stochastic analysis shows the relative large value for the deterministic coefficient at low substrate temperature. Hence, surface diffusion is small and, contrary to the high-temperature cases, it cannot be a governing parameter for the destabilization, at low substrate temperature. This behavior is different from what is known for the common crystalline types of growth such as organic epitaxial or metal on metal growth models. On the other hand, our stochastic analysis shows the large magnitude of the random noise coefficient points to a time-independent process directly linked to the deposition process itself. This interpretation is consistent with the fact that roughening destabilization sets in only for large deposition rates, *i.e.* under conditions where surface diffusion effects become suppressed due to a reduction of the available diffusion time for each molecule. However, still a mechanism for the roughening destabilization is needed.

As pointed out by Shevchik and explicitly modeled by Raible *et al.*, for the case of amorphous semiconductors, the substrate has a significant influence on the particle trajectory in the gas phase [18–21]. In order to explain the experimentally observed phenomena of moundlike growth in amorphous thin films, Raible *et al.* have suggested a generalized nonlinear stochastic model. They have, indeed, considered the comparison with Kardar-Parisi-Zhang (KPZ) growth equation. In the Raible *et al.* model it is demonstrated that the governing term for the growth of surface mounds is proportional to the deposition rate times the typical length scale of inter-particle forces. This states that the attractive interactions as well as the deposition rate will give rise to the development of moundlike structures. Therefore, attractive interactions between particle and substrate cause not only an acceleration of the particles in front of the substrate, but also a deflection of the particle trajectory toward the local surface normal. If surface diffusion is suppressed through low temperature or short diffusion times (high deposition rate), destabilization takes place. Thus molecules are steered to surface protrusions which receive enhanced particle flux while surface depressions experience a reduced particle flux. This way the formation of mounds in amorphous semiconductors thin film has been explained.

As discussed above, attractive interaction between molecules is playing an important role in growth of hills and destabilization. For the case of amorphous organic growth, in this paper, we need to consider that organic molecules interact exclusively via van der Waals interaction [9–11]. For the growth of organic crystalline films, the influence of attractive van der Waals interaction between substrate and organic molecules has been studied for different cases. However, the effect of such interactions on the roughening destabilization of amorphous organic thin film still needs to be considered. Here, we suggest that the deflection of the molecular trajectory due to the

van der Waals interactions may be of special importance in amorphous organic growth. The strength of particle deflection depends i) on the range of the potential, ii) on the acceleration it experiences normal to the surface and iii) on its initial speed. A far-reaching potential, a large acceleration in this potential and a low initial speed will maximize the deflection effect. i) Taking into account that the attractive force on the molecules diminishes with z^{-4} , z being the normal distance to the surface, thus the particle trajectory starts to be influenced already at large distances from the surface. This far-reaching van der Waals potential can maximize the deflection effect. ii) Organic molecules with their extended π -electronic systems possess large polarizabilities, which are increasing strongly with the molecular mass. This increase is almost linear for the case of molecules built from identical groups. The acceleration within the potential is thus more likely to increase than to decrease with molecular mass. iii) Besides this attractive potential, the initial speed of the molecules in the gas phase is the other important parameter which influences the strength of the deflection. The initial speed of the molecule is given by the square root of its thermal energy divided by its mass. Large organic molecules have an average $E_{kin} = 3/2k_bT$, as do atoms. However, organic molecules have relatively low temperatures of evaporation and therefore small thermal energies. For the case of α -NPD growth through OVPD the molecules are transferred by the carrier gas with a temperature 289 °C being much lower than typical evaporation temperatures of 1000 °C used in inorganic growth. In addition, organic molecules usually possess a large mass. For the case of α -NPD it is $m = 588.7$ amu. Both the small thermal energy and the large mass thus favor a strong-deflection effect.

Finally we note that, even under the high pressure growth conditions of OVPD, the mean free path of molecules is of the order of 1 μ m. This value is still considerably larger than the length scale of the morphology instabilities which is of the order of 10 nm. Hence, although the concentration gradient in the OVPD chamber is higher than for vacuum deposition, it can not be considered as the source for the observed instabilities and the dependence of morphology on rate and substrate temperature. However, the approximate range of van der Waals inter-molecular interactions is of the order of 10 nm, and hence comparable to the length scale of the observed instabilities.

Conclusions. – In conclusion, we find a surprising roughening of the growth front in amorphous organic thin film growth at high temperature and low deposition rate through dewetting and island formation and at low temperature and high deposition rate through the deflection effect of the surface potential on the particle trajectory. This is assumed to be of special relevance in organic thin film growth and calculations to quantitatively determine its magnitude would be highly desirable. However, at the two moderate temperatures of 25 °C and 45 °C, there is a compromise between deposition rate

and diffusion process. For these samples, the substrate temperature is insufficient to form molecular agglomerates in the initial growth stage; yet, it is sufficient to smooth surface fluctuations.

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