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DEMONSTRATION OF EPITAXY IN VAPOR DEPOSITED BIPHENYL ON Al_2O_3

Zackery E. Moreau*, Katie L. Nili* and A.M. Nishimura†

Department of Chemistry, Westmont College, Santa Barbara, CA 93108

Abstract

A thin underlayer of biphenyl in a particular conformer was prepared by vapor deposition onto a single crystal of cryogenically cooled Al_2O_3. Then a thick epilayer was deposited. From previous studies the spectroscopic signatures for the various conformers of biphenyl in the solid are known and can be used to identify the species that is responsible for the epilayer fluorescence. The conformer of the overlayer was observed to be controlled by the conformer of the substrate and thereby demonstrating epitaxy in biphenyl.

†corresponding author: nishimu@westmont.edu

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Introduction

Epitaxial growth of crystals on solid substrates is one of many commerical application of chemical and physical vapor deposition (1). The understanding of factors that influence the morphology of thin films of organic compounds during vapor deposition would be helpful in obtaining the desired crystal form of the epilayer (2-4). These organic molecules that are used in such applications as in semiconductors such as pentacene and graphene are typically on the larger size, the former being one of the smallest (5). In fact studies of epitaxy in smaller organic molecules such as those having one or two benzene rings have been limited in the literature, presumably because their higher vapor pressures make them commercially less useful. Although biphenyl itself would not be a candidate for commerical applications, its derivatives are being used for organic wires and organic semiconductors such as diodes and transistors (5). The catalyst of this study was that understanding how crystallization occurred from vapor deposition of small molecules such as biphenyl might be extrapolated to larger molecules.

Biphenyl was chosen for this study because of its unique geometry in that the dihedral angle between the two planar phenyl groups can vary (6-8). In the gas phase, the dihedral angle is 45° due to the competition between the steric hindrance of the ortho-hydrogens and the π-electrons that can delocalize if the phenyl groups were co-planar (8,9). For the solid at room temperature, the two rings are in a double minimum potential and statistically centered at 45° (7). When solid biphenyl is cooled to ~ 45 K, it is known to undergo a phase transition from planar to twisted conformation (10).

In previous studies that were done on vapor deposited biphenyl, the conformers that biphenyl assumed were found to be identifiable by matching their spectroscopic signatures with biphenyl derivatives whose structures were known (11-13). In this way λ_{max} at 320, 345 and 370 nm were assigned to the twisted, planar and excimers, respectively (11-13). For example, when biphenyl was vapor deposited onto the Al_2O_3 substrate at 110-125 K, the fluorescence from this amorphous adlayer had a λ_{max} of 320 nm where the twisted form dominated (11-14). Subsequent to the disorder-to-order transition that occurred during the temperature programmed desorption (TPD) experiment, the fluorescence red-shifted and the λ_{max} was at 345 nm with the biphenyl in the planar conformation (11-14). More recently, the excimer of biphenyl with a λ_{max} of 370 nm was formed by controlling the deposition temperature. (11,12). Reported here is an application of the spectral signatures to study the effect that substrate molecules have in the homoepitaxial growth of epilayers of biphenyl.

Experimental

Biphenyl of the highest purity (> 99%) was purchased from a commercial source (Sigma-Aldrich, St. Louis, MO). It was placed in a sample holder attached to one end of a precision leak valve for vapor deposition. Details of the experimental set up have been previously published (10-13) and only a brief summary is given here. The ultra-high vacuum chamber had a background hydrogen base pressure of 1 x 10^{-9} Torr. A single crystal of Al_2O_3 (0001) (Crystal Systems, Inc., Salem, MA) was suspended on the lower end of a liquid nitrogen cryostat via copper post on either side of the Al_2O_3 with a sapphire spacer for electrical and thermal isolation. Resistive heating of the Al_2O_3 was done by sending current through a thin tantalum foil that was in thermal contact with the substrate. A type-K (chromel/alumel) thermocouple (Omega, Norwalk, CT) that was also in thermal contact with the Al_2O_3 monitored the temperature. Process control during the TPD experiment was accomplished by a program written in LabVIEW (National Instruments, Austin, TX) that incorporated a PID (proportional-integral-derivative) feedback algorithm that linearly incremented the temperature of the Al_2O_3 crystal.

During the TPD the program also took the fluorescence spectra every 300 ms in real time from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) that was sensitive in the ultra-violet. Manipulation of the array of spectra as a function of temperature by a MATLAB (Mathworks, Natick, MA) template yielded the WRTPD (wavelength resolved TPD) that are shown in the figures. To ensure a clean surface, the Al_2O_3 was heated to 300 K after each run. Temperature ramps to higher temperatures did not indicate any other adsorbates.

The activation energy for desorption, E_a, was calculated by Redhead analysis (15) in which a first-order desorption kinetics as described by King (17) was assumed and is based on the mass spectral peak desorption temperature, T_p (16). The uncertainties in the desorption temperatures lead to a propagated error in the activation energies of ± 2%.

Finally, the LabVIEW program received data from a residual gas analyzer so that both the deposition and the desorption of biphenyl could be monitored. The surface coverages, Θ, in monolayers (ML) were calculated by calibrating the integrated mass spectral peaks to an optical interference experiment. The interference experiment yielded accurate rate of deposition with coverage error of ± 30%, and is described in detail elsewhere (13).

Results and Discussion

The peak desorption temperature, T_p, of neat biphenyl at low coverages (~ 20 ML) was 222 K. First-order desorption was assumed and the activation energy for desorption, E_a, was calculated to be 57.6 kJ/mol (15-17). Upon deposition, excitation of neat biphenyl on the Al_2O_3 surface with a high-pressure Hg lamp caused the amorphous biphenyl to fluoresce with a λ_{max} of 320 nm. As can be seen from Figure 1, when the surface temperature was linearly ramped in a TPD experiment, the adlayer underwent a disorder-to-order transition at 157 K (solid arrow in inset to Figure 1), where λ_{max} red-shifted to 345 nm and the overall intensity decreased. Since energy hopping is nonradiative, the reduction in intensity arose partly from the ordered planar biphenyl that became energy carriers for the trap sites from which fluorescence occurred (14).

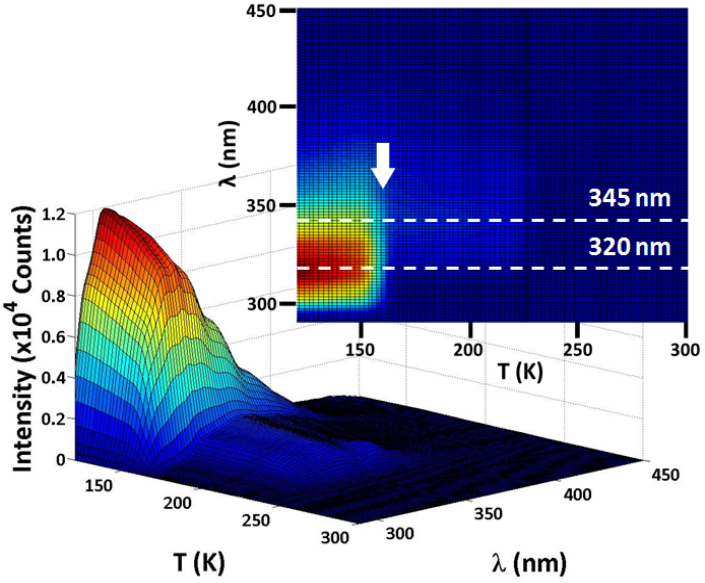

Figure 1: Wavelength-resolved TPD of biphenyl with a λ_{max} at 320 nm. The disorder-to-order transition occurred at about 157 K (solid arrow) and λ_{max} shifted to 345 nm. $\Theta_{biphenyl}$ ~ 94 ML. Inset: Top view. Dotted lines show the monomer emission of planar biphenyl at λ_{max} of 345 nm and the twisted conformer at λ_{max} at 320 nm.

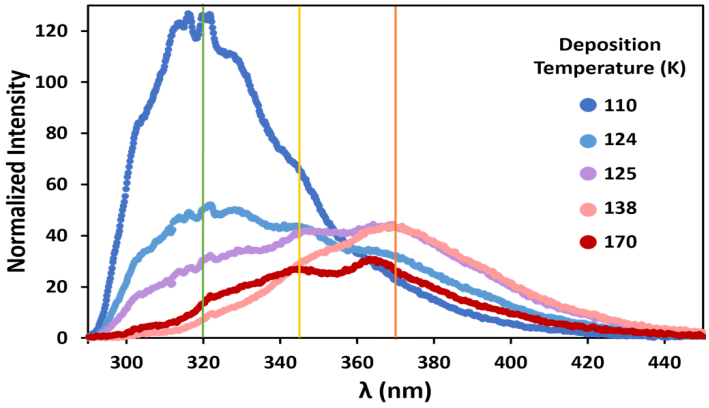

Figure 2. Fluorescence spectra of biphenyl at 110 K after deposition at different temperatures (Legend on right). For comparison, the fluorescence intensities were normalized to the biphenyl coverage. Vertical linesshow the λ_{max}'s for the various conformers are: green = 320 nm (twisted), orange = 345 nm (planar), red = 370 nm (excimer, planar).

To prepare the substrate in the desired conformer, deposition was done at precise surface temperatures. Figure 2 shows the fluorescence spectra of biphenyl as a function of deposition temperature. The fluorescence spectrum at 110 K for the WRTPD shown in Figure 1 is plotted in dark blue and the spectrum is that of the twisted conformer with a λ_{max} of 320 nm. As the deposition temperature is raised to 124 K, the spectrum shown in light blue changed to reveal the planar conformer at a λ_{max} of 345 nm and the appearance of excimer at λ_{max} of 370 nm. (The vertical lines were drawn to emphasize the temperatures at which the various conformers of biphenyl are observed: green = 320 nm for the twisted conformer, orange = 345 for the planar conformer and orange = 370 nm for the excimer). When biphenyl was deposited at 125 K (plotted in purple), the excimer began to form in larger quantity. At 138 K (in pink) the fluorescence originated from the excimer fluorescence. When the deposition temperature was raised to 170 K (in red), only the planar conformer of biphenyl gave rise to an observable fluorescence.

To demonstrate homo-epitaxy, the biphenyl excimer and various conformers of biphenyl were formed as underlayer substrate with thicknesses of ~ 10-30 ML by controlling the deposition temperature as determined from Figure 2. The surface was then allowed to cool to about 110-120 K. Then the epilayer of biphenyl was vapor deposited either at 110-120 K or at 138 K. If deposited at the former temperature, the twisted conformer would be expected and if the latter, excimer would normally be expected to form from what was observed for neat adlayers. As evidenced by the WRTPD, the conformer of the epilayer molecules was identical to

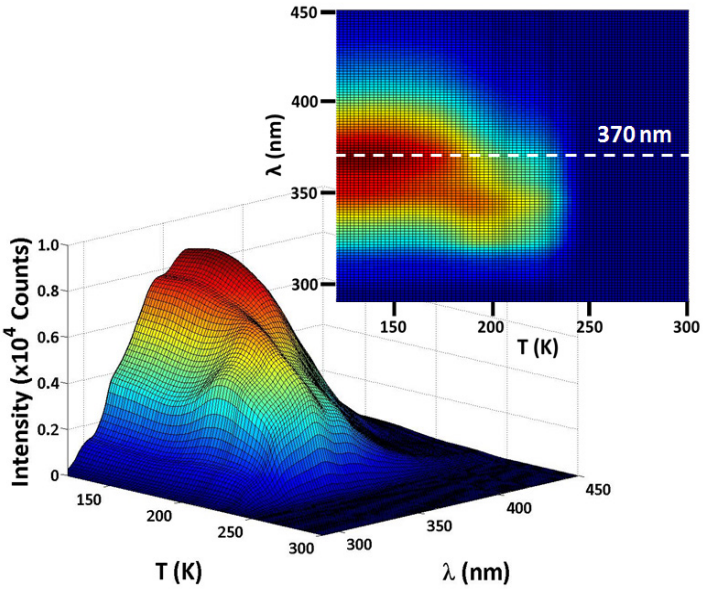

Figure 3. Wavelength-resolved TPD of epitaxially formed biphenyl with the substrate $\Theta_{biphenyl}$ ~ 10 ML that was deposited at 138 K to form the excimer with λ_{max} of 370 nm. The overlayer $\Theta_{biphenyl}$ ~ 455 ML was deposited at 119 K that would normally have a twisted conformer with λ_{max} of 320 nm, but instead expitaxially grew as excimer. Inset: top view that show the biphenyl excimer at 370 nm that blue shifts to the planar ordered biphenyl at 345 nm.

that of the base layer. Representative WRTPD of these are shown in Figure 3 and 4. In Figure 3 the underlayer of ~ 10 ML of biphenyl was deposited at 138 K to form the excimer. Then an overlayer of ~ 455 ML of biphenyl was deposited at 119 K where the twisted conformer would have been expected. Instead, the epilayer exhibited excimer fluorescence in the planar amorphous conformer.

In order to asertain the thermal stability of the planar conformer that formed when the adlayer was deposited at 170 , biphenyl was deposited at this temperature. When cooled to 110 K, the WRTPD showed fluorescence solely from the ordered planar conformer. So that if epitaxy occurred on a similarly prepared substrate the epilayer would be expected to be in the planar conformation. In Figure 4, the WRTPD of epitaxially formed biphenyl with the substrate of $\Theta_{biphenyl}$ ~ 20 ML that had been deposited at 170 K. The eiplayer was deposited at 116 K with $\Theta_{biphenyl}$ ~ 590 ML where the overlayer would be expected to be in a twisted conformer with λ_{max} of 320 nm. Instead the epilayer expitaxially grew with a planar conformer that resulted in *both* planar species, ordered planar biphenyl at λ_{max} of 345 nm *and* planar excimer with λ_{max} of 370 nm. The presence of the latter was because excimers in general form with planar conformations (18).

In summary, the following observations were made:
1, When the underlayer substrate was deposited at 138 K, the temperature that favored the formation of biphenyl excimer, then cooled to 110-120 K and the epilayer deposited at 110-120 K, the epilayer was that of the biphenyl excimer and not of the twisted conformer that was observed for neat biphenyl deposited at that lower temperature.
2. Planar biphenyl result in two ways: a) When the underlayer of biphenyl was annealed at 170 K which is past the disorder-to-order transition temperature and cooled to 110-120 K *or* b) if the deposition temperature of the underlayer was 170 K and cooled to 110-120 K and if the epilayer was then deposited at 138 K and cooled to 110-120 K. It should be noted that when a biphenyl adlayer that has been prepared by deposition at 110-120 K, annealed at 170 K, and allowed to cool to the original 110-120 K, the WRTPD indicated fluorescence solely from planar biphenyl. In other words, once the adlayer underwent the disorder-to-order transition, the stable adlayer was the ordered planar biphenyl. The conclusion is, that in biphenyl, the base layer determined the conformer of the epilayer.

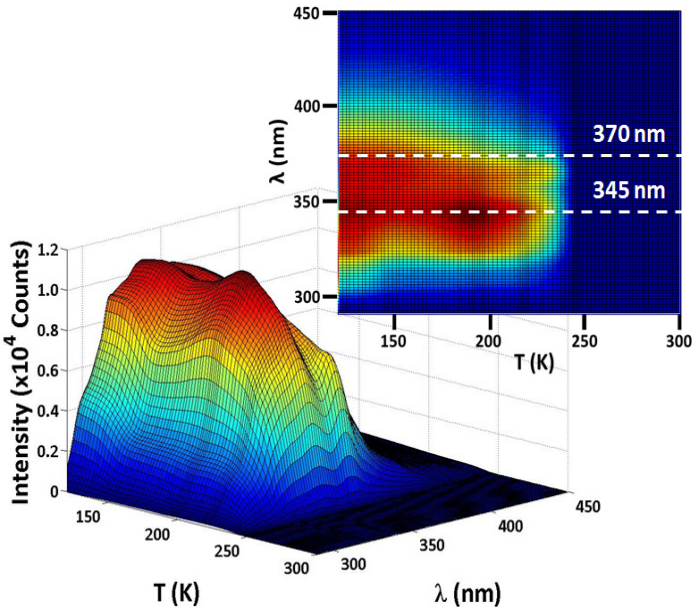

Figure 4. Wavelength-resolved TPD of epitaxially formed biphenyl with the substrate of $\Theta_{biphenyl}$ ~ 20 ML that had been deposited at 170 K and then cooled to 116 K, at which temperature the overlayer of biphenyl was deposited until $\Theta_{biphenyl}$ ~ 592 ML was achieved. The overlayer would normally have a twisted conformer with λ_{max} of 320 nm, but instead expitaxially grew with a planar conformer that resulted in both ordered with λ_{max} of 345 nm and excimer with λ_{max} of 370 nm. Inset: top view.

Although epitaxy is generally the norm in vapor deposition, a demonstration that epitaxy does occur for a small molecule such as biphenyl is noteworthy. Being able to spectroscopically identify all three forms of biphenyl made this molecule an ideal choice in the study of epitaxy by vapor deposition.

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References

(1). G. Witte and C. Woell. *Journal of Materials Research*, **2004**, 19, 1889-1916.
(2). C. Li, Y. Zhang, Q. Ji, J. Shi, Z. Chen, X. Zhou, Q. Fang, Y. Zhang. *2D Materials*, **2016**, 3, 35001-35008.
(3). P. Friederich, V. Rodin, F.von Wrochem and W.Wenzel. *ACS Applied Materials & Interfaces*, **2018**, 10, 1881-1887.
(4). B. Xu, B.Varughese, D. Evans and J. Reutt-Robey. *J. Phys. Chem. B*, **2006**, 110, 1271-1276.
(5). C. Joachim, J.K. Gimzewski and A. Aviram, *Nature*, **2000**, 408, 541-548.
(6). A. Almenningen, O. Bastiansen, L. Fernholt, B.N. Cyvin, S.J. Cyvin and S. Samdal. *J. Mol. Struct.*, **1985**, 128, 59-76.
(7). G.P. Charbonneau and Y. Delugeard. *Acta Crystallographica B*, **1976**, 32, 1420-1423.
(8). F. Grein. *J. Phys. Chem. A*, **2002**, 106, 3823-3827.
(9). A. Almenningen, O. Bastiansen, L. Fernholt, B.N. Cyvin, S.J. Cyvin, S.J. Sandal, *J. Mol. Struct*., **1985**, 128, 59-76.
(10). H. Cailleau, A. Girard, F. Moussa, CM.E. Zeyen, *Solid State Comm*., *1979*, 29, 259-261.
(11). M.K. Condie, C. Kim, Z.E. Moreau, B. Dionisio, K. Nili, J. Francis, C. Tran, S. Nakaoka and A.M. Nishimura, *JUCR*, **2020**, 19, 14-17.
(12). M.K. Condie, Z.E. Moreau and A.M. Nishimura *JUCR*, **2019**, 18, 15-18.
(13). M.K. Condie, B.D. Fonda, Z.E. Moreau and A.M. Nishimura, *Thin Solid Films*, **2020**, 697, 137823-137828.
(14). B.D. Fonda, Z.I. Shih, J.J. Wong, L.G. Foltz, K.A. Martin and A.M. Nishimura, *JUCR*, **2018**, 17, 32-35.
(15). P.A. Redhead. *Vacuum*, **1962**, 12, 203-211.
(16). F.M. Lord and J.S. Kittelberger. *Surf. Sci.*, **1974**, 43, 173-182.
(17). D.A. King. *Surf. Sci*., **1975**, 47, 384-402.
(18). J.B. Birks. Photophysics of Aromatic Molecules, John Wiley & Sons Ltd., New York, NY (1970), pp. 301-370.