Vapor phase deposition of oligo(phenylene ethynylene) molecules for use in molecular electronic devices

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The field of molecular electronics is often limited by nonreproducible electrical device characteristics and low yields of working devices. These limits may result from inconsistencies in the quality and structure of the monolayers of molecules in the devices. In response, the authors have developed an ultrahigh vacuum vapor phase deposition method that reproducibly assembles monolayers of oligo(phenylene ethynylene) molecules (the chemical backbone of many of the molecules used in molecular electronics). To improve the structure and purity of the monolayer, the vapor phase assembly is performed in an ultrahigh vacuum environment using a low temperature organic thermal cell. Because vapor phase assembly does not require the use of solvents, a potential source of contamination is eliminated. The absence of solvents also permits the fabrication of complex device architectures that require photoresist patterning prior to the molecular assembly. Characterization via ellipsometry, x-ray photoelectron spectroscopy, and scanning tunneling microscopy shows that the monolayers are dense, chemisorbed, ordered, and chemically pure.
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I. INTRODUCTION

In the past decade, many groups have made headway fabricating molecular electronic test devices.[1–18] These devices exhibit a range of interesting electrical behaviors, including electrical switching with memory[2,8,19–21] and negative differential resistance[2–4] that have potential for use in logic and memory devices. With few exceptions,[22,23] the field of molecular electronics is plagued by problems including a lack of device consistency between groups and low device yields. Although problems may be partly attributed to differences in molecular test structures, an additional factor may be nonreproducible quality and/or structure in the devices' molecular monolayers.

Some of the differences in monolayer quality and structure likely result from the fact that most research groups currently use "solution phase" assembly. For solution phase assembly of molecules with thiol end groups on a gold-coated substrate, the substrate is placed into a solution of the molecules dissolved in an organic solvent. The substrate is left in the solution for 24–48 h, allowing the molecules to self-assemble on the substrate surface. Then, the substrate is removed and rinsed with another organic solvent [such as tetrahydrofuran (THF)] to remove any molecules that had physisorbed on the monolayer. This method of assembly introduces the possibility of the monolayer becoming contaminated by organic solvents. Because the active area of the monolayer in a typical molecular device is composed of only 1000–10 000 molecules, any monolayer contamination can compromise device functionality and consistency.

Solution phase assembly is also limited by the use of organic solvents and their incompatibility with the photolithography techniques required for more complex device architectures. One of the photolithography techniques that will probably be required for complex device architectures is gold on photoresist lift-off. This is because gold is a widely used molecular device contact material, and lift-off is one of the simplest and most effective patterning methods for gold. However, because gold lift-off requires a prepatterning of the photoresist prior to molecular assembly, the photoresist is exposed to the solvents used in solution phase assembly. These solvents can dissolve the organic resists and rinse them away. Additionally, the dissolved photoresist can contaminate the assembled monolayer.

Other groups perform "gas-phase" assembly where the substrate is placed in a closed container of air or nitrogen and the molecules are heated in the same container to produce a gas, which assembles on the substrate.[24–26] Although this method can eliminate the use of solvents, it is difficult to control the purity and consistency of the gas. This method has similar contamination and consistency issues as observed with solution phase deposition and has shown the tendency to produce multilayers, rather than a monolayer.[24]

In this article we present a reproducible method of molecular monolayer deposition that was performed in an ultra-

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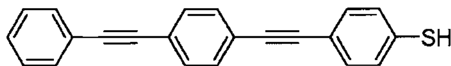

FIG. 1. Oligo(phenylene ethynylene) used in these UHV self-assembly experiments.

high vacuum (UHV) solvent-free environment using a special low temperature thermal cell. The compound used in the assembly was a simple oligo(phenylene ethynylene) (OPE) with a thiol end group (see Fig. 1). This was chosen because OPEs are the chemical backbone of most of the molecules that have exhibited functional electrical behaviors, such as switching, in test devices.[1–21] The UHV environment was a modified molecular beam epitaxy (MBE) chamber, underscoring the compatibility with traditional fabrication protocols. Extra precautions were taken to ensure that the molecules remained intact during vaporization, including the use of a specialized low temperature thermal cell with excellent temperature control. To further reduce contamination, the molecular charge was purified utilizing a distillation-based method facilitated by the UHV environment. Postassembly ellipsometry, x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM) confirmed the vapor-assembled monolayer's quality and structure.

II. EXPERIMENT

The substrates used for the vapor phase assembly of OPEs were 50 mm silicon wafers (001) coated with a 5 nm thick titanium adhesion layer and a 200 nm thick gold layer. The metals were evaporated using a separate e-beam evaporator. These gold-coated substrates were cleaned with a piranha etch (concentrated sulfuric acid and hydrogen peroxide in a volume ratio of 3:1) prior to being loaded into the UHV chamber. The substrates that were destined for STM analysis were flame annealed using a hydrogen-oxygen flame prior to molecular assembly.

The OPE was synthesized using standard protocols.[27] For solution phase assembly of OPEs, it is common to use molecules with the sulfur end groups that are "protected" with an acetyl group to reduce the chance of thiol oxidation and degradation prior to use. However, since the solutions used in the deprotection step could be a source of contamination and since the solid material is far more stable (less prone to oxidative coupling) than the molecules in solution, we used unprotected molecules (i.e., free thiols with no acetyl group, Fig. 1). Nonetheless, we took precautions to limit the molecules' exposure to light and air. The molecules were stored in a freezer in a nitrogen environment and were exposed to air and light only for a few minutes as required to load them into the thermal cell, after which they were placed in a dark UHV environment. Approximately 10–20 mg of OPE molecules were loaded into the quartz crucible in the thermal cell at a time.

The vapor phase assembly of the OPE molecules was performed in a modified molecular beam epitaxy chamber with a base pressure of less than 9×10^{-9} Torr. The chamber was pumped by a turbomolecular pump, which included nitrogen-purged bearings to prevent molecular clogging. Because high temperatures could have caused molecular decomposition, traditional UHV gauges (such as Bayert-Alpert gauges) were eliminated in favor of a cold cathode gauge. Finally, to keep molecules from condensing in this gauge and interfering with its readings, it was heated to 80 °C using a band heater.

We utilized a low temperature thermal cell for the molecular assembly that was purchased from MBE-Komponenten[28] to improve temperature control. This enhanced temperature control was essential because thermal gravitational analysis and differential scanning calorimetry indicated that, for certain OPE-based molecules, there was as little as a 10 °C difference between vaporization and decomposition temperatures. Traditional thermal cells are not designed to operate at low temperatures. When such cells are operated at low temperatures (below 300 °C), the radical fall in radiative heat dissipation (due to the Stefan-Boltzmann law, which predicts a T^4 dependence) makes them very prone to temperature overshoot. With such overshoot, molecular decomposition temperatures can easily be exceeded. The low temperature cell that we use makes use of liquid metal heat transfer, along with balanced heating and cooling elements. This cell could operate at our typical temperatures (approximately 100–130 °C) with less than 0.4 °C of overshoot.

In situ molecular source purification was achieved by first increasing the temperature of the thermal cell to 1–2 °C above the desired temperature for the molecular vaporization (as determined by trial and error using various temperatures). Typically during this source purification, the deposition chamber pressure would increase from base pressure to approximately 6×10^{-7} Torr. Over time, this pressure would then fall back to the base pressure, indicating that volatile contaminants had been eliminated from the source. This pressure burst was attributed to dissipation of contaminants because subsequent vaporization of OPEs produced no increase in chamber pressure. Unlike the contaminants, OPE molecules apparently condense on the first surfaces with which they come into contact, never reaching our remotely sited pressure gauge. Thus after more than 20 molecular vaporization experiments, not only were chamber base pressures maintained but there was no degradation in molecular device results. For these reasons, we chose to not regularly bake the UHV chamber after venting. We instead employed a very quick molecular recharging routine that involved venting the chamber to atmospheric pressure using point-of-use purified nitrogen, and a pump down back to vacuum within 10 min.

The molecular films were assembled by varying the flux of molecules to the substrate by changing either the exposure time or the source temperature (and hence flux rate). For each experimental run, the temperature of the thermal cell was ramped up to 80 °C, and the substrate was loaded into the deposition chamber with the gold side facing the source. The molecular source was then elevated (using a bellows system on the thermal cell) to a distance of approximately 8 cm from the center of the sample, the source shutter was

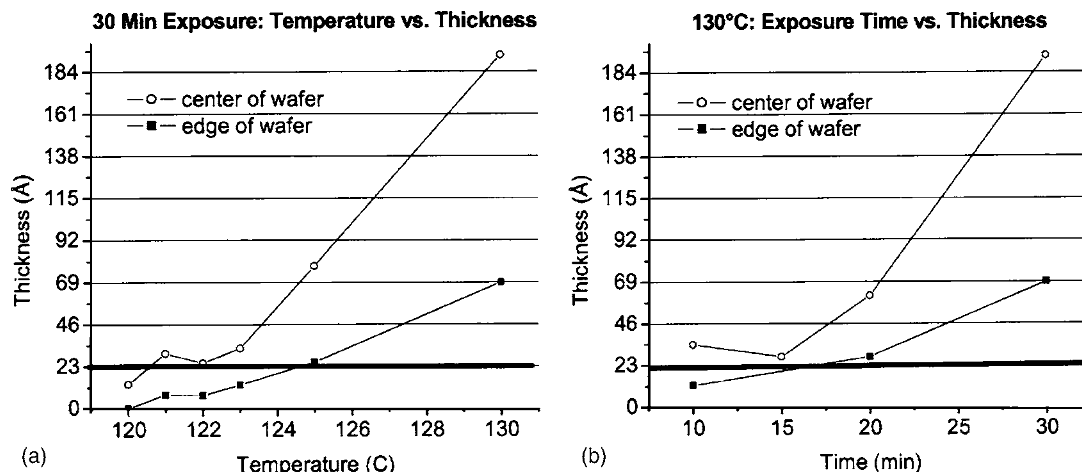

FIG. 2. (a) Ellipsometry-determined molecular layer thicknesses vs temperature for samples exposed for 30 min. (b) Thicknesses vs time for samples exposed at a constant temperature of 130 °C. The line at 23 Å is the approximate expected molecular thickness for the thiolate chemisorbed on Au.

opened, and the source temperature was increased to the final vaporization temperature. The conditions required for a chemisorbed monolayer were determined by varying the source temperature and assembly time and then characterizing the film.

The film thickness was measured using a single wavelength (632.8 nm laser) Gaertner Stokes ellipsometer. The n and k values were taken from control substrates without exposure to molecules. The thickness was modeled as a single absorbing layer ($n=1.55$, $k=0$) on top of an infinitely thick substrate (fixed n_s). All of the values were averaged over three measurements with a deviation of approximately ±2 Å per 1×1 cm^2 sample. Measurements were performed on the center of the 50 mm wafers, as well as on the edge of the wafer farthest from the source. The center samples were approximately 8 cm from the source, whereas the edge pieces were approximately 9.5 cm from the source.

XPS was performed using a Quantera x-ray photoelectron spectroscopy (XPS) scanning microprobe. The takeoff angle was 45°, and a 114.8 W monochromatic Al x-ray source was applied for all of the measurements. All XPS peaks were referenced to the Au $4f$ major peak at 84.0 eV.

To verify that the monolayer was regular and ordered, scanning tunneling microscopy (STM) was performed using a Molecular Imaging PicoPlus scanning probe microscope. All samples that were used for STM consisted of 200 nm of gold evaporated on 5 nm of Ti (for adhesion) on a 500 nm thick silicon dioxide layer on silicon. After the gold was evaporated and prior to the molecular assembly, these substrates were flame annealed to enlarge grain sizes for improved imaging. The oxide layer between the silicon substrate and the Ti/Au layer acted as a physical barrier and prevented migration of silicon during flame annealing.

III. RESULTS AND DISCUSSION

The assembled films were first evaluated by ellipsometry to verify molecular coverage. This characterization showed that a variety of conditions produced a film with a thickness of approximately 23 Å (the thickness expected for 1 ML of OPE on Au).[29] Figure 2 shows the film thickness for various source temperatures with a constant exposure time (a), as well as for a constant source temperature with various exposure times (b). As one can see in Fig. 2(a), 1 ML thick films were produced at the center of the wafer when it was exposed to OPE molecules heated to temperatures between about 121 and 123 °C for 30 min. Monolayer thick films were observed at the edge of the wafer when it was exposed to molecules that were heated at 125 °C for 30 min. For a constant evaporation source temperature, Fig. 2(b) shows that single monolayer films were produced in the center of the wafer using a 15 min exposure to a 130 °C source.

In order to investigate the composition of the films that were thicker than a monolayer, we rinsed the thicker films with THF. THF should rinse away the physisorbed molecules while leaving chemisorbed monolayers intact. The results for

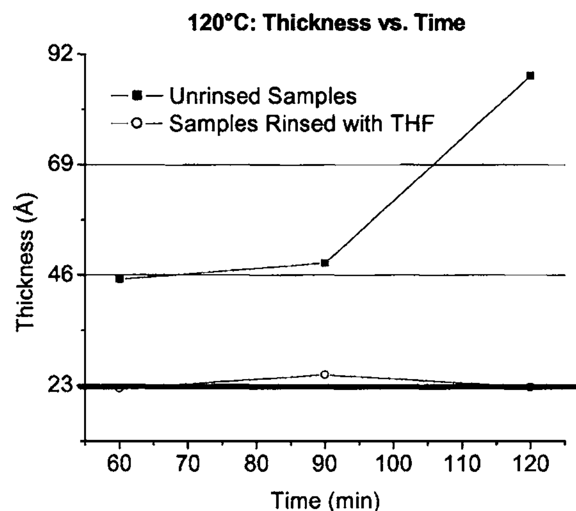

FIG. 3. OPE samples both unrinsed and rinsed with THF. The line at 23 Å is the approximate expected molecular thickness for the thiolate chemisorbed on Au.

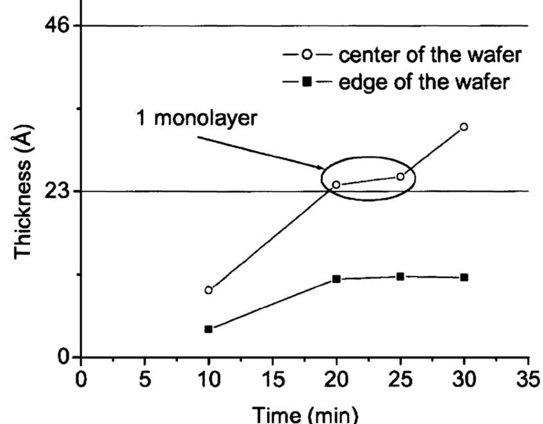

FIG. 4. Thickness vs exposure time for a constant source temperature of 120 °C. This figure shows that the expected thickness for a monolayer (approximately 23 Å) was achieved for exposures of 20–25 min. Note: This figure is for samples assembled using an OPE source that was reloaded with molecules after samples were assembled for Figs. 2 and 3. The line at 23 Å is the approximate expected molecular thickness for the thiolate chemisorbed on Au.

OPE films before and after rinsing are shown in Fig. 3. As one can see from the figure, while films had a variety of thicknesses prior to rinsing, all were approximately 23 Å thick after rinsing. (Thus, we confirmed that 23 Å was the approximate thickness of a chemisorbed monolayer and that after a chemisorbed monolayer of molecules was assembled, additional molecules physisorbed on top of this initial monolayer.) These physisorbed molecules could be rinsed away with THF, leaving a chemisorbed monolayer. Nevertheless, looking forward, it would be desirable to eliminate the need for postdeposition rinsing; this would both simplify processing and eliminate a possible source of contaminant reintroduction. Further, for vapor phase deposition, it would allow us to progress directly to the deposition of the top contact material.

Ultimately, we were able to establish a process window in which we could consistently and reproducibly assemble a monolayer of OPE molecules without rinsing the film. Figure 4 shows ellipsometry thickness data for exposures between 10 and 30 min to a 120 °C OPE evaporation source. Over a fairly wide window between 20 and 25 min, single monolayer films were reproducibly achieved. Although settings had to be slightly readjusted each time the cell was reloaded, from that point onward, parameters were quite stable. In fact, for a single molecular load, we were able to assemble more than 30 samples without any change in the conditions required to achieve a monolayer. These data not only offer a high-yield device processing window but also indicate a significant tendency toward true self-limiting monolayer growth for vapor deposited OPE molecules. The next challenge was to confirm that vapor phase assembled monolayers were uncontaminated, chemisorbed, and had ordered regular structures.

In order to confirm that the self-assembled monolayers were also chemisorbed and chemically pure, we next performed XPS. The XPS of films that were less than or equal to 23 Å thick (as determined by ellipsometry) showed that all of the sulfur end groups of the molecules were bound to gold, indicating that all of the molecules were chemisorbed to the gold surface [see Fig. 5(a)]. However, the XPS of the films thicker than 23 Å showed peaks for bound sulfur as well as unbound sulfur end groups [see Fig. 5(b)], indicating that the samples with a thickness greater than that expected for a single monolayer had both chemisorbed and physisorbed molecules. This supported our interpretation of THF rinsing experiments above that samples with an ellipsometry thickness of 23 Å were indeed a complete chemisorbed monolayer and the thicker samples consisted of a chemisorbed monolayer covered with physisorbed molecules.

XPS also showed that the OPE monolayers were uncontaminated and thus verified that vapor phase deposition was a clean assembly method. The XPS spectrum in Fig. 6 is the survey scan for a vapor phase assembled monolayer of OPEs

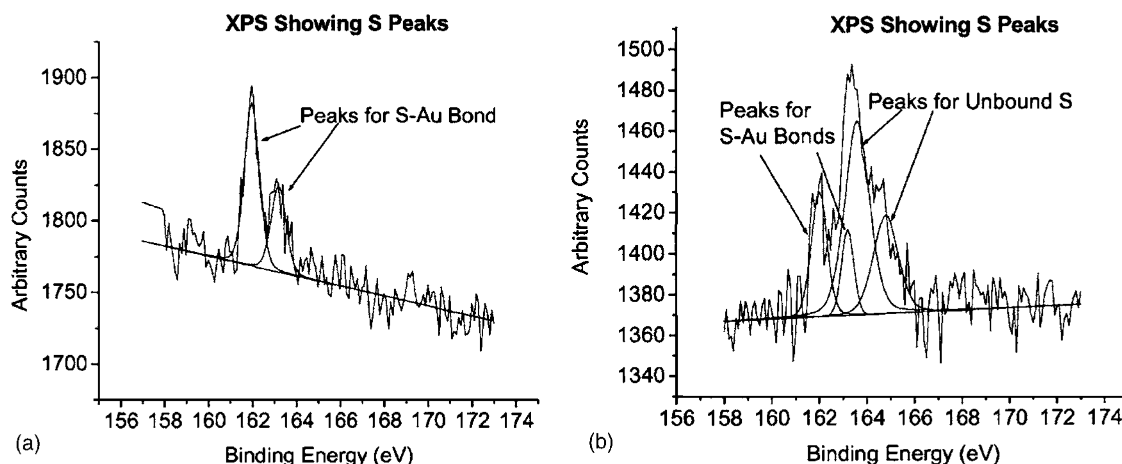

FIG. 5. (a) XPS of a 23 Å thick sample that showed bound sulfur peaks. (b) XPS of a sample thicker than 23 Å that showed both the bound and the unbound sulfur peaks.

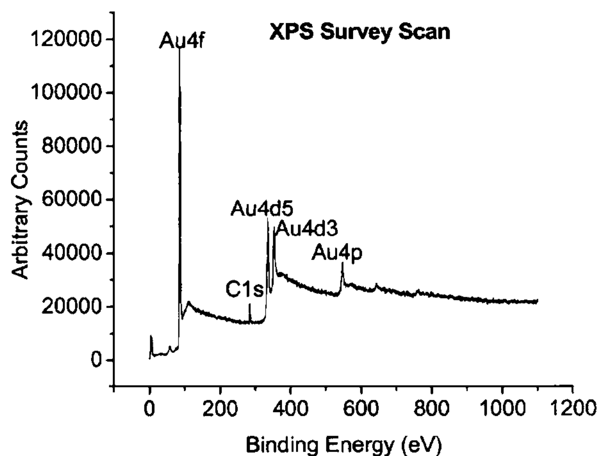

FIG. 6. XPS survey spectrum of a 23 Å thick sample showing only peaks due to the carbon in the OPEs, the Au substrate, and the sulfur end group.

that is 23 Å thick. The only detectable peaks in this spectrum are for gold and carbon. These peaks may be attributed to the substrate (Au) and the molecular backbone (C). There is no obvious sulfur peak in the spectrum because of the low sensitivity to sulfur; the sulfur peak can be obtained only after intensive multiplex scans [see Fig. 5(a)]. Close inspection of the entire spectrum showed no additional peaks, confirming the purity of the monolayer.

When we imaged the deposited films with STM, all samples 23 Å or thicker showed molecular order (as indicated by the "striping" in Fig. 7). Previous work shows that the observation of striping with a pitch of approximately 6–12 Å indicates that the monolayer has the desired root 3 superlattice and is well ordered.[30,31] Films slightly thinner than a monolayer (as determined via ellipsometry) also occasionally showed order when imaged with STM. This may have been because STM showed local order, whereas ellipsometry showed the average monolayer density of a much larger area. The observed pitch of the striping (see Fig. 7) was approximately 7 Å, which is the expected pitch for a dense, upright, chemisorbed monolayer of OPEs.[30–32] Although molecules physisorbed to the surface in a lying down configuration could result in STM with striping, the pitch from this striping would be at least twice the length of the molecules (more than 46 Å for the OPEs).[30,31] Thus, STM showed that the OPE monolayer assembled via vapor phase was composed of the expected ordered herringbone structure of chemisorbed, dense, upright molecules as would be desired for use in molecular electronic devices.

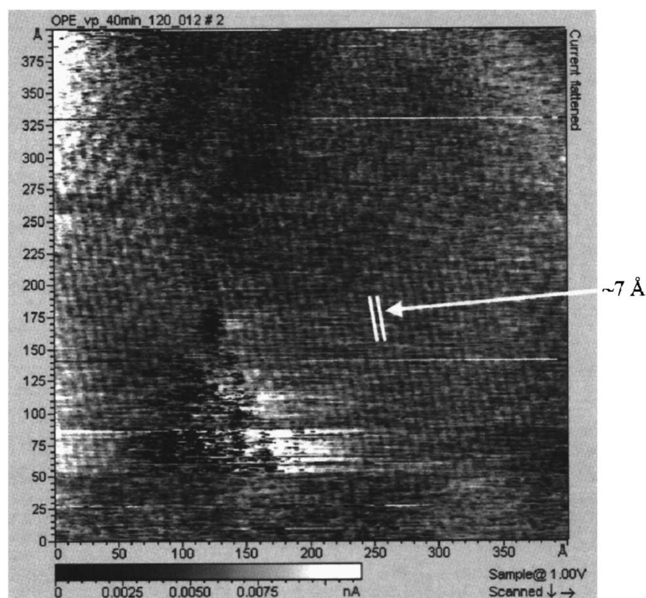

FIG. 7. STM image of a sample of the OPE molecules on gold using a Molecular Imaging PicoPlus with Pt/Ir tip. "Striping" in image is indicative of ordering of the monolayer.

This work establishes a novel method of vapor phase assembly of unfunctionalized OPE molecules, but may also be applicable to the assembly of OPE-based molecules that are electrically enhanced via chemical functionalization. Due to the narrow window between the vaporization temperatures and decomposition temperatures of many of these molecules, the temperature precision of the established vapor phase technique will be essential. If the gap between the vaporization and the decomposition temperatures for any one type of molecule is too small, it may be possible to first vaporize the molecular backbones and then perform *in situ* functionalization prior to, during, or after monolayer assembly.

IV. CONCLUSIONS

In conclusion, we have demonstrated a method for molecular assembly that reproducibly forms an ordered, chemisorbed, uncontaminated, dense monolayer of OPE molecules for use in molecular electronic devices. This vapor phase method of assembly should not only improve device reproducibility and yields but can also be used for the fabrication of devices that require photoresist patterning prior to molecular assembly. Now established, vapor phase assembly can be expanded to the assembly of more electrically functional OPE-based molecules.

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