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Simplifying *in vacuo* Optical Measurements of CVD Processes Using Vacuum-Compatible Optical Fibers

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Abstract

In situ optical measurements during chemical vapor deposition (CVD) processes can offer insight into the chemical reactions and electronic phenomena that are occurring during a process. However, the tooling to make these measurements can be complex, difficult to align, and may even require a redesign of the entire vacuum deposition chamber. Herein, we present a setup that allows for *in situ* optical measurements using vacuum compatible fiber optics that only require a singular conflat feedthrough, eliminating the need for optical viewports and alignment of external light sources/detectors. Proof of performance is shown with a neutral density filter and an exemplary application of vapor doping a conjugated polymer (poly-3-hexylthiophene, P3HT) using vapor-phase $TiCl_4$.

I. Introduction

In situ optical measurements of chemical vapor deposition (CVD) processes have been used for many years. For example, in 1988 Koller *et al.* used IR reflection absorption spectroscopy to monitor the PECVD growth of SiO_2.[1] In 2002, Frank *et al.* demonstrated the ability of *in situ* IR absorbance to provide information about the atomic layer deposition (ALD) of AlO_x using trimethyl aluminum and D_2O.[2] Such *in situ* measurements can both provide new insights into

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the mechanisms of a process and real-time monitoring for process feedback. *In vacuo* measurements also allow for direct detection of phenomena without exposure to the contamination and atmosphere of an ambient environment. Such *in vacuo* measurements are especially invaluable to ALD processes to understand the mechanisms of each half-cycle without breaking vacuum.

However, these *in situ* measurements commonly require a specialized reactor that is expressly designed to accommodate the optics necessary for such measurements. These reactors usually include the appropriately positioned windows or viewports capable of transmitting light into and out of the reactor. If an existing vapor deposition chamber does not already have the appropriately aligned flanges or viewports, then significant re-engineering or a completely new chamber construction may be necessary to introduce *in situ* optical measurements. Here, we demonstrate the use of vacuum-compatible optical fibers to perform optical absorbance measurements that only need a single conflat feedthrough.

In situ optical fibers have been used in prior work to actively monitor CVD reactions. Three broad categories of such use cases exist. Researchers have used tilted fiber Bragg gratings (TFBG) on bare optical fibers that themselves are deposited on through a CVD reaction to determine uniformity and thickness.[3] Another similar use case takes advantage of surface plasmon resonance to measure the sputter deposition rate of TiO_2.[4] Finally, Zhou et al. developed a method of depositing on the end of a single-mode optical fiber that resulted in the development of a Fabry-Pérot interferometer that could be used to determine film thickness.[5] Although these techniques are useful and informative, they all rely upon

depositing the film directly on the optical fiber, instead of using the optical fibers to probe a sample. In this shop note, we demonstrate the use of *in situ* vacuum-compatible optical fibers that are connected through a conflat feedthrough to make real-time absorption measurements of a vapor deposition process on a thin film sample. Importantly, this setup requires only a single feedthrough port with no specific placement requirements, enabling its facile addition to many reactor chambers.

II. Experimental Setup

Figure 1 shows a diagram of this fiber optic setup with the spectral transmittance in the bottom left. The critical parts for constructing this setup are listed in Table 1, including manufacturer and part numbers. For our setup, two optical fibers are attached to a single 2 ¾" conflat tee, fed through a single 2 ¾" conflat port on the reactor chamber. Here we use conflat optical feedthroughs with SMA 905 adaptors that can attach to standard optical fibers. External to the chamber, one fiber connects to the light source while the other connects to the detector. An Ocean Insights DH-2000 light source with a deuterium and halogen bulb and an Avantes Avaspec-ULS2048CL-EVO-RS detector were used for this purpose. This setup could be space-economized even further with a single 2 ¾" conflat, dual fiber optical feedthrough. Inside the chamber, each fiber is connected to a sample holding stage that meets the needs of the experimental design. In our case, we have chosen a commercially available transmission holder with two collimating lenses (an Accu-glass Collimating kit). The position of the sample holding stage is limited only by the length of the rather flexible *in situ* optical fibers. We have the conflat optical feedthroughs

attached to the side of a 1 ft^3 cubic chamber while the sample holder rests on the bottom of the chamber. In general, the sample holder can be mechanically affixed in any position desired.

The path through which the light beam travels is as follows: light source, *ex situ* optical fiber, SMA adapter, optical conflat feedthrough, vented SMA adapter (vented for vacuum compatibility), *in situ* optical fiber, collimating lens, and thin film sample. After the sample, the light travels through those same parts in the reverse order ending in a light detector (in place of the light source). Note that the sample holder shown in light gray inside the red box comes with both collimating lenses shown. Additionally, the spectral transmittance for our setup used is shown in the bottom left of the figure. Use of different light source and detectors should allow for collection of data at higher wavelengths. The large spikes in intensity at ~485, 585 and 655 are Balmer-series lines due to the deuterium bulb used, not an artifact of the *in situ* setup. Figure 2 shows a photo of the setup used to secure the sample along with the collimating lenses and optical fibers. For this specific sample holder, the substrate size is limited to ~0.5 cm wide and < 0.5 cm in thickness.

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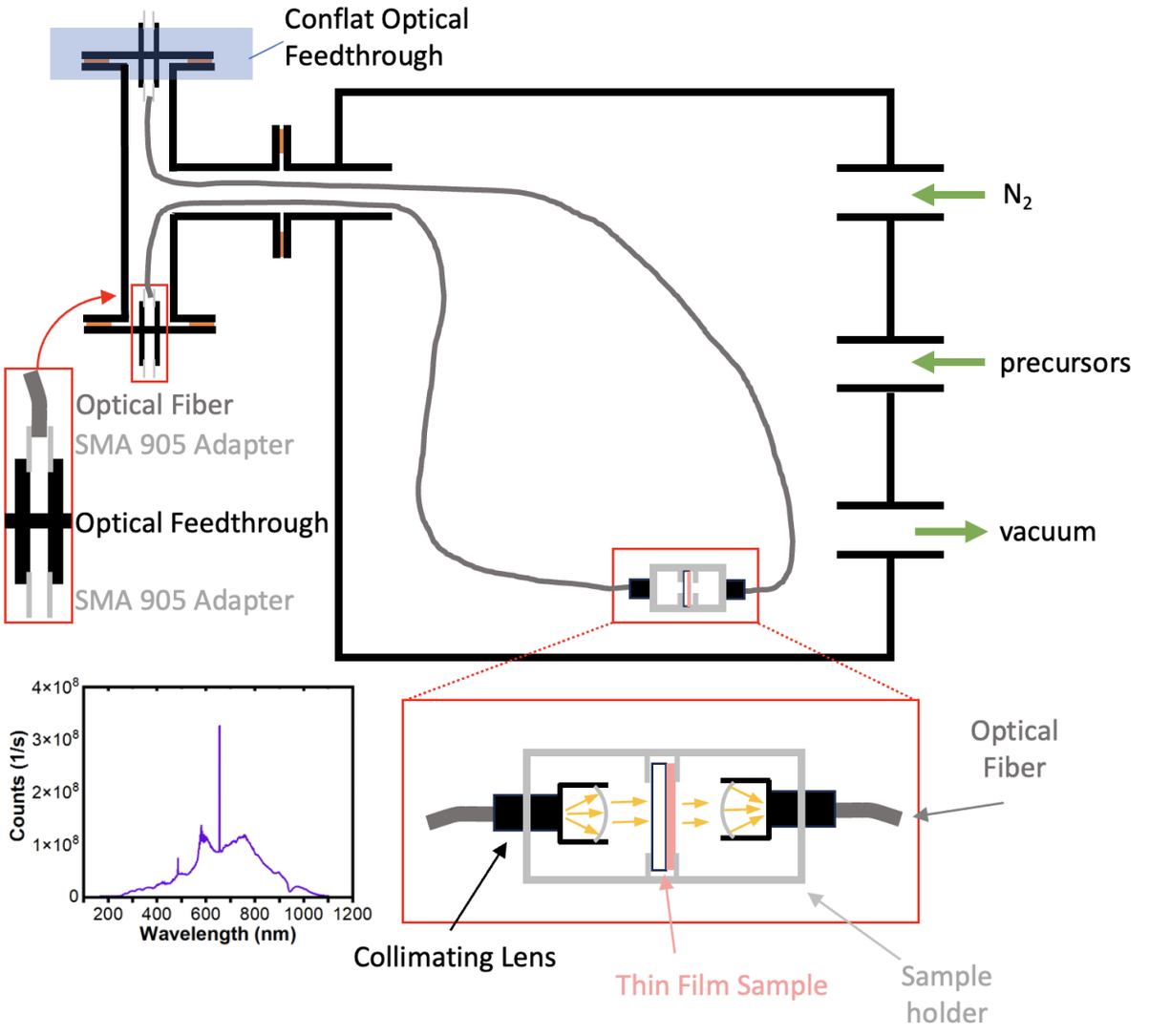

Figure 1. Depiction of a vacuum-based vapor deposition chamber with an *in situ* optical absorbance setup using vacuum-compatible optical fibers and without any viewports. Additionally, the spectral transmittance allowed by the setup for the light source and detector used is shown in the bottom right.

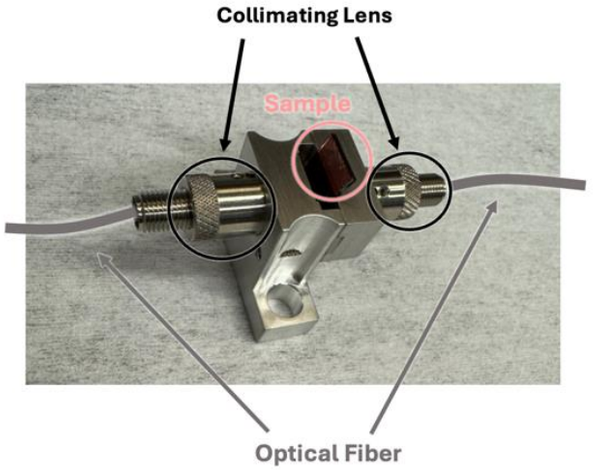

Figure 2. Photo of sample holder showing the collimating lenses, optical fibers and sample holder. The collimating lenses and sample holder are sold as a single component.

Table I. Table of essential parts with the respective manufacturer and part number.

Part	Manufacturer	Part #	Wavelength Range (nm)
Conflat Fiber Optic Feedthrough	Thorlabs	VC2L6S	400-2400
Sample holder (includes 2 collimating lenses)	Accu-glass	112694	190-2500
Optical Fiber – add SS braid	Accu-glass	6-601147	400-2200
SMA 905 Adapter – vented	Accu-glass	105450	
SMA 905 Adapter	Accu-glass	105451	

Table 1 also shows the wavelength ranges for the various components. Here, the optical fibers are the limiting components for wavelength range, as their transmission is rated up to 2200 nm, while the optical lenses and conflat feedthroughs are able to transmit to 2500 and 2400 nm respectively. If deeper into the UV is of interest, optical components with transmission to 200 nm are also commercially available (from e.g., Accu-glass). This wide range of wavelengths makes this setup flexible for a wide range of applications. The maximum operating temperature for all the *in vacuo* components is 250°C, which may not be sufficient for every CVD process but is compatible with many ALD processes. Another

concern of note is whether the CVD process will coat the lenses. Similar limitations must be managed in systems using viewports and will depend on the exact experimental design.

This particular setup was purchased for ~ $2500 in the fall of 2024, making the setup reasonably economical. Moreover, the components most likely to fail are the optical lenses and/or optical fibers. These components are easily replaced with no need to alter any of the vacuum seals (e.g., conflats). The initial setup also only requires replacing a single conflat flange, and its location has no significant locational restraints.

III. Demonstration

To validate this *in vacuo* measurement setup's feasibility, UV-Vis absorption spectra are collected from a 0.3 OD (optical density) neutral density (ND) glass filter from Edmund Optics in both ambient atmosphere and under *in situ* vacuum conditions. Figure 3 plots the absorption spectra for the ND filter measured for: (1) *ex situ* in ambient atmosphere, (2) *in situ* under vacuum at room temperature, and (3) *in situ* under vacuum at 80 °C. The reference spectrum in all cases is the direct light source. Note that the ND filter has a blocking wavelength range from 400-700 nm and is the limiting factor for the wavelength range shown for Figure 3. Figure 3a plots the raw absorbance spectra for the three conditions, showing nearly identical absorbance in each condition. Figure 3b plots the percent difference in absorbance for each of the *in situ* measurements (at room temperature and 80 °C) relative to the *ex situ* measurement. Here we see the difference is less than 5% over the entire wavelength range measured. As some validation of the setup's durability, we did not measure any significant shift in the ND filter spectrum after 10 vapor

infiltration experiments (see below). Furthermore, the spectral transmittance variation after these 10 vapor infiltration experiments was within error of the light source used, indicating minimal degradation of the setup.

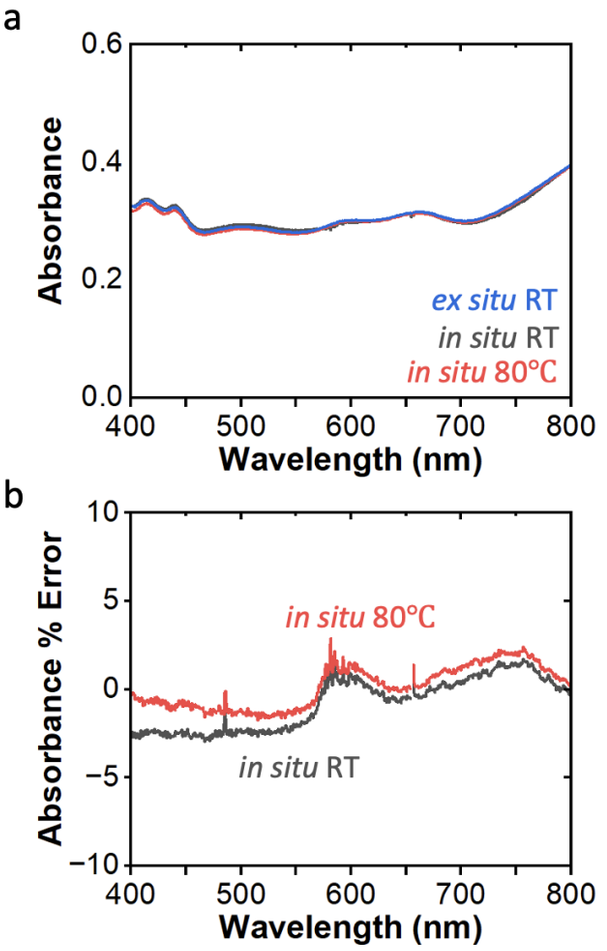

Figure 3. (a)UV-Vis absorbance spectra for a 0.3 OD ND filter performed *ex situ* (blue), *in situ* under vacuum at room temperature (black) and *in situ* under vacuum at 80°C (red). (b)UV-Vis absorbance % difference spectra where the *in situ* under vacuum at room temp and at 80°C samples are referenced back to the *ex situ* measurement.

To demonstrate real-time CVD process monitoring, Figure 4 presents UV-Vis spectra collected from a semiconducting poly(3-hexylthiophene) (P3HT) film on a glass substrate that is vapor doped with $TiCl_4$ at 80 °C at increasing exposure times (all of which are collected during a single vapor doping process). Evident in these spectra is the decrease in

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absorbance of the π-π* transition (~520 nm) and an increase of the polaronic absorbance (> 650 nm). Both of these spectral changes are consistent with the conjugated polymer film becoming more electrically doped (higher carrier concentration).[6-8] The reaction that occurs is a redox reaction where the $TiCl_4$ removes an electron from the P3HT backbone, leading to generation of a polaronic charge carrier. The exact doping mechanism is rather complex and not discussed here, but the reaction between $TiCl_4$ and P3HT has been documented to be a doping reaction wherein the Ti does not bond directly to the polymer and therefore the changes in absorbance are from doping of the polymer.[6] The increase in absorbance near 250-300 nm is contributed to incorporation of $TiCl_4$ (eventually converted to TiO_2 upon water dosing), though this is slightly beyond the rated wavelength range of the equipment and should be interpreted cautiously.[9] Consequently, the decreases in absorption ~520 nm and increase ~650 nm should not be contributed to either $TiCl_4$ incorporation or TiO_2 deposition. The measured percent difference in absorbance (~8%) is notably greater than any error at the wavelength range (1 - 2.5% error), showing that the vapor-phase doping of conjugated polymers can be measured even for a weak dopant such as $TiCl_4$.

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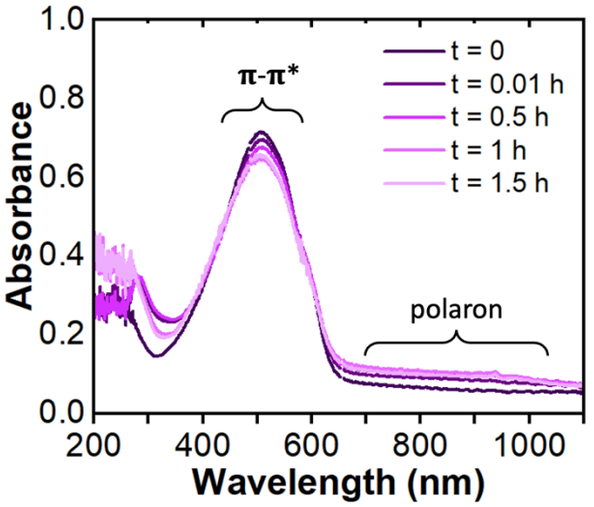

Figure 4. *In situ* UV-Vis spectra collected from a P3HT film being vapor doped with $TiCl_4$ in a vacuum chamber at 80 °C for varying exposure times (0, 0.01, 0.5, 1, and 1.5 h).

IV. Conclusions

This shop note has presented an alternative method for measuring *in situ* optical absorption phenomena during CVD processes without the need for aligned external viewports. This setup requires access to just a single conflat flange and can be used for many types of vapor deposition processes. The extent to which the optical fibers can withstand exposure to various precursors has not been rigorously tested, but it seems capable of withstanding several pulsed cycles without significant change in optical performance. The setup should be broadly applicable with minor modifications to monitor any spectral features between 200 and 2200 nm, with some possibility to expand farther into the IR to do vibrational spectroscopies given the proper optics, light sources, and detectors.

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Author Declarations

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Li Zhang: Conceptualization (lead); Data curation (lead); Formal Analysis (lead); Investigation (lead); Methodology (lead); Project administration (equal); Validation (lead); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal). **Mark Losego:** Funding acquisition (lead); Project administration (equal); Resources (lead); Supervision (lead); Writing – review & editing (equal).

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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