

A Liquid-Phase Quartz Crystal Microbalance for Photovoltaics Research

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ABSTRACT

Processes involving solid surfaces and liquid reactants are ubiquitous in the semiconductor industry, and photovoltaics is no exception. Examples include the chemical bath deposition of CdS buffer layers in Cu(In,Ga)Se₂ and CuInS₂ devices, a process that is used in virtually every commercially available CIS-based module. Aqueous etching is used for anti-reflective texturing of silicon cells, and is also used in the cleaning, defect etching, and native oxide removal for that particular PV material. Research on next generation quantum dot-based solar cells frequently uses simple solution-based methods for the growth and modification of the quantum dots. In all of these examples, a liquid is used to remove or deposit very thin, sometimes atomically thin, layers on the surface of a solid, and the nature of the chemical and physical changes that take place at that interface are critical to the proper functioning of the finished photovoltaic device. Despite the widespread use of liquid processes in research and in industry, there are few characterization techniques suitable for in-situ and real-time investigations of the solid-liquid interface. We have recently finished constructing a new, low-cost tool based on a quartz crystal microbalance for investigations of liquid processes that are of interest to the PV community. The tool consists of a liquid-phase QCM, pumps, valving, reaction vessels, membrane contactors for control of dissolved gases, and a PC-based control system, and can be used in continuous flow cell mode or in a batch reaction scheme. Because the system has been integrated with the NREL Surface Analysis Team's cluster tool, films either grown or modified with this new tool can be transferred without fear of atmospheric contamination to a suite of surface analytical techniques for further study. This paper will describe the new tool, its capabilities, potential pitfalls with its use, initial results, and possible future research directions.

INTRODUCTION

Quartz crystal microbalances (QCMs) are heavily used tools in vacuum deposition processes because of their relatively low cost and their ability to accurately and sensitively measure mass changes in real time. Use of QCMs in liquid environments is less common but over the past decade has become more important because of the development of oscillator control circuitry capable of maintaining stable oscillation in crystals under heavy viscous loading by liquid environments and non-rigid films. Use of QCMs in liquids has also benefited from increasingly sophisticated theoretical treatments of oscillators. Early work includes that by Sauerbrey [1], who developed the

following simple relationship for resonators operating in vacuum:

$$\Delta m = \frac{(f_q - f) \sqrt{\rho_q \cdot \mu_q}}{2n \cdot f^2} \quad (1)$$

Equation 1 assumes that deposited films have the same acousto-elastic properties as quartz. Here Δm is the mass per unit area in g/cm², f_q is the resonant frequency of the unloaded crystal in Hz, f is the frequency of the loaded crystal in Hz, ρ_q is the density of quartz (2.648 g·cm⁻³), μ_q is the shear modulus of quartz (2.947 x 10¹¹ g·cm⁻¹·sec⁻²), and n is the number of the harmonic at which the crystal is driven. For the 5 MHz crystals used in our apparatus which are driven at their first harmonic, this translates to a sensitivity of 5.66 x 10⁷ Hz·g⁻¹·cm⁻².

For thick films of the piezoelectric materials ZnO and CdS studied in this paper, Sauerbrey's original assumptions fail. Lu and Lewis [2] extended Sauerbrey's work to include the mechanical properties of the film being deposited on or removed from the quartz crystal surface:

$$\Delta m = \left(\frac{N_q \cdot \rho_q}{\pi \cdot R_z \cdot f} \right) \cdot \tan^{-1} \left[R_z \cdot \tan \left[\pi \cdot \left(\frac{f_q - f}{f} \right) \right] \right] \quad (2)$$

where N_q is a frequency constant for the crystal and R_z is the acoustic impedance ratio of the quartz and film material and =

$$\frac{\rho_q \cdot \mu_q}{\rho_f \cdot \mu_f} \quad \text{where } \rho_f \text{ is the density of the film}$$

and μ_f is the film shear modulus. The Lu and Lewis relationship was incorporated in the software written to control our apparatus because ρ_f and μ_f are known for common materials such as ZnO and CdS. Note that determination of the coverage of an organic molecule using this relationship requires using values for both ρ_f and μ_f . Typically these are not well known. For this reason, coverage of the organic molecule studied here was performed using Equation 1.

Operation of a QCM in liquid causes a frequency shift [3] due solely to the liquid's density and viscosity:

$$\Delta f = -f^{3/2} \sqrt{\frac{\eta_L \cdot \rho_L}{\pi \cdot \mu_q \cdot \rho_q}} \quad (3)$$

where η_L is the liquid viscosity and ρ_L is the liquid density. Equation 3 predicts a large frequency shift of 721 Hz upon immersing a 5 MHz crystal in distilled water at room temperature. Using Equation 2 and the density and lattice constants of ZnO, it can be shown that this frequency shift translates to ~ 43 Zn-O bilayers, much more than the thickness of a single organic monolayer. To achieve sub-monolayer sensitivity we have minimized these frequency shifts due to changes in liquid density and viscosity by designing our apparatus such that the reagents contacting the crystal may be changed without withdrawing the crystal from the liquid environment. In addition we have used dilute (2-5 mM) solutions so that there are minimal differences between the properties of the pure solvents (water and ethanol) and solutions made from them.

Our previous work with II-VI materials and interest in nanoparticle surface chemistry has led to the initial testing of our apparatus with two systems: ZnO + self-assembled monolayers (SAMs) of organic molecules and CdS chemical deposition. In this paper we report on results with the ZnO-SAM system. There have been several reports of tuning injection barriers and absorber morphology in organic electronic devices using SAMs on metals (see i.e. [[4-6]]). Much less is known about SAMs on oxide surfaces and how they might be used to improve PV devices. By appropriate selection of terminal functional group, Appleyard et al. were able to produce positive and negative work function changes on phosphonic acid SAM functionalized indium tin oxide (ITO) and thereby tune injection barriers in organic devices [7]. Hanson et al. showed how a thiophenephosphonic acid could be used to enhance hole injection in OLED devices [8]. Lao used carboxylic acid functionalization of ZnO nanobelts for similar improvements in energy level alignments [9]. We have chosen the phosphonic acid moiety as a surface linking group because of its advantages over more common silane and thiol chemistry that include better resistance to hydrolysis and polymerization in solution as well as less of a dependence on surface hydroxyl content [10]. Finally, the chemical similarity of the alkane phosphonic acid used here to the corresponding alkane thiol could allow the first determinations of the acousto-elastic properties of these molecules.

EXPERIMENTAL

A schematic of the QCM-based apparatus operating in flow-cell mode is shown in Figure 1. Except for the pumps, the system is inside the glove-box portion of cluster tool that has been described in previous publications.[11, 12] All wetted materials except for the QCM sensor are of fluoropolymer or polypropylene construction. Liquid reagents can be transported to the flow cell or a batch reactor either by active pumping with one of two computer controlled peristaltic pumps or by gravity feed as shown on the two right-hand reagent containers. Reagents are first passed through a set of membrane contactors (model EF-Micro from Dianippon Ink and Chemical), devices that allow the removal or addition of dissolved gases in the streams. The contactors consist of a high surface area hydrophobic membrane that is permeable to low molecular weight molecules such as oxygen and carbon dioxide. Reagents flow over one side of the

membrane and dissolved gases diffuse through the membrane into a vacuum that is maintained on the other side. The contactors were found to be necessary when performing experiments

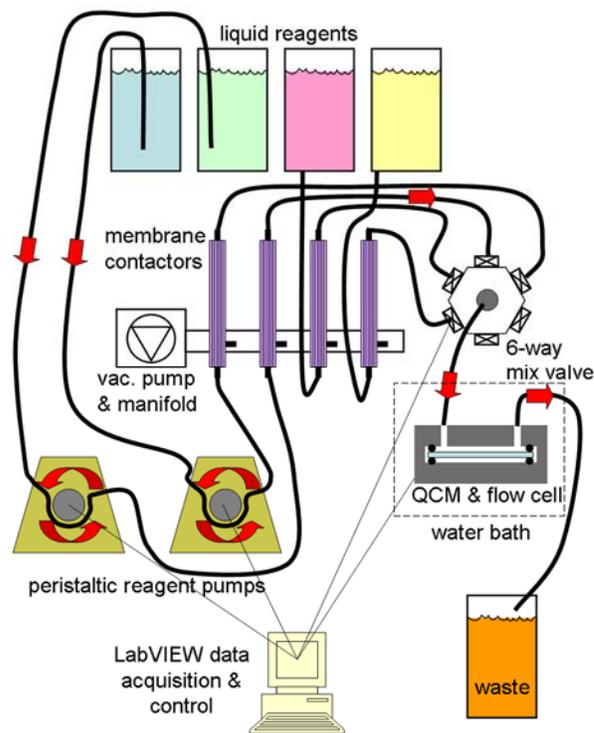


Figure 1. Schematic of QCM-based flow reactor

at elevated temperature because heating gas-saturated reagent streams caused the formation of bubbles, which in turn cause spurious readings in the QCM sensor. After passing through the contactors, reagents flow through a six-inlet, one-outlet solenoid operated mixing valve. In the case of the gravity fed solutions, flow is initiated by actuation of the corresponding solenoid. If the apparatus is set up for flow cell mode as depicted in the schematic, reagents next flow across a Mactek 5 MHz AT-cut QCM crystal that has been coated with the material to be investigated, ZnO in the initial work reported here. If the QCM is being used in a batch reactor, i.e. for control and monitoring of a CdS chemical bath deposition (CBD), the flow cell is replaced by an open crystal holder that is immersed in a standard CBD water-jacketed beaker into which reagents are dispensed. The entire system, including a Mactek RQCM crystal monitor, is controlled with National Instruments hardware and with software written in LabVIEW. Frequency changes in the crystal were converted to film thicknesses every 50 ms according to the relation developed by Lu and Lewis.[2] Polished SiO₂-coated QCM crystals were purchased from Mactek Inc. and were sputter coated with 500 nm of undoped ZnO at ~ 200 °C. For the ZnO experiments conducted in the flow cell, 5 mM ethanolic solutions of NH₄Cl and n-hexylphosphonic acid were used and experiments were conducted at room temperature.

RESULTS AND DISCUSSION

Although the initial use of the QCM was as a real time and in-situ thickness sensor in chemical bath depositions of CdS, the focus of this paper is on results obtained while operating the apparatus in a flow cell mode. Flow cell operation allows minimizing or avoiding complications with operating a QCM in liquids that are not seen with vacuum operation. In addition to the mass of the crystal, the oscillation frequency of a liquid QCM is dependent on the solution viscosity, density, hydrostatic pressure, and film roughness, the latter coming into play because a porous film can entrain liquid. Additional factors include temperature dependent stress on the crystal from the crystal holder, temperature dependent resonance frequency of the crystal itself, and bubble formation with the flow cell during operation at elevated temperature. Figure 2 shows both the effects of hydrostatic pressure and of bubble formation.

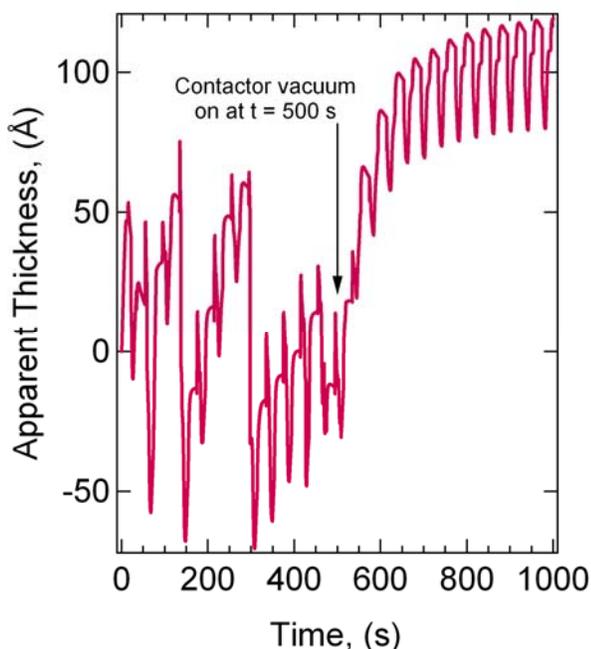


Figure 2. Spurious thickness readings caused by hydrostatic pressure and bubbles, and the effects of degassing the liquid stream.

These data were taken with the computer toggling the flow of room temperature distilled water on for 20 s and off for 20 s with the water bath being held at 65 °C. Without the membrane contactors working, air-saturated water moves into the temperature bath, is heated, and a mixture of bubbles and gas passes by the QCM sensor. By turning on the vacuum to the membrane contactor manifold, noise in the QCM signal that is due to in-line bubble formation is eliminated, and the signal that is due to the periodically changing hydrostatic pressure is recovered.

Figure 3 shows flow cell data taken with a QCM crystal that was coated with 500 nm of sputter-deposited

ZnO. The red trace, consisting of about 150,000 thickness readings, shows the change in ZnO thickness as a result of etching with dilute ethanolic NH_4Cl and using the pulse sequence of 1) ethanol rinse 2) ethanol injection 3) ethanol rinse 4) NH_4Cl injection. Noise spikes due to valve actuation and the 10 s rinse and 25 s injections are visible; between the spikes the flow cell is in a static condition and etching or adsorption involves only the small volume with the cell (0.1 ml). During the NH_4Cl etching cycles, ZnO is being removed at $0.008 \pm 0.001 \text{ \AA/s}$.

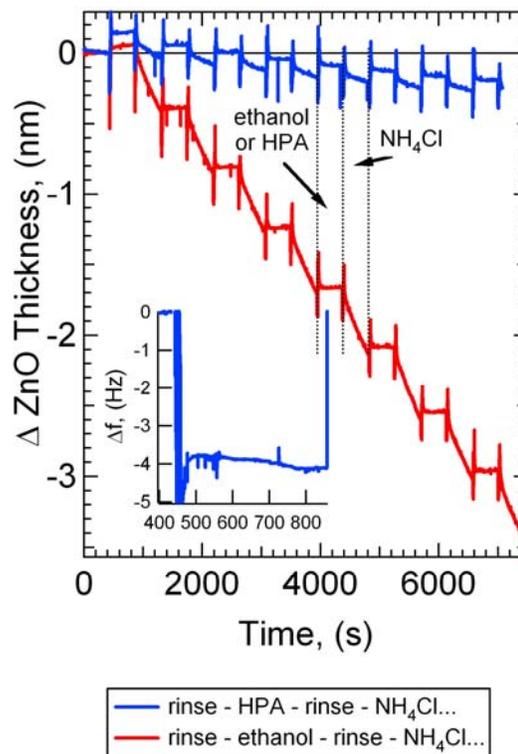


Figure 3. ZnO etching and etch blocking by SAM of alkanephosphonic acid.

The blue trace of Fig. 3 is QCM output from the same ZnO surface using the pulse sequence 1) ethanol rinse 2) n-hexylphosphonic acid (HPA) injection 3) ethanol rinse 4) NH_4Cl injection. The initial rise from zero in the plot indicates that HPA is adsorbing on the ZnO surface. The blue trace in the inset is the corresponding decrease in crystal frequency during this first cycle. Use of Equation 1 on this portion of the data results in a coverage of 2.6×10^{14} molecules/ cm^2 , which is about 0.24 monolayers (ML) if 1 ML is defined as the number of atoms/ cm^2 on a c-axis oriented ZnO crystal (1.1×10^{15}). Attachment of an electrically insulating hydrophobic molecule such as HPA to ZnO is expected to inhibit attack by a hydrophilic Brønsted acid such as NH_4Cl . The fact that the etch rate over the full 7000 s long reaction sequence is a factor of ~8 smaller than the control experiment (red plot) is evidence that the hexylphosphonic acid has been attached to the ZnO surface, and shows that an n-alkyl group even as short as the hexyl group can add corrosion resistance to a TCO.

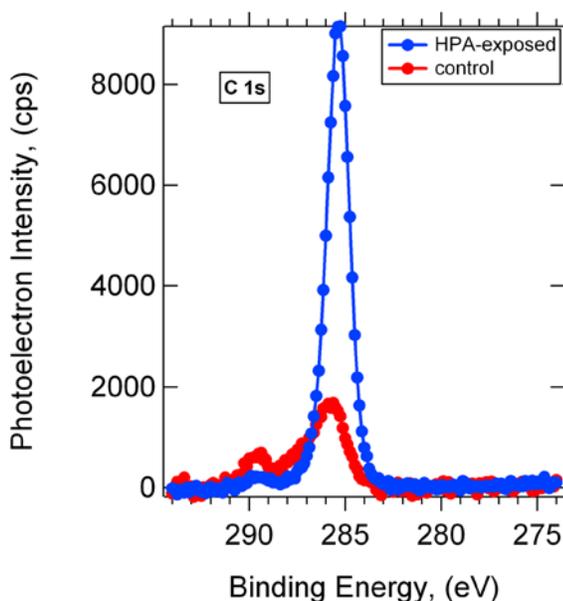


Figure 4. Carbon 1s XPS spectra of ZnO and ZnO-HPA SAM.

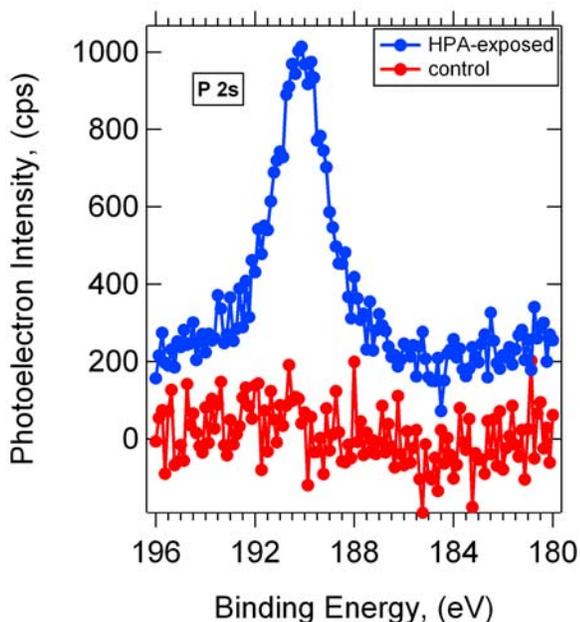


Figure 5. Phosphorus 2s XPS spectrum of ZnO and ZnO-HPA SAM.

Figure 4 is x-ray photoelectron spectroscopic data for the carbon 1s region of a ZnO control film exposed to ethanol only (red trace), and a ZnO film exposed to the HPA-ethanol film for several hours and then rinsed with copious amounts of ethanol (blue trace). The large increase relative to the control film in the amount of carbon in the HPA-exposed film is ascribed to the hexyl group of the HPA. Further confirmation that the ZnO film has been functionalized with HPA is found in Figure 5,

XPS spectra of the phosphorus 2s region, which show the presence of phosphorus only in the HPA-exposed film.

CONCLUSIONS

We have built a new instrument based on a QCM for the study of chemical reactions occurring between solid surfaces and liquids. The design of the instrument allows sensor artifacts to be reduced to the point where atomic scale phenomena are easily observed. Although one limitation of the instrument is that the solid to be studied must be deposited on a QCM crystal, stable oscillation was achieved on three different crystals sputter coated with ZnO and it is believed that any material can in principle be investigated with this apparatus as long as its growth temperature does not exceed the $\alpha \rightarrow \beta$ quartz phase transition of 573 °C. We have used the apparatus to demonstrate functionalization of the ZnO surface with an organic molecule, n-hexylphosphonic acid, and how that molecule affects the corrosion of ZnO in the presence of a weak acid. Further work with this tool will include using it to investigate the aqueous analog of atomic layer deposition, the so-called "SILAR" deposition method [13], and exploiting the features of a flow cell set-up [14] to understand the kinetics of PV-relevant solid-liquid processes. In addition, quantification of the SAM coverage via XPS or other independent means would allow determination of shear moduli of these types of films, values that are otherwise difficult to obtain and that would allow the rapid and accurate quantification of organic layers via low cost and simple QCM-based equipment. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337 with the National Renewable Energy Laboratory.

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