High-throughput functional thin film characterization with in situ data analytics and real-time feedback

Dissertation proposal

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Abstract

Advances in data analytics and combinatorial processing have enabled rapid design and synthesis of a broad range of novel functional materials. Before their deployment in commercial or industrial applications, these materials must undergo characterization of structure and functionality under a broad range of ambient environmental conditions. To facilitate high-throughput characterization of film functionality, we developed an integrated multi-functional environmental system (IMES) and associated workflow at Center for Nanophase Materials Sciences. IMES enables simultaneous multi-sample screening of electrical, gravimetric and optical properties across an ultra-wide (mHz-THz) frequency excitation band. The system has been used to characterize functionality of a broad range of materials including metal oxides, carbon nanotubes, graphene, MXenes, biomolecules, conjugated polymers and ionic liquids. Multidimensionality of the environmental parameter space (temperature, pressure, humidity) and characterization modes (electrical, optical, gravimetric) create unique challenges for data processing and experimental design. To address these challenges and reduce redundancies in researcher-led experiment planning, this proposal aims to assess the feasibility of using in situ data analytics in a feedback loop to enable semi-autonomous computer-controlled sample testing. The proposed research will be addressed in three stages:

1. Integration of data processing into experimental control software for real-time analytics and modeling of thin film response.
2. Feedback of film response into control software for automated dynamic tuning of measurement settings and environmental conditions.
3. Extension of real-time data processing and feedback to include gravimetric, electrical, and optical characterization modes with data processing offloaded to a remote server for ensuring scalability of the system.

The resulting experimental control software will perform automated experimental design and streamlined data analysis by employing machine learning, physical modelling, and advanced statistics. Deployment of the system will enable a pathway toward autonomous thin film characterization, reducing labor-intensive researcher-directed experiment planning and data analysis.

Background and significance

Advances in thin film synthesis, multilayer patterning, and 3D micro-additive manufacturing have enabled the development of a broad range of emerging technologies with unprecedented functionality and portability, including low-cost sensors for internet of things (IoT) networks, smart textiles, flexible displays, microelectromechanical systems (MEMS), and lab-on-a-chip diagnostic biomedical devices[1-2]. Future improvements in device functionality and miniaturization will be primarily driven by design, discovery and deployment of novel materials[3-5] using combinatorial methods and machine learning[6-9] with guidance from comprehensive materials databases[10-13] such as those assembled by the Materials Genome Initiative[14].

Although discovery and design of materials has been accelerated by high-performance computing, wide availability of data, and automated synthesis techniques, testing of material functionality generally requires human-based screening and remains highly inefficient[15-16]. Characterization of functional properties and assessment of long-term film stability are often the most challenging steps to automate in the materials characterization workflow[17] and represent a primary bottleneck in the roughly 20-year process from materials discovery to commercial deployment[16-18]. Automated sample characterization remains challenging due to the broad range of functional film materials which must undergo screening (nanoparticles, nanotubes, two-dimensional materials, polymers, ionic liquids, and oxides), and use of a wide variety of chemical (chemical vapor deposition, atomic layer deposition) or physical (spin-coating, sputtering, pulsed laser deposition) deposition techniques which contribute to significant heterogeneity between samples.

Stand-alone off-the-shelf instruments are generally unsuitable for high-throughput materials testing because they lack the flexibility to accommodate different sample geometries, specific experimental procedures, and customized batch data processing routines. Efficient multi-functional material characterization requires a dedicated in-situ diagnostics system which allows simultaneous probing of multiple film functionalities[19] and provides capabilities for simultaneous multi-sample testing and control of ambient environmental conditions, including pressure, temperature, humidity, and light intensity for assessing the environmental response and long-term stability of functional films.

Precise control of ambient environment is critical for reproducible thin film characterization. The poor electrical and morphological stability of many functional thin film materials limits their suitability for adoption in commercial or industrial applications. Due to nanometer-micrometer scale thicknesses and inclusion of patterned microstructures, low-dimensional materials, and microporous materials, functional thin films often exhibit surface area to volume ratios which are significantly higher than those of corresponding bulk materials. This results in functional mesoscale behavior which is dominated by surface and interface effects rather than bulk properties, increasing susceptibility to interaction with the ambient environment.

Film stability is particularly important in the context of emerging organic electronics and low-dimensional materials. Functional organic films offer promising alternatives to traditional silicon-based device components because of their low cost, mechanical flexibility, and compatibility with solution-based processing, which enables low-cost large-area flexible technologies including organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic thin film transistors (OTFTs), and a wide range of organic thin film bioelectronics and sensors[20-23]. Conjugated polymers, graphene, carbon nanotubes and phthalocyanines rely on delocalized π-systems for charge transport[20] which promotes thermodynamic stability but often results in strong reactivity with oxidizing species like oxygen and water. Long-term stability of organic materials is often limited by their rate of oxidation, which can lead to loss of conjugation, decreased charge carrier density, and introduction of electronic scattering sites[21, 24-25]. Surface energy decreases during adsorption of gas or vapor molecules under typical thermodynamic conditions, resulting in chemical doping which can compromise electronic stability[26], while thermal fluctuations and incident radiation can result in chemical and electronic doping, polymer chain scission, and photobleaching.

While thin film interaction with ambient environment adds complexity to functional materials characterization, design of environmentally-responsive thin films is crucial for development of sensor technologies IoT devices, autonomous vehicles, industrial process control, environmental monitoring, and biomedical applications[21]. Chemical sensing comprises an important functionality for many nanomaterials and functional organic materials because of their high surface areas and strong response to gas/vapor and light. Typical commercial gas sensors rely on metal oxide films which require elevated temperatures for maintaining sensor reversibility. In contrast, thin film sensors based on conducting polymers and small organic molecules are often deposited at room temperature by simple solution-based deposition or printing, which significantly lowers the cost of sensor fabrication. Polymer-based chemical sensors may be operated at room temperature, which increases portability and decreases energy requirements associated with sensor operation[27], while specific analyte sensitivity can often be tuned by tuning modifying film polymerization or chemical functionalization[28].

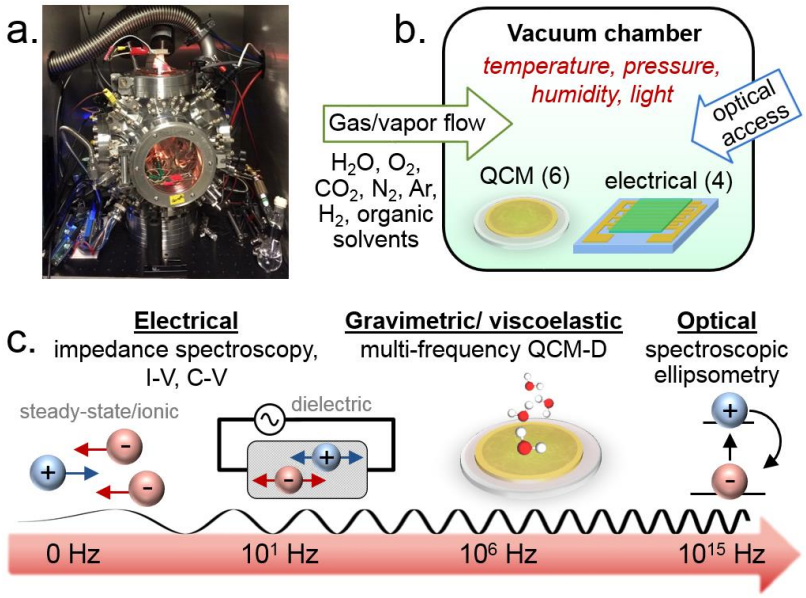

Figure 1. (a) IMES system developed at CNMS designed for high-throughput multi-functional film characterization. (b) The measurement chamber allows environmental control of temperature, pressure, gas/vapor flow, humidity and light, and is capable of (c) simultaneous electrical, optical, and gravimetric measurements using multiple channels across a broad frequency range.

Current progress

To address challenges related to high-throughput materials characterization under controlled environment, an integrated multi-functional environmental system (IMES) was developed at CNMS (Figure 1a). The system enables multi-modal film characterization inside a vacuum chamber while a two-gas mixing system delivers gas/vapor compositions at controlled pressures and flow rates (Figure 1b). The gas injection system performs automated delivery of precise gas/vapor analyte conditions and relative humidity (RH) by flowing mixtures of O_2, H_2O, CO_2, N_2, Ar, or H_2 + Ar. Temperature is controlled by a heating plate mounted inside the chamber with embedded thermocouples. A quartz optical window allows for sample heating and surface activation by infrared (IR) and ultraviolet (UV) sources mounted outside the chamber. The system contains over 50 channels for electrical feedthroughs, enabling impedance spectroscopy, current-voltage (I-V), cyclic voltammetry (C-V), and back-gating transistor measurements on multiple samples simultaneously. Additional electrical channels are dedicated to multi-harmonic quartz crystal microbalance with dissipation monitoring (QCM-D) for multi-sample gravimetric and viscoelastic measurements. Two optical fiber feedthroughs provide one channel for optical diagnostics. The combination of DC-bias electrical measurements (0 Hz) with electrical impedance (mHz – MHz), multi-frequency QCM (MHz – 100 MHz), and optical diagnostics (THz) enables multi-functional film characterization across an ultra-broad frequency range (Figure 1c). Pumping the camber to 10^{-4} Torr vacuum before and after measurements allows environmental response to be referenced to film behavior under vacuum, enabling clear differentiation between inherent film behavior and that resulting from doping by gas/vapor molecules. Data acquisition and control of source-measure units, QCM electronics, optical spectrum acquisition, and environmental conditions inside the chamber are controlled through a central dedicated LabVIEW user interface, which allows real-time display of measured data and

automated control of environmental conditions. The IMES system has been successfully used to investigate multi-functional environmental response of broad range of thin film materials including carbon nanotubes[29], ion-intercalated MXenes[30], conjugated polymers[31-32], organic semiconductors[33-34], polymer-nanotube composite films[35], perovskites[36], proteins[37] and metal oxides[38-39].

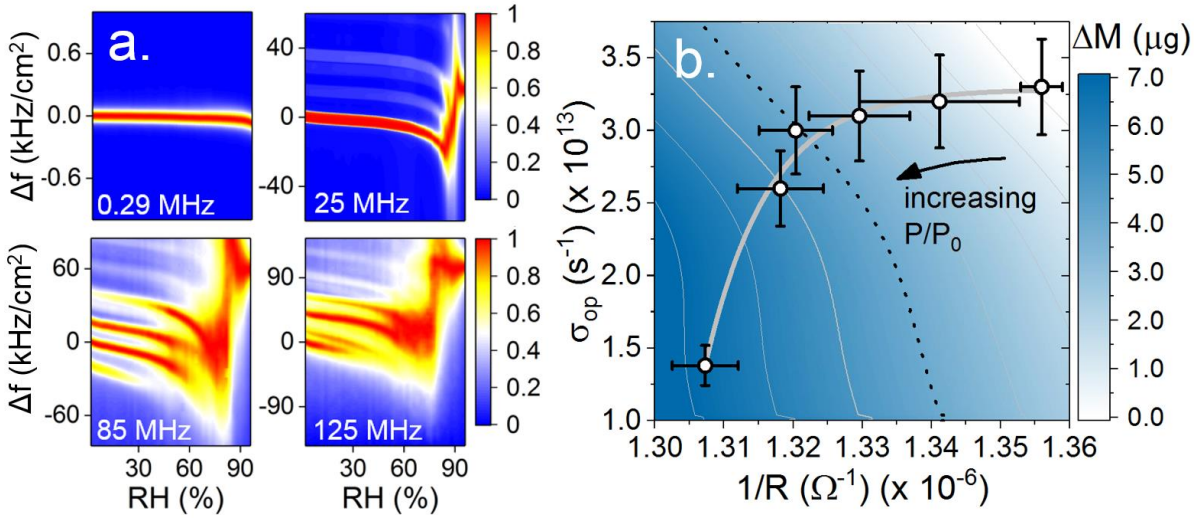

Figure 2. (a) Example of high-dimensional QCM data showing film response to relative humidity (RH, x-axis), frequency dependence (ΔF, y-axis), normalized conductance (color bar), and crystal overtone number (resonant frequency of overtone displayed in lower left-hand corner of each panel). (b) Example of simultaneous multi-modal data channels including electrical (inverse electrical resistance [1/R], x-axis), optical (optical conductivity [σ_{op}], y-axis), and gravimetric (mass change [ΔM], color bar) modes during film exposure to increasing water vapor partial pressures (P/P_0). Figure (b) is reproduced from ref.[33].

Current Challenges

Although the IMES system enables automated environmental control and data acquisition, two primary workflow challenges remain. The first challenge is associated with manual experiment planning. Before initiating an experiment, a sequence of environmental testing conditions must be manually designed and entered in the central IMES software to allow for automated temporal control of temperature, ambient pressure, relative humidity, analyte gas/vapor flow, and intensity of auxiliary light sources. Design of experimental conditions becomes particularly complex during multi-sample testing due to variation in the environmental sensitivity, response time, and reversibility of different samples. Exploration and design of a multi-dimensional environmental parameter space, which for example may be represented as a three-dimensional grid of varying humidity levels, oxygen partial pressures, and temperatures, requires further complexity and significantly increases the duration of experiments and human-led planning and preparation. Along with selection of appropriate environmental testing conditions, a broad range of

measurement parameters and instrument settings must be determined and set manually prior to each experiment. Important measurement settings which must be selected by an experienced researcher include I-V and C-V scanning directions, step sizes, and sweep rates, and AC and DC bias voltages, frequency ranges, sampling rates, and integration times for impedance spectroscopy and QCM measurements. Challenges associated with manual experiment planning suggest that automated optimization of experimental conditions and measurement settings would lead to increased experimental throughput due to a reduction in redundant experimental procedures and time spent by human researchers for manual tuning of experimental settings.

The second major challenge related to automation of high-throughput thin film characterization is associated with data processing, analysis and modeling. Simultaneous acquisition of electrical, optical, and gravimetric measurements results in a complex data stream which may contain channels consisting of one-dimensional (e.g. time-dependent electrical resistance), two-dimensional (e.g. frequency-dependent electrical impedance spectra), or higher-dimensional (harmonic-dependent multi-frequency QCM impedance spectra) data. Experiments running concurrently may require different integration times for high-resolution measurements, resulting in final output data which contains inconsistent time-referenced indices. Across different characterization modes and output file formats, data must be efficiently timestamp-referenced to enable matching of thin film response to the specific environmental conditions present at the time of acquisition. Examples of multi-modal and high-dimensional datasets are shown in Figure 2. In Figure 2a, normalized QCM conductance (color bar) is plotted as a function of frequency (Δf) and relative humidity (RH) at 0.29 MHz, 25 MHz, 85 MHz, and 125 MHz crystal resonances. A single QCM experiment can involve measurement of conductance spectra at 15 different crystal overtones under a 2-96% RH range, which may produce over 5 GB of data when multiple samples are measured simultaneously. In Figure 2a, response of sulfonated copper phthalocyanine film to changing water vapor partial pressure (P/P_0) is compared across three different modalities: optical (optical conductivity, σ_{op}) electrical (inverse electrical resistance, 1/R), and gravimetric (mass change of the film, ΔM). Unfolding the multi-modal response in Figure 2a required use of 5 different laboratory instruments: a QCM controller, spectroscopic ellipsometer, source-measure unit, gas flow controller, and electronic butterfly valve for precise control of partial pressure. Analysis of output data from multiple instruments with different file formats generally requires manual intervention and post-processing by an experienced human researcher. However, manual post-processing of data often cannot occur until after completion of an experiment and may require hours or days depending on the number of samples, measurement techniques, and size of the environmental parameter space which was probed. After initial data processing and analysis, a preliminary understanding of sample response may be formulated. Preliminary results often shed light on flaws in the experimental design such as suboptimal instrument settings or poor variation in environmental conditions. Experimental design can then be improved in a follow-up experiment, but this iterative process is prohibitively labor-intensive and time-consuming. After appropriate experiments are designed and deployed, formal data

analysis and physical modeling may require days or weeks. The time-consuming process of manual post-experiment data organization, formatting, analysis, and modeling represents a critical bottleneck in the high-throughput experimental workflow.

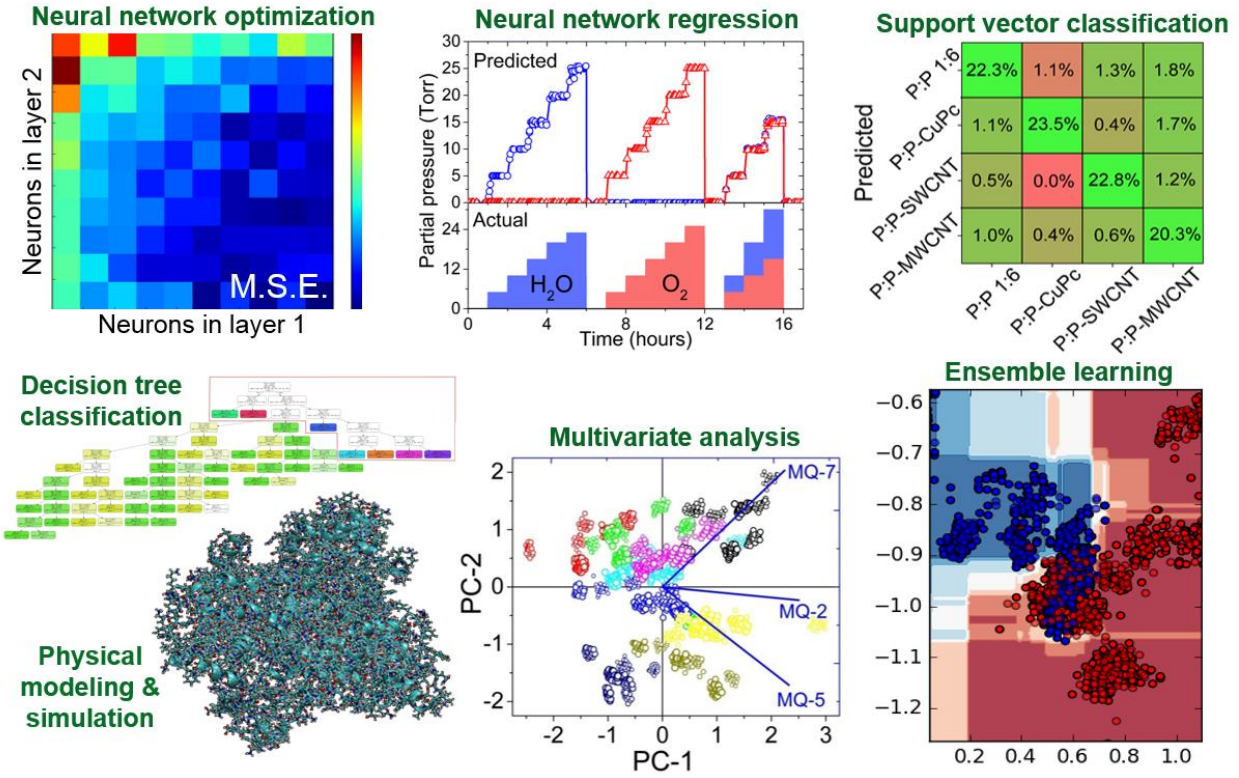

Figure 3. Examples of ex situ machine learning and physical modeling performed on data collected using the IMES workflow. Neural network regression and support vector classification images are reproduced from ref.[35]. Physical modeling and simulation image is reproduced from ref.[40].

Proposed Research

Some of the challenges associated with high-throughput materials characterization may be mitigated by incorporation of computer-based decision-making and real-time data analytics into experimental control software. Machine learning and algorithmic-based methods for control of data acquisition and processing have shown promise for increasing efficiency of functional materials screening[38, 40-42], leading authors of a 2018 Materials Acceleration Platform (MAP) report to conclude that their primary research goal is to create and deploy laboratories that "autonomously design, perform, and interpret experiments"[43]. Computer-controlled experiments may reduce redundancies in sequential human-designed experiments and provide a valuable supplement to labor-intensive researcher-led experiment planning. Combining in situ data analytics with computer-based planning allows sending of feedback to experimental control systems, enabling iterative experimental design based on real-time response of samples under

test. Experiments which incorporate fully-automated in situ data analytics allow researchers to observe model parameter evolution in real-time, enabling rapid hypothesis formation and assessment which reduces the need for lengthy data processing after experiment termination. Additionally, researchers would have access to unexplored benefits of mixed-mode analytics in which output from multiple functionality characterization channels may be viewed simultaneously. To supplement tradition physical and statistical models, a variety of regression-based machine learning (ML) algorithms including artificial neural networks (ANNs), random forests (RFs), and support vector regressions (SVRs) may be used to enable more accurate modeling and prediction of nonlinear high-dimensional data. Machine learning has been successfully applied to materials science in fields of materials design and discovery[6, 44] and microscopy[45], and has been implemented in post-processing of data streams produced during IMES-based experiments for gas discrimination and materials identification[35], biomolecule classification[37], deconvolution of pressure and humidity[31], and classification of ambient environmental conditions[38] (Figure 3). However, the use of most ML algorithms requires lengthy pre-processing procedures and is therefore limited to applications which may be deployed only after termination of active experiments. For full advantages of ML-based analytics to be realized, preprocessing and modeling of data must be performed in situ using automated routines to enable real-time prediction of material response.

This proposal is designed to assess the feasibility of supplementing or replacing experienced researchers with a system of iterative physical models and self-learning algorithms for efficient design of experimental conditions and automated initiation and termination of experimental procedures. Data processing and analysis which is typically performed after completion of an experiment will be integrated into IMES control software for streamlining post-experimental procedures and enabling rapid interpretation of experimental results. An example of a computer-controlled experimental workflow is shown in Figure 4. In the standard workflow (left panel), a human must design experimental conditions, process data, and manually apply models to data after each experiment to optimize settings for the next iterative experiment. These time-consuming procedures (represented by red boxes) are eliminated by use of a computer-controlled workflow (right panel), which utilizes automated data processing, analysis, and feedback for more efficient data collection and model-building. The goal of the proposal is to demonstrate a working prototype of a computer-controlled thin film characterization experiment in which results from in situ data analytics are used as inputs for iterative self-learning of optimal experimental conditions. This goal will be addressed in three stages:

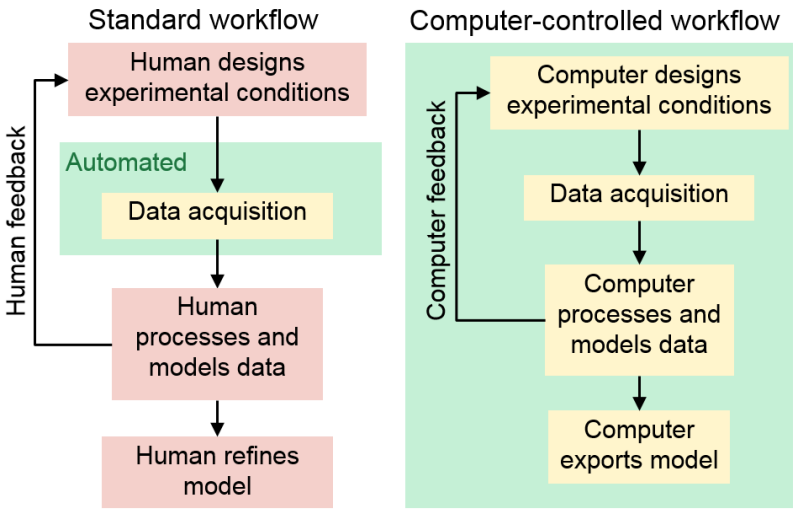

Figure 4. Standard experimental workflow (left) and computer-controlled workflow (right). Red boxes represent time- or labor-intensive procedures. Boxes inside green region are automated by control software. The goal of the proposal is to automate all time-intensive processes in the workflow.

Stage 1: Integrate custom QCM software currently used for post-experiment data processing, physical modeling, and machine learning into IMES control software. The QCM provides an attractive system for in situ data analytics because of its rich multi-frequency spectral data output which may be modeled using equivalent electrical resonator circuits[46] and acoustic viscoelastic representations[47-48]. For real-time preprocessing of QCM data, conductance spectra will be smoothed using a second-order univariate spline fit. Peaks in the smoothed spectrum will be detected automatically using a custom peak-detection algorithm written in Python. For equivalent electrical circuit modeling, resonant peaks in QCM impedance spectra will be fitted to the Butterworth Van Dyke (BVD) resonator circuit model[46], allowing extraction of position, width, and equivalent RLC values associated with each resonant peak. Multi-frequency response will be used to estimate the relative contributions of mass change and viscoelastic change to total frequency shift using Kanazawa's model for response of QCM in contact with a fluid[48]. Changes in peak position (Δf) and peak width (ΔD) will be used as inputs for solving simultaneous equations for film shear modulus (μ) and viscosity (η) using the continuum mechanics approach elucidated by Voinova and coworkers[47]. In situ analysis of multi-frequency QCM spectra will enable real-time display of Δf, ΔD, $\Delta\mu$, $\Delta\eta$, and equivalent ΔR, ΔL, and ΔC values.

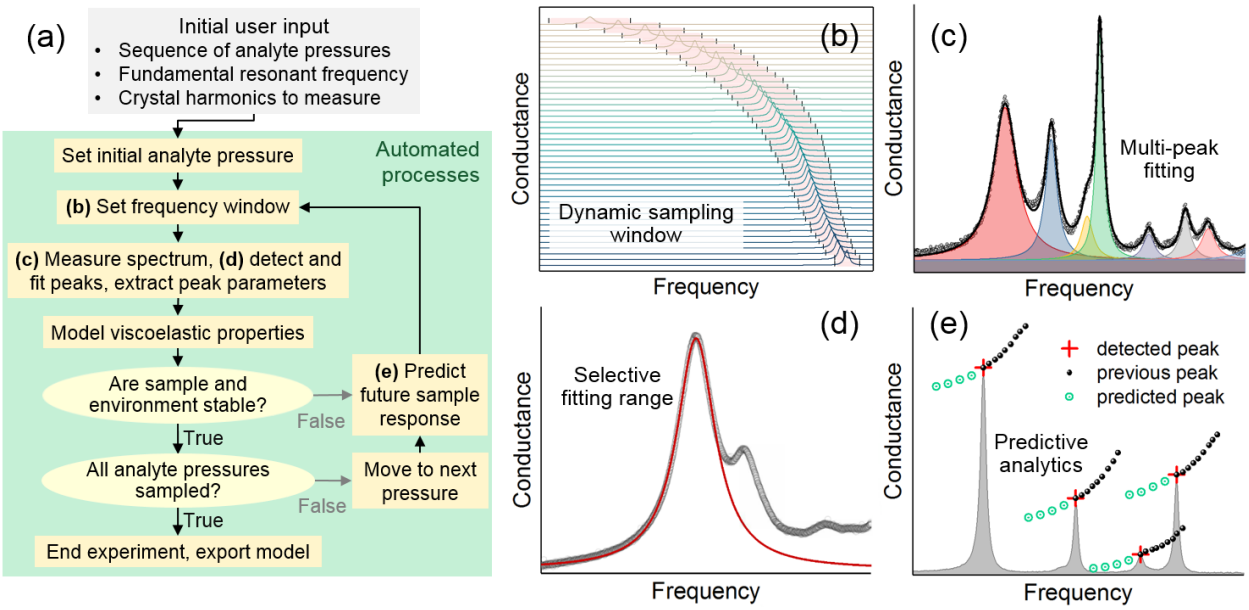

Figure 5. (a) Flowchart describing incorporation of real-time analytics and modeling into a feedback loop for semi-autonomous experimental design of QCM experiments under varying analyte pressures. User input (gray box) is used to initiate the experiment, which uses in situ modeling of QCM response to (b) automatically select the appropriate frequency measurement sampling window, (c) perform multi-peak fitting of conductance spectra to allow (d) subtraction of spurious overtone peaks and selective fitting of main resonant peaks, and (e) perform modeling for prediction of future sample response.

Stage 2: Demonstrate working prototype of feedback-controlled QCM experiment by enabling IMES to control instrument settings and change environmental conditions iteratively using results from real-time modeling and analysis. Calculated parameters from QCM experiments and their derivatives with respect to changes in environment (pressure, temperature, relative humidity) will be used as feedback for automated adjustment of experimental control software. The system will use a sequence of analyte pressures, the fundamental crystal resonant frequency, and a list of crystal harmonics of interest as the only user inputs (Figure 5a). Initial frequency measurement windows will be set automatically based on the resonant frequency of the crystal and crystal harmonics of interest. The peak position and peak width calculated at each crystal harmonic will be used to adjust bandwidth of the measured frequency range, enabling a self-learning, iterative, dynamic frequency window which tracks position of the resonant peak and ensures that tails of the peak are not truncated due to shifts outside of the measured frequency window (Figure 5b). Multi-peak fitting of conductance spectra (Figure 5c) will allow subtraction of contributions from auxiliary overtone peaks, resulting in a selective-fitting procedure which ensures that the shape of the main peak fit is not distorted by the presence of spurious modes (Figure 5d). By modeling the change in peak positions over time, the software will predict positions of the next peaks to further improve selection of the center and bandwidth of the next measured frequent widow (Figure 5e).

Peak intensities and the baseline conductance will be used for estimating signal-to-noise ratio (SNR) of the QCM impedance spectra. The SNR will be used as feedback to the central control software for iterative adjustment of integration time and sampling rate. For real-time autonomous control of environmental conditions during the experiment, changes in positions and widths of the resonant peaks at each crystal harmonic will be used to calculate the derivative of BVD model parameters with respect to changes in ambient environment (i.e. temperature, pressure, relative humidity). Environmental conditions which result in the most significant spectral response will be identified and used as feedback for the control software so that they can be re-sampled at higher resolution to efficiently capture details in the dynamics of film response.

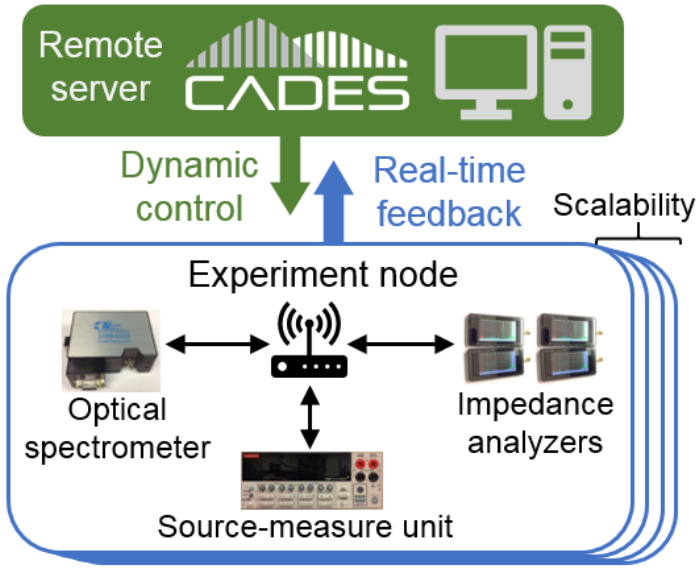

Figure 6. Schematic of workflow for remote server-controlled experiment node which enables autonomous film characterization using simultaneous optical, electrical, and gravimetric modes. The experiment node streams data to the CADES remote server, where it is processed and used for real-time feedback for designing dynamic experimental conditions. The system allows adding an arbitrary number of experiment nodes, enabling significant scalability.

Stage 3: Run semi-autonomous thin film characterization experiments by extending in situ data processing and feedback to include analysis of electrical and optical modes. Results from modeling of electrical and optical thin film response will be used to supplement QCM response for feedback into environmental control software, enabling semi-autonomous characterization experiments. Environmental conditions and measurement settings will be determined iteratively using dynamic feedback from simultaneous gravimetric, electrical, and optical data streams (Figure 6). The system will offload data to the Compute and Data Environment for Science (CADES) remote server where it will be processed and modeled. Results from analysis will be transmitted to the experiment node where they will be used for dynamic control of instruments for adjustment of measurement settings and environmental conditions. A single CADES virtual machine may control several experiment nodes, enabling significant scalability of the system.

During measurement and analysis of QCM impedance spectra as described in stages 1 and 2, concurrent measurements of electrical impedance, I-V, and C-V characteristics will be carried out on films deposited on interdigitated electrodes. Maximum sweep voltage will be determined automatically based on measured film current and rate of change of current with respect to applied voltage. Frequency range and applied AC voltage in impedance measurements will be determined by measured sample impedance and SNR in impedance spectra. Electrical impedance data will be fitted to an appropriate equivalent circuit model based on the shape and number of semi-circles detected in the Nyquist plot. Optical absorption/transmission spectra will be analyzed using the spectral fitting tools previously developed for analysis of QCM conductance spectra (Figure 5). Intensity of excitation light, measured wavelength range, and integration time will be controlled autonomously using feedback from previously measured optical spectra. The resulting system will be a fully-autonomous scalable multifunctional film characterization tool with native capability for in situ data analytics and modeling.

Summary

Rapid materials discovery and development relies on high-throughput functional characterization of thin film materials under a broad range of ambient environmental conditions. To automate rapid film characterization, we developed an integrated multi-modal environmental system (IMES) at Center for Nanophase Materials Sciences. Primary challenges related to operation of IMES include design, planning, and optimization of experimental measurement conditions and processing, analysis, and modeling of multi-modal characterization data. To address these challenges, we propose to integrate data processing and analytics into central IMES software for creating a feedback loop between material response and experimental control. This goal will be addressed in three stages:

1. Integration of gravimetric data processing and analysis into experimental control software for real-time analytics and modeling.
2. Feedback of gravimetric modeling into experimental settings for automated tuning and optimization of measurement parameters and environmental conditions.
3. Extension of real-time feedback to include electrical and optical characterization modes and offloading of data to a remote server for enabling increased stability of the system.

Development of the computer-controlled IMES feedback system will allow efficient experimental design and real-time data analytics for significantly increasing throughput of multi-functional thin film characterization experiments under a broad range of ambient environmental conditions. The resulting instrument suite and central control software will represent a significant advance toward creation of a system capable of carrying out autonomous design, execution, and analysis of experiments.

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