Fundamentals and Technology of Multifunctional Materials and Devices
Room On Demand - Session C1

Optical Materials: Design, Synthesis, Characterization, and Applications

C1-1 INVITED TALK: Measurement of Feature Dimension and Shape for Nanowire Test Structures Using Mueller Matrix Spectroscopic Ellipsometry based Scatterometry and Small Angle X-Ray Scattering*, Alain C. Diebold (adiebold@sunypoly.edu),* SUNY Polytechnic Institute Albany, USA **INVITED**

One of the most difficult measurement challenges is non-destructively determining the feature dimensions and shape for complicated 3D structures. An interesting and challenging example structure is the Nanowire Test Structure which is used to develop etch processes which produce vertically stacked nanowires from a multi-layer film stack of Si/SixGe1-x/Si/SixGe1-x/Si .(1, 2, 3) This presentation will review Mueller Matrix Spectroscopic Ellipsometry based scatterometry which uses the Rigorous Coupled Wave Approximation (RCWA) to solve Maxwell's equations for a model structure and the resulting Mueller Matrix elements are compared to experimental results. We also present the use of critical dimension –small angle X-ray scattering characterization. This method uses high energy synchrotron X-Ray scattering to obtain diffraction results from the same periodic array used for scatterometry.

References

[1] Alain C. Diebold, Anthony Antonelli, and Nick Keller, Perspective: Optical measurement of feature dimensions and shapes by scatterometry, APL Mat. **6**, (2018), 058201. doi: 10.1063/1.5018310.

[2] Sonal Dey, Alain Diebold, Nick Keller, and Madhulika Korde, Mueller matrix spectroscopic ellipsometry based scatterometry simulations of Si and Si/SixGe1-x/Si/SixGe1-x/Si fins for sub-7nm node gate-all-around transistor metrology, Proc. SPIE 10585, Metrology, Inspection, and Process Control for Microlithography XXXII, 1058506 (6 June 2018); doi: 10.1117/12.2296988

[3] Madhulika Korde, Subhadeep Kal, Cheryl Pereira, Nick Keller, Aelan Mosden, Alain C. Diebold, Optical Characterization of multi-NST Nanowire Test Structures using Muller Matrix Spectroscopic Ellipsometry (MMSE) based scatterometry for sub 5nm nodes, Proc. SPIE Metrology, Inspection, and Process Control for Microlithography XXXIII, (2019).

C1-3 Optical Probing of Vanadium Oxide Thin Film Composition and Phase*, M. Junda,* ***Nikolas Podraza (nikolas.podraza@utoledo.edu),*** University of Toledo, USA

Vanadium oxides have a range of compositions and phases made possible by multiple valence states of vanadium and the high defect tolerance of some phases. Several types of vanadium oxides have found application or are of interest as imaging layers in infrared sensors (VO_x), phase change materials (VO_2), and electrodes for energy storage (V_2O_5). For each application, different optical and electronic characteristics are required which depends strongly upon the chemical composition, crystal structure (if applicable), and amorphous vs. crystalline ordering of the material. Optical property variations with these characteristics are complicated but enable the use of spectroscopic ellipsometry as a diagnostic of film deposition, post-deposition processing, and operational use. Here, infrared to ultraviolet range spectroscopic ellipsometry is performed on vanadium oxide materials to extract the optical response in the form of the complex dielectric function spectra and relate its characteristics to amorphous film composition, crystal phase after annealing, and changes during temperature driven phase transformations. Amorphous VO_x films are deposited via reactive sputtering of a pure vanadium target in an $Ar+O_2$ ambient onto glass substrates at room temperature. Composition is deduced from variations in the amorphous phase complex dielectric functions. Initially amorphous films are then annealed into polycrystalline materials with the phase dictated by starting composition; in two examples room temperature orthorhombic V_2O_5 and monoclinic VO_2 are produced from initially amorphous x = 2.5 and 2.0 VO_x, respectively. VO_2 exhibits temperature-dependent opto-electronic properties resulting from a metal-insulator transition (MIT) at the easily accessible temperature of ~67ºC from the rutile phase at high temperatures to the monoclinic phase at room temperature. Taking advantage of this switching capability, VO_2 is used for infrared imaging, thermochromic infrared-selective filtering in windows, and has shown potential to be useful in memory and transistor computing electronics. *In situ* SE measurements of VO_2 films are collected as a function of temperature over the infrared to the ultraviolet (0.08 – 5.9 eV) spectral range. In addition to determining the optical response of the metallic and semiconducting VO_2 phases, incremental changes in the complex optical response are tracked as VO_2 is cycled through the MIT.

C1-4 INVITED TALK: Metrology for Emerging Semiconductor Devices and Processes*,* ***Ndubuisi George Orji (ndubuisi.orji@nist.gov),*** National Institute of Standards and Technology (NIST), USA **INVITED**

As semiconductor device design undergoes a transformation from laterally-aligned to vertically-aligned gates, and from CMOS-based to beyond CMOS-based architectures, the increased number of materials and device-structure complexity pose new challenges for the metrology needed for characterization and process control. Patterning techniques such as extreme ultraviolet (EUV) lithography, which is expected to be the leading-edge high-volume lithography method for the next decade, also pose a host of measurement problems. In addition, new architectures, such as those based on 2D heterostructures, crossbar memristors, and carbon nanotubes have been proposed. Although the metrology and process control tools needed for some of these new architectures are not yet developed, the challenges are well known. These include smaller sizes, hard-to-obtain optical properties, materials and films with low imaging contrast, and atomic scale defects, among others.

This confluence of small dimensions, new materials and processes, and complex structures requires new approaches. This talk will give an overview of key metrology and characterization requirements for emerging semiconductor devices and processes. The goal is to highlight possible solutions and approaches.

One approach is hybrid metrology, which refers to the use of different techniques to determine the value of a parameter. The large number of process-control parameters for new and proposed device structures means that no single instrument has the required level of resolution, range, and sensitivity needed to adequately characterize the material properties and three-dimensional structure of the devices. I will describe some of the benefits of hybrid metrology and show application examples. I will also describe metrology needed for EUV lithography. Feature sizes and tolerances from EUV lithography are now approaching a level where the molecular size of the resist material affects the printability and size variability of the final features. These variabilities, which are stochastic in nature and show up as surface, linewidth and line edge roughness and defects, are in some cases beyond the detection limits of optical inspection tools.

The importance of metrology in semiconductor manufacturing cannot be overstated. This is underscored by the number of processes where the unavailability of adequate metrology could be a potential showstopper. Although some emerging semiconductor devices fall under this category, there are a variety of new and old techniques and approaches that could be helpful in addressing their metrology needs.

C1-6 Chemical Bath Deposition of ZnO Nanorods on Ion-plated ZnO:Ga Seed Layers and Their Structural, Photoluminescence and UV Light Detecting Properties*,* ***Tomoaki Terasako (terasako.tomoaki.mz@ehime-u.ac.jp),*** *S. Obara, N. Hashikuni, S. Namba,* Ehime University, Japan*; M. Yagi,* National Institute of Technology (KOSEN), Kagawa College, Japan*; Y. Furubayashi, T. Yamamoto,* Research Institute, Kochi University of Technology, Japan

Zinc oxide (ZnO) has many excellent properties, such as a wide band gap (E_g) of ~3.37 eV, a large exciton binding energy of ~60 meV, high transparency, piezoelectricity and thermoelectricity. Among various techniques for preparing the ZnO nanostructures, we have paid our attention to chemical bath deposition (CBD) because this technique is usually performed at low temperatures (<100 °C), which allows us to use polymers as substrate materials. In our previous paper, successful CBD growth of vertically aligned ZnO nanorods (NRs) on ion-plated Ga doped ZnO (IP-GZO) seed layers has been reported. Moreover, we reported that the PEDOT:PSS/CBD-ZnO NRs heterostructures exhibited rectifying characteristics in dark and photocurrent under the light illumination [1]. In this paper, structural and PL properties of the NRs and the device performance of the PEDOT:PSS/ZnO NRs/GZO heterostructures will be discussed in terms of the average width of the NRs (W_{av}).

The ZnO NRs layers were grown on the IP-GZO seed layers by CBD using the aqueous solution of 0.05 M $Zn(NH_3)_2{\cdot}6H_2O$ and 0.05 M $C_6H_{12}N_4$. Bath temperature was kept at ~86 °C. The growth time was varied in the range of 5-360 min. The PEDOT:PSS layers were deposited on the NRs layers by spin-coating (3000 rpm, 30 sec), followed by thermal annealing in the air at 80 °C for 20 min.

It was confirmed that the photocurrent was effectively generated by the illumination of the UV light corresponding to the E_g of ZnO, indicating that both the electrons and holes contributed to the photocurrent generation. It was also found that the increase in W_{av} led to the decrease in the barrier height (Φ_B) and the increase in ideality factor (n). The larger the W_{av}, the lower the density of the surface states capturing electrons by forming adsorbed oxygen molecular ions (O_2^-s). Therefore, the band bending at the surface region becomes smaller with the increase in W_{av} [2]. Time response curves for the PEDOT:PSS/CBD-ZnO NRs heterostructures exhibited very long response and recovery times, which cannot be explained without the help of the surface reaction. These results indicate that the adsorption and desorption of the O_2^-s to the surfaces of the NRs dominate the device performance [3].

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References: [1] T. Terasako *et al.*, Thin Solid Films 677 (2019) 109-118. [2] S. Shi *et al.*, J. Appl. Phys. 109 (2011) art. no.103508. [3] C. Soci *et al.*, Nano Lett. 7, (2007) 1003-1009.

C1-7 IR Mirror Coating for Evacuated Thermal Collectors: Design and Optical Characterization*,* ***Daniela De Luca (daniela.deluca@na.isasi.cnr.it)****,* UniNa and CNR-ISASI, Italy*; E. Di Gennaro,* UniNa Università degli studi di Napoli "Federico II", Italy*; C. D'Alessandro, A. Caldarelli, D. De Maio, E. Gaudino,* UniNa and CNR-ISASI, Italy*; M. Musto,* UniNa Università degli studi di Napoli "Federico II", Italy*; R. Russo,* CNR-ISASI, Italy

Capturing solar radiation as high-temperature heat in solar thermal devices is challenging, especially if flat panels are used instead of concentrating systems. While a high-vacuum encapsulation helps suppressing the conductive and convective losses, the radiative term rise with temperature, according to the Planck's law of blackbody radiation.

To reduce that loss and increase the panel efficiency, we propose an optimized infrared mirror coating. The underlying mechanism is based on the cold-side external photon recycling: the mirror has to be highly reflective in the mid-IR region, to reflect and thus recapture infrared emission back at the absorber. On the contrary, in the visible and near-IR region it has to be highly transparent, to transmit the incident solar power. To obtain its best configuration, optical simulations have been performed and results showed that the best configuration is reached if a rugate filter design is used. Rugate filters are made of alternating layers of dielectric materials, with a continuous and periodic variation of the refractive index as a function of optical thickness.

Previous theoretical [1] and experimental works [2] show that the continuous profile of a rugate filter can be approximated by a reduced number of layers with steps in the refractive indices. Here, we extend prior works and include a realistic set of materials for ease of fabrication.

The Physical Vapor Deposition (PVD) technique has been used for thin films deposition of Si-based materials, i.e. Silicon Oxides, Oxynitrides, and Nitrides. Their strong dependence on the environmental conditions during deposition (pressure, gases flux,...) allow us to obtain different refractive indices from the same cathode of Si, meeting the limitation of most deposition tools on the number of target available.

We present here the optical characterization of the produced samples, including measurements performed with the ellipsometer, integrating sphere connected to an optical spectrum analyser, profilometer, and FTIR spectroscope. This analysis is useful to deeply study all the additional parameters (thickness, roughness, refractive index coupling and matching) that can interfere with the optical and physical properties of the materials. Preliminary results on multilayer structures are also shown and compared, with the aim of choosing the most promising ones for the realization of the final structure.

[1] Baumeister, P., Appl. Opt.25,2644–2645 (1986), doi: 10.1364/AO.25.002644

[2] De Luca, D. et al., Proc. SPIE 11496, New Concepts in Solar and Thermal Radiation Conversion III, 1149605 (2020), doi:10.1117/12.2574604

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