

Thin Film

Room 2022 - Session TF-ThM

Fundamentals in Thin Film Deposition

Moderator: M.C.M. Van De Sanden, Eindhoven University of Technology, The Netherlands

8:00am **TF-ThM1 Tilted Fiber Texture in Aluminum Nitride Thin Films**, *J.M.E. Harper*, University of New Hampshire, US; **D. Denz**, University of New Hampshire; *J.W. Hoehn, F. Chen*, Seagate Technology Inc.

We report a strong dependence of fiber texture tilt angle on the angle of deposition and gas composition in aluminum nitride (AlN) thin films prepared by reactive magnetron sputtering in N₂/Ar mixtures. Texture distributions were measured using x-ray pole figures. For fully nitrated films, deposited with N₂ flow of 15% of the total flow, the AlN c-axis fiber tilt angle increases steadily with deposition angle, with the c-axis approximately aligned with the deposition direction. At a deposition angle of 64° from normal, a second population of grains appears with c-axis perpendicular to the main population, corresponding to a-axis alignment with the deposition direction, as reported by Rodriguez-Navarro et al. We measured the c-axis AlN tilt angle as a function of N₂ flow ratio for a deposition angle of 42° from normal, and found that the c-axis remains perpendicular to the substrate for a N₂ flow ratio up to 12%, and then abruptly shifts towards the deposition direction for a N₂ flow ratio above 12%. We also identified a range of deposition parameters at lower N₂ flow in which an amorphous phase of AlN is formed. We attribute the tilted fiber texture to the energetic atom flux causing less damage and resputtering in grains oriented with open channeling directions, compared with non-channeling directions in AlN. The abrupt change in fiber tilt angle vs. gas composition is attributed to adatom mobility being quenched above 12% N₂ flow. @FootnoteText@ @footnote 1@A. Rodriguez-Navarro, W. Otano-Rivera, J.M. Garcia-Ruiz, R. Messier, and L.J. Pilione, J. Mater. Res., Vol. 12, No. 7, 1689 (1997).

8:20am **TF-ThM2 CVD of Titanium Diboride using Single Source Precursor**, **N. Kumar**, *Y. Yang, W. Noh, G. Girolami, J. Abelson*, University of Illinois Urbana-Champaign

TiB₂ is a mechanically hard, metallic ceramic with a bulk melting temperature of 3220 °C and electrical resistivity of 10 μΩ·cm. Thin films of TiB₂ have been used as wear resistant protective coatings in magnetic storage media and other applications. TiB₂ has also been investigated as a possible liner material and/or contact electrode in microelectronics. CVD growth of TiB₂ can be accomplished using halide based precursors, but this process is inherently corrosive and requires substrate temperatures in excess of 600°C. Girolami et al. previously synthesized the halogen free, single source precursor Ti(BH₄)₃dme. This talk will focus on the CVD of TiB₂ films using this precursor, including the deposition kinetics, film microstructure, diffusion barrier properties and conformality on trench shaped substrates. Films were grown at substrate temperatures ranging from 170 to 800 °C. Films grown at lower temperatures are X-ray amorphous whereas films grown at 800°C are polycrystalline. Film growth starts at temperatures as low as 170 °C on SiO₂ substrates. The growth rate is 2 nm/min below 200°C, 4 nm/min for intermediate temperatures, and 2.5 nm/min at 800 °C. There is no nucleation delay as measured by in situ ellipsometry, even at the lowest growth temperatures. For the lowest and highest growth temperatures, the films are nearly stoichiometric and have C and O contents lower than 5 at. % as measured by AES. In the intermediate temperature range the films have B/Ti ratio < 2 and the C and O contents are > 10 at. %. Low temperature films have a dense columnar microstructure as evaluated by SEM. For a 40 nm thick film, the RMS roughness by tapping mode AFM is 1.5 nm. The electrical resistivity is 265 μΩ·cm. The film also performed well as a diffusion barrier to prevent Cu diffusion into Si for temperatures as high as 600 °C.

8:40am **TF-ThM3 Fundamentals in Thin Film Pulsed Laser Deposition: Growth Control at an Atomic Level**, **D.H.A. Blank**, University of Twente and MESA+ Institute for Nanotechnology, The Netherlands **INVITED** Pulsed Laser Deposition (PLD) is attractive for research on complex oxides because it is fast and one can easily investigate a wide range of different materials and compositions. Currently, a major issue in the growth of oxide materials with PLD is the control of the surface morphology. For most

materials it is necessary to control the thickness and roughness of the thin films down to an atomic scale. Such well-controlled growth can also be used to manufacture artificially layered structures of, e.g., ferroelectric materials. In this way it is possible to create a whole new class of materials. It would be possible to create materials tailor-made to applications. Such materials are also ideal for the purpose of understanding the physics and the search for materials with even yet not-known properties. Much effort is put in the deposition of excellent textured layers without grain boundaries. In general the properties of highly oriented films approximate the properties of single crystals. Single or multi-layer structures require a well-conditioned process technique. The deposited layers must have a large homogeneity with well-defined material properties, smooth surfaces, and, in the case of oxides, the correct oxygen stoichiometry. Growth monitoring became possible even at relative high deposition pressures using ellipsometry and so-called high pressure Reflecting High Energy Electron Diffraction (RHEED). These developments have helped to make PLD a grown-up technique to fabricate complex materials and structures. With our development of HP RHEED PLD we are able to control the growth of these materials and to introduce new growth manipulations, like pulsed laser interval deposition. At present, extremely sharp and homogeneous interfaces can be realized and this is, for example, yet utilized in SrTiO₃/LaAlO₃ interfaces and artificial ferroelectric structures. In this presentation I like to show these unique techniques and the obtained results to design complex materials 'on demand'.

9:20am **TF-ThM5 Solvation Effects in the Kinetics of Supercritical CO₂ Based Deposition of Metal Oxide Thin Films**, **Q. Peng, K.J. Park, D. Hojo, D. Barua, G.N. Parsons**, North Carolina State University

Supercritical CO₂ (scCO₂) offers unique solvent properties for metal-organic deposition, such as high solubility, high diffusion rate, zero surface tension, and high penetration ability. In our work, supercritical carbon dioxide process has been successfully used to deposit a variety of metal oxides including Ga₂O₃, Al₂O₃, ZrO₂, FeO_x, Cr₂O₃, Co₃O₄, and WO_x thin films on native oxide silicon wafer from direct pyrolysis of organometallics. Conformal and reflective metal oxide films with good adhesion have been obtained. The kinetics of Al₂O₃ and Ga₂O₃ deposition has been studied to show the mechanism of scCO₂ based deposition process. For example, for Al₂O₃ deposition from Al(acac)₃, the deposition rate at 200°C is observed to be 10nm/min, compared to <1nm/min for typical vacuum based CVD from the same precursor. Similar results were observed for Ga₂O₃ thin film from Ga(acac)₃. Moreover, an overall activation energy of 60-70 kJ/mol and 80-85 kJ/mol were observed for pyrolysis of Al(acac)₃ and Ga(acac)₃ in scCO₂ phase, respectively, which are less than typical values obtained in vacuum CVD. Solvation energy of stabilization of the reaction transition state is suggested as the main reason for the enhanced surface reaction rates. The reduced kinetic barrier will be discussed in terms of relative polarity of the solvent and transition state structure. The solvation effect of scCO₂ can enable lower process temperature to enable material processing on temperature-sensitive surfaces.

9:40am **TF-ThM6 Formation of c-Si/a-Si:H Interfaces Studied by Real-Time Second-Harmonic Generation, Spectroscopic Ellipsometry, and Infrared Spectroscopy**, **J.J.H. Gielis, P.J. van den Oever, B. Hoex, M.C.M. Van De Sanden**, Eindhoven University of Technology, The Netherlands; **W.M.M. Kessels**, Eindhoven University of Technology, The Netherlands, Netherlands

The properties of crystalline silicon / amorphous silicon (c-Si/a-Si:H) interfaces are of key importance for new developments in solar cell research, e.g. to obtain high efficiency silicon heterojunction (SHJ) solar cells or diffused emitter solar cells with an excellent level of surface passivation. We have studied the interface formation between H-terminated Si(100) and a-Si:H in a hot-wire chemical vapor deposition process (HWCVD). The interface formation has been studied in real-time for films between 5 and 70 nm using three different optical diagnostics simultaneously. Spectroscopic ellipsometry (SE) has been used to determine the optical properties of the a-Si:H, the film thickness and the surface roughness evolution and gives insight into the nucleation phase of film growth. Information on the hydrogen bonding modes and hydrogen depth profile in the film has been obtained by attenuated total reflection (ATR) infrared spectroscopy. Second-harmonic generation (SHG), a nonlinear optical technique sensitive to surface and interface states, has been used both in real-time and spectroscopically in the fundamental photon energy range of 1.33-1.75 eV. In this range the SHG signal is governed by two-photon resonances related to modified Si-Si bonds in the

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surface and interface regions of the c-Si and a-Si:H. The spectral width of the resonances provides a distinction between c-Si and a-Si:H. The spectra indicate that the SHG signal is generated mainly at the c-Si/a-Si:H interface. From the real-time experiments detailed information into the c-Si/a-Si:H interface formation is obtained, such as: the nucleation of a-Si:H islands on the c-Si along with SiH_x surface species, the occurrence of film 'closure', and the appearance of bulk SiH_x together with a correlation with the SHG signal. On the basis of these observations key aspects of the c-Si/a-Si:H interface formation will be discussed.

10:00am **TF-ThM7 Kinetic Pathways Leading to Layer-By-Layer Growth: A Multibillion Time-Step Molecular Dynamics Study**, *V. Chirita, D. Adamovic, E.P. Münger, L. Hultman*, Linköping University, Sweden; *J.E. Greene*, University of Illinois, Urbana

We employ multibillion time-step embedded-atom method molecular dynamics simulations to study homoepitaxial growth of Pt(111) during low-energy (5 - 50 eV) Pt irradiation at 5 eV intervals. We deposit 5 monolayers at 1000K and with fluxes corresponding to deposition rates of 5x10⁴ @super 5 @ μm/min and 5x10⁴ @super 4 @ μm/min, i.e. only 3, respectively 2, orders of magnitude higher than experimental rates used in electron beam-physical vapor deposition (EB-PVD). To analyze the results we calculate normalized anti-phase intensities, as measured in reflection high-energy electron diffraction (RHEED), and detect a 3-dimensional (3D) growth mode for energies of up to 20 eV. However, for E = 20 eV and higher, the RHEED intensities signal the transition to layer-by-layer growth mode. In order to determine the mechanism responsible for the observed change in the growth mode we isolate, with unprecedented accuracy, the effects of irradiation-induced processes from thermally activated mass transport during deposition. We find that for all energies irradiation events are completed within 10 ps following impacts while thermal migration is not affected by the deposition energy. We provide direct evidence that the energy threshold observed at 20 eV (and observed in many experimental studies) is entirely due to the atomic processes induced by the irradiation process, in the first 10 ps following the arrival of energetic species. Adatom scattering, surface channeling, dimer formation and cluster disruption are identified as primary mechanisms responsible for 2-fold and 5-fold increases in intra-, respectively interlayer, mass transport rates as irradiation energy is increased from 10 to 20 eV. The same kinetic pathways, leading to an even more clear transition from 3D to layer-by-layer growth, are identified in μs-long (multibillion time step) MD simulations carried out at fluxes approaching experimental conditions. Our results should apply to most fcc (111) metallic planes and have added significance in the low-temperature regime, where thermal processes are exponentially depressed, as it will be discussed.

10:20am **TF-ThM8 Interpretation of the Roughness in Au(111) Polycrystalline Films**, *E. Rodríguez-Canas*, Instituto de Ciencia de Materiales de Madrid (CSIC), Spain; *J.A. Aznarez*, Instituto de Física Aplicada (CSIC), Spain; *E. Vasco, J.L. Sacedon*, Instituto de Ciencia de Materiales de Madrid (CSIC), Spain

Recently, the surface morphology of columnar polycrystalline Au(111) films grown by thermal evaporation on native SiO_x-covered Si(100) has been investigated by scanning tunneling microscopy (STM). The STM images reveal that the surface can be broken down into columnar-assembled paraboloidal-like elements. The analysis method based on the surface decomposition into single elements introduces a complete set of statistical parameters related to the elements shapes and allows to quantitatively characterize the Au(111) growth front. The height distribution curves of the imaged surfaces are described by means of an explicit expression of these shape parameters, which are connected with phenomena that control the columnar growth and the growth front evolution. After summarizing these results, we will show that the usual roughness or interface width can be decomposed as an algebraic expression of the statistical set of parameters. This expression allows to decompose the roughness into components with well-defined meanings. The roughness expression is applied to analyze the scaling laws of the roughness with deposition time in the Au(111) films and it is successfully compared with the experimental results. We extend the roughness analysis method proposed here to surface morphologies formed from elements with other shapes (e.g., conical- or spheroidal cap-like elements). The application of the method is suitable for columnar as well as for growth fronts composed by mounds. The relation of the components of the roughness with the various kinds of growth models is discussed. @FootnoteText@ @footnote 1@ J. L. Sacedon, E. Rodríguez-Canas, C. Munuera, A. I. Oliva, and J. A. Aznarez, Phys. Rev. B 72, 195413 (2005).

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