Thin Films
Room 303C - Session TF-MoA
Mechanical Properties of Thin Films

Moderator: B.L. French, College of William and Mary

2:00pm **TF-MoA1 Nano-Mechanical Properties of a "Solid Liquid"*, J.E. Houston,*** Sandia National Laboratories

Understanding the unique properties of nano-phase materials requires analysis of the mechanical properties at the nano-scale. Since many such materials involve the inclusion of small particulates in a polymer matrix, it is important to be able to analyze the viscoelastic behavior of the matrix in the region adjacent to the particulates, the so called â?ointerphaseâ? region. Scanning probes have the potential to be very important for this type of analysis. However, such applications are made difficult because of the critical role played by contact mechanics in the process, and at the nano-scale this quantity is not directly observable. In this presentation, an example of such an analysis is outlined involving a classic viscoelastic material, which is often referred to as a â?osolid liquidâ? or â?odilatantâ? material, but is more commonly known under the popular name â?oSilly PuttyTMâ? (trademark: Binney and Smith). This material is unusual because it exhibits elastic behavior over short experimental times (high Deborah numbers) and viscous properties over long times (low Deborah numbers). The results are presented in terms of transient relaxation measurements, using both lyophilic and lyophobic tips, followed by a Fourier analysis to obtain the broad-range frequency response. These results are directly compared with more classical bulk rheological measurements. While these initial results are not done at the true nano-scale, the discussion will include an assessment of the potential, and contact-mechanics difficulties, involved in proceeding to that regime. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:20pm **TF-MoA2 Structure and Properties of Exothermic Metal Multilayers*, D.P. Adams,*** *C. Tigges, M.A. Rodriguez, T. Buccheit,* Sandia National Laboratories

Multilayer thin films composed of reactive material pairs are currently of interest for brazing, joining and other applications. As shown extensively by Weihs et.al. several thin film material systems can be stimulated such that a rapid, self-propagating reaction occurs within a multilayer. These layers have great potential for joining, because they act as a localized, short-lived heat source. In this talk, we evaluate the properties and microstructure of two multilayer systems, Co/Al and Pt/Al, which have vastly different heats of formation. Each material system was deposited by magnetron sputtering to thicknesses in excess of 1 micron having different designs. Propagation velocities were measured by high-speed photography for both material systems, and speeds are shown to depend on bilayer thickness, premixed volume, heat of formation and substrate thermal properties. Critical thicknesses required for propagation (when attached to substrates) have been identified and are described through comparison with analytical models. Secondly, we discuss the microstructure and mechanical properties of reacted films. New (previously not reported) phases have been found after exhibiting a self-propagating exothermic reaction. For example, rhombohedral AlPt has been produced in reacted Al/Pt multilayers. We currently attribute this to the rapid quench rate following reaction to high combustion temperatures. The mechanical properties (hardness, toughness) of reacted films are also investigated, because these are critical to future applications. Attempts are made to relate these properties to reacted film microstructure.

2:40pm **TF-MoA3 A Nanometrics Feasibility Approach to Reliable Devices*, W.W. Gerberich*,** *W.M. Mook, J.M. Jungk, M.J. Cordill,* University of Minnesota **INVITED**

Rapid advances in LIGA structures and other approaches to MEMS devices could be achieved by fast turn-around screening. This could be achieved on appropriate length-scale test samples fabricated by MBE (molecular beam epitaxy), CVD (chemical vapor deposition), ALD (atomic layer deposition), and electrochemically-produced small volumes. Using nanoindenters as either indenters or compression testers, we have already demonstrated that films, nanospheres, and thin-walled nanoboxes of Au, Ti and Si can exhibit three or four levels of length scale.@footnote 1@ These and further developments regarding possible computational and combinational approaches will be discussed. @FootnoteText@ @footnote 1@W.M. Mook, "Geometry and Surface State Effects on the Mechanical Response of Au Nanostructures," Zeiss Metalkunde (2004) in press.

3:20pm **TF-MoA5 Properties and Applications of Boron Carbide Thin Films*, Y. Chen*,** *C.A. Freyman, Y.-W. Chung,* Northwestern University

Boron carbide thin films have been synthesized with pulsed dc magnetron sputtering using a boron carbide target in an ambient of pure argon. We examined the effect of substrate bias and pressure on the surface roughness and hardness of these films. Wear rates and coefficient of friction data were also obtained. As expected, an optimum substrate bias results in the atomic scale surface topography and highest nanoindentation hardness (about 40 GPa). Under normal ambient conditions, boron carbide films result in lower friction coefficient, most likely due to the formation of boric acid as a solid lubricant, reported earlier by Erdemir and coworkers. The high hardness, smooth topography and low friction even in moist environments suggest that boron carbide may be a better protective overcoat for disk drive systems.

3:40pm **TF-MoA6 Mechanical Stress in PVD Deposited Chromium Films*, G.C.A.M. Janssen,*** Delft University of Technology, The Netherlands, Netherlands*; J.-D. Kamminga, S.Y. Grachev,* Netherlands Institute for Metals Research, The Netherlands

Thin films on substrates are usually in a stressed state. Apart from the well understood thermal stress - stress occurring due to different thermal expansion coefficient of layer and substrate in combination with an elevated deposition temperature - intrinsic stress can occur resulting from the growth and/or microstructure of the film. In this presentation the mechanisms behind both tensile and compressive intrinsic stress are discussed. A set of chromium films was deposited at room temperature using PVD. These films have a microstructure in zone 2 of the Thornton model. The grain boundary density is high near the substrate-film interface and lower higher up in the film. In fact the grain boundary density as function of height in the film follows a power law. We have shown that tensile stress and grain boundary density co-develop with film thickness. This observation proves the generation of tensile stress at grain boundaries. We calculated the amount of grain boundary shrinkage responsible for the generation of tensile stress to be 0.013 nm. Films deposited at higher Ar pressure exhibit a different power law dependence on thickness. TEM revealed dense grain boundaries and small grains for the films deposited at low pressure and porous grain boundaries, separating larger feather like grains, for films deposited at higher pressures. Grains in those films have less interaction and generate less stress. Stresses in films deposited under a bias voltage were tensile for thin films and compressive for thick films. This is due to a combined effect of atomic peening, leading compressive stress and grain boundary shrinkage leading to tensile stress. It is shown that the dependence of the total stress on film thickness is described by a thickness dependent tensile term and a thickness independent compressive term.

4:00pm **TF-MoA7 Development of Zrb@sub 2@ and Hfb@sub 2@ Hard Coatings by CVD from Single Source Precursors*, S. Jayaraman*,** *E.J. Klein, Y. Yang, L. Nittala, J.R. Abelson, D.Y. Kim, G.S. Girolami,* University of Illinois at Urbana-Champaign

The transition metal diborides ZrB@sub 2@ and HfB@sub 2@ are "metallic ceramic" materials with excellent properties, including high melting temperature (> 3000 °C), low electrical resistivity (9 µm@ohm@cm for ZrB@sub 2@), high thermal conductivity (23 Wm@super -1@K@super -1@ for ZrB@sub 2@), high hardness (20 and 29 GPa for ZrB@sub 2@ and HfB@sub 2@, respectively), and great corrosion resistance. This makes them attractive candidates for monolithic or nanocomposite based hard coatings. However, there have been relatively few attempts to deposit transition metal diboride coatings by chemical vapor deposition (CVD). Here, we investigate ZrB@sub 2@ and HfB@sub 2@ growth by CVD using the single-source precursors Zr[BH@sub 4@]@sub 4@ and Hf[BH@sub 4@]@sub 4@ over the substrate temperature range 200-1000 °C. At temperatures < 500 °C, we direct a flux of atomic hydrogen, generated by a remote plasma source, onto the growth surface in order to promote the removal of excess boron and improve stoichiometry. For deposition temperatures < 500 °C the films appear to be amorphous in X-ray diffraction; for higher temperatures crystalline peaks are detected. The crystalline films are strongly textured with either (0001) or (10@super-@10) planes normal to the growth direction and display characteristic microstructures. Initial experiments on trench coverage at low temperatures show that film growth is conformal. We will report the hardness of ZrB@sub 2@ and HfB@sub 2@ films determined by nanoindentation and the relationship between the hardness, crystallinity, and microstructure. We will also outline the prospects for the growth of nanocomposite hard coatings in this materials system.

4:20pm **TF-MoA8 Effects of Sulfur Addition to Magnetron Sputtered a-C:H Thin Films**, ***C.A. Freyman**, Y.-W. Chung,* Northwestern University

Amorphous hydrogenated carbon films (a-C:H) have shown ultra low friction coefficients ($\mu<0.01$) in dry nitrogen testing environments. The ultra low friction properties degrade with the addition of water vapor to the testing environment. In this work, we explore the effects of sulfur addition to magnetron sputtered a-C:H films on elastic modulus, hardness and tribological properties as a function of relative humidity in the testing environment. Film microstructure and chemical state of sulfur have been investigated with transmission electron microscopy and electron energy loss spectroscopy. Hydrophobicity of these films are obtained via contact angle measurements. These studies show that with appropriate control of the film-substrate interface, sulfur addition of a few atomic percent is sufficient to reduce the adverse effect of humidity on friction.

4:40pm **TF-MoA9 RF MEMS Beam Stiffness Measurement Using Nanoindentation**, ***J. Vella**, S. Pacheco, P. Zurcher,* Freescale Semiconductor

With wireless communications being a major technology driver for semiconductors, on-chip integration of analog functions that are often based on passive components is crucial for reduced system form factor, higher performance, improved functionality, and reduced cost. MEMS-based resonators promise to deliver smaller and more easily integrated IF and RF filters and oscillators. The operating frequency of such filters and oscillators is defined by the mechanical resonant frequency and is given by @omega@@sub n@=@sr@(k/m), where @omega@@sub n@ is the natural resonant frequency, k is the beam stiffness and m is the beam mass. Thus, direct determination of the beam's stiffness is paramount for the design of MEMS-based resonators. The stiffness, k, can be determined for a fixed-fixed beam under a concentrated load at its center using the following equation: k=16Ew@sub r@(h/L@sub r@)@super 3@, where E is the Young's modulus of the beam material, w@sub r@, h, and L@sub r@ are the width, thickness, and length of the fixed-fixed beam, respectively. This study compares modeled beam stiffness predictions with nanonindentation measurements. A 20 µm radius diamond tip is used to deflect a resonator laminate beam composed of tantalum nitride and silicon oxynitride. Nanoindentation loads are used to induce elastic deflection of the resonator beam. The unloading portion of the nanoindentation load versus deflection curve directly yields the beam stiffness. This measurement technique was used to determine the stiffness of several resonator beam designs. Stiffnesses in the 900-5000 N/m range were measured and were within 10% of the calculated values using the above stiffness equation. In addition, derived stiffnesses from measured beam resonant frequencies (as per the resonant frequency equation above) further confirm the nanoindentation measurements.

5:00pm **TF-MoA10 Effect of Trimethylsilylation on the Film Stress of Nanoporous Silica Ultralow-k Film Stacks**, ***F.M. Pan**,* National Chiao Tung University, Taiwan*; A.T. Cho,* National Nano Devices Laboratories, Taiwan*; J.Y. Chen, L. Chang,* National Chiao Tung University, Taiwan*; K.J. Chao,* National Tsing Hua Univerisity, Taiwan

In advanced dual damascene interconnect structures, ultralow-k dielectrics must be integrated with etch stop and barrier layers, and, therefore, interfacial properties of the film stacks are critical to process yield and reliability of interconnects. In this work, the film stress and effective dielectric property of self-assembled nanoporous silica overcoated by various dielectric thin layers were studied. The nanoporous silica was prepared by spin-coating the sol-gel precursor on the silicon wafer, followed by baking and calcination. Due to the film shrinkage during thermal treatments, the as-prepared nanoporous silica films have a tensile film stress. In order to improve the dielectric property, the nanoporous silica thin film was exposed to hexamethyldisilazane (HMDS) vapor for trimethylsilylation, and a dielectric constant lower than 1.95 could be obtained. The film stress became less tensile after the HMDS treatment. The decrease of the tensile stress can be ascribed to the spring-back effect resulting from the introduction of bulky trimethylsilyl groups in the nanoporous silica layer. Three different capping layer, Si@sub 3@N@sub 4@, SiO@sub 2@ and @alpha@-SiC:H films were separately deposited on the nanoporous film at 300@sup o@C. When directly deposited on the Si wafer, all the three capping materials show compressive stress. While the capping layers were deposited on the as-calcined nanoporous silica, the film stress of the SiO@sub 2@ and Si@sub 3@N@sub 4@ layers was so large that the capping layers cracked. On the other hand, when the capping layers were deposited on the HMDS treated nanoporous silica, the film stacks showed no mechanical failure and the effective dielectric constant could be lower than 2.2. This study suggests that trimethylsilylation of the nanoporous silica low-k dielectric can effectively improve the integrity of the three film stacks in terms of mechanical strength and dielectric property.

Author Index

Bold page numbers indicate presenter