Thursday Morning, October 28, 1999

Thin Films Division Room 615 - Session TF-ThM

Nanophase Thin Films

Moderator: J.S. Zabinski, Air Force Research Laboratory

8:20am TF-ThM1 Thin Films from Slow and Energetic Cluster Impact, H. Haberland, University of Freiburg, Germany INVITED

An intense beam of clusters can be produced by first sputtering atoms into an argon atmosphere and then forming the clusters into a beam. Deposition rates of about 5 ML are observed for clusters between 1000 and 12.000 atoms of all metals tried so far (Ag, Al, Cu, Co, Mo, Ti, TiN, Pd) as well as for Si. Up to one third of the beam can be charged, so that an intense beam of cluster ions can be produced. Mass spectroscopy is used to determine the cluster size. Several examples will be discussed; e.g. Co clusters embedded in a Ag matrix for magnetic applications, Ag clusters in a SiC matrix for a two-dimensional conductor, etc. If the clusters impinge on the substrate with high kinetic energy (up to 30.000eV) they are deformed on impact and form a well adhering, smooth thin film. Unusual properties are observed: e.g. golden TiN films produced at room temperaturs, or well adhering metal films on Teflon, etc. Molecular Dynamics simulation are used to explain these unusual properties.

9:00am TF-ThM3 Spark-Processing - A Novel Technique to Prepare Light-Emitting, Nanocrystalline Silicon Films, *R.E. Hummel,* University of Florida INVITED

Scientists are constantly searching for new processing techniques which are capable of modifying the properties of materials. This could yield alternative characteristics that may lead eventually to new consumer products or, more importantly, provide a better understanding of nature. Such a new technique is spark-processing, which has been shown to change remarkably the optical properties of silicon (and other materials). Specifically, spark processing (sp) creates a substance which transforms Si into a strongly photo-luminescing and cathodoluminescing material (in contrast to ordinary Si which is not light emitting). The resulting material is extremely stable against high temperature annealings, HF etching, and laser irradiation. The emission wavelengths range from violet to green to red, depending on the processing parameters. Further, sp-Si is ferromagnetic (compared to conventional Si which is diamagnetic). A new photoresitive device has been created from sp-Si which, upon impingement of light, increases or decreases its resistivity depending on geometric variables. Sp-Si is produced by high frequency, high voltage, low current electric pulses which are applied for a short time between a Si substrate and a counter electrode.

9:40am TF-ThM5 Interesting Properties of Nanophase Films Deposited from a High-rate, Nanoparticle Beam, F.K. Urban III, A. Khabari, A. Hosseini-Tehrani, P. Griffiths, Florida International University

Nanophase thin films have been deposited by sputtering target material into a chamber designed and operated to promote condensation of the sputtered species into nanoparticles. Flowing argon and helium gas are used to sputter and assist condensation. Particle size and numbers depend on the nucleation rate, condensation rate, and time available for these processes. Films have been deposited from copper, cobalt, molybdenum, and composite copper-cobalt targets. The work to be reported here explores soft-landed nanoparticle films using no acceleration. The soft landed films are porous with nanocrystalline structure from about 5 to 10 nm crystallites. Properties of films are different from bulk and film literature values. The change in film structure with acceleration will be reported. SEM, TEM, AES, RBS, and AFM results will be presented.

10:00am TF-ThM6 Simulation of Fundamental Physical Phenomena in the Deposition of Nanophase Thin Films using a Sputtering Based Source, F.K. Urban III, A. Hosseini-Tehrani, A. Khabari, P. Griffiths, Florida International University

Recently, nanophase thin films have been deposited by sputtering target material into a chamber designed and operated to promote condensation of the sputtered species into nanoparticles. Interesting optical and magnetic properties has been reported for these films. It has been recognized that quantum size effects are most consistent with observed data. The structure of the film and the grain size determines the film properties. In this work, the classical nucleation theory has been used to understand the processes involved in the nucleation and condensation of the particles. A detailed analysis of the nanoparticle beam energy has been

carried out by deflecting, accelerating the beam and comparing the experimental data with simulations by SIMION computer code. Results of simulations and comparison to measuremnts and to the resulting depositd films will be presented.

10:20am **TF-ThM7 Deposited Porous Silicon on Insulator Substrates**, A.K. Kalkan, S.H. Bae, H. Li, **S.J. Fonash**, The Pennsylvania State University

High porosity crystalline Si thin films have been directly deposited using a high density plasma approach at temperatures as low as 100°C. These films exhibit the same unique properties, such as visible luminescence and gas sensitivity, that are seen in electrochemically etched Si (i.e., porous Si). The ultimate advantage of our low temperature direct deposition approach is that now porous Si films can be obtained on any substrate including plastics, XRD identifies our films, deposited by ECR-PECVD, as crystalline with no preferential orientation. TEM shows our as-deposited porous Si films consist of a periodic array of uniformly sized rodlike columns normal to the substrate surface in a void matrix. A typical rod diameter is 80 Å and a typical rod separation is 30 Å. Unlike other previously obtained columnar films, these rodlike columns are not tapered but have a constant diameter. We have demonstrated this structure is fully controllable and have varied the porosity up to ~80% by varying the deposition conditions. We have also found that the porosity can be further increased by reducing the diameter of the Si columns by hydrogen ECR-plasma etch exposures after deposition. Red and orange photoluminescence has been observed from our high porosity films. Furthermore, a large and fast conductivity response to certain vapor or gas ambients has been found. In particular, in the case of humidity, a weak response was found up to a threshold humidity level. Above this level a steep exponential increase in conductivity of 3-4 orders of magnitude was observed. The onset of this steep increase was found to occur at higher humidity levels as the porosity is increased. A saturation is observed at relative humidity levels above 75%. Sensitivity for acetone and isopropyl alcohol was observed also for films in the higher porosity range. This implies the sensitivity for larger molecules may be enabled by increasing the void size.

10:40am TF-ThM8 Optical Properties of Chiral Thin Film Nanostructures and Composites, S.R. Kennedy, J.C. Sit, M.J. Brett, University of Alberta, Canada

We have fabricated porous, chiral thin films with distinct helical nanostrucutures of dimension 300nm pitch and 100nm separation. The geometry of these microstructures can be easily controlled by careful substrate motion using the GLancing Angle Deposition (GLAD) technique.@footnote 1@ Because of their nanometer size scale, these helices give rise to optical phenomena, such as the wavelength specific rotation of linearly polarized light, or optical activity. Analysis of films has found that optical properties are functions of film material and thickness as well as helical pitch and radius. All of these characteristics can be accurately controlled during the deposition process to tailor the film's properties to the desired wavelength regime and rotatory power. For example, we have measured a peak rotation of 2.0° at a wavelength of 480nm when polarized light is incident normal to the plane of the film. The porosity of GLAD thin films has also allowed us to fill gaps surrounding the nano-helices with fluids to enhance the film properties. By filling the films with substances of varying indices of refraction, we were able to modify the rotational effect. In addition to filling with non-active fluids, we investigated the effect of combining optically active nematic liquid crystals with our chiral films. @FootnoteText@ @footnote 1@Robbie, K., & Brett, M. J., Nature, v13, 616 (1996).

11:00am **TF-ThM9 Solid State Electrochromic Devices for Thermal Emittance Control**, *C.L. Trimble*, *E. Franke*, *M.J. DeVries*, University of Nebraska, Lincoln; *J.S. Hale*, J.A. Woollam Company; *J.A. Woollam*, University of Nebraska, Lincoln

Thin films of crystalline Li@sub x@WO@sub 3@ (0@<=@ x @<=@ 0.5) allow modulation of IR reflectance within the spectral region from 2 to 30µm depending on the amount of inserted Li ions. Weakly crystalline or amorphous NiO thin films maintain a highly IR transparent state upon Li intercalation. By changing the reflectance of the Li@sub x@WO@sub 3@ layer in contrast to the supporting device layers, electrochromic devices with variable IR emittance can be built. We study a solid state electrochromic device consisting of a five layer stack on glass substrates with a layer sequence: electrode/a-Li@sub x@NiO/Ta@sub 2@O@sub 5@/c-Li@sub x@WO@sub 3@/electrode. The layers are deposited by reactive dc and rf magnetron sputtering at various substrate temperatures, total gas pressures, and oxygen partial pressures, in high-vacuum conditions. Lithium is electrochemically inserted into WO@sub 3@ using a

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1N LiClO@sub 4@/propylene carbonate solution. WO@sub 3@, NiO, and Ta@sub 2@O@sub 5@ are deposited on glass/ITO, or Si substrates. The structural and optical properties of the as-deposited thin films, as well as the Li intercalated WO@sub 3@ and NiO single layers are investigated by XRD, AFM, and IR ellipsometry, in-situ and ex-situ UV-VIS ellipsometry, and IR reflectance measurements. The WO@sub 3@, NiO, and Ta@sub 2@O@sub 5@ thin film optical constants are obtained in the IR and VIS spectral region. Electrochromic devices are designed with consideration of the single layer thin film properties. To predict the device IR emittance modulation performance IR reflection and transmission of the colored and bleached devices are measured. The device switching and memory behavior are tested. The Li depth distribution within the electrochromic devices is investigated by secondary neutral mass spectroscopy (SNMS).@footnote 1@ @FootnoteText@ @footnote 1@ Research supported by BMDO contract #DSAG60-98-C-0054 and NASA Epscor Research Center contract #NCC5-169.

11:20am TF-ThM10 Correlation Between Phase Constituency and Near Ultraviolet Optical Absorption in Nanophase Titania Films, J.D. DeLoach, G. Scarel, University of Wisconsin, Milwaukee; C.R. Aita, University of Wisconsin, Milwaukee, US

Titania forms coexisting nanocrystalline and vitreous structures in films grown at room temperature. This study's goal is to correlate fundamental optical absorption edge characteristics with nanophase constituency of titania films. Films with coexistent rutile, anatase, and vitreous constituents were sputter deposited onto fused silica, and post-deposition air-annealed at 700 and 1000 @super o@C to affect phase changes. X-ray diffraction was used for phase identification, and UV spectrophotometry was used to determine the optical absorption coefficient at the onset of interband transitions. The absorption coefficient was modeled using the coherent potential approximation, with Gaussian site disorder introduced into the valence and conduction bands of a perfect virtual crystal. Two parameters of the disordered crystal were defined: the optical band gap, E@sub x@, and the slope of absorption edge, E@sub o@. The results are discussed in terms of two extreme cases: (1) Films containing a large rutile volume fraction (0.70-1) share a rutile virtual crystal, with E@sub g@=3.22 eV. Data for these films were combined with single crystal data to develop an expression interrelating E@sub g@, E@sub x@, and E@sub o@. This expression is applicable to any structure with a rutile virtual crystal. The relationship between structural disorder (i.e., volume fraction of vitreous material) and electronic disorder (i.e., E@sub o@), is consistent with the CPA model. (2) Films with a small rutile volume fraction (0.02-0.17), and hence a large anatase+vitreous component, share a non-rutile virtual crystal, with E@sub g@=3.41 eV. The effect of increasing the structural disorder (i.e., rutile volume fraction), in these films is to shift E@sub x@ to lower values, which is consistent with the CPA model. Furthermore, anatase and vitreous components were modeled using the same non-rutile virtual crystal, indicating these structures have a common short-range order in these films.

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