

Thin Films

Room 306 - Session TF-WeA

Fundamentals of Thin Films

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

2:20pm TF-WeA2 PECVD Silicon Nitride Nucleation Kinetics Impact on Device Scaling, A. Raviswaran, P. Keswick, Cypress Semiconductor

Plasma enhanced chemical vapor deposition of silicon nitride is a commonly used process in the microelectronics industry for etch stop and passivation layers. As the device dimensions continue to shrink along Moore's law, the silicon nitride thickness is also reduced to meet device requirements. So controlling the silicon nitride thickness and stoichiometry is critical as the gate length and contact width are affected by the thickness and etch rate of the silicon nitride layer used as etch-stop. The current study helps understand the initial stages of nucleation and growth of the PECVD silicon nitride and contributes significantly to better controlling the deposition of very thin silicon nitride layers used in device fabrication. Silicon nitride films with thickness ranging from 37 Å (deposition time of 1 sec) to 450 Å was deposited on Si wafers at 400 °C. Spectral data collected using an ellipsometer shows that as the thickness of the film increases, a transformation is observed in the spectral profile at about 200 Å thickness. AFM, SEM and cross section TEM show that the films are continuous (no 3D cluster growth) at 37 Å. In contrast to reports on LPCVD silicon nitride, the PECVD nitride deposition rate is found to increase with a reduction in deposition time and does not show an incubation time. The refractive index of these films is found to increase with a decrease in film thickness. XPS analysis shows that the thinner films are silicon rich. The 85 Å film with RI of 2.17 has a Si/N ratio of 0.947 and the 340 Å film with RI of 1.95 has a Si/N ratio of 0.928. Evaluation of hydrogen in the film by FTIR and HFS (in progress) will further help understand the impact of hydrogen on the nucleating film properties. The nucleation of a 2D Si-rich layer is attributed to high PECVD deposition rate (relative to surface diffusion) and lower bond strength of Si-H relative to N-H bonds in the reactant gases.

2:40pm TF-WeA3 Transition Metal Diborides by CVD: Super-Conformal, Epitaxial, Diffusion Barrier, and Super-Hard Films, J.R. Abelson, University of Illinois at Urbana-Champaign

INVITED

Transition metal diborides are metallic ceramic materials with high electrical conductivities, refractory melting temperatures, and high hardness. Despite these attractive properties, the boride compounds have been overlooked in thin film science and technology relative to the carbides and nitrides. We employ the single-source, impurity-free precursors Hf(BH₂)₄, Zr(BH₂)₄ and Cr(BH₂)₄ to deposit stoichiometric thin films of HfB₂, ZrB₂, and CrB₂ by chemical vapor deposition. This talk highlights recent results on film microstructure, properties, and deposition mechanisms, which are analyzed using spectroscopic ellipsometry, line-of-sight mass spectroscopy, and trench coverage. Films grown at substrate temperatures of 200-300°C are diffraction amorphous and super-conformal in deep (20:1) trenches. The conformality is a consequence of site blocking which greatly lowers the precursor sticking coefficient. HfB₂ and ZrB₂ films are excellent diffusion barriers that prevent the mixing of Cu and Si during annealing up to 600°C. At growth temperatures \geq 500°C the films are crystalline and adopt a strong preferred orientation, including a normal texture on SiO₂ and pseudo-epitaxy on crystalline silicon (100) and (111) substrates. The latter may be good templates for heteroepitaxial growth of GaN, as previously reported. Amorphous HfB₂ can be crystallized by annealing at temperatures \geq 600°C. The post annealed films have an equiaxed, nanocrystalline structure with grain diameters of < 100 Å. Such films exhibit nanoindentation hardness as high as 40 GPa, exceeding the reported bulk value of 29 GPa. We create multilayered structures by periodically introducing a flux of atomic nitrogen during growth. This creates thin mixed phase layers that are softer; the ratio of hardness to modulus can be adjusted and the overall toughness increased.

3:20pm TF-WeA5 Sputter Deposition of Silicon Oxynitride for Waveguide Applications, J.G. Sandland, A. Eshed, L.C. Kimerling, Massachusetts Institute of Technology

Silicon oxynitride (SiON) is an ideal waveguide material because the SiON materials system provides substantial flexibility in composition and refractive index. SiON can be varied in index from that of silicon dioxide

($n=1.46$) to that of silicon-rich silicon nitride ($n\sim 2.3$). This flexibility in refractive index allows for the optimization of device performance by allowing trade-offs between the advantages of low-index contrast systems and the benefits of high-index-contrast systems. We present sputter processing as an alternative to traditional CVD processing of SiON. We explore a co-sputtered deposition from a silicon oxide and a silicon nitride target, and reactive sputtering process from a silicon nitride target in oxygen ambient. Silicon nitride sputtered from a silicon nitride target is also investigated. Models were developed predicting the index and composition as function of deposition conditions. A materials study is provided that shows sputtered SiON to be a homogeneous material that gives good control of refractive index. Reactively sputtered SiON is shown to be Si-rich. These sputtered materials investigated for use as a core material in optical waveguides. Low loss waveguides are demonstrated for both co-sputtered and reactively sputtered depositions. Losses below 1 dB/cm are shown for co-sputtered deposition ($n=1.65$). These waveguide losses are then related back to our sputtering model, and silicon dangling bonds are shown to contribute to the losses in the waveguides.

3:40pm TF-WeA6 ALD-like Deposition of High Quality SiO₂ Film at 200°C using Organic Silicon Source Gas and Highly Concentrated O₃ Gas, T. Nishiguchi, N. Kameda, Y. Morikawa, M. Kekura, Meidensha Corporation, Japan; H. Nonaka, S. Ichimura, National Institute of Advanced Industrial Science and Technology, Japan

One of the technical issues to be solved to fabricate a high performance flexible poly-silicon (p-Si) TFT is the development of the technique of high-quality gate dielectric (SiO₂) film formation even as low as 200 °C. Although plasma enhanced CVD using an organic silicon source / O₃ gas is now widely used, the further reduction of impurity incorporation such as carbon and OH is required. Focusing on the high reactivity of O₃ to organic molecules even at low temperature, we have carried out an ALD-like process by supplying an organic silicon source gas and highly concentrated (100%) ozone (HC-O₃) gas to a vacuum (< 1 Pa) processing chamber alternately and cyclically. The SiO₂ deposition rate on Si substrate was typically 1 nm per cycle in case of hexamethyldisilazane (HMDS) gas supply of 50 Pa and HC-O₃ gas supply of 1,000 Pa at 200 °C. As-deposited film was stoichiometric SiO₂ with no Si-CH₃ bond detected by infrared absorption spectroscopy. Leakage current through the film was satisfactory low, i.e. lower than 10⁻⁷ A/cm² for 3 MV/cm electric field application. However, a film deposited with a higher deposition rate contained a few wt. % Si-OH bonds and H₂O molecules. We have already confirmed that a UV-light irradiation to Si substrate through an O₃ atmosphere serves to enhance the chemical reaction at Si surface because of the generation of an excited state oxygen atom in gas phase as well as the temperature rise of uppermost Si region. We are now investigating that the usage of UV irradiation together is effective for achieving both high quality film formation and high deposition rate.

4:00pm TF-WeA7 Strontium Oxide Template Monolayers by Surface Reactions of Metal-Organic Precursors with Si(100), A.C. Cuadra, D. Sklar, B.G. Willis, University of Delaware

The crystalline structure of strontium titanate (SrTiO₃) consists of alternating 'sublayers' of SrO and TiO₂. Investigations by molecular beam epitaxy using elemental sources have shown that the heteroepitaxy of SrTiO₃ on Si(100) 2x1 surfaces can be nucleated with the SrO/Si(100) interface. This talk presents the experimental approach for monolayer growth of a SrO 'template' on a Si(100) 2x1 surface using strontium dipivaloylmethanate [Sr(dpm)₂] and water precursors as the sources of Sr and oxygen, respectively. To nucleate SrO on Si(100), the surface chemistry of the substrate must be tuned to direct the surface reactions of the strontium metal-organic precursor. Following native oxide desorption, dissociative chemisorption of H₂O is carried out in UHV to hydroxyl terminate Si(100) and initiate two-dimensional nucleation of the metal oxide while avoiding incubation periods common to the atomic layer deposition (ALD) of metal oxides. Metal oxide growth has been correlated to the concentration of hydroxyl groups on the substrate surfaces because they facilitate ligand exchange from the surface. Results show that thick SrO films with low carbon contamination can be grown on Si(100) and SiO₂ terminated with hydroxyl groups through wet chemical methods; this talk focuses on the initial SrO nucleation layer. In situ Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and reflection high energy electron diffraction (RHEED) are used to investigate the crystalline quality of the nucleation monolayers and to verify the epitaxial orientation of SrO films on Si(100) 2x1 surfaces.

Wednesday Afternoon, November 2, 2005

@footnote 1@ G.Y. Yang, et al., Journal of Material Research, 17 (1), 204-213 (2002)@footnote 2@ R.L. Puurunen, Applied Surface Science, 245, 6-10 (2005).

4:20pm **TF-WeA8 Texture Evolution during Shadowing Growth of Ru Nanorods**, *F. Tang¹, T. Karabacak, G. Churamani, G.-C. Wang, T.-M. Lu*, Rensselaer Polytechnic Institute

A detailed study of texture evolution during oblique angle deposition of ruthenium vertical nanorods by dc magnetron sputtering is presented. The Ru nanorods have diameters less than 130 nm and lengths ranging from ~ 40 to ~ 480 nm. We used reflection high energy electron diffraction (RHEED) to characterize texture and demonstrated that RHEED can be a powerful tool to follow the growth front of texture evolution. The diffraction patterns showed that the nanorods developed into a strong vertical (100) texture unlike the usually observed (002) texture of conventional Ru films grown by normal incidence deposition. Furthermore, through the quantitative analysis of the RHEED patterns, it was found that the dispersion angle, $\Delta\theta$, of the texture evolved into a power law relationship with respect to time t before its saturation, $\Delta\theta \sim t^p$, where $p = -0.49 \pm 0.01$. This is shown for the first time that the power law relationship exists not only in the process of morphology evolution but also texture evolution under oblique angle deposition. The analyses of SEM and TEM images reveal the column competition growth, column dispersion, and the single crystal structure of the individual nanorod. We correlate the evolution of column dispersion angle to the evolution of the texture dispersion angle. We also simulated the evolution of the column dispersion angle based on a modified needle model. The exponent of the power law relationship obtained from the simulation was consistent with experimental value and almost independent of the initial simulation conditions, which may indicate a universal scaling behavior. *F.T. is the recipient of the Harry Meiners Fellowship.

4:40pm **TF-WeA9 Microstructural Characterization of Single Crystal Ferromagnetic Shape Memory Films**, *T.C. Shih, S. McKernan, S.K. Srivastava, J.Q. Xie, R.D. James, T.W. Shield, C.J. Palmstrom*, University of Minnesota

Microstructure and martensitic phase formation behavior are known to be important for magnetic-field-induced-strain in ferromagnetic shape memory alloys. Transmission electron microscopy (TEM) has been used to examine the microstructure and martensitic transformation behavior of non-stoichiometric Ni-Mn-Ga and Co-Ni-Ga post-growth-released single crystal films grown by molecular beam epitaxy (MBE) on GaAs (001). The twin and precursor tweed structures observed in the TEM images are of particular interests. The film compositions were determined using Rutherford backscattering spectrometry (RBS), particle-induced X-ray emission (PIXE), energy dispersive spectroscopy (EDS), and wavelength dispersive spectroscopy (WDS). For a thin film with nominal composition $\text{Co}_{50}\text{Ni}_{25}\text{Ga}_{25}$, convergent beam electron diffraction patterns indicated that the austenite exhibited primarily B2 ordering with additional weak L_2 ordering at room temperature. Sharp satellite reflections appeared at $1/6$ the spacing of the $\{220\}$ reflections around the $\{220\}$ spots along the $\langle 100 \rangle$ directions at ~250 K, with the evidence of high-density striations or tweed contrast observed in the dark-field images. The tweed contrast became more pronounced on cooling, accompanied by increasing intensity of the four additional reflections. On further cooling and stabilizing at 100 K, no twin structure was observed. For thin films with nominal composition $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25}$, $\text{Ni}_{50}\text{Mn}_{30}\text{Ga}_{20}$, and $\text{Ni}_{53}\text{Mn}_{25}\text{Ga}_{23}$, the martensitic transformation temperatures showed linear dependence with increasing average valence electron concentration per atom (e/a). Each specimen transformed into different microstructures with the microtwins ranging from 10 nm to 80 nm. This presentation will emphasize the influence of composition and epitaxial growth conditions on the resulting microstructure of the FSMA films before and after being released from the substrates.

5:00pm **TF-WeA10 Vinyltrimethylsilane (VTMS) as a Probe of Chemical Reactivity and Surface Structure of a TiCN Diffusion Barrier Deposited on Silicon**, *L. Pirolli, A.V. Teplyakov*, University of Delaware

This study presents the first molecular level investigation of chemical reactivity of a surface of an amorphous diffusion barrier film deposited on a Si(100)-2x1 single crystal. Vinyltrimethylsilane (VTMS) is chosen as a probe molecule because of its role as a ligand in a common copper deposition precursor, hexafluoroacetylacetonato-copper-

vinyltrimethylsilane. Surface chemistry of vinyltrimethylsilane (VTMS) on TiCN-covered Si(100)-2x1 has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR), Auger electron spectroscopy (AES), thermal desorption mass spectrometry, and computational analysis. On a film deposited at 600 K, VTMS adsorbs molecularly at cryogenic temperatures even at submonolayer coverages, the major pathway for its temperature-programmed evolution is desorption. Adsorption at room temperature leads to chemisorption via a double bond attachment. The desorption studies combined with the computational analysis suggest that the adsorption of VTMS occurs preferentially in two configurations: across the surface C-Ti bond and on a corner Ti, but not across the Ti-N bond.

¹ TFD Student Award Winner

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