Plasma Science
Room: C-103 - Session PS+TF-ThM

Plasma Enhanced Deposition
Moderator: T.M. Klein, University of Alabama

8:20am **PS+TF-ThM1 The Correlations between Gas Phase Chemistry, Material Properties, and Device Characteristics of PECVD ZrO_2 Thin Films**, ***B. Cho***, *J.P. Chang*, University of California, Los Angeles

We investigated ZrO_2 as a replacement dielectric film of SiO2 for dynamic random access memory (DRAM) capacitor. We used ECR-PECVD process to deposit ZrO_2 films on p-Si (100) wafers with zirconium tetra-tert-butoxide (ZTB; $Zr(OC_4H_9)_4$) as an organometallic precursor, Ar as a carrier of the precursor vapor, and O_2 as an oxidant. Optical emission spectroscopy (OES), Langmuir probe, and quadrupole mass spectrometry (QMS) were used to characterize the plasma. Using QMS, we identified all oxidation states of Zr and found the compositional abundance shifted from Zr metal and monoxide to Zr dioxide and trioxide with the increase in O_2 /Ar flow rate ratio (O_2 /Ar). Based on the results, we proposed the oxidation and the decomposition reaction mechanisms of ZTB precursors. The as-deposited films obtained without any heating had monoclinic and tetragonal polycrystalline phases based on the grazing incidence x-ray diffraction analysis. High resolution transmission electron microscopy showed that the polycrystalline phase of ZrO_2 was interspersed with amorphous phase and that interfacial layer was formed between the ZrO_2 and the substrate Si. Static secondary ion mass spectrometry showed that Zr concentration was uniform across the bulk ZrO_2 film from both oxygen-rich and oxygen-deficient conditions but Si/Zr ratio was much higher in the interfacial layer obtained in the oxygen-rich condition. This suggested that the oxygen-rich condition resulted in more SiO_2-like interfacial layer. X-ray photoelectron spectroscopy (XPS) showed that stoichiometric ZrO2 film was obtained while an interfacial layer containing Si-O bond was formed even without any O_2 addition to the plasma.

8:40am **PS+TF-ThM2 Low-Temperature Plasma Migration Enhanced Epitaxy of $CuInSe_2$ on GaAs**, ***B.J. Stanbery***, *S. Kincal, S. Kim, T.J. Anderson, O.D. Crisalle*, University of Florida

A comparison of migration-enhanced epitaxial growth[1] of $CuInSe_2$ on GaAs at 350°C with either a thermal cracker or ECR helicon plasma selenium source demonstrates both improved crystallinity and enhanced selenium incorporation using the plasma cracker. Mass spectrometric characterization of the flux from the effusion source coupled to a magnetic-mirror confined 2.45GHz plasma cracker shows 50% enhancement of the Se monomer to dimer flux ratio compared to the thermal double-oven with its cracking zone operating at 1200K, and no measurable ion flux outside the plasma source. Samples grown using the ECR plasma cracker were characterized by a number of differences from all other growth experiments that used the thermal source. The improvement of $CuInSe_2$ epilayer crystallinity is confirmed by the XRD data irrespective of the atomic [Cu]/[In] ratio of the resultant films, which exhibit an order of magnitude reduction in incoherent scattering compared to samples grown with the thermal source, particularly at low angles. Films grown with the plasma source that contain excess copper yield compositions that lie well into the selenium-rich domain of the equilibrium ternary phase field, with little indication of diffraction corresponding to the Cu_2Se binary compound which coexists in equilibrium with $CuInSe_2$ when the overall composition is copper-rich. In contrast, such a peak is always seen in significantly copper-rich layers grown with the thermal source. The higher level of selenium incorporation resulting from MEE growth with the plasma source is discussed in the context of a recent theoretical lattice defect model for $CuInSe_2$ that predicts a significant reduction in the electrical compensation ratio of indium-rich $CuInSe_2$ incorporating a stoichiometric excess of selenium.[2]

[1] Y. Horikoshi, et al., Jap. J. Appl. Phys. 25, L868 (1986).

[2] B.J. Stanbery, Ph.D. Dissertation, U. Fl.(2001).

9:00am **PS+TF-ThM3 2-Dimensional Plasma Simulation of Reactive Physical Vapor Deposition of Metal Nitride**, ***D. Zhang***, *S. Samavedam, J. Schaeffer, R. Martin, P.L.G. Ventzek, P. Tobin*, Motorola Inc.

Reactive physical vapor deposition (RPVD) of metal nitride has been used for interconnect barrier and metal gate deposition due to its relative simplicity in process implementation and lower contamination compared to other deposition techniques requiring chemical precursors. As the electrical properties (e.g. work function, resistivity) of deposited film are sensitive to film characteristics (e.g. composition), optimal process control based on in-depth mechanistic understanding is critical for reactive PVD to meet product requirements. This has motivated our development of a 2-dimensional plasma model for RPVD of metal nitride films. The RPVD model is based on the 2-dimensional Hybrid Plasma Equipment Model (HPEM) developed at the University of Illinois.[1] Plasma is approximated as a fluid in HPEM. A target surface nitridation model (TSNM) has been developed to be self-consistently coupled with HPEM. The TSNM uses a site balance algorithm to address neutral adsorption, desorption by ion sputtering, and surface coverages. An effective sputtering yield for the target is used to account for the effect of target nitridation. The model has been applied to study reactive TiN and Ti_xAl_yN deposition using a parallel-plate PVD tool. It is found that athermal neutrals are the dominant source for deposition. Target nitridation impacts deposition rate by reducing sputtering yield. For Ar and N_2 source gases with a constant total flow, the model derived the dependency of deposition rate with N_2 flow that is in good agreement with experiments. Impact of various process parameters (gas mixture, power, pressure) on deposition characteristics will also be discussed in this work.

[1] P. Subramonium and M. J. Kushner, J. Vac. Sci. Technol. A 20, 325 (2002).

9:20am **PS+TF-ThM4 Expanding Thermal Plasma for SiO_2 Films: A Chemistry-controlled Process and an Insight into the Deposition Mechanism**, ***M. Creatore***, *M. Kilic, K. O'Brien, M.C.M. Van de Sanden*, Eindhoven University of Technology, The Netherlands

SiO_2 PECVD by means of organosilicon/O_2 mixtures has shown its versatility in many fields, as e.g. IC/MEMS, photonics, optics, mechanics, food packaging. However, some issues concerning the deposition process remain unresolved. For example, the deposition precursors have not been unambiguously identified, hampering a direct correlation between plasma species densities and film composition. The remote expanding thermal plasma (ETP) is introduced as a simplified approach to get insight into the hexamethyldisiloxane (HMDSO)/O_2 deposition process. HMDSO is injected downstream in the expanding argon plasma (generated in a dc cascaded arc) by means of a ring. Because of the expansion, the electron temperature drops to about 0.3 eV: electron-induced dissociations are negligible and the chemical activity is controlled by the (Ar^+, e^-) flow from the arc. The ETP has led to a step-by-step entirely chemistry-controlled process (no ion bombardment) from silicone-like to C-free and dense SiO_2 films, at competitive growth rates (8 nm/s). A multidiagnostics approach has been applied to study the fragmentation and reactions of HMDSO. Cavity Ring Down Spectroscopy (CRD) has been used for OH, CH and CH_3 radicals detection in HMDSO/O_2 plasmas. Together with Mass Spectrometry, CRD has shown that the Si-C bond in the HMDSO molecule appears to break only at very high Ar^+ flux (high arc Ar flow rate and current). Milder conditions favour the Si-O and C-H bond scissions. Films are characterized by means of IR absorption spectroscopy, in situ single wavelength ellipsometry and ex situ spectroscopic ellipsometry. In the presentation the relation between the film properties and the plasma characterization will be addressed.

9:40am **PS+TF-ThM5 Plasma Production of Silicon Clusters and Nanocrystalline Silicon Particles : A New Route for Nanostructured Silicon Thin Films**, ***P. Roca i Cabarrocas***, Ecole Polytechnique, France **INVITED**

The study of silane plasma deposition is important due to the large number of large area devices based on amorphous silicon. When transferring research results to production, deposition rate, uniformity, and powder formation are key issues. In this respect, the study of square-wave modulated discharges revealed that silicon nanocrystals (powder precursors) can be produced even at room temperature. This result has motivated for the work on plasma conditions near the onset of powder formation, to produce better-structured silicon thin films in which silicon clusters, and crystallites formed in the plasma contribute to deposition. Among the nanostructured materials we produced thus far, most work has focused on polymorphous silicon films because they share the high optical absorption of a-Si:H while having improved transport properties. In this presentation we review our recent work on the production, the characterization, and the study of devices based on this new material. The challenging issue of nanoparticle detection in the plasma is addressed with new techniques such as cavity ring down and impedance measurements. Moreover, in situ ellipsometry was used to study the growth and to determine the thermal gradient for which nanoparticles can reach the substrate. In conclusion, the precise control of the size and concentration of nanocrystalline silicon particles in the plasma opens the way to the nanoelectronics field in which the plasma-produced nanocrystallites can be passivated, coated, and incorporated into devices such as non-volatile memories. This is in our opinion an important challenge for the plasma community in the next few years.

10:20am **PS+TF-ThM7 Correlation between Cluster Amount and Qualities of a-Si:H Films for SiH_4 Plasma CVD**, ***K. Koga***, *K. Imabeppu, M. Kai, A. Harikai, M. Shiratani, Y. Watanabe*, Kyushu University, Japan

Recently, clusters below a few nanometers in size formed in SiH_4 high frequency discharges have been pointed out to be a possible cause of light-induced degradation of hydrogenated amorphous silicon (a-Si:H) films. Hence, suppression of cluster growth is an important issue for depositing high quality a-Si:H films at a high rate. To realize such suppression, we have developed a cluster-suppressed plasma CVD method utilizing gas flow and gas temperature gradient.[1] The following results have been obtained in our experiments. 1) Even under so-called device quality conditions, a large amount of clusters (> 10^4 cps) exist in the conventional plasma CVD reactor. 2) Microstructure parameter $R\alpha$ of a- Si:H films decreases with decreasing the cluster amount. The developed cluster-suppressed plasma CVD reactor can decrease both $R\alpha$ and cluster amount below detection limits of our measurement systems ($R\alpha$< 0.003 and cluster amount < 0.001 cps, respectively). These results suggest that a-Si:H films of high qualities can be prepared at a high deposition rate by suppressing the cluster growth. 3) A ratio of cluster amount to deposition rate for a discharge frequency of 60 MHz is 1/20 of that for 13.56 MHz, indicating that the VHF discharge is effective in suppressing cluster growth. 4) Preliminary evaluation of fill factor (FF) of a n^+Si/a-Si:H/Ni Schottky solar cell using a-Si:H films of $R\alpha$= 0.057 shows the high initial value FF_i= 0.57 and high stabilized value after-light soaking FF_a= 0.53, compared to FF_i= 0.51 and FF_a= 0.47 of cell using conventional device quality a-Si:H films of $R\alpha$~ 0.1.

[1] K. Koga, M. Kai, M. Shiratani, Y. Watanabe and N. Shikatani, Jpn. J. Appl. Phys., 41, L168 (2002).

10:40am **PS+TF-ThM8 Plasma and In Situ Film Diagnostic Study of Amorphous and Microcrystalline Silicon Deposition**, ***W.M.M. Kessels***, *J.P.M. Hoefnagels, Y. Barrell, P.J. Van den Oever, M.C.M. Van de Sanden*, Eindhoven University of Technology, The Netherlands

Our comprehensive investigation of the film growth process of amorphous silicon (a-Si:H) from a remote H_2/SiH_4 plasma has recently also been extended to microcrystalline silicon (µc-Si:H). This material is of particular interest for applications in thin film solar cells and thin film transistors because of its higher stability. In this contribution we will compare the absolute densities of the different silane radicals, as determined from cavity ringdown spectroscopy, for the two plasma regimes yielding the two different materials. Moreover, the surface reaction probability of the silane radicals will be presented as obtained under real deposition conditions (e.g., as a function of substrate temperature) by time-resolved cavity ringdown experiments. >From this information, it is, for example, revealed that Si, SiH, and SiH_3 radicals have approximately an equal contribution to µc-Si:H growth, unlike a-Si:H film growth which is almost completely governed by SiH_3. Furthermore, we will present 'film depth-information' with respect to hydrogen bonding, hydrogen concentration, and other structural film properties as has been obtained by in situ monitoring of film growth by attenuated total reflection infrared spectroscopy and spectroscopic ellipsometry. This powerful combination of diagnostics applied to the well-characterized plasma conditions has revealed a rather homogeneous hydrogen distribution throughout the film (also for µc-Si:H) apart from an initial incubation phase corresponding to interface/surface layer formation. The interface thickness and surface roughness increase with increasing deposition rate but decrease with increasing substrate temperature. New insights into the film growth process of both materials will be discussed.

11:00am **PS+TF-ThM9 Mechanism of Hydrogen-Induced Crystallization of Amorphous Silicon Thin Films**, ***S. Sriraman***, *E.S. Aydil, D. Maroudas*, University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) films are used in solar cells, displays, and imaging devices. The a-Si:H films undergo chemically-induced structural transformation from a state of disorder to order (crystallinity) when exposed to H atoms from an H_2 plasma at temperatures lower than those required for thermal annealing; exposure to an H_2 plasma is used as a post-deposition treatment step for plasma-deposited a-Si:H films. In addition, nc-Si:H films can be grown during plasma deposition by heavily diluting the SiH_4 feed gas with H_2. Though several hypotheses have been proposed, the mechanism behind the H-induced disorder to order transition still remains unclear. The atomic-scale processes behind this structural transition are analyzed through molecular-dynamics (MD) simulations of repeated H atom impingement on a-Si:H films. These films were grown through MD by repeatedly impinging SiH_3 radicals on an initially H-terminated Si(001)-(2x1) surface. The evolution of the Si-Si radial distribution function during H exposure of the film showed gradual appearance of peaks corresponding to the coordination shells of crystalline Si, indicating a transition from disorder to order. Detailed structural analysis after H exposure revealed the presence of a nanocrystalline region embedded within the amorphous Si matrix. The structural transformation is mediated by H atoms that diffuse into the a-Si:H film and insert into strained Si-Si bonds to form intermediate bond-centered H (Si-H-Si) configurations. This results in local structural relaxation of these strained Si-Si bonds. The energetics of H insertion into strained Si-Si bonds and its implications in the structural relaxation of the amorphous phase are discussed. The existence of bond-centered H(D) in a-Si:H films exposed to H(D) atoms from a $H_2(D_2)$ plasma also was verified experimentally through in situ infrared spectroscopy.

11:20am **PS+TF-ThM10 On the Roughness Evolution during Remote PECVD of Amorphous Silicon**, *M.C.M. Van de Sanden*, ***A.H.M. Smets***, *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

The roughness evolution during the growth of hydrogenated amorphous silicon is studied in situ by means of single wavelength ellipsometry. The roughness measurements are corroborated by ex situ spectroscopic ellipsometry and Atomic Force Microscopy on films having thickness in the range from 30 up to 3000 nm. The films were deposited by means of the expanding thermal plasma, a remote plasma technique. Silane is injected downstream in an Ar/H_2 plasma. From detailed measurements in the gas phase it is established that the dominant radical contributing to the film growth is the silyl radical with minor contributions from other radicals such as Si, SiH and H. The self-bias is small which characterizes the a-Si:H growth from this dominantly SiH_3 source as purely chemical in origin. The roughness evolution is analysed by means of the scaling properties of the surface as first proposed by Family and Vicsek.[1] It is found that the surface width scales with film thickness d as $d^{ß}$. β, the dynamic scaling exponent, is determined as function of substrate temperature and growth rate. A cross-over from random deposition ($\beta = 1/2$) at low substrate temperatures, to a deposition process in which surface diffusion dominates the roughness evolution is observed. The scaling universality class of the roughness development of the growth of a-Si:H shows great similarity with, e.g., Molecular Beam Epitaxy of crystalline silicon. The activation energy from beta vs. substrate temperature is determined from comparing the data with a solid-on-solid model and is about 1 eV. This value is much higher than expected on basis of the conventional growth models for a-Si:H, in which the weakly adsorbed SiH_3 radical is assumed to rule the roughness evolution. The implications for the growth model of a-Si:H will be discussed.

[1] F. Family and T. Vicsek, J. Phys. A 18 L75 (1985).

11:40am **PS+TF-ThM11 Detailed Study of Chemistry of Ar/C_2H_2 Plasma and Consequences For the a-C:H Film Growth**, *J. Benedikt, R.V. Woen*, ***M.C.M. Van de Sanden***, Eindhoven University of Technology, The Netherlands

The role of hydrocarbon radicals during the deposition of a-C:H films is studied in an Ar/C_2H_2 remote expanding thermal plasma (ETP) reactor. C, C_2 and CH radicals are detected by means of cavity ring down spectroscopy (CRDS) at different plasma conditions and at different positions downstream from the thermal plasma source. A broadband absorption (BBA) is observed in the 250 - 520 nm region. Acetylene and diacetylene (C_4H_2) are monitored with a residual gas analyser. A simple plasma chemistry model is developed to explain measured data. The plasma chemistry is governed by argon ion induced dissociation of acetylene molecules. Main product of this reaction is the ethynyl (C_2H) radical, which can further react either with argon ions or with acetylene, depending on the ratio between the flux of argon ions and the flux of acetylene into the reactor. The BBA is due at least two species: most likely candidates are C_2H radical and C_4H_2 molecule. In-situ real-time ellipsometry was used to determine growth rate and refractive index of the films grown. Our preliminary conclusion is that C_2H radical is a growth precursor for high quality hard diamond-like a-C:H films; a-C:H films with slightly lower hardness but faster growth rate were also deposited using a C_4H_2 rich plasma. The loss probabilities of the ethynyl radical and diacetylene molecule are determined from time dependent CRDS. The probabilities can be used to monitor the relative importance of the ethynyl radical vs. diacetylene in the growth of a-C:H.

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