Plasma Science and Technology
Room 315 - Session PS+TF-TuM

Plasma Enchanced Chemical Vapor Deposition

Moderator: D.C. Guerin, Naval Research Laboratory

8:20am **PS+TF-TuM1 PECVD, From the Laboratory to Mass Production, *J.P.M. Schmitt*[1],** Unaxis Management Incorporated, Switzerland **INVITED**

After a rapid recall of the "alchemist" age of gas decomposition by an electrical arc, the gradual birth of PECVD is described in the early 70's. The richness of PECVD potential was then realised creating expectations for a long list of potential applications. Soon after the first industrial applications of PECVD were demonstrated. A look back at the pioneering days of PECVD allows to identify and discuss the key attributes of PECVD that made (and keep) this technology attractive for film coating. In the early 80's PECVD was hype and was the objet of active research. Basic research teams activity focused on the complex mechanisms involved in the PECVD process. First were understood the basic steps such as electron induced molecular dissociation and particle-surface processes. It is only later that far more complex mechanisms such as dust formation were found to be also extremely important. The status of knowledge on basic mechanisms will be reviewed. In the last 15-20 years a wide variety of configurations for the plasma reactors were tested. Instead of a complete zoological classification of all variations, we relate various classes of plasmas with their most marking attributes to the PECVD process key mechanisms. If in the 80's PECVD was already at work in mass production plants, it is in the 90's that a full set of production related problems were actively addressed. Self-cleaning was found a highly desirable ability for a PECVD tool. This requirement combined with high throughput demand led to new classes of equipment and processes. The application field of PECVD also stretched from the food industry the most sophisticated high tech industry. PECVD is today facing new challenges. The glass substrate size for the flat display industry is about to exceed 2m@super 2@ still requiring good uniformity and high throughput. PECVD has also the opportunity to prove itself into new fields such as semiconductor epitaxy or deposition of organic based films with functional groups.

9:00am **PS+TF-TuM3 Plasma-enhanced Deposition of Silicon and Metal Oxynitride Films in a High-density Ammonia Discharge***, Z.G. Xiao,* ***T.D. Mantei,*** University of Cincinnati

Silicon, titanium, zirconium, and chromium oxynitride films have been grown in a high-density electron cyclotron resonance (ECR) ammonia discharge. The organosilicon deposition precursors for silicon oxynitride were hexamethyldisiloxane and tetramethylsilane, while the organometallic deposition precursors for metal oxynitride were titanium (IV) isopropoxide and tetrakis(dimethethlyamino)titanium, zirconium 2-methyl-2-butoxide and zirconium t-butoxide, and bis(ethylbenzene)chromium. The plasma-grown films had nanoindentation hardness values of 12 - 14 GPa for SiN, 20 - 28 GPa for TiN, 17 - 21 GPa for ZrN, and 25 - 31 GPa for CrN. Deposition growth rates were 40 - 50 nm/min for silicon oxynitride and 10 - 20 nm/min for the metal oxynitrides. X-ray photoelectron spectroscopic (XPS) analyses showed the nitrogen content of silicon, titanium, and zirconium oxynitrides to be 31% - 38%, while the CrN nitrogen content was 15%. The SiN films grown from hexamethyldisiloxane were colorless and transparent while films grown from tetramethylsilane had the characteristic dark color of Si@sub 3@N@sub 4@. The TiN and ZrN films had the characteristic brass and white gold colors of TiN and ZrN reference samples while the CrN samples were gray. The SiN films lasted 800 hours in an ASTM B117 accelerated salt-fog corrosion test without visible corrosion, and the TiN and ZrN films lasted 1000 hours without visible color change or corrosion.

9:20am **PS+TF-TuM4 Identification of the Growth Precursors for Hydrogenated Amorphous Carbon Growth***, J. Benedikt*[2]*, R.V. Woen, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The plasma chemistry and plasma composition of argon/acetylene expanding thermal plasma, used for fast (up to 70 nm/s) hydrogenated amorphous carbon (a-C:H) film deposition, was studied by means of Cavity Ring Down absorption Spectroscopy and Mass Spectrometry. Since the electron temperature in expanding thermal plasma beam is low (less than 0.3 eV) electron impact processes can be neglected and acetylene dissociation is argon ion induced. The C@sub 2@H radical was identified as the main growth precursor for hard (14 GPa) diamond-like a-C:H films. It was shown that under conditions where most of acetylene molecules are decomposed into C, CH and C@sub 2@ radicals, the a-C:H films are soft and polymer-like. Furthermore it was observed that good a-C:H films can be grown also under conditions when C@sub 4@H@sub 2@ molecules are the main plasma chemistry product and when reactive radicals as C@sub 2@H has already reacted away with acetylene in the gas phase. The mass spectrometry measurements of C@sub 4@H@sub 2@ molecule in the background of the plasma shows that C@sub 4@H@sub 2@ density depends on the wall condition (argon plasma activated or hydrogen plasma passivated) suggesting that C@sub 4@H@sub 2@ is one of the contributors to the film growth. C@sub 2@H and C@sub 4@H@sub 2@ as possible precursors for a-C:H growth is confirmed by recent Molecular Dynamics simulations which reveal reaction probabilities close to one for both species.

9:40am **PS+TF-TuM5 Characterization of TaN Diffusion Barrier Layers Prepared by Chemical-Enhanced Physical Vapor Deposition (CEPVD)***, N. Li*[3]*, D.N. Ruzic,* University of Illinois, Urbana-Champaign

CEPVD of TaN is a novel process attempting to deposit diffusion barrier layers with both high conformal step coverage (as in CVD) and superior quality (as in PVD). The experiments are performed by sputtering a Ta target in a modified conventional PVD instrument and simultaneously adding a certain amount of chemical precursor, TBTDET, in the vicinity of the substrate at elevated temperature (330@degree@C) in combination with a carrier gas (N2), reducing agent (H2), non-reactive sputtering gas (Ar) and a RF-powered secondary ionization plasma. Different combinations of RF power, N2, H2, Ar flow and bias voltage result in distinct resistivity regimes. Increasing H2 flow rate from 5 sccm to 10 sccm allows more hydrocarbon formation and thus results in significant resistivity variation. The addition of 10sccm Ar increases target sputtering and more Ta flux, producing film with relatively lower resistivity (5200 Î¼-cm compared to 62,000 Î¼-cm). The addition of Ar also produces a more columnar and porous structure. N2 flow rate determines precursor residence time and so controls growth density and deposition rate. Biasing the substrate with -60 V drops resistivity one order of magnitude. Patterned wafers with various trench aspect ratios are lined to compare the step coverage under different processing conditions. Four point probe, SEM, AES, XRD and XPS are utilized to characterize the film properties and the analysis reveals the balance between energetic Ta flux, TBTDET breakup and impurity volatilization. The synergy between PVD and CVD is clearly demonstrated.

10:20am **PS+TF-TuM7 Anisotropic Cu Deposition using Plasma Chemical Vapor Deposition***, **M. Shiratani**, K. Takenaka, M. Takeshita, M. Kita, K. Koga, Y. Watanabe,* Kyushu University, Japan **INVITED**

We have demonstrated complete filling of trenches by anisotropic Cu deposition, in which Cu is filled preferentially from the bottom of the trenches, using plasma chemical vapor deposition.@footnote 1@ The key to realize the anisotropic deposition is kinetic energy and flux of ions irradiating on the surface, since the deposition rate increases with increasing the kinetic energy and fluxes. Previously, by using H-assisted plasma CVD we have realized conformal deposition of smooth 20 nm thick Cu films in trenches as well as conformal filling of trenches.@footnote 2@ Although the Cu films have a low as-deposited resistivity of of 1.85 μ@ohm@cm and a strong adhesion strength above 10 MPa to the TiN layer, conformal filling results in a small crystal grain size below half of the trench width and in a seam where impurities of high concentration remain. The anisotropic deposition offers a possibility to overcome such shortcomings for the conformal filling together with two additional interesting features. One is the fact that deposition rate increases with decreasing the width of a trench. The other is a self-limiting deposition by which deposition stops automatically just after filling completely a trench. This feature may realize a LSI fabrication processes without the chemical mechanical polishing, being attractive for the Cu-porous low-k interconnects. @FootnoteText@@footnote 1@ K. Takenaka, et al., Matr. Sci. Smiconductor Processing 5, 301 (2003).@footnote 2@ M. Shiratani, et al., Sci. and Technol. of Adv. Mater. 2, 505 (2001).

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[1] **AVS 50th Anniversary Invited Speaker**

[2] **PSTD Coburn-Winters Student Award Finalist**

[3] **PSTD Coburn-Winters Student Award Finalist**

11:00am **PS+TF-TuM9 Pulsed-plasma Deposition of Silicon Dioxide in a High Density Oxygen Discharge**, ***Y. Qi***, *T.D. Mantei,* University of Cincinnati

Hard clear silicon dioxide films have been grown from octamethylcyclotetrasiloxane (OMCTS) at low substrate temperatures in a pulse-modulated high density electron cyclotron resonance (ECR) oxygen plasma. The input microwave power at 2.45 GHz was pulse-modulated with repetition frequencies from 20 Hz to 20 kHz, duty ratios (on-time/period) from 5% to 100%, and peak microwave power levels from 800 W to 2400 W. The resulting films were SiO@sub 2@-like with Si-O bonds and Si:O ratios close to 1:2. The deposition growth rates were almost independent of frequency for all pulse repetition frequencies from 20 Hz to 20 kHz. The growth rates increased strongly as the peak pulse power was increased; with a 50% duty ratio, the growth rate was 0.5 - 0.6 mm/min with 800 W peak power, increasing to 0.8 - 0.9 mm/min at 1600 W peak power. The coating hardness values decreased with pulsed operation as the average input microwave power decreased. Deposition substrate temperatures were significantly lowered as the duty ratio (and thus the average power) decreased, e.g., substrate temperatures were 140°C - 150°C after 10 minutes of deposition with 1600 W of continuous microwave power, dropping to 90°C with a 50% pulse duty ratio and 1600 W peak power. Results from current experiments on pulsed low temperature growth of metal nitride and teflon coatings will also be discussed.

11:40am **PS+TF-TuM11 Secondary Plasma Based Debris Mitigation for Next-Generation 13.5nm EUVL Sources**, ***B. Jurczyk***, *D.N. Ruzic, E. Vargas-Lopez, M. Neumann, M. Williams, C. Chrpbak, S. Taj,* University of Illinois at Urbana-Champaign

Next-generation EUV photolithography machines (>25kW-class) require order of magnitude improvements in debris removal for component lifetime and stable operation. Discharge plasma light sources, such as the dense plasma focus, are leading candidates for EUV. The Illinois Debris-mitigation Experiment and Applications Laboratory (IDEAL) consists of a dense plasma focus discharge source operating on order of 25 J/pulse, 100 Hz rep rate, and 4 kV. Argon and Helium gases have been tested to generate plasma environmental conditions similar to that experienced by industry. The secondary-plasma-based debris mitigation technique is presented; a concept pioneered from iPVD reactors at the University of Illinois. Sputtered electrode and chamber component debris is re-ionized in the secondary plasma region and removed with the application of electric fields prior to the collection optics. A helical resonator inductive coil generates the secondary plasma with minimal coil self-biasing for decrease erosion. A dual-channel foil trap, with independently biased plates (0-1kV), collects debris from the secondary plasma region. The foil trap is positioned to vary aspect ratios from 1:1-to-16:1 to correlate with gas pressure effects. Results from in-situ high-precision quartz-crystal-oscillators, ex-situ surface characterization (XPS, Auger, Profilometry, etc.), secondary plasma characterization, and collection optic protection factors are presented for a series of mitigation schemes.

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