Friday Morning, November 6, 1998

Thin Films Division
Room 310 - Session TF-FrM
Thin Film Deposition from Chemical Precursors

Moderator: A. Belkind, Stevens Institute of Technology

8:20am **TF-FrM1 Annealing of Copper Electrodeposits***, **C.H. Seah**, S. Mridha,* Nanyang Technological University, Republic of Singapore*; L.H. Chan,* Chartered Semiconductor Manufacturing Ltd., Republic of Singapore

Cu is the best metallization candidate to replace Al and its alloys because of its lower resistivity and better electromigration resistance. Significant progress has been made in building multilevel Cu interconnection systems for advanced microelectronics. As a result, it is important to understand how the morphology of the electroplated Cu films and its properties change after annealing at high temperatures. The properties of annealed electroplated Cu films, together with the diffusion barrier performance, have been studied. Electroplating of Cu films was performed onto p-Si with Cu and W seed layers. The barriers film are either TiN, Ta or TaN. The specimens were then annealed at 600 and 700°C in N@sub 2@ atmosphere for grain growth study. The average grain size of the as-plated Cu films was found to be different; larger Cu grains were formed on W seed layer compared to that formed on Cu (600 vs 200 nm). After annealing, all the Cu films recrystallized readily and grain growth occurred. Regardless of the initial grain size of the electroplated Cu films, the final grain size after annealing was found to be similar in both seed materials. The grain sizes were about 1.0 and 1.2 µm after annealing at 600 and 700°C respectively. The driving force for grain growth is the surface energy release from elimination of grain boundaries and thus achieving an equilibrium state. The annealed films produced a layered microstructure, together with the presence of pinholes and cavities. Results show that all the diffusion barriers remained intact after annealing at 600°C. The CVD TiN barrier appeared to fail at 700°C annealing if the film stack contains only 100 Å thick barrier layer. The resistivity of the electroplated Cu films was also found to be reduced from 2.1 microhm-cm to 1.9 microhm-cm after annealing at both temperatures.

8:40am **TF-FrM2 Polymerized C-Si Films on Metal Substrates: Cu Adhesion/Diffusion Barriers for ULSI?***, L. Chen, **J.A. Kelber**,* University of North Texas

The increasing demands of ULSI have created a need for Cu diffusion/adhesion barriers which are consistently effective at thicknesses of several hundred angstroms or less. Further, the integration of Cu with low-dielectric polymers requires the reliable adhesion at the Cu/polymer interface. We have recently synthesized polymeric C-Si films which are resistant to thermal diffusion of Cu at temperatures below 800 K, even at thicknesses less than 100 Å. These films also show potential for providing a covalently bonded interphase between Cu and, e.g., fluoropolymer dielectrics. The films are created by electron or UV photon bombardment of condensed vinyl silane derivatives. The films are not SiC, and have chemical compositions very close to those of the vinyl silane precursors (e.g., Si:C = 1:4 for vinyltrimethylsilane(VTMS)-derived films). TPD data show that polymerization occurs via the vinyl group. Films derived from VTMS are adherent and stable on Ta substrates until 1000 K in UHV. Diffusion of Cu is not observed below 800 K. Cu adhesion to the substrate is relatively good, with dewetting of deposited overlayers occuring only at temperatures above 600 K in UHV. Perfluorobenzene moieties can also be incorporated into the growing film with good thermal stability, indicating that these films have potential to adhesively couple Cu surfaces to vapor-deposited fluoropolymer films. Opportunities for molecular tailoring of electronic and mechanical properties via systematic variation of precursor structure will be discussed.

9:00am **TF-FrM3 Ultra High Rate, Wide Area, Plasma Polymerized Films from High Molecular Weight/Low Vapor Pressure Liquid or Solid Monomer Precursors***, **J.D. Affinito**, M.E. Gross, P.A. Mounier, S. Stockhause,* Pacific Northwest National Laboratory **INVITED**

A new process has been developed for the high rate vacuum deposition of solid films from high molecular weight/low vapor pressure liquid, or even solid, monomer precursors. The gas resulting from the flash evaporation of a liquid monomer mixture, or from a suspension of liquid monomer and insoluble solid particles, is used as the support medium for a glow discharge in a Plasma Enhanced Chemical Vapor Deposition-like (PECVD) process. Due to the high molecular weight/low vapor pressure nature of the precursors, the plasma of the flash evaporated gas cryo-condenses at extremely high rate on substrates at ambient, and higher, temperatures. Upon condensation the liquefied plasma immediately begins to polymerize to form a solid film due to the high concentration of radicals and ions contained in the liquid film. The process has been successfully implemented in a vacuum roll coating system in a roll-to-roll deposition process. Polymer films, and Molecularly Doped Polymer (MDP) composite films of polymer and light emitting organic molecules, have been deposited at thickness' ranging from 0.1 microns to 24 microns at webs speeds as high as 100 linear meters per minute. This new deposition process will be discussed along with some properties of the films fabricated with this new process.

9:40am **TF-FrM5 Effects of Temperature (350 - 25°C) on OH Incorporation and Electrical Performance of Plasma Deposited Silicon Dioxide Thin Films for Applications on Plastic Substrates***, **A. Gupta**, C.G. Makosiej, G.N. Parsons,* North Carolina State University

Very low temperature PECVD SiO@sub 2@ may be useful on plastic substrates for gate dielectrics for polysilicon thin film transisitors, or for barrier or insulating layers in organic LED displays. We have used SiH@sub 4@/N@sub 2@O/He/H@sub 2@ mixtures in a parallel plate rf plasma CVD reactor to form SiO@sub 2@ on silicon, and examined the effect of substrate temperature between 350°C and 25°C, rf power, and gas ratios on the chemical composition, refractive index, etch rate, chemical stability, deposition rate, and I-V and C-V characteristics. Low temperature films have also been deposited on PET and polycarbonate substrates to examine adhesion and stress. Films deposited at 350°C show good insulating properties with breakdown fields >8 MV/cm. As temperature is decreased to 100°C, an increase in charge trapping is observed. The decrease in temperature also results in an increase in deposition rate from 65 to 100 Å/min, and a decrease in refractive index from 1.47 to 1.43, indicating a less dense structure. Infrared spectroscopy shows a correlation between OH concentration and the Si-O stretch peak position. At 90W, as the temperature decreases from 350 to 250°C, the Si-O stretch mode position decreases from 1063 to 1056 cm@super -1@, indicating an increase in bond strain. As temperature is decreased from 250 to 25°C, the Si-O peak increases from 1056 to 1065 cm@super -1@, due to an increase in OH incorporation during deposition. After deposition, the OH concentration increases with ambient exposure, and decreases slightly during annealing at 300°C. Process variations, including H@sub 2@ and He dilution, and time modulated deposition and H@sub 2@ exposure cycles to decrease OH incorporation have been tested. Films with less OH in the as deposited condition show a greater resistance to post-deposition oxidation, and show improved electrical properties. Films with good leakage characteristics (

10:00am **TF-FrM6 Structural and Electrical Properties of SrTiO@sub 3@ Thin Films Prepared by Plasma Enhanced MOCVD***, D.O. Kim, **Y-.B. Hahn**,* Chonbuk National University, Korea

Dielectric SrTiO@sub 3@ ultra thin films having 30 - 75 nm thickness were deposited on Pt/Si and Ir/Si substrates by plasma enhanced MOCVD using high purity Ti(O-i-C@sub 3@H@sub 7@)@sub 4@, Sr(tmhd)@sub 2@ and O@sub 2@. The structural and electrical properties of SrTiO@sub 3@ films were studied in terms of crystallinity, microstructure, current leakage, and dielectric constant. For the case of Pt/Si substrate, the peaks of (100) and (111) SrTiO@sub 3@ together with TiO2 and SrCO@sub 3@ peaks started to appear at 500 @super o@C, and at 550 @super o@C for (110) and (211) peaks without TiO@sub 2@ and SrCO@sub 3@ peaks. For Ir/Si substrate, peaks of (100) SrTiO@sub 3@ and TiO@sub 2@ appeared at 500 @super o@C, and at 550 @super o@C for (110), (111) and (210) SrTiO@sub 3@. Dielectric constants decreased as the film thickness decreased. The leakage current density of the SrTiO@sub 3@ films decreased with increasing deposition temperature up to 550 @super o@C, but somewhat increased at > 550 @super o@C. It was found that the electron current was limited by tunneling effect for films thinner than 30 nm, but limited by Schottky emission for films thicker than 30 nm. The electron affinity and depletion layer of SrTiO@sub 3@ films, based on the electron current mechanism, were 4.0-4.3 eV and 15 nm, respectively.

10:20am **TF-FrM7 Thermal Stability of MOCVD TiN/PECVD SiOF Interface for Cu Metallization***, **K.H. Kim**, S.J. Park, G.S. Lee,* Louisiana State University

RC delay based on Al and SiO@sub 2@ interconnection system comprises a great portion of the total delay as circuit density increases. RC delay can be reduced by using low resistance metal or low dielectric constant insulator, or both. Thus, Cu and SiOF are preferred to be used as low resistance and low dielectric materials, respectively. However, Cu metallization system needs a stable diffusion barrier. Meanwhile, it is known that the properties of MOCVD TiN film are affected largely by the substrate material. In this study, we investigated the interface stability of MOCVD TiN/PECVD SiOF film for the possibility of integration. The SiOF film of 100 nm thickness was deposited using TEFS with Ar as a carrier and O_2 as a reactant. The MOCVD TiN film of 50 nm thickness was coated using TDEAT and He carrier at substrate temperature of 350°C. The TiN/SiOF film was annealed in the temperature range of 200 - 600°C for 30 min. in vacuum. The effect of annealing was investigated by FTIR, four point probe, C-V measurement, and AES. It was observed that the sheet resistance of the TiN film increased and the dielectric constant of the SiOF film decreased at annealing temperature above 500°C. After the TiN film was removed from the annealed TiN/SiOF film, FTIR showed unknown peak which increased as a function of annealing temperature. The results of C-V measurement also showed unstable interface at annealing temperature above 500°C. We demonstrated that the properties of MOCVD TiN/PECVD SiOF film were affected by annealing, which may be due to diffusion and interaction at interface.

10:40am **TF-FrM8 Assessment of As-deposited Polycrystalline Silicon Films on Polymer Substrates using ECR-PECVD***, **S.H. Bae**, S.J. Fonash,* The Pennsylvania State University

As-deposited polycrystalline silicon (poly-Si) films have been successfully grown on polymer substrates at 120 and 200 °C using ECR (Electron Cyclotron Resonance) PECVD. PES (polyethersulfone) and PET (polyethylene terephthalate) substrates have been used in this work. To block diffusion and degassing from the polymer substrates, 1000 Å ECR-PECVD silicon nitrides (refractive index = 1.9) have been coated on the substrates prior to Si film depositions. Then, Si films have been deposited with SiH_4/H_2 ECR plasmas. The structural, opto-electric and electrical characteristics of Si films have been assessed by X-ray diffraction, photoluminescence, and electrical conductivity measurements, respectively. X-ray diffractions for 3500 Å Si films grown at 120 and 200 °C have shown (111), (220), (311) and (331) peaks which are the primary diffraction peaks of crystalline Si materials. We have explored the effect of the 13.56 MHz RF substrate bias during growth of Si films. According to X-ray diffraction patterns, low RF substrate bias and high substrate temperature are favorable for high degree of crystallinity of Si films. It is noted that RF substrate bias during ECR plasmas may tailor electrical properties of as-deposited poly-Si films; as the RF substrate bias is applied and increased, conductivities are improved and activation energies are decreased. In photoluminescence spectra of Si films, the intensity of luminescence is enhanced as RF bias is increased. Since intensity of photoluminescence is related to defect density of Si films; the more defects offer the more alternative paths for non-radiative recombination which compete with radiative recombination paths, enhancement of photoluminescence intensity with applying RF bias may mean that degree of defect passivation during Si film growth is controlled by RF substrate bias.

11:00am **TF-FrM9 A Novel Method For Determining Kinetic Rate Expressions For CVD Processes Using a Combination of Step Coverage Measurements and Computer Simulation***, E.J. McInerney, **G. Ramanath**, D.C. Smith,* Novellus Systems

There is an increasing need for understanding reaction kinetics and mechanisms during chemical vapor deposition (CVD) to accurately predict deposition rate, uniformity, step coverage, and reactor throughput. We present a novel method for determining reliable kinetic rate expressions by a combination of transport modeling and experimental measurements of step coverage and planar deposition rate. We demonstrate the method by applying it to W CVD during H_2 reduction of WF_6 to elucidate -- for the first time -- two distinct kinetic mechanisms operating in different WF_6 flow regimes. Rate expressions deduced from deposition rate measurements on planar geometries often fail to accurately predict step coverage due to incorrect assumptions of near-surface concentration N_s of reactants. As direct measurements are difficult, modeling species transport in the reactor is necessary to estimate N_s. However, this method by itself is inadequate because small errors in the model can lead to large errors in the rate expression. In our method, we obviate the limitations of traditional modeling by utilizing experimentally measured step coverage values to model species transport within topological features in addition to that in the reactor. In this way N_s is calculated self-consistently, allowing the determination of the reaction order n and kinetic mechanisms. Despite numerous studies of the H_2-WF_6 reaction over the last 30 years, the order of WF_6 concentration dependence on W deposition rate has been unresolved between n=0, 1/6, and 1. Our results reveal two distinct mechanisms: at high WF_6 flows the rate is HF desorption limited (n=1/6), while at low flows WF_6 adsorption is the limiting step (n=1).

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