Thin Film
Room: B4 - Session TF2-MoM

Metals and Nitrides (ALD/CVD)
Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am TF2-MoM1 ALD of Metal Chalcogenide Thin Films, M.A. Leskela, T. Hatana, M.J. Heikkila, V.J. Pore, M.K. Rituala, University of Helskini, Finland

ALD of metal sulphide thin films has been known since the discovery of the technology in early 70s whereas ALD of metal selenide and telluride films has been limited because of a lack of precursors that would at the same time be safe and exhibit high reactivity as required in ALD. In this presentation we show that alkylsilanes of tellurium and sulphur can be used as tellurium and selenium precursors in thermal ALD. Compounds with a general formula (Et3Si)2Te and (Et3Si)2Se react with various metal halides producing metal telluride and selenide thin films. Sb2Te3, GeTe and GeSb2Te5 films can be deposited by ALD at 90 °C using (Et3Si)2Te, SbCl3 and GeCl3·C2H4O as precursors. All three precursors exhibit a typical saturative ALD growth behaviour. The GeSb2Te5 films show excellent conformity on a high aspect-ratio trench structure. Many other selenide and telluride films can be deposited by ALD using alkylsilanes of tellurium and selenium as precursors. Those deposited in this work include ZnTe, Bi2Te3, ZnSe, Bi2Se3, InSe and Cu2Se. The growth temperature has in some cases been 400 °C showing the thermal stability of these new Se and Te precursors. Growth rates of these binary chalcogenide films are typically between 0.5 and 1 Å/cycle. Other metal precursors than chlorides are also possible in the selenide and telluride depositions, as exemplified by the use of GeBr2 and Sb(OEt)3.

9:00am TF2-MoM3 Molybdenum ALD and Mo/W Alloy Growth Using MoF6, WF6 and Si2H6 as the Reactants, D. Seghete, A.S. Cavanagh, S.M. George, University of Colorado at Boulder

Metal ALD using thermal chemistry is limited and based on combustion reactions (Ru, Pt), organic or H2 reduction (Cu, Pd) or fluorosilane elimination (W). Molybdenum (Mo) is a refractory metal that has applications in alloys, catalysis and electronics. Mo ALD can be achieved with fluorosilane elimination chemistry using MoF6 and Si2H6 as reactants. This process is similar to W ALD using WF6 and Si2H6 as reactants. This study reports Mo ALD using a quartz crystal microbalance (QCM) to monitor the growth of the Mo ALD films and Mo/W alloy films in a high wall viscous flow reactor.

QCM studies showed that Mo ALD is self-limiting for both MoF6 and Si2H6 reactants. MoF6 produces a large mass gain and Si2H6 produces a small mass loss. A mass gain of 535 ng/cm2 per cycle was observed at 120 °C when both reactant exposures were in saturation. Although long MoF6 residence times were observed on the surface, the Mo ALD growth per cycle was independent of purge time. The Mo film growth reached a linear regime after a short nucleation period of only 3–4 cycles on Al2O3 ALD surfaces. X-ray reflectivity (XRR) experiments confirmed linear Mo ALD growth versus number of cycles. A growth per cycle of 6.4 Å/cycle was measured at 120 °C. The average density of the Mo films was 8.7 g/cm3 and there was excellent agreement between the QCM and XRR experiments. The temperature dependence of the Mo ALD growth per cycle was investigated from 90 °C to 150 °C. X-ray photoelectron spectroscopy confirmed negligible F concentrations in the Mo ALD films. However, higher Si concentrations were observed in the Mo ALD films compared with W ALD films. The variation of Si content in the Mo ALD films was examined versus growth temperature and dosing conditions. Various Mo/W alloys can be produced by alternating Mo ALD and W ALD. These alloys can eliminate crystalline grain growth that occurs in the pure metals. This reduction of crystalline grain growth relieves the internal mechanical stress that develops in pure W ALD films.


Ruthenium thin films were deposited by pulsed chemical vapor deposition from bis(N,N-di-tert-butylacetamidinato) ruthenium(II) dicarbonyl and O2. Highly conductive, dense, conformal and pure thin Ru films can be deposited when oxygen exposure E0 approaches a certain low threshold (E0 = E0, max). When E0 > E0, max, the films peel off silica substrates, perhaps due to recombinative desorption of O2 at the film/substrate interface. Ruthenium films grown on tungsten substrates show very strong adhesion, > 17 J m2, and no evidence for any oxidized interlayer between the Ru and the W. Thus the low oxygen exposure does not oxidize the tungsten substrate surface during Ru deposition. Analysis by an atomic probe microscope shows that the crystallites are nearly free of carbon impurity (<0.1at.%), while a low level of carbon (~0.5at.%) is segregated near the grain boundaries. The atom probe microscope also shows that a small amount of O impurity (0.3at.%-0.5at.%) is distributed uniformly through the crystallites and the grain boundaries.

10:00am TF2-MoM5 Thermal and Remote Plasma ALD of Ru from CpRu(CO)2Et and O2, N. Leick, B.O.F. Verkuiljen, E. Langereis, Eindhoven University of Technology, The Netherlands, S. Ruuchow, SAFEC Hitec Limited Power Road, UK, F. Rozeboom, NXP Semiconductors Research, The Netherlands, M.C.M. van de Sanden, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

Ruthenium (Ru) is regarded as an electrode candidate on ultrahigh-k SrTiO3 dielectric films for future high-density trench capacitors. To achieve conformal film growth, remote plasma deposition (ALD) of Ru is investigated. To this end, the use of an oxidizing reactant is desired to avoid electronic degradation of the interface properties of SrTiO3 as found when using a NH3 plasma for Ru ALD or when using thermal ALD TiN as electrode. Thermal ALD of Ru using O2 gas, however, generally results in a pronounced nucleation delay and high surface roughness. The current work aims at depositing ALD Ru using an O2 plasma in order to improve the film nucleation and to try to obtain smoother films. Using the novel CpRu(CO)2Et precursor and O2, both thermal and remote plasma ALD of Ru were studied in the same reactor at wafer temperatures up to 200 nm. Unlike thermal ALD, the Ru film growth by remote plasma ALD does not rely on the dissociative chemisorption of O2 on the Ru surface and good film nucleation is expected by providing O radicals from the gas phase. In situ spectroscopic ellipsometry, x-ray reflectometry and diffractometry, and electrical measurements clearly show this benefit of the O2 plasma. The Ru films almost immediately nucleate for the plasma-based process, whereas the thermal process showed a nucleation delay of approximately 100 cycles. Once film growth has started, the growth per cycle (1 Å/cycle), the effective growth rate (20 Å/cycle) for >5 nm thick films, and the polycrystalline structure are similar for both ALD processes. However, despite the drastically improved nucleation, the remote plasma ALD Ru films show higher roughness values than the thermal ALD Ru films (roughness of 13 nm and 8 nm for 20 nm thick films, respectively). To elucidate this unexpected phenomenon, the film nucleation and surface reactions were examined. Mass spectrometry provided insight into the reaction products (CO, CO2, CH4 and H2O mainly) and, therefore, into the surface chemistry during both ALD processes. Optical emission spectroscopy delivered information on the species created during plasma exposure. A reaction mechanism will be proposed for these oxygen-based ALD Ru processes that accounts not only for the differences in nucleation, but also relates to the roughness development of the Ru films.


Atomic layer deposition (ALD) provides the unique and powerful capability to blend materials at the atomic scale for tuning and optimizing the properties of the resulting mixed layers. The ALD of mixed metal-oxide layers to maximize the charge storage capacity of dielectric materials is well known, but the ALD of mixed metal films is less well explored. The capability to synthesize mixed-metal layers with tunable physical and chemical properties could benefit numerous applications such as catalysts, hydrogen storage, corrosion resistance, and microelectronics, and the ALD of metal laminate nanostructures offers the possibility of core-shell structures and near surface alloys. In this study, we examine the ALD of platinum-iridium (Pt-Ir) mixed metal layers. The platinum ALD uses alternating exposures to (methylcyclopentadienyl) trimethylplatinum and oxygen while the iridium ALD uses alternating exposures to iridium(III) acetylacetonate and oxygen. The similar chemistries and process conditions for these pure metals facilitates ALD of the mixed metal layers. Furthermore, the tendency of Pt to form discrete nanoparticles on oxide supports makes this material attractive for catalytic application. We examine the Pt-Ir mixed metal ALD using in situ quartz crystal microbalance and quadrupole mass spectrometer measurements to investigate the growth mechanism for the pure and mixed materials as well as the effect of mixing on the metal nucleation and growth. In addition, ALD Pt-Ir films were prepared on planar substrates and examined with a variety of techniques to evaluate the thickness, morphology, crystal
of the primary thin film constituents. One process observed in the first cycles of growth is the shift in the position of the N(1s) peak, from a binding energy of cu. 398.9 eV to 397.2 eV. The former binding energy corresponds well to that reported for –N(R)2 species (398.6), while the latter is close to that reported for TaN (397.5) and Ta2N5 (396.9). As a final example, we will consider growth of TaN on SiO2 and porous low-k substrates modified with interfacial organic layers. We have found that adsorption of a branched polymer possessing a high density of –NH2 species on the porous dielectric increases both the initial uptake of Ta[N(CH3)2]x in the first half cycle, and the growth rate per cycle. Here an important issue concerns the fate of the IOL—does the ALD thin film quickly and uniformly cover the IOL, or are there reactions between the ALD precursors and the IOL? We find that the fate of the IOL depends strongly on the density and spatial distribution of reactive groups in the organic layer. We will discuss the implications of these observations concerning the use of IOLs as nucleation promoters in ALD.

11:20am TF2-MoM10 Interconnect Reliability Improvement by Selective CVD of Co Capping Layer on SAM Treated Copper/Low-k Surface. H.B. Bhandari, H. Park, R.G. Gordon, Harvard University

Electromigration in copper interconnects is a surface phenomenon and therefore becomes a dominant reliability concern as the Cu line widths are narrowed to accommodate the continuing scaling of interconnect structures. Reliability can be improved by applying a layer of cobalt metal on the top surface of Cu lines, thereby improving its adhesion to an overlying etch-stop layer such as silicon nitride. Thus selective deposition of Co metal on ultra narrow Cu lines integrated in low-k dielectric is of critical importance in preserving the electrical performance of future integrated circuits. Here we propose a chemical vapor deposition process for applying Co thin films selectively on Cu surfaces. XPS showed complete coverage by Co films less than 2 nm thick on Cu substrates. The selectivity of the Co deposition was confirmed by Cu line to line leakage measurements on long interdigitated comb structures. Further enhancement of Co selectivity was achieved by employing self-assembled monolayers (SAMs) to passivate low-k surfaces. XPS and TEM characterizations indicate that low-k surfaces treated with (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane or Si2H6 as a precursor and reactant, respectively, as a novel and systematic method to conformally coat an electrically conductive material on complex fiber architectures. By ALD processing, a uniform coating of tungsten was achieved at a temperature of 180 °C on quartz tissues with fibers ranging in diameter from 250 nm to 3 μm. A deposition rate of 3.4 Å/cycle was measured by deposition of tungsten on Si coated with ~80 Å of ALD Al2O3. The tungsten growth nucleation period on the quartz tissue is predicted to be similar to tungsten growth on Al2O3. Scanning electron microscopy showed only minor cracking of the tungsten film coating on the quartz fibers, even after handling. The resistivity of ALD tungsten thin films grown on Al2O3 was < 200 μOhm cm, and measurements show similar resistivity values for the tungsten deposited on the quartz fiber. Electronic transport differences in measurement of resistivity and the subsequent mechanisms for conductive pathways through fiber bundles compared to monolithic structures will be discussed. These results suggest new opportunities in the use of ALD processing to create electronically active fiber systems.
Authors Index

Bold page numbers indicate the presenter

— A —
Alvis, R.: TF2-MoM4, 1

— B —
Bhandari, H.B.: TF2-MoM10, 2

— C —
Cavanagh, A.S.: TF2-MoM3, 1
Christensen, S.T.: TF2-MoM6, 1

— E —
Elam, J.W.: TF2-MoM6, 1
Engstrom, J.R.: TF2-MoM11, 2

— G —
George, S.M.: TF2-MoM3, 1
Gordon, R.G.: TF2-MoM10, 2; TF2-MoM4, 1

— H —
Hatanpaa, T.: TF2-MoM1, 1
Heikkila, M.J.: TF2-MoM1, 1
Hughes, K.J.: TF2-MoM11, 2
Jur, J.S.: TF2-MoM9, 2

— L —
Langereis, E.: TF2-MoM5, 1
Leick, N.: TF2-MoM5, 1
Leskela, M.A.: TF2-MoM1, 1
Lin, Y.: TF2-MoM4, 1

— N —
Na, J.-S.: TF2-MoM9, 2

— R —
Ritala, M.K.: TF2-MoM1, 1
Roozeboom, F.: TF2-MoM5, 1
Rushworth, S.: TF2-MoM5, 1

— S —
Seghete, D.: TF2-MoM3, 1

— U —
Ulfig, R.M.: TF2-MoM3, 1

— V —
van de Sanden, M.C.M.: TF2-MoM5, 1
Verkuijlen, R.O.F.: TF2-MoM5, 1

— W —
Wang, H.: TF2-MoM4, 1
Wang, X.: TF2-MoM4, 1