

# Thermal and Remote Plasma ALD of Ru from CpRu(CO)<sub>2</sub>Et and O<sub>2</sub>

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cathode current were monitored. Increasing the gas flow rate from 10 sccm to 100 sccm caused the cathode current to decrease by ~25%, but on reversing the flow rate, the cathode current did not go back up along the same curve, instead exhibiting a hysteretic behavior. A similar trend was observed for the change in oxygen partial pressure between 0 and 20% as well. The width and position of the hysteresis curve depends on the relative values of the gas flow rates and the oxygen partial pressures. VO<sub>x</sub> thin films deposited at various points along the hysteresis curve were evaluated using four-probe resistivity measurements over a wide temperature range. The room temperature resistivity of the films varied by more than six orders of magnitude and was found to have a progressive dependence on the cathode current. Structural characterizations such as X-ray diffraction and transmission electron microscopy studies indicated that the microstructure changes gradually from nano-crystallite to amorphous nature with the increase in total gas flow rate and/or oxygen partial pressure.

11:20am **TF1-MoM10 Compositional and Structural Evolution of Sputtered Ti-Al-N**, *P.H. Mayrhofer, L. Chen, M. Moser*, Montanuniversitaet Leoben, Austria, *Y. Du*, Central South University, China

The compositional and structural evolution of Ti-Al-N thin films as a function of the total working gas pressure ( $p_T$ ), the N<sub>2</sub>-to-total pressure ratio ( $p_{N_2}/p_T$ ), the substrate-to-target distance (ST), the substrate position, the magnetron power current ( $I_m$ ), the externally applied magnetic field, and the energy and the ion-to-metal flux ratio of the ion bombardment during reactive sputtering of a Ti<sub>0.5</sub>Al<sub>0.5</sub> target is investigated in detail. Based on this variation we propose that the different poisoning state of the Ti and Al particles of the powder-metallurgically prepared Ti<sub>0.5</sub>Al<sub>0.5</sub> target in addition to scattering and angular losses of the sputter flux cause a significant modification in the Al/Ti ratio of the deposited thin films ranging from ~1.05 to 2.15. The compositional variation induces a corresponding structural modification between single-phase cubic, mixed cubic-hexagonal and single-phase hexagonal. However, the maximum Al content for single-phase cubic Ti<sub>1-x</sub>Al<sub>x</sub>N strongly depends on the deposition conditions and was obtained with  $x = 0.66$ , for the coating deposited at 500 °C,  $p_T = 0.4$  Pa, ST = 85 mm, and  $p_{N_2}/p_T = 17\%$ . Our results show, that in particular, the N<sub>2</sub>-to-total pressure ratio in combination with the sputtering power density of the Ti<sub>0.5</sub>Al<sub>0.5</sub> compound target has a pronounced effect on the Al/Ti ratio and the structure development of the coatings prepared.

## 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. Hatanpaa, M.J. Heikkila, V.J. Pore, M.K. Ritala*, University of Helsinki, Finland

INVITED

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 selenium can be used as tellurium and selenium precursors in thermal ALD. Compounds with a general formula (R<sub>3</sub>Si)<sub>2</sub>Te and (R<sub>3</sub>Si)<sub>2</sub>Se react with various metal halides producing metal telluride and selenide thin films. Sb<sub>2</sub>Te<sub>3</sub>, GeTe and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> films can be deposited by ALD at 90 °C using (Et<sub>3</sub>Si)<sub>2</sub>Te, SbCl<sub>3</sub> and GeCl<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> as precursors. All three precursors exhibit a typical saturative ALD growth behaviour. The Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> films show excellent conformality 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, Bi<sub>2</sub>Te<sub>3</sub>, ZnSe, Bi<sub>2</sub>Se<sub>3</sub>, In<sub>2</sub>Se<sub>3</sub> and Cu<sub>2</sub>Se<sub>y</sub>. 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 GeBr<sub>2</sub> and Sb(OEt)<sub>3</sub>.

9:00am **TF2-MoM3 Molybdenum ALD and Mo/W Alloy Growth Using MoF<sub>6</sub>, WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> 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 H<sub>2</sub> 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 MoF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> as reactants. This process is similar to W ALD using WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> 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 hot wall viscous flow reactor.

QCM studies showed that Mo ALD is self-limiting for both MoF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> reactants. MoF<sub>6</sub> produces a large mass gain and Si<sub>2</sub>H<sub>6</sub> produces a small mass loss. A mass gain of 535 ng/cm<sup>2</sup> per cycle was observed at 120°C when both reactant exposures were in saturation.

Although long MoF<sub>6</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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/cm<sup>3</sup> 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.

9:20am **TF2-MoM4 Vapor Deposition of Ruthenium Thin Films from an Amidinate Precursor**, *H. Wang, X. Wang, Y. Lin, R.G. Gordon*, Harvard University, *R. Alvis*, FEI Company, *R.M. Ulfing*, Imago Scientific Instruments

Ruthenium thin films were deposited by pulsed chemical vapor deposition from bis(*N,N'*-di-*tert*-butylacetamidinato) ruthenium(II) dicarbonyl and O<sub>2</sub>. Highly conductive, dense, conformal and pure thin Ru films can be deposited when oxygen exposure E<sub>O</sub> approaches a certain low threshold (E<sub>max</sub>). When E<sub>O</sub> > E<sub>max</sub>, the films peel off silica substrates, perhaps due to recombinative desorption of O<sub>2</sub> at the film/substrate interface. Ruthenium films grown on tungsten substrates show very strong adhesion, > 17 J m<sup>-2</sup>, 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 (<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.%) is distributed uniformly through the crystallites and the grain boundaries.

9:40am **TF2-MoM5 Thermal and Remote Plasma ALD of Ru from CpRu(CO)<sub>2</sub>Et and O<sub>2</sub>**, *N. Leick, R.O.F. Verkuijlen, E. Langereis*, Eindhoven University of Technology, The Netherlands, *S. Rushworth*, SAFC Hitech Limited Power Road, UK, *F. Roozeboom*, 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* SrTiO<sub>3</sub> dielectric films for future high-density trench capacitors. To achieve conformal film growth, atomic layer 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 SrTiO<sub>3</sub> as found when using a NH<sub>3</sub> plasma for Ru ALD or when using thermal ALD TiN as electrode. Thermal ALD of Ru using O<sub>2</sub> gas, however, generally results in a pronounced nucleation delay and high surface roughness. The current work aims at developing ALD of Ru using an O<sub>2</sub> plasma in order to improve the film nucleation and to try to obtain smoother films. Using the novel CpRu(CO)<sub>2</sub>Et precursor and O<sub>2</sub>, both thermal and remote plasma ALD of Ru were studied in the same reactor at wafers up to 200 mm. Unlike thermal ALD, the Ru film growth by remote plasma ALD does not rely on the dissociative chemisorption of O<sub>2</sub> 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 O<sub>2</sub> 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 the film growth has started, the growth per cycle (1 Å/cycle), the electrical properties (20 μΩcm for >5 nm 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