Thermal and Remote Plasma ALD of Ru from CpRu(CO)2Et and O2

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The compositional and structural evolution of Ti-Al-N thin films as a function of the total working gas pressure ($p_{w}$), the N$_2$-to-total pressure ratio ($p_{N2}/p_T$), 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$_{60}$Al$_{40}$ 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-metallographically prepared Ti$_{60}$Al$_{40}$ 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 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 alkylsiline sulfurselenides and selenides can be used as tellurium and selenium precursors in thermal ALD. Compounds with a general formula (R$_3$Si)Te and (R$_3$Si)Se react with various metal halides producing metal telluride and selenide thin films. Sh$_{2}$Te$_{3}$, GeTe and Ge$_{2}$Sb$_{2}$Te$_{5}$ films can be deposited by ALD at 90 °C using (Et$_3$Si)$_2$Te, SbCl$_5$, and GeCl$_3$-CH$_3$OH as precursors. All three precursors exhibit a typical saturative ALD growth behaviour. The Ge$_{2}$Sb$_{2}$Te$_{5}$ films show excellent conformity on a high aspect-ratio trench structure. Many other selenide and telluride films can be deposited by ALD using alkylsiline sulfurselenides and selenium as precursors. Those deposited in this work include ZnTe, Bi$_2$Te$_3$, ZnSe, Bi$_2$Se$_3$, In$_2$Se$_3$ and Cu$_2$Se. 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$_3$ and Sb(OEt)$_3$.

9:00am **TF2-MoM2** Molybdenum ALD and Mo/W Alloy Growth Using MoF$_6$, WF$_6$, and SiH$_4$ as 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$_2$ reduction (Cu, Pd) or fluorosilanes elimination (W). Molybdenum (Mo) is a refractory metal that has applications in alloys, catalysts and electronics. Mo ALD can be achieved with fluorosilane elimination chemistry using MoF$_3$ and SiH$_4$ as reactants. This process is similar to ALD using WF$_6$ and SiH$_4$ 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$_3$ and SiH$_4$ reactants. MoF$_3$ produces a large mass gain and SiH$_4$ produces a small mass loss. A mass gain of 355 ng/cm$^2$ per cycle was observed at 120°C when both reactant exposures were in saturation.

Although long MoF$_3$ residence times were observed on the surface, the Mo ALD growth per cycle was independent of particle number. Mo ALD film growth reached a linear regime after a short nucleation period of only 3-4 cycles on Al$_2$O$_3$ 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$^3$ 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.