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

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Published in: Proceedings of the 56th international American Vacuum Society Symposium & Exhibition (AVS 56) 8-13 November 2009, San Jose, California

Published: 01/01/2009

Document Version
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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, thin films deposited at various points along the hysteresis curve were evaluated using four-point 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, Montanuniversitat 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 (pT), the N2-to-total pressure ratio (pN2/pT), the substrate-to-target distance (ST), the substrate position, the magnetron power current (Ip), the externally applied magnetic field, and the energy and the ion-to-metal flux ratio of the ion bombarding during reactive sputtering of a Ti80Al20 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 Ti0.5Al0.5 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 xAl1-xN strongly depends on the deposition conditions and was obtained with x = 0.66, for the coating deposited at 500 ºC, pT = 0.4 Pa, ST = 165 mm, and pN2/pT = 17%. Our results show, that in particular, the N2- to-total pressure ratio in combination with the sputtering power density of the Ti80Al20 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. Hiekilla, 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 (R3Si)2Te or (R3Si)2Se react with various metal hydrides producing metal telluride and selenide thin films. Sn2Te5, GeTe and Ge2Sb2Te5 films can be deposited by ALD at 90 ºC using (Et3Si)2Te, SbCl3 and GeCl3-C6H6O2 as precursors. All three precursors exhibit a typical saturation ALD growth behaviour. The Ge2Sb2Te5 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, Bi2Te3, ZnSe, Bi2Se3, In2Se3 and Cu2Se. The growth temperature has in some cases been 400 ºC 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 GeBr3 and Sb(OTe)3.

9:00am TF2-MoM3 Molybdenum ALD and Mo/W Alloy Growth Using MoF6, WF6 and SiH4 as Reactants. 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 SiH4 as reactants. This presentation is similar to ALD using WF6 and SiH4 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 MoF6 and SiH4 reactants. MoF6 produces a large mass gain and SiH4 produces a small mass loss. A mass gain of 535 ng/cm2 per cycle was observed at 120 ºC 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 MoF6 dosage. 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 120ºC. 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 ºC to 150 ºC.

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{(c5V3-d-tetra-butylicatamidinato) ruthenium(II) dicarbonyl and O2. Highly conductive, dense, conformal and pure thin Ru films can be deposited when oxygen exposure EtO approaches a certain low threshold (Eto). When Eto > Eto, 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 W oxygen exposure does not oxidize the tungsten substrate 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.%) is distributed uniformly through the crystallites and the grain boundaries.