Nanostructured composite thin films with tailored resistivity by atomic layer deposition

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ABSTRACT

We have developed a new type of thin film composite material comprised of Mo:Al₂O₃ consisting of conducting metal nanoclusters embedded in an insulating Al₂O₃ matrix. These nanocomposite thin films were prepared by atomic layer deposition (ALD). Quartz crystal microbalance (QCM) experiments performed with various Mo cycle percentages revealed that the Mo ALD inhibits the Al₂O₃ ALD and vice versa. Despite this inhibition, the relationship between Mo content in the films and cycle percentage was close to expectations. Depth profiling X-ray photoelectron spectroscopy (XPS) showed that the Mo:Al₂O₃ films were uniform in composition and contained Al, O and metallic Mo as expected, but also included significant F and C. Cross sectional TEM revealed the composite film structure to be metallic nanoparticles (2-3nm) embedded uniformly in an amorphous Al₂O₃ insulating matrix. The resistivity of these composite films could be tailored in the range of 10⁴ - 10¹² Ohm-cm by adjusting the Mo ALD cycle percentage. These nanocomposite films have been used as resistive coatings in microchannel plate (MCP) fabrication and as charge-drain coatings in micro-electron-optical devices. Here we report the ALD growth characterization, and application of these of Mo:Al₂O₃, films.

Keywords: ALD, resistive layer, QCM, molybdenum, aluminum oxide, nanostructures

1. INTRODUCTION

Thin film composite materials that combine conducting and insulating components have been utilized for a wide variety of applications such as resistive layers for electron multipliers such as microchannel plates,[4-8] resistive memories,[9-15] electro-chromic devices,[16-18] biomedical devices,[19-23] and charge dissipating coatings on micro-electromechanical systems (MEMS) devices.[19-23] The physical and electrical properties of composite thin films can be tailored by adjusting the relative proportions of the metal and insulating constituent materials. Amongst the numerous thin film deposition methods, atomic layer deposition (ALD) is a technique for growing complex layers in a precisely controlled manner with many unique advantages.[3, 24, 29, 30] ALD is based on a binary sequence of self-limiting chemical reactions between precursor vapors and a solid surface. Because the two reactions in the binary sequence are performed separately, the gas phase precursors are never mixed and this eliminates the possibility of gas phase reactions that can form particulate contaminants and cause non-self-limiting chemical vapor deposition. This strategy yields monolayer-level thickness and composition control. The self-limiting aspect of ALD leads to continuous pinhole-free films, excellent step coverage, and conformal deposition on very high aspect ratio structures. ALD processing is also extendible to large area substrates and batch processing of multiple substrates and used in semiconductor industry to deposit various thin film layers.[34]

Here we describe composite thin films synthesized by combining the ALD processes for molybdenum (Mo) and aluminum oxide (Al₂O₃). Our study focused on (a) the ALD of Mo:Al₂O₃ nanolaminates comprised of alternating, distinct layers of these two materials and (b) synthesizing more thoroughly mixed Mo:Al₂O₃ composites. The primary goal is to achieve unique electrical properties distinct from either material in their bulk forms. This approach has been employed previously for the ALD of metal oxide composite materials including ZnO-Al₂O₃[25, 26] and Nb₂O₅-Ta₂O₅,[27, 28] but to our knowledge our group is the first to study metal-metal oxide (Mo:Al₂O₃ and W:Al₂O₃) nanocomposites by ALD[29, 30]. The low temperature ALD process yields nanocrystalline Mo with an electrical resistivity of ρ ~10⁴ Ω-cm, while ALD Al₂O₃ is an excellent amorphous insulator with a resistivity of ρ ~10¹⁵ Ω-cm[31]. This contrast offers the potential for an extremely wide range of tunable resistance values. In addition, ALD Al₂O₃ has a high breakdown electric field[31] and this attribute is beneficial in high voltage operating devices such as MCPs where the electric fields can be >10⁶ V/m. Both Mo and Al₂O₃ ALD can be performed under similar process conditions including the deposition temperature, and this simplifies the task of combining these materials.

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materials into composite layers. In addition to the wide variance in electrical properties, Mo and Al$_2$O$_3$ have very different physical and chemical properties. As a result, by modulating the proportion of Mo in the Al$_2$O$_3$ matrix, we expect that the optical, mechanical, and electrical properties of Mo:Al$_2$O$_3$ composite layers can be broadly adjusted. Finally, ALD Al$_3$O$_6$ has been extensively studied whereas very little work done on ALD Mo$^{[25]}$. In summary, there are many reasons for exploring Mo:Al$_2$O$_3$ composite layers by ALD.

Here, we present the ALD synthesis of Mo:Al$_2$O$_3$ nanocomposite films to evaluate the effect of the ALD process parameters on the growth, composition, and electrical properties of the resulting films. We employed in-situ quartz crystal microbalance (QCM) measurements to perform a phenomenological study on the growth behavior of these films. We intend to conduct and report more detailed studies aimed at unraveling the mechanism of Mo:Al$_2$O$_3$ ALD in the future.

2. EXPERIMENTAL

Depositions of Al$_2$O$_3$, Mo, and composites of Mo:Al$_2$O$_3$ were carried out at 200°C in a hot walled viscous flow ALD reactor described previously$^{[3, 29, 32]}$. This reactor was equipped with a quartz crystal microbalance (QCM) that facilitated in-situ studies of the ALD processes. The TMA (97%, Aldrich), deionized H$_2$O, Si$_2$H$_6$ (99.998%, Aldrich) and WF$_6$ (99.8%, Aldrich) precursors were maintained at room temperature. The ultrahigh purity N$_2$ carrier gas flow was set to 300 sccm which provided a base pressure of 1.0 Torr in the ALD reaction chamber as measured by a heated Baratron pressure gauge (MKS model 629B). The Mo:Al$_2$O$_3$ composite films were deposited on n-type Si(100) substrates ranging in size from 1x1 cm coupons up to full 300 mm wafers. Prior to ALD, the substrates were cleaned using a 10 min ultrasonic treatment in acetone. For the Al$_2$O$_3$ substrates ranging in size from 1x1 cm coupons up to full 300 mm wafers. Prior to ALD, the substrates were cleaned using a 10 min ultrasonic treatment in acetone. For the Al$_2$O$_3$ ALD, the precursors TMA and H$_2$O were alternately pulsed in the continuously flowing N$_2$ carrier flow with the timing sequence: (1s TMA dose - 5s N$_2$ purge - 1s H$_2$O dose - 5s N$_2$ purge). The TMA and H$_2$O partial pressures during the dosing were 0.2 Torr and 0.3 Torr, respectively. Similarly, the Mo ALD used alternating exposures to MoF$_6$ and Si$_2$H$_6$ with the timing sequence: (1s Si$_2$H$_6$ dose - 5s N$_2$ purge - 1s MoF$_6$ dose - 5s N$_2$ purge), with partial pressures of 0.25 Torr and 0.05 Torr for the Si$_2$H$_6$ and MoF$_6$, respectively. These conditions for the Al$_2$O$_3$ and Mo ALD provided the self-limiting growth as verified by in-situ QCM measurements.

In-situ QCM measurements were performed to examine the Mo:Al$_2$O$_3$ composite ALD using different ALD Mo to Al$_2$O$_3$ cycle ratios. The QCM measurements typically used longer N$_2$ purge times of 10s to allow the QCM signals to stabilize after each precursor exposure. The thicknesses of Mo:Al$_2$O$_3$ layers on Si were determined using ex-situ spectroscopic ellipsometry (Alpha-SE, J. A. Woollam Co.). Transmission electron microscopy (TEM) analysis was performed by Evans Analytical Group (EAG, Sunnyvale, CA). TEM samples were prepared using the in-situ FIB lift out technique on an FEI Strata Dual Beam FIB/SEM. The samples were capped with a protective layer of carbon prior to FIB milling. The samples were imaged with a FEI Tecnai TF-20 FEG/TEM operated at 200kV in bright-field (BF) TEM mode, high-resolution (HR) TEM mode, and nano-beam diffraction (NBD) mode. The composition of the Mo:Al$_2$O$_3$ composite layers was determined by depth profiling X-ray photoelectron spectroscopy (XPS, Evans Analytical Group). The relative Mo content in the Mo:Al$_2$O$_3$ composite films was determined using X-ray fluorescence spectroscopy (XRF, Oxford ED2000).

The resistance of the Mo:Al$_2$O$_3$ layers was determined by performing current-voltage (I-V) measurements using a Keithley Model 6487 current-voltage source. To facilitate I-V measurements on these highly resistive coatings, the films were deposited on insulating substrates with lithographically patterned comb structures comprised of interdigitated Au electrodes with a 2µm spacing. These comb structures provided an effective contact area of 80000 squares, and an equivalent boost in current compared to conventional four-point probe measurements$^{[29]}$.

3. RESULTS AND DISCUSSION

Al$_2$O$_3$ ALD can be accomplished using alternating exposures to trimethyl aluminum (TMA) and H$_2$O$^{[26]}$. Mo ALD can be performed using alternating exposures to Si$_2$H$_6$ and MoF$_6$ $^{[25]}$. The surface chemistries for the individual half-reactions of the Mo and Al$_2$O$_3$ ALD have been examined in detail previously $^{[25, 26]}$. In contrast, the surface chemistry for Mo:Al$_2$O$_3$ composite ALD is largely unexplored and is most likely complex due to the unique reactions that occur during the frequent transitions between the two materials. It is well known that Al$_2$O$_3$ ALD is mediated by surface hydroxyl (OH) groups$^{[26]}$, while Mo ALD occurs via the sacrificial exchange of Si by Mo where the surface is partially F-terminated after both half-reactions$^{[25]}$. In contrast, the reaction of TMA with F terminated surface species is unknown, but a recent publication demonstrated that alternating exposures to niobium
pentafluoride and TMA yielded films comprised of niobium carbide, niobium fluoride, aluminum fluoride, and amorphous carbon\(^{[33]}\).

In-situ QCM measurements were performed to examine pure Mo and Al\(_2\)O\(_3\) ALD, as well as the influence of the Mo ALD cycle ratio on the growth of the Mo:Al\(_2\)O\(_3\) composite layers. We define the Mo cycle ratio as: \(\%\text{Mo} = \text{Mo}/(\text{Mo}+\text{Al}_2\text{O}_3)\times100\) where Mo and Al\(_2\)O\(_3\) are the relative numbers of TMA/H\(_2\)O and Si\(_2\)H\(_6\)/MoF\(_6\) ALD cycles performed, respectively. Representative QCM measurements for the Al\(_2\)O\(_3\) ALD are shown in Fig. 1a. The average steady state mass step size for Al\(_2\)O\(_3\) is 35 ng/cm\(^2\)/cycle. Ex situ ellipsometry measurements for the ALD Al\(_2\)O\(_3\) films deposited on Si(100) substrates yielded a growth rate of 1.21 Å/cycle. Similarly, representative QCM measurements for the Mo ALD are presented in Fig. 1b and show an average steady state mass gain of 840 ng/cm\(^2\)/cycle. The ALD Mo films adhered poorly to the Si(100) substrate, but the adhesion was excellent when a thin (50-60Å) ALD Al\(_2\)O\(_3\) layer was deposited first on the Si(100) substrate. Mo thin film on the Al\(_2\)O\(_3\) passivated Si(100) yielded a growth rate of ~10 Å/cycle as determined by ellipsometry.

![Figure 1](http://proceedings.spiedigitallibrary.org/ss/doi-lookup?doi=10.1007%2F978-3-319-01262-2_47)

**Figure 1.** In-situ QCM measurements recorded at 200°C for: (a) Al\(_2\)O\(_3\) and (b) Mo ALD. The steady state average mass deposited for Al\(_2\)O\(_3\) = 35 ng/cm\(^2\)/cycle, and for Mo = 840 nm/cm\(^2\)/cycle.

As expected, the Mo:Al\(_2\)O\(_3\) composite QCM data yielded a more complex pattern compared to the measurements of the pure Mo and Al\(_2\)O\(_3\) ALD. Figure 2a shows the QCM measurements for a Mo:Al\(_2\)O\(_3\) composite film prepared using 10% Mo cycles. In this particular case, there are 9 Al\(_2\)O\(_3\) ALD cycles and 1 Mo ALD cycle, and this combination of cycles is denoted as one “super cycle”. As clearly visible in Fig. 2a, the repetition of this super cycle resulted in a very repeatable pattern in the mass gains. The calculated mass gains for the individual ALD cycles of Mo and Al\(_2\)O\(_3\) are plotted in Fig. 2b. This plot shows that every super cycle of Mo:Al\(_2\)O\(_3\) deposited a similar amount of mass on the QCM sensor. The QCM step-sizes for the composite material were substantially below those of the pure ALD Al\(_2\)O\(_3\) and Mo. After each Mo ALD cycle, the Al\(_2\)O\(_3\) ALD yielded ~16 ng/cm\(^2\)/cycle and this mass gain increased gradually up to the steady state value of ~34 ng/cm\(^2\)/cycle after 9 Al\(_2\)O\(_3\) ALD cycles. The average mass added for these 9 Al\(_2\)O\(_3\) cycles was 21 ng/cm\(^2\)/cycle which is 40% lower than the steady state value for pure Al\(_2\)O\(_3\). Similarly, the Mo ALD yielded a mass increment of 250 ng/cm\(^2\)/cycle within each super cycle, a value that was 70% lower than the steady state mass gain observed for the pure Mo. The same growth inhibition behavior was observed by QCM for other %Mo values during the Mo:Al\(_2\)O\(_3\) composite film ALD. The QCM step sizes were influenced strongly by relative number of Mo to Al\(_2\)O\(_3\) ALD cycles, and this has a profound influence on the resistivity of the Mo:Al\(_2\)O\(_3\) nanocomposite layers.
Figure 2: In-situ QCM measurements performed during the ALD of Mo:Al₂O₃ composite layer using 10%Mo ALD cycles (a). Mass changes produced by individual ALD cycles as calculated from Fig.2a (b). The dashed line at 35ng/cm² and the solid line at 840ng/cm² indicate the average steady-state mass per cycle values for pure Al₂O₃ and Mo ALD, respectively.

Figure 3: XPS depth profile from Mo:Al₂O₃ composite layer showing atomic concentrations of O, Al, Si, F, Mo, and C (a). XPS spectrum of the Mo 3d spectral region showing the characteristic peaks for metallic Mo (b).

The composition of the Mo:Al₂O₃ composite films was determined using XPS depth profiling and RBS (data not shown) measurements of films prepared on Si(100) substrates. XPS depth profile from Mo:Al₂O₃ composite layer is composed of O, Al, Si, F, Mo, and C (Fig.3a). Based on the surface chemistries for the ALD Al₂O₃ and ALD Mo in the composite layers, the presence of F and C is unexpected and likely originates from the unique chemistry that occurs upon transitioning between the Mo and Al₂O₃ ALD process. The Mo3d spectral region confirms the characteristic of mostly metallic Mo but also existence of sub-oxide (Mo⁺⁴) states in the film[34]. These findings, when combined with the QCM and FTIR measurements (data not shown here), suggest that the TMA reduces the adsorbed MoOFₓ species to form AlF₃ and metallic Mo. In addition, the C and F presence in the films is similar to that in a previous study which concluded that alternating exposures to niobium pentafluoride and TMA produced films comprised of NbF₅, NbC, C, and AlF₃[33].
Figure 4: Higher resolution cross-sectional TEM image including the substrate-film interface of Mo:Al$_2$O$_3$ composite layer on Si(100) (a). The interface between the Si substrate and the Mo:Al$_2$O$_3$ composite film shows an amorphous region attributed to the Si native oxide and the initial Al$_2$O$_3$ ALD cycles. A nano-beam diffraction (NBD) measurement acquired from the composite film region exhibit diffuse rings consistent with crystalline nanoparticles (b). Top-down TEM image of Mo:Al$_2$O$_3$ composite film is comprised of 2-3 nm particles (dark spots) embedded in a oxide matrix (c).

Figure 5: ALD Mo:Al$_2$O$_3$ composite films: Resistivity determined by current-voltage measurements versus Mo cycle percentage (a), Temperature dependence resistance measurements (b), Current density vs. Electric field plot and Current density vs. square root of electric field plot.
Next, the microstructure of the Mo:Al$_2$O$_3$ composite film with 10% Mo was evaluated using TEM analysis. Fig. 4a shows a cross-sectional TEM image including the substrate-film interface. The film appears dense, uniform and continuous and the top surface is relatively smooth and parallel to the Si substrate surface. Nano-beam diffraction (NBD) measurements acquired from the composite film region (Fig. 4b) exhibit diffuse rings consistent with crystalline nanoparticles. More importantly, Fig. 4c shows that Top-down TEM image of the Mo:Al$_2$O$_3$ composite film is comprised of 2-3nm particles (dark spots) embedded in a lower density amorphous matrix. Close inspection of the particles reveals weak lattice fringes.

The electrical resistivity of the Mo:Al$_2$O$_3$ composite films was determined using current-voltage measurements of films deposited on comb structures, and the results are shown in Fig. 5a. It is clear that the resistivity of the Mo:Al$_2$O$_3$ composite films can be tuned over a very broad, 6-decade range by adjusting the Mo cycle percentage. The electrical transport mechanism in Mo:Al$_2$O$_3$ layers shows the Frenkel-Pool emission$^{[30]}$ type conduction behavior Fig. (b-d) where the current density at higher electric fields on a semi-log plot follows a linear relation (Fig. 4d). Figure 4b shows a strong temperature dependence of the I-V data: as the temperature of the layer increases, the current decreases in an exponential fashion. The details of transport properties are reported elsewhere$^{[30]}$.

The range of resistivity values achieved by these coatings in Fig. 5a, ($\sim 10^{4}$-10$^{10}$ Ohm cm) is particularly useful for applications in electron multipliers and charge drain coatings. For electron multiplier application we have used these resistive coatings to functionalize borosilicate micro-capillary glass array wafers, an alternative strategy for MCP manufacturing using ALD to impart the necessary conductivity and secondary emission properties$^{[2, 3]}$. We have also implemented these resistive nanocomposites coating in electron-optical micro-electro mechanical systems (MEMS) devices. Electrostatic charging is a challenging problem in electron-optical MEMS devices. The ALD nanocomposite films with adjustable resistance are an excellent candidate for charge drain coatings. We have demonstrated their benefit in the reflective electron beam lithography (REBL) Nanowriter, a high throughput, direct-writing, maskless lithography tool under development at KLA-Tencor$^{[30, 35]}$.

4. SUMMARY

We have developed Mo:Al$_2$O$_3$ nanocomposite coatings consisting of conducting, metallic nanoparticles embedded in an amorphous dielectric matrix. These films are prepared by ALD using alternating exposures to TMA and H$_2$O for the Al$_2$O$_3$ ALD, and alternating MoF$_5$/Si$_2$H$_6$ exposures for the Mo ALD. By varying the relative ratio of ALD cycles for the Mo and the Al$_2$O$_3$ components in the film, we can tune precisely the resistance of these coatings over a very broad range from $10^4$-10$^{12}$ Ohm-cm. We employed in-situ QCM to understand the ALD growth mechanism for the Mo:Al$_2$O$_3$ nanocomposite films. Cross-sectional TEM revealed the film structure to be metallic nanoparticles (2-3nm) embedded in an amorphous Al$_2$O$_3$ matrix. We utilized these nanocomposite coatings to functionalize microcapillary glass array wafers to fabricate large-area MCPs suitable for electron multiplier application. In a second application, we have applied these resistive films as charge drain coatings in electron-optical MEMS devices for a prototype electron beam lithography tool, and obtained high resolution electron beam patterns without charging artifacts.

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6. REFERENCES


