Atomic Layer Deposition of Ultrathin and Continuous Metal Films

Steven M. George

Depts. of Chemistry and Mechanical Engineering, University of Colorado
Boulder, Colorado 80309; Steven.George@Colorado.edu

ABSTRACT

The atomic layer deposition (ALD) of ultrathin and continuous metal films is very challenging. This paper describes a general procedure that can yield an ultrathin and continuous metal ALD film using a W ALD adhesion layer.

INTRODUCTION

Atomic layer deposition (ALD) is a thin film growth process based on sequential, self-limiting surface reactions [1]. ALD usually yields films that are conformal to the initial substrate. However, the ALD of metal films typically produces metal nanoparticles during initial film growth instead of continuous and ultrathin metal films [2].

The production of metal nanoparticles can be explained by a number of factors including lack of proper surface functional groups for chemical reaction during ALD, poisoning of the initial substrate by ligands from the ALD precursors, and the high surface energy of the deposited metal relative to the underlying substrate. Consequently, ALD leads to metal films that nucleate as metal islands. Continuous ALD metal films are not observed until these islands eventually grow together.

The ALD of ultrathin and continuous metal films is possible under the right circumstances. The most important factor is the use of an adhesion layer that has a higher surface energy than the surface energy of the desired metal film. In this case, the desired metal will "wet" the adhesion layer because the resulting surface energy is lower than the initial surface energy. This paper will illustrate this concept using W ALD as an adhesion layer for the deposition of ultrathin and continuous Pt ALD films.

EXPERIMENTAL

W has a surface energy of ~3.5 J/m^2 which is one of the highest surface energies for metals [3]. In contrast, Pt has a much lower surface energy of ~2.5 J/m^2 [3]. To obtain the deposition of ultrathin and continuous Pt ALD films, we first use Al_2O_3 ALD to coat the initial substrate. W ALD is subsequently deposited as an ultrathin and continuous film on Al_2O_3 ALD because of the unique chemistry between one of the W ALD precursors, WF_6, and Al_2O_3 [4]. Pt ALD is then deposited on the W ALD adhesion layer using (methylcyclopentadienyl)-trimethyl platinum and H radicals from a H_2 plasma [5].

RESULTS & DISCUSSION

The deposition of continuous and ultrathin Pt ALD films on flat substrates is demonstrated using ex situ x-ray photoelectron spectroscopy (XPS) and x-ray reflectivity (XRR) measurements [5]. The XPS and XRR studies versus the number of Pt ALD cycles are consistent with the layer-by-layer growth of a continuous Pt ALD film on the W ALD adhesion layer at Pt ALD film thicknesses of ≥1.5 nm.

Relative XPS atomic fractions from the Pt and W XPS signals versus the density-adjusted Pt film thickness on the W ALD adhesion layer are shown in Figure 1 [5]. The dashed line shows the prediction assuming a layer-by-layer growth mechanism for Pt ALD. XRR results also confirm that the Pt ALD film has a density of ~100% of the bulk Pt density at a film thickness of ~1.5 nm.

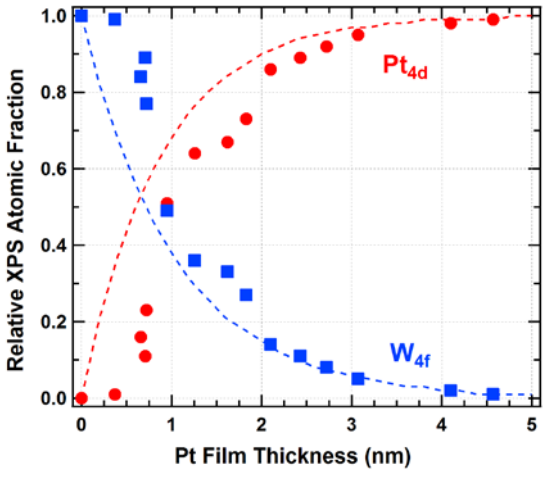

Figure 1. Relative XPS atomic fractions from the Pt and W XPS signals versus the density-adjusted Pt film thickness on the W ALD adhesion layer.

978-1-4799-5018-8/14/$31.00 ©2014 IEEE

Authorized licensed use limited to: SLUB Dresden. Downloaded on October 09,2024 at 02:20:45 UTC from IEEE Xplore. Restrictions apply.

The layer-by-layer growth of Pt ALD films has also been studied by in situ spectroscopic ellipsometry (SE) [6]. Under the proper H_2 plasma conditions, the Pt ALD growth is immediate and linear with Pt ALD cycles. Figure 2 shows the Pt film thickness and density versus the number of Pt ALD cycles [6]. The H_2 plasma exposure was 10 s and the H_2 pressure was 11 mTorr. The Pt ALD has a growth rate of 0.2 Å/cycle. Ex situ XPS analysis is consistent with the in situ SE results. Ex situ XRR analysis is also consistent with the in situ SE results. The XRR results also confirm that the density of the Pt film is ~100% of bulk density at a film thickness of ~1.5-2.0 nm.

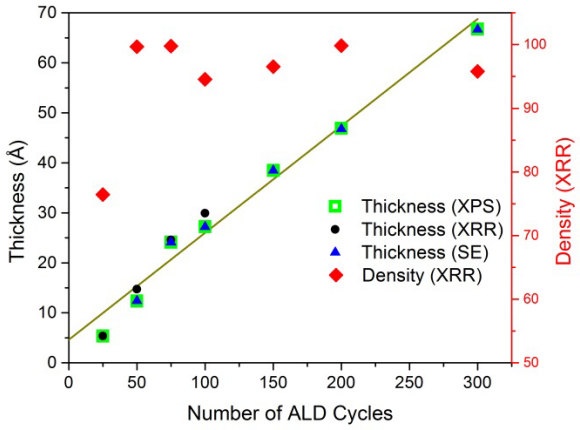

Figure 2. Pt film thickness and density versus the number of Pt ALD cycles. The Pt film thickness was measured using SE, XRR and XPS.

Continuous and ultrathin Pt ALD films have also been deposited on two high surface area substrate materials. Transmission electron microscopy (TEM) showed uniform and continuous Pt films with a thickness of ~3-5 nm on TiO_2 particles. Pt ALD was also deposited on 3M nanostructure thin film (NSTF) which is a substrate of carbon nanofingers. Analysis by TEM with electron energy loss spectroscopy (EELS) revealed W ALD and Pt ALD films with thicknesses of ~3 nm that were continuous and conformal to the 3M NSTF substrate.

CONCLUSION

This concept of using W ALD as an adhesion layer for the deposition of ultrathin and continuous metal films should be applicable to other metals because W has one of the highest surface energies for metals. For example, the deposition of ultrathin and continuous Cu ALD films should be possible on the W ALD adhesion layer because Cu has a much lower surface energy of ~1.8 J/m^2 [3].

ACKNOWLEDGEMENTS

This work was funded by General Motors Research and Development and the Defense Advanced Research Project Agency (DARPA). Advanced Energy, Inc. provided the plasma sources used for this research.

REFERENCES

[1] S.M. George, "Atomic Layer Deposition: An Overview", *Chemical Reviews* 110, 111-131 (2010).

[2] L. Baker, A.S. Cavanagh, D. Seghete, S.M. George, A.J.M. Mackus, W.M.M. Kessels, Z.Y. Liu and F.T. Wagner, "Nucleation and Growth of Pt Atomic Layer Deposition on Al_2O_3 Substrates Using (Methylcyclopentadienyl)-Trimethyl Platinum and O_2 Plasma", *Journal of Applied. Physics* **109**, 084333 (2011).

[3] L. Vitos, A.V. Ruban, H.L. Skriver and J. Kollar, "The Surface Energy of Metals", *Surface Science* **411**, 186-202 (1998).

[4] R.A. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al_2O_3", *Journal of Applied. Physics* **105**, 074309 (2009).

[5] L. Baker, A.S. Cavanagh, J. Yin, S.M. George, A. Kongkanand and F.T. Wagner, "Growth of Continuous and Ultrathin Platinum Films on Tungsten Adhesion Layers Using Atomic Layer Deposition Techniques", *Applied Physics Letters* **101**, 111601 (2012).

[6] A.S. Cavanagh, L. Baker, J.W. Clancey, J. Yin, A. Kongkanand. F.T. Wagner and S.M. George, "In Situ Characterization of Plasma-Assisted Pt ALD on W ALD Adhesion Layers with Spectroscopic Ellipsometry", *ECS Transactions* **58**(10), 19-26 (2013).

Authorized licensed use limited to: SLUB Dresden. Downloaded on October 09,2024 at 02:20:45 UTC from IEEE Xplore. Restrictions apply.