

Contamination in vacuum coatings due to water vapor
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Abstract

At last year's conference, we examined a series of aluminum films intentionally contaminated with varying amounts of water vapor. The resulting structure and chemistry of those films were explored using transmission electron microscopy. Those results beg two questions: 1) how much contamination do I have, and 2) how much contamination can my product tolerate? The method to answer to the first question is straightforward and will be described. The second question is application specific and more challenging but will be responded to with a pair of samples that bracket the boundary between good and bad. The results will help us understand why we can get good coatings using a high speed, industrial roll-to-roll metallizer at pressures in the 10^{-4} Torr region (and higher), while we need much lower pressures in our lab-scale bell-jar evaporators. It's all about the impingement rates of the metal atoms and the water molecules.

Introduction

Last year we [1] discussed making Al films deliberately contaminated with water vapor in a variety of ways. The power in that presentation was the scanning transmission electron microscopy images that provided insights into both the physical morphology and chemical stoichiometry of the various film samples. Figure 1 is a sample image-pair from that presentation showing a typical "good" sputtered Al film; the left image shows a columnar microstructure; the right image shows small amounts of oxygen at either surface. Note that these images are for a thick, sputtered aluminum film with intentional contamination from water vapor. There's more oxygen in the film than normal.

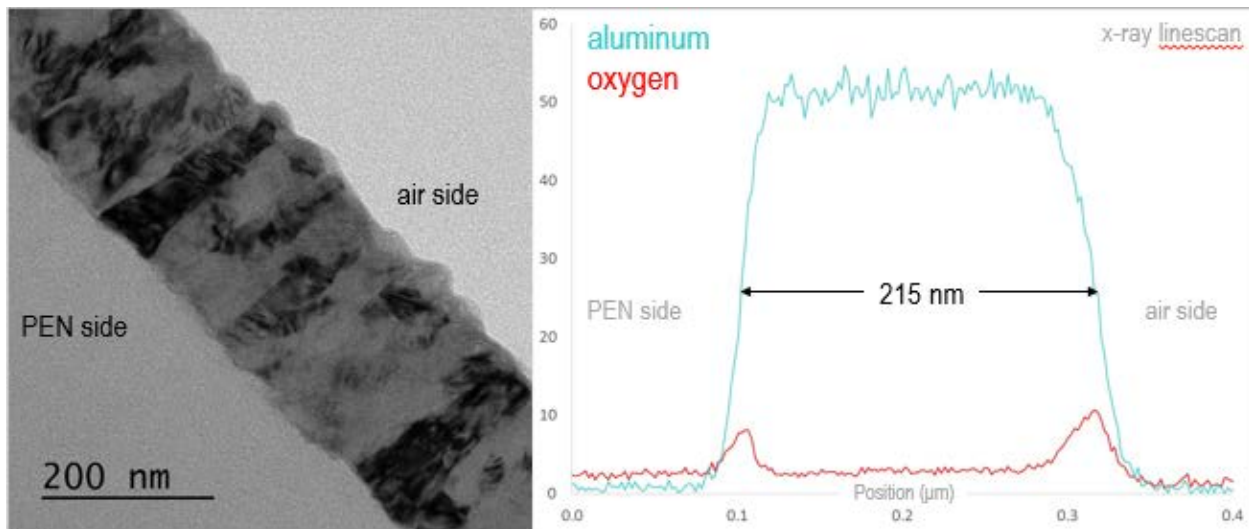


Figure 1. S/TEM cross section of a thick sputtered aluminum film on the left and the x-ray line scan showing its chemical composition on the right. For more details, see reference 1.

Several years ago, we presented a paper [2], that included scanning transmission electron microscopy images of evaporated aluminum films prepared in an industrial roll coater. All the films regardless of thickness, from 6 to 38 nm, had oxide layers at both surfaces that were ~3 nm thick.

Here we share a simple method to estimate the amount of contamination in any given coating process and estimate how much contamination is too much. To make the results specific, we will

focus on aluminum coatings deposited in a roll coater onto polymer film substrates which are contaminated with water vapor, but the method works in a much wider range of vacuum coating applications.

We begin with the conclusion: that the amount of water vapor, the water vapor partial pressure, that causes a problem depends on the rate of aluminum atoms arriving at the substrate surface, how fast we are coating. Specifically, the higher the aluminum rate, the higher the water vapor pressure the system can tolerate. In responding to the how much is too much question, we will use a specific coating example to bracket the amount of water vapor contamination that was found to be tolerable and a higher amount that was found to be “too much.”

In this paper, the amount of contamination will be characterized by the ratio of the amount of the contaminant (water vapor molecules) hitting our substrate . . . divided by the amount of our intended material (aluminum atoms) hitting our substrate. We will use the impingement rates for each material to build the ratio, looking first at aluminum, then water vapor.

Estimating the impingement rate of aluminum atoms

It's relatively easy to show that the impingement rate of aluminum atoms on the substrate in a roll coater is given by,

$$I [\text{atoms/cm}^2/\text{sec}] = \frac{\text{Thick}[\text{nm}] \times (\text{Density}/\text{AtomicWt}) \times \text{Speed}[\text{ft}/\text{min}] \times 10^{15}}{\text{CoatingApertureWidth}[\text{ft}]} \quad (1)$$

where I is the impingement rate, Thick is the film thickness, Density and Atomic Weight take their usual meanings, Speed is the web speed, and Coating Aperture Width is the distance in the web movement direction over which the substrate is coated.

I have used this formula for years in my training classes and have always disliked the large 10^{15} multiplier at the end which is needed for the particular units chosen. The large multiplier can be eliminated if one thinks microscopically instead of macroscopically, that is, if one expresses the impingement rate in units of atoms/nm²/sec instead of per cm²,

$$I [\text{atoms/nm}^2/\text{sec}] = \frac{\text{Thick}[\text{nm}] \times (\text{Density}/\text{AtomicWt}) \times \text{Speed}[\text{ft}/\text{min}] \times 10}{\text{CoatingApertureWidth}[\text{ft}]} \quad (2)$$

The ratio of density (g/cm³) to atomic weight (g/mole) in the numerator is called the molar density. The value for aluminum is 0.1 (moles/cm³). Using this value in Equation 2, we get the very simple result,

$$I [\text{atoms/nm}^2/\text{sec}] = \frac{\text{Thick}[\text{nm}] \times \text{Speed}[\text{ft}/\text{min}]}{\text{CoatingApertureWidth}[\text{ft}]} \quad (3)$$

Using metric units does not change the formula so long as the Speed is in [m/min] and the Coating Aperture Width is in [m].

Other materials have different densities and atomic weights, but for materials commonly used in vacuum evaporation, their ratios differ only modestly from that of aluminum, 0.1 moles/cm³; see Figure 2. The molar densities range from 0.06 to 0.16. Using a value of 0.1 may be adequate for many purposes.

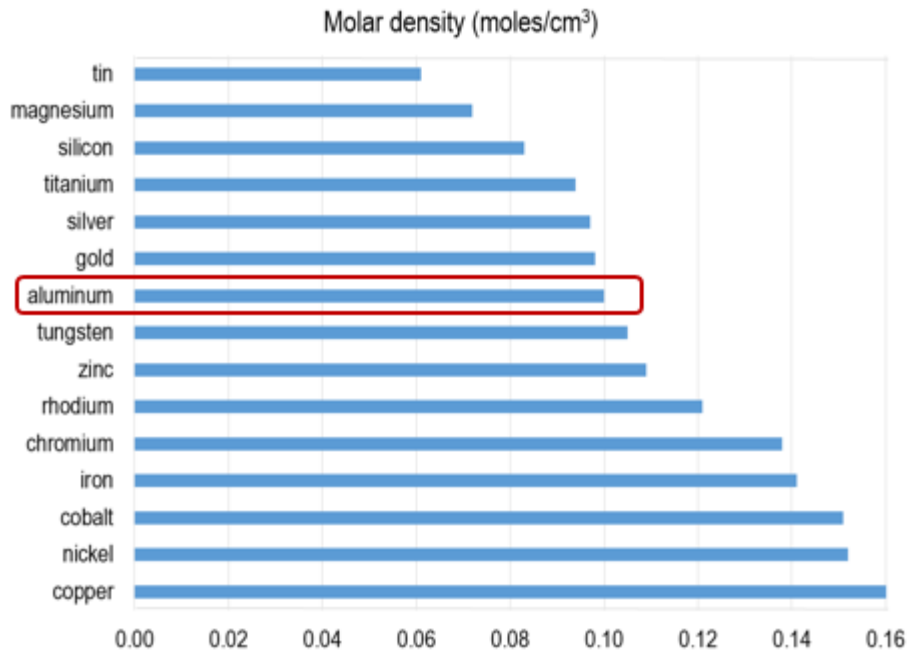


Figure 2. Molar densities for commonly used vacuum evaporation materials.

I choose values for inputs to Equation 3 that give a convenient result: Thick = 40 nm; Speed = 1000 ft/min; and Coating Aperture Width = 1 ft; the result:

$$I = 40,000 \text{ atoms/nm}^2/\text{sec}. \quad (4)$$

Estimating the impingement rate of water vapor molecules

It's important to note that, unless you are deliberately adding gas or have an air leak, water vapor is the ONLY gas in our systems while at coating pressures. If you have access to a residual gas analyzer on your metallizer, it will confirm this. Lacking a residual gas analyzer, the following thought experiment may be convincing.

All the atmospheric gasses are pumped away while pumping from atmospheric pressure down to operating vacuum level. Water vapor is continuously released from our substrates by outgassing and from our internal chamber surfaces by desorption. The time constant for outgassing and desorption can be minutes to hours, even with heating. After the atmospheric gasses are gone, there's only water vapor.

The rate of gas molecules hitting ALL surfaces in our chambers is given in any number of textbooks,

$$I [\text{molecules/cm}^2/\text{sec}] = 3.8 \times 10^{20} \times P [\text{Torr}] \quad (5)$$

where I is the impingement rate, and P is the pressure. If we take a typical pressure for a metallizer as 1×10^{-4} , the impingement rate is 4×10^{16} molecules/cm²/sec. If we again convert to area in nm², instead of cm², we get 4×10^2 molecules/nm²/sec = 400 molecules/nm²/sec.

Estimating the amount of contamination

As noted above the amount of contamination for our purposes is the ratio of the water vapor impingement rate to the aluminum atom impingement rate. For our example,

$$\text{Ratio (H}_2\text{O/Al)} = 400/40,000 = 1/100$$

We will see below that this ratio is small enough to give good quality metallic films. It's been said (by an author whose identity is forgotten) that only one molecule of water in ten reacts with a freshly deposited aluminum surface. If that were true, then a case with an impingement rate ratio of 1/100 would mean only 1 in 1000 aluminum atoms is converted to oxide.

How much contamination is too much?

We respond to this question by comparing two samples made under nearly identical conditions. The samples were prepared in a box coater using an electron beam evaporation source, whose rate was accurately controlled using a quartz crystal monitor. As the system was pumped down, the aluminum evaporation rate was stabilized while the sample shutter was closed. When the system pressure reached 1×10^{-6} Torr, the shutter was opened for the several seconds it took to deposit a 6 nm thick aluminum film. The pressure changed by a negligible amount during the actual deposition. At 1×10^{-6} Torr the water vapor impingement rate, by the formula above, is 4 molecule/nm²/sec.

The first film was deposited at an aluminum rate of 0.7 nm/sec, which corresponds to an aluminum atom impingement rate of 42 atoms/nm²/sec. The ratio of water molecules to aluminum atoms was $4 / 42 = 1:10$. The film was conducting, with a sheet resistance of 55 ohms/sq. and a metallic grey color.

The second film was deposited at 0.2 m/sec, which corresponds to an aluminum atom impingement rate of 12 atoms/nm²/sec. The ratio of water molecules to aluminum atoms was $4 / 12 = 1:3$. This film was insulating, with a sheet resistance beyond the 2×10^6 ohm / sq. capabilities of the meter used, and was brown in color, indicating a conversion of the aluminum to an oxide.

In summary, a metallic, aluminum film was formed for water molecules / Al atoms = 1:10, and an insulating, aluminum oxide film was formed for water molecules / Al atoms = 1:3.

All this discussion and math is based on averages and the assumption of both uniform and equilibrium conditions. But those conditions are not typical.

1. Our coatings are seldom uniform over the coating aperture; typically the rate at the leading and trailing edges is (much) lower than that at the center; thus those areas are more susceptible to contamination.
2. In high rate evaporation, getter pumping by evaporated atoms in the deposition zone reduces the local background gas pressure, with the result that the gauge at the chamber wall does not reflect the pressure in the deposition zone.
3. In high rate evaporation, the local density of aluminum atoms forms a region of (much) higher pressure and lower mean free path. The pressure of the Al flux may sweep out water molecules and reduce the diffusion of water molecules into the coating zone.
4. In high rate sputtering, the energy from the sputter source heats the gas above the source and may (dramatically) reduce the local gas density.

Can we operate our roll coaters at still higher pressures?

One might read the above material and conclude that we could eliminate contamination and tolerate operating at still higher chamber pressures if we could coat fast enough. Unfortunately we

would then need to deal with the effects of the shrinking mean free paths with increasing pressure. At 10^{-4} Torr the mean free path = 500 mm; at 10^{-3} Torr the mean free path = 50 mm; at 10^{-2} Torr the mean free path = 5 mm. Scattering becomes a problem at these higher pressures.

Conclusions

Using the concepts of impingement rates, we have built a simple model to estimate the amount of water-based contamination of an aluminum film deposited in a roll coater based on chamber pressure and coating thickness, web speed, and coating aperture width. We have experimentally defined the ratios of the water vapor impingement rate to the aluminum atom impingement rates that produce good and poor aluminum coatings. In this we learn that web coaters operating in the 500+ ft/min speed range can routinely produce high quality films in the 10^{-4} pressure range, while lab scale box coaters must use pressures significantly lower to produce good films. We also saw that coating at pressures in the 10^{-3} and higher range may produce films with little contamination if the coating rate is high enough, but the films would be likely be compromised by scattering of the aluminum atoms, resulting in reduced rates and possibly defective coatings.

References

1. Donald J. McClure and Stuart McKernan, "Vacuum-deposited aluminum thin films in gray, black, brown and whitish and their underlying causes," *Converting Quarterly*, 2017 Quarter 1, page 42; or *Proceedings, Society of Vacuum Coaters*, TBD (2017); or send the author an email for a copy.
2. Donald J. McClure and Nick Copeland, "Evaporated aluminum on polyester: optical and electrical properties as a function of thickness," *Fall Meeting of the Association of Industrial Metallizers, Converters, and Laminators* (2010); also www.convertingquarterly.com 2011 Quarter 2, pg. 66; and, "Evaporated aluminum on polyester: optical and electrical properties as a function of thickness and time," *Proceedings, Society of Vacuum Coaters*, 634 (2011).