

Sputtered Aluminum and the Water Vapor Problem

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Abstract

The percent reflectance of highly reflective and opaque aluminum metal films has been known for well over half a century to depend on low vacuum pressures and high deposition rates. It has been relatively clear that this is because water vapor reacts with the energized aluminum to form what is likely to be a hydrated aluminum oxide or alumina. This, in turn, "dilutes" the aluminum metal and reduces the reflectance of the film. Some of that history is reviewed here. The procedures are described whereby such a process was adjusted to obtain highly reflecting sputtered aluminum on randomly sized and shaped plastic parts in reasonably short production times from atmospheric pressure back to atmospheric pressure.

Introduction

Georg Hass reported much of the seminal work on evaporated aluminum as a mirror surface. He published a survey and review article[1] in 1955 which gives much of the history: "The first evaporated mirror coatings were prepared by Pohl and Pringsheim in 1912; but it was not until about 1930, when high-speed vacuum pumps and tungsten heating elements for evaporation were developed, that the vacuum coating technique began receiving considerable attention. Important contributions towards the development of satisfactory techniques for evaporating metals in a high vacuum were made between 1930 and 1937 by Ritschl, Strong, Cartwright, Williams, and Auwaerter. The most important advancement of this period was Strong's discovery of a practical method for evaporating pure aluminum." The reference to Strong is Ref. 2 in this present paper.

In 1936, John Strong and E. Gaviola[3] reported that aluminum films up to "a thickness of 4 wave-lengths are generally free from bloom (a milky appearance of the surface)." Beyond that the aluminum mirrors became more scattering. They also commented that "bloom seems to be associated with low vacuum." These things still appear to be true in current experience, now over 80 years later.

Strong also showed another interesting finding where they "photographed" the amount of evaporation of aluminum from a tungsten filament by a 0.5 mm hole in a mica sheet which was paced one inch from the filament, followed by a glass plate positioned one inch farther on. Figure 1 is reproduced from Ref. 3 and shows as Strong says "far more vapor comes from the sides of the U than from the drop. This means that

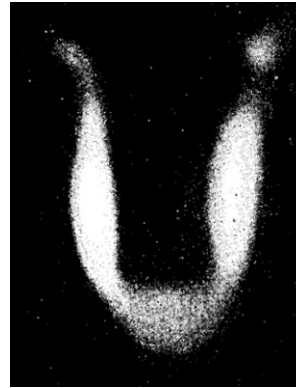


Fig. 1: "Self photo of aluminum evaporating from a tungsten filament[3]."

most of the aluminum flows out over the surface of the tungsten wire where the temperature is higher."

In 1949, Hass and Scott[4] reported on SiO₂ protected aluminum mirrors. They stated that "the temperature of the mirror form when depositing aluminum should not be greater than 150C to avoid harmful roughness." This is consistent with one of Strong's mentions of "blooming." They also reported that "a thin protective film of aluminum oxide is formed on aluminum when it is exposed to

air (thickness about 50A after one month)." They further reported that "Heating in air substantially reduces the reflectivity of unprotected aluminum mirrors because of oxidation," but "SiO₂-protected aluminum mirrors on glass and metal bases are not adversely affected by prolonged heating in air at temperatures up to 400C."

Hass sums up with things that are still true: "It is well known that the optical properties of all evaporated films are strongly influenced by many factors such as speed of deposition, pressure during the evaporation, thickness of the coating, angle of evaporation, temperature of the substrate and finally, aging in air. All factors should be investigated to obtain optimum conditions for film preparation."

Hass also makes a salient comment for our current work: "Most of the change in reflectance is due to the oxidation of aluminum in air and takes place within the first month. The oxide films formed on aluminum in air under normal conditions are only 40 to 100 A thick. Such thin oxide films affect the reflectance of aluminum much more in the ultraviolet than they do at longer wavelengths."

Hass, et al.[5] stated that "High speed of evaporation is probably the most important single factor in producing aluminum coatings of the highest reflectance. This is especially true in the extreme ultraviolet." Hass et al.[6] further emphasized that "Six factors affecting the extreme ultraviolet reflectance of aluminum are: speed of evaporation, pressure, thickness of the deposited film, purity of the aluminum, substrate temperature during deposition, and aging conditions." They further showed the importance of material purity and that "Iron was the major impurity in the 99.5% sample, while in the 99.88% sample there were approximately

equal amounts of iron and silicon." They also said that "For substrate temperatures higher than 50C, the specular reflectance decreases significantly with increasing temperature. For example, a temperature change from 50C to 200C reduces the reflectance at 2200 Å from 91% to 81%, at 1600 Å from 73% to 58%, and at 900 Å from 18% to 15%." It is conjectured that the temperature effect is mostly from more reactivity of the aluminum with oxygen.

Hass and Tousey[7] described fast, bloom-free, one-micron thick coatings for grating blanks. They also reported that the oxidation rate of aluminum increases upon irradiation by ultraviolet, and that the oxidation rate increase depends upon the humidity of the air surrounding the surface.

Hass and Waylonis[8] determined the optical constants of aluminum from 220-650nm.

Canfield, Hass, and Waylonis[9] studied the protection of aluminum with a MgF₂ over-coating. They found it very beneficial, and also that the loss of reflectance of a mirror surface caused by oil adsorption can be recouped by rinsing the mirror with clean ether, acetone, or Freon TF (Dupont) or by a collodion cleaning. A combination of rinsing with one of the above-mentioned liquids followed by a collodion cleaning proved to be most successful.

Adriaens and Feuerbacher[10] provided a very interesting report on aluminum deposition at much lower pressures than other reports. By carrying out evaporation in a vacuum of 10⁻¹⁰ Torr, slow evaporation rates for the coating could be used without oxidation. They report that "The initial pressure was about 2×10⁻¹⁰ Torr which rose to ~2×10⁻⁹ during evaporation of the aluminum at a rate of 10-20 Å/sec and dropped down again to below 5×10⁻¹⁰ Torr within 30 sec after completion of the deposition. The LiF and MgF₂ were out-gassed for several minutes and evaporated at a rate of approximately 10 Å/sec at a pressure of ~10⁻⁹ Torr. No dependence of evaporation speed on reflectance could be found." This seems to be a valuable confirmation that the effects of oxygen (from water vapor) during aluminum deposition are the primary factor in reducing the reflectance of the bare aluminum coating.

Hutcheson, et al.[11] further supported the findings that "The Al + MgF₂ films did not show any significant degradation of vacuum ultraviolet reflectance with aging, regardless of MgF₂ deposition conditions, even after storage either in a desiccator or in ambient air for periods as long as 5 months. Previous work has shown that MgF₂-protected Al mirrors are very stable and are not generally affected by exposure to atmosphere or even ultraviolet or electron irradiation."

Schmauder, et al.[12] showed in the reproduced Fig. 2 here, the effect of excess thickness of aluminum which is consistent with the observations of Strong and Hass.

Vergason and Gaur[13] reported on the roughness of various sputtered metals including aluminum, as seen in Fig. 3, showing an increase of roughness with thickness which is

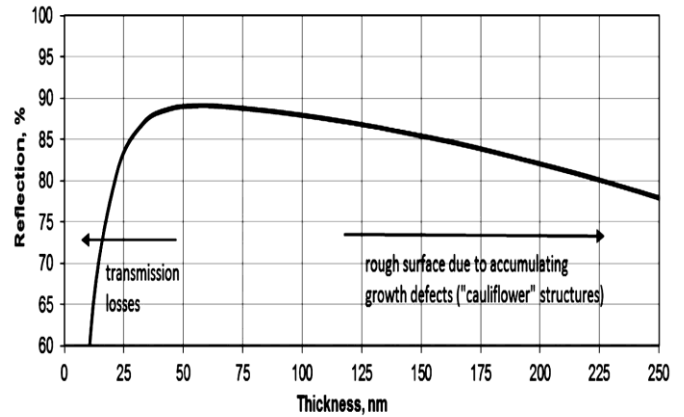


Figure 2: Reflection development of PVD aluminum layers over layer thickness, schematic.[12].

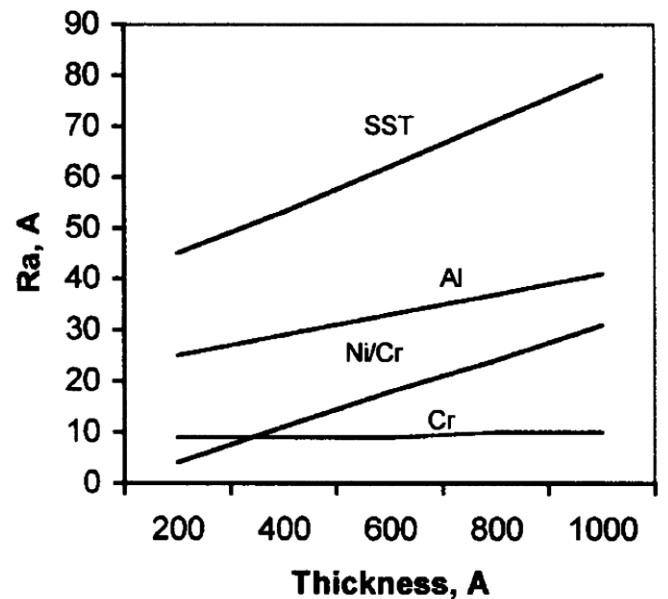


Figure 3: Thickness vs Total Roughness (Ra) via Sputtering[13].

similar to previous findings with evaporated aluminum. This roughness should lead in the extreme to "bloom," or haze, or scattering, and thereby a loss of the percent of specular reflection.

In 1978, Springer and Catlett[14] reported on a scholarly set of experiments on evaporated aluminum at deposition pressures from 10⁻⁶ to 10⁻⁴ Torr at rates from a few Å/second to 70Å/second. They used XPS and Auger techniques to determine the ratio of oxygen to aluminum in the films produced. Figure 4, is redrawn from their results, where the straight line is the mean of their data points which are the open circles and triangles. The plethora of other points are from the current work and will be discussed below. Springer and Catlett showed that the included oxygen can be approximately 1:1 with the aluminum at pressures of 1×10⁻³ Torr, and the pressure needed to be less than 1×10⁻⁴ Torr for the oxygen content to be less than 1% of the aluminum. They commented

that, "The total transparency of the film deposited at the highest water partial pressure was extremely striking." They further say that, "Evidently the hydrogen evolution indicates cracking of the water molecule at the surface of the fresh film deposit. The product of this water dissociation is thought to be a mixture of oxide and hydroxide." They concluded that: "Of the gasses investigated, only oxygen and water showed any significant chemical activity."

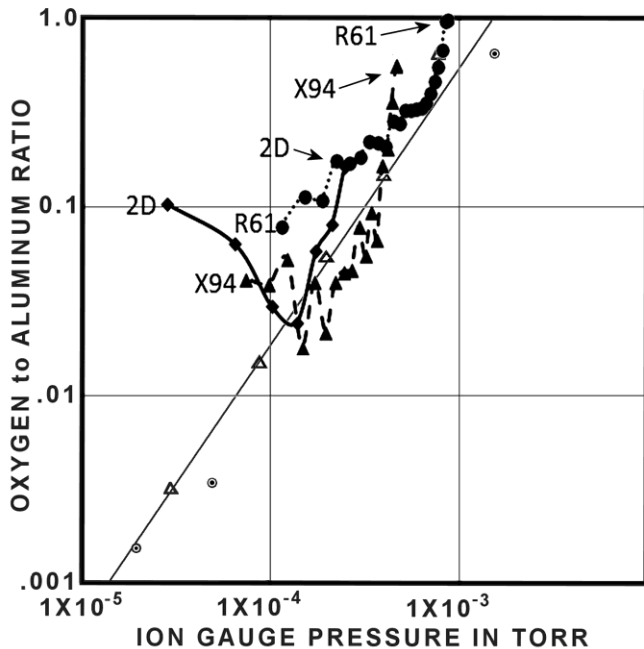


Figure 4: Oxygen to aluminum ratio versus water vapor pressure in aluminum evaporation[14].

The Airco book edited by Russell Hill[15], and first published in 1976, shows that sputtering of aluminum had come of age by that time and was being used in the semiconductor industry. Hartsough, and McLeod[16] published their work to sputter aluminum mirrors (and add SiO₂ and TiO₂ layers to enhance the reflection). They published another paper[17] at that time about sputtering 1.2µm thick aluminum for semiconductor purposes. Their observations for sputtering of 100 nm thick aluminum films in the first paper[16] were consistent with the above observations for evaporated films. They said that "The influence of deposition rate was not explored in detail, but rates above 12 nm/s were found to give the high reflectances, although reflectance did not decrease significantly at lower rates. However, reflectance was sensitive to background gas in the system. An air leak, which raised the base pressure of the system from 1×10⁻⁶ to 1×10⁻⁵, caused a 4.5% decrease in the average visible reflectance of a film made at 12 nm/s."

The System

The system used for the current investigation was produced by the DynaVac Company[18] for LexaLite[19] to rapidly aluminize plastic parts and deposit a top layer of HMDSO for protection of the aluminum. Figure 5 is a photo of the system.

There are two doors to allow unloading and loading parts on one door while the parts on the other door are being coated.

The system is pumped by a Leybold Rough Pump and Blower, Pfeiffer ATH 1600 Mag Lev Turbopump, Pfeiffer LRS1 Turbo Backing Pump, PolyCold PFC 552HC, and a Meissner Coil. The Meissner Coil is in front of the Turbopump but behind the high vacuum valve, so that it does not need to be defrosted with every cycle.

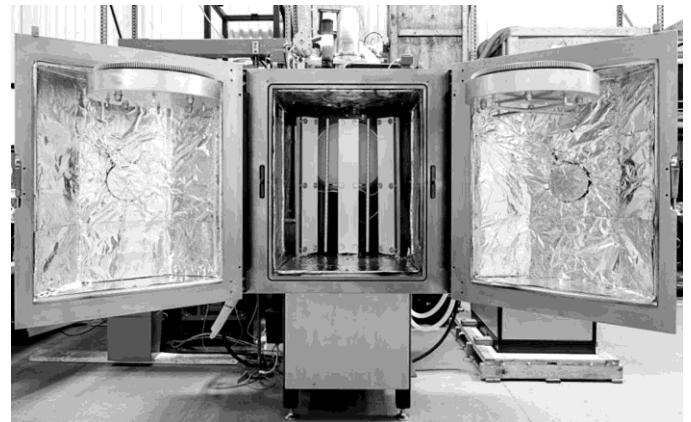


Figure 5: The System built by DynaVac[18] for LexaLite[19].

The aluminum is sputtered by two linear 5" x 30" magnetron cathodes on each side of the chamber with 30kW power supplies. The process gasses of argon and oxygen are provided through mass flow controllers as needed. The maximum deposition rate is approximately 1.7 nm/second.

The Process

The system has a computer data acquisition system which (when requested) stores all of the salient process parameter readings as often as requested (typically every second in this process). This was found to be a **very** valuable tool.

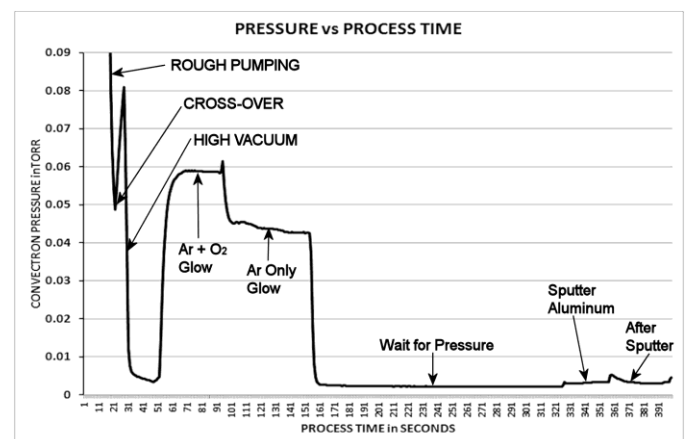


Figure 6: Convectron Gage total pressure reading through the whole process.

Figure 6 shows the total pressure reading of the Convectron Gage on the system through the whole process. The sputtering of the aluminum occurs from about 324 to 360 seconds in this particular example.

The loaded chamber is rough-pumped to a cross-over pressure of 50 microns and the HiVac valve opened at less than 30 seconds. The chamber is at a pressure of 3×10^{-3} Torr by the end of one minute from the start. The process starts when some predetermined pressure is reached on an ion gauge, such as 3×10^{-5} Torr. An RF glow with a mix of argon and oxygen is done and then a glow with only argon. The glow is stopped and the chamber is pumped for a time to recover a good vacuum, and then the sputtering with only argon is done at maximum power for a specified time to deposit the aluminum thickness needed.

The Problem

The problem presented itself as a low percent reflectance (%R) and occasional haze on production parts. Upon consideration of the issues discussed above, it was apparent that the automated process parameters needed to be adjusted to reduce the pressure prior to start of sputtering in order to reduce the water vapor content during sputtering.

Figure 7 is a vertically expanded view of the sputtering section of three cases like that of Fig. 6 to better examine the sputter phase and after sputter phase of the process. The sputtering starts at the near left on this plot and the pressure is seen to rise. When the sputtering ceases the pressure rises rapidly. The interpretation of these data is that the sputtering "cracks" the residual water vapor in the plasma into H and OH, and the aluminum getters the OH to form Al_2O_3 and possibly $Al_2O_3 \cdot H_2O$ or related forms. The energy of this process is also thought to heat the residual water vapor and drive off adsorbed water from surrounding walls, fixtures, parts, etc., thus increasing the process pressure. This is thought to be the cause of the rapid rise in pressure after the sputtering stops. This spike in pressure has been observed to correlate directly with the chamber pressure just before the start of sputtering, which is believed to be mostly water vapor.

The Gencoa [20] company in the UK provided one of their Optix Sensor units for testing. This is an optical plasma emission monitoring system which provides information on the relative partial pressures of various gasses similar to that provided by a Residual Gas Analyzer (RGA). The Optix Sensor operates over the total pressure range of 1×10^{-6} mbar to 0.5 mbar, which was well suited for this process.

Figure 8 is a plot of the data from the Optix for a typical sputtering run. The solid black line is the OH reading, and the dotted line is the OH reading divided by the H reading, times 30 to match the two curves. The dotted line is considered a good representative of the water vapor partial pressure in the system. The drop in the solid OH line during sputtering phase

is thought to be a demonstration of the aluminum getting the OH to make Al_2O_3 , etc. The lower grey line for oxygen also shows that the oxygen is getterd by the sputtering aluminum.

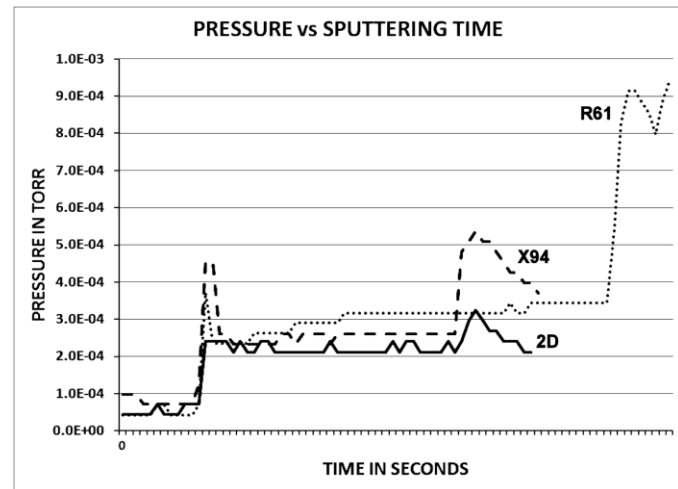


Fig. 7: Vertically expanded view like Fig. 6, showing the sputtering step and following pressure rise.

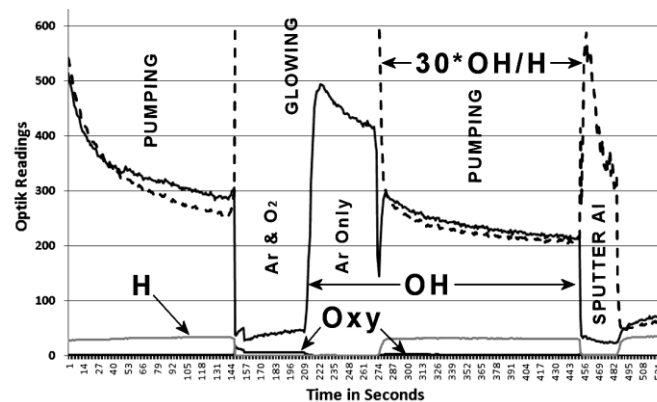


Figure 8: Composite plot of Optix data for various gasses during a typical process run.

The Solution

Various parameters were optimized using Design Of Experiments (DOE) methodology to remove haze, maximize reflection, minimize process time, and maximize adhesion on various polymer substrates. The major contributor to %R and haze was found to be the pressure reached before starting the sputtering part of the process. The time to achieve this pressure could be traded off with resulting %R. The maximum %R is limited by its nature to about 91% in the visible spectrum, and if the requirements were only to be 85 %R or greater, then shorter cycle times could be used. Figure 9 shows these results for three selected samples.

Three representative samples from the various sets of experiments were analyzed using Auger Electron Spectroscopy by Geller MicroAnalytical Laboratory, similar to the work of Springer and Catlett[14]. These three samples had

reflectances of 75.4%, 77.2%, and 87.2% resulting from starting pressures of 11.3×10^{-5} , 7.3×10^{-5} , and 2.8×10^{-5} Torr.

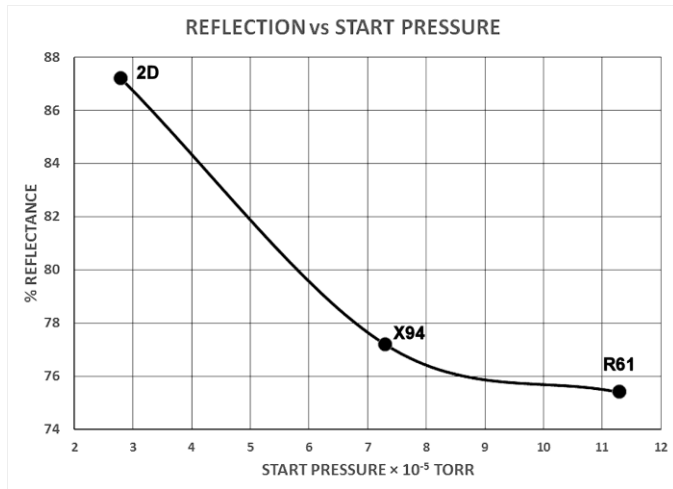


Fig. 9: Best %reflectance of aluminum coating as a function of pressure before the start of sputtering phase.

The oxygen and aluminum percentages measured by Auger are shown in Fig. 10 for these three samples. It was a surprise to see that the 2D sample which was sputtered for the same time and power as the X94 sample was only half as thick. This might somewhat effect the accuracy of some of the observations here.

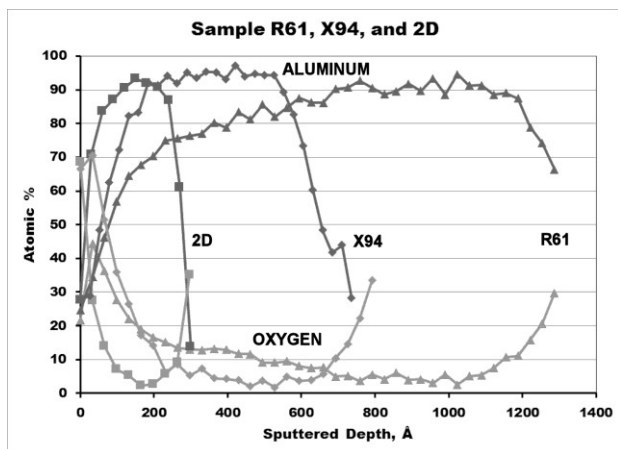


Fig. 10: Atomic percent of aluminum and oxygen from Auger analysis of the three samples versus sputter depth .

The oxygen to aluminum ratios for the three samples are plotted in Fig. 11 for comparison and also for application to Fig. 4. Note that the oxygen percent and oxygen to aluminum ratios rise from right to left in Figs. 10 and 11, or the start to end of the sputtering. These data are plotted on Fig. 4 versus the measured pressures through the deposition. It will be noted that these are generally consistent with the work of Springer and Catlett. The starting pressures are to the lower left in Fig. 4, and the pressures at the end of the sputtering are to the upper right. The starting pressures for each of the three

samples are seen at the left end of each of their plots, where 2D is the lowest, X94 is next, and R61 is the highest. The final pressures for each are all seen to be above and to the right, and they are in the same order. The 2D and X94 both move to lower ratios of oxygen to aluminum in their first few points before moving to higher ratios. The somewhat different start of the first few points of the 2D sample may be due to the gettering effect of the aluminum on the pressure at the start of the sputtering of that sample.

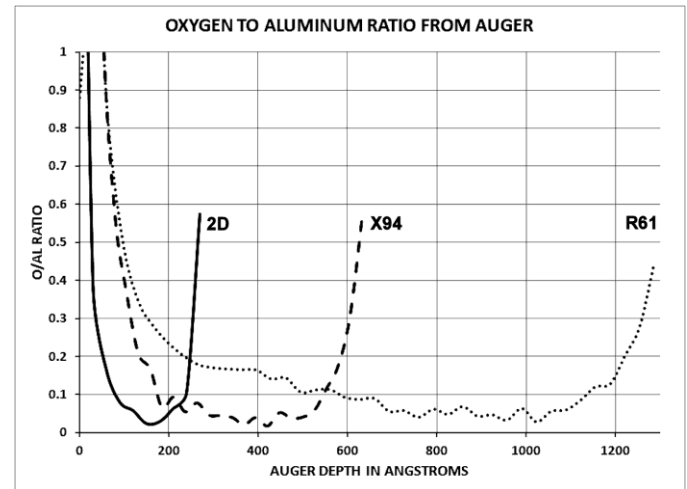


Fig. 11: Atomic percent ratio of aluminum and oxygen from Auger analysis of the three samples versus sputter depth.

Conclusions

To obtain high reflectance (85% at 550 nm) from sputtered aluminum with the type of equipment used in the present report, it is necessary to be below 3.5×10^{-5} Torr before the start of the sputtering. To get close to the theoretical best at over 91%, it is probably necessary to start at below 1.0×10^{-5} Torr. It appears that the pressure rises in the chamber due to the energy of the sputtering liberating more water vapor from the surfaces in the chamber. As a result of this, it appears advisable to only deposit the minimum thickness of the aluminum necessary as fast as practical to maximize the reflectance. Otherwise, the reflectance may reduce with increasing thickness as implied by the increase in the oxygen to aluminum ratio as seen in Figs. 10 and 11. The observations of this current work appear to be consistent with the historical works reported in the references.

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