Retarding the Growth of Oxide on Aluminum Thin-Films

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ABSTRACT

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Aluminum (Al) is the best choice for next generation broadband mirrors because it has high reflectance over a wide range of wavelengths. However, the far ultraviolet ($\lambda < 120$ nm) range has not been explored much since aluminum oxide is absorptive in that range. Fluoride protective layers have been used in the past to prevent oxidation, but limit the range of wavelengths that can be clearly observed. These protective layers also make studying the reflectance of Al in the UV range difficult. This paper explores the rate at which aluminum oxidizes in different storage environments. Samples were stored in liquid nitrogen (LN₂), hexane and dry ice environments. Oxide thicknesses were measured using variable-angle, spectroscopic ellipsometry (VASE). Rates of oxidation during storage were compared with oxidation in ambient lab air. It is shown that LN₂ retards oxidation by a factor of 500, hexane by a factor of 200 and dry ice by a factor of 40. The results shows that aluminum oxidation can be significantly retarded. This opens up possibilities of ultra-thin protective layers, which would allow the far uv to be observed by space telescopes.

Keywords: Mirror Storage, Thin-Films, Oxidation, Far-Ultraviolet, Aluminum, Longevity, Fluoride

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Chapter 1

Introduction

1.1 Background

Aluminum (Al) is the most promising candidate for future broadband mirrors because of its unmatched high reflectance from deep ultraviolet (DUV), through the visible and infrared (IR) wavelengths (see Fig. 1.1). Two of NASA's potential upcoming space observatory projects, the



Figure 1.1 The reflectance of different metals commonly used as mirrors because of their high reflectance in the visible range. Of these, aluminum has the highest reflectance across the infrared, visible and near UV spectrum. Figure copied from [1].



Figure 1.2 This graph shows the different spectral lines of hydrogen. The Lyman series are in green and are in the UV range, Balmer series is in the visible range and the Paschen series in the infrared range. For this reason, to see the Lyman series, the mirror must have high reflectance in the UV. Figure copied from [2].

Large UV/Optical/IR Surveyor (LUVOIR) and the Habitable Exoplanet Observatory (HabEx), depend on being able to observe a wide spectrum of electromagnetic radiation. More specifically, these two projects need mirrors that are able to observe into the Lyman Ultraviolet range (LUV, 91.2 nm – 121.6 nm). The Lyman wavelengths are emitted when the electron in a hydrogen atom transitions from a high energy state, down to the ground state (see Fig. 1.2). Since hydrogen atoms makes up the largest percentage of the observable universe.Not being able to detect the Lyman series means there is a lot of information that cannot be explored.

Current mirror technology on the Hubble Space Telescope (HST) consists of a magnesium fluoride (MgF₂) protective layer over the Al which keeps the reflectance above 115 nm high but causes reflectance to drop to around 15% at wavelengths below 110 nm [3]. Metal fluoride protective



Figure 1.3 The reflectance of aluminum at different wavelengths with no oxide, 1 nm of Al_2O_3 and 5 nm of Al_2O_3 . The vertical lines correspond to the different Lyman wavelengths, starting at 122 nm, with the Lyman limit at 91.2 nm. Increasing thickness of Al_2O_3 makes observing these wavelengths much more difficult. Figure adapted from [4].

layers are used to prevent oxidation of the aluminum, but each has a characteristic wavelength below which they are opaque. These protective layers are used to combat the formation of aluminum oxide which occurs rapidly when Al is exposed to the atmosphere of Earth. Even a thin layer of oxide decreases the Al mirror's reflectance in the far UV range. It can be calculated that even a 1 nm layer of Al_2O_3 will decrease the reflectance of the mirrors from 90% (unoxidized) by over 20% (1 nm) below 120 nm [4] (see Fig. 1.3).

1.2 Motivation

This decrease in reflectance is an issue because the mirrors used on space telescopes are stored for a long duration (more than a year) before being launched into space. It has been shown that oxidation of aluminum follows a logarithmic trend [5, 6]. Thus, they will necessarily have protective fluoride overcoats. But how thick must those overcoats be? Our group has experience in studying the oxidation of aluminum under ultrathin fluoride coatings, particularly aluminum fluoride (AIF₃) [4, 5, 7]. If ultrathin fluoride films could be made sufficiently tight, preventing the aluminum from oxidizing, they might be suitable for LUV applications [8, 9]. However, at the present the aluminum under such coatings does oxidize, albeit at a much slower rate than bare aluminum. It would be helpful to find ways to store samples for the purpose of shipping them from one lab to another without them changing significantly and to store them in the lab for future reference.

1.3 Experimental question

This question this paper examines is as follows: does the storage environment affect the rate of oxide growth on bare Al and AlF₃-coated mirrors, and if so, what is that rate? The environments studied were: liquid nitrogen (LN₂), hexane, dry ice and dry laboratory air (dew point < 273K). Another intent of this study is to understand the growth kinetics of Al₂O₃ on bare Al and under a protective fluoride layer. We chose to use bare Al samples to better examine environmental ways of retarding oxide growth on the least complicated mirror surface before turning to coated mirrors.

Chapter 2

Experimental Methods

In the following chapter, I discuss how the samples were made and stored and how I was able to determine the effects of storage on the growth rate of aluminum oxide. Section 2.1 discusses the thermal evaporation techniques used to make the samples. In section 2.2, I explain the different storage environments. In sections 2.3 and 2.4 I note how samples were measured and what we did to understand the change that took place in the samples.

2.1 Deposition of aluminum samples

The thermal evaporator I used was a Veeco glass bell jar resistive heater thermal evaporator. Using a hoist system the top of the chamber can be lifted up so that the inner chamber, shown in figure (2.1), can be accessed. This thermal evaporator has the capability of depositing up to three different source materials during one 'run' without breaking vacuum. Only one source was used to deposit aluminum onto the sample substrates during the deposition process.

The sample substrates were cleaved from a 200 mm diameter Si(100) wafer coated with about 300 nm chemical vapor deposition (CVD) Si₃N₄. The CVD Si₃N₄ dielectric layer on the substrate functioned as the interference layer (IL) [5, 10]. The samples were approximately 30 mm by 30 mm



Figure 2.1 Inside of the evaporation chamber. 1: The connection points for the evaporation boats. 2: A lower shutter which can cover one evaporation boat while the other is being deposited on the substrate. 3: INFICON quartz thickness monitor. 4:The upper shutter used to control when the samples have material deposited on them. 5: the platen which samples were secured to.

rectangles. I chose this size so that the samples would fit into the liquid nitrogen dippers, explained in section 2.2.1. During evaporation the samples were secured to a 40 cm diameter platen. This sample platen has threaded holes drilled into it, like an optical breadboard. Screws and washers were threaded through these holes to secure the sample on it. The samples needed to be secure, because the platen is loaded into the chamber such that the samples are face down, towards the evaporation source. The platen is secured, sample side down, in the chamber above the top shutter (item 5 in Fig 2.1).

The evaporation source material was a piece of 99.9% pure aluminum wire. This wire was inserted into a F7-3X tungsten coil (RD Mathis), connected to a variable voltage source via copper busbars (item 1 in Fig 2.1). The lower shutter (item 2 in Fig 2.1) was positioned so that the atoms from the aluminum would have a clear path to the sample substrate. While the source aluminum was being heated to be ready for deposition, the upper shutter (item 4 in Fig 2.1) was positioned in front of the samples. This insured that no aluminum would be deposited on the substrate before deposition thickness was being monitored. The rate of deposition was measured using an INFICON quartz crystal thickness monitor (item 3 in Fig 2.1).

2.2 Storage environments

Storing aluminum mirrors in ambient lab conditions does not prevent oxidation of the Al, which changes the desired reflectance of the aluminum mirror. Our experiment tried to limit the growth of this oxide by storing aluminum samples in different environments. These environments are liquid nitrogen (LN_2), the hydrocarbon, hexane, and dry ice.

2.2.1 Liquid nitrogen



Liquid nitrogen was chosen for its cryogenic purposes. Many biological samples can be stored for long periods of time in LN_2 dewars. LN_2 is a cryogenic environment free of gaseous oxygen. In the cryogenic environment of the LN_2 , oxidation should not occur or occur much less than in air. Since LN_2 in a dewar is 77 K at sea level, the low temperature does not provide much molecular kinetic energy. We believe that this lack of energy, coupled with minimal gaseous oxygen means that oxidation will occur at a much slower rate.

Figure 2.2 Liquid nitrogen dewar used to store samples in. 1: the neck core tube used to keep out contaminants while ensuring no pressure build up. 2: Dippers which allowed specific samples separation.

The LN_2 dewar that I stored our samples in, is similar to a typical dewar used to store biological samples. The mouth of the dewar is not very wide, with foam necktube core (item 1 in Fig. 2.2) used to prevent contaminants, including air, from entering while also preventing pressure build up. Dippers were used to store samples in the LN_2 , the diameter of each is 35 mm. A sample was placed in a dipper and then lowered into

the dewar (item 2 in Fig. 2.2). Up to six dippers could be stored in the dewar at one time. I labeled each dipper to identify which samples it contained. This facilitated calculating the total time in storage.

During the course of this experiment, different benefits of working with LN_2 were found, as well as some downsides. LN_2 can be a great low oxygen environment, and it is a low temp. Both of these features make it a great candidate for preventing the growth of oxide. Samples were easily stored in the dewar, and the LN_2 lasted for a couple weeks before it needed to be refilled. However, storage in LN_2 has its limits. It is tricky to move the dewar since it is not sealed. LN_2 also cannot be sealed due to pressure build up, so shipping samples in LN_2 would require special equipment and handling.

2.2.2 Hexane storage

Hexane was one method for providing a low oxygen, ambient temperature storage environment. Storing samples this way was intended to have a comparison for the storage in LN_2 . By comparison of the oxide growth in hexane vs. LN_2 , it could be determined if temperature affected oxide growth rates. Hexane was put into a wide mouth glass jar and the samples were then placed in it. The jar had a screw top lid that kept contaminants out of the hexane. Samples were removed using wafer tweezers and gently shaken so that excess hexane was removed from the surface.

Hexane was easy to work with for this experiment. It did not require any specific containers, and did not need to be refilled over the course of this experiment. However, it is flamable and a liquid, which would make shipping samples in hexane difficult.

2.2.3 Dry ice

Dry ice was considered as a storage environment once the experiment for the other two storage environments was already underway. Dry ice is ideal for shipping things that need to be kept at a low temperature, and the carbon dioxide will displace the ambient air in the container.

Samples were taken from LN_2 storage, measured via ellipsometery This and then put into the dry ice environment. An insulated styrofoam shipping box was used to house the dry ice. The samples were sandwiched between two layers of lint free Kimmwipes. Dry ice was packed above and below the samples. I replaced the dry ice every few days because otherwise all the dry ice would sublimate and leave the sample exposed to air.



Figure 2.3 Hexane storage consisted of a glass jar with a screw top lid. This jar was filled with hexane and the samples place into the liquid.

Dry ice eliminates the problems for shipping samples that both LN₂ and hexane environments

have. However, dry ice is trickier to maintain over long periods of time of how quickly the dry ice sublimates.

2.3 Measurement of oxide growth

Measurements of the thickness of the oxide layer were made using variable-angle spectroscopic ellipsometry (VASE) over a 190-1688 nm wavelength range, between angles 70 and 80 degrees (with 5 degree increments). I made these measurements on a J.A. Woollam M-2000D ellipsometer. A measurements were made right before each sample went into storage. Measurements were not taken while the samples were in LN_2 and hexane storage. The samples stayed in storage for differing amounts of time before I took them from storage and stored them in ambient air. I measured each sample right after it was removed from storage, with successive measurements made at increasing intervals of time. The intervals of time followed a logarithmic trend. This allowed each sample to act as its own control. The effect on the growth of oxide could be noted after and during storage. After analysis (see sec. 2.4) this showed the difference between oxide growth during storage and normal oxide growth behavior.

2.4 Sample Characterization

Analysis of the data was done using the CompleteEASE® software also from J.A. Woollam Company. The model that was used consisted of a top layer of oxide, the deposited aluminum and the substrate layers. In my study, the substrate layers were not important in the model. Due to the thickness of the aluminum layer, the light was absorbed before it could interact with the substrate layers and reflect from the back interface. The layers were in descending order, were 1nm silicon dioxide (SiO₂), 300 nm silicon nitride (Si₃N₄) and the silicon (Si) substrate [10].

At first, since the alumina layer was so thin, I used the sapphire optical constants from literature.

However, this proved to be inaccurate, since the alumina (Al₂O₃) formed during oxidation is unlikely to be the same as sapphire and gave unrealistically thick layers of alumina (> 4 nm). This model was also inconsistent when analysis was done on successive measurements of the same sample, randomly varying between each measurement. To deal with this, the oxide layer was calculated as part of the as-deposited material which gave consistent results for successive measurements. The oxide layer was parameterized as a Cauchy layer, $A_0 + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$, with an Urbach tail. To obtain the constants for the alumina model, I took the ellipsometric data from all the samples at all stages of oxidation and used a "multi-sample analysis" (MSA). The MSA fit the oxide constants for all stages of growth.

Under the oxide layer is the deposited layer of aluminum. Film thickness, deposition conditions and grain sizes all affect the behavior of the free electrons in the thin aluminum layer. For this reason, the aluminum layer is treated differently than a dielectric [6]. Four to six Gaussian oscillators and a UV pole were used to model the aluminum layer. I used a 7-oscillator model from the CompleteEASE® software as a starting point for the model. The parameters of the aluminum were set as part of the study and the same model was used for successive measurements of each given sample. Each sample was modeled the same way. An effective medium approximation (EMA) was investigated as a means of accounting for the possibility that oxygen that may have penetrated the aluminum along grain boundaries causing oxidation inside the layer. For samples stored in hexane, the void part of the EMA layer was replaced with polyethylene, to represent hexane absorbed into the aluminum layer by way of capillary action.

Chapter 3

Results and Discussion

The question I investigated was this: does storage in environments that are low oxygen, at reduced temperature or both, retard the oxidation during the time that it is stored? For example if, after storage in a medium for 150 hours, the amount of oxidation were found to be the same as one stored in air for 5 hours, that would be a retardation factor of 1/30. Meaning a similar sample stored for 600 hours in the medium, one could expect it would experience the same amount of oxidation as one stored 20 hours in ambient air. That is the meaning of a retardation factor. I calculated the retardation factor for the three difference storage environments.

My investigation of the effect of storage conditions on the oxidation of bare Al samples went as follows: For any given sample, after storage for a long period of time with no disruptions, we removed the sample from storage, and measured it via VASE. Then the sample was not returned to storage. Instead it remained in lab air and was measured via VASE periodically as time went on. This provided a means to estimate the retardation in aging each individual sample may have enjoyed relative to one in air for the same time due to its storage in another environment. The growth of Al_2O_3 , if any, could be noted right after removal from storage. It could then be compared to the Al_2O_3 growth which occurs later when the sample is stored in air. If the oxidation behavior of Al were affected by the deposition conditions doing this allowed the samples to act as their own control. Thus, the growth of Al_2O_3 could be examined for the stored condition first, and then in the air. The most significant deviation from logarithmic oxidation was noticed in the sample stored in LN_2 for a period of > 300 hours. Since the oxidation did not follow logarithmic growth during storage, retardation is present. The specifics of each environment will now be considered.

3.1 Liquid Nitrogen

The effects of LN_2 on the retardation of Al_2O_3 during storage is best seen visually. To do this the apparent aluminum oxide thickness was plotted as a function of elapsed time since deposition (see Fig. 3.1. The thickness of the apparent oxide when the sample was first removed from the deposition chamber is less than one nanometer, the first data point on the graphs. A small amount of oxide is expected even right after deposition due to the rapid oxidation that occurs when the sample is taken from the evaporation chamber. The sample was then placed in liquid nitrogen for over 3000 hours before it was removed and placed in air. The points at the right are the measured thicknesses after it was removed and sat in air. the point of the left and those and the right do not lie on the same curve. The only way to make these show a coherent trend is to assume that oxidation did in fact slow down or cease while the sample was stored in LN_2 . Fig. 3.2 shows the same data assuming that the 3343 hours in LN_2 corresponded to no time at all. That is, when all of the time that the sample was in liquid nitrogen is counted as though it never happened, then the thicknesses with time appears to follow a logarithmic growth curve. While this is a better fit, it has a defect. It has two thicknesses for zero hours. This is clearly not true either.

Assuming that the change in the oxidation is logarithmic [5,6], for all measurements after the first, the time in storage was replaced with an adjusted time, such that the R^2 value was closest to 1 (see Fig. 3.3). The best logarithmic fit occurred when the time in LN₂, 3343 hours, was modeled as about 6 hours of time in air. The value of time, 6 added to the air time of all of the points after

storage was the amount of time that was most likely "equal to" the amount of time that the sample spent in the LN₂. Fig. 3.3 is a graph of the R^2 values as a function of the time adjustment value that we used. The R^2 value reaches a maximum of .996 the effective time in air is 6 hours. Using this approximation, the retardation factor for LN₂ is 1/500. This was calculated by

$$RF = \frac{A}{S}.$$
(3.1)

Where RF is the retardation factor, A is the best adjsted time, and S is the time in storage. This formula (Eq. 3.1) is the same used to calculate the retardation factor of hexane and dry ice.

While only the charts for one Al sample are shown here, the same trends were seen for the other samples stored in LN_2 . In Fig. 3.4 the best retardation factor of the samples stored in LN_2 are shown together. The adjusted time for the three samples sit on a straight line. The fact that these points lie on a straight line with an intercept very close to zero indicates that the concept of a retardation factor may have some validity. The slope of the graph is 2.14×10^{-3} , meaning that the rate of oxide growth in LN_2 is about 1/500 the rate of that in air for bare Al samples.



Figure 3.1 This plot shows the apparent thickness of Al_2O_3 vs time since deposition. The storage time has no adjustments made to it. The growth doesn't follow a logarithmic trend.



Figure 3.2 This plot shows what the trend would look like if the time in LN_2 storage was considered to be zero, meaning complete retardation of oxide growth. this follows a logarithmic trend more closely than considering no retardation of oxide growth in storage.



Adjusted Time (hrs: Retardation Factor *3343)

Figure 3.3 The adjusted time, found by multiplying the time in storage by different retardation factors, versus the R squared value of a logarithmic fit.



Figure 3.4 This plot shows the best adjusted time for the three samples that were stored in LN_2 . The slope between the points is the retardation factor. The adjusted time shoes that 500 hours in LN_2 equals 1 hour of time in air.



Figure 3.5 When the time in storage is multiplied by 1/500 (the retardation factor), the growth accurately follows a logarithmic trend. The 3343 hours in storage was accounted for as around 6 hours in air.



Figure 3.6 This is the data for Al_2O_3 growth on a sample stored in hexane. This sample was stored for 1824 hours. It also does not follow a logarithmic trend. This means that some retardation of oxide growth occurred while in storage.

3.2 Hexane

Are there liquids which at room temperature exclude water and/or oxygen? These are thought to be the two primary actors in the oxidation of aluminum. When placed in water hexane will not dissolve. Oxygen and water are both mostly insoluble in hexane. Thus, hexane is a candidate room temperature medium that may retard aluminum oxidation. Different bare aluminum samples were stored in the hydrocarbon hexane (C_6H_{14}) at room temperature to study the effects of storage in a low-oxygen environment at room temperature. The samples that were stored in hexane were treated as those in LN₂. Sample 200328 C4 was stored in hexane for 1824 hours; then it was removed, measured and left in air for subsequent VASE measurements. The thickness versus time analysis was then done in the same way was done for the LN₂ samples as explained above.

Fig. 3.6 shows that there is a retardation effect is similar to that of liquid nitrogen, but less



Figure 3.7 Finding the best retardation factor for hexane. The retardation factor that makes hexane growth best fit logarithmic trends is 1/200. This is from the adjusted time of 7-11 hrs giving the best R^2 values. 1824 hrs in hexane is equivalent to roughly 9 hours in air.



Figure 3.8 This plot shows the trend of oxide growth with the hours of hexane storage multiplied by the retardation factor of 1/200, to an adjusted 9 hours. With the new adjusted time, it follows the logarithmic trend nicely.



Figure 3.9 Samlpe was taken out of LN_2 storage after 2928 hours, measured and then stored in dry ice. Successive measurements were taken during dry ice storage, because the dry ice sublimated quickly.

pronounced. Fig. 3.7 shows the best fit curve for the 1824 hours in hexane is equivalent to about 9 hours in air. This is 0.5% of the time that it was in hexane, meaning for every 100 hours in hexane, it is equivalent to about 0.5 hours in air. This is a significant reduction in the rate of "oxide" growth, compared to the rate at which it oxidizes in air. Storage in hexane is an effective way to retard the growth of "oxide" but not quite as effective as liquid nitrogen.

Thus, it can be seen that the retardation of $Al_{@}O_{3}$ growth in hexane is 1/200 of that in air. Fig. 3.8 shows the data taken from a smaple stored in hexane with the 1824 hours adjusted to around 9 hours. It fits the logarithmic trend much better with the retardation factor adjusting the time in storage.

3.3 Dry Ice

The LN_2 and hexane environments are great for long term storage. However, sending samples stored in LN_2 or hexane across the country to be analyzed at a different lab is quite difficult. Pressurized containers are dangerous and an open container is subject to spilling. This led to an investigation of the viability of using dry ice to slow the rate of growth Al_2O_3 in bare Al samples, because dry ice can be used in shipping and will not spill easily. The sample was stored in LN_2 for 2928 hours before it was taken out, measured and then put in dry ice storage.

The dry ice sample was placed into a dry ice shipping box. The sample was sandwiched between dry ice, with newspaper and lint free cloth isolating the sample from contact with the dry ice. Every two to three days the dry ice was replaced. The sample was kept as cold as possible during the refills and the refilling process was done as fast as possible. The sample was exposed to the atmosphere for less than 2 minutes each time the dry ice was replaced, but was not given the opportunity to warm up. Only a few data points were collected for the dry ice storage because it was exposed to air over a weekend when all the dry ice sublimated. Data taken for this dry ice sample was different than the others. VASE measurements were taken during the storage process. This means sample was taken from storage, measured and then put back in storage.

As seen in Fig. 3.9, the data does not fit well when the time in storage is not changed by a retardation factor. Since sample was stored in two different mediums, two different retardation factors were used to fit the data to a logarithmic curve. In order to find the retardation factor in dry ice, the time in LN₂ has been adjusted from 2928 hours to 5.86 hours in accordance to our findings in earlier for the ratio of oxidation growth in LN₂ vs air for bare Al (1/500 as in Fig. 3.4. With the time in LN₂ adjusted accordingly, a retardation factor of dry ice could be found through fitting the data. The best logarithmic fit (Fig.3.11 happens when the time in dry ice has been multiplied by a retardation factor of 1/40. The peak R^2 value occurring when the 335 hours in dry ice is adjusted by the retardation factor to 8.3 hours of equivalent time in air.



Figure 3.10 The growth best follows a logarithmic trend when the 335 hours of dry ice storage is considered as 8.3 hours in air. Dry ice has a retardation factor of 1/40.



Figure 3.11 With the storage in both LN_2 and dry ice adjusted by their respective retardation factors, the oxide growth follows a logarithmic trend.

3.4 Conclusion

The data shows that the storage of bare Al mirrors in these low oxygen / cryogenic environments significantly retards the growth of Al_2O_3 . By comparing the amount of oxide growth on several films in each of the environments, the oxide growth was shown to be retarded by a constant factor for each medium. Variable-angle, spectroscopic ellipsometry was used to do find the oxide thickness. This factor was quantifiable for each medium and labeled as the retardation factor. A logarithmic model was used to account for the amount of oxide growth. To get the samples stored in LN_2 to match the model, the time in storage was changed by a factor of 1/500. The time in hexane storage was changed by a factor of 1/200 and the time in dry ice was changed by a factor of 1/40. This study contributes to the body of knowledge on preservation of aluminum mirrors, by bringing forward some ways in which oxidation of aluminum can be slowed.

3.5 Future Work

The findings of this research show that there are environments that can slow the rate at which oxide forms on aluminum. I plan on expanding upon these findings by studying the effects on oxidation in other environments. One of these environments is sealed gas containers, full of nitrogen or argon. Since dry ice is easily shipped, I want to improve the storage method in dry ice to increase the retardation factor. My research so far has focused on bare aluminum. I want to know what effect storage in different environments has on aluminum samples that have fluoride layers on top, as this is most likely to be the composition of future mirrors used in space telescopes.

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