3-3: Ultra Thin Film Barrier Layer for Plastic OLED

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Abstract

Fabrication of barrier layer on PES substrate and plastic OLED device by atomic layer deposition are carried out. Simultaneous deposition of 30nm of AlO_x film on both sides of PES gives film MOCON value of 0.0615g/m^2.day (@38°C, 100% R.H). Introduction of conformal AlO_x film by ALD resulted in enhanced barrier properties for inorganic double layered film including PECVD SiN_x. Preliminary life time to 91% of initial luminance (1300 cd/m^2) for 100nm of PECVD SiN_x/30nm of ALD AlO_x coated plastic OLED device was 260 hours.

1. Introduction

The flexible Organic Light Emitting Diodes (OLEDs) have attracted much attention as the next-generation display.[1] It has been recognized that the development of thin film barrier layers for OLED and flexible substrates would be the key technology for the realization of flexible OLEDs.[2] Although the requirement of barrier layer for OLED display is not elucidated clearly, it has been understood that long-lived flexible OLEDs need a moisture barrier layer which transmits less than 10^{-6} g/m^2.day of water.[3]

It has been reported that multi layer combinations of polymer and inorganic dielectric layer can be more than three orders of magnitude less permeable to water and oxygen than an inorganic single layer. Several groups reported multi-layered barrier including inorganic thin films fabricated by plasma enhanced chemical vapor deposition (PECVD) or sputtering. [4,5]

Our group reported a new approach to the oxide barrier layer of flexible OLED substrates using conventional traveling wave reactor typed atomic layer deposition (ALD)[6] and plasma enhanced ALD (PEALD)[7]. ALD is a technique that a binary reaction is split into two self-limiting chemical reactions in a repeated alternate deposition sequence. Although ALD based on the surface chemical reactions can minimize the structural imperfection in the films and substrate damage, resulting in high quality barrier layer, the low growth rate is the main drawback for the application of barrier layer. In addition, use of water vapor or ozone in traveling type ALD method and oxygen plasma in PEALD method for the precursor of O, made us hesitate to apply ALD-deposited AlO_x films as the barrier layer of OLED device directly.

However, we show that just nanometer order of aluminum oxide single film deposited by ALD technology has superior barrier properties and is suitable even for the device barrier layer. In addition, we optimized the structure of barrier layer for plastic OLED, consisting of PECVD deposited SiN_x and ALD deposited AlO_x.

2. Experiments

Aluminum oxide thin films with thickness in the range of 10nm~50nm were grown on PES substrate in a 12 x 16 inch large traveling wave ALD reactor with nitrogen as carrier gas in the temperature range of 80-150°C . Trimethylaluminum (TMA) and H_2O were used as precursors of Al and O, respectively. The sequence of pulses for one cycle is TMA (0.5s)/ N_2 (0.8s)/ H_2O (0.5s)/ N_2 (2.5s). Water vapor transmission rates (WVTR) were measured for both PES substrate and aluminum oxide coated samples on a 50 cm^2 active sample area at 38±2 °C, 100% R.H. using MOCON permatran-W1A for 72 hrs. Morphological properties were examined by scanning electron microscope (SEM) and AFM. UV-vis spectra were taken using Hitachi U-3501 spectrophotometer. Device structure of OLEDs grown by vacuum thermal deposition is PET/ ITO/ 20nm MTDATA/ 40nm NPD/ 60nm Alq/ 2nm LiF/ 75 nm Al.

3. Results and Discussion

The dependency of barrier properties of AlO_x films on the deposition temperature and thickness were investigated. With the considerations of slow deposition rate of the ALD method and application of barrier layer in OLED packaging, we focused on the measuring WVTRs of ultra thin aluminum oxide films deposited at lower than 150°C. Table 1 shows the results. While most of inorganic single layers deposited by other chemical or physical methods showed proper barrier properties with the thickness higher than 100nm, single aluminum oxide film deposited by ALD at 90°C showed excellent barrier property of 0.3031 g/m^2.day of MOCON value even with the thickness of 30 nm.

One of the main advantages of traveling wave typed ALD is the ability of film coating on both sides of substrate or device simultaneously. The PES substrate coated both sides with 30nm of AlO_x has 0.0615 g/m^2.day MOCON value that is the lowest value for single inorganic layer with the thickness less than 100nm. Simultaneous both sides coating can also reduce the film stress caused by the difference of coefficients of thermal expansions between the plastic substrate and the dielectric film.

The formation of conformal film by ALD resulted in coverage of pin-holes in other inorganic or organic layer. Deposition of 20nm of AlO_x on the MOCON test-failed SiN_x thin film gave barrier property of double layer as low as the limited value of MOCON, which indicates the decoupling effect of ALD deposited AlO_x film.

Superior step coverage property of ALD grown AlO_x film can even be applied to the coverage of negative angle sloped separator used in the passive matrix OLED panel.

Table 1. The dependence of AlO_x film on the substrate temperature and reaction cycle

Temperature (°C)	Reaction cycle	WVTR (g/m^2.day@ 38°C)	[a]WVTR (g/m^2.day@ 38°C)
80	200	1.25	
	300	0.409	0.0615
	400	0.141	
	500	0.102	
90	300	0.303	
100	300	0.214	0.0276

[a] WVTR of PES coated both sides with AlO_x

The surface SEM images of the different thickness of aluminum oxide films on PES are shown in Figure 1. ALD grown aluminum oxide thin films showed flat morphology and also good adhesion to the plastic substrate. When thin films are used for the device packaging, it would be very important for films to have good adhesion to different materials such as metal, organic materials, and substrate.

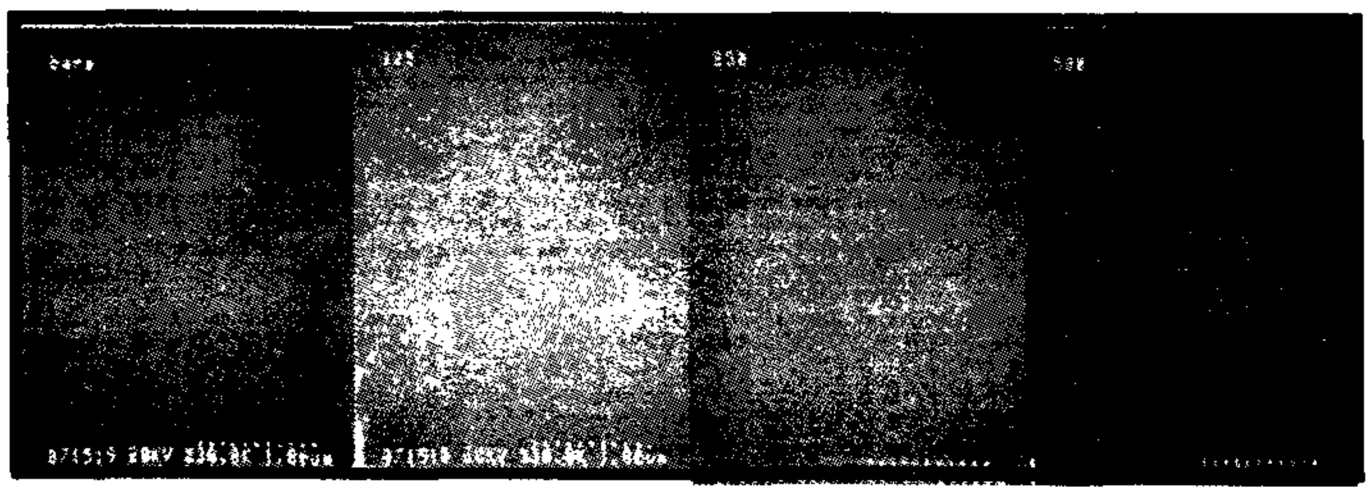

Figure 1. SEM images of bare and AlO_x coated PES subsrates

One of the major advantages of ALD method is no formation of pin-hole on the film. However, we found defect from the AlO_x film grown at 150°C and presented in Figure 2. This might come from the substrate out-gassing.

Figure 2. Defects found in AlO_x film deposited at 150°C

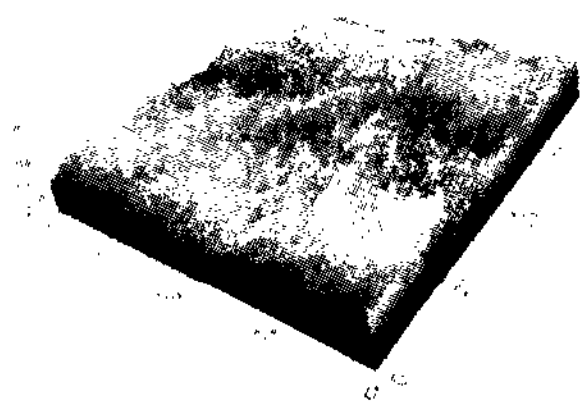

Figure 3. AFM image of AlO_x coated PES

Figure 3 showed atomic force micrograph (AFM) of aluminum oxide coated PES substrate. The RMS surface roughness of 50nm-thick aluminum oxide was 3.38 Å. The transmittance of the AlO_x coated film for the whole visible light range is more than 85% with the air reference and higher value than that of bare PES substrate with the PES reference.

We tested ALD-grown aluminum oxide film for the barrier layer of plastic OLED device with emitting area of 2 x $2mm^2$. The OLED was prepared on a PET substrate by the vacuum evaporation and 1μm thick parylene film and 30 nm thick AlO_x were deposited continuously in a separated reactor at R.T. and 80°C, respectively. The OLED device was exposed to the air at each step. Parylene was coated to prevent direct contact of water vapor to the OLED materials.

It is known that organic layers, especially hole transport layer, are crystallized at the temperature higher than 55°C to induce degradation of device. Therefore most of researchers tried to deposit barrier layer at lower than 50°C. However, AlO_x deposition carried out at 80°C on the parylen coated device did not show any significant difference in emitting images of plastic OLED devices. Several dark spots are observed right after parylene deposition and grow bigger as following AlO_x film deposition is carried out. This may be due to the exposure of device to the air between each deposition step. In addition, process time for ALD takes more than 2 hours just to reach the reaction temperature since there is no load-lock chamber. If the process could be carried out in ALD equipped with load-lock chamber, the formation of dark spot could be prevented. For the glass device packaging, even with this long process time, we could not see any formation of dark spot by deposition of AlO_x film directly on top of the OLED.

Figure 4 shows the typical electric characteristics of OLED device. The AlO_x coated devices showed no big changes in L-V, I-V and efficiency compared to those of the bare device.

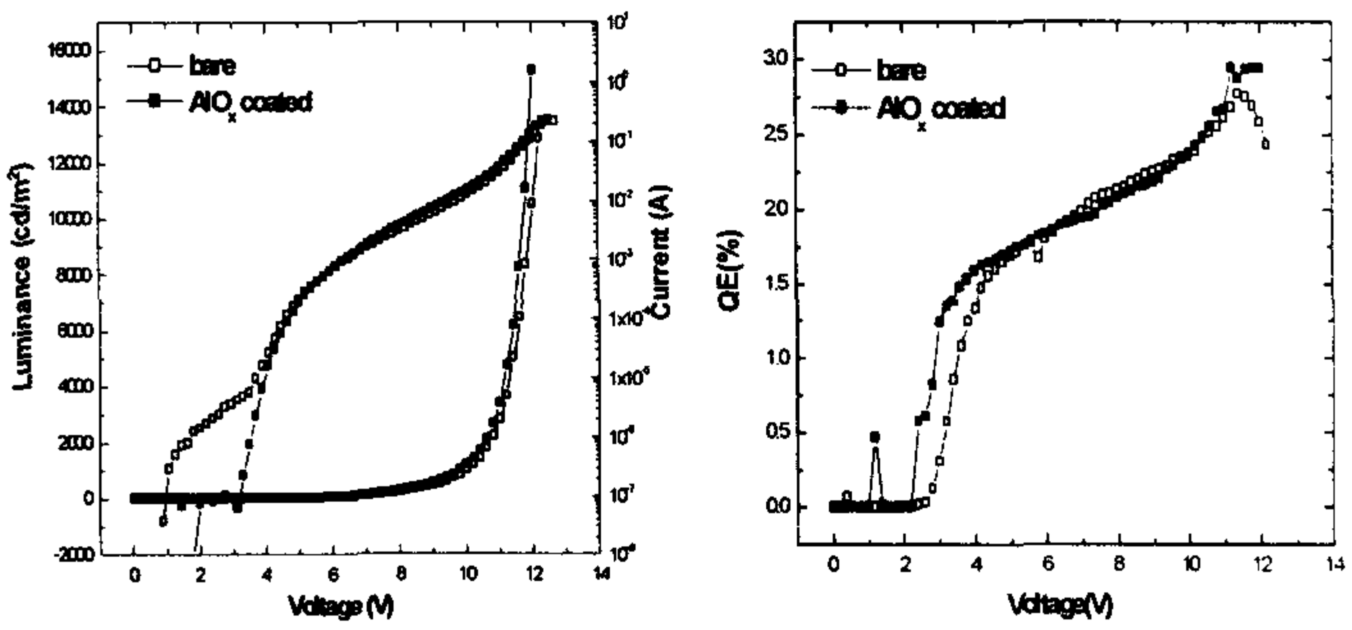

Figure 4. The electrical characteristics of bare OLED and 30nm AlO_x coated OLED.

The life times of bare and thin film coated devices were measured at initial luminance of 1300 cd/m^2 under continuous constant current of 1mA in air at RT. Figure 5 shows the decrease of average EL luminance of single emitting pixel of bare OLED device and barrier coated device fabricated on PET substrate. While the life time of bare device is less than 24 hours and that of PECVD deposited SiN_x coated device is 35 hours, 30nm-AlO_x

coated plastic OLED device maintains 83% of initial luminance for 130 hours. Degradation of OLED is mostly due to the formation of new dark spots and growth of existent dark spot size.

In ALD process, precursors including water vapor, oxygen plasma, or TMA are pulsed for just less than 0.5 second for each cycle in a reactor size larger than 12". Therefore, the damage of OLED device caused by precursors could be minimized compared to other plasma enhanced deposition methods such as PECVD or sputtering.

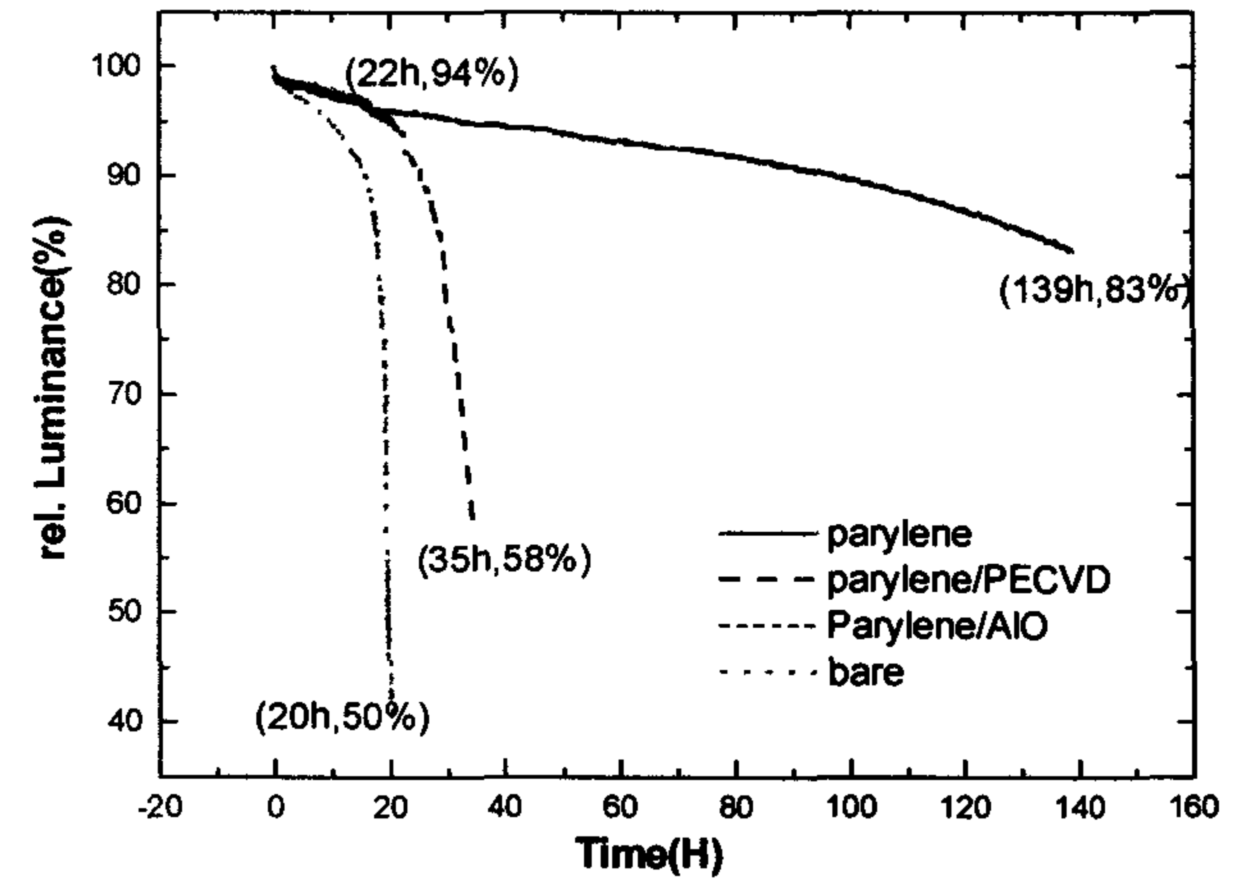

Figure 5. Lifetime of AlO coated OLEDs (initial luminance of 1300 cd/m2) at driving current of 1mA.

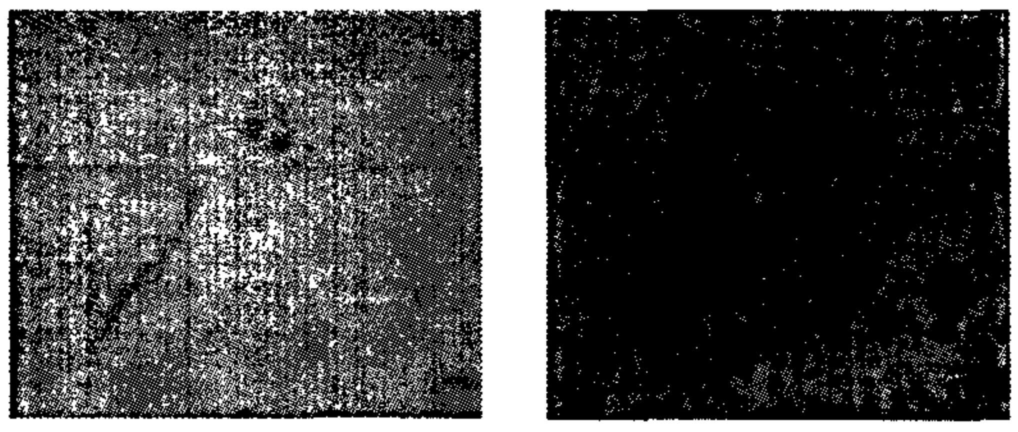

Figure 6. CCD images of a light emitting area of the AlOx coated plastic OLED device before and after the driving at 1mA to give 50% reduction of first luminance under 24°C, 45% RH.

Since ultra thin ALD deposited film showed pin-hole decoupling effect as the micro-order thick organic film does, we adapted inorganic bi-layer system for the barrier.

The SiN_x film was deposited on parylene coated OLED device at room temperature under the plasma power of 25W with the gas ratio of N_2(400sccm) /SiH_4(4sccm) /NH_3(26sccm) /H_2(100sccm) /He(300sccm). Even though the SiN_x film deposited at RT showed poor barrier property due to the pin-holes, additional deposition of AlO_x by ALD method enhance the film quality greatly.

Figure 7 shows life time of OLED device packaged by SiN_x/AlO_x double thin film layers. While the SiN_x coated OLED showed rapid decay, life time of SiN_x (100nm)/AlOx (30nm) double layer coated OLED to 90% of initial luminance (1300cd/m^2) was 260 hours. The use of ALD deposited AlO_x thin film for the barrier layer can not only reduce the total thickness of barrier layer and also increase the life time of plastic OLED device significantly.

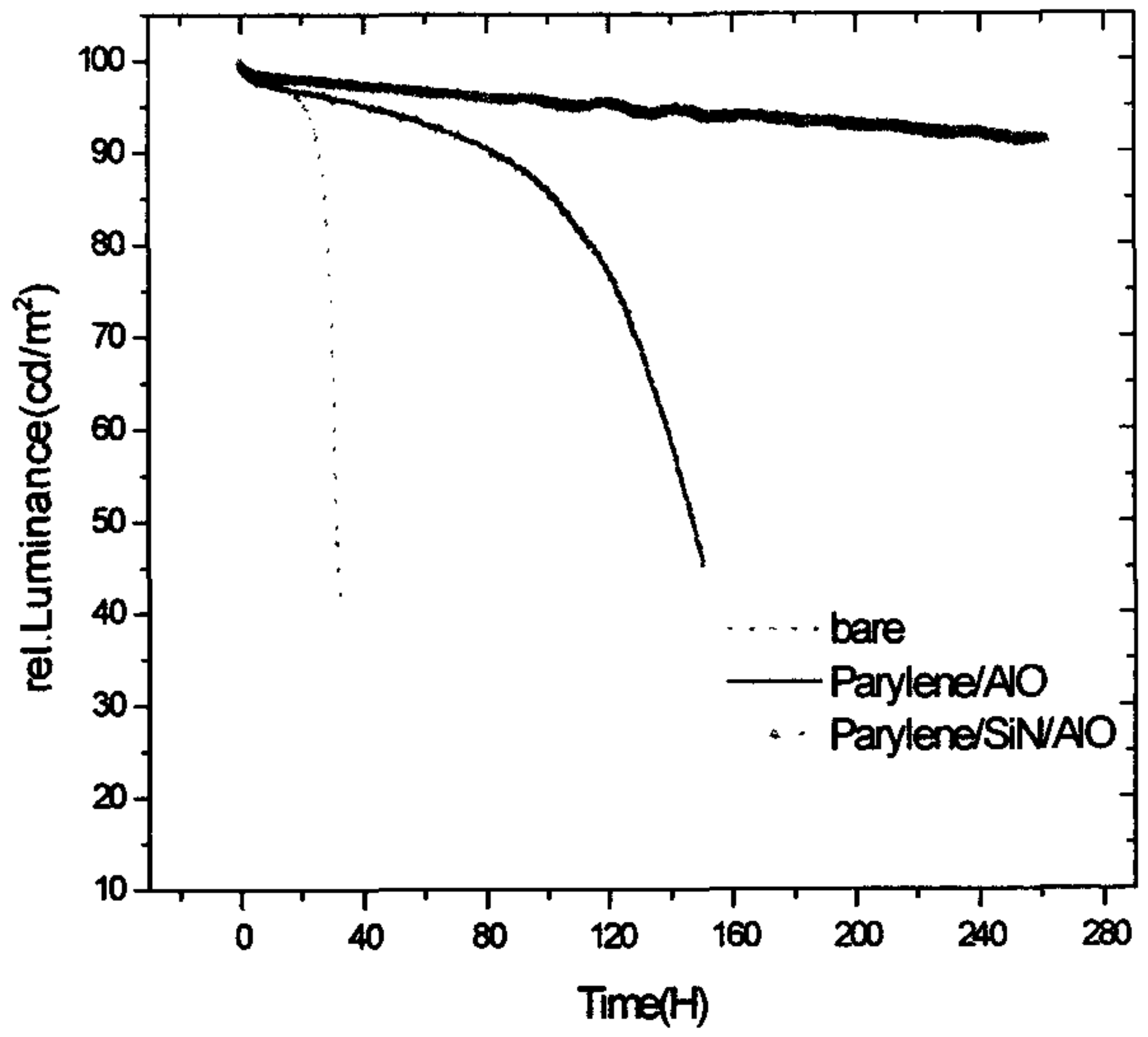

Figure 7. Lifetime of double layer coated OLEDs (initial luminance of 1300 cd/m2) at driving current of 1mA

4. Conclusion

The encapsulation of plastic OLED device with the films deposited by the ALD method has been carried out for the first time. Since AlO_x films with even 30nm-thickness shows superior barrier properties, it is considered that ALD technology is suitable for barrier layer fabrication. Due to the effect for decoupling of defect, introduction of ALD deposited AlO_x film can significantly enhance barrier properties for both substrate and plastic OLED device with ultra thin thickness. Further studies are under investigation for the effects of oxygen precursor of AlO_x process on the characteristics of plastic OLED devices.

5. Acknowledgements

The Korea ministry of Information and Communications financially supported the accomplishment of present work.

6. References

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