

# Study on Aging Effect of Optical Film under High Intensity of UV Exposure

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**Keywords:** Material Aging, UV Exposure, I-line, Anti-reflective Film, Reflective Film.

**Abstract:** In the semiconductor industry, for lithography system the reflective film coated on the mirror and the anti-reflective film coated on the correction lens in the projection lens module were usually irradiated by the high intensity of I-line light, and the optical film will gradually age and become matte after using a period of time. In order to investigate the ingredient variation and aging effects of the optical film caused by i-line light, a UV light irradiation environment was built with an optical power of 80 mW. In the experiment, the reflective and anti-reflective film was coated on the BK-7 glass and irradiated by 24 to 120 hours. Then, the reflectivity/transmittance and the ingredient of optical film was measured and analyzed. The reflectivity and transmittance of optical film varied after 24 hour irradiation and decreased approximately 1.67 and 0.9 wt% after 120 hours irradiation, respectively. In addition, the results obtained from the focused ion beam (FIB) system indicated that the ingredient of oxygen of both films increased and the anti-reflective film ruptured evidently under 120 hours of irradiation. The results from the manuscript can serve as reference information for durability evaluation of optical film employed in the projection lens module in the semiconductor industry.

## 1 INTRODUCTION

In the gas film forming method, it can be further divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD) based on the principle of film formation. The physical vapor deposition method utilizes a physical mechanism such as heating or atomic sputtering of a palladium material to form a film. (Marszalek et al., 2015) The chemical vapor deposition method uses a chemical mechanism such as the gel coating to form a film. When the coating process is carried out, the coating material is turned into the ion state by an electron gun or resistance heating. Since the coating machine is in a high vacuum state, the coating material of the ion state can smoothly attach to the substrate. (Martin, 1986)

The optical film can be divided into the reflective (Folta et al., 1999) and anti-reflective film (Jeong et al., 2004), and which are widely applied in the various optical system, including lithography, laser, solar cells, sensors and so on. (Wiesinger et al., 2018) On these systems, the quality of optical film would affect the efficiency of the systems. Therefore, the stability of the film is an important parameter for

all optical components, and the coating parameter such as the vacuum degree, material, and its thickness would affect the film quality and optical performances such as the reflectivity or transmittance (Raut et al., 2011) of optical components. (Su et al., 2017) Generally, the multilayer film (Lien et al., 2006) is matched with a high refractive material and a low refractive material and formed the reflective or anti-reflective film. (Krogman et al., 2005) High refractive materials usually included TiO<sub>2</sub> and HfO<sub>2</sub> (Franta et al., 2011), and low refractive materials included SiO<sub>2</sub> and MgF<sub>2</sub>. (Rajan et al., 2016) For example, the alternate layer with two materials were often used to generate the film with high reflectivity or transmittance. (Dubey and Ganesan, 2017) However, the operating environment such as UV light, particle, temperature, humidity of the optical film in different applications would also affect the film quality and optical performance of optical components. (Ulaeto et al., 2017) When the optical film was irradiated by the light with high brightness and high energy such as mercury lamp or laser source (Li et al., 2014), the film would be damaged by the instantaneous heat. (Botha et al., 2017) Hence, the anti-thermal and

mechanical ability of the optical film was analyzed to evaluate the aging effect of optical film induced by high power of light irradiation. Yaghubinia et al., (2016) enhanced the photovoltaic performance of planner perovskite solar cells by using localized surface Plasmon (LSP) effect of a silver-alumina core-shell nanoparticles as a dopant in the perovskite layer. Tozoni et al., (2017) and his colleagues found that the photoluminescent blend was characterized by optical absorbance and steady-state photoluminescence spectroscopy. The PMMA/MEH-PPV blend film presented high homogeneity and high photoemission intensity. The PMMA/MEHPPV blend film photodegradation curve also presented a biexponential time decay behavior with a long time  $t_1=16.67$  hours and a fast time  $t_2=1.40$  hours. Moreover, the PMMA/MEH-PPV blend film photodegradation in function of sample exposure time to the blue-light excitation curve presented long biexponential time decay. Soãres (2018) found the optically levered reflection resolved on a nanometer resolution displacement sensor, enables the analysis of spindle axial and rotational error, stage linear error, the impact of these error-motion components on a diamond tool edge and its progression to wear, while inspecting the compliance of the product to the desired surface finish and shape. Scanning optical scatterometry is utilized to image and analyze edges, surfaces, defects, and thin film structure. In order to ensure the quality and stability of the film, some reliability experiments were conducted (Magnozzi et al., 2018). For both reflective film and anti-reflective film, some experiments of optical system applications were investigated. These studies indicated that the morphological changes of the film and the thickness distribution of multilayer coatings also affected its quality and performance (Poirié et al., 2017).

In the present study, we built a high intensity of UV lighting module and used to irradiate the BK-7 glass that coated the reflective and anti-reflective film. The coating parameters of films such as the thickness and material of each layer was the same in the correct lens and mirror of ourselves developed projection lens module. Then the optical properties of films such as the reflectivity and transmittance were measured by UV-VIS spectrophotometer and compared to the original film that without light irradiation. In addition, the aging effect was also observed from the tiny variation included the ingredient and film strength that measured by the Energy Dispersive Spectrometer (EDS) of focused ion beam (FIB) system. The measured results

quickly provide a reference information for evaluating the aging situation and its durability of films coated on the mirror and correction lens in the actual projection lens.

## 2 EXPERIMENTAL SYSTEM

### 2.1 Preparation of Optical Film on Substrate

In order to simulate the reflective and anti-reflective film coated on the lens of the projection lens module in the semiconductor industry. The same parameter of each layer on the lens was coated on the experimental tested sample, which was the BK-7 glass with a diameter of 25.4 mm and thickness of 5 mm. The schematic of coated reflective and anti-reflective film on BK-7 glass and the thickness and material of each layer was shown in Fig. 1 and summarized in Table 1-2, which was the dielectric film.

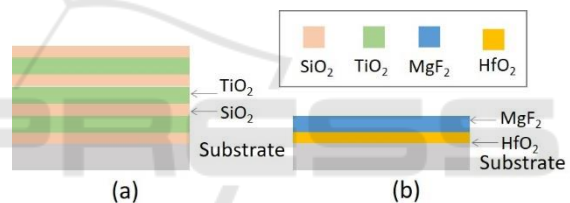


Figure 1: Schematic of (a) reflective and (b) anti-reflective film coated on BK-7 glass substrate.

The reflectivity of reflective film in the simulation of the coating software was higher than 97 % at wavelength of 365 nm and higher than 92 % at wavelengths of 355-375 nm, and the transmittance of anti-reflective film in the simulation was higher 99% at wavelength between 290 nm to 450 nm.

Table 1: Coated material and thickness of anti-reflective film.

Material	Thickness (nm)	layer
HfO <sub>2</sub>	20.03	1
MgF <sub>2</sub>	18.70	1
HfO <sub>2</sub>	36.41	1
MgF <sub>2</sub>	67.69	1
Total	142.83	4

Table 2: Coated material and thickness of reflective film.

Material	Thickness (nm)	layer
SiO <sub>2</sub>	32.97	1
TiO <sub>2</sub>	39.72	2*6
SiO <sub>2</sub>	65.94	
TiO <sub>2</sub>	39.72	1
SiO <sub>2</sub>	98.92	1
Total	805.57	15

### 2.2 Irradiation on Optical Film

In this study, a 5X5 square matrix LED panel was designed with 25 UV LEDs (365 nm) illuminated on the surface of 3 samples. One sample was taken every 24 hours, and after the third sample was irradiated for 72 hours, the surface element change of the three samples was analyzed.

In addition, the optical film coated on the BK-7 glass was placed on the stage and faced to the UV LED light under the irradiation distance of 10 mm (Fig. 2), which the optical power on the optical film of testing sample that measured by the power meter (Thorlabs, PM200) was 80 mW. Therein, the temperature and humidity of the experimental environment were 22°C and 66 %, respectively. The irradiation time of the tested sample was ranged from 24 hours to 120 hours in the intervals of 24 hours.

The stability of the UV source was also concerned to evaluate the uniformity and stability of the illumination during the irradiation time. Before performing the experiment, this study uses a voltage mode to supply current, and the power meter was used every hour to determine the illumination stability.

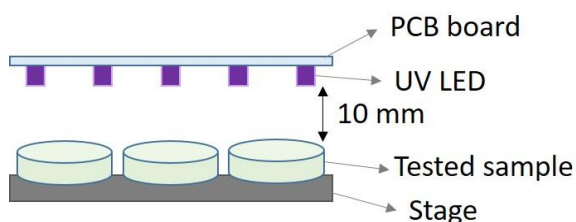


Figure 2: Schematic of experimental setup of UV light irradiation on optical film coated on glass substrate.

## 3 EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 Optical Properties of Optical Film

The spectrophotometer (PerkinElmer, Lambda 900) was used to measure the transmittance and reflectivity of the anti-reflective and reflective film, respectively. Before the measuring process, a calibration sample was employed to calibrate the measured value. From the measured results, the actual transmittance of the anti-reflective film coated on the BK-7 glass at i-line spectrum, wavelength of 355-375 nm, ranged from 88.48 to 93.48 %. Especially, the transmittance was higher than 90 % from the wavelength of 359 nm, and which was 91.99 % at a wavelength of 365 nm.

After the UV light irradiation, the transmittance of optical film gradually decreased, and the dropped value was larger than 1 % at the wavelength of 321 nm to 363 nm after 120 hour irradiation, shown as Fig. 3. The range of drop value in i-line spectrum was 0.76- 1.24 %, and it dropped 0.90 % and the transmittance decreased to 91.08 % at the wavelength of 365 nm, shown as Fig. 4.

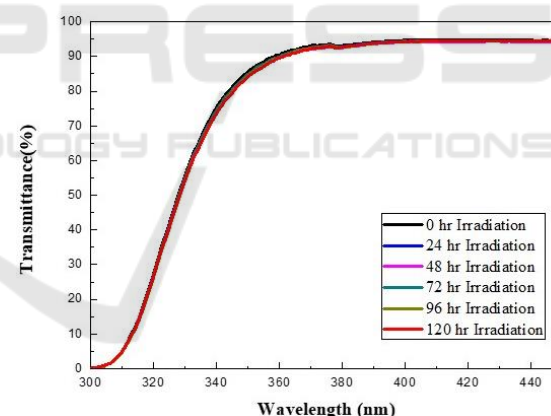


Figure 3: Variation of transmittance of optical film at the wavelengths of 300-450 nm over 120 hours of light irradiation.

In addition, the reflectivity of optical film that without irradiation was ranged from 96.73 to 104.34 % at the wavelength of 355 to 375 nm; especially, which was 103.32 % at 365 nm. The caused reason of the measured value higher than 100 % was the reflectivity of optical film was higher than the calibration sample (Taylor, 2009 and Optical Reference Laboratory, 2012). Hence, the variation of the measured value between the without irradiation and under several hours of irradiation was analyzed.

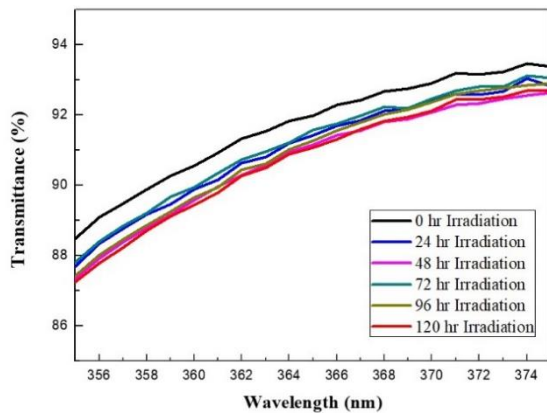


Figure 4: Variation of transmittance of optical film at the wavelengths of 355-375 nm over 120 hours of light irradiation.

The results showed that the reflectivity of optical film under 24 to 96 hour irradiation was not varied evidently, and which decreased significantly after 120 hours of irradiation, show as Fig. 5.

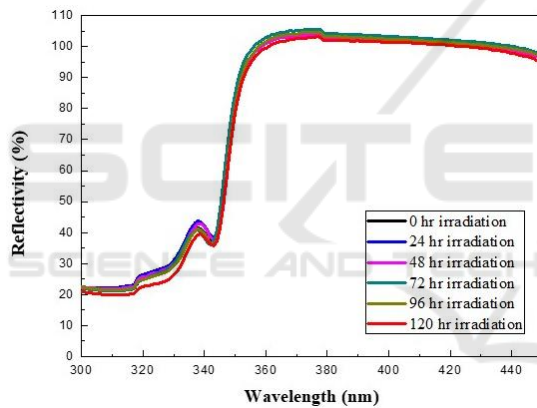


Figure 5: Variation of reflectivity of optical film at the wavelengths of 300-450 nm over 120 hours of light irradiation.

The maximum variation of reflectivity between 0 hr and 120 hr irradiation was 3.13 % at a wavelength of 331 nm. The drop range was 1.21 to 1.89 % in i-line spectrum with wavelength of 355-375 nm; especially, the value was approximately 1.67 % at 365 nm, shown as Fig. 6.

### 3.2 Material Aging Analysis

Due to the non-conductive material of optical film and BK-7 glass, the platinum (Pt) was coated on the tested sample under the current of 10 mA and 80 seconds. Then the FEI Helios Nanolab 660 dual-beam microscope that combined the field emission scanning electron microscope and focused ion beam

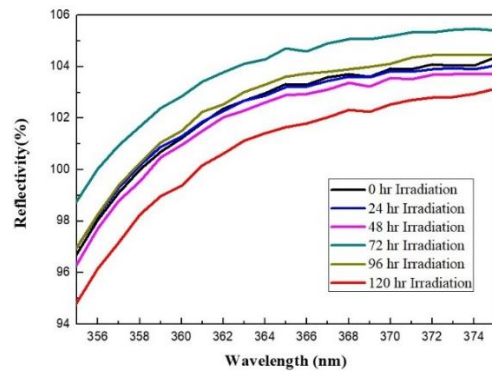


Figure 6: Variation of reflectivity of optical film at the wavelengths of 355-375 nm over 120 hours of light irradiation.

was employed to acquire the surface image of optical film and analyze the ingredient of material. The 1 kV of the electron beam was employed to acquire the top view images and 10 kV was used in intergradient analysis. When the material gradually become aging, the proportion of oxygen will be enhanced. From the elemental analysis, you can see the difference in oxygen, and the rest of the elements are smaller. Therefore, in this volume focuses on the changes in oxygen.

From the ingredient results, the oxygen (O) increased after the UV light irradiation, and which the increased range was 0.9 – 5.0 % in weight under various irradiation times, shown in Fig. 7 and summarized in Table 3. The O has the largest in the initially 24 hours and gradually be stable. Respect to the transmittance of the optical film, it dropped drastically in the initial 24 hours light irradiation, and the degree of declining reduced.

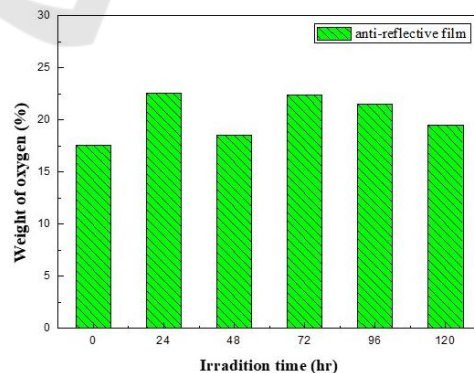


Figure 7: Variation of oxygen of anti-reflective film under different light irradiation time.

From the top view of optical film and magnified by 200,000 X, the images showed that the surface was completely under the excitement of the electron

Table 3: Summarized of weight of various atom of anti-reflective film under different irradiation time.

Time (hr) \ Atom (wt%)	0	24	48	72	96	120
Hf	27.5	27.3	28.7	27.3	27.7	27.6
O	17.6	22.6	18.5	22.4	21.5	19.5
Si	15.1	18.8	15.0	19.8	19.1	17.4
F	12.5	12.2	18.3	12.0	12.3	12.6
Pt	11.8	3.3	4.1	2.8	3.7	6.8
Mg	7.8	5.9	7.8	5.9	6.2	7.2
K	3.1	3.8	3.0	3.9	3.7	3.7
Na	2.7	3.2	2.7	3.2	3.2	2.9
Ca	1.9	2.8	1.8	2.6	2.6	2.3

beam. However, the surface with UV light irradiation was ruptured while the electron beam was focused on the optical film, and it became seriously with the increase of irradiation time, shown as Fig. 8. It indicated that the film was aged after the UV light irradiation, and the mechanical strength of film decreased simultaneously.

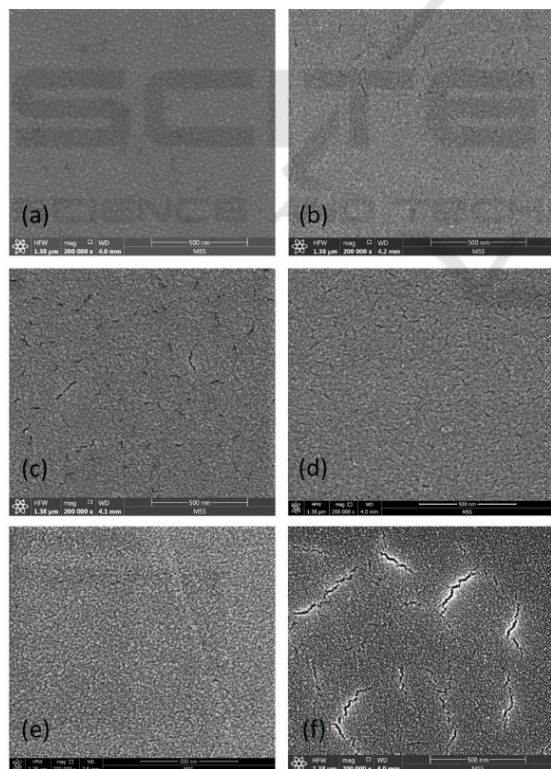


Figure 8: Top view of anti-reflective film under (a) 0 hour, (b) 24 hour, (c) 48 hour, (d) 72 hour, (e) 96 hour and (f) 120 hour of light irradiation.

The ingredient of reflective film also showed that the atom O increased approximately 0.3 – 2.4 % in weight after the UV light irradiation, summarized in Table 4 and shown in Fig. 9. Besides, the atom of silicon (Si) and titanium (Ti) increased less than 0.6 wt% and 0.5 wt%, respectively. It indicated that the reflective film will be affected and become oxidation and aging by the UV light. The top view showed that the reflective film was not ruptured by the electron beam (Fig. 10) owing to the total thickness of reflective film was 5 times thicker than the anti-reflective film. Hence, the better mechanical strength of the film can be obtained and the aging time will be extended.

Table 4: Summarized of weight of various atom of reflective film under different irradiation time.

Time (hr) \ Atom (wt%)	0	24	48	72	96	120
O	42.8	44.5	45.2	44.3	44.0	43.1
Si	22.4	23.0	22.2	22.6	22.2	22.5
Ti	20.7	20.9	20.6	20.7	20.2	21.2
C	5.0	2.7	5.2	5.2	7.2	5.2
Pt	5.7	5.2	3.8	3.8	3.3	4.6
Ag	3.4	3.7	2.9	3.4	3.1	3.5

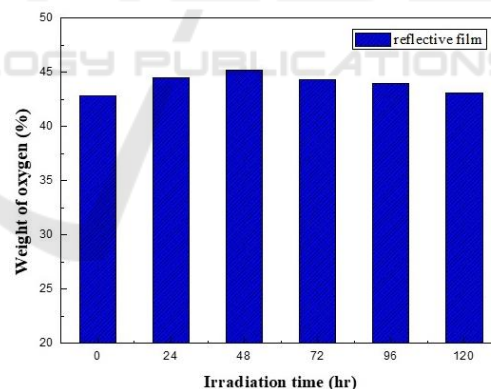


Figure 9: Variation of oxygen of reflective film under different light irradiation time.

From the above results, the optical film would be oxidation and aged under the UV light irradiation, and the surface gradually ruptured and caused the transmittance or reflectivity decreased. Hence, the parameter of each coating layer can be adjusted to obtain a film with high performance and low aging and oxidation degree. In addition, the durability of optical film and the performance of the lens could be evaluated from the results of more irradiation time in the future.

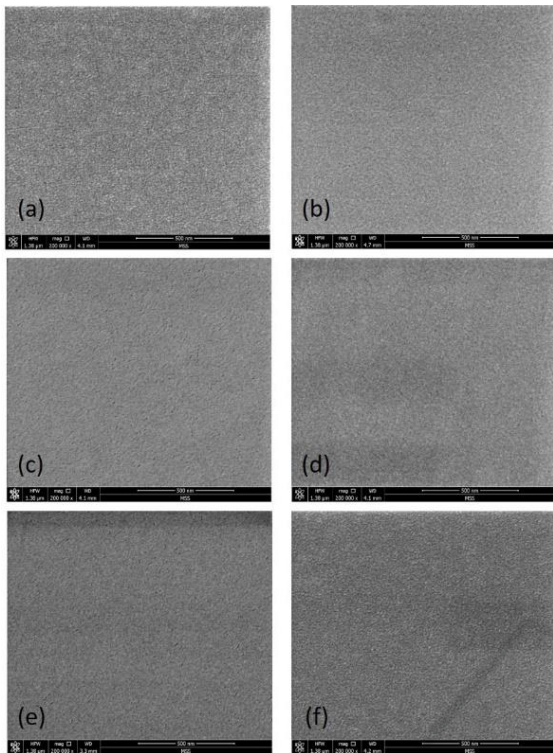


Figure 10: Top view of reflective film under (a) 0 hour, (b) 24 hour, (c) 48 hour, (d) 72 hour, (e) 96 hour and (f) 120 hour of light irradiation.

## 4 CONCLUSIONS

In this study, we built a UV light irradiation environment to investigate the oxidation and aging effects of the optical film included reflective and anti-reflective film coated on the BK-7 glass substrate. Under the UV light irradiation, the optical property like the transmittance of anti-reflective film and reflectivity of reflective film and its ingredient and surface appearance would be changed. The transmittance and reflectivity of optical film at i-line spectrum (355-375 nm) dropped 0.76-1.24 % and 1.21-1.89 %, respectively. In addition, the oxygen increased approximately 0.9- 5.0 wt% and 0.3-2.4 wt% in anti-reflective and reflective film after the 24 -120 hour light irradiation; additionally the surface of reflective was not easy to be ruptured and has better mechanical strength because it's high thickness of film. From the presented results, the coating parameters of film should be redesigned to reduce the degree and speed of film aging, and the exposure dose may be adjusted according to the aging degree, optical property and performance of projection lens in the real lithography process. The

results can provide the reference information for the designer and manufacturer of lithography equipment in the semiconductor industry.

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