Impact Assessment about UV- and AO-Irradiated Silicone Contaminants through Optical Property Measurement

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Abstract

In order to clarify the influences of atomic oxygen (AO) or the interaction between ultraviolet rays (UV) and AO to optical properties of silicone contaminants, UV- and AO-irradiated silicone contaminants were evaluated through optical property measurement. RTV-S691, a silicone adhesive with low volatiles content and minimum outgassing behavior for space utilizations, was used as an outgassing source, and two optical materials (magnesium fluoride and zinc selenide) were used for collecting contaminants from the RTV-S691. Optical properties were examined by Fourier transform infrared spectroscopy and Ultraviolet-visible-near infrared spectroscopy. RTV-S691 was heated to 125°C, while the two optical materials used for collecting contaminants were maintained at 25°C. The results show that UV- and AO-irradiation have impacted the optical properties of silicone contaminants, for example, some optical spectral peaks were disappeared by AO irradiation.

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1. Introduction

It is known that molecular contaminants derived from organic materials impair the performance of solar arrays, thermal control surfaces, and optical components. Moreover, some of space environmental factors are known to influence the various properties of contaminants. For example, ultraviolet rays (UV) cut chemical bonds of organic materials, and atomic oxygen (AO) reacts in chemical changes with organic materials¹). In the previous work, Japan Aerospace Exploration Agency (JAXA) developed three identical units of the micro-particles capturer and space environment exposure device (MPAC &SEED) on the exterior of the Russian service module on the International Space Station for exposure test against such elements of the space environment as high-energy radiation particles, atomic oxygen, space dust and ultra-violet radiation particles²). The growth of contamination was observed on all MPAC&SEED units after they had been retrieved3). The degradation of throughput data was observed by the Optical Telescope Assembly (OTA) that had been on-board satellite named HINODE (formerly called Solar-B), which is an observational satellite launched on September 22, 2006 and equipped with three advanced solar telescopes; solar optical telescope (SOT), X-ray telescope (XRT) and EUV imaging spectrometer (EIS). The tendency of the degradation could not be explained with only the deposition of contaminants without considering the influence of the space environment⁴⁾.

The contaminants may receive influences from space environments with similar order of factors in effect. It is important for us to understand the impacts of such contaminants and the degrading impacts of space environmental factors, especially on optical properties. However, the impacts caused by AO or the interaction between UV and AO on the optical properties of contaminants remains largely unknown. Thus, in order to clarify the influences of AO or the interaction between UV and AO on the optical properties of silicone contaminants (well-known contaminants in orbit), UV- and AO-irradiated silicone contaminants were investigated for two optical materials of zinc selenide (ZnSe) and magnesium fluoride (MgF₂) in this work, and their optical characteristics have been examined by fourier transform infrared (FT-IR) spectroscopy and ultravioletvisible-near infrared (UV-Vis-NIR) spectroscopy.

2. Experimental

2.1 Experimental Conditions

Table 1 gives an overview of the optical materials along with the experimental conditions in this work. Two common optical materials of ZnSe and MgF_2 were selected for collecting contaminants. The reasons to select them are that ZnSe is an optical material with high transmittance against visible ranges to far-infrared region and MgF_2 is also an optical material with high transmittance in vacuum within the regions between ultraviolet, visible, and infrared region. Their optical properties were evaluated to clarify the influences of UV- and AO-irradiation to contaminants through the measurements by FT-IR spectroscopy and UV–Vis–NIR spectroscopy for ZnSe and MgF₂, respectively.

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Material	Dimensions, mm	Sample No.	UV irradiation	AO irradiation
ZnSe	φ 25×t 1	Z-1	0	0
		Z-2	0	×
		Z-3	×	0
		Z-4	×	×
MgF_2	φ 25×t 1	M-1	0	0
		M-2	0	×
		M-3	×	0
		M-4	×	×

 Table 1
 Optical materials and irradiation condition for each samples in this work.

o: irradiated, ×: non-irradiated

2.2 Experiment Flow

Figure 1 shows the experimental flowchart in this work, which procedures are carried out with the steps of (1) preparation of optical materials, (2) deposition of contamination on the optical materials, (3) UV irradiation, (4) AO irradiation and (5) Evaluation explained as follows;

(1) Preparation of Optical Materials

After both samples (ZnSe and MgF₂) were cleaned with ultrasonic cleaning using ethyl alcohol, thermal drying was proceeded in vacuum less than 3 kPa at 150 degree C (°C) for six hours. ZnSe was selected for obtaining absorption spectrum data of the infrared region, while MgF₂ was chosen to obtain absorption spectrum data in the ultraviolet visible region.

(2) Depositing Contamination on Optical Materials

Given its use as an adhesive between solar cells to support the substrate, the room-temperature-vulcanising (RTV) adhesive No. S691 (RTV - S691; Wacker Asahikasei Silicone Co., Ltd.) was selected as the silicone outgassing source. The RTV-S691 has been used as an outgassing source, because the silicone adhesive is widely used for bonding solar cells and supporting the

substrate of solar cells in spacecraft.

Due to depositing the contaminants from RTV-S691 on the optical materials, the outgas measuring test was carried out with the Outgas Measuring System (ULVAC, Inc.) following ASTM-E595⁵) which is a standard of American Society for Testing and Materials about outgas measurement. Silicone adhesive RTV-S691 was heated to 125°C, while the optical materials for collecting silicone contaminants were maintained at 25°C. The thermal condition used was in reference to ASTM E595⁵). All optical materials were contaminated on one side equally in terms of area (314 mm²).

(3) UV Irradiation

After being contaminated with silicone contaminants from the RTV-S691, the optical materials were irradiated with UV. The UV irradiation was conducted in a high-vacuum chamber equipped with an Xe lamp⁶) (Yamashita Denso Corporation). **Table 2** outlines the UV irradiation conditions that emulated the results of passive space environment measurement⁷), ⁸). The UV flux and fluence levels were measured by a multispectral radiometer. The contaminated side of optical materials was



Fig. 1 Experimental flowchart

Table 2UV irradiation conditions

Item	Parameter
Light source	Type UXL-2501YA 2.5 kW Xe short-arc lamp
Irradiation wavelength, nm	250 - 500 ^{‰1}
Irradiation intensity, UV-sun ^{**2}	10
UV irradiation fluence, ESD ^{**3}	30

*¹ The flux of region less than 250 nm was reduced using a lamp coating to avoid the creation of ozone. A dichroic mirror (which reflects UV and reduces the wavelength of the IR region) significantly increased the temperature.

** 2 1UV-sun = 11.8 mW/cm² (Integration of spectral intensity of 200-400 nm in orbit⁹)

 **3 1ESD (Equivalent sun days) = 1.02×10^3 J/cm² (Fluence of UV irradiation per day: in orbit, 200–400 nm)

irradiated with UV. The sample numbers Z-3, M-3, Z-4 and M-4 were put in an unsealed aluminum case to prevent their exposure to UV and then set in the high-vacuum chamber for exposing to the same environment without UV irradiation. Thus, as shown in Table 1, the samples of Z-1, M-1, Z-2 and M-2 were irradiated with UV, whereas those of Z-3, M-3, Z-4 and M-4 were not directly irradiated with the UV. Samples are commonly heated during the UV irradiation; therefore, the surface temperature of the optical materials was monitored and regulated to keep under 25°C by cooling the backsides of the optical materials with water flow in this work.

(4) AO Irradiation

After the UV irradiation, AO irradiation was provided to the optical materials by the AO source of the Combined Space Effects Test Facility^{10), 11}. This facility has a laser detonation AO beam source. Kapton H film made by DuPont was used as the AO monitoring sample. Since the erosion yield (E_K) of the Kapton H is known as $3.0 \times 10^{-24} \text{ cm}^3/\text{atom}^{12}$), the total AO fluence (F) can be estimated by measuring the mass loss (Δm_K) of Kapton H after AO irradiation tests using the equation (1)¹³,

$$\mathbf{F} = \frac{\Delta \mathbf{m}_K}{A_K \rho_K E_K} \tag{1}$$

where A_K and ρ_K are the exposure area and the density of Kapton H, respectively. The former is 314 mm² and the latter is 1.42 g/cm³ in the present work. The value of F is then 6.5×10^{20} atoms/cm² with the value of Δm_K tested (average: 8.6 mg); the AO average flux is 5.5 x 10^{15} atoms/cm² · s and the AO beam average speed is 8.1 km/s. These AO irradiation conditions also emulate the results of passive space environment measurement^{7),} ⁸⁾. The contaminated side of optical materials was irradiated with AO. The samples of Z-2, M-2, Z-4 and M-4 were put in an unsealed aluminum case to prevent their exposure to AO, and then set in the Combined Space Effects Test Facility for exposing to the same environment without AO irradiation. In summary, the samples of Z-1 and M-1 were irradiated with UV and AO, those of Z-2 and M-2 were irradiated with UV only, Z-3 and M-3 were irradiated with AO only, and Z-4 and M-4 were irradiated without UV and AO (cf. Table 1).

(5) Evaluation

The mass of all optical materials was measured by using the microbalance (XP6, Mettler Toledo International Inc.) before and after depositing contamination, in order to confirm that the enough contaminants were deposited on the optical materials for measuring the optical properties.

The effects on the optical properties of UV- and AO-irradiated silicone contaminants were investigated by using an FT-IR spectrometer (Spectrum One, PerkinElmer Japan Co., Ltd.) in wavenumber region from 400 cm⁻¹ to 5000 cm⁻¹ with the resolution of 4 cm⁻¹ and a UV–Vis–NIR spectrometer (U-4100, Hitachi High-Technologies Corporation) in wavelength range between 190 nm and 2500 nm with 1 nm resolution. The optical properties were investigated before and after depositing contamination, and also before and after UV and/or AO irradiation.

3 Results and Discussion

3.1 Mass Measurement

Table 3 shows the mass of each optical material before and after depositing contamination, and the deposition thickness. Deposition thickness was calculated under the assumption that the contaminants deposited homogeneously on the surface of optical materials by using the specified values (deposition area: 314 mm², density of contamination¹⁴): 1 mg/mm³). Actually contaminants are deposited as droplets on the surface of materials, resulting in the deposition thickness are thicker than the calculated values. As a result, the mass measurement results show that the optical materials are sufficiently deposited with silicone contaminants for investigating the optical properties.

3.2 **Optical Properties**

The FT-IR spectra of silicone contaminants on ZnSe were measured in the wavenumber range of $5000-400 \text{ cm}^{-1}$, and the UV–Vis–NIR spectra of silicone contaminants on MgF₂ were measured by UV–Vis–NIR spectroscopy in the wavelength range of 190–2500 nm. Figure 2 shows the FT-IR spectra of silicone contaminants; Figure 3 shows the UV–Vis–NIR spectra of silicone contaminants.

Optical material	Sample					
	No.	Irradiationcondi tions	Before	After	Δ (After-Before)	Deposition thickness, nm
ZnSe MgF ₂	Z-1	UV,AO	2686.842	2687.083	0.241	767.516
	Z-2	UV	2702.741	2702.924	0.183	582.803
	Z-3	AO	2773.342	2773.553	0.211	671.975
	Z-4	Non	2600.021	2600.22	0.199	633.758
	M-1	UV, AO	1663.301	1663.543	0.242	770.701
	M-2	UV	1662.096	1662.321	0.225	716.561
	M-3	AO	2428.507	2428.770	0.263	837.580
	M-4	Non	2437.888	2438.134	0.246	783.439

 Table 3
 Mass of optical materials before and after depositing contamination and deposition thickness



(b) Spectra between 2800 cm⁻¹ and 3600 cm⁻¹

(c) Spectra between 400 cm⁻¹ and 1600 cm⁻¹

Fig. 2 FT-IR spectra of ZnSe selected as one of the optical materials in this work

----- : irradiated by UV and AO (Z-1), ---- : irradiated by UV (Z-2), ------ : irradiated by AO (Z-3), ------ : non-irradiated (Z-4).

The peaks can be clearly found for a part of samples around the regions shown with arrows.

There are three spectral peaks that are not observed at a part of the optical materials (the spectral peaks are indicated by arrows in **Fig. 2**). The spectral peaks at 1400 cm⁻¹ and 2900 cm⁻¹ in **Fig. 2(a)**, **2(b)** and **2(c)** disappeared in the spectra of Z-3 (irradiated with AO only); however, these peaks were retained in the spectra of Z-1 (irradiated with UV and AO), Z-2 (irradiated with UV only), and Z-4 (not irradiated). In this work, spectral peaks did not disappear in the spectra of Z-1 (irradiated with UV and AO), thereby making it difficult to consider AO erosion as the cause of this spectral discrepancy. An oxidation reaction that occurred upon AO irradiation may have caused the peaks to disappear.

The broad spectral peak in the vicinity of wavenumber 3400 cm^{-1} in **Figure 2(a)** appeared in the spectra of Z-1 (irradiated with UV and AO) and Z-3 (irradiated with AO only), but was not present in the spectra of Z-2 (irradiated with UV only) and Z-4 (not irradiated). The broad spectral peak was derived by –OH as

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in the previous experimental results.

Given the facts, the appearance of the broad spectral peak is thought to result from the oxidization of silicone contaminants caused by AO irradiation. As a result of the FT-IR spectra of silicone contaminants, oxidation reaction is considered the main reaction of AO irradiation to silicone contaminants.

The transmittance of M-1 (irradiated with UV and AO), M-2 (irradiated with UV only), and M-3 (irradiated with AO only) was degraded, as compared with that of M-4 (non-irradiated) in the range of 280 nm–500 nm in **Fig. 3(b)**. The difference between the UV–Vis–NIR spectra of M-1 (irradiated with UV and AO) and M-2 (irradiated with UV only) in the wavelength range of 190 nm–380 nm in **Fig. 3(b)** indicates that AO irradiation improved the degradation caused by UV irradiation. Similarly, in the region between wavelength range of 190 nm and 210 nm in **Fig. 3(b)**, the difference between the UV–Vis–NIR spectra of M-3 and M-4 shows that AO irradiation



(b) UV-Vis-NIR spectra between 190 nm and 640 nm

Fig. 3 UV-Vis NIR spectra of MgF₂ selected as one of the optical materials in this work

improved the degradation of silicone contaminants. As a result, erosion or oxidation by AO irradiation is considered to improve the degradation of silicone contaminants caused by UV, especially at a low wavelength, but such an effect does not occur in the same wavelength range when there is no degradation of contaminants caused by UV.

Joyce A. Dever et al. reported that polymers react with AO via initial reactions of bond dissociation or oxidation, and that UV can lead to the crosslinking of polymer surfaces¹). In the same way, by comparing the results of both FT-IR *a*nd UV–Vis–NIR spectra, cross-linking reaction ⁴) is considered the main reaction of UV irradiation to silicone contaminants in this work. And oxidation reaction⁴ is considered the main reaction of AO irradiation to silicone contaminants in this work. This means that the sites susceptible to erosion caused by AO are limited in terms of silicone contaminants.

4. Conclusion

UV- and AO-irradiated silicone contaminants were evaluated through optical property measurement. As a result, the following points have been confirmed.

- 1) The main reaction of UV irradiation to silicone contaminants is cross-linking reaction.
- 2) The main reaction of AO irradiation to silicone contaminants is oxidation reaction.
- Erosion or oxidation caused by AO irradiation is considered to improve the degradation of silicone contaminants caused by UV, especially at a low wavelength.

Although it has been clarified the influences of AO or the interaction between UV and AO on the optical properties of silicone contaminants, investigations for much longer duration have to be carried out. The confirmed impacts of silicone contaminants by UV and AO irradiation is considered only against equivalent exposure worth of UV- and AO-irradiation emulating results of passive space environment measurement for around one year. Therefore, it is important to investigate higher levels of UV- and AO-irradiated silicone contaminants useful for actual missions for more than one year, and so later experiments will be planned with higher irradiation levels of UV and AO.

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