Optical properties of Ta_2O_5 single layer and ultraviolet reflective film under ultraviolet irradiation*

XU Lingmao (徐岭茂)[1], **HE Yanchun** (何延春)[1], **LI Kun** (李坤)[1], **ZHOU Hui** (周晖)[1]**, **WANG Ying** (王颖)[2], **XIONG Yuqing** (熊玉卿)[1], **and DAI Shuwu** (代树武)[2]

1. Science and Technology on Vacuum Technology and Physics Laboratory, Lanzhou Institute of Physics, Lanzhou 730001, China

2. Beijing Institute of Spacecraft System Engineering, Beijing 100094, China

(Received 15 October 2020; Revised 14 November 2020)

Tantalum pentoxide (Ta_2O_5) and ultraviolet reflective (UVR) multilayer films were deposited on quartz glass substrates by an electron beam evaporation system equipped with a hall ion source, respectively. The optical properties of Ta_2O_5 film and the UVR film under the vacuum ultraviolet irradiation were investigated. It is found that the mean transmittance of the Ta_2O_5 thin film decreased in the 300—500 nm region. The refractive index and extinction coefficient of the single layer increased during the range of 300—1 000 nm, with the variation rate of refractive index less than 1%, which is mainly due to the larger surface roughness and variation of the chemical state of Ta atoms on the surface caused by the irradiation. The mean reflectance of UVR film decreased from 96.5% to 95.4% during the range of 290—450 nm, indicating that the Ta_2O_5 and UVR films have excellent vacuum ultraviolet irradiation resistant properties.

Document code: A **Article ID:** 1673-1905(2021)08-0464-4

DOI https://doi.org/10.1007/s11801-021-0157-8

Ultraviolet reflective (UVR) film can be applied to the surface of solar cell arrays and thermal control film on the spacecraft to reduce the thermal effect caused by ultraviolet absorption, in which existence of UV irradiation, gamma rays, protons, and neutrons could cause variation of both optical materials' properties and optics' performance[1,2]. The inductive change of optical constants of thin film will lead to the deterioration of transmittance or reflectance of multilayers containing such materials[3]. Moreover, the film with large roughness can absorb atmospheric contaminants or propellants from spacecraft which result in degradation of optics performance[4,5].

Tantalum pentoxide (Ta_2O_5) thin films have been widely used in spectral modulation due to its interesting properties, including high refractive index, chemical stability at high temperatures and wide transparent region[6-9]. Coupled with low refractive index optical film, the interferential stacks have been used or have potential applications in interference filter, anti-reflection films, reflective film, and other spectral elements[10-12]. The behavior of Ta_2O_5 film and multilayers under proton and gamma irradiation had been studied by researchers[13], while the behavior of Ta_2O_5 film and UVR film under ultraviolet irradiation is little investigated, which would make sense in addressing these problems in the context of advanced manufacturing of optical films used in space.

In this study, Ta_2O_5 and UVR films are deposited on quartz substrates by an electron beam evaporation system, respectively. Then optical properties and vacuum ultraviolet irradiation resistant properties of Ta_2O_5 and UVR films are investigated. The surface morphologies of Ta_2O_5 film are observed by an atomic force microscope (AFM) before and after the UV radiation, X-ray photoelectron spectroscopy (XPS) are examined to investigate the chemical bonding of surface. It is found that the Ta_2O_5 and UVR films have excellent vacuum ultraviolet irradiation resistant properties which can be used in optics for space applications.

Specimens of quartz glass with a size of Φ30 mm^2 and thickness of 1 mm were selected as substrates. Ta_2O_5 single film with designed thickness of 400 nm and designed UVR film were coated by an electron beam evaporation system (Model JASOC 1350) equipped with a hall ion source (Telemark, ST-3000). Before depositing, substrates were cleaned by ion beam to activate the surface. During the coating process, the vacuum is 1.0×10^{-2} Pa, deposition temperature is 523 K, the deposition rates of Ta_2O_5 and SiO_2 are 3 Å/s and 8 Å/s, respectively. A thin film deposition controller (INFICON XTC/3)

* This work has been supported by the Joint Astronomical Fund of National Science Foundation of China (No.U1731113), and the Foundation of Science and Technology on Vacuum Technology and Physics Laboratory (No.ZD171902).

** E-mail: zhouhui510@sina.com

equipped with a quartz crystal was applied to monitor the thickness. The optical properties were measured by a spectrophotometer (PerkineElmer, Lamda950) with an 8° fixed angle absolute reflectance accessory. The surface morphology, chemical bonding of Ta_2O_5 films were observed by an atomic force microscope (Oxford, MFP-3D Origin) and X-ray photoelectron spectroscopy (Kratos, AXIS Ultra DLD), respectively. The vacuum ultraviolet irradiation experiment was processed on the ultraviolet irradiation device (UV-1, irradiation spectral range of 200—400 nm). The vacuum ultraviolet irradiation intensity is 2 000 ESH (equivalent solar hour), the vacuum is 5×10^{-4} Pa, and the accelerating factor is 4~5, all irradiated samples are kept below 373 K with a temperature control system to eliminate the effects of high temperature.

The transmittance of quartz substrate and Ta_2O_5 single layer measured before and after ultraviolet irradiation with total dose of 2 000 ESH are shown in Fig.1. As can be seen in Fig.1(a), the degradation of transmittance of the quartz substrate below 500 nm can be noticed, there is no deterioration of transmittance between 500 nm and 1 000 nm. This is attributed to the color center and other types of defects induced by the irradiation which has a similar mechanism with Gamma irradiation[2,13,14]. Therefore, the transmittance of Ta_2O_5 thin film is normalized to the transmittance of quartz substrate to eliminate the substrate influence as illustrated in Fig.1(b). It can be seen that the mean transmittance of Ta_2O_5 thin film decreases from 81% to 79.4% in the 300—500 nm region, and it remains 86.7% in the 600—1 000 nm region after the ultraviolet irradiation.

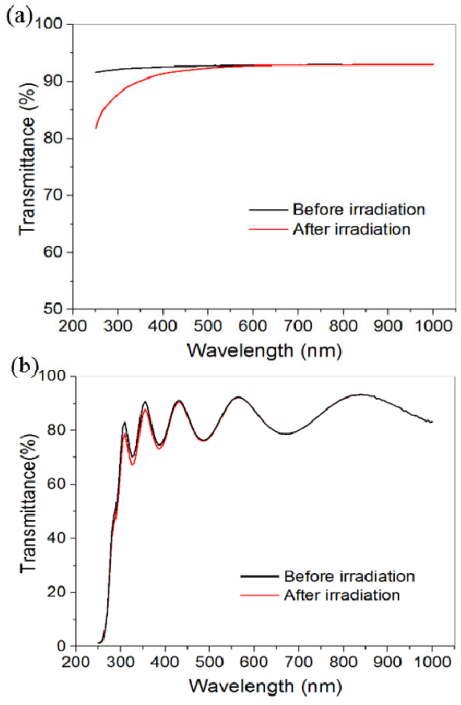


Fig.1 The transmittance of (a) quartz substrate and (b) Ta_2O_5 single layer measured before and after ultraviolet irradiation

Fig.2 shows the refractive index and extinction coefficient of Ta_2O_5 thin film before and after ultraviolet irradiation during the range of 300—1 000 nm obtained by full spectrum inversion fitting method[15]. It can be seen that the refractive index increases after the irradiation during the range of 300—1 000 nm, in particular, it increases from 2.091 4 to 2.111 6 at wavelength of 500 nm with a rate of variation less than 1%. It is observed that the extinction coefficients decrease from 300 nm to 400 nm, and the trend is consistent both before and after the irradiation. During the range from 400 nm to 1 000 nm, the extinction coefficients can be neglectable due to they are approximate to zero. After irradiation, the extinction coefficients also increase during the range from 300 nm to 400 nm, from 1.4×10^{-5} to 3.12×10^{-5} at wavelength of 400 nm in particular.

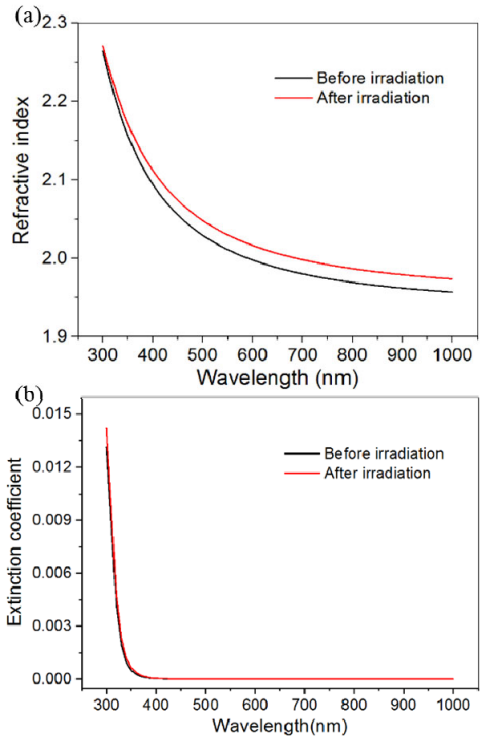


Fig.2 (a) Refractive index and (b) extinction coefficient of Ta_2O_5 thin film before and after ultraviolet irradiation during the range of 300—1 000 nm

To untangle the surface morphology of Ta_2O_5 thin film, the film is characterized by AFM with a non-contact mode in ambient conditions, the scan area was 5 μm×5 μm. Fig.3(a) and (b) show the 2D and 3D AFM images of Ta_2O_5 samples before and after irradiation, respectively. The morphology observed in the AFM images is measured in multiple regions for each film and confirmed to be similar and uniform. A smooth surface with no presence of grains or facets is observed, excluding the presence of a poly-crystalline phase for Ta_2O_5 and thus confirming their amorphous nature. As can be seen in the Fig.3(a), the surface morphology is uniform before

the irradiation. The average surface roughness R_a and root mean square roughness (*RMS*) are estimated to be 0.56 nm and 0.69 nm for the sample as-received, 0.48 nm and 0.6 nm for the irradiated film, respectively. These roughness values of all the samples are quite low and in good agreement with those reported for other amorphous films[16,17]. The mean width of the mounds increased after irradiation, moreover, with some high peaks and crystal defects, indicating that UV irradiation change the surface morphology of the sample. This may due to the sputtering effect caused by irradiation which not only results into the change of surface morphology, but also some microdefects.

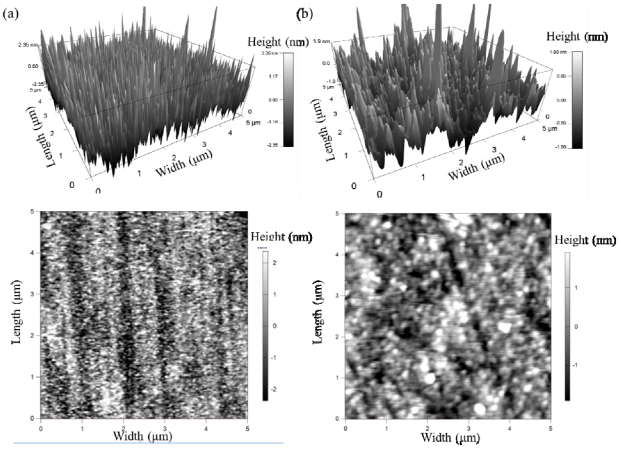
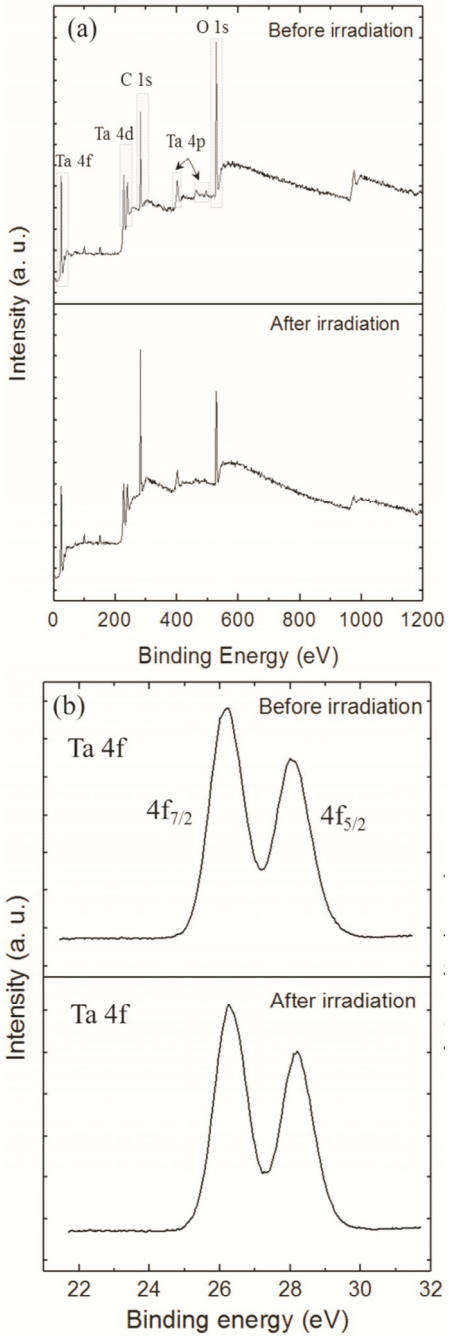


Fig.3 AFM images of Ta_2O_5 thin film (a) before and (b) after ultraviolet irradiation

To investigate the variation of chemical bonding, XPS wide scan spectra, the Ta 4f region, and the O 1s region of Ta_2O_5 thin films before and after ultraviolet irradiation are illustrated in Fig.4. Photoelectron binding energies are calibrated at the C ls binding energy of the hydrocarbon at 284.8 eV. All the expected peaks are present in Fig.4(a), three different orbitals of tantalum (4f, 4d, and 4p) are observed as well as the O 1s peak, ascribed to the deposited oxide, and the C 1s peak is present attributed to atmospheric contamination. XPS wide scan spectrum does not reveal any further contamination besides C presence. After irradiation, the C 1s peak increases due to the larger surface roughness which may be more sensitive to the contamination. In the contrary, O 1s peak decreases after irradiation which is due to the reduced concentration of oxygen on the surface thin layer.

From Fig.4(b), we can see that the Ta 4f core level exhibits as a doublet peak which can be deconvoluted into two peaks located at 26.30 eV, 28.19 eV, 26.19 eV, and 28.07 eV for the Ta_2O_5 films before and after irradiation, respectively. It signifies that the Ta 4f splits into Ta $4f_{7/2}$ and Ta $4f_{5/2}$ due to the spin-orbit splitting (SOS), and exhibits a separation energy of about 1.9 eV and an area ratio of 1.3[7,18]. The binding energy of Ta 4f peak reduces about 0.1 eV after the irradiation, illustrating that variation of chemical state of Ta atoms on the surface[19]. Fig.4(c) depicts the O 1s photoelectron spectra of the film before and after the irradiation. The O 1s peak can be resolved into two Gaussian peaks. The first peak consisted of an intense peak located at 530.44 eV and 530.49 eV for the film as received and after irradiation, respectively, which is the characteristic peak of the O^{2-} species occurring in Ta_2O_5. After the irradiation, the binding energy of the O^{2-} 1s increased 0.05 eV due to the presence of sub-oxides, which has been investigated as an effect of oxygen vacancies[20].

A thin film of SiO_2 was also deposited on fused silica, even though the evaluation of its behavior is not easy, its transmittance being similar to the substrate transmittance. The behavior of the UVR film containing Ta_2O_5 and SiO_2 layers was then investigated. The UVR films are comprised of 31 layers with a thickness of 1.5 μm, and the



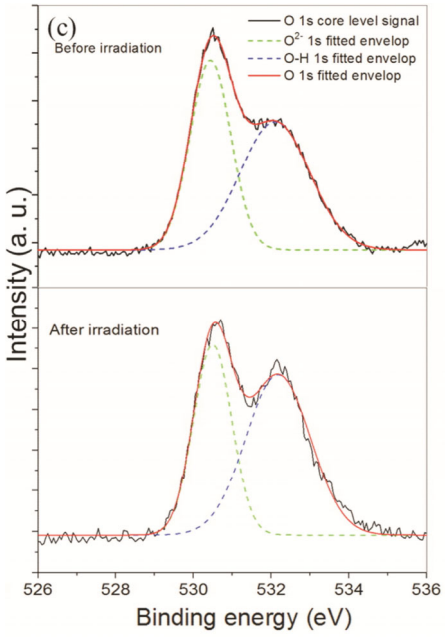


Fig.4 XPS wide scan spectra in (a) the Ta 4f region, (b) and (c) the O 1s region of Ta_2O_5 thin films before and after ultraviolet irradiation

thickness ratio of Ta_2O_5 to SiO_2 film is 0.68. Ta_2O_5 and SiO_2 films are deposited alternately, in which the first and the last layer are Ta_2O_5 films prepared by the process mentioned above. The reflectance spectra are reported in Fig.5 before and after UV irradiation. A slight absorption in the ultraviolet can be noticed, the mean reflectance of UVR film between 290—450 nm decrease from 96.5% to 95.4%. The observed changes could be explained by the variation of the properties of Ta_2O_5 and SiO_2 films.

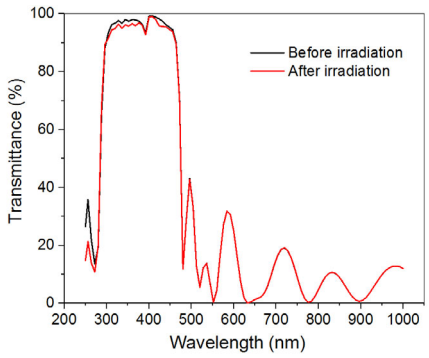


Fig.5 The reflectance spectra of UV reflective coating measured before and after ultraviolet irradiation

After irradiation, the mean transmittance of the substrate and Ta_2O_5 thin film decreased in the 300—500 nm region, the mean reflectance of UVR film between 290—450 nm decreased from 96.5% to 95.4%. The refractive index and extinction coefficient of the Ta_2O_5 film obtained by full spectrum inversion fitting method increase, with the variation rate of refractive index is less than 1%, indicating that UVR and Ta_2O_5 thin films have excellent vacuum ultraviolet irradiation resistant properties. The variation of surface roughness and chemical state of Ta atoms after irradiation increase of light scattering and further give rise to the changes of optical properties. The results will lay a good foundation for the application of UVR and Ta_2O_5 thin films in space.

References

[1] Sharma N, Kumar VP, Kumar M, Kumari N, Karar V and Goswamy JK, Optik **202**, 163697 (2020).
[2] Mannequin C, Tsuruoka T, Hasegawa T and Aono M, Applied Surface Science **385**, 426 (2016).
[3] Bright TJ, Watjen JI, Zhang ZM, Muratore C, Voevodin AA and Koukis DI, Journal of Applied Physics **114**, 083515 (2013).
[4] Shakoury R, Rezaee S, Mwema F, Luna C, Ghosh K and Jurečka S, Optical and Quantum Electronics **52**, 95 (2020).
[5] Sertel T, Sonmez NA, Cetin SS and Ozcelik S, Ceramics International **45**, 11 (2019).
[6] Lee C-C and Jan D-J, Thin Solid Films **483**, 130 (2005).
[7] Korkos S, Xanthopoulos NJ, Botzakaki MA, Drivas C, Kennou S and Ladas S, Journal of Vacuum Science & Technology A **38**, 032402 (2020).
[8] Pellicori SF, Martinez CL, Hausgen P and Wilt D, Applied Optics **53**, A339 (2014).
[9] Marshall CD, Speth JA and Payne SA, Journal of Non-Crystalline Solids **212**, 59 (1997).
[10] Chen X, Bai R and Huang M, Optical Materials **97**, 109404 (2019).
[11] Chaneliere C, Autran JL, Devine RAB and Balland B, Materials Science & Engineering R-Reports **22**, 269 (1998).
[12] Shakoury R and Willey RR, Applied Optics **55**, 5353 (2016).
[13] Di Sarcina I, Grilli ML, Menchini F, Piegari A, Scaglione S and Sytchkova A, Applied Optics **53**, A314 (2014).
[14] Leyderman A, Weil JA and Williams JAS, Journal of Physics and Chemistry of Solids **46**, 519 (1985).
[15] Xu LM, Zhou H, Zhang KF, Zheng J, Li K and Wang JZ, Journal of Infrared and Millimeter Waves **37**, 11 (2018).
[16] Stenzel O, Wilbrandt S, Schlegel R, Böhme M and Kaiser N, Thin Solid Films **542**, 295 (2013).
[17] Huang TW, Lee HY, Hsieh YW and Lee CH, Journal of Crystal Growth **237**, 492 (2002).
[18] Atanassova E and Spassov D, Applied Surface Science **135**, 71 (1998).
[19] Simpson R, White RG, Watts JF and Baker MA, Applied Surface Science **405**, 79 (2017).
[20] Tsuchiya T, Imai H, Miyoshi S, Glans PA, Guo J and Yamaguchi S, Physical Chemistry Chemical Physics **13**, 17013 (2011).