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Slow-positron annihilation analysis on optical degradation of ZnO white paint irradiated by protons*

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Abstract: The optical degradation in ZnO white paint under low energy proton exposure was investigated in terms of slow-positron annihilation spectroscopy. Experimental results show that with increasing proton fluence, the *S*-parameter of the Doppler broadening spectrum gradually decreases, and the *W*-parameter increases. The slope plot of the fitting *S*-*W* changes under the proton exposure. The decrease of *S*-parameter can be attributed to a decrease of zinc vacancy content and the formation of quasi-positroniums. The quasi-positronium is viewed as a bounded state of a singly ionized oxygen vacancy (trapping an electron) with a positron, the formation of which could reduce the positron annihilation rate and thus the *S*-parameter. The decrease of *S*-parameter demonstrates the amount increase of singly ionized oxygen vacancy of ZnO white paint caused by proton irradiation. The change of the *S*-*W* plot slope is related to the transformation of doubly ionized oxygen vacancies into singly ionized oxygen vacancies under proton irradiation.

Key words: slow-positron annihilation; optical degradation; ZnO white paint; protons

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The service behavior of thermal control coatings is an important factor affecting the reliability of thermal control systems for spacecraft[1-2]. There exists a large amount of protons with energies smaller than 200 keV in the Earth's radiation belts, which can cause radiation-damage of thermal control coatings[3]. ZnO-type white paint is a typical thermal control coating possessing low solar absorptance and high semi-spherical emissivity, and extensively used in spacecrafts. It is believed that the optical degradation of ZnO-type white paint under proton exposure is primarily associated with the change of oxygen vacancies in the ZnO pigment[4-8]. Under the proton exposure, the lattice oxygen atoms in ZnO can obtain energy higher than the bonding energy of lattice due to their collision with the incident protons, escaping from the lattice to become free oxygen thus to form the doubly ionized oxygen vacancies V_O^{**} (without trapping an electron). During proton exposure, the electron-hole pairs can be generated along the paths of incident protons, and each V_O^{**} is ready to trap and bind an electron. As a result, the V_O^{**} transforms into a singly ionized oxygen vacancy (V_O^{*}) and the V_O^{*} gradually becomes a primarily radiation-induced defect. The required energy for a photon to make the electron in V_O^{*} jump into conduction band is just within the visible wavelength region, leading to an increase of absorptance for visible light. Therefore, optical degradation occurs with increasing V_O^{*} content.

The oxygen vacancies are point-defects with atomic scale. The positron annihilation spectroscopy (PAS) with slow-positron beams is a powerful and sensitive technique to examine micro-defects in materials[9-10]. The distribution of defects in the surface or sub-surface layers of samples can be examined by controlling the incident slow-positron beam energy[11]. When a positron is implanted into materials, it can be annihilated with an electron, emitting two γ-quanta of 511 keV. The momentum of the annihilated positron-electron pair

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causes the Doppler broadening of annihilation radiation. The defects such as vacancies and dislocations often carry equivalent negative-charges. In the materials containing defects, a freely diffusing positron can be readily localized or trapped by the defects due to Coulomb interaction. The trapping will lead to a narrowing of momentum distribution of the positron-electron pairs. Such a change can be examined by the parameters S and W of the Doppler broadening spectra. The parameters S and W characterize the annihilation fraction of the positrons with low momentum electrons (valence electrons) and high momentum electrons (core electrons), respectively. The localization of positrons at defects will increase the fraction of the positrons annihilated with valence electrons and decrease that annihilated with core electrons. As a consequence, the parameter S increases and W decreases.

This study aims to examine the change in the slow-positron annihilation spectrum under the exposure of protons with energies lower than 200 keV, and to reveal the relation between point-defect evolution and optical degradation of ZnO-type white paint.

1 Experiment

The experimental samples of ZnO white paint are 20 mm in diameter and 150 μm in thickness, which are coated on Al substrate. The diameter of ZnO pigment particles ranges from 0.4 to 0.9 μm. The binder is an organic silicone containing a small amount of addition agents.

The proton irradiation was performed in a simulator with the energies of 30 to 200 keV. Samples were placed in a chamber with vacuum of 10^{-4} Pa. The proton beam was perpendicular to the sample surface. The energy of protons was chosen as 90 keV, and the flux 5×10^{11} cm$^{-2}\cdot$s^{-1}. The fluence varied in the range of 5×10^{14} to 1×10^{16} cm^{-2}. There was a liquid nitrogen screen inside the test chamber, and the temperature on sample surface was measured to be (298$\pm$5) K during the proton irradiation.

The slow-positron annihilation testing was conducted at room temperature with a slow-positron beam equipment at University of Science and Technology of China[11]. In the measurement system, the β^+ decay of ^{22}Na radioactive source was used to produce positrons, which were slowed down and transmitted through a vacuum pipe of a magnetic control system to get a slow positron beam with an energy of 24 eV. The beam size was smaller than 10 nm, and the energy divergence was less than 2 eV. The implantation depth of the slow positron beam in the samples could be varied by changing the negative high voltage on sample holder. The information of the 511 keV annihilated photons was collected using a high purity Ge detector (ORTEC-GEM-1075), which had an energy resolution of 1.2 keV (FWHM) for the 514 keV γ-rays of ^{85}Sr. Spectra were measured with a total count number of 5×10^{15} for every value of energy. The parameters S and W were used to describe the characteristics of the annihilation spectra. The S-parameter is defined as the ratio of the counts in central energy region around 511 keV to the total counts of spectrum. The W-parameter is the ratio of the wing area to the total area under spectrum. The parameters S and W can demonstrate the information of the low-momentum electrons and the high-momentum ones in materials, respectively.

2 Results and discussion

2.1 Change in optical properties

Fig. 1 shows the pristine reflective spectrum (a) and the change in spectral reflectance $\Delta\rho_\lambda$ as a function of proton fluence (b) for ZnO white paint. It is indicated that the optical degradation mainly occurs in the visible region after the 90 keV proton irradiation. With increasing proton fluence, the intensity of the absorption band increases and the spectral reflectance of samples decreases. The absorption band shifts to longer wavelengths (red shift) and widens due to the proton irradiation.

The solar absorptance α_s is an important parameter to characterize thermal control coatings, and can be obtained according to the following equation[12]:

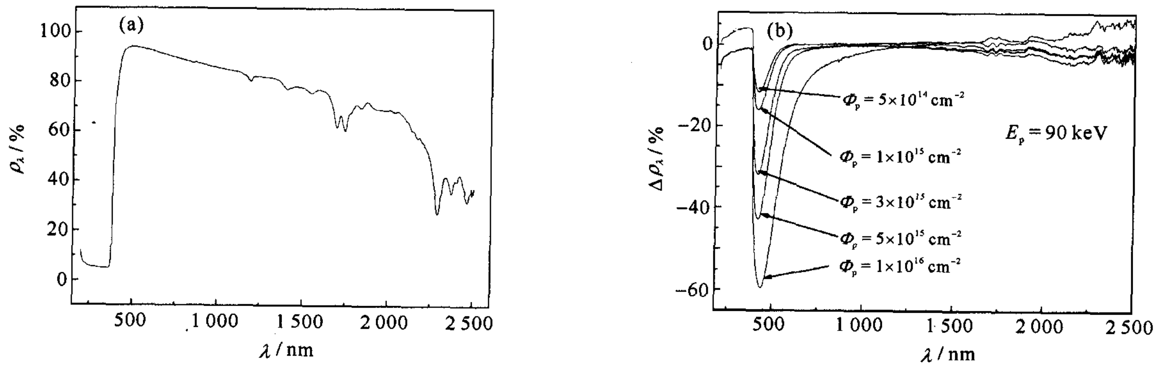

Fig. 1 Pristine reflective spectrum (a) and the change in spectral reflectance $\Delta\rho_\lambda$ (b) *vs* proton fluence for ZnO white paint

$$\alpha_s = 1 - R_s = 1 - \sum_i^n \rho_\lambda / n \tag{1}$$

where R_s is the solar reflectance, ρ_λ is the spectral reflectance and n is chosen as 24. Table 1 shows the change in solar absorptance $\Delta\alpha_s$ as a function of proton fluence for the ZnO white paint samples. $\Delta\alpha_s$ increases with increasing fluence.

Table 1 Change in solar absorptance $\Delta\alpha_s$ *vs* proton fluence for ZnO white paint

proton energy/ keV	flux/ ($cm^{-2} \cdot s^{-1}$)	fluence/ cm^{-2}	$\Delta\alpha_s$
		5×10^{14}	0.016 7
		1×10^{15}	0.021 3
90	5×10^{11}	3×10^{15}	0.048 4
		5×10^{15}	0.075 6
		1×10^{16}	0.149 4

2.2 Slow-positron annihilation analysis

Figs. 2 and 3 show the S and the W parameters as a function of positron implantation energy for the ZnO white paint irradiated by 90 keV protons, respectively. With increasing the proton fluence, the S-parameter decreases, whereas the W-parameter increases. This phenomenon indicates that under the proton exposure, the annihilation fraction of positrons with valence electrons decreases, and that with core electrons increases. Also, it can be seen in Fig. 2 that the S-parameter first ascends, and then shows a descending trend followed by leveling off above the positron energy of approximately 3 keV. The implantation depths of positrons with lower energies are small and a portion of them might diffuse to the sample surface. The annihilation of positrons at the surface results in an increase of the S-parameter. When the energy is high enough, the implantation depths of positrons increase obviously, reducing the probability of the positrons to diffuse to the surface. Thus, almost all the positrons with higher energies can be annihilated in the ZnO interior. In such a case, the lifetime of positrons is longer than those annihilated at the sample surface.

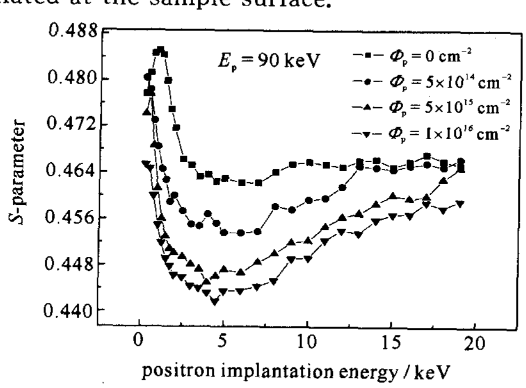

Fig. 2 S-parameter *vs* positron energy for ZnO white paint irradiated by 90 keV protons

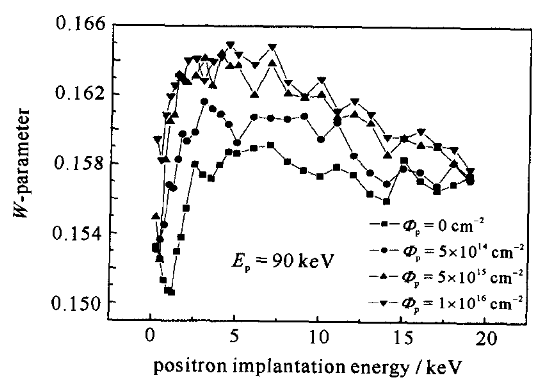

Fig. 3 W-parameter *vs* positron energy for ZnO white paint irradiated by 90 keV protons

The S-W plot can be used to identify the types of defects trapped by positrons in materials. If only one type of defect exists in the sample, the S-W plot can be fitted as a straight line. Fig. 4 shows that the slope of the S-W plot for ZnO white paint changes under proton exposure. The slope is about $-0.338\ 3$ for the pristine sample, and changes into approximately −0.316 2 after the irradiation with the fluence of 5×10^{15} cm^{-2}. This illustrates that the primary type of defects is not the same before and after the proton irradiation.

2.3 Discussion

The slow-positron annihilation technique is often used to characterize the defects induced by ion-implantation in ZnO[9-11,13-16]. In general, positrons can be freely annihilated in perfect crystals. If some defects (such as vacancies, dislocations, microvoids, etc.) exist in materials, the positrons are ready to be trapped by the defects, forming an annihilation of trap state. It seems that the proton exposure would induce a large amount of vacancy-type defects in the surface or sub-surface layers to create trapping centers of positrons. The more the radiation induced defects, the stronger the trapping effects, and thus the *S*-parameter would be increased. However, Fig. 2 shows that with increasing proton fluence, the *S*-parameter decreases for the irradiated ZnO white paint. It is known that the defects in ZnO lattice generally are oxygen vacancies V_O, zinc vacancies V_{Zn} and oxygen interstitials O_i. Previous work[9-11,13-16] shows that V_{Zn} is an effective trapping center of positrons. The repulsion between positrons and ions could be reduced due to the presence of V_{Zn}. The redistribution of electrons at defects would generate a negative potential to trap positrons. Hence, the positrons are easier to be annihilated at V_{Zn}. During the proton irradiation, V_{Zn} content decreases in the ZnO white paint, as confirmed by our previous work[6-8]. The area ratio of the V_{Zn} peak to the whole spectrum gradually reduces with increasing proton fluence. Therefore, under the proton exposure, the *S*-parameter should descend.

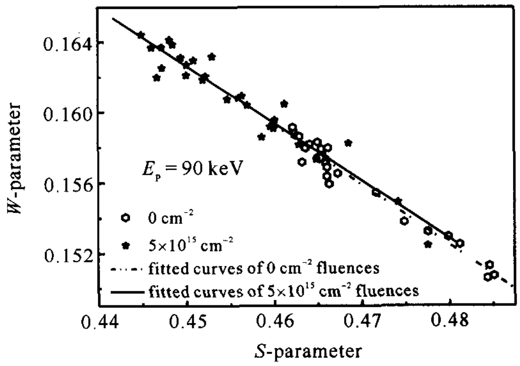

Fig. 4 *S*-*W* plots for ZnO white paint before and after proton irradiation with fluence of 5×10^{15} cm^{-2}

In addition, the decrease of *S*-parameter due to proton exposure can be related to the formation of singly ionized oxygen vacancies (V_O^*). Our previous work[6-8] also demonstrates that during proton irradiation, the area ratio of the V_O^{**} peak to the whole spectrum decreases, whereas that for the peak V_O^* increases. It is believed that the proton exposure could lead to a transformation of V_O^{**} into V_O^*. V_O^{**} is the primary point-defect in ZnO white paint before proton irradiation, and V_O^* is the primary point-defect in the irradiated samples for higher fluences. V_O^{**} (catching no electron) carries equivalent positive charges and could not trap positrons. But V_O^* (catching an electron) can trap a positron, forming a quasi-positronium of bounded state (a negative ion vacancy + an electron + a positron).

The relatively stable state formed by a positron trapping an electron is referred to as positronium (Ps), similar to a hydrogen atom. The positronium has longer lifetime, and can reduce the fraction of positron annihilation and the *S*-parameter. Thus, under the proton exposure, the *S*-parameter decreases with increasing V_O^* content. The transformation from V_O^{**} into V_O^* due to proton irradiation can also be confirmed, to some extent, by the slope change of the *S*-*W* plot as shown in Fig. 4.

3 Conclusion

ZnO white paint is a typical thermal control coating extensively used on spacecraft. In order to further reveal the damage mechanism caused by protons with energies smaller than 200 keV, which exist in a large amount in the Earth's radiation belt, an analysis of slow-positron annihilation was conducted. It is shown that the *S*-parameter decreases with increasing proton fluence, and the slope of *S*-*W* plot changes under the exposure. The decrease of *S*-parameter due to the proton irradiation can be attributed to two main reasons. One is related to the decrease of V_{Zn} content, and the other to the formation of V_O^*. V_{Zn} is an effective center of positron annihilation, and V_O^* can be viewed as quasi-positronium with longer lifetime than the positron.

Therefore, either a decrease of V_{Zn} content or an increase in V_O^* amount could relieve the positron annihilation effect, and thus reduce the *S*-parameter.

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质子辐照 ZnO 白漆光学退化的慢正电子湮没分析

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摘 要： 采用慢正电子湮没光谱研究低能质子辐照下 ZnO 白漆的光学退化。研究结果表明，随质子辐照注量的增加，多普勒展宽谱的 *S* 参数逐渐减小，*W* 参数逐渐增大。质子辐照下 *S-W* 参数拟合曲线的斜率发生改变。*S* 参数的减小可以归结为锌空位含量的减少以及准正电子素的形成。准正电子素（单电离氧空位（捕获一个电子）+正电子）的形成，能够降低正电子湮没的速率，导致 *S* 参数减小。*S* 参数的减小证实了质子辐照导致 ZnO 白漆中单电离氧空位数量的增加。*S-W* 参数拟合曲线斜率的变化可以归结于质子辐照下双电离氧空位向单电离氧空位的转变。

关键词： 慢正电子湮没； 光学退化； ZnO 白漆； 质子