Optical characteristics and mechanical properties of optical thin films on weathered substrates

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Thin films used for optical components require improvements in their mechanical properties and long-term stability. We examine the influence of substrate weathering on optical thin films. The light scattering of TiO_2 thin films increased as the substrate is weathered. The light scattering of the TiO_2 thin film formed by ion-assisted deposition (IAD) is smaller than that of the TiO_2 thin film formed by electron beam deposition (EBD).

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Thin films used for optical components require improvements in their mechanical properties and long-term stability. This has been achieved through the optimization of their mechanical properties, such as stress, hardness, and adhesion[1]. However, the weathering of the substrate also affects the properties of the thin films, and thus monitoring this weathering is important. However, other than visual examination the methods for measuring weathering all rely on sophisticated instruments and are destructive. We have focused on developing a new method for detecting substrate weathering not visible to the human eye.

Optical glass (BK-7) and super white glass (D253) were used as substrates. The composition of these substrates is shown in Table 1. Weathering was artificially simulated in an environmental testing apparatus, and was verified by using a nanoindentation tester (ENT-1100a, Elionix). A weathered and an unweathered surface were created by gluing two substrates together before subjecting them to the simulated environmental exposure. The optical properties and mechanical properties of the samples were measured again after the environmental exposure, in order to compare them with the initial properties. The weathering of the substrate was monitored by spectrometry, nanoindentation testing[2], and atomic force microscopy (AFM). The thin films were deposited on the weathered substrates. Two vapor deposition techniques were used to deposit the TiO_2 and SiO_2 films: ion-assisted deposition (IAD) and electron beam deposition (EBD). The optical characteristics and mechanical properties of the films were measured in order to determine the effect of substrate weathering on the thin films. We have previously proposed an alternative measurement method that can be used to evaluate light scattering from spectral data[2]. This method uses a spectrometer with an integrating sphere to measure all the light transmitted through the thin film and the transmitted light that was scattered. The light scattering spectrum can then be calculated from the following expression:

[(scattered light) / (all transmitted light)] × 100 (%).

Table 1. Composition of Substrate

	BK-7	D263
SiO_2 (wt.%)	71.0	64.2
Al_2O_3 (wt.%)	—	3.0
CaO (wt.%)	—	—
NaO_2(wt.%)	8.0	7.2
K_2O (wt.%)	8.0	6.4
BaO (wt.%)	3.0	3.1
ZnO (wt.%)	—	7.1
Fe_2O_3 (wt.%)	—	—
MgO (wt.%)	—	—
SO_3 (wt.%)	—	—
B_2O_3 (wt.%)	10.0	8.9
Young's Modulus (10^3 kg/mm^2)		
	9.28	7.29

The light scattering after deposition was subtracted from the light scattering before deposition to give the light scattering of the film. Moreover, X-ray diffraction (XRD), AFM, and scanning electron microscopy (SEM) were used to determine the cause of the increase in light scattering.

Weathering that could be confirmed by visual examination was present in the BK-7 sample after 24 h of simulated environmental exposure, and after 48 h in the D263. The optical scattering properties in the samples did not change after the environmental exposure, even when the weathering was visible. However, the nanoindentation method showed that the hardness of the BK-7 sample started to change after 6 h of environmental exposure (Fig. 2) and the hardness of the D263 sample started to change after 24 h (Fig. 3)

The displacement of the surface roughness was measured by AFM (Figs. 4 and 5). The surface roughness of the BK-7 sample started to change after 15 h of environmental exposure (Fig. 4), and the surface roughness of D263 started to change after 24 h (Fig. 5).

The surface states of the BK-7 and D263 samples were measured by SEM (Figs. 6 and 7). Weathering was confirmed from the SEM image after 6 h of environmental exposure for the BK-7

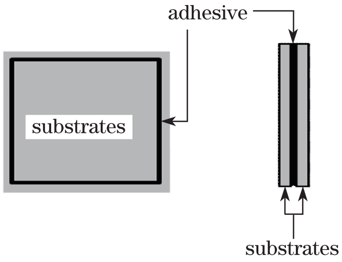

Fig. 1. Adhesive bonding of substrates.

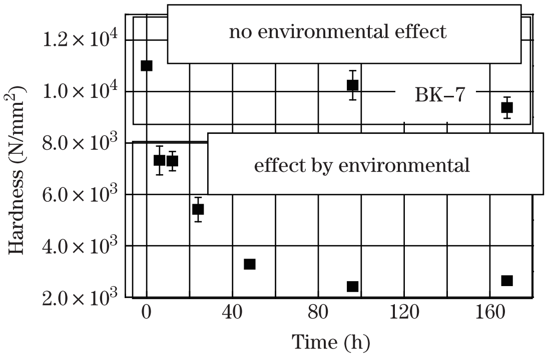

Fig. 2. Change in hardness of glass (BK-7) after environmental testing.

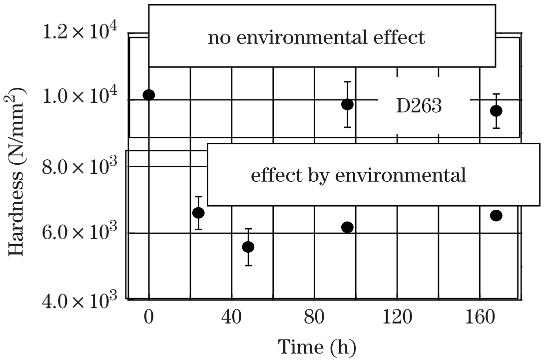

Fig. 3. Change in hardness of glass (D263) after environmental testing.

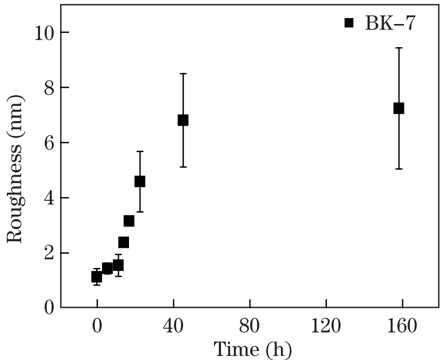

Fig. 4. Change of surface roughness of substrate by weathering (BK-7).

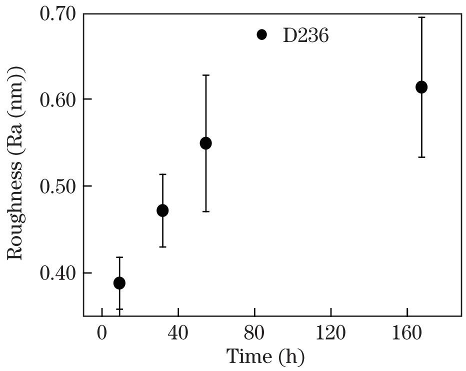

Fig. 5. Change of surface roughness of substrate by weathering (D263).

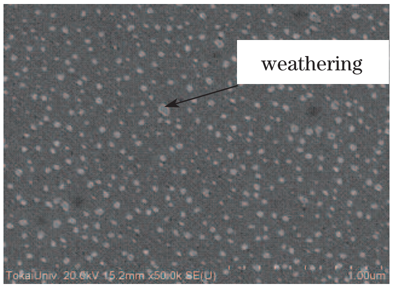

Fig. 6. SEM image of glass (BK-7) surface after 6 h environmental testing.

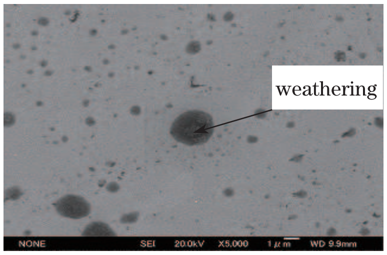

Fig. 7. SEM image of glass (D263) surface after 24 h environmental testing.

sample (Fig. 6), and after 24 h for the D263 sample (Fig. 7). Therefore, the nanoindentation method effectively detected weathering that was not visible to the human eye.

TiO_2 and SiO_2 were then deposited on the substrates after the weathering was measured. The light scattering of the TiO_2 thin film formed on BK-7 by EBD is shown in Fig. 8 and those of the TiO_2 thin film formed on BK-7 by IAD are shown in Fig. 9. The light scattering of the TiO_2 thin film increased with the weathering of the substrate. The light scattering of the SiO_2 thin film formed on BK-7 by EBD is shown in Fig. 10, and that of the SiO_2 thin film formed on BK-7 by IAD is shown in Fig. 11. The light scattering of the SiO_2 thin film increased with the weathering of the substrate and was smaller than that of the TiO_2 thin film. The light scattering of the TiO_2 and SiO_2 thin films formed by IAD changed less than that of the films formed by EBD. These observations may be affected by the SiO_2 thin film being amorphous, whereas TiO_2 is crystalline.

The effect of the thin film crystal structure on light scattering was evaluated using XRD. The XRD

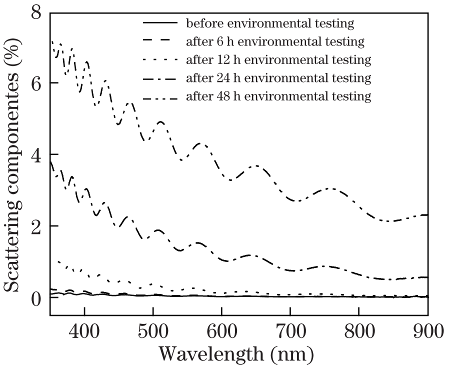

Fig. 8. Light scattering spectra (TiO_2 single layer EBD method 150 °C).

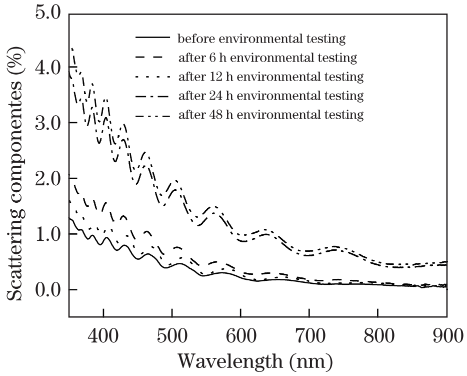

Fig. 9. Light scattering spectra (TiO_2 single layer IAD method 150 °C).

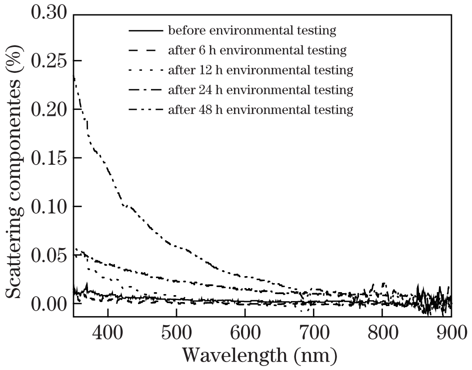

Fig. 10. Light scattering spectra (SiO_2 single layer EBD method 150 °C).

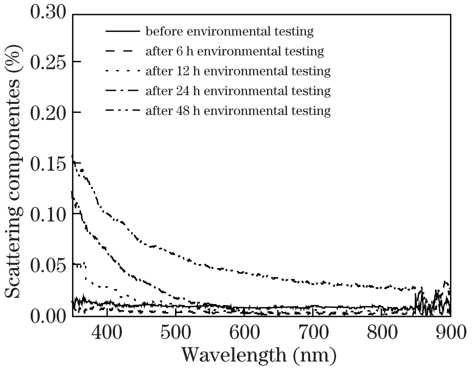

Fig. 11. Light scattering spectra (SiO_2 single layer IAD method 150 °C).

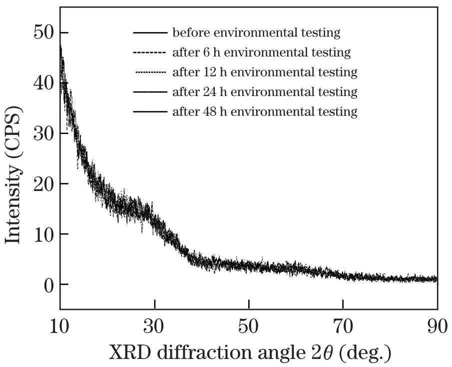

Fig. 12. XRD spectra (TiO_2 single layer EBD method).

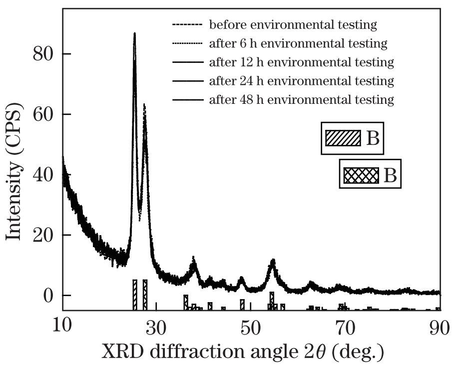

Fig. 13. XRD spectra (TiO_2 single layer IAD method).

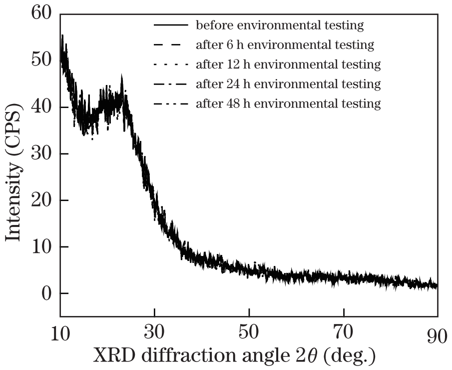

Fig. 14. XRD spectra (SiO_2 single layer EBD method).

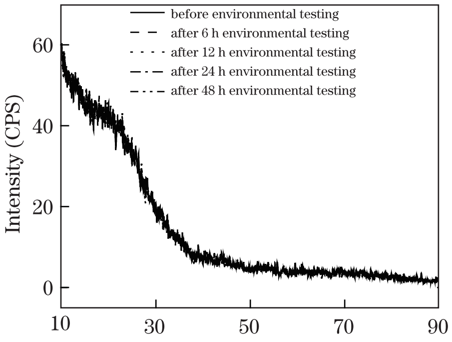

Fig. 15. XRD spectra (SiO_2 single layer IAD method).

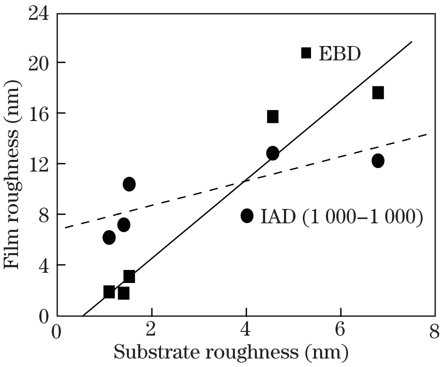

Fig. 16. Surface roughness of substrate versus surface roughness after coating (TiO_2).

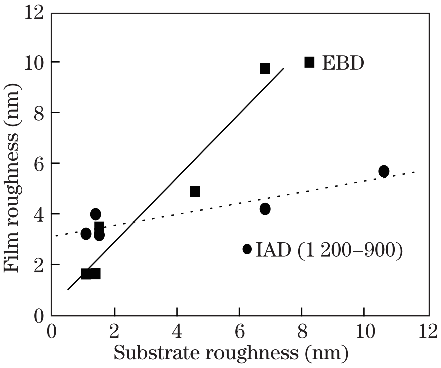

Fig. 17. Surface roughness of substrate versus surface roughness after coating (SiO_2).

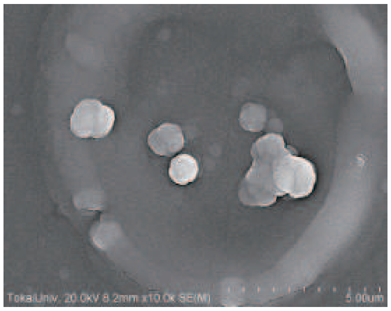

Fig. 18. SEM image of TiO_2 single layer surface after 48 hour environmental testing (EBD method).

diffraction spectra of the TiO_2 thin film formed by EBD and IAD (Figs. 12 and 13), and of the SiO_2 thin film formed by EBD and IAD (Figs. 14 and 15) show that the crystal structure of the films is not changed by substrate weathering.

The influence of the surface roughness of the substrate on the surface roughness of the thin films was measured by AFM. The surface roughness of the TiO_2 and SiO_2 thin films formed by EBD and IAD increased with the surface roughness of the substrate (Figs. 16 and 17), but was independent of the thin film material. The increase in the surface roughness of the films fabricated by IAD was lower than those fabricated by EBD.

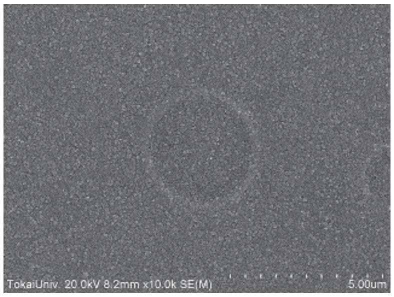

Fig. 19. SEM image of TiO_2 single layer surface after 48 hour environmental testing (IAD method).

The effect of the structure on the surface of the film was measured by SEM. The SEM images of the TiO_2 thin film formed by EB and by IAD on the substrate following 48 h of environmental exposure are shown in Figs. 18 and 19. Nodules occurred around areas of weathering in the thin film formed by EBD. In contrast, the thin film formed by IAD did not develop nodules. The formation of nodules affects the control of the surface roughness in thin films.

In conclusion, the weathering which arose after a short period of environmental exposure can not be detected by visual examination; the weathering is successfully measured by the nondestructive nanoindentation and AFM methods; no changes in the crystal structure of the films are observed during substrate weathering; the light scattering of the SiO_2 thin film is smaller than that of the TiO_2 thin film; the generation of nodules and light scattering is suppressed by IAD.

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References

1. C. T. Chuang, C. K. Chao, R. C. Chang, and K. Y. Chu, J. Mater. Process. Technol. **201,** 770 (2008).
2. M. Bai, K. Kato, N. Umehara, and Y. Miyake, Thin Solid Films **377-378,** 138 (2000).