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Nobuyuki Koike
Koji Sasaki
Takatoshi Yamada
Naoki Hanashima
Akio Takada
Motofumi Suzuki

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Nobuyuki Koike,[a,*] Koji Sasaki,[a] Takatoshi Yamada,[a] Naoki Hanashima,[a] Akio Takada,[a] and Motofumi Suzuki[b]

[a]Dexerials Corporation, 30 Kaganosakai, Takaraeniida, Nakada-cho, Tome-shi, Miyagi 987-0622, Japan

[b]Kyoto University, Department of Micro Engineering, Kyoto 615-8540, Japan

Abstract. We investigated the optical characteristics and microstructures of wave plates composed of $Ta_2O_5(100 - x) + TiO_2(x)$ and prepared by the so-called serial bideposition technique. While a single-layer film prepared by conventional oblique deposition technique has a tilted columnar structure (i.e., tilted optical axis), a serial bideposition film has a narrow, long columnar structure; this ensures that the optical axis of the film is along the quasinormal to the substrate, thus reducing haze. The influence of using additives with Ta_2O_5 was investigated as well. It was found that additive TiO_2 improves optical transmittance at shorter wavelengths. For verifying the advantage of this type of wave plates, quarter wave plates with optimized TiO_2 content were fabricated and their optical performance and reliability were evaluated against those of organic-type wave plates. The results show that the inorganic wave plate prepared by serial bideposition is advantageous for applications where high-transmittance and high-temperature durability are essential. [DOI: 10.1117/1.JNP.8.083991]

Keywords: serial bideposition; oblique deposition; wave plates; practical applications.

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1 Introduction

The demand for optical devices with high-light resistance and thermal durability is increasing because requirements such as increased luminescence and miniaturization of liquid crystal display (LCD) projectors. Polymer-based wave plates are widely used in LCD projectors. They contain organic materials that degrade easily under long, intense exposure to light from a super-high-pressure mercury lamp. Therefore, wave plates of inorganic materials with high-light resistance and high-thermal durability are required for those applications.

It is well known that obliquely deposited thin films can be applied to wave plates.[1–4] The oblique deposition can lead to the formation of birefringent layers on any substrate at low cost without size limitation. Because these wave plates are composed of inorganic materials, superior thermal durability is expected.

High transmittance and exact control of retardation value are extremely important for using wave plates with obliquely deposited films in practical optical instruments. Several researchers have reported solutions[2,4] for improving the transmittance, which depends on the smaller birefringent, Δn, and, occasionally, on film haze.[1]

Several studies have reported that the retardation films prepared by the serial bideposition technique[4–6] have nanostructural growth perpendicular to the substrate, and can therefore be used for increasing Δn. Film thickness could decrease at high values of Δn. Moreover, Motohiro et al.[2] suggested that the columnar growth normal to the substrate can reduce polarization-dependent reflection, which occurs owing to the interface of bilayered retardation films[1] and is obstructive in some applications.[7] Meanwhile, Motohiro and Taga[1] explained that the nature of haze can

*Address all correspondence to: Nobuyuki Koike, E-mail: Nobuyuki.Koike@dexerials.com

be attributed to agglutination of the columns; therefore, if columnar structures are considerably smaller than the wavelength of light, the resulting haze value is very low.

Serial bideposition films consist of numerous individual thin layers. Hence, it is possible that haze can be reduced by inhibiting column agglutination. However, there have been few reports on the relationship between the birefringent and the transmittance of serial bideposition films.

In addition, we noticed the effect of the composition of serial bideposition films on their optical properties. The birefringence values of several materials' oblique deposition films were reported,[1,4] and large Δn were obtained for Ta_2O_5, TiO_2, ZrO, and CeO_2 when deposited at lower temperatures. Furthermore, Motohiro and Taga mentioned that obliquely deposited Ta_2O_5 films show high transmittance in the visible spectrum range.[1] In contrast, there have been few attempts to investigate the effect of element addition on the optical properties of obliquely deposited film.

Several studies reported that the addition of TiO_2 to Ta_2O_5 thin films prepared by chemical vapor deposition[8] or radio frequency magnetron sputtering deposition[9] can improve the films' insulating properties. It is considered that this improvement occurs owing to the compensation of oxygen vacancies[8] contained in Ta_2O_5 films evaporated at lower temperatures.[10–13] We consider that this result implies the addition of TiO_2 to Ta_2O_5 films could improve the films' transmittance by compensating for oxygen vacancies with serial bideposition films.

In this paper, we present the microstructures and optical properties of serial bideposition films. Then, we clarify the effect of Ta_2O_5 with TiO_2 additive. Finally, to verify the advantages of the above configuration, we demonstrate an inorganic quarter wave plate with high transmittance, thermal durability, and light resistance. The novelty of this paper is in production of very practical inorganic wave plates prepared by the serial bideposition technique.

2 Experiments

Serial bideposition films of $Ta_2O_5(100-x) + TiO_2(x)$ ($0 \leqq x \leqq 100$ wt%) were formed on a glass substrate with an EB source placed at a source-to-substrate distance of 1000 mm under a pressure of 5×10^{-4} Pa. During evaporation, deposition angle, α, measured from the surface normal, was fixed to 70 deg, while the azimuth was rapidly switched by 180 deg with each deposition of a 5–1600-nm-thick layer, t_1. Serial bideposition films with a total thickness, t_{Ta2O5}, of 800–1600 nm were prepared by repeating 0–200 cycles of each deposition, and subsequently annealing at 200° C in air. Passivation layers of SiO_2 and antireflection coatings of SiO_2/Nb_2O_5 are formed on the serial bideposition films using a magnetron sputtering system.

Microstructures and compositions of serial bideposition films were investigated by scanning electron microscopy (SEM) and energy dispersive x-ray spectrometry, respectively. The transmittance and reflectance were measured using a double-beam spectrophotometer in the wavelength range of 400–700 nm with polarized light. For reflectance measurements, the angle of incidence of light was 5 deg, and the spectra of specularly reflected light were acquired. In contrast, transmittance spectra were measured for normal incidence. Diffuse scattering in the off-specular or off-normal directions was negligible. The birefringence was evaluated using a phase-retardation measurement system with a rotating analyzer.

Humidity resistance was evaluated by measuring the transmittance of the serial bideposition films, which were maintained at 60°C and 90% R.H for different storage times and then maintained at 23°C for 24 h. Light resistance properties were evaluated by measuring the transmittance of serial bideposition films irradiated with a light intensity of $0.6\ W/mm^2$ from a high-pressure mercury lamp for different storage times and then maintained at 23°C for 24 h.

3 Results and Discussions

3.1 *Microstructures*

Figure 1 shows the morphology of the serial bideposition $Ta_2O_5(100-x) + TiO_2(x)$ ($x = 5$ wt%) film for $t_1 = 7$ nm and $t_{Ta2O5} = 1500$ nm. Figures 1(a) and 1(b) show the SEM images of the cross-sectional views parallel to the deposition plane of the Ta_2O_5 flux

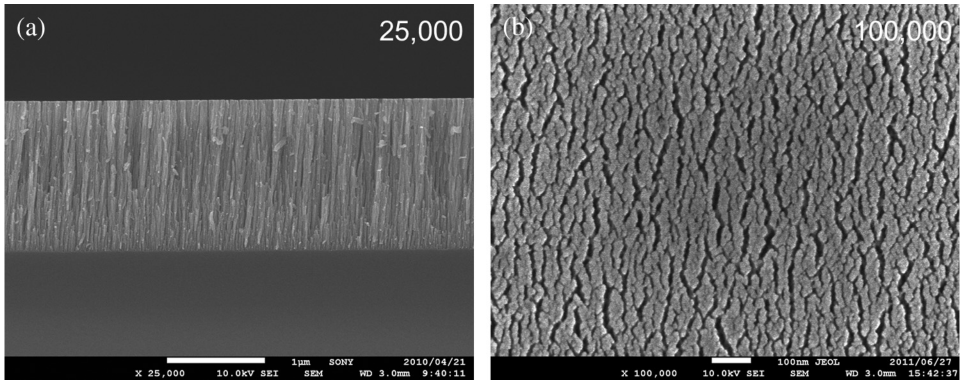

Fig. 1 SEM Image of (a) cross section (b) top view of the sample of $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 5$ wt%) serial bideposition film.

and the top view, respectively. It is observed that the serial bideposition film is composed of narrow, long, columnar structures, and that many bundles and gaps derived from the columnar structures were along the normal to the Ta_2O_5 flux deposition plane.

This surface morphology can be observed even on a Ta_2O_5 film prepared by conventional oblique deposition. In the case of serial bideposition, the shadowing area lies alternately in front of and behind the columns, and, accordingly, the intercolumn gaps are widened, and bundles are formed more visibly.[6] Therefore, the degree of anisotropy of the surface morphology is considerably higher than that of a conventional obliquely deposited film.

3.2 *Optical Properties*

The birefringence and transmittance loss of the $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 5$ wt%) serial bideposition film at the wavelength of 550 nm as a function of thickness t_1 with $t_{Ta2O5} = 1500$ nm are shown in Fig. 2, in which the plot of $t_1 = 1500$ nm is equivalent to the film prepared by conventional oblique deposition. Transmittance loss was calculated by subtracting the sum of transmittance and reflectance from 100%.

As for the birefringence, Δn increases with decreasing t_1 when t_1 is less than 70 nm, whereas it remains same as that of the conventional oblique deposition film when t_1 is more than 70 nm. With serial bideposition, Hodgkinson and Wu[4] explained that structural growth occurs in plate-like columns perpendicular to both the deposition plane and the substrate when individual layers are thin. In the case of such a structure, Hodgkinson et al. estimated a 100% increase in Δn for a packing density $p = 0.60$ using equation for form birefringence.[14] This value coincides with an increase in the Δn of serial bideposition $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 5$ wt%) films, as shown in Fig. 1. In our case, it is considered that the plate-like columns grow when t_1 is less than 10 nm.

The transmittance loss is the least at around $t_1 = 6$ nm, and it seems to be unchanged for $t_1 > 10$ nm. For $t_1 < 10$ nm, agglutination of the columnar structures of a stack of individual

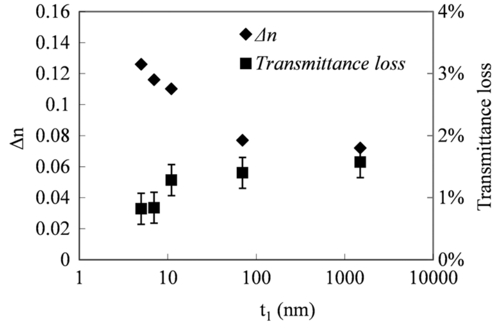

Fig. 2 Δn and transmittance loss as a function of thickness t_1.

thin layers whose directions alternate could be prevented, thus reducing haze. Moreover, it is considered that the narrow, long columns standing normal to the substrate instead of being inclined, as with conventional oblique deposition, reduced the amount of light reflected off the interface. As the result, the transmittance loss is decreased because $t_1 < 10$ nm. The transmittance loss for both orthogonal polarizations is decreased. This result shows that the serial bideposition films can not only achieve larger Δn but also decrease the transmittance loss compared with conventional obliquely deposited films.

3.3 *Influence of TiO_2 Addition*

The optical transmittance of $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 0 - 100$ wt%) serial bideposition films as a function of TiO_2 composition is shown in Fig. 3, in which the rhombuses, squares, and triangles indicate the transmittance averaged over the wavelength ranges of 680–600, 590–520, and 510–430 nm, respectively. Thickness values of $t_1 = 7$ nm and $t_{Ta2O5} = 6000$ nm were selected so that the influence of additive on transmittance could be recognized easily. As seen in the figure, the transmittance is maximized at $x = 5$–15 and decreases at both $x < 5$ and $x > 30$; particularly, the transmittance is improved in the wavelength range of 51–430 nm at $x = 5$–15, respectively.

Saitoh et al. revealed that a low concentration of TiO_2 doping in a Ta_2O_5 film by chemical vapor deposition could reduce the leakage current of the film.[8] In that case, they explained that oxygen vacancies are possibly compensated for by Ti^{4+} ions, which are substitutionally incorporated into Ta^{5+} sites in the film.[8] This suggests that the transmittance improvement of serial bideposition films at lower TiO_2 doses is due to a decrease in the number of oxygen vacancies in the Ta-Ox.

Although the exact mechanism responsible for this improvement is yet to be found and we need further experiments to reveal the same, it is considered that adding a small amount of TiO_2 to Ta_2O_5 can reduce the resulting film's transmittance loss. The serial bideposition film with a lower dose of TiO_2 in Ta_2O_5 is potentially applicable to wave plates in applications requiring high transmittance.

3.4 *Properties of Wave Plate Application*

Figures 4(a) and 4(b) show the retardation and transmittance/reflectance spectra of $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 5$ wt%) serial bideposition films with antireflection coatings for $t_1 = 7$ nm and $t_{Ta2O5} = 800$ nm. The retardation of 115 nm at $\lambda = 460$ nm, which corresponds to a quarter wave plate for the wavelength, is achieved. In the wavelength range of 430–510 nm, the transmittance and reflectance averaged over $\lambda = 430$–510 nm were more than 99% and less than 0.5%, respectively.

Figure 5 shows the angle dependence of the retardation of a serial bideposition film at $\lambda = 460$ nm. Rotation around the fast axis increases the retardation, whereas rotation around the slow axis decreases the retardation. In addition, angle dependence is symmetrical about 0 deg.

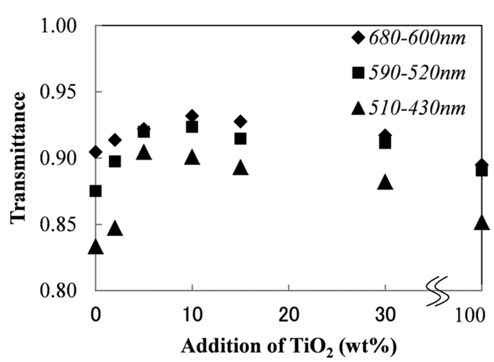

Fig. 3 TiO_2 composition dependence of transmittance of $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 0 - 100$ wt%) serial bideposition films.

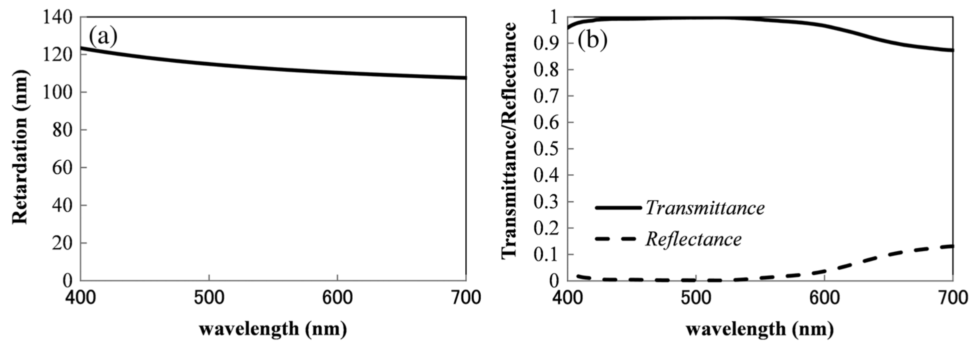

Fig. 4 (a) Retardation and (b) Transmittance/reflectance spectra of $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 5$ wt%) serial bideposition film with antireflection coating for $t_1 = 7$ nm and $t_{Ta2O5} = 800$ nm.

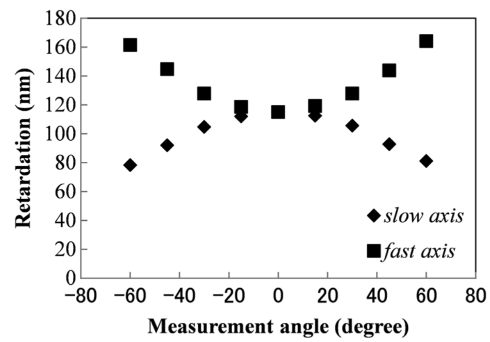

Fig. 5 Measurement angle dependence of retardation of serial bideposition $Ta_2O_5(100 - x)+$ $TiO_2(x)$ ($x = 5$ wt%) film.

In the case of conventional obliquely deposited films, angle dependence is asymmetric around 0 deg.[1,3] In the case of a serial bideposition film, angle dependence is symmetric because narrow, long columnar structures perpendicular to the substrate are formed, as shown in Fig. 1(b).

This angle dependence of serial bideposition films corresponds to the homogeneous biaxial indicatrix. Although serial bideposition films are composed of numerous individual thin layers, they can be considered as a homogeneous single layer with an optical axis parallel to the substrate because each layer of the stack has a thickness that is a fraction of the operating wavelength.

This result offers the following advantage. Optical devices are preferred to have left-right symmetric optical properties when they are used for optical instrument using luminance fluxes that have a definite incidence angle such as LCD projectors. Asymmetric optical properties lead to uneven luminance, and hence, the quality of the projected image deteriorates. Therefore, serial bideposition films with symmetric properties are applicable to wave plates mounted inside actual optical instruments.

3.5 *Wave Plate Reliability*

Figure 6 shows the change in the averaged transmittances of serial bideposition films with or without the passivation layer at a temperature of 60 °C and relative humidity of 90% (i.e., humidity resistance test). The transmittance decreases monotonically with time without the passivation layer and is lowered by 20% after 500 h, whereas it remains unchanged with the passivation layer.

Figure 7 shows changes in the transmittance with time under irradiation from a light intensity of 0.6 W/mm^2 (i.e., light resistance test). For comparison, a conventional organic wave plate was tested as well.

Our inorganic wave plate with a serial bideposition film showed significant/superior robustness to irradiation, and there was no degradation in its optical characteristics or appearance.

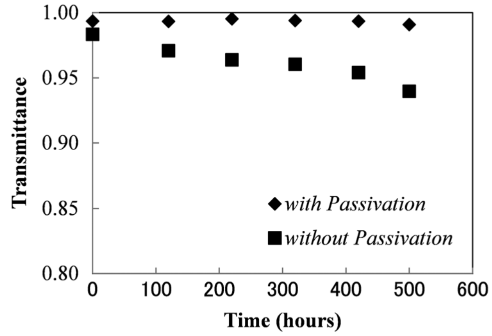

Fig. 6 Transmittance of serial bideposition films as a function of time under humidity condition.

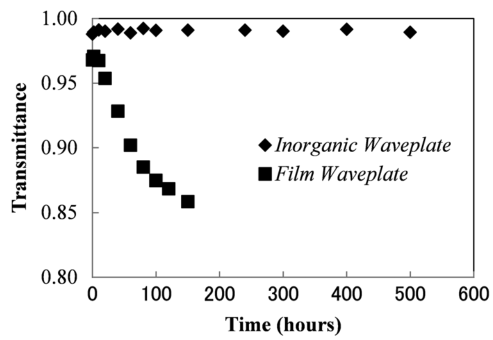

Fig. 7 Transmittance of wave plates as a function of time in light resistance test.

Conversely, the transmittance of the organic wave plate deteriorated rapidly, and it finally burned out after 200 h of irradiation. As a result, it is shown that our fully inorganic wave plates with a serial bideposition film is advantageous for applications in which it is used under either/both high-humidity or high-power light irradiation.

4 Conclusion

We investigated the optical characteristics and microstructures of serial bideposition $Ta_2O_5(100 - x) + TiO_2(1 - x)$ ($0 \leqq x \leqq 100$ wt%) films. The dense, narrow, and long columns that grow quasiperpendicular to the substrate give rise to higher birefringence and lower transmittance loss compared with conventional obliquely deposited films.

Additionally, we investigated the effect of TiO_2 addition to Ta_2O_5. It was found that a small amount of additive can improve the film's optical transmittance, especially at shorter wavelengths.

We demonstrated a fully inorganic quarter wave plate with the serial bideposition film of $Ta_2O_5(100 - x) + TiO_2(x)$ ($x = 5$ wt%), which achieved both high transmittance and low reflectance at $\lambda = 430$–510 nm, as well as symmetric angle dependence of retardation. Finally, we showed the superior durability of our wave plate under both high-humidity and high-power light irradiations. It is expected that the developed wave plates can be applied to applications requiring high transmittance and long-term operation stability under high temperatures.

Acknowledgments

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Nobuyuki Koike has been working on the development of inorganic devices with submicron structures in Dexerials Corporation, Japan.

Koji Sasaki has been working on the development of inorganic devices with submicron structures in Dexerials Corporation, Japan.

Takatoshi Yamada has been working on the development of inorganic devices with submicron structures in Dexerials Corporation, Japan.

Naoki Hanashima has been working on the development of inorganic devices with submicron structures in Dexerials Corporation, Japan.

Akio Takada has been working on the development of inorganic devices with submicron structures in Dexerials Corporation, Japan. He is a member of Japan Society of Applied Physics.

Motofumi Suzuki is an associate professor at Kyoto University, Japan. His current research interests include the optical properties of nanostructured thin films and the synthesis of novel nanostructures. He is a member of SPIE.