

New dielectric material, zirconium oxide-based film, for an interface layer of a phase-change optical disk

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Abstract

In the layer stack of a phase-change optical disk, dielectric materials play important roles to realize long cycle number and environmental stability. Dielectric films such as ZnS-SiO₂ and Ge-N have been utilized for optical disk systems having a red laser. In this paper, we will report a new dielectric film, a zirconium-based oxide, suitable for systems with a blue-violet laser. The ZrO₂-based film simultaneously shows a high transparency at $\lambda=405\text{nm}$ and a fine adhesiveness with phase-change films. Accordingly, it has greatly contributed to realize the world-first product of the dual-layer type rewritable phase-change optical disk with 50GB capacity.

1. Introduction

In the layer stack of a phase-change optical disk, dielectric materials play important roles. They protect the plastic substrate from the thermal damages, protect the phase-change film from the external moisture, prevent the inter-layer atomic diffusion and improve cycle-ability, and produce optical interference to optimize the optical properties. Thus, the dielectric films such as ZnS-SiO₂¹⁾ and Ge-N²⁾ have been reported to bring superior results for the optical disks utilizing a red laser. However, few studies have been carried out on dielectric materials for a blue-violet laser. Naturally, the film thickness that corresponds to a certain optical length, λ/n (n : refractive index), becomes smaller with a decrement of the optical wavelength, λ . In addition, optical absorption of a dielectric material increases as usual. It means that the mechanical strength and thermal resistivity of optical disks will be extremely worse for blue-violet laser.

Accordingly, we developed new dielectric films suitable for blue-violet laser systems. The newly developed dielectric film, zirconium-based oxide, shows a fine effect as an interface film for an optical disk using blue-violet laser. Especially, it greatly contributed to develop dual-layer type rewritable optical disk, since the laser-incident side layer (Layer 1) of the disk inherently requires dielectric films with a high optical transparency and a high thermal stability.

In this paper, optical properties of the new dielectric film are shown as compared with some other materials. Furthermore, the successful results of the film application to the 50GB-capacity dual-layer Blu-ray Disc (BD) will be described.

2. Experiments

Our guiding principles for searching new dielectric films were determined as follows; i.e., 1) the material films will be highly transparent at a blue-violet wavelength, 2) their melting point will be sufficiently higher than that of recording film, 3) they will possess a superior adhesiveness to a recording film, and 4) no significant atomic diffusions will be produced between neighboring films by the repetitious laser heating.

Experiments were carried out as following procedures. First, some candidates of dielectric materials (single oxides, nitrides, carbides and fluorides) were selected out based on the above-mentioned guiding principles (2). Then, these materials were filmed on each quartz glass 20 nm in the thickness by radio frequency sputtering, and their complex optical constants ($n-ik$, n is refractive index and k is extinction coefficient) were measured with an ellipsometer at the wavelengths of 405 nm and 660 nm. Thirdly, using the optical constants, experimental disks were prepared for the each candidate dielectric film and the adhesiveness between GeSbTe and the interface film were examined. For this examination, each experimental disk has only Layer 1 (L1) on 1.1 mm thick polycarbonate substrate. That is, film stack of cover layer (75 μ m)/ZnS-SiO₂/interface-film/GeSbTe (6nm)/interface-film/Ag-alloy (10nm)/TiO₂($\lambda/8n$), is formed directly on plastic disk substrate not on Layer 0 (L0) stack as shown in Fig. 1.

Substrate (1.1t)
TiO ₂ ($\lambda/8n$)
Ag-alloy (10nm)
Interface film
Ge-Sb-Te (6nm)
Interface film
ZnS-SiO ₂
Cover layer (0.075t)

Fig. 1. Cross-section of the experimental Layer 1 disk.

Each material candidate was examined as the interface films on the both sides of GeSbTe film. The films were successively deposited on a polycarbonate substrate by sputtering method and a cover layer was adhered on the top. The disk specimens were left to stand for 200 hours in an environmental test chamber with a setting condition of 90 degrees Celsius and 80 % of relative humidity. After taking out the samples from the environmental test chamber, they were observed using microscope.

For the possible materials, thermal resistance was examined using thermal desorption mass spectroscopy (TDMS). Here, we prepared Si substrate samples with a thick film of about 1 μ m by sputtering method. In this method, each sample was continuously heated in a high vacuum chamber and ion intensity desorbed from the sample was detected. By investigating the kind of ion and its intensity, some changes such as crystallizations or decompositions can be seen. Thus, we can estimate the thermal resistance of these material films.

At last, performances such as CNR (carrier to noise ratio), limit-equalized jitter value (LEQ-jitter) and direct-overwrite-cyclability were evaluated. In this case, we prepared complete dual-layer disk specimen with both of L0 and L1, and evaluated the recording performance of each L1 based on the 25GB capacity condition of rewritable Blu-ray Disc format ver.1.0. The disk structure was shown in Fig. 2. Thickness of each film was optimized so as to maximize the transmittance and optical contrast defined by $(R_{\text{cry}}-R_{\text{amo}})/(R_{\text{cry}}+R_{\text{amo}})$, where the R_{cry} and R_{amo} denote reflectivities at the crystalline and the amorphous areas from the Layer 1, respectively³⁾.

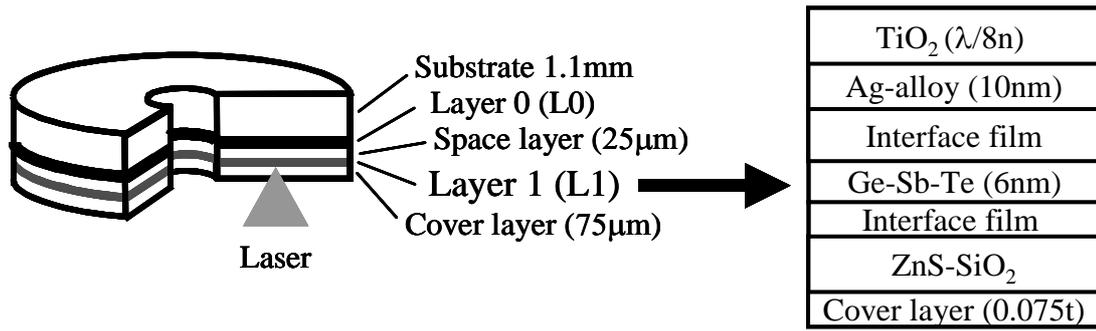


Fig. 2. Dual-layer structure and cross-section of the experimental Layer 1 disk.

3. Results and discussion

Table 1 shows melting points cited from reference books ⁴⁾, the experimentally obtained optical constants of the thin film samples at 405 nm and 660 nm, and the test results of the adhesiveness. As can be seen in the table, for example, SiC has fine adhesiveness but k value is too large for blue-violet laser. For LaF₃, n value is too small. In the case of Ta₂O₅ and Nb₂O₅, they have proper optical constants, but they are poor in adhesiveness. GeN-based film is almost transparent at 660 nm; however, the extinction coefficient is somewhat large, 0.22, at 405 nm. ZrO₂-based film is almost transparent at 405nm. ZrO₂-based film and GeN-based film show good adhesiveness. Consequently, only a ZrO₂-based film achieves all items and is the most possible candidate for interface films. Most of another oxides, nitrides, carbides and fluorides delaminated from GeSbTe or their optical constants were not proper.

Table 1. Experimentally obtained optical constants of the thin film samples at 405 nm and 660 nm and the evaluation results of adhesiveness of the disk samples.

		ZrO ₂ -based	GeN-based	SiC	LaF ₃	Ta ₂ O ₅	Nb ₂ O ₅
Tm (C) (Bulk)		2700	Decomposition	2700	1500	1900	1500
n-ki	λ= 405 nm	2.33- 0.06i	2.38- 0.22i	3.03-0.33i	1.69-0.05i	2.20-0.02i	2.47-0.01i
	λ= 660 nm	2.18-0.04i	2.21- 0.07i	2.86-0.07i	1.68-0.03i	2.06-0.02i	2.23-0.01i
adhesiveness		Yes	Yes	Yes	No	No	No

Figure3 shows the results of TDMS. The black line shows desorption of nitrogen gas from GeN-based film and the gray line shows that of oxygen gas from ZrO₂-based film. In the case of GeN-based film, a large desorption of nitrogen gas can be seen, and we can suppose that some decomposition will be produced at around 700 C. On the other hand, in the case of ZrO₂-based film, there is no apparent peak till 1000 C. It reveals ZrO₂-based film has very high thermal stability.

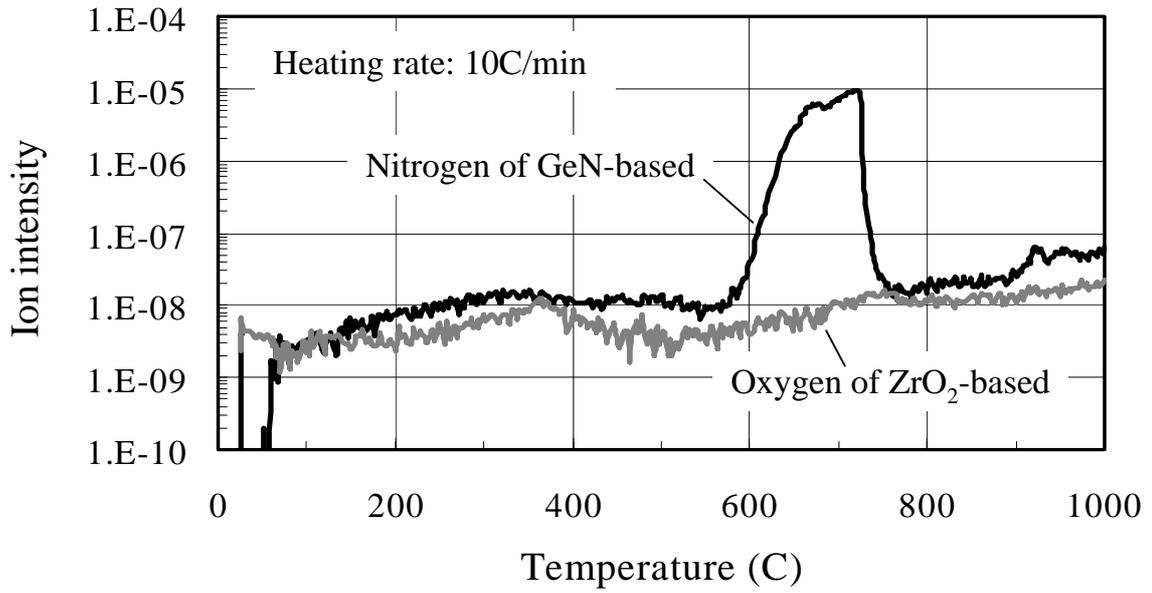


Fig. 3. Result of TDMS (Thermal Desorption Mass Spectroscopy) of ZrO₂-based film and GeN-based film.

Table 2 shows the experimentally obtained optical properties of the disk samples. For the disk with ZrO₂-based film, a high transmittance of exceeded 50 % and a large optical contrast of exceeded 0.8 are achieved. On the other hand, for the disk with GeN-based film, transmittance remains below 50 % and optical contrast is also less than 0.8. This is originated from the difference of optical constant between these two materials that are shown in Table 1.

Table 2. Optical parameters of the sample disks (experimental).

Material of interface film	Experimental				
	Transmittance(%)		Reflectivity(%)		
	Cry.	Amo.	Cry.	Amo.	Contrast
ZrO ₂ -based	50.9	52.3	5.6	0.4	0.87
GeN-based	47.6	49.2	5.6	1.0	0.70

Figure 4(a) and 4(b) show the CNR and the LEQ-jitter of Layer 1, respectively. In both figures, the open circles show the case for ZrO₂-based film and the solid circles show the case for GeN-based film. The Layer 1 with ZrO₂-based film achieves 47 dB of CNR and 6.7 % of LEQ-jitter. On the contrary, the values for Layer 1 with GeN-based film remain 45 dB and 7.3 %, respectively. We think these differences come from the difference of optical contrast between these two materials just explained above. We think that this result indicates that the jitter value of the optical disk will be improved by adopting more transparent dielectric material for the interface films.

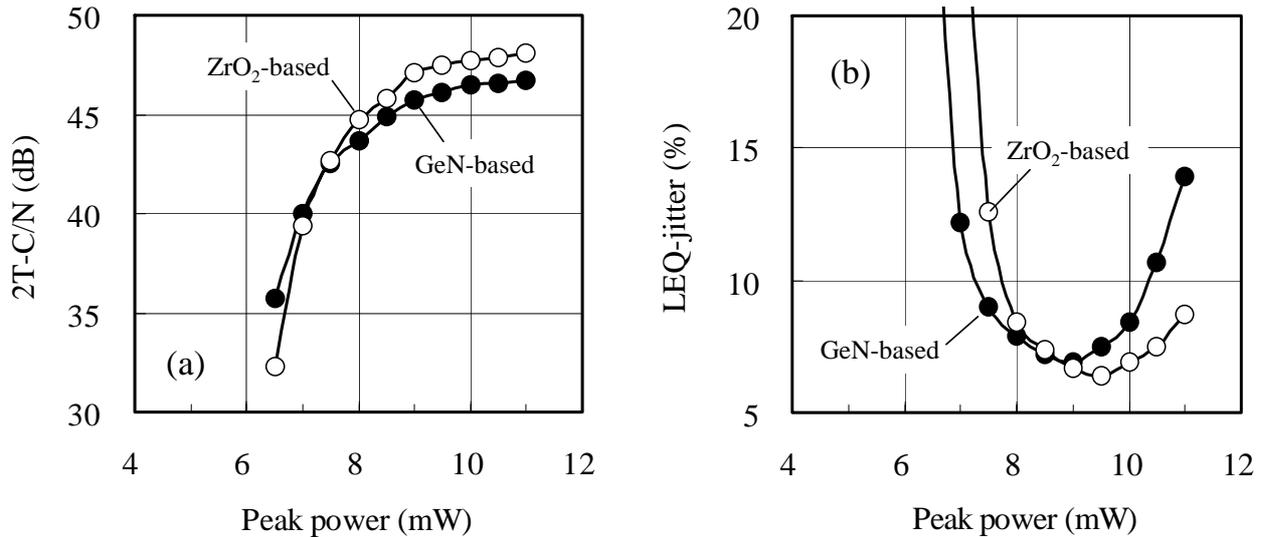


Fig. 4. Comparison of (a) CNR and (b) LEQ-jitter between a Layer 1 with ZrO₂-based films and that with GeN-based films.

Figure 5 shows cycle characteristics of the disk samples. As shown in the figure, The disk with GeN-based film shows only 2000 of direct overwrite cycle number; on the other hand, the disk with ZrO₂-based film shows more than 10000 of that. It is supposed that high transparency and high thermal stability of the ZrO₂-based film will work to maintain good cycle-ability. On the other hand, the small cycle number of the disk with a GeN-based film will be caused by a heat damage of the GeN-based film itself. This is because it has somewhat large optical absorbance in the blue-violet wavelength region for Blu-ray Disc whilst it is very transparent at red wavelength region for DVDs.

4. Conclusion

It is confirmed that for using a laser with high-energy wavelength such as blue-violet region, interface films should be transparent and heatproof. We obtained a dielectric material, ZrO₂-based film, is very suitable for blue-violet laser providing the superior properties. The film shows both of high transparency at 405 nm and fine adhesiveness with a recording film. Thus recording media with semitransparent at blue-violet laser and good recording characteristics can be developed and rewritable dual-layered media can be realized.

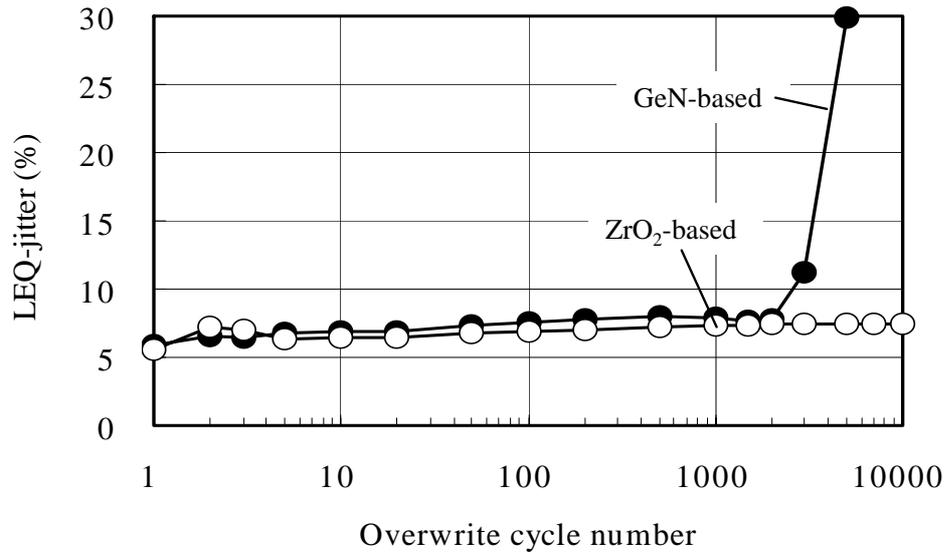


Fig. 5. Comparison of the cyclability between a Layer 1 with ZrO₂-based films and that with GeN-based films.

References

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