# Ultra-Multilayered Optical Recording Using Electrochromic Material

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**Abstract**

To achieve ultra-multilayered optical recording using electrochromic(EC) materials as recording layers, deposition conditions of Tungsten oxide ($WO_3$) film and a transient response of coloring were examined. A Tungsten oxide film sputter-deposited with a sintered target could contain more than 99% of $WO_3$ phase by adding 5 sccm of $O_2$ to 70 sccm of Ar. Transmittivity of an EC cell at 550nm fell from 80% to 30% under an applied voltage of +1.3 V for 90s. This very slow speed of coloring, that is, selection of each recording layer will be discussed based on cross sectional TEM analysis of an EC cell.

The possibility of a rewritable recording in an EC film is considered. The novel and potential approach to rewritability which originates in phase change is proposed.

**Keywords:** multilayered, optical recording, rewritable, electrochromic, $WO_3$

## 1. Introduction

An optical recording capacity of more than 25 GB per recording layer was achieved by introducing technologies such as an objective lens with an NA of 0.85, a laser with a wavelength of 405 nm and a track pitch narrower than 0.4 µm. In addition these technologies, the MPEG-2 encoding system must be used and the bit rate must be reduced to 50 Mbps to record broadcast-use HDTV (High Definition Television) video signal for 45 min. But, a bit rate of 1.2 Gbps is necessary to record the non-compressed, that is, full-bit HDTV video signal. Even if an ultra-high bit rate has been attained in a recording material, a huge recording capacity is needed for practical broadcast-use such as covering news or producing program contents.

A multilayer recording system is a powerful and attractive candidate for increasing recording capacity. A rewritable dual-layer phase change disk with a capacity of 50 GB has been reported by Yamada[1) ], and, a recording capacity reached 100 GB in the case of a write-once disk with quadruple recording layers.[2)] In these media, recording layers must be separated from each other by a distance of about 25 µm to access optically only one recording layer. This separation limits the number of recording layers in a multi-layer disk. Since the sum of thickness of recording layers, dielectric layers and other layers can be neglected compared to the separation between adjacent recording layers, the sum of the thickness of the surface cover layer and spacers must be smaller than the variable range of the focusing point. For example, this range is from 70 to 110 µm in the disk tester introduced in our laboratory. So, the maximum number of recording layers is two when the thickness of spacer and cover layer is tuned to 25 µm and 70µm, respectively. That is, 70+25x2＞110, in this case.

An experiment of reproducing an HDTV video with a total data transfer rate of 140 Mbps, which corresponds to HDCAM, using a two-head system was exhibited at the Open House of NHK Science & Technical Research Laboratories last year. Furthermore, an integrated optical disk camera for HDTV broadcast-use was released for the first time in the world at Open House 2004. This system can record HDTV video with a bit rate of 50 Mbps for 45 minutes on a disk with a diameter of 120 mm and a capacity of 23 GB using the MPEG-2 4:2:2P@HL encoding. Although it would be extremely difficult, a non-compressive HDTV signal should be recorded as a video material at studio to transmit contents to the home as high definition as possible. When a non-compressed HDTV signal is recorded for one hour on a disk, the recording capacity is estimated 500 GB. That is, 25 recording layers each with a capacity of 20 GB would be required for this item in the specifications. If the thickness of a spacer is about 25 µm, this number of recording layers is absolutely impossible in one disk.

A novel multi-layer optical recording disk was recently proposed by Terao et al.[3),4)] Their unique and hopeful idea introduced an electrically selective method into an optical recording technology to access only one recording layer by adopting an electrochromic material as the recording layer.

Tungsten oxide ($WO_3$) is known to exhibit electrochromic properties and has been applied to display devices and glare-free inner mirrors of cars. This paper reports on an optical recording disk comprised of several dozen recording layers with $WO_3$ as the recording material. The possibility of reversible phase transition at the electrochromic layer and related rewritability of recording is discussed. An electrochromic cell with an absorption wavelength of 450 nm was prepared. When DC voltage of +1.3V was applied to the cell, transmittivity varied from 80% to 30%.

## 2. Electrochromism and applications in $WO_3$

The coloring reaction in $WO_3$ is explained by the following chemical formula and Fig.1.

$$WO_3 + xM^+ + xe^- \rightleftharpoons M_xWO_3 \qquad 1)$$

$WO_3$ is a cathodic electrochromic material which colors blue, so called "tungsten blonds" with reduction. A $WO_3$ crystal exhibits a perovskite structure and there exists a vacancy inside as shown in Fig.1. A cation sent from the adjacent solid electrolyte which is the origin of coloring occupies this vacancy. Then, if this vacancy does not exist, electrochromism might not appear in $WO_3$..

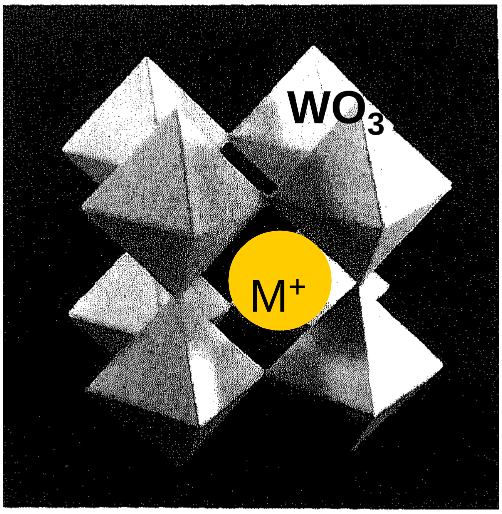

**Fig.1 Perovskite and cation**

A cathodic electrochromic material and anodic one are combined in practical electrochromic devices[5] as shown in Fig.2. $Ta_2O_5$ is used as a solid electrolyte in this example. The plus ion $H^+$ and the minus ion $OH^-$ co-exist in the $Ta_2O_5$ layer. Even if only a $WO_3$, that is a cathodic electrochromic material, layer was stacked on a $Ta_2O_5$ layer and the bias voltage was applied through ITO, $H^+$ cannot easily enter the $WO_3$ layer because the minus ion OH- also exists in the same layer. If a high bias voltage is applied, a transparent electrode can play a part of counter electrode reaction layer. However, it may be difficult to apply a high bias voltage to an optical disk rotating at high speed. It is therefore necessary to select a simple layer structure and an accompanying transparency or a low bias voltage.

Authors' group performed experiments which included deposition of $WO_3$ and confirming the coloring of prepared electrochromic cells. This paper introduces the results, and discusses the new approach to building rewritability into an electrically selective multi-layered optical recording disk.

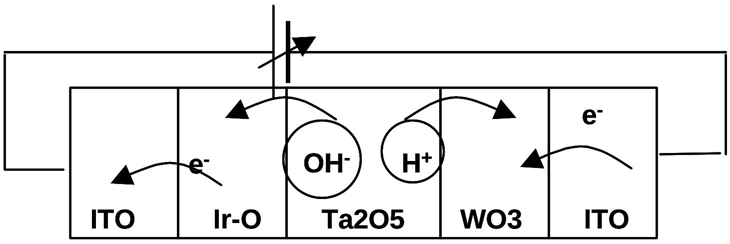

**Fig.2 Example of electrochromic cell**

## 3. Experiments

Firstly, electrochromism was visually confirmed using a commercial inner mirror for cars. A $WO_3$ film is adopted as an electrochromic layer in this mirror. Next, the time and frequency dependency of transmittivity of transparent electrochromic cells, in which $WO_3$ is used, were measured under DC bias voltage of 0, +1.5 and –1.5 V. The bias voltage dependency of reflectivity reduction of a reflective electrochromic cell was measured in a coloring state. This type was prepared for static recording experiments which progress to a disk sample. The detailed layer and intra-layer structure of above samples will be described in the next section based on the results of TEM observations.

Some amount of oxygen should be introduced in sputtering gas to compensate for the reduced reaction in a sputtering process and to ensure stoichiometry in an oxide film. A tungsten oxide film was sputter-deposited on a quartz substrate from a $WO_3$ sintered target using an RF magnetron sputtering apparatus with a mixture of Ar and oxygen. The chemical state of a film was characterized with XPS. Sputtering conditions are listed in Tab.1.

| Ar(sccm)/O2(sccm) | Pressure(Pa) | Power(W) | Time(min) |
|---|---|---|---|
| 70/0 | 0.7 | 200 | 60 |
| 70/5 | 0.7 | 200 | 60 |
| 70/7 | 0.7 | 200 | 60 |
| 70/10 | 0.7 | 200 | 60 |

**Tab.1 Sputtering conditions**

**4. Results and Discussion**

Electrochromic materials such as $WO_3$ have been developed and applied to display devices, light resistive glass, sunglasses, glare-free inner mirrors for cars and camera finders. The commercial inner is shown in Fig.3. A reflectivity is reduced by applying a DC bias voltage of +3 V and a driver is protected from the headlight glare of oncoming cars.

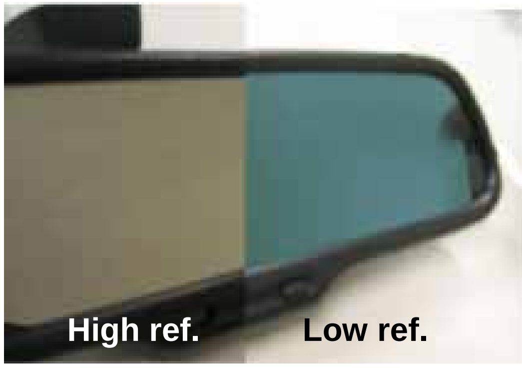


**Fig.3 Glare-free inner mirror using WO3 electrochromic cell**

The contrast between a coloring state and a breaching state and the transparency at a breaching state are important in the case of applying an electrochromic cell to optical recording. Transmittivity of a $WO_3$ electrochromic cell, which exhibits electrochromism as shown in Fig.4, was measured. The transmittivity reduces from 80 % to 30 % for 90 sec upon applying a DC bias voltage of +1.5 V. This long time for reduction in transmittivity is attributed to the resistance of transparent electrodes, ITO. These samples were prepared through the process used to manufacture the inner mirror in Fig.3. Instantaneous reduction of reflectivity of a mirror is dangerous for the driver and others. Therefor, the resistance of ITO is tuned to several dozen ohms so that the reflectivity changes slowly. A transient response can be improved for an optical disk by reducing the resistance of ITO to the order of several ohms. The difference in transmittivity between a breached and a colored state should be as large as possible for a highly-sensitive recording. A transmittivity in a breached state should ideally be almost 100 % for ultra multi-layered optical recording. Although the transmittivity is 80 % in this sample, this value could constitute a hurdle to the number of recording layers.

**before coloring at o V** **colored at 1.3 V** **breached with shorting**

**Fig.4 Breaching and coloring states in a transparent WO3 EC cell**

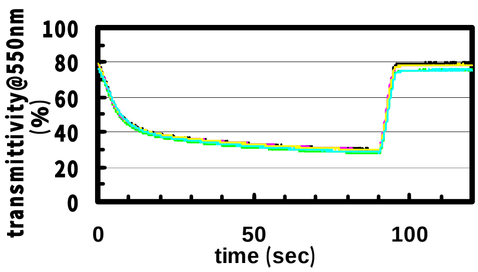


**Fig.5 Transmittivity dependence on time. Applied voltage is +1.5 V(colored) and –1.5 V (breached).**

Fig.6 is a TEM image of a cross-sectional sample of a transparent $WO_3$ electrochromic cell. An ITO electrode, an Ir oxide layer, a tantalum oxide layer which acts as an solid electrolyte, a $WO_3$ layer and an ITO electrode layer are stacked in this order on a glass substrate. However, the upper electrode, ITO, had been torn off during sample preparation. It is often explained that a cation occupies the vacancy in a perovskite structure when an electrochromic material colors. EDX analysis was performed in a TEM observation to investigate the effect of a crystalline structure of electrochromic material on electrochromism. Both Ir oxide and $WO_3$ appeared to be amorphous from this result. Fig.5 and 6 conclusively show that an amorphous inorganic electrochromic material is practically porous and numerous vacancies contributes to the coloring state. Coloring in a crystalline electrochromic material has not been confirmed yet in our laboratory. This experiment might propose a model which enables rewritability in an electrochromic material.

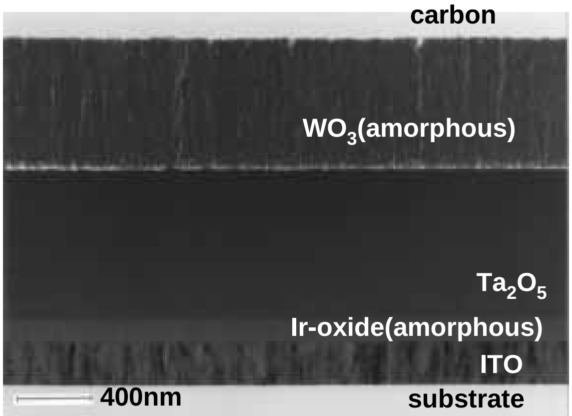


**Fig.6 Cross-sectional TEM image of a transparent WO3 electrochromic cell**

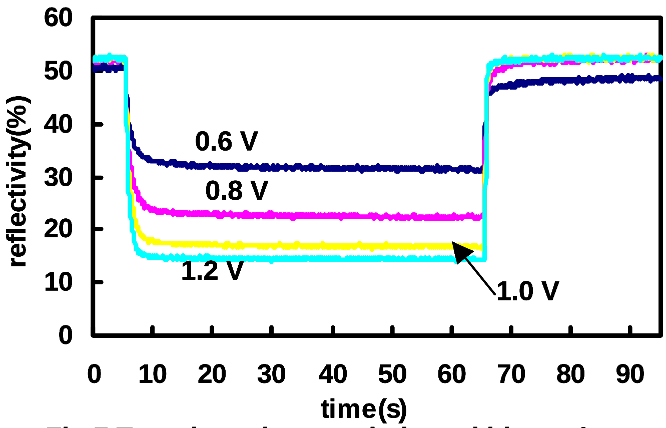


**Fig.7 Transient characteristic and bias voltage dependence of electrochromism in reflective electrochromic cell**

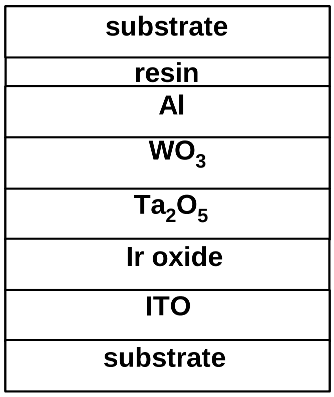


**Fig.8 Schematic layer structure of reflective electrochromic cell**

The transient characteristic of the reflected electrochromic cell and its bias voltage dependence are shown in Fig.7. The schematic layer structure of this sample is shown in Fig.8. This sample was made for a static recording experiment. Because a resistance of Al which acts as the upper electrode is in the order of several ohms, which is rather lower than that of ITO, the reflectivity decreases more drastically than in the transparent sample shown in Fig.5.

A company made these samples based on specifications designed by NHK. We attempted to sputter-deposit $WO_3$ to prepare a future disk sample, using a $WO_3$ sintered target and an RF magnetron sputtering apparatus. Samples were made under a ratio of Ar to $O_2$ from 70/0 to 70/10 (sccm). An as-deposited film was characterized by XPS and the compositional ratio of $WO_3$, other oxide, that is $WO_x$, and W metal was estimated. The results are shown in Fig.9. When an Ar flow and an $O_2$ flow are 70 sccm and 0, respectively, W metal phase does not exist and 95.5 % of $WO_3$ phase occupies the as-deposited W oxide film. When 5 sccm of $O_2$ are mixed with 70sccm of Ar, the compositional ratio of $WO_3$ becomes 99.5 %. It is concluded from Fig.9 that 5 sccm of $O_2$ is sufficient to obtain almost $WO_3$ single phase when a sintered W oxide target is used, and a pressure of sputtering gas and a sputtering power are 0.7 Pa and 200 W, respectively.

The original concept for mark formation, erasing and rewritability in an electrically selective multi-layered optical recording disk is proposed in the next section.

## 5. Proposal for rewritability

Which is a better material with a high contrast of transparency between a breached and a colored state, an amorphous or a crystalline electrochromic material? This problem has not been solved yet in our laboratory. However, experimental results clearly show are that the electrochromic layers of a transparent electrochromic cell are amorphous and that cell is breached with shorting electrodes. These results suggested a means of achieving rewritability in an electrochromic recording layer. That is, we noticed that there exist cations in an electrochromic material which is colored. We therefore considered that a breached mark might be formed and erased if cations could be squeezed out of and return to an electrochromic layer. What force can squeeze cations? There are two candidates.

One is the creation and annihilation of vacancies which may be accompanied with phase transition in a electrochromic material, and another is a potential difference through the solid electrolyte layer. In a $WO_3$ film, can phase transition occur under a laser power and over time as in the case of chalcogenide materials? A melting point of $WO_3$ is almost 1500 C[6], whereas the melting point of chalcogenide materials is about 600 C, so it is difficult for high-speed phase transition to occur under a low power as in chalcogenide materials. Thus, we tried to establish a rewritability in a electrochromic material based on potential difference.

A schematic diagram regarding a proposed solid electrolyte and accompanied mark formation is shown in Fig.10. Recording on an electrochromic layer is only to make a breached mark. How can it be made under a finite bias voltage? Let's return to Fig.4, which introduce the coloring and the breaching state in the transparent electrochromic cell. In the right-hand photograph, cations and electrons were discharged and the coloring electrochromic layer was breached by shorting electrodes. Is it possible to make a shorting path only in the irradiated part of a recording layer? A novel composite electrolyte was contrived to realize a ultra-partial shorting path. This electrolyte is composed of a conventional electrolyte and a phase change material as shown in Fig.10. GeSbTe in an electrolyte layer is amorphous, that is, a resistance is high at an initial state. When a laser irradiates and focuses on the colored electrochromic layer to record, heat directly generated from GeSbTe and bias heat from electrochromic layer cause GeSbTe to change to the crystalline phase. The resistance of GeSbTe, which is used in Ovonic memories, then decreases by $10^3 \sim 10^5$ ohms. The potential difference through the ultra-partial composite electrolyte layer on which the laser focused becomes very small. In this region, cations are expected to return to the composite electrolyte layer and a breached mark is formed in the electrochromic

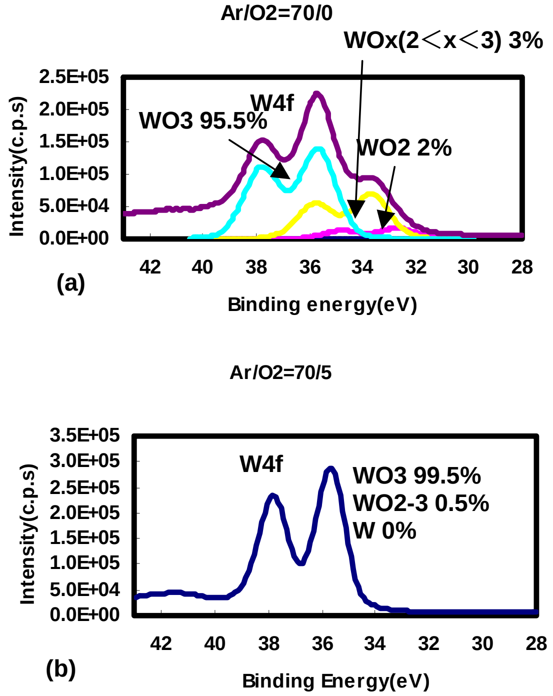


**Fig.9 XPS spectra of $WO_3$ films**

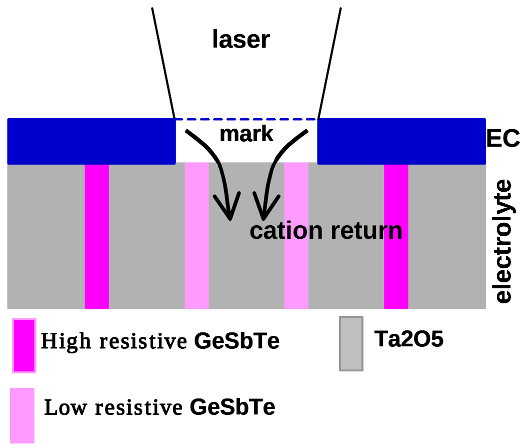


**Fig.10 Solid electrolyte composed of $Ta_2O_5$ and GeSbTe**

layer. A breached mark returns to the colored state by irradiating a region rather wider than the mark and by changing GeSbTe to amorphous. This is the erasing process. A rather wide region in a recording layer should be irradiated to obtain sufficient bias heat from the electrochromic layer. A breached mark over crystalline GeSbTe cannot generate bias heat. Insolubility between GeSbTe and $Ta_2O_5$ was confirmed in our laboratory from X-ray small-angle scattering measurements of a GeSbTe/$Ta_2O_5$ multi-layered film. So, sufficient rewrite cyclability is obtained in an electrochromic multi-layered disk that has the composite solid electrolyte layer as shown in Fig.10.

## 6. Conclusion

The electrochromic multi-layered optical disk is a potential candidate medium with a recording capacity of several hundred GB. There are many advantages with this type of memory as compared other three-dimensional memory systems such as holographic memory. For example, the process of manufacturing the medium, the substrate, signal processing, format and disk tester are almost the same as those for conventional optical disks.

Only a write-once type has been reported until now. In view of not only recording capacity but also various uses in broadcasting such as recording contents, news gathering and editing, rewritability must never be compromised. In this work, the electrochromism of inorganic electrochromic material, $WO_3$ was introduced for the electrically selective multi-layered optical recording disk, and a method of achieving rewritability was proposed. The authors anticipate that various proposals for rewritable electrically selective multi-layered optical recording will be developed.

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