The Development of Functional Thin Films and Sputtering Target Materials for Electronic Devices

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Sputtering is widely used in the production of electronic devices such as liquid crystal displays (LCDs), optical media, magnetic media and semiconductors. The Kobelco Research Institute, Inc. has been participating in the sputtering target business since 1993. The technical development group of Kobe Steel has developed the new materials for the business. This article introduces Al-Nd alloys for LCDs and Ag-Nd-Cu alloys for optical media. Also described is a unique method of spray-forming to fabricate the Al alloy targets.

Introduction

Sputtering targets provide thin-film materials deposited by the sputtering method. Kobelco Research Institute, Inc. started the target material business in 1993 and its competitive strength exists in the approach of originally developing high-performance film-materials before providing the target-materials required to make the films. The research and development group of Kobe Steel is responsible for the development of original thin-films and has contributed to the steady growth of the business in cooperation with the Kobelco Research Institute, Inc. This article summarizes the developments, current statuses and futures of Al-Nd and Ag-Nd-Cu alloys, which have found lucrative applications in LCD panels and optical storage media respectively. Also described is the spray-forming process used in the production of Al-Nd alloy targets.

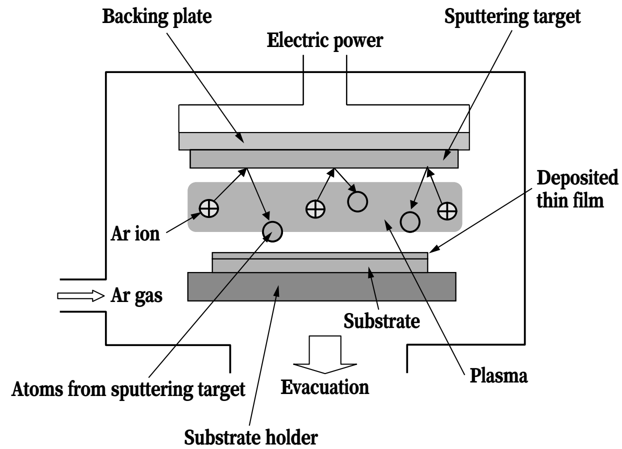


Fig. 1 Sputtering process

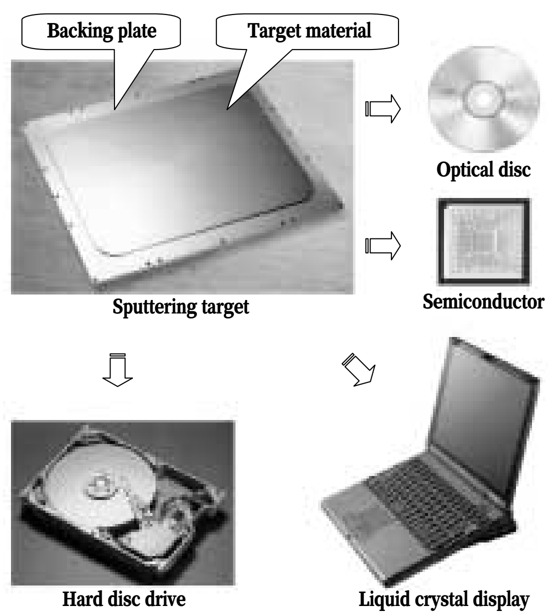


Fig. 2 Sputtering target and it's application

1. Sputtering process, target materials and their applications

1.1 Principle of sputtering process

The principle of the sputtering process is shown in **Figure 1**. Argon plasma is formed between a substrate and target material and atoms constituting the target material are sputtered out by energetic argon atoms impacting against the sputtering target. The sputtered atoms are deposited on the substrate, forming a thin film on the substrate's surface.

Figure 2 shows a typical appearance of the sputtering target and several application fields. Most target materials are in the shapes of plates and are sheet-brazed (or bonded) to the surfaces of the cooling plates (called backing plate) supplied by the users. The general size of the target material for LCD is 500 to 1,300 mm square with thickness of 6 to 16 mm.

As shown in Figure 2, sputtering processes are used in the production of various electronic devices such as LCD panels, optical storage media, magnetic recording media and semiconductor devices, and have become an important process supporting our daily activities.

1.2 Outline of film materials for LCD wiring and optical-disk reflective layer

Among all the application fields of the sputtering process, the LCD panels are expected to expand their markets especially in the office automation and home electric appliances. Above all the thin-film transistor LCD (TFT-LCD), which uses transistors to switch pixels, has become the mainstream of LCDs with its high response and finesse of the display.[1] In most cases, aluminum alloys are used for the thin-film wirings, which transmit switching signal to the TFT, and their characteristics affect the performances of TFT-LCD significantly. The wiring film is sputtered onto a glass substrate, patterned into stripes of approx. 10 μm wide and 0.3 μm thick by etching, and connections are made to both to the pixel TFTs and to the control ICs installed at the perimeter of the panel.

The optical storage media, which have become major pre-recording media replacing videotapes, provide another major application field of target materials. Reflective layers of Ag are used for the optical storage media, including the current mainstream DVD and the next-generation high-density recording, including Blu-ray disc and HD-DVD. The reflective layers are ultra-thin films of 10 to 20 nm and their optical properties and durability affect the reliability of the media.

2. Development of Al-Nd alloy for LCD panel wiring

2.1 Background of development

Around 1989 the LCD panel manufacturers suffered from the issue of wiring resistivity. **Figure 3** shows the relation between the resistivity of interconnection thin-film and the LCD panel size.

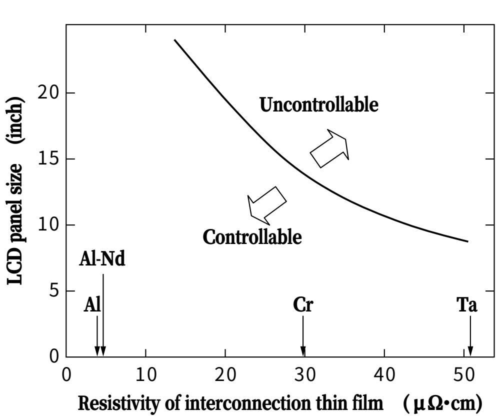


Fig. 3 Resistivity of interconnection thin film and controllable panel size

At that time refractory metals such as pure chromium and pure tantalum were used for the wiring, limiting the applicable panel size. Considering the increasing panel size in the future, the panel manufacturers desired to use aluminum alloys which have lower resistivities. However, use of pure aluminum for the wiring-film resulted in formation of small blisters called "hillock" during the heating process required for the LCD manufacturing and ended up with issues such as shorting of wires.

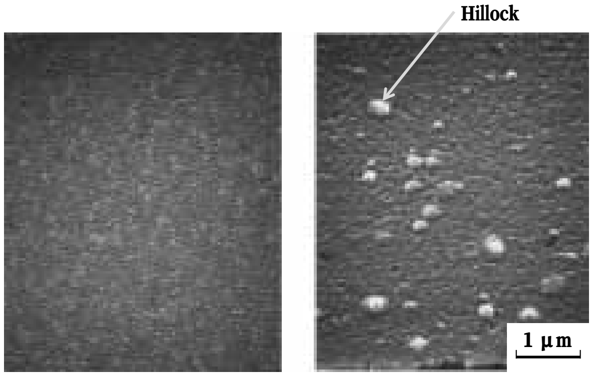
We started development of wiring thin-films having low resistivities in the hope of starting business of target materials for sputtering such films. The goal was set at the development of a film material having resistivity of less than 6 μΩ•cm with no "hillock" at 400℃.

2.2 Development of Al-Nd alloy film

The formation of hillock, then the main subject, was analyzed first to elucidate the formation mechanism. As a result, it was found that the differential thermal expansion between the glass substrate and aluminum wiring-film causes compressive residual stress in the film, providing driving force for aluminum atoms to diffuse along the grain boundaries and to form protrusions, the hillocks.[2] It was also found that the driving force of residual stress and the grain-boundary diffusion can be controlled by alloying. On the other hand, the alloying inevitably increased resistivity, making the trade-off between the resistivity and hillock to be the major subject of the development.

The alloy design was based on a concept of using the heating process of LCD manufacturing as an annealing process to reduce resistivity, and we succeeded in achieving both the low-resistivity and hillock prevention by addition of Nd into Al.[3]

Generally the sputtered thin film forms an almost uniform oversaturated solid-solution. Nd has an extremely low solid solubility limit in the equilibrium condition, however, it forms oversaturated solid-solution in the Al-Nd thin film.[4] Nd in the oversaturated solid-solution is considered to migrate into the grain boundaries during the heating, inhibiting the grain-boundary diffusion of Al and alleviating the compressive stress in the film. It has also been clarified that the oversaturated Nd is completely precipitated out as the intermetallic compound (Al_4Nd), reducing the resistivity down to the level of pure aluminum. **Figure 4** indicates the hillock prevention effect of Nd addition and **Figure 5** shows decreases of resistivities at elevated temperatures.



(a) Al-2at%Nd
Film thickness : 3,000 Å
Annealing condition : 400℃×1 h

(b) Pure Al
Film thickness : 3,000 Å
Annealing condition : 300℃×1 h

Fig. 4 Hillocks on thin film surface

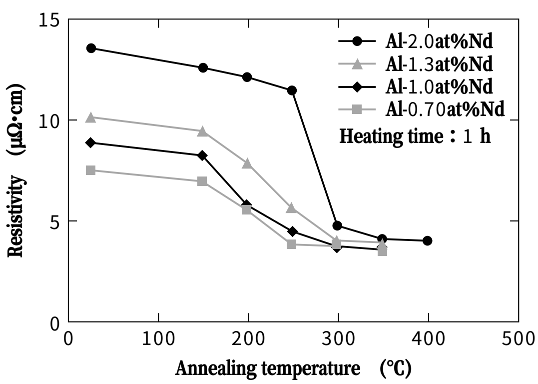


Fig. 5 Decrement of resistivity of interconnection thin film by annealing

Table 1 Relationship between Nd content and hillock free heating temperature

Heating condition	Observation of hillock			
	Al-0.7at%Nd	Al-1.0at%Nd	Al-1.3at%Nd	Al-2.0at%Nd
150℃×1.0 h	○	○	○	○
200℃×1.0 h	○	○	○	○
250℃×1.0 h	○	○	○	○
300℃×1.0 h	×	×	○	○
350℃×1.0 h	×	×	×	○
400℃×1.0 h	×	×	×	○

○ : Hillock free
× : Hillock is observed

Table 1 summarizes the relation between the amount of Nd addition and the observation of hillock. The Al-2at%Nd alloy was selected to be the most suitable alloy because the heating at around 350℃ is required for the manufacturing of LCD panels and heating at this temperature lowers the resistivity to almost a level which is constant, regardless of the Nd content, as shown in Figure 5. The alloy is used as a standard wiring material by many LCD panel manufacturers.

Our Al-Nd alloy currently holds the largest share in the wiring film material for the LCD panel and we will continue to propose and supply new materials based on new concepts such as Al alloys for dry etching and Al alloys for direct contact.

3. Development of Ag alloy for optical-disk reflective layers

3.1 Background of development

Recording densities and capacities of optical storage media are increasing as the media progress from CD to DVD, to Blu-ray Disc and to HD-DVD. The trend calls for high performance of the reflective layers comprising the disc. Au and Al-alloys are used for the reflective layers conventionally, while Ag has been considered to be the most suitable of all materials for the reflected layer, since Ag has the highest reflectivity and lowest absorption for the wavelength commonly used for the optical storage. However, pure Ag film lacks significantly in environmental durability compared to pure Au film and Al alloy films.[5] The low durability of the pure Ag film is due to aggregation caused by the migration of the Ag atoms at low heating temperatures, which is enhanced in humid environment.[6), 7)]

We started developing a Ag alloy film having high durability with low aggregation and high optical characteristics, in the hope of making the alloy the second pillar of business after Al-Nd alloy for LCD panel wiring. The goal was set at the development of a film with reflectivity higher than 90% (wavelength 650 nm) and no aggregation in 80℃-90%RH environment.

3.2 Development of Ag-Nd-Cu alloy

We started the development with studies on the aggregation behavior of pure Ag film.

Figure 6 shows scanning electron micrographs (SEM) of Ag films (thickness; 20 nm) before and after an environmental test (80℃, 90%RH, 48 hrs). The film after the aging test shows aggregation. It was clarified that the aggregations consist only of pure Ag and contain no reaction product such as oxide, indicating that they are caused by the diffusion of Ag atoms itself, changing the film from flat to island shape.

Based on the concept that the aggregation in a Ag alloy film is affected by the mobility of Ag in the film, alloying elements were chosen to improve the thermal resistance of the Ag alloy through observations of the microstructure. As a result, additions of Nd and Cu were found to be very effective in improving the thermal resistance of the

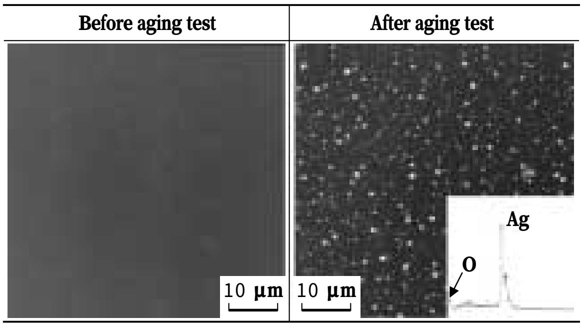


Fig. 6 Ag aggregation after aging test

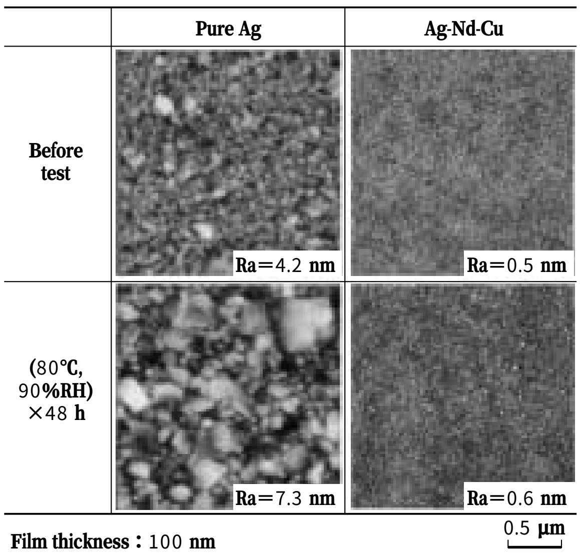


Fig. 7 Effect of Nd addition on aggregation in Ag alloy films

alloy.[8)]

Figure 7 shows atomic-force-micrographs (AFM) of the surfaces of pure Ag and Ag-0.7at%Nd-0.9at%Cu alloy (ANC) film before and after the environmental test. The pure Ag surface shows aggregation and increase of the surface roughness, while the ANC retains original smoothness of the surface even after the testing, showing good resistance against aggregation. The reflectivity after the environmental test determines the reliability of the optical disc reflective layer, and the changes in reflectivity before and after the testing were examined in relation to the Nd content (**Figure 8**). The reflectivity of pure Ag film is reduced significantly after testing, while the reflectivity reduction is decreased with increasing Nd content and becomes saturated above approx. 0.4 at% of Nd content. The result indicates that addition of Nd higher than 0.4% prevents aggregation of Ag alloy film with minimal reduction of reflectivity.

The Nd content was optimized based on the above result and Ag-0.7at%Nd-0.9at%Cu alloy was developed as an alloy having both the high

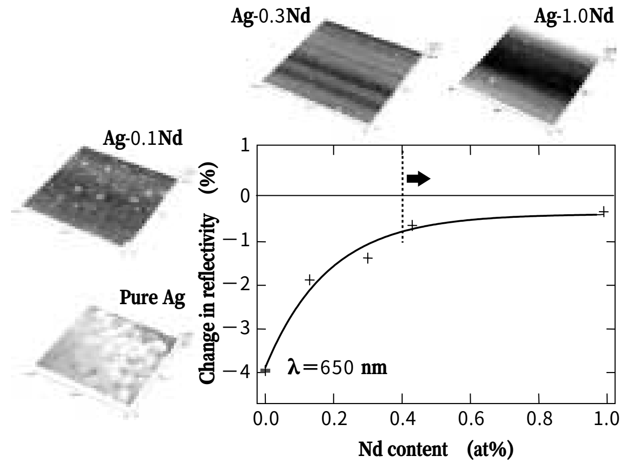


Fig. 8 Relationship between Nd contents and change in reflectivity after aging test

reflectivity and durability in humid and heated environments. The material has been recognized as a durable Ag alloy by media manufacturers, and has been applied to volume products including DVD-R, RW and BD-RE. New developments are being made on reflective layers based on a new concept and also on optical storage media materials for the next-generation recording.

4. Production of target materials by spray-forming

The target materials require such characteristics as uniformity of compositions, fine and homogeneous microstructure, and purity. In case of the target material for LCD panels, special emphasis is made on the refinement and homogeneity of the microstructure. This is due to the fact that the LCD panel calls for higher sputtering power density compared to other applications, which increases the tendency for inhomogeneous microstructures of the target material to form undesired particulates on the substrate surface. The particulates are generally called the "splash" and directly reduce the yield of the LCD panel production, and thus the demands for target materials with fine and homogeneous microstructures are becoming stronger and stronger.

We studied the application of the spray-forming process to make the microstructure fine and homogeneous and introduced the basic technology from Osprey Co, of the UK in 1991. After this introduction we spent about 3 years establishing the production technologies of aluminum alloys[9)] and transferred the technology to the Kobelco Research Institute, Inc. in 1998.

Figure 9 shows a schematic diagram of the spray-forming. As in the case of the conventional

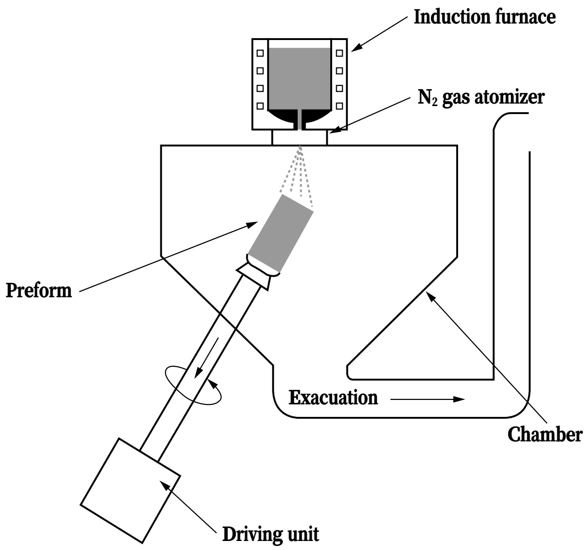


Fig. 9 Schematic diagram of spray forming method

melt/cast technology, the raw material is first melted in an induction furnace. The crucible in the furnace has a hole of approx. 5 mm in diameter at the bottom to allow the metal to flow into the chamber where the molten metal is blown by nitrogen into small droplets. The droplets are accumulated in liquid form on a collector and solidify there to form an ingot or a pre-form. The pre-form is somewhat porous and is consolidated further by HIP (Hot Isostatic Pressing) to 100% density.

The process is featured by its rapid solidification rate, because the metal solidifies in small droplets, and by the homogeneity of the solidified metal, which is the reflection of the uniformity of the molten state. In case of Al-Nd alloy, the average grain-size of the pre-form is about 2 μm and the size of Al-Nd intermetallic compound is about 1 μm. **Figure 10** shows microstructures of target materials prepared by different processes. The microstructure of the spray-formed material is distinguishably finer and more homogeneous, making the target material less susceptible to splashes and easier to use.

The conventional processes of melting/casting and powder-metallurgy can be replaced by the spray forming to produce target materials with fewer splashes.

Conclusions

Traditionally, the thin-film materials used in devices such as LCD panels and optical discs have been developed by the device manufacturers, and the material manufacturers have been responsible only for the development of the production process of the material specified by the device manufacturers. We broke this tradition and have developed technologies to evaluate and design thin-films to provide competitive target materials that meet our ONLY ONE, NUMBER ONE policy. More recently, we have made a step forward in the material design from the one based on the film-property to those based on thin-film processes and device characteristics. We will continue to improve our technologies to provide products that attract our users based on new concepts which lead the trend in LCDs and optical discs.

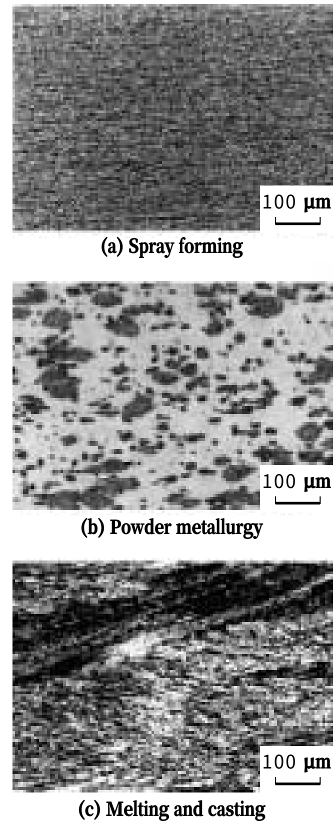


Fig. 10 Comparison of microstructure of Al-2at%Nd sputtering target by production method

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