ISSN 0429-8284

Whole Number 224

e-Front runners

FUJI ELECTRIC REVIEW

1
2009 VOL.55

Magnetic Recording Media
Photoconductors

Fuji Electric Group

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REVIEW

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Cover photo:

Hard disk drives are positioned as the primary type of information recording device due to their advantages of large capacity and low bit cost. As a result of a recent significant technical breakthrough known as the perpendicular magnetic recording method, one terabyte large-capacity drives (equipped with three 3.5-inch disks having the capacity of 334 GB/disk) are feasible, new markets are being created for commercial electronics applications such as hard disk recorders, and future market growth is forecast.

Fuji Electric was one of the first companies to commercialize perpendicular magnetic recording media, and quickly implemented a vertically integration of its production line and is responding to the expanding market.

The cover photo shows typical group of familiar application products. The creation of mobile products that fully utilize the small size and large capacity of hard disk drives is anticipated.

FUJI ELECTRIC REVIEW vol.55 no.1 2009
date of issue: February 20, 2009

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Current Status and Future Outlook for Magnetic Recording Media

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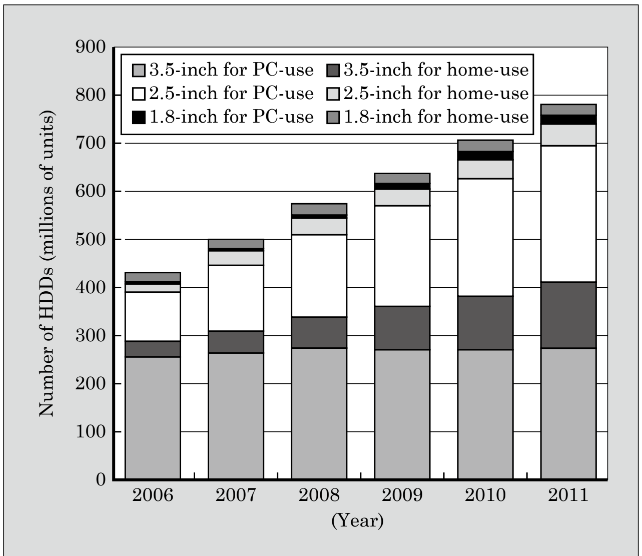
1. Introduction

With the commercialization of hard disk drives (HDDs) employing perpendicular magnetic recording technology, areal densities are once again increasing at faster rates and are growing by approximately 40% per year, new products such as HDD recorders (for non-PC use) and portable music players that advantageously utilize the large capacity and small size of these drives have been created, and the HDD market is continuing to expand (Fig. 1[(1)]). Moreover, HDDs are manufactured in 3.5-inch, 2.5-inch and other sizes according to their intended use, i.e., whether for stationary applications or mobile applications. Market trends for each size of magnetic recording media are described below.

For 3.5-inch HDDs, the arrival of 1 terabyte (TB) large-capacity drives is creating a new market for HDD recorders and for applications with IT companies that operate Internet portal sites such as Google*1 and Yahoo!*2 This market is called "near line storage" and represents a group of products (requiring relatively low-cost and large capacity HDDs) that connect the desktop PC to a server. Media manufacturers expect this market to have significant volume since each drive is equipped with 3 to 4 disks. As a result, the market for 3.5-inch HDDs is growing at an annual rate of more than 9%.

Fig.1 HDD market forecast



2.5-inch HDDs are increasing in popularity as notebook PCs achieve higher functionality and as a result of lower costs due to intense competition among HDD manufacturers, and this market is growing at an annual rate of more than 20%. In the future, as areal densities increase and recording capacities exceed 250 gigabytes (GB), the installation of 2.5-inch HDDs in desktop PCs becomes increasingly likely.

1.8-inch HDDs are used in the specialized market for portable music players such as the iPod*3 and are also creating a new market for ultra-slim notebook PCs. Competition from semiconductor memory technology, however, is expected to prevent large future growth of this market.

Small size HDDs such as 0.85-inch and 1.0-inch drives are expected to be installed in portable music players and cell phones, but market share will be lost to semiconductor memory, which has the advantages of lower cost, better resistance to mechanical shocks, and lower power consumption.

In order for the HDD market to continue its steady growth, larger capacities must be achieved and the cost-per-bit advantage compared to semiconductor memory must be maintained.

This paper discusses the status of technical development and the future outlook for Fuji Electric's magnetic recording media.

2. Technical Trends of Magnetic Recording Media

Longitudinal recording method, the former mainstream method for recording, has reached its limita-

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*1: Google is a trademark or registered trademark of Google Inc. in the United States and other countries.
*2: Yahoo! is a trademark or registered trademark of Yahoo! Inc. in the United States and other countries.
*3: iPod is a trademark or registered trademark of Apple Inc. in the United States and other countries.

Fig.2 Timing of market deployment of new technology products

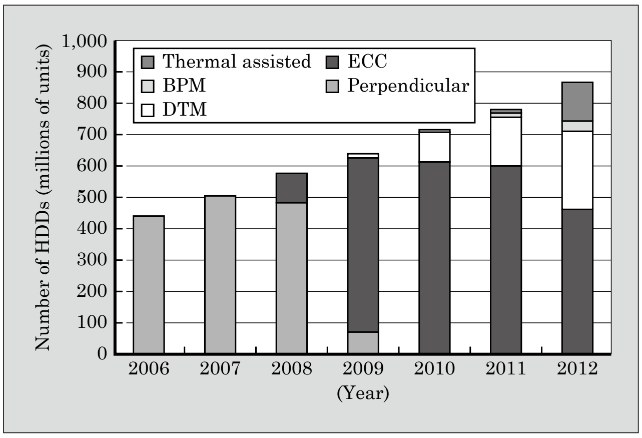
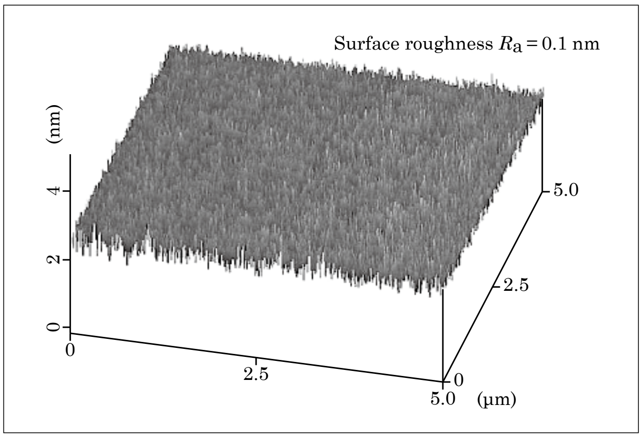


Fig.3 Surface topography of aluminum substrate for perpendicular magnetic recording media (AFM image)



tion for higher areal density, and from 2006 to 2007 was successively replaced by the perpendicular magnetic recording method. Fuji Electric commercialized the industry's first 2.5-inch glass perpendicular magnetic recording media (80 GB/disk) in 2006 and the industry's largest capacity (334 GB/disk) 3.5-inch aluminum magnetic recording media in 2007. Fuji Electric is presently manufacturing 3.5-inch products with 160 GB/disk, 250 GB/disk and 334 GB/disk capacities, and 2.5-inch products with 120 GB/disk and 160 GB/disk capacities. In 2008 there was a migration from the previous perpendicular magnetic recording media to ECC (exchange-coupled composite) perpendicular magnetic recording media (ECC media) capable of higher areal densities, and the development of 3.5-inch 500 GB/disk and 2.5-inch 250 GB/disk products are planned.

The new key technologies presently being developed in order to realize higher areal densities are as follows.

(a) Super smooth surface finishing technology
(b) ECC media
(c) DTM (discrete track media)
(d) BPM (bit pattern media)
(e) Thermal assisted media

Figure 2 shows a forecast of the timing of product development using these new technologies. As in the case of perpendicular magnetic recording media, Fuji Electric aims to be an industry leader for these new technologies and is advancing their development.

3. Technical Development Trends of Magnetic Recording Media

3.1 Super smooth surface finishing technology

To increase the recording density, the spacing between the R/W (read/write) element and the magnetic layer of the media should be as small as possible. In a 3.5-inch HDD, stable flying performance by the magnetic head is required at flying heights of 3.0 to 4.0 nm for 334 GB/disk media, at 2.5 to 3.0 nm for 500 GB/disk media, and at 2.0 nm for higher capacity disk media. Moreover, because of the heat generated in the vicinity of the R/W element and the mechanism used to control narrowly the spacing with the magnetic layer, the absence of surface micro-defects and projections is required in order to ensure stable flying characteristics. Fuji Electric independently develops and manufactures aluminum substrates, and in response to these types of requests, is independently developing aluminum substrates having high levels of smoothness and cleanliness suitable for perpendicular magnetic recording media, and is also applying proprietary texture technology to realize even smoother surfaces. (See Fig. 3.)

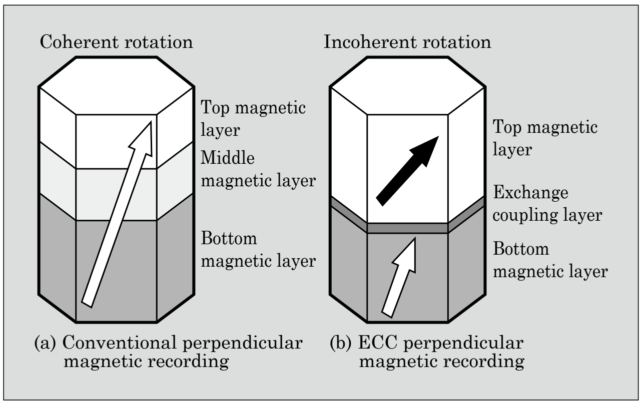
For glass substrates, as in the case of aluminum substrates, Fuji Electric's proprietary texture technology realizes the highest level of surface smoothness in the industry. In addition to surface smoothness, Fuji Electric has also developed washing technology that removes extremely minute and small amounts of residue, enabling finishing to a clean surface. Surface finishing technology and washing technology both contribute to long-term reliability and help distinguish Fuji Electric from its competitors.

3.2 ECC media

Limitations of the recording density of conventional perpendicular magnetic recording media are coming into view. ECC media products, capable of even higher recording densities, were deployed in 2008. One problem in achieving higher recording densities is a phenomenon known as adjacent track erasing, whereby adjacent tracks on both sides of a recorded track are erased during recording. The magnetic field from the head is obliquely incident on adjacent tracks, and the conventional perpendicular magnetic recording media is characteristically predisposed to magnetization reversal when exposed to an obliquely incident magnetic field. Increasing the density in the track direction and reducing the spacing between tracks causes the problem of adjacent track erasing to become more noticeable.

As shown in Fig. 4, ECC media features a structure

Fig.4 Structure of conventional perpendicular magnetic layer and ECC perpendicular magnetic layer



provided with coupling layer for controlling exchange coupling energy between the top and bottom magnetic layers, whereby the top magnetic layer which is predisposed to magnetization reversal reverses first and then the bottom magnetic layer, which is resistant to magnetic reversal, is encouraged to reverse so as to facilitate writing. Also, the ECC media has the significant advantages of being resistant to magnetic reversal when exposed to an oblique magnetic field and of being highly resistant to adjacent track erasing when the track density is high.

The ratio of the magnetic anisotropy K_u values of the bottom and top magnetic layers is important for ECC media, and the development of the materials used in these layers is a key factor. Fuji Electric is advancing its proprietary ECC media development work, and expects to be able to realize recording capacities greater than 750 GB/disk for 3.5-inch media.

3.3 DTM

As explained for ECC media, increasing the density in the track direction causes the tracks to become closer to one another and cause mutual interference. With DTM, semiconductor lithographic technology is used to pattern the magnetic layers, and this technology isolates adjacent tracks as shown in Fig. 5 to increase the density in the track direction. Technical development is presently underway, and the following items are important when etching a structure formed from deposited magnetic and protective layers.

(a) Reliability when etching the magnetic layer
(b) Limiting cost increases due to added processes

Issues associated with (a) include corrosion performance, head flyability, and so on. Issues associated with (b) include the capital investment to install semiconductor processing equipment and the limited number of times the servo pattern master can be used.

Fuji Electric completed development of the basic processes in the first half of 2008, started-up a pilot line in the second half of 2008, and aims to commercialize products in the first half of 2009.

Fig.5 Comparison of conventional media and DTM

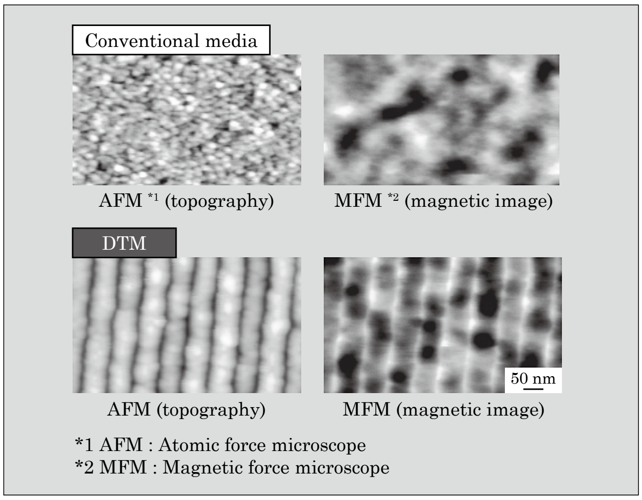
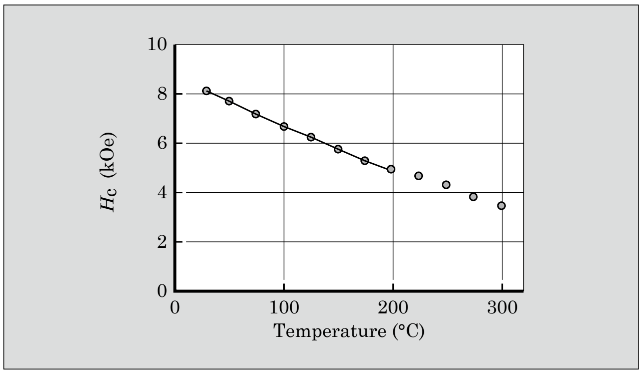


Fig.6 Temperature dependence of H_c



3.4 Thermal assisted recording media

The coercivity H_c of magnetic recording media is dependent on temperature, and for example, as shown in Fig. 6, H_c decreases by approximately 20 Oe for a 1 °C rise in temperature. H_c decreases at high temperatures and increases at low temperatures.

Previously, media in which H_c did not change in response to temperature fluctuations was sought. However, thermal assisted recording media is based on a contrary philosophy and utilizes the temperature dependency of H_c to increase the recording density.

Increasing the recording density typically results in smaller-sized individual bits and instability due to thermal fluctuations. To ensure thermal stability, H_c must be increased. If H_c is increased, however, the head magnetic field will have difficulty writing. To overcome these contradictory characteristics, a laser element is attached to the head, and when writing, the light irradiated from the laser causes temperature to rise at the part to be recorded instantaneously, and H_c decreases to facilitate the writing operation. After returning to room temperature, the H_c has a high value, and thermal stability can be ensured. For example, in a magnetic layer having an H_c of 8 kOe at room temperature, the H_c drops to 5 kOe when irradiated with laser light, the head magnetic field is applied at that instant, and the magnetization of the magnetic layer can be reversed.

Thermal assisted media faces the following two challenges.

(a) Development of materials and processes having a large H_c temperature dependence

(b) Durability of the protective layer and lubricant film against heating by laser irradiation

Fuji Electric is advancing materials development for these types of magnetic layers, protective layers and lubricant films, and aims to commercialize thermal assisted recording media.

4. Postscript

2008 was the year in which our approach to post-perpendicular magnetic recording media gained momentum. So that HDDs continue their stable market growth over the long-term, recording densities must continue to increase and the cost-per-bit advantage compared to semiconductor memory must be maintained.

Based on the core technologies described in this paper, and in cooperation with customers, head manufacturers, equipment manufacturers and materials manufacturers, Fuji Electric intends to achieve early commercialization of these products, and contribute to the expansion of the HDD market.

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Perpendicular Magnetic Recording Media with Aluminum Substrate

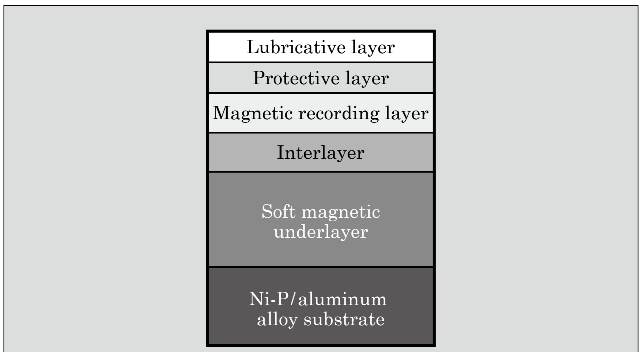
Shinji Takei †
Naoki Hara †

1. Introduction

Hard disk drives (HDDs) have been used in practical applications since 1956. Their areal densities have been increased rapidly in recent years. This trend is expected to continue at an annual rate of increase approximately 40%. As a result of this sort of remarkable increase of areal density, the method of longitudinal magnetic recording has reached its areal density limit due to a trade-off between low noise performance and thermal stability, and the perpendicular magnetic recording method, first proposed by Iwasaki et al.[1] in 1975, has emerged as an alternative to longitudinal magnetic recording. Perpendicular magnetic recording is characteristically dissimilar to longitudinal magnetic recording, namely, its thermal stability increases as areal density increases and is therefore well suited, in principle, for high areal densities. In the Spring of 2005, HDDs that utilized perpendicular magnetic recording technology were released commercially, and in 2006, Fuji Electric began mass-producing perpendicular magnetic recording media.

Fuji Electric has been working to develop perpendicular magnetic recording media since 1999. By concentrating on the development of perpendicular magnetic recording media that simultaneously realize low noise performance, and good thermal stability and writability, which had presented significant challenges for commercialization, has attained commercial viability. Figure 1 shows an example of the layer structure of perpendicular magnetic recording media. A SUL (soft underlayer), inter-layer, magnetic recording layer and protective layer are deposited sequentially on an aluminum substrate, and then the protective layer is coated with a lubricative layer. These layers are typically formed from several thin films.

Fig.1 Layer structure of perpendicular media



This paper describes the required substrate performance for use with perpendicular magnetic recording media, the development of sputtering techniques for the SUL, inter-layer, magnetic recording layer and protective layer of perpendicular magnetic recording media, which use completely different materials and layer structure from that of longitudinal magnetic recording media, and the status of development of aluminum perpendicular magnetic recording media at Fuji Electric.

2. Substrate for Perpendicular Magnetic Recording Media

Substrates used for aluminum perpendicular magnetic recording media, as in the case of substrates for conventional longitudinal magnetic recording media, are polished after a Ni-P film is been plated on an aluminum alloy, but differ from substrates for longitudinal magnetic recording media in terms of surface roughness. With longitudinal magnetic recording media, in order to improve the electromagnetic transfer characteristics, the magnetic moment must be oriented in the circumferential direction of a substrate, and a texturing process to provide a certain degree of controlled roughness is applied in the circumferential direction. On the other hand, with perpendicular magnetic recording media, if the easy axis of the SUL is oriented in the circumferential direction, leakage flux from adjacent tracks during recording may possibly cause erasure, and therefore a circumferential orientation is not desirable. Moreover, the texturing process in the circumferential direction is also undesirable since there is increased likelihood that the easy axis of the SUL, which needs to be oriented in the radial direction, will also become aligned in the circumferen-

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tial direction. Additionally, in order to realize higher areal densities of magnetic recording media, the spacing between the magnetic layer and the magnetic head for recording and playback must be reduced to achieve a lower flying height of the head, and a smoother substrate surface is sought. To reduce the surface roughness, Fuji Electric uses a circumferential texturing process which is easy to implement, and also adopts a texturing process that is controlled to achieve a roughness below a certain level.

With magnetic recording media, long-term reliability is sought, but there is a potential risk of micro corrosion due to particles adhered to the substrate surface. For this reason, in addition to a substrate surface smoothing process, a cleaning process is also extremely important.

Fuji Electric is also developing and producing aluminum substrates, and the ability to implement a continuous series of processes from substrate manufacturing to polishing, cleaning, sputtering and finally to evaluation is a tremendous advantage for developing aluminum perpendicular magnetic recording media.

3. Sputtering Technology

3.1 SUL

One major difference between perpendicular recording media and longitudinal recording media is that perpendicular recording media has a SUL. The existence of the SUL provides significant advantages including the ability to establish a magnetic field for the head that is 1.5 times the magnitude as that of the longitudinal recording method. Consequently, however, the required thickness of the SUL exceeds one-half of the total film thickness of the perpendicular magnetic recording media. In consideration of the ease of manufacture and cost, the SUL is preferably made as thin as possible. To realize a thinner SUL, the design of the inter-layer and the magnetic recording layer play important roles, but the most effective method is to increase the saturation magnetic flux density B_s of the SUL. The first generation of perpendicular magnetic recording media typically used Co-based alloy amorphous films such as CoZrNb and CoZrTa. Co-based alloy thin films were used because they have relatively high levels of B_s and corrosion resistivity, and could easily provide the necessary amorphous structure for the SUL. However, the B_s of CoZrNb and CoZrTa ranges from approximately 1.1 to 1.3 T, and is not as large as the maximum value of 2.3 T for a magnetic material.

The B_s of the SUL can be increased by adding Fe (B_s = 2.1 T), but corrosion resistivity decreases as the amount of Fe additive increases. Adding paramagnetic materials such as Cr, Ta and Nb to increase the corrosion resistivity will cause the B_s level to drop, thereby making it pointless to add Fe in the first place.

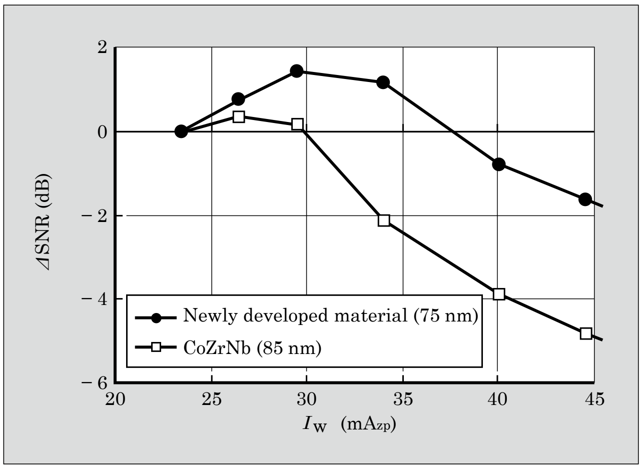
Fuji Electric conducted an investigation of SUL materials based on theoretical considerations, and succeeded in developing a structure having a high B_s level while maintaining high corrosion resistivity and an amorphous structure. Table 1 shows a comparison of the characteristics of the newly developed material versus those of CoZrNb, which has typically been used in the past. The B_s level was raised to 1.5 T, an increase to approximately 1.4 times the 1.1 T B_s of CoZrNb. As magnetic recording media, this newly developed material showed good corrosion resistivity, with less Co corrosion than CoZrNb. Additionally, cross-sectional images obtained by X-ray diffraction (XRD) and transmission electron microscopy (TEM) were analyzed, and the results exhibited a good amorphous structure.

Figure 2 shows the write current dependency of the standard value of signal-to-noise ratio (SNR), which is an indicator of the read/write (R/W) performance. SNR values for both SUL materials are shown normalized with reference to the SNR when the write current is 23 mA. In the case of CoZrNb, the SNR rapidly deteriorates as the write current increases. However, with the newly developed material, the deterioration in SNR is minimized, despite having a thinner film thickness as compared to CoZrNb. This behavior is believed to be attributable to the B_s level of CoZrNb, which is not so high when the write current is large, and as a result, the magnetic flux generated from the magnetic head causes the SUL magnetization to saturate completely. Therefore, the SUL made of CoZrNb is unable to fulfill its role as a magnetic circuit, and magnetic leakage flux that does not pass through the SUL causes recorded signals to be erased. On the other hand, with the newly developed SUL material, since the B_s level is high, magnetic flux generated from the

Table 1 Comparison of SUL materials

	B_S (T)	Co corrosion (ng/cm^2)	Crystal structure
Newly developed material	1.5	0.006	Amorphous
CoZrNb	1.1	0.018	Amorphous

Fig.2 Write current dependency of normalized SNR



magnetic head returns to the magnetic head without saturating the magnetization of the SUL and without erasing any signals.

Use of the newly developed material enabled a successful reduction in SUL film thickness to approximately 70% the conventional thickness and a significant boost in manufacturing ease. Additionally, the corrosion resistivity improved dramatically and the reliability of perpendicular magnetic recording media also improved.

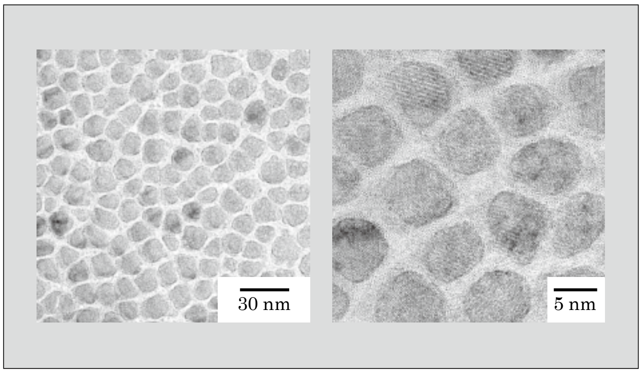
In addition to increasing the B_s level of the SUL, appropriately control of the soft magnetic performance and magnetic anisotropy is crucial for improving the performance of perpendicular magnetic recording media, and therefore, Fuji Electric is actively advancing the development of such control.

3.2 Inter-layer

The inter-layer is used to enhance the crystalline orientation and segregation of the magnetic recording layer. Ideally, individual grains in the magnetic recording layer are grown epitaxially with a 1:1 correspondence on top of the grains in the inter-layer. Accordingly, in order to increase the density of the magnetic recording media, the grain size of the magnetic recording layer must be reduced. Although the grain size of the inter-layer must be reduced, refining the grain size makes the orientation and segregation become susceptible to deterioration. Therefore, Fuji Electric uses a multilayer inter-layer method to refine the grain size while improving orientation and segregation. This method separates the functionality by forming separate layers for refining grain size, for improving crystalline orientation and for improving segregation. For this purpose, the necessary material design is carried out and the sputtering process is optimized with high precision.

Figure 3 shows an in-plane TEM image of perpendicular magnetic recording media being developed by Fuji Electric. At the start of mass-production of magnetic recording media (corresponding to an areal density of 120 Gbits/in^2), the grain size was approximately 7 nm, but the material presently being developed has a grain size of less than 6 nm, a successful refinement in size of approximately 20%. Additionally, the TEM image shows good segregation characteristics. From the results of analysis using XRD, the c-axis distribution $\Delta\theta_{50}$ was verified to be rather good at approximately 2.5 degrees.

Fig.3 In-plane TEM image



Moreover, the capability to maintain the above-mentioned characteristics while making the inter-layer as thin as possible is the key to improving the write performance and manufacturing ease of the magnetic recording media. Fuji Electric has successfully realized the world's thinnest inter-layer film and is able to mass-produce perpendicular magnetic recording media that is highly competitive.

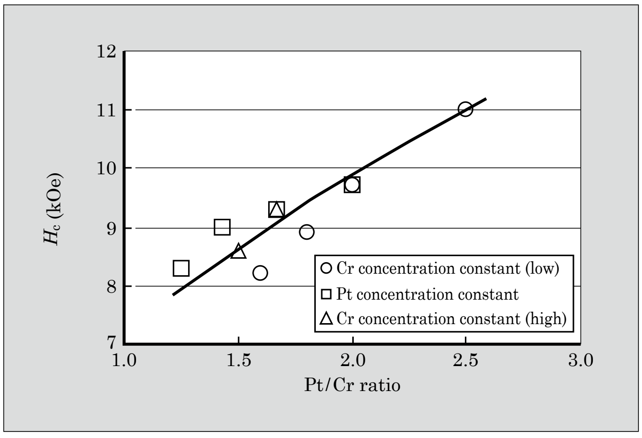
3.3 Magnetic recording layer

Fuji Electric pioneered the use of CoPtCr (granular magnetic material) with an SiO_2 additive as magnetic layer material and has actively issued announcements[(2), (3)] describing such achievements as the realization of perpendicular magnetic recording media having a large uniaxial magnetic anisotropy constant K_u and a favorably segregated structure , and the good recording and playback characteristics and high thermal stability that are exhibited.

In the granular magnetic layer structure, individual grains of CoPtCr are surrounded by non-magnetic amorphous SiO_2 and results in reduced magnetic interactions between CoPtCr grains and lower noise. In order to fabricate a thin film having a favorably segregated structure, the amount of SiO_2 additive is an important factor, but the sputtering process which includes doping with additional gas and the concentration thereof, control of the doping timing, and so on is extremely critical. Fuji Electric's ongoing development efforts are focusing on this sputtering process.

Moreover, as described above, in order to improve the performance of perpendicular magnetic recording media, the size of grains in the magnetic recording layer is refined as a result of the refinement of grain size in the inter-layer, but in doing so, thermal stability becomes a problem. As a consequence of the smaller size of crystalline grains, the volume V of each crystal

Fig.4 Pt/Cr ratio dependence of H_c



becomes smaller and the value of K_uV/kT (where k: Boltzmann's constant, T: absolute temperature), which indicates thermal stability, decreases. One way to boost thermal stability would be to increase the thickness of the magnetic recording layer and increase V, but in consideration of the balance between the magnetic head and write performance, simply increasing the film thickness is not a good idea. Thus, the K_u of the magnetic recording layer must be increased. Figure 4 shows the change in coercivity H_c according to the ratio of Cr and Pt contained in the magnetic recording layer. Although H_c and K_u do not always have a 1:1 correspondence, K_u exhibits a similar trend as H_c and therefore the direction of change in K_u can be ascertained by observing the change in H_c. Increasing the percentage of Pt in the film causes H_c to increase nearly linearly, and this demonstrates that increasing the Pt percentage is also an effective means for increasing K_u. However, simply increasing the amount of Pt in the magnetic recording layer will lead to higher noise and poorer SNR characteristics. Therefore, the film composition must be designed in consideration of the balance with other elements such as Cr and SiO_2.

Furthermore, important factors for achieving good performance in the magnetic recording layer include, in addition to the layer composition, the layer structure and the above-mentioned sputtering process, and development of the magnetic recording layer must proceed with a comprehensive consideration of all of these factors. This is Fuji Electric's area of expertise.

3.4 Protective layer

The protective layer, as its name states, is formed to protect the magnetic recording media. Owing to the synergistic effect derived from the prevention of corrosion in the magnetic recording layer and the provision of a lubricative layer that is coated on top of the protective layer, the protective layer functions to protect the magnetic layer from abrasive wear from the head. Carbon film, sputtered by ordinary CVD (chemical vapor deposition), is suitable for use as the protective layer. Generally, a thinner protective layer leads to an improved SNR due to a small spacing between the magnetic layer and head. However, susceptibility to Co corrosion increases rapidly as the protective layer becomes thinner. Or in other words, corrosion resistivity deteriorates rapidly when the protective layer is made thinner. Thus a tradeoff relation exists between SNR and Co corrosion characteristics.

Consequently, there is a need for development of a high-density carbon film that enables a reduction in the thickness of the protective layer without increasing Co corrosion. In response to this need, equipment for manufacturing high-density carbon film has been developed, but as of the present point in time, has not yet been put into practical use.

Meanwhile, by using the conventional CVD method directly and modifying the sputtering process, Fuji Electric has succeeded in developing high-density carbon protective film. Figure 5 shows the relationship between Co corrosion and protective layer thickness in perpendicular magnetic recording media that has been manufactured by this newly developed process. Results obtained by using the current process are also shown on the same graph. The results show that by increasing the density of the protective layer, corrosion resistivity equivalent to that of the current process can be obtained even for film thicknesses on the order of 3 nm. Additionally, Fig. 6 shows the protective layer dependence of SNR in perpendicular magnetic recording media that has been manufactured using the newly developed process. Also shown on this graph is the SNR obtained when using the current process. Use of the new process improves not only the film density, but also improves the head flyability, i.e., enables lower flying heights, so as to realize an improved SNR for the same protective film thickness. Thus, the newly developed process for improving protective film density enables the manufacture of magnetic recording media that exhibits good corrosion resistivity and a favorable SNR even in thin film areas. Fuji Electric will continue to advance this development work in order to realize thinner films in the future, and simultaneously, is also working to develop new sputtering methods for

Fig.5 Protective layer thickness dependence of Co corrosion

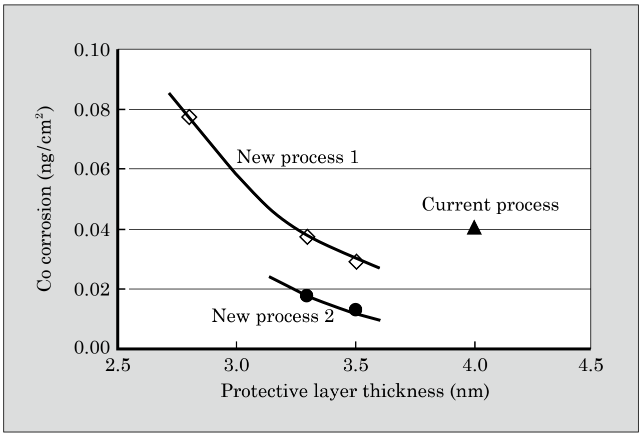
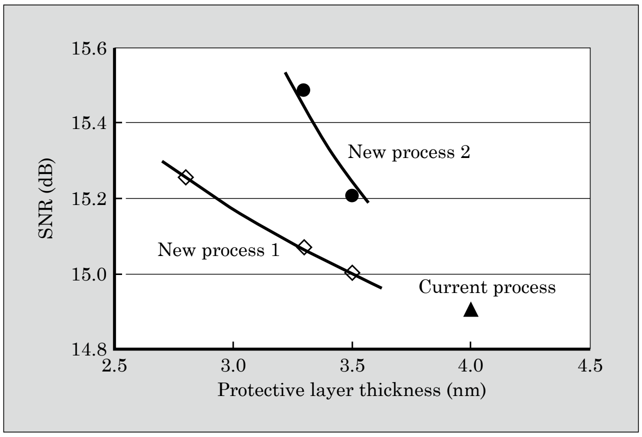


Fig.6 Protective layer dependence of SNR



realizing even thinner films.

4. Postscript

Fuji Electric has been mass-producing perpendicular magnetic recording media since the Spring of 2006, and was the first company in the industry to advance a production line that supports perpendicular media, and then to transition production from longitudinal to perpendicular media. At present, perpendicular magnetic media accounts for more than 90% of Fuji's total production. In the future, Fuji Electric intends to continue to pursue highly productive processes in order to realize even higher density of perpendicular magnetic media, and will actively continue to develop leading-edge technology.

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Perpendicular Magnetic Recording Media with Glass Substrate

Tadaaki Oikawa †
Yoshifumi Ajishi †
Hiroyuki Uwazumi †

1. Introduction

Hard disk drives (HDDs), not limited to applications in external recording devices for use with personal computers, are recently being used increasingly in commercial electronics (CE) applications such as recording devices for car navigation systems, game devices and other information appliances. The HDDs installed in such CE devices are required to be compact in size, and mainly use 2.5-inch and 1.8-inch size magnetic recording media with glass substrates.

Furthermore, owing to recent developments of digitized information, larger and larger quantities of data are being handled, and HDDs that are more compact yet have larger capacity are being requested of the HDD market.

Responding to the market needs for more compact size and larger capacity, in 1999 Fuji Electric began developing perpendicular magnetic recording media that used a perpendicular recording method(1) instead of the longitudinal recording method that had been in use previously, and pioneered the development of CoPtCr-SiO_2 granular perpendicular magnetic recording media(2), the mainstream perpendicular magnetic recording media currently on the market. Fuji Electric is presently advancing development toward higher recording densities by optimizing the manufacturing process, materials and layer structure of the CoPtCr-SiO_2 granular perpendicular magnetic recording media.

This paper describes Fuji Electric's efforts toward achieving higher recording density in the development of CoPtCr-SiO_2 granular perpendicular magnetic recording media, and also introduces the latest read-write evaluation technology which is indispensible for furthering the efficient development of perpendicular magnetic recording media.

2. Challenges in Realizing Higher Recording Density of CoPtCr-SiO_2 Perpendicular Magnetic Recording Media

In perpendicular magnetic recording media, the simultaneous realization of high thermal stability and low media noise is essential for realizing higher recording density. Namely, the challenge for realizing higher recording density is to reduce the recording bit volume V while increasing the aniaxial magnetic anisotropy constant K_u so that the magnetic energy, expressed as the product K_uV of the K_u value and the recording bit V, is maintained.

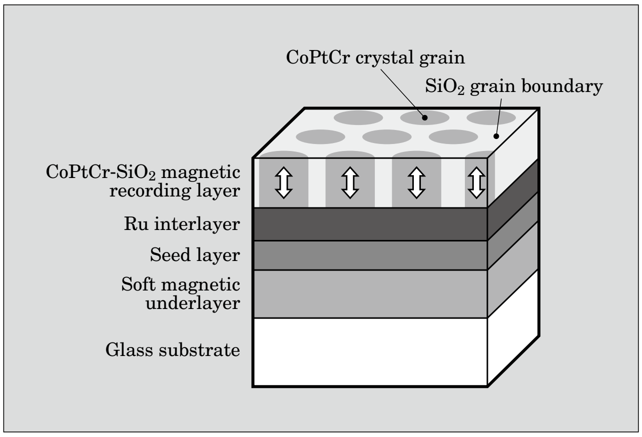
† Fuji Electric Device Technology Co., Ltd.

3. Efforts Toward Achieving Higher Recording Density in Perpendicular Magnetic Recording Media

3.1 Layer structure of CoPtCr-SiO_2 glass perpendicular magnetic recording media

CoPtCr-SiO_2 glass perpendicular magnetic recording media, as shown in Fig. 1, has a layer structure in which the characteristic soft magnetic underlayer of the perpendicular magnetic recording media is formed on a glass substrate, and formed above the underlayer are a seed layer and an interlayer for the purpose of controlling the grain size and crystalline orientation of the recording layer. Then, the CoPtCr-SiO_2 granular perpendicular magnetic recording layer, after having been formed, is covered by sequentially laminated overcoat layers of carbon, and finally the surface is coated with a lubricative layer.

Fig.1 Layer structure of CoPtCr- SiO_2 perpendicular magnetic recording media with glass substrate



3.2 Design of the composition of the CoPtCr-SiO_2 magnetic recording layer for higher recording density

(1) SiO_2 content and reduced media noise

In order to overcome the challenges encountered in realizing higher recording density in CoPtCr-SiO_2 perpendicular magnetic recording layer media, we examined the composition of the CoPtCr-SiO_2 granular perpendicular magnetic recording layer. With CoPtCr-SiO_2 perpendicular magnetic recording media, the media characteristics change significantly according to the percent composition of elements Pt and Cr and of SiO_2 with respect to Co in the magnetic recording layer, and therefore, the compositional design of the magnetic recording layer is a critical factor for achieving higher recording density. Consequently, we examined the effect of each of the above elements upon the media characteristics, and determined design guidelines for the magnetic recording layer composition.

To reduce media noise in CoPtCr-SiO_2 perpendicular magnetic recording media, it is important to improve the magnetic isolation among magnetic crystal grains while reducing the size of those magnetic crystal grains. In the control of magnetic crystal grain size, individual crystal grains of the magnetic recording layer must be grown epitaxially on the interlayer crystal grains in a 1:1 correspondence. Accordingly, in order to reduce the crystal size in the magnetic recording layer, the crystal size of the interlayer must also be reduced.

On the other hand, magnetic isolation among the magnetic crystal grains is thought to be dependent upon the amount of SiO_2 (grain boundary width) segregated to the grain boundary that surrounds the magnetic crystal grains. In other words, by increasing the amount of SiO_2 content, the grain boundary becomes thicker and as a result, isolation among the magnetic crystal grains is improved and a reduction in media noise can be expected.

Figure 2 shows cross-sectional TEM (transmission electron microscope) images of the interlayer of CoPtCr-SiO_2 perpendicular magnetic recording media and of the CoPtCr-SiO_2 perpendicular magnetic recording layer when the amount of CoPtCr-SiO_2 content is changed. Also, Fig. 3 shows a schematic drawing of the change in crystal grain size and of the layer structure of the magnetic recording layer in CoPtCr-SiO_2 perpendicular magnetic recording media as obtained from cross-sectional TEM images. The crystal grain size shown in the drawing is the sum of the boundary width and the actual magnetic crystal grain size. In the composition range of 0 to 11 at% SiO_2 content, the crystal grain size, including the grain boundary width, remains nearly unchanged, but as the amount of SiO_2 content increases, the actual magnetic crystal grain size, which does not include the grain boundary width, decreases steadily, and the grain boundary width increases proportionally. This region corresponds to the range extending from points (a) to (b) in the schematic drawing of Fig. 3.

Fig.2 Cross-sectional TEM images of CoPtCr-SiO_2 perpendicular magnetic recording layers

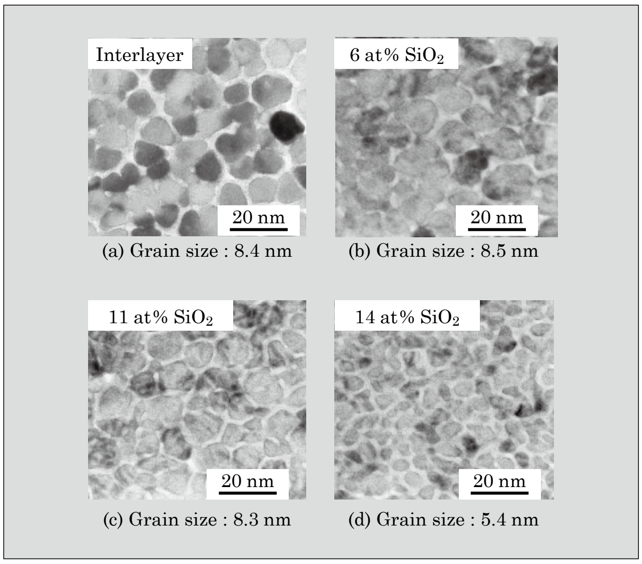
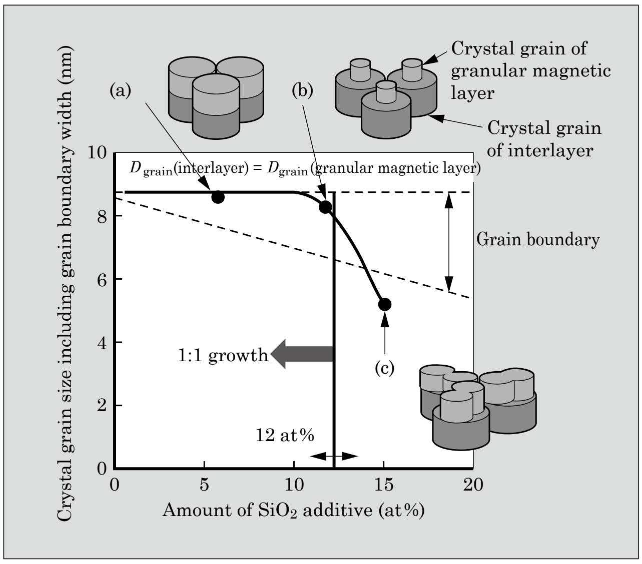


Fig.3 Schematic diagram of change in grain size and layer structure of CoPtCr-SiO_2 perpendicular magnetic recording layer



In this type of SiO_2 composition range, the crystal grain size of the interlayer and the crystal grain size of the magnetic recording layer (grain boundary width + magnetic crystal grain size) are approximately the same value, and as a result we can infer that the growth of one crystal grain in the magnetic recording layer on top of one crystal grain in the interlayer is implemented with a 1:1 correspondence. Moreover, from actual cross-sectional TEM images, clearly formed grain boundary structures and improved the segregation among crystal grains can be verified.

However, in the composition range where the SiO_2 content in the magnetic recording layer exceeds

12 at%, the crystal grain size in the magnetic recording layer decreases suddenly, and cross-sectional TEM images show deterioration in the degree of segregation of grains at several locations. Thus, in such a composition range where the SiO_2 content in the magnetic recording layer exceeds 12 at%, as can be seen in the schematic drawing of Fig. 3(c), multiple magnetic crystal grains having a small grain size and poor segregation are formed on top of a single crystal grain in the interlayer, and cross-sectional TEM images show the layer structure to be non-uniform. In other words, in compositions having a high concentration of SiO_2, the crystal size in the magnetic recording layer cannot be controlled by the crystal size of the interlayer. Namely, the optimal amount of SiO_2 to add to the magnetic recording layer depends on the crystal size in the interlayer, and the use of a magnetic recording layer composition containing this optimal amount of added SiO_2 enables a reduction in media noise.

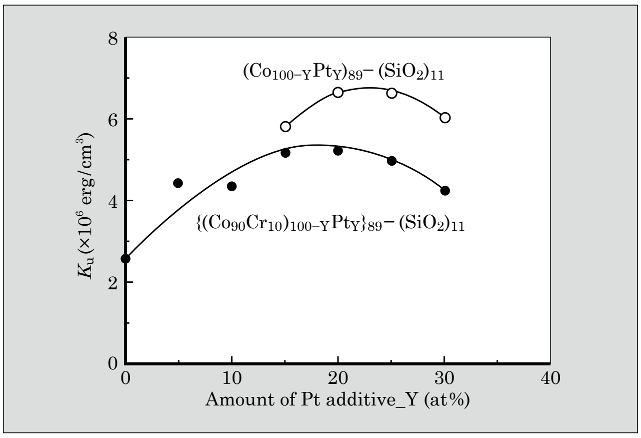
Given these findings, in order to achieve higher recording density in CoPtCr-SiO_2 perpendicular magnetic recording media, design guidelines for the magnetic recording layer composition increase the amount of SiO_2 added to the magnetic recording layer in order to decrease the actual magnetic grain size, which does not include the grain boundary width. Also, it is important to implement precise process control so as to maintain a 1:1 grain growth correspondence between the crystal grains in the magnetic recording layer and the refined and small-size crystal grains in the interlayer.

(2) Pt content and higher K_u value

A reduction in magnetic crystal grain size in order to realize higher recording density, however, leads to deterioration of the thermal stability. Accordingly, in order to increase the recording density of CoPtCr-SiO_2 perpendicular magnetic recording media, the K_u value must be increased to ensure the value of the thermal stability indicator of K_uV/kT (where V: volume of magnetic crystal, k: Boltzmann's constant, and T: absolute temperature). The K_u value of the perpendicular magnetic recording media depends largely on the amount of Pt added to the magnetic recording layer.

Figure 4 shows the dependency of the K_u value according to the amount of Pt content in CoPtCr-SiO_2 perpendicular magnetic recording media and in CoPt-SiO_2 perpendicular magnetic recording media, which does not have any Cr content. In the magnetic recording layer of the perpendicular magnetic recording media that was studied, the Cr content was fixed at 10 at% and the amount of SiO_2 additive was fixed at 11.2 at%. Regardless of whether Cr was added to the magnetic recording layer, the K_u value reached a gradual maximum when the amount of Pt additive was in the vicinity of 15 to 25 at%. Since media noise is large for the CoPt-SiO_2 alloy by itself, Cr is added and has the effect of reducing media noise, but even with a magnetic recording layer composition in which the Cr content is 10 at%, the K_u value of 5.3×10^6 erg/cm^3 is large. In compositions having a high Pt content, the lower K_u value is believed to be attributed to the formation of a fcc (face-centered cubic lattice) phase in the crystal grain.

Fig.4 Change in K_u value according to amount of Pt additive in CoPtCr-SiO_2 perpendicular magnetic recording media



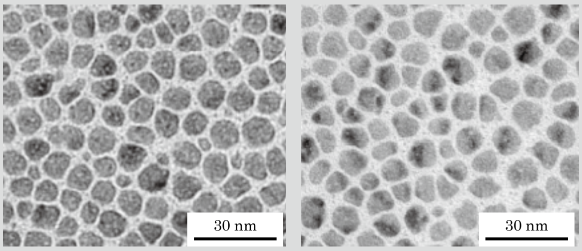
Thus, the K_u value of CoPt-SiO_2 perpendicular magnetic recording media can be controlled to a suitable value by the amount of Pt additive. However, increasing the amount of Pt in order to raise the K_u value leads to an increase in media noise. Therefore, when adding an amount of Pt to the magnetic recording layer, so that the desired media characteristics can be obtained for the required recording density, it is important that the magnetic recording layer composition be designed in consideration of and in balance with the percent of Co content.

4. Improved Media Characteristics by Optimizing the CoPt-SiO_2 Magnetic Recording Layer Composition

The example below describes the case in which, based on the abovementioned design guidelines for the magnetic recording layer, the CoPtCr-SiO_2 granular perpendicular magnetic layer composition was optimized for the material and crystal grain size of the existing interlayer in order to improve the media characteristics and realize a higher recording density.

Figure 5 shows cross-sectional TEM images of the magnetic recording layers in media that uses a magnetic recording layer having a conventional composition and in the CoPt-SiO_2 perpendicular magnetic recording media that uses a new magnetic recording layer developed by optimizing the magnetic recording layer composition. Except for the change in magnetic recording layer composition, both types of perpendicular recording media were fabricated with the same sputtering conditions. Both types of media exhibited the same total grain size of approximately 8.3 nm, which is the sum of the actual magnetic crystal grain size plus the grain boundary width. Because these values are approximately the same as the crystal grain

Fig.5 Cross-sectional TEM images of $CoPtCr\text{-}SiO_2$ perpendicular magnetic recording layers



Crystal grain size not including grain boundary width : 6.5 nm
Grain boundary width : 1.7 nm

(a) Conventional magnetic recording layer composition

Crystal grain size not including grain boundary width : 6.1 nm
Grain boundary width : 2.2 nm

(b) New magnetic recording layer composition

size of the interlayer, the individual crystal grains in the magnetic recording layer are assumed to grow in a 1:1 correspondence with the crystal grains of the interlayer. Moreover, although the total grain sizes were approximately the same, the magnetic crystal grain size and grain boundary width were 6.1 nm and 2.2 nm, respectively, in the new composition media and were 6.5 nm and 1.7 nm, respectively, in the convention composition media, indicating that the grain boundary width increased and the magnetic grain size was refined as a result of the optimization of the composition. These findings suggest that the initial objective of improving magnetic isolation among magnetic crystal grains and enhancing media characteristic can be attained. Therefore, we compared media characteristics of these types of perpendicular magnetic recording media.

Table 1 shows the values of coercivity H_c and signal-to-noise ratio (SNR) for these perpendicular magnetic recording media having different recording layer compositions. The H_c value for media having a conventional composition was of 8.2 kOe, while the H_c value for the new composition media was 9.3 kOe, thereby verifying an approximate 1 kOe increase in the H_c value. Moreover, a comparison of the SNR value also revealed an improvement of approximately 0.4 dB in the SNR value of the new composition media.

These findings clearly demonstrate that by optimizing the magnetic recording layer composition so as to closely match the interlayer material and crystal grain size, the media characteristics can be improved significantly. These findings are the results of improved magnetic isolation due to the increased grain boundary width which has been verified by cross-sectional TEM images. Applying these techniques, 2.5-inch media having a 160 GB capacity and a recording density of 250 Gbits/in^2 was commercialized in 2007.

However, in order to achieve next-generation 2.5-inch media with 250 GB capacities and recording densities of 400 Gbits/in^2 and above, further refinement of the interlayer's crystal grain size, which determines the magnetic crystal grain size, and optimization of the sputtering process and magnetic recording layer composition to refine the magnetic crystal grains and improve magnetic isolation are necessary, and such development is ongoing.

Table 1 H_c and SNR values of $CoPtCr\text{-}SiO_2$ perpendicular magnetic recording media

	Coercivity	Signal to noise ratio
	H_C (kOe)	SNR (dB)
Conventional magnetic recording layer composition	8.2	14.3
New magnetic recording layer composition	9.3	14.7

5. Evaluation Techniques for Perpendicular Magnetic Recording Media

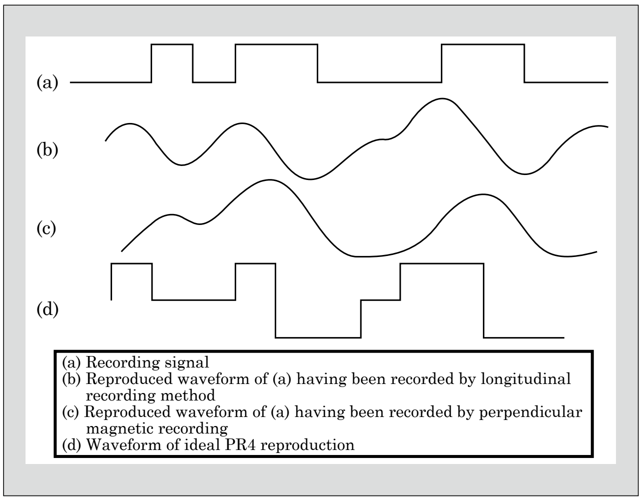
5.1 Evaluation of perpendicular magnetic recording media characteristics

Important factors for realizing higher recording densities in present-day HDDs include the establishment of perpendicular magnetic recording, and the advancement of technology for a media recording layer that simultaneously achieves both refinement and thermal stability, advancement of magnetic head technology for switching the magnetic field abruptly, reduction in spacing loss due to FOD (flying on demand) technology, and signal reconstruction techniques based on PRML (partial response maximum likelihood). Based on empirical knowledge acquired from the era of longitudinal recording, media characteristics had formerly been evaluated by examining the widely-known SNR value and analog signals such as overwrite, but because the signal processing carried out within an actual HDD was not considered, this type of media evaluation was inadequate as a technique for realizing higher recording densities. Here, as a representative evaluation indicator for magnetic recording media, an evaluation technique is introduced that identifies inherent problems in the widely used MF (middle frequency)–SNR and rectifies those problems.

5.2 Differences with conventional media from the perspective of record and reproduction

PR4 is a PRML method that is widely used in the reproduction signal processing of present-day HDDs. The PR4 method subtracts from an input signal string a string that has been shifted by two bits, and then outputs the result, and is based on a design philosophy of actively utilizing the mutual interference from signals of adjacent bits and obtaining the sign inversion of adjacent bits, i.e., a differential waveform. Essentially, this method was designed to make full use of the characteristics of longitudinal magnetic recording media in which magnetic flux leakage outside the media occurs at magnetic transition locations only, but with the popularization of perpendicular magnetic recording, this signal processing method continues to be used

Fig.6 Examples of reproduced signal waveforms of a recorded signal



even today.

Figure 6 shows (a), the recording signal waveform, and the results of signal processing to generate (c), a reproduced waveform of signal recorded by perpendicular magnetic recording, and (d), a reproduction waveform using the PR4 method. In the case of the PR4 method, in order to obtain the final PR4 output waveform from the relation between the actual recording signal and the reproduction signal, PR4 equalization is implemented using a FIR (finite impulse response) filter provided after the reproduction signal sampling. Specifically, in order to obtain the PR4 equalization signal y_n from the reproduction signal string $\{x_n\}$, equation (1) is computed with the FIR being expressed as a numerical sequence $\{a_n\}$.

$$y_n = \Sigma a_{n-k} x_k \quad \cdots\cdots (1)$$

A numerical sequence $\{a_k\}$ (FIR filter) is selected so that the waveform approaches the ideal PR4 waveform during this process. As shown in Figs. 6(a) and (b), with longitudinal magnetic recording, the record signal waveform and the reproduction signal waveform have a differential relationship, and the abovementioned FIR filter provides only compensation processing, but with perpendicular magnetic recording, the FIR filter is actually responsible for the differential processing.

Another significant difference with longitudinal magnetic recording media is the dependency on the SUL. The SUL not only facilitates recording by absorbing magnetic fields from the head during recording, but also has the effect of amplifying the signal during reproduction as a result of the polarization that occurs due to the recording magnetization. This polarization differs according to the magnetization switching distance and also according to the media structure. For example, the polarization increases for media having a shorter distance between the recording layer and SUL, and polarization also increases as the magnetization switching distance becomes longer, and since only low recording density signal intensities are amplified, the resolution appears to decrease. The FIR filter provided in a perpendicular magnetic recording HDD also implements restoration processing in consideration of the inter-symbol interference due to the SUL polarization.

5.3 Problems with the MF-SNR

MF-SNR, a typical evaluation index for magnetic recording media, is the ratio of recording signal intensity for 2-bit recording and reproducing to the noise intensity obtained by integrating the spectrum up to the 1-bit inversion frequency. This index is closely correlated to the error rate and has been highly regarded ever since the era of longitudinal magnetic recording. As described above, the MF-SNR used with perpendicular magnetic recording is different than the signal processing implemented with an actual HDD, and therefore the correlation with the error rate may be questioned.

With longitudinal magnetic recording, the waveform of a reproduction signal, i.e., the magnetic field that reaches the magnetic head from the media, closely resembles the signal of a waveform reproduced by the PR4-method, but differs significantly from that of perpendicular magnetic recording, and accordingly, the waveform of the signal to be evaluated, after having passed through a filter, differs from the waveform of a directly measurable signal prior to passing through the filter. Moreover, the reproduction signal waveform of perpendicular magnetic recording media is influenced by the media's structural factors, such as the SUL and interlayer thickness, and the FIR filters will be different if these factors are different. Accordingly, when evaluating perpendicular magnetic recording media, it is desirable to estimate a suitable FIR filter for each media, and then to evaluate the signal quality after the signal has passed through the filter.

5.4 Method of SNR evaluation by FIR filter transmission signal processing

A method of evaluating the SNR according to a signal that has passed through a filter, and the effectiveness of this method, are described below. First, the frequency dependence (linear recording density dependence) of the reproduction signal intensity is measured and the impulse response is computed, and then an inverse transformation applied to obtain an equalization filter. A filter obtained thusly is converted to the frequency domain by applying a Fourier transform, and is then multiplied by the reproduction signal power spectrum obtained from a spectrum analyzer, and the spectrum of the signal after having passed through the filter is obtained. The series of signal processing steps are shown in Fig. 7.

For an MF signal that has been recorded onto Fuji Electric's perpendicular magnetic recording media, Fig. 8 shows the noise spectrum of a reproduction signal as obtained by a spectrum analyzer and the noise spectrum after multiplication with a PR4 equalization

Fig.7 Signal processing steps with perpendicular magnetic recording

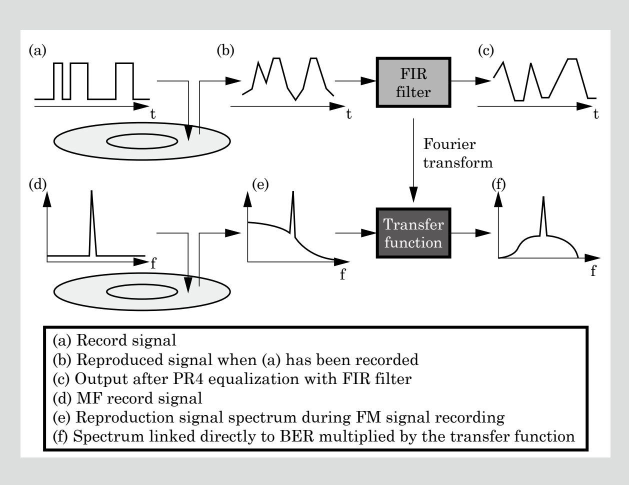
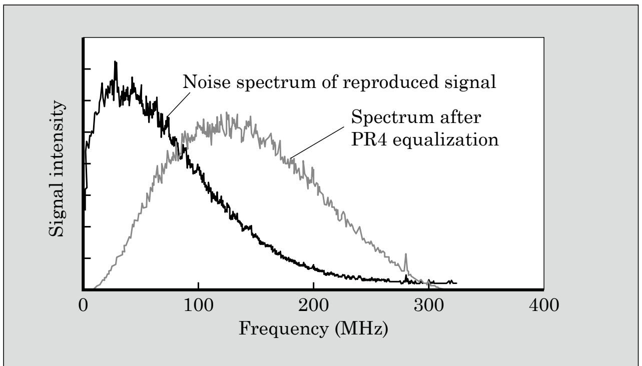


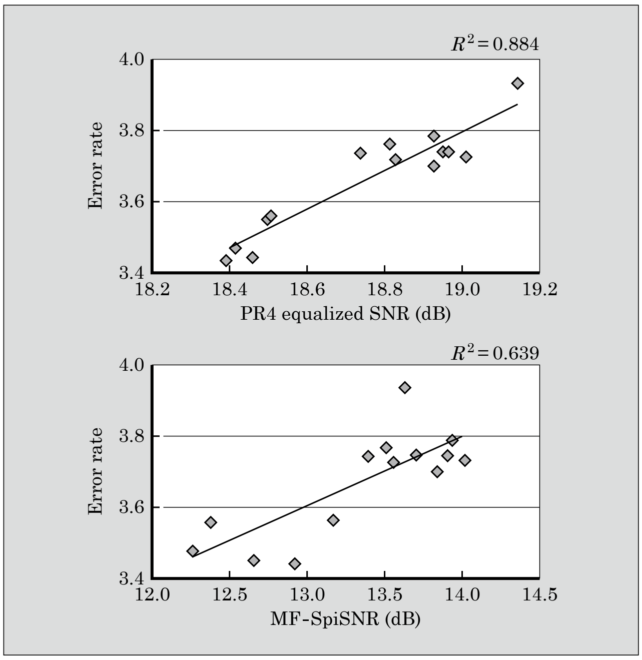
Fig.8 Noise spectrum after multiplication by PR4-equalized filter



filter. The noise intensity of the reproduction signal itself is concentrated in the low frequency region, but there is no effect on the SNR after PR4 equalization, and noise increases in the MF vicinity, and therefore the reduction of noise in the MF vicinity is important.

Figure 9 compares ordinary MF-SNR and PR4 equalized SNR values evaluated for various types of perpendicular magnetic recording media having different structures or compositions with actually measured error rate values. Using the SNR evaluation method described herein and only the additional hardware of a spectrum analyzer, dramatic improvements in the error rate which expresses the digital reproduction quality and the response thereto were observed.

Fig.9 Relationship between each SNR and measured error rate



6. Postscript

In order to respond in a timely manner to market requests for larger capacity HDDs, Fuji Electric is promoting close cooperation with external parties while advancing the development of higher recording density in perpendicular magnetic recording media. However, for the realization of recording densities greater than 1 Tbits/in^2, there is a limit to the extent that improvements can be made to the existing perpendicular magnetic recording media structure, and some sort of technical breakthrough is needed. In the future, technical development will shift its focus toward next-generation technologies such as discrete track media and thermal assist media, and Fuji Electric intends to establish these technologies at an early stage.

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(2) Oikawa, T. et al. Microstructure and magnetic properties of CoPtCr- SiO_2 perpendicular recording media, IEEE Trans. Magn., vol.38, 2002, p.1976-1978.

ECC Media Technology

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TuQiang Li †
Yoshiyuki Kuboki †

1. Introduction

Two years have already elapsed since Fuji Electric began mass-producing perpendicular magnetic recording media, and now perpendicular media accounts for a majority of Fuji's manufactured media. Areal density levels had stagnated at slightly more than 100 Gbits/in^2 with the longitudinal recording system, but progress is being made in the transition to perpendicular recording, and HDDs having areal densities on the order of 250 Gbits/in^2 are presently being mass-produced. Meanwhile, laboratory demonstrations of areal densities greater than 500 Gbits/in^2 have been reported, and areal densities are increasing at an annual rate of approximately 40% in mass-production and in the laboratory. Assuming that HDD areal densities will continue to increase at this rate, areal densities will reach 500 Gbits/in^2 in mass-production and 1 Tbits/in^2 in the laboratory during 2009. These types of high areal densities will be extremely difficult to realize by enhancing only the existing perpendicular media, and some sort of technical breakthrough is needed.

In order to increase the areal density, the track width must be reduced and the bit length shortened. To reduce the track width, the magnetic pole width of the recording head is made narrower, but this causes the recording field to decrease. Increasing the saturation magnetization B_s of the soft magnetic material used at the magnetic pole tip causes the recording field to increase, but the B_s value of the presently-used material is already approaching its theoretical limits and therefore this approach is not desired. In other words, with an increase in areal density, the recording head is predicted to become unable to perform write operations. On the other hand, in order to shorten the bit length, the magnetic reversal unit of the recording layer in the media must be reduced, but a smaller magnetic reversal unit leads to lower thermal stability. Namely, there is increased risk of erasing stored recorded data. Thus, to ensure thermal stability even when the magnetic reversal unit is small, the anisotropy of the magnetic material used in the recording layer may be increased. If anisotropy is increased, the magnetic field required for the recording, i.e., the switching field, will be increased further. As described above, an increase in the recording field of the head cannot be expected in the future, and therefore increasing the switching field of the media will cause the head to become unable to perform write operations. Thus, the three properties of "higher density", "write-ability" and "thermal stability" are difficult to achieve simultaneously, and this problem is known as the "tri-lemma of perpendicular media." The reason for mentioning the necessity of a breakthrough at the beginning of this paper is because a solution to this tri-lemma is thought to be difficult to achieve by extending the conventional implementation.

To solve this tri-lemma and realize higher densities, several candidate technologies including thermal assist recording and patterned media have been mentioned, and one such possibility having been proposed is ECC (exchange-coupled composite) media.(1) The results of simulations have been reported(2) as realizing up to the 1 Tbits/in^2 level, and show promise for the next-generation technology. Moreover, unlike thermal assist recording which requires that the head be equipped with a heat source and patterned media which requires that each bit must be physically segregated by microfabrication technology or the like, ECC media can be realized without any significant changes to the media or head, and is therefore highly advantageous from the perspectives of cost and manufacturing technology.

This paper describes the structure and features of ECC media and also discusses the development status of Semi-ECC media at Fuji Electric and future challenges for this media.

2. ECC Media

2.1 Principles and features of ECC media

Prior to discussing ECC media, we shall roughly estimate the media switching field when the specifications for 1 Tbits/in^2 level are satisfied. Using the same assumptions(2) as Greaves et al., and a crystal grain size of approximate-

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ly 6.5 nm which is the magnetic reversal unit, a magnetic layer thickness of 13 nm, and a $K_u V/kT$ value of approximately 60 (where K_u: uniaxial anisotropy constant, V: activation volume, k: Boltzmann's constant, T: temperature), a simple computation of K_u yields a value of approximately 5×10^6 erg/cm^3. Here, by setting the saturation magnetization M_s of the magnetic crystal grains to 750 emu/cm^3, the switching field in consideration of the demagnetization field can be roughly approximated as ranging from H_0 to 17 kOe. This is much larger than the switching fields of media presently being used in applications. It is also much larger than the 12 to 13 kOe magnetic field of the head considered with the method of Greaves et al.[(2)], and therefore recording cannot be accomplished with these specifications. Consequently, we concluded that media which satisfies the 1 Tbits/in^2 level specification cannot be manufactured with a simple structure. The thermal stability must be maintained while the switching field is reduced, and ECC media, with which this is feasible, is described below.

Figure 1 shows a schematic drawing of ECC media. The recording layer of the ECC media is constructed from 3 layers: a soft layer, a hard layer and a layer for controlling the exchange coupling energy between these layers. In the case of an ordinary laminated film, the soft layer and hard layer would be directly laminated together, but the provision of an interlayer between these soft and hard layers and suitable control of the exchange coupling energy enable the switching field to be decreased without decreasing the thermal stability.

Figure 2 shows the simulated interlayer coupling energy dependency of the switching field H_{sw} and the energy barrier E_b/kT. This calculation, similar to the method of Inaba et al., uses a simplified 2-spin model that sets a single spin for each magnetic layer for 1 grain. In the figure, the horizontal axis shows that coupling becomes weaker as the interlayer coupling energy approaches 0, and that the coupling becomes stronger as the interlayer coupling energy increases. For example, in the case of direct coupling without an inserted interlayer for controlling the coupling energy between layers, the characteristics become similar to those on the right edge of the figure, and in the case where the interlayer coupling is completely cut-off, the characteristics are as shown for an interlayer coupling energy of zero. Moreover, the figure shows that thermal stability increases as the energy barrier becomes larger. From Fig. 2, it can be seen that as the interlayer coupling energy is increased from 0, the switching field drops once and establishes a minimum, and then rises again and eventually saturates.

At its minimum value, the switching field falls to approximately one-half the value as at the time of direct coupling, and since the energy barrier does not change at this time, we found that the switching field could be reduced without changing the energy barrier. In other words, an easy-to-record media that maintains its thermal stability was realized. The control of interlayer coupling energy in the region indicated by arrows in Fig. 2 is important for obtaining these types of results with ECC media.

Fig.1 Schematic diagram of ECC media

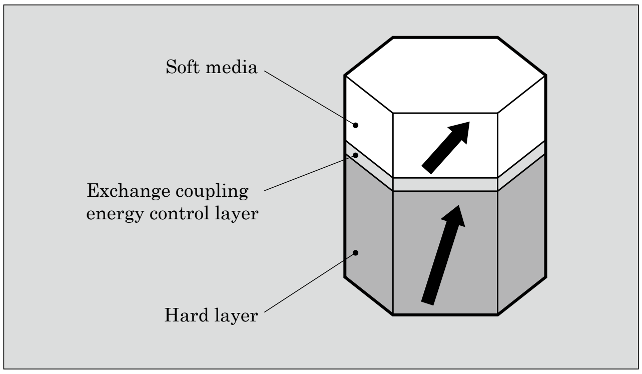
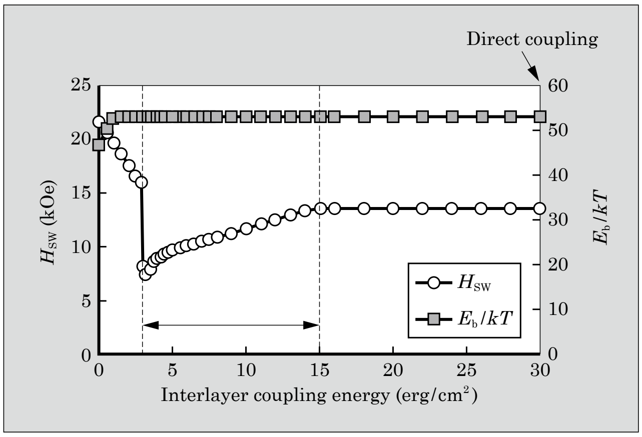


Fig.2 Exchange coupling energy dependency of switching field and energy barrier



2.2 Semi-ECC media

To fully utilize the advantages of ECC media and achieve high areal density, the following two measures are necessary.

(a) Increase the K_u of the hard layer (for example, set the K_u to at least 10^7 erg/cm^3)
(b) Increase the thickness of the soft layer (for example, set the thickness of the soft layer to at least half of the total thickness of the recording layer)

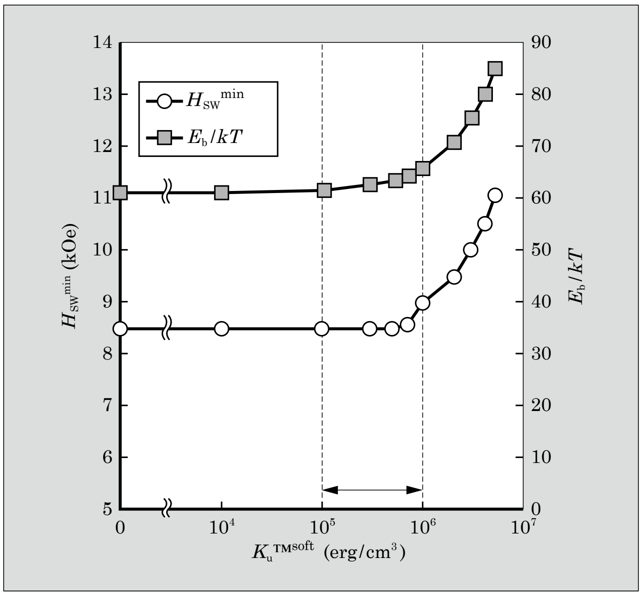
The reasons for the above are as follows.

(a) When the K_u of the hard layer is increased, thermal stability will increase, but the switching field will also increase.
(b) Increasing the thickness of the soft layer enables the switching field to be reduced significantly.

However, the following challenges exist.

(a) A practical magnetic material having a high K_u value and low noise and that satisfies requirements has not been found.
(b) Increasing the thickness of the soft layer is technically difficult.

Fig.3 K_u^{soft} dependency of minimum switching field and energy barrier



Thus, as a step toward a transition to ECC media, we examined media structures that do not use a soft layer.

Figure 3 shows K_u^{soft} dependency of the soft layer on the minimum switching field H_{sw}^{min} and energy barrier E_b/kT. The minimum switching field is shown as the switching field (Fig. 2) that becomes a minimum when the interlayer coupling energy is changed. Moreover, here, the hard layer K_u is set to 6×10^6 erg/cm^3, which is a value that can be realized even with a CoPtCr-SiO_2 granular magnetic layer[(3), (4)]. From Fig. 3, it can be seen that even when not using a completely soft magnetic layer with a soft layer K_u of 0, as long as $K_u^{soft} < 5 \times 10^5$ erg/cm^3, then there will be no change in the minimum switching field and the energy barrier. Moreover, both the minimum switching field and the energy barrier exhibit a sudden tendency to increase for values of $K_u^{soft} > 1 \times 10^6$ erg/cm^3. These results demonstrate that the selection of a semi-hard layer with a K_u^{soft} of 1×10^6 (erg/cm^3) as the soft layer enables ECC media that does not exhibit a large increase in the switching field and has only a slight increase in the energy barrier to be obtained. Fuji Electric calls this Semi-ECC media and is working to advance its development. Chapter 3 describes characteristics of actual prototypes of Semi-ECC media. Hereinafter, the layer provided between magnetic layers and that controls the coupling energy (Fig. 1) is referred to as the coupling layer.

3. Characteristics of Semi-ECC Media

3.1 Magnetic characteristics

Figure 4 shows the changes in the Kerr loop when the coupling layer thickness is changed, and Fig. 5 shows the coupling layer thickness dependency of the coercivity H_c and saturation magnetic field H_s. Here, the K_u values of the hard layer K_u^{hard} and $K_u^{semi\text{-}hard}$ of the semi-hard layer are approximately 5×10^6 erg/cm^3 and 1×10^6 erg/cm^3, respectively, and the composition and thickness of the magnetic layers are constant so that only the thickness of the coupling layer is changed. So as to correspond with Fig. 2, Fig. 5 is plotted with the coupling layer thickness set to zero for direct coupling, and the coupling layer thickness increasing along the horizontal axis in the direction toward the left side. The interlayer coupling energy increases along the horizontal axis in the direction towards the right side, and corresponds to Fig. 2. Moreover, the Kerr loops assigned numbers ①, ② and ③ in Fig. 4 correspond to the same numbers shown in Fig. 5. These results showed that if the interlayer coupling energy increases, i.e., if the coupling layer thickness decreases, then the switching field (at the level matching H_s) of the prototype Semi-ECC media falls once to reach a minimum value and then increases, and exhibits the same behavior as that predicted by simulation. More-

Fig.4 Kerr loop of Semi-ECC media

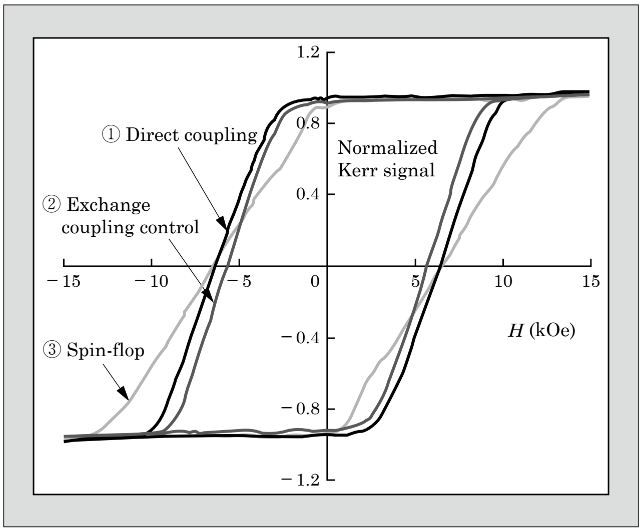
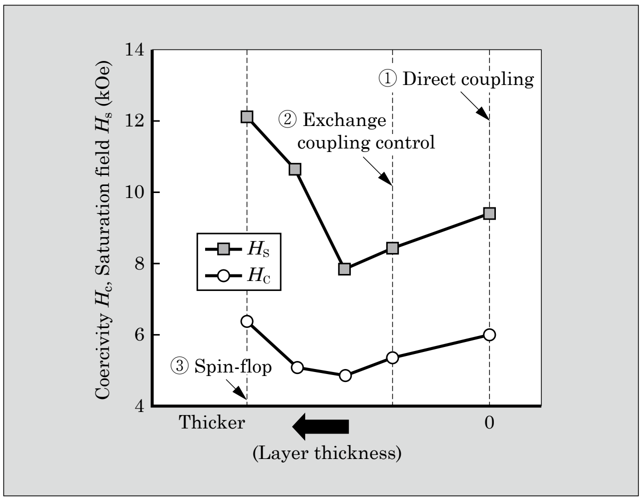


Fig.5 Coupling layer thickness dependency of H_c and H_s



over, it can be seen that in the case of direct coupling (①) and in the case where the interlayer coupling energy is controlled to near the minimum of the switching field (②), there are no significant differences in the shape of the Kerr loops, but in the region (③) where H_c and H_s increase dramatically, the Kerr loop assumes a two-step configuration, and its slope is also small (Fig. 4). In ③, at the region of the step, the magnetization of the semi-hard layer is believed to switch reversibly, and as a result, the switching field does not fall sufficiently. In Fig. 2, in order to increase the switching field in a region where the interlayer coupling energy is low, i.e., in a region of weak coupling (interlayer coupling energy < 3 erg/cm^2), a magnetization reversal process as in ③ is implemented.

These findings demonstrated the feasibility of manufacturing Semi-ECC media having the magnetic characteristics predicted through simulation. Therefore, next, we evaluated the read-write (R/W) performance and investigated whether write-ability and other characteristics had actually been improved.

3.2 R/W performance

Here, as in section 3.1, samples were manufactured without changing the composition and thickness of the magnetic layers, and with only the coupling layer thickness being changed. Since the write performance clearly deteriorates in a spin-flop state (③ of Figs. 4 and 5), this time, the thickness of the coupling layer was controlled so as to remain in a spin-flop free region on the Kerr loop.

Figure 6 shows the coupling layer thickness dependency of magnetic characteristics and R/W performance of the prototyped Semi-ECC media. Here, the coupling layer thickness increases along the horizontal axis in the direction to the right side. The magnetic characteristics in Fig. 6 show that H_c and H_s steadily decrease as the coupling layer thickness increases from the directly coupled state. This corresponds to the region extending from ① to ② in Fig. 5. At the maximum, H_c decreases by approximately 2.6 kOe (41%) and H_s decreases by approximately 3.6 kOe (35%), and a strong effect on "write-ability" is obtained. On the other hand, as the coupling layer thickness increases, although H_c and H_s steadily decrease, it can be seen that both the reverse overwrite (R-O/W: overwriting high density recorded data with low density data) and MF-SNR (middle frequency signal-to-noise ratio) have a tendency to increase up to a maximum value and then to decrease. At the maximum, R-O/W and MF-SNR are improved by approximately 20 dB and 2.3 dB, respectively, and a strong effect on R/W performance was verified. These results demonstrate that the adoption of a Semi-ECC structure leads to improvement in not only the magnetic characteristics but also the R/W performance.

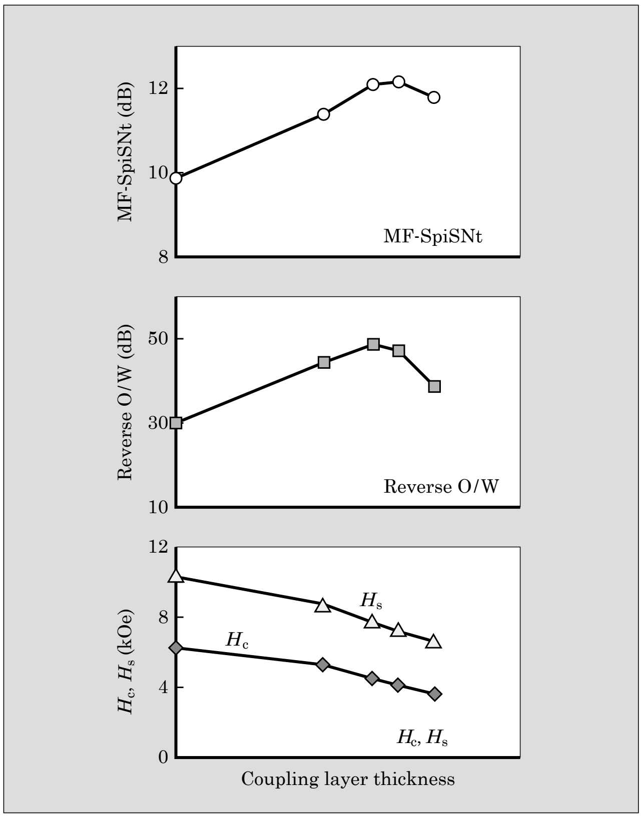
The reasons for differences in the magnetic characteristics and R/W performance when using coupling layer thicknesses in this region could not be clarified, but are presumed to be caused by the following.

(a) With Kerr loop measurements obtained using measuring times of approximately 30 seconds, noticeable steps and the phenomenon of increasing H_s were not observed. This is believed to be caused by successive reversals that occur due to the influence of thermal fluctuation of the two layers sandwiching the coupling layer.

(b) During extremely short time periods on the order of several nanoseconds, however, such as when recording with the head, thermal fluctuations have little effect and therefore a magnetic reversal behavior different from that during measurement of the Kerr loop is exhibited. In other words, there is the possibility that spin-flop states are being created dynamically.

In closing, the following section describes future challenges to be overcome in order to produce Semi-ECC media suitable for use in practical applications.

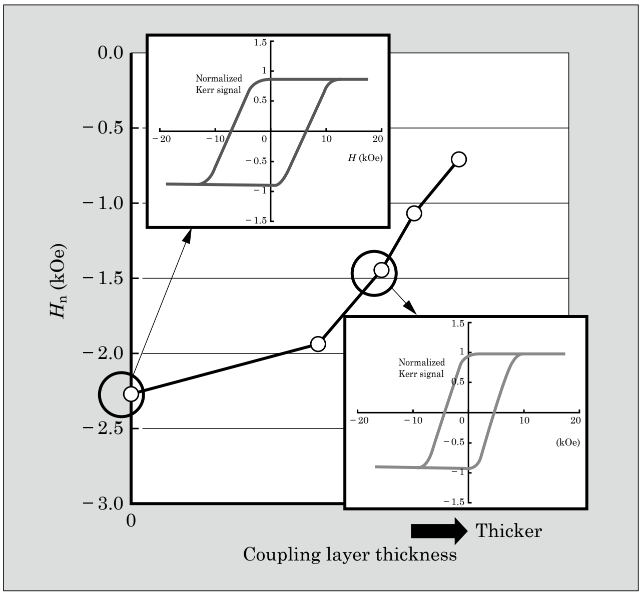
Fig.6 Coupling layer thickness dependency of magnetic characteristics and read-write performance



3.3 Future challenges

Figure 7 shows the coupling layer thickness dependency of the nucleation field H_n in the Semi-ECC media that exhibited the R/W performance described in section 3.2 above. H_n corresponds to the "shoulder" portion of a Kerr loop, and the larger the overhang on the minus side, the higher tolerance to the thermal fluctuation and stray fields. Similar to the tendencies

Fig.7 Coupling layer thickness dependency of H_n



of H_c and H_s in Fig. 6, Fig. 7 shows that the absolute value of H_n decreases as the coupling layer thickness increases. Under the conditions in which R-O/W and MF-SNR are at maximum values in Fig. 6, H_n is only approximately − 1.5 kOe and is insufficient in consideration of the thermal stability and a resistance to stray fields. In order to ensure a suitable value of H_n, increasing the K_u of the hard layer is effective, but as described above, it is not easy to increase the K_u in material that is suitable for practical use and exhibits noise low. Moreover, in addition to the specific challenge of ensuring a suitable H_n value in Semi-ECC media, achieving higher density presents several other challenges. The future challenges are enumerated below.

(a) Ensure a suitable H_n value
(b) Search for low-noise and high K_u magnetic material, or improve a process to realize lower noise in high K_u material
(c) Refine the magnetic layer crystal grain size or magnetic reversal unit

4. Postscript

A prototype of Semi-ECC media was manufactured, and a reduction in the switching field and an improvement in R/W performance were verified. In order to attain a level suitable for practical application, however, challenges clearly remain. Fuji Electric intends to overcome these remaining challenges through searching for suitable materials and improving manufacturing processes. In addition to the Semi-ECC structure, Fuji Electric is also verifying the excellent R/W performance that can be obtained from a laminated structure[4] provided with a K_u gradient. We also want to investigate new layer structures, such as a combination of this laminated structure and Semi-ECC.

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Glossary Hard layer and soft layer, Kerr loop, Reverse O/W and MF-SpiSNt

■ Hard layer and soft layer

The hard layer performs the role of stabilizing the recording, and is formed from permanent magnet material having a high coercivity H_c. Meanwhile, the soft layer performs the role of facilitating the recording, and is formed from material having a low H_c and relatively large permeability. ECC media suitably adjusts the coupling force between these layers to combine the attributes of both.

■ Kerr loop

When the surface of magnetized material is exposed to linearly polarized light, the polarization plane of the reflected light rotates. This is known as the magneto-optical Kerr effect (MOKE). The rotation angle is proportional to the magnitude of the magnetization, and therefore, a loop resembling the magnetization curve can be obtained by measuring the rotation angle while applying an external field. This is known as the Kerr loop. For perpendicular magnetic recording media, measurement of the magnetization curve is difficult due to the effect of a soft underlayer (SUL), and therefore the MOKE, which can be measured in a nondestructive manner, is often used to evaluate magnetic characteristics.

■ Reverse O/W and MF-SpiSNt (Explanation of vertical axis of Fig. 6 on page 20)

Reverse overwrite (R-O/W) is the ratio of the record signal and erase signal strengths when overwriting on low density data high density recorded data. Higher R-O/W values indicate better “write-ability.”

MF-SpiSNt is the signal-to-noise ratio at one-half the maximum recording frequency. Higher MF-SpiSNt values indicate that bits can be recorded at higher densities.

Present Status and Future Prospects for Photoconductors

Mitsuru Narita †

1. Introduction

In today's changing business environment, the social responsibilities of corporations with regard to globalization, deregulation, structural reform and environmentally friendly practices are becoming more important. Under these circumstances, the provision of new products and valuable product services is important in order to compete successfully in the global market. For these types of business activities, IT is becoming an increasingly important tool to be used, and the popularization of the Internet is driving rapid advances in IT. Consequently, network-connected offices and home environments are also changing, and the importance of information transmission and reception capability is increasing.

For example, the network functions of image input/output-capable devices such as cell phones, personal computers, printers, digital copiers, electronic paper and scanners are rapidly being advanced. Under these circumstances, printers and copiers that display and record color information and images provide a role of growing importance.

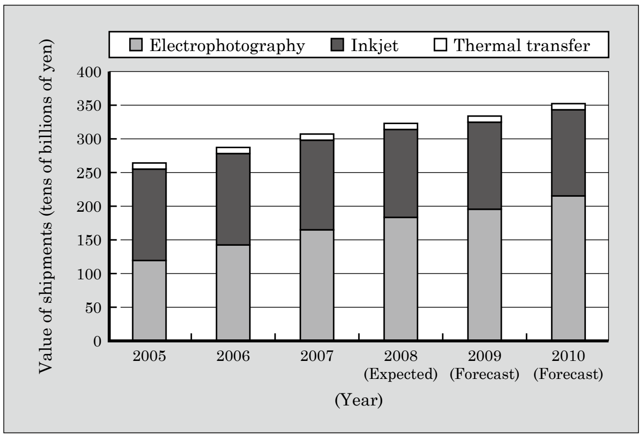
This paper describes the market trends of these printers and copiers and, as a subset thereof, the trends of electrophotographic printers and copiers, and also provides an overview of Fuji Electric's photoconductors that correspond to these trends.

2. Market Trends of Printers and Copiers

As a means of communicating text and images, soft copies (displayed images) and printed hard copies (printouts of the information) have been used.

Technology for soft copies, as typified by liquid crystal and organic EL (electroluminescence) displays, has made amazing advances and will come into even wider use in the future. Hard copies use paper media, the consumption of which is continuing to grow steadily, and various reasons can be given to explain this continued growth, but the major factors are believed to be paper's ability to combine various functions such as display, write, save and transmission, and also paper's inherent characteristics of being a lightweight and easy-to-use media.

Fig.1 Changes in worldwide value of shipments of color hard-copy machines



In the computer output sector, hard copy methods are broadly classified into an inkjet method which is popular for personal use and an electrophotographic method which is popular for office use. The inkjet has the features of inexpensive device cost, color compatibility and special-use paper, while the electrophotographic method has the features of low running cost, speedy operation and of compatibility with ordinary paper.

Figure 1 shows the market forecast for various types of color hard copy machines. In 2007, the overall color hard copy market exhibited an approximate 7% year-on-year increase. The electrophotography market, however, driven by increased demand for color printers and color copiers, experienced even larger growth of approximately 16%. Large future growth is forecast for electrophotography. Inkjet printers and electrophotography will become competing technologies in the future, but by fully utilizing the advantages of each, future growth is expected for both methods.

3. Trends of Electrophotography

The demand for color electrophotographic printers

† Fuji Electric Device Technology Co., Ltd.

and copiers has been trending upwards for the past several years, and especially due to the aforementioned advances in networking, colorization is progressing and demand for both types is continuing to increase. Also, structural changes in these printers and copiers are expected in the future in order to extend applications to the high-speed light printing field and to provide reduced power consumption and other technological advances in response to changes in the business environment.

3.1 Printers

Trends for shipments of electrophotographic-type monochrome printers, color printers, monochrome copiers and color copiers are shown in Fig. 2. In 2007, the shipment volume increased by 8% year-on-year for monochrome printers, but even more rapid was the 25% year-on-year increase for color printers. Large future increases in the shipment volume of color printers are forecast, and the market is expected to expand.

Fig.2 Changes in worldwide volume of shipments of electrophotographic devices

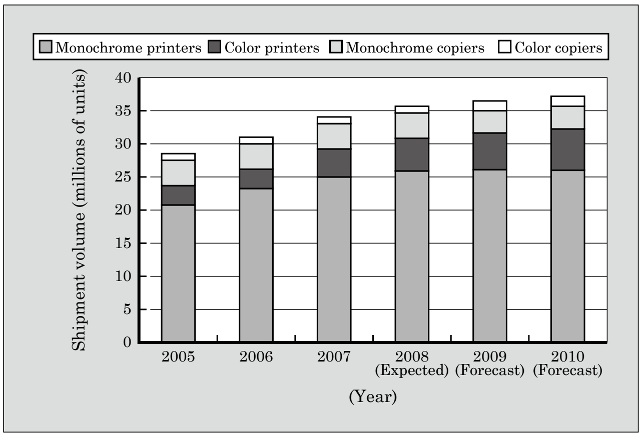
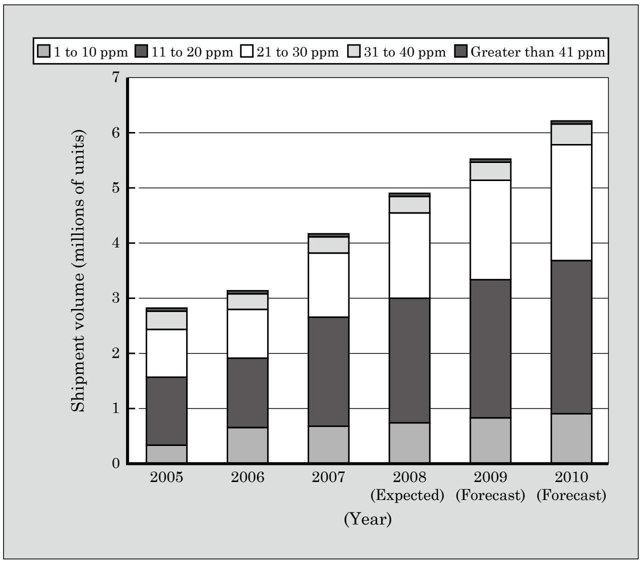


Fig.3 Changes in worldwide volume of shipments of color laser printers by speed



As can be seen in Fig. 3, color printers having output speeds of 10 ppm (pages per minute) and less experienced little growth, and 11 ppm and higher speed printers are expected to become the mainstream in 2007 and beyond. In this scenario, rather than the printing method used by low-speed copiers (4 cycle engine method) wherein a single photosensitive drum sequentially prints 4 colors, the method used by high-speed copiers (tandem engine method) wherein four photosensitive drums are arranged in series and each photosensitive drum prints a single color is expected to become the mainstream method.

The photoconductors used in color printers are required to provide high image quality, and in particular, high resolution and the required stable light attenuation characteristics for good color reproducibility. Moreover, especially in the tandem method above, the photoconductors are required to provide high dimensional accuracy in order to suppress color drift by the four colors.

Another trend in the printer industry is the progress toward light printing. On-demand printing is becoming more prevalent with increased information networking. Specifically, on-demand printing is used for small lot printing of newspapers, magazines, catalogs, and for onsite printing, and this is a new field that leverages the high-speed and convenience of electrophotographic printing. The photoconductors used in this field are required to provide high sensitivity and high-speed response corresponding to the printing speed, a suitable durability for the service life, and the high resolution sought for offset printing. Positive charge single-layer photoconductors, having a degree of resolution that does not deteriorate even if their outer film is removed, have been reported as the optimal photoconductors. Also, high resolution printers that use liquid toner instead of conventional dry toner have been announced, and photoconductors suitable for these printers are also being developed.

3.2 Copiers

The trend toward digitization is also advancing in the copier field. Figure 4 shows the changes in the worldwide volume of copier shipments. The overall shipment volume is trending toward saturation. Within this overall trend, however, shipments of color digital copiers are increasing while shipments of monochrome digital copiers are decreasing. The saturation is a result of printers being increasingly provided with MFP (multifunction peripheral) capabilities, and being positioned in the marketplace as an alternative to copiers. Figure 5 shows changes in the worldwide volume of shipments of copiers by speed. High-speed printers having image output rates of 21 cpm (copies per minute) and above show healthy growth, but those having output rates of 20 cpm and below exhibit a decreasing trend. The photoconductors used in copiers are required to provide such characteristics as high-speed re-

Fig.4 Changes in worldwide volume of shipments of copiers

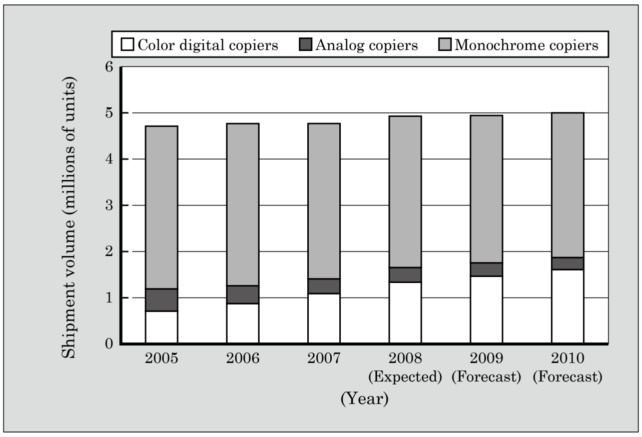
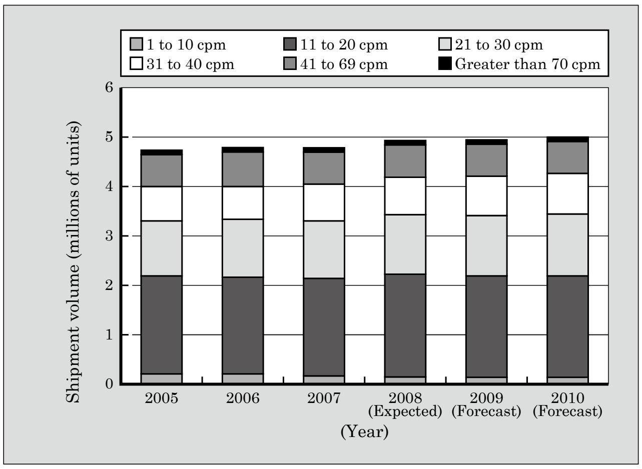


Fig.5 Changes in worldwide volume of shipments of copiers by speed



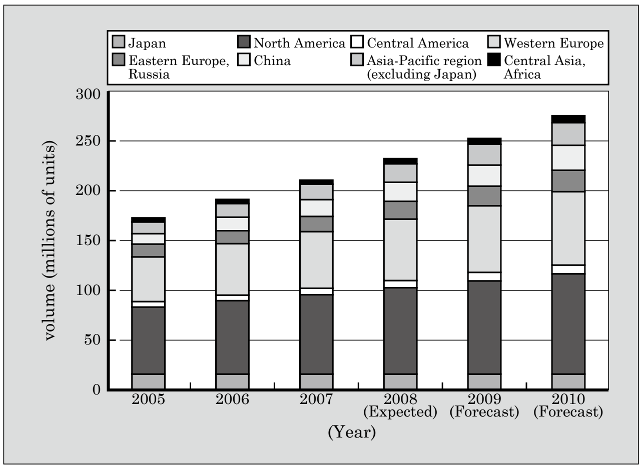
sponse, high durability and a wide range of gradation levels for reproducing half tones in graphic images, and to realize light attenuation characteristics suitable for copier processes.

3.3 Photoconductors

The types of photoconductors used in the above-mentioned electrophotographic printers and copiers include organic photoconductors (OPC), selenium photoconductors, amorphous silicon photoconductors and so on. Figure 6 shows the changes in worldwide volume of production of these photoconductors. Healthy growth at a annual rate of approximately 8% is shown. Moreover, the majority of consumption is presently concentrated in North America and Western Europe, but in the future, demand is expected to increase in Eastern Asia, Russia, China and the Asia Pacific regions. Driven by the increasing usage of color printers, on-demand printers and digital copies, in the future, a new market may be formed for electrophotographic devices that use these photoconductors, and further growth is anticipated.

The photoconductors characteristics necessary to support future new advances are summarized below.

Fig.6 Changes in worldwide volume of production of photoconductors



(a) Color printers: High resolution, color reproducibility, high precision
(b) On-demanding printing: High sensitivity, high-speed response, high durability
(c) Digital copiers: High-speed response, high durability, wide range of gradation levels

4. Overview of Fuji Electric's Products

Fuji Electric commercialized and began selling selenium photoconductors in 1973 and OPCs in 1988. Subsequently, Fuji Electric quickly and flexibly responded to the rapid advances in electrophotographic technology and expanded its business globally to include the development, production and sales of photoconductors, which are the core parts of printers and copiers, and to the peripheral devices.

Fuji Electric has three production sites, a domestic site in the Matsumoto area of Japan, U.S. Fuji Electric Inc. in the US, and Fuji Electric (ShenZhen) Co., Ltd. in the ShenZen area of China. In the first half of 2006, OPC production was integrated into the ShenZen area production work to support worldwide demand more efficiently.

Fuji Electric (ShenZhen) Co., Ltd. is the site of production for magnet rollers, toner cartridges and other peripheral products. At present, many printer manufacturers and copier manufacturers have located their equipment assembly operations in China and other Asian countries, and the production of photoconductors and their peripheral components in China is thought to provide considerable convenience.

4.1 OPCs

Fuji Electric is poised to respond to the diversified needs of customers and has prepared a product lineup of various types of photoconductors compatible with the light source wavelengths of printers and copiers so that clear images can be obtained.

Table 1 lists Fuji Electric's OPC product line-up.

Table 1 OPC product lineup

Type	Features		Uses
	Charging polarity	Layer structure	
Type 8	Negative	Stacked-layer type	Printer, facsimile, multifunction device
Type 9	Negative	Stacked-layer type	Analog copier
Type 10	Negative	Stacked-layer type	Digital copier, multifunction device
Type 11	Positive	Single-layer type	Printer, facsimile, multifunction device, light printing

(1) OPCs for use in printers

Fuji Electric has commercialized the type 8 OPC for use in printers, and has prepared a product lineup capable of supporting a wide range of potential responses and sensitivities, for low-speed printers to high-speed printers. For organic material (charge generating material, charge transporting material, and so on) in particular, Fuji Electric continues to work toward developing computer-assisted molecular design technology and other material design technologies, dispersion techniques for coating and liquefying material and coating technology for finishing OPCs, and is able to support a wide range of customer needs such as providing the high level of resolution and color image reproducibility characteristics required for color printers.

In order to reduce the amount of toner consumption, Fuji Electric focused on the adhesion of the photoconductor and toner and proposed various physical properties from the perspectives of both the photoconductor and the toner.

As for the dimensional accuracy of the drum, advances in element tube processing technology and the high precision design of the gears have enabled the realization of excellent rotational stability.

(2) OPCs for use in copiers

Two series of photoconductor products have been commercialized, type 9 for use in analog copiers and type 10 for use in digital copiers.

For copier-use, Fuji Electric has arranged a lineup of OPC products that satisfy the requested high-speed response, high durability and range of gradation levels, and is working to develop and design new materials in order to further improve the characteristics of these OPCs. In particular, OPCs for use in digital copiers are strongly requested to provide a long service life and good electric potential stability, and as a result of molecular design technology for OPC binder material and various additive technologies for electric potential stability, high performance photoconductors have been commercialized.

(3) Positive charge single-layer OPC

While expanding the series of photoconductor products compatible with the negative charge method, Fuji Electric is also working to develop a positive charge type photoconductor that facilitates the realization of higher picture quality and helps reduce the amount of ozone emission in the environment. To realize such a photoconductor, the development of electron transport material having high mobility was essential. Fuji Electric succeeded in independently synthesizing the materials, and then commercialized them in 1999.

As is well known, positive charge type OPCs generate low amounts of ozone, even when corona discharge is used for the charging process, and because light absorption and charge generation occur at the surface of the photoconductor, positive charge type OPCs enable higher resolution.[1] Furthermore, compared to the stacked-layer type, positive charge single-layer OPCs have better response and environmental characteristics, and use a simple coating process that improves their ease of manufacture. To fully utilize these characteristics, applications to monochrome printers, color printers and on-demand printers are being advanced, improvements are being made to realize higher sensitivity and the application range is being expanded to also include high-speed printers.

4.2 Peripheral products

Using electrophotographic process technology which has been cultivated over many years, Fuji Electric designs, develops and produces process units that integrate the charging unit, of which a photoconductor is the core component, the developing unit and the cleaning unit for electrophotographic printer and copiers. In particular, owing to advances in element tube processing technology for photoconductors, and advances in miniature surface processing technology and thin film coating technology, the developing sleeve used for the developing unit is being installed in both monochrome printers and color printers.

5. Postscript

As a result of the evolution and progress of the Internet, the use of electrophotographic technology in digital and color applications is increasing by leaps and bounds. Performance expectations are increasing for photoconductors to achieve more vivid image quality and higher durability. In response to these market requests, Fuji Electric will undertake the challenge of improving material design technology, commercialization techniques and production technology, and intends to develop technology that is beneficial to our customers. We will also concentrate the collective power of all the Fuji Electric groups to strengthen our technical capabilities, and provide high performance and highly reliable products in response to customer needs.

Reference

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Material Technology for Organic Photoconductors

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Seizo Kitagawa †
Shinjiro Suzuki †

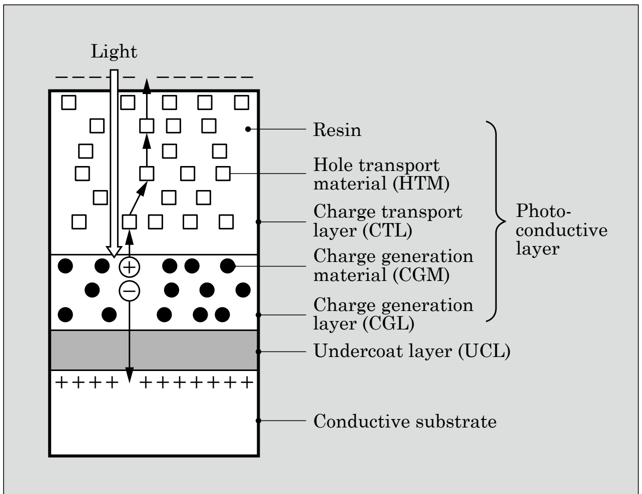
1. Introduction

In recent years, as the trends toward digitization, coloration and network connectivity have advanced for printers, copiers, facsimile machines, printing presses and other electrophotographic equipment equipped with photoconductors, government and business documents as well as personal documents are increasingly highly dense and contain large amounts of information, and the number of pages to be output is also increasing.

Accompanying these market trends are requests for photoconductors to provide higher sensitivity, higher responsiveness, higher resolution and higher stability, and to be smaller in size and have lower cost. In order to satisfy these requests, Fuji Electric is commercializing organic photoconductors having various characteristics.

This paper presents an overview and describes the characteristics and progress of materials technology and chemical technology, which are fundamental technologies for these organic photoconductors.

Fig.1 Layer structure of negative charge multilayer type OPC



2. Organic Photoconductors

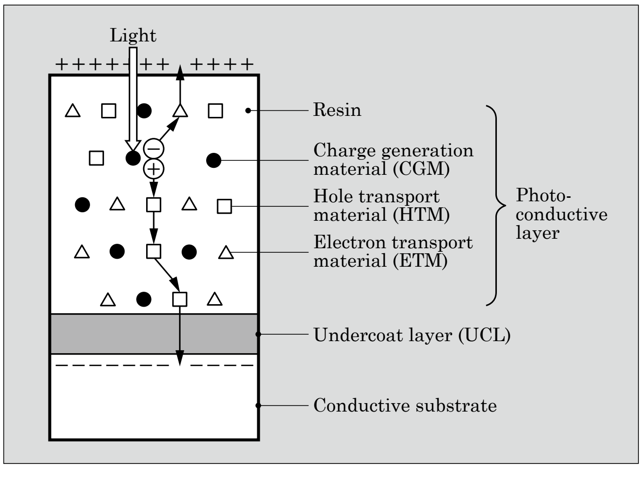
Organic photoconductors (OPCs) utilize the potential difference created on a photoconductive surface to form an image, and in principle, the polarity of the potential, whether positive or negative, makes no difference.

An OPC having an image forming potential that is positive is called a positive charge type OPC, and if negative, is called a negative charge type OPC. Figure 1 shows a negative charge multilayer type OPC, and Fig. 2 shows the layer structure and operating principles of a positive charge monolayer type OPC.

The negative charge multilayer type OPC has a function-separated multilayer structure and is fabricated by first providing an undercoat layer (UCL) made of resin or the like on a conductive substrate such as an aluminum tube, and then providing a charge generation layer (CGL), formed from charge generation material (CGM) and resin or the like, on the UCL, and then providing a charge transport layer (CTL), formed from a hole transport material (HTM), which is a type of charge transport material (CTM), and resin or the like, on the CGL.

The positive charge monolayer type OPC is fabricated by providing, as necessary, a UCL made of resin or the like on a conductive substrate such as an alumi-

Fig.2 Layer structure of positive charge monolayer type OPC



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num tube, and then providing a photosensitive monolayer of CGM, HTM, and electron transport material (ETM), which is a type of CTM, on the UCL.

Moreover, positive charge multilayer type OPCs are also being developed, and have a structure, for example, in which a CTL formed from HTM, resin and the like is provided between the UCL and photosensitive layer of the positive charge monolayer type OPC.

When the surface of a photosensitive layer is charged by corona discharge or contact electrification and then exposed, both positive and negative charges are generated at the CGM. The positive charges travel through the HTM, and in the case of a negative charge type OPC, arrive at the photosensitive layer surface, or in the case of a positive charge type OPC, the positive charges pass through the CTL and UCL and arrive at the substrate. On the other hand, negative charges, in a negative charge type OPC, pass through the UCL and arrive at the substrate, while in a positive charge type OPC, the negative charges travel though the ETM and arrive at the photosensitive layer surface. As a result, the surface charge on a photoconductor is neutralized, and the potential differences between exposed and unexposed areas cause the formation of electrostatic latent images. Subsequently, latent images are visualized with the toner (colored resin ink powder), and then processes for transferring, heating, melting and fixing the toner to paper are performed to generate a hard copy.

3. Material Technology, Chemical Technology

3.1 OPC material

Table 1 lists the main materials used in OPCs. Such materials include UCL material, functional materials such as CGM, HTM, ETM and the like, film formation material such as various resins, additives for high-performance, etc.

For OPCs to become widely accepted in the marketplace, the performance of each material, i.e., functional material, film formation material, additives, etc., must be designed for optimal mutual balance, and this is one of the challenges of OPC materials technology. Fuji Electric is able to leverage its proprietary materials technology to not only provide materials that satisfy current market needs, but also to provide new functions that expand the market.

(1) UCL materials

UCL materials are requested to provide such diverse functions as adhesion with the conductive substrate, a smoother conductive substrate surface, charge blocking, easy application of an overcoat layer, and stability of the UCL coating solution. These functions are realized with conductive materials, film formation materials, additives, and the like.

Fuji Electric uses proprietary molecular design technology to develop and apply new high-performance film formation materials, and aiming to realize even higher resistance to humidity and higher resistance to dielectric breakdown, continues to advance the development of new materials.

(2) CGL materials

CGL materials are requested to provide such diverse functions as adhesion with the UCL, a large quantum effect in response to the exposure light, charge blocking, easy application of an overcoat layer, and stability of the CGL coating solution. These functions are realized with charge generation materials, film formation materials, additives, and the like.

Fuji Electric uses proprietary synthesis reaction technology and process control technology to develop and apply high-performance and highly stable charge transport materials. Aiming to achieve compatibility with even higher sensitivities and color gamma characteristics, Fuji Electric continues to advance the development of new materials.

(3) CTL materials

CTL materials are requested to provide such diverse functions as adhesion with the CGL, good charge retention, good charge injection performance, good transport of the injected charge, printing durability, resistance to oxidizing gases, resistance to greases and oils, and stability of the CTL coating solution. These

Table 1 Typical OPC materials

Layer		Constituent material	
Photosensitive layer	Charge transport layer (CTL)	Hole transport material (HTM)	Arylamines, hydrazones, stilbenes, benzidines, etc.
		Electron transport material (ETM)	Azoquinones, etc.
		Film formation material	Polycarbonates, polyesters, polystyrenes, etc.
		Additive	Materials for enhancing photoconductor characteristics, ancillary materials for film formation, materials for suppressing deterioration of the coating solution, etc.
	Charge generation layer (CGL)	Charge generation material (CGM)	Phthalocyanines, azos, etc.
		Film formation material	Polyvinylacetates, polyketals, etc.
		Additive	Materials for enhancing photoconductor characteristics, ancillary materials for film formation, materials for suppressing deterioration of the coating solution, etc.
Under coat layer (UCL)		Conductive material	Metal oxides, etc.
		Film formation material	Polyamides, polyesters, melamines, etc.
		Additive	Materials for enhancing photoconductor characteristics, ancillary materials for film formation, materials for suppressing deterioration of the coating solution, etc.

functions are realized with charge transport materials, film formation materials, additives, and the like.

Fuji Electric uses proprietary molecular design technology to develop and apply additives that prevent the deterioration of coating solutions and OPC and additives that enhance durability. Aiming to achieve even higher durability and higher image quality, Fuji Electric continues to advance the development of new materials.

3.2 Molecular design technology

Figure 3 shows an example of the molecular design process flow. In the past, this design work was implemented experimentally and then verified.

In recent years, as a result of improved computational algorithms and higher speed computers, computer-assisted molecular design technology has been utilized in practical applications.[1] Fuji Electric is installing molecular design systems, and is configuring proprietary hardware, improving software, setting parameters, and analyzing data in accordance with OPC materials to establish computer-assisted molecular design technology and to shorten the development time. Aiming to further increase OPC functionality, this computer-assisted molecular design technology is being applied to develop such new materials as functional materials, polymeric materials, additives and the like.

3.3 Synthesis technology

(1) Synthesis reaction technology

Molecularly-designed OPC material is synthesized by chemical techniques, and a synthesis reaction having the highest possible purity and yield must be selected.

For example, high purity and high yield synthesis reactions have evolved using synthesis route design technology such as retrosynthesis[2], which deconstructs a final target material to identify constituent raw materials, and innovative high reactivity reactions such as Suzuki reactions[3] that use new catalysts.

Fuji Electric also uses appropriate catalysts, which are an important element of Suzuki reactions, to establish highly functional, low cost synthesis reactions that are also safe and that restrict sudden increases in the synthesis reaction temperature.

(2) Process control technology

The process control during synthesis requires a shift from the perceived emphasis on chemical material synthesis to that of electronics material synthesis.

Figure 4 shows an example of temperature control during a synthesis reaction. For a set value, OPC material having a certain function could not be synthesized under the condition of a $\pm 0.5\,°C$ temperature allowance during a stable reaction, but under the condition of a $\pm 0.1\,°C$ temperature allowance, a material having the intended function was obtained with a high yield.

Fuji Electric utilizes plant technology and process control technology to manufacture OPC material according to the precise process control for synthesis reactions as used by electrical machinery manufacturers.

3.4 Purification technology

Table 2 lists an example of purification technology. Purification technology is essential for realizing the full functionality of an OPC.

Fuji Electric utilizes individual purification tech-

Fig.4 Relation between process temperature control and yield

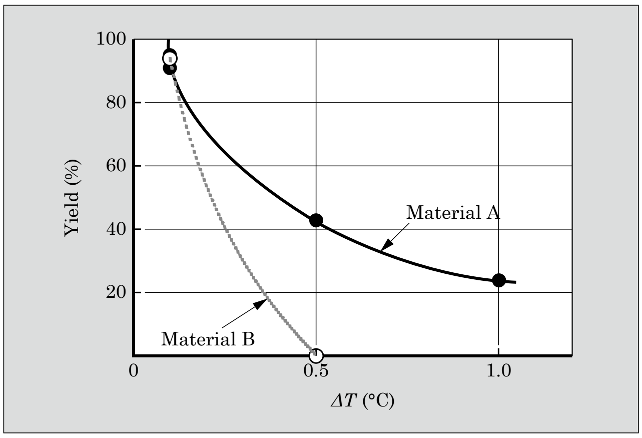


Fig.3 Example of molecular design process flow

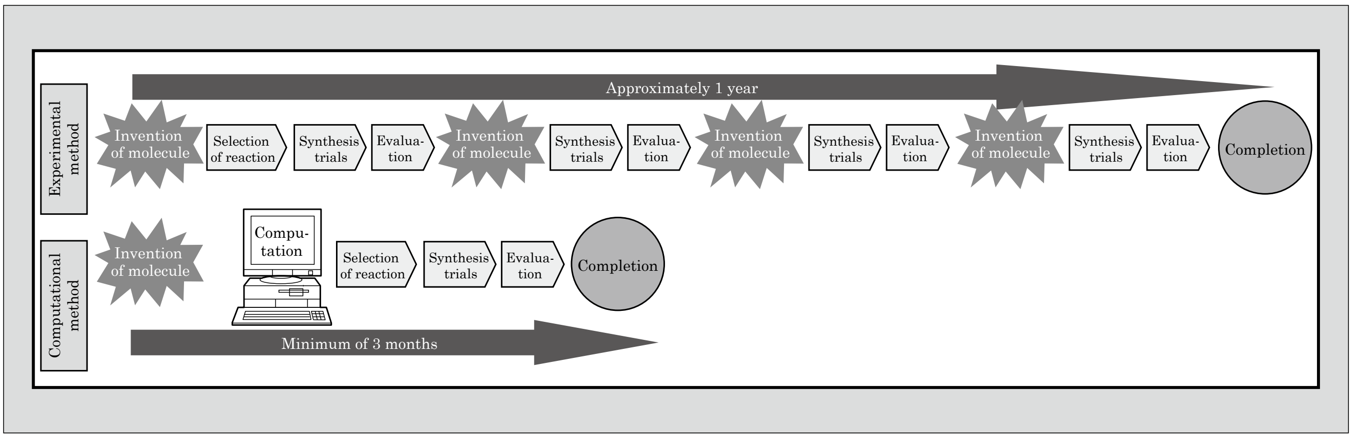


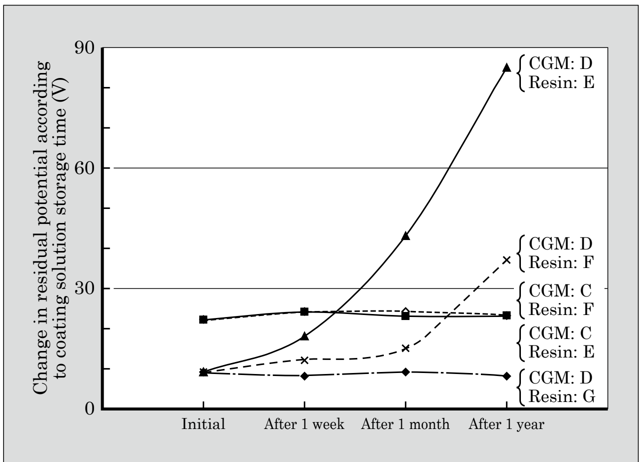
Table 2 Typical purification technology

Purification principle	Purification method
Solubility	Recrystallization, etc.
Distribution of absorption and desorption	Charcoal absorption, alumina absorption, silica gel absorption, zeolite absorption, column chromatography, etc.
Boiling point	Distillation at normal pressure, vacuum distillation, etc.
Sublimation point	Vacuum sublimation, etc.

Table 3 Typical material inspection technology

Inspection-related technology	Inspection method
Separation technology	High performance liquid chromatography, ion chromatography, gel permeation chromatography, etc.
Optical analysis technology	Infrared absorption spectra, UV-VIS absorption spectra, X-ray diffraction spectra, atomic absorption spectra, spectra of laser light scattered by particles, etc.
Thermal analysis technology	Melting point, differential scanning calorimetric spectra, etc.
Mass analysis technology	Mass spectra, time-of-flight mass spectra, etc.

Fig.5 Deterioration-suppressing effect of coating solution



nologies such as recrystallization, column chromatography, distillation, and sublimation according to the intended objective, and carefully monitors clean room and plant site conditions and controls the water and air quality to maintain and improve quality.

3.5 Materials inspection technology

Table 3 shows an example of materials inspection technology. Various technologies, such as chromatographic analysis technology, optical analysis technology, thermal analysis technology, mass analysis technology, and the like are used according to the objective.

Moreover, about petroleum-derived materials, depending on where crude oil for their ingredients was produced, whether in Saudi Arabia, Sumatra, Texas, the North Sea or elsewhere, despite appearing to be the same compounds, they often exhibit different behavior during a synthesis reaction or during OPC production, and therefore the inspection of materials is important.

Fuji Electric believes materials inspection technology to be important in order for electronic materials to realize enhanced functions, stable quality and lower cost in OPCs, and also performs strict inspections according to a list of inspection items.

Table 4 Safety verification system

Verification stage	Verifying organization	Verification method
Molecular design	Fuji Electric	Elimination of known dangerous structures
Synthesis design	Fuji Electric	Verification of raw material impurities, by-products, etc.
Coating solution design	Third party	Ames test, acute toxicity, etc.
Photoconductor design	Third party	Test method suited for laws of destination country

3.6 Coating solution technology

Figure 5 shows an example of a dispersion enhancement technology, which is one type of coating solution technology. The coating solution is placed into an environment in which it is extremely susceptible to deterioration due to contamination by and exposure to dust, aluminum filings, coating film filings, coating applicator filings, moisture, oxygen and the like.

With the development of a deterioration-suppressing additive for the coating solution, Fuji Electric is able to select a wider range of suitable materials since the deterioration of coated OPC material can be prevented. Accordingly, the coating solution has been perfected for realizing enhanced functionality and stabilized quality in an OPC.

3.7 Safety technology

Table 4 lists the safety verification systems. Safety verification is essential for new OPC material.

Safety, in accordance with the laws of the destination country and Fuji Electric's regulations, is verified by third parties at key development sites.

3.8 Environmental technology

Table 5 lists the major environment-related laws. As interest in the international environment increases, compliance with new laws in the EU (European Union) and China, and with the new toxic material designation of organic cyano compounds in Japan is necessary.

By developing and applying materials having a low environmental impact, a deterioration-suppressing additive for the coating solution, a solvent recovery system, and the like, Fuji Electric has realized a manufacturing system that is sensitive to the global environment, and has a low environmental impact and generates low amounts of waste.

Table 5 Environment-related laws, etc.

Country/ organization	Environment-related laws, etc.
Japan	Law Concerning Examination and Regulation of Manufacture and Handling of Chemical Substances (Chemical Substances Control Law) Existing chemical substance list
USA	TSCA: Toxic substances control act Existing chemicals list (TSCA inventory)
EU (European Union)	Council directive 92/32/EC amending for the seventh time Directive 67/548/EEC relating to the classification, packaging and labeling of dangerous substances EINECS: European Inventory of Existing Commercial Chemical Substances
	RoHS: Restriction of the use of certain Hazardous Substances in electrical and electronic equipment
China	New chemical substance environmental control regulation Name recording of existing chemical substance
	The Administration on the Control of Pollution Caused by Electronic Information Products

3.9 Evaluation technology

Table 6 lists photoconductor evaluation technology. Appropriate evaluation technology is essential for the development of OPC materials.

Fuji Electric possesses technology for evaluating the electrical characteristics, image characteristics, temperature and humidity characteristics, and durability characteristics of photoconductors since selenium photoconductors, and is moving ahead with development that combines materials technology and photoconductor technology.[4]

4. Postscript

Utilizing proprietary materials technology and chemical technology, Fuji Electric develops and produces OPC materials, and then supplies them as OPC products.

These OPC materials are being developed and produced using proprietary computer-assisted molecular design technology and materials technology, and by collectively using the plant technology, process control technology and other chemical technologies of affiliated and partner companies.

Table 6 Evaluation technology

Evaluation item	Measuring instrument, etc.
Initial electric characteristics	Photoconductor potential simulator
Photo-induced discharge characteristics	Photoconductor potential simulator
Resistance to oxydizing gases	Photoconductor potential simulator
Strong light fatigue electrical characteristics	Photoconductor potential simulator
Mobility	Charge time-of-flight tester
Electrical characteristics of actual machine	Commercially available printer, etc.
Transfer image characteristics	Photoconductor transfer simulator
Temperature/humidity environment characteristics	Photoconductor potential simulator
Coating solution lifespan characteristics	Photoconductor potential simulator
Durability characteristics	Photoconductor durability simulator
Appearance characterization	Color difference meter, etc.
Surface crack characteristics	Grease and oil tester
Photosensitive layer adhesion characteristics	Cross-cut tester (Japanese Industrial Standard)

In the future, Fuji Electric intends to raise the overall functional level of OPC materials so as to enhance the image quality, ease of use, cost-performance tradeoff and environmental friendliness of equipment that uses OPCs and to increase the level of customer satisfaction.

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(4) Registed patent numbers, USP5837410, KRP455821.

Organic Photoconductors for Printers

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1. Introduction

With the recent advances in information technology (IT), applications for electrophotographic printers continue to expand for both personal use and business use. Moreover, printers are also being required to provide more advanced functionality, i.e., higher speed printing that supports the higher speeds of information processing, colorization and higher resolution that support more diversified types of information, and smaller size devices and maintenance-free operation that support the requests for reduced cost of information processing.

Moreover, the technology for each of the electrophotographic charging, developing, transferring and fixing processes is becoming more diverse in response to such requirements.

In order to realize the required level of performance for electrophotographic printers, Fuji Electric is developing, manufacturing and enriching its product line of negative charge type and positive charge type organic photoconductors (OPC), and is expanding this market. This paper presents an overview of Fuji Electric's OPC products and describes their features.

2. Negative Charge Type OPC "Type 8"

2.1 Product overview

Negative charge type OPCs have the layer structure shown in Fig. 1, and in order to provide compatibility with various amounts of exposure energy, Fuji Electric offers three OPC product lines of low, medium and high sensitivity. By controlling the material and layer thickness, Fuji Electric is able to regulate sensitivity over the wide range of 0.15 to 1.50 μJ/cm^2 at − 100 V photo sensitivity, as shown in Table 1.

Figure 2 shows representative spectral sensitivity characteristics for low, medium and high sensitivity type of OPCs. All types exhibit nearly the same sensitivity in the 600 to 800 nm wavelength region and are compatible with typical LD (laser diode) and LED (light emitting diode) light sources.

By combining these charge generation layers (CGL) with various charge transport layers (CTL), OPCs can be provided for a diverse variety of processes in low-speed to high-speed printers.

Fig.1 Layer structure of negative charge type OPC

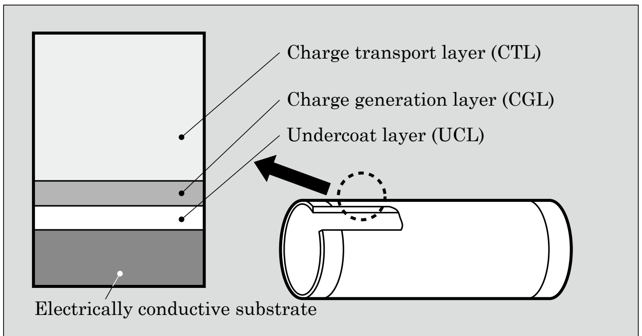
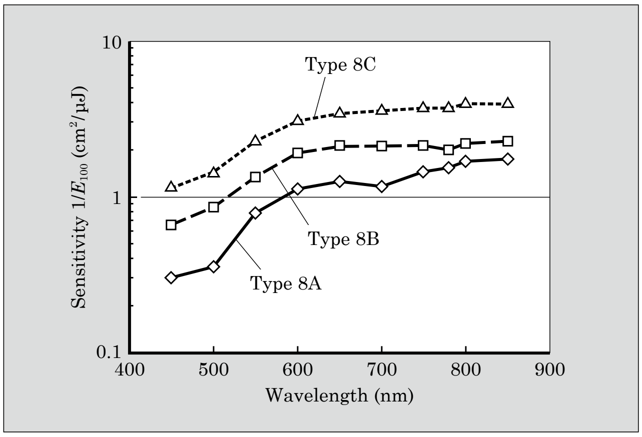


Table 1 Overview of negative charge type OPC products

Type	Sensitivity* (Exposure energy to −100 V)
8A (Low sensitivity)	0.70 to 1.50 μJ/cm^2
8B (Medium sensitivity)	0.40 to 0.80 μJ/cm^2
8C (High sensitivity)	0.15 to 0.40 μJ/cm^2

*Sensitivity indicates the required exposure energy for the surface potential to discharge from −600 V to −100 V

Fig.2 Spectral sensitivity characteristics of negative charge type OPCs



† Fuji Electric Device Technology Co., Ltd.

Using Fuji Electric's proprietary conductive substrate processing technology and coating technology, the negative charge type and the positive chargie type OPCs can be manufactured with external diameters of 20 to 262 mm and lengths of 236 to 1,000 mm, and these products are being deployed over a wide range of applications, from A4-sheet printers to A0 plotters.

2.2 Product features

Printer-use OPCs must exhibit five required performance characteristics: high-speed, color imaging, high resolution, small size and maintenance free operation. Specifically, the technical challenges associated with each performance requirement can be categorized as shown in Fig. 3. Characteristics of each item are described below.

(1) High-speed response

In order for small-diameter OPCs (having a diameter of 20 to 30 mm) to be suitable for use in high-speed printers capable of printing longitudinally-fed A4-size sheets at a rate of 35 ppm or higher, the surface potential at areas exposed to light must be uniform during the exposure-development time, which is 50 ms or less in a typical processing machine. Accordingly, Fuji Electric is preparing a high-speed charge transport material (CTM) having mobility of 2×10^{-5} cm^2/V·s for use in practical applications. Moreover, Fuji Electric is also completing the development of a high mobility material of 8×10^{-5} cm^2/V·s to support even higher speeds.

Figure 4 shows the dependency of the surface potential after exposure on the exposure-development time for typical CGL/CTL combinations. Moreover, a type 8C "SH" OPC that uses CTM having a super high-speed carrier mobility exhibited characteristics suitable for practical application at exposure-development times of up to 40 ms.

(2) High definition

OPCs for use in color imaging, high resolution printers and multi-function peripherals (MFPs) are required to have color reproduction capability for color images and tone reproduction capability for monochrome images. Moreover, as document output becomes increasingly diverse, a higher level of image quality than in the past is desired. Fuji Electric is developing and commercializing OPCs in which the photo-induced discharge characteristics are optimized for various machine processes. Figure 5 shows an example of photo-induced discharge characteristics according to OPC type. This characteristic is largely dependent on the charge transfer performance of the CTM and the efficiency of carrier injection between layers, and can therefore be regulated according to the combination of UCL, CGL and CTL.

As printers continue to advance toward higher quality images, small potential differences on the OPC surface have become easier to reproduce in the image as contrasts in image density, and OPCs, in addition to having a photo sensitive layer of uniform thickness, are also desired to be relatively unaffected by the application of a reverse polarity at transfer sites and the increase in residual potential at sites of continuous exposure. To reduce potential differences, Fuji Electric is developing new materials for use and optimizing them in the UCL, CGL and CTL functional layers.

When a cartridge is replaced or when paper jams

Fig.3 Required OPC characteristics and technical challenges

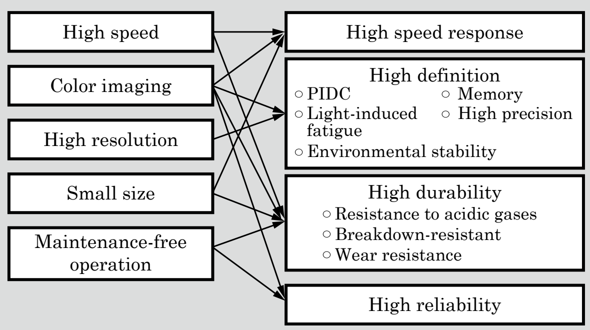


Fig.4 Photoresponsivity of negative charge type OPC

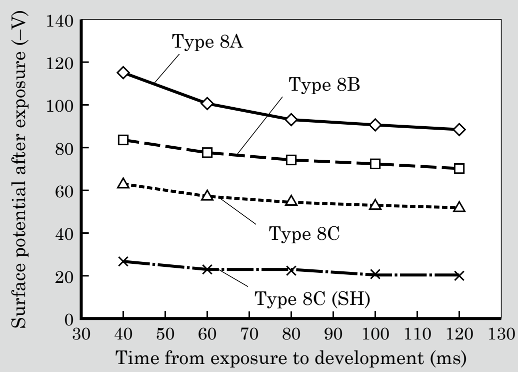
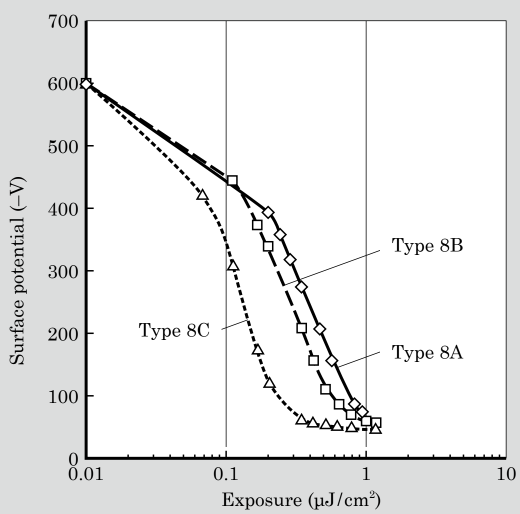


Fig.5 Photo-induced discharge of negative charge type OPC



occur, the OPC may be exposed to indoor light or sunlight and therefore an OPC that is largely unaffected by such light exposure is required for the general market. Fuji Electric combines CGL and CTL layers to realize OPCs whose image quality is largely unaffected by exposure to indoor lighting such as fluorescent lights, and that are suitable for use in practical applications.

Color printers that print by overlaying four colors require relatively high dimensional precision in order to prevent out-of-color-registration problems. Fuji Electric possesses technology for processing OPC-use element tubes, which have a run-out of 50 μm or less and straightness of 20 μm or less, and that are suitable for use in these types of color printers, and has established a system for supplying high precision plastic flanges.

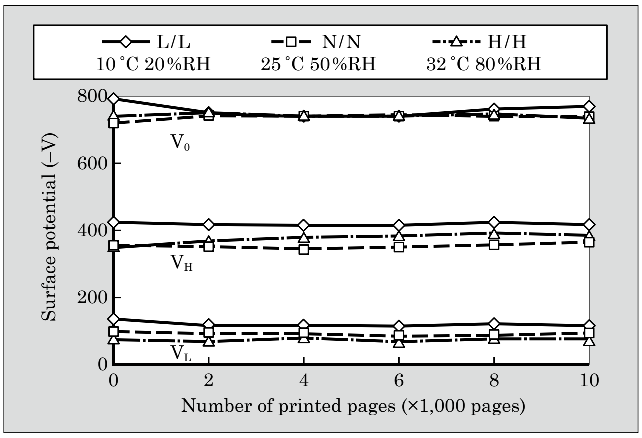
In order to maintain the initial image quality, the OPCs are desired to have characteristics that exhibit little change in response to environmental changes and printing. Using a commercially available contact electrification-type laser printer equipped with a 24 mm-diameter OPC, 10,000 A4-size longitudinally fed sheets were each printed under the environmental conditions of normal temperature and normal humidity (N/N: 25 °C and 50%RH), low temperature and low humidity (L/L: 10 °C and 20%RH), and high temperature and high humidity (H/H: 32 °C and 80%RH), and the surface potential was measured after every 2,000 sheets. This data is shown in Fig. 6. In all of these environments, favorable characteristics were exhibited without any significant change in surface potential.

(3) Technology for higher durability

OPCs must be resistant to the ozone gas generated by the chargers used in printers and to other active gases in the environment.

Various anti-oxidizing agents and other additives are used in OPCs. Increasing the amount of an additive usually improves the resistance to acidic gases but also leads to increased residual potential and also negatively affects other electrical characteristics. To ensure resistance to acidic gases, Fuji Electric has developed CTM that exhibits almost no deterioration and a proprietary additive that has little effect on electrical characteristics.

Fig.6 Surface potential stability during environmental life test for negative charge type OPC



The method of contact electrification is widely used in medium- and low-speed printers, however improved resistance to dielectric breakdown, comparable to that of the scorotron non-contact electrification method, is strongly required. Since launching a UCL equipped with an interference suppressing function in 1995, Fuji Electric has been working to develop OPCs with improved resistance to dielectric breakdown and improved environmental characteristics. Fuji Electric is presently developing UCL products that exhibit excellent environmental characteristics and the same degree of resistance to breakdown as an anodized layer, and is endeavoring to improve the overall performance of OPCs, including the CGL and CTL layers.

Factors that determine the useful service life of an OPC include abrasion from contact parts such as the developing system, the paper and the cleaning blade, scratches that cause printing defects, and the adhesion (filming) of toner and paper dust particles on the OPC surface, and accordingly, OPCs are required to exhibit properties of low wear, high hardness and low filming. Fuji Electric is independently developing wear-resistant resin and lubricative resin, and appropriately combines these resins to provide OPCs optimized for each process.

(4) High reliability

OPCs are desired to maintain stable characteristics in a variety of environments and are also desired to remain stable in response to external mechanical and chemical stresses.

During the stage of materials development, Fuji Electric independently establishes a list of inspection items, and then in the course of development, evaluates the reliability, including long-term storage characteristics, for each product in order to develop and produce highly reliable OPC products.

3. Positive Charge Type OPC “Type 11”

3.1 Overview of Fuji Electric’s products

Fuji Electric is developing positive charge type OPC products that provide higher image resolution and are more effective against ozone than the typical negative charge multi-layer type OPCs.

When designing CTM for positive charge use, the required characteristics are more difficult to realize than in the case of CTM for negative charge use. Fuji Electric is commercializing positive charge type OPCs that combine photoconductor technology with positive-charging-use CTM which has been developed through the application of computational chemistry techniques and synthetic organic chemistry techniques.

Table 2 lists Fuji Electric’s line-up of type 11 positive charge type OPC products. Figure 7 shows the

Table 2 Overview of positive charge type OPC products

Type	Feature	Recommended machine (pages/minute)	Printing life (converted to A4 intermittent printing, 30 mm external diameter)
Type 11A	Low-speed type	< 12	20,000 pages
Type 11B	Medium-speed type	10 to 18	30,000 pages
Type 11C	Medium & high-speed type	12 to 24	140,000 pages
Type 11D	High-speed, high printing durability	≥ 30	200,000 pages (converted to 120 mm external diameter & A4 continuous printing, up to 1 million pages can be used)

Fig.7 Spectral sensitivity characteristics of positive charge type OPCs

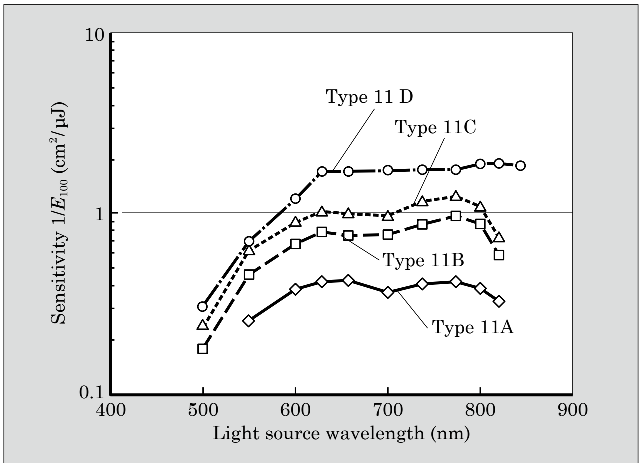
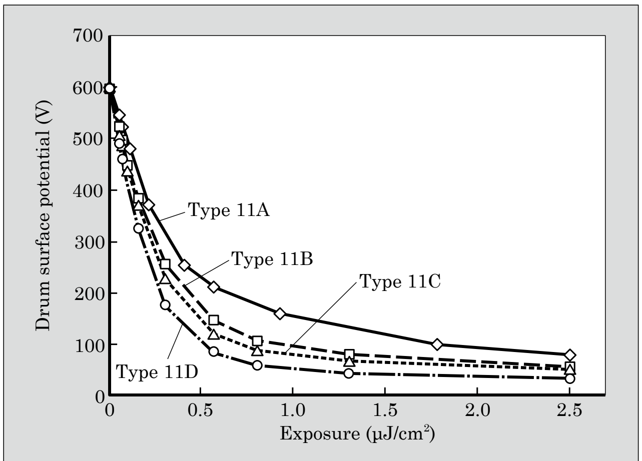


Fig.8 Photo-induced discharge characteristics (PIDC) of positive charge type OPCs



spectral sensitivity characteristics of types 11A to 11D. All of the positive charge type OPCs exhibit essentially the same sensitivity in the 600 to 800 nm wavelength region, and are compatible with typical LD and LED light sources. Moreover, sensitivities over the wide range of half-decay exposure from 0.15 to 0.38 μJ/cm² are provided as shown in Fig. 8, and are suitable for use with low-speed (15 ppm and lower) printers to high-speed (35 ppm and higher) printers. In particular, as shown in Table 3, due to performance improvements of each functional material, the type 11D realizes enhanced OPC characteristics, and is able to satisfy the growing demands for high sensitivity and high-speed response.

Table 3 Relation between characteristics and material of type 11D

Characteristic	Characteristic of material
High sensitivity	CGM→increased quantum efficiency
High-speed response	HTM → increased hole mobility ETM→increased electron mobility
High strength	Resin binder →higher glass transition temperature →increased surface hardness
Resistance to breakdown	UCL→thicker layer (electrically conductive control)

3.2 Characteristics of positive charge type OPC products

As has been described for negative charge type OPCs, positive charge type OPC product characteristics and their associated technical challenges are described below.

(1) High-speed response

Figure 9 shows the photoresponsivity of positive charge type OPCs. Any of these positive charge type OPCs can be used with devices in which the time from exposure to development is 75 ms. In particular, the type 11D, even 30 ms after exposure, exhibits little rise in the potential at light exposure areas, and is suitable for use with small-size high-speed printers having shorter times from exposure to development.

(2) High definition

Positive charge type OPCs are well suited for use in high resolution applications since the absorption of exposure light and the subsequent generation of charge occurs near the OPC surface and there is little scattering and diffusion of exposure light and charge within the photosensitive layer. Figure 10 shows the results of measuring the electrostatic latent image width at the sites of 1-dot exposure writing. Spreading of the latent image can be observed in the negative charge type OPC, and indicates the extent of the high resolution performance of the positive charge type OPC.

The optimal regulation of the UCL and GTL, even during endurance testing, enables better uniformity of the halftone image quality and suppresses the phenomenon of residual images.

As for light-induced fatigue characteristics, regardless of the OPC type, exposure to light at 1,000 lx for 10 minutes caused little change in the dark area voltage, and the recovery time after the light exposure was quick.

Figure 11 shows the environmental characteristics

Fig.9 Photoresponsivity of positive charge type OPCs

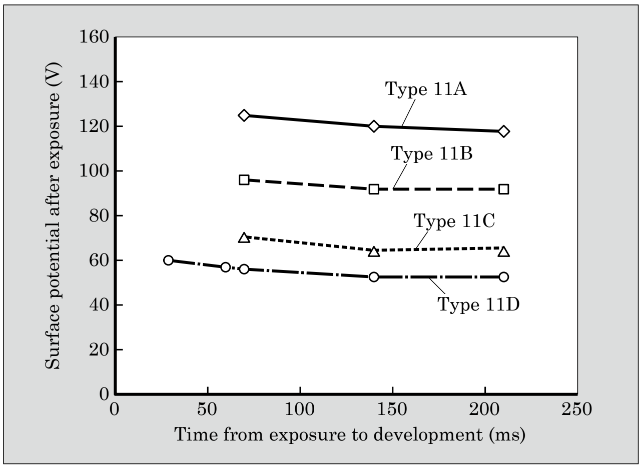


Fig.10 Comparison of 1-dot latent image for positive charge type and negative charge type OPCs

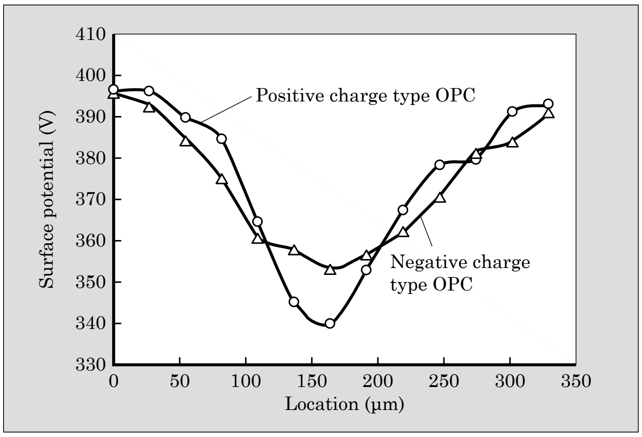


Fig.11 Environmental dependency of light area voltage V_L and dark area voltage V_D for positive charge type OPCs

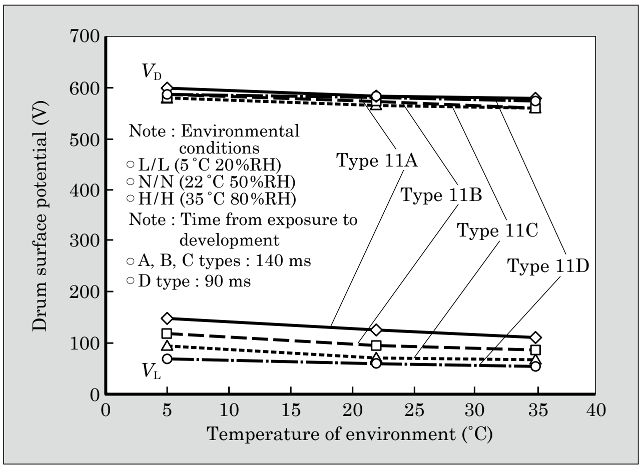


Fig.12 Ozone characteristics

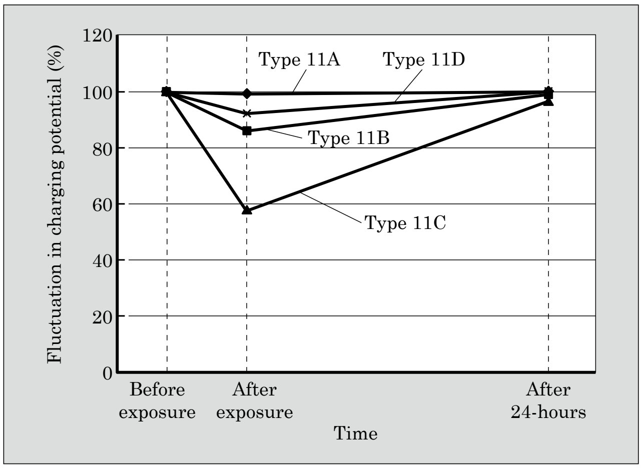


Table 4 Change in characteristics due to reliability test of positive charge type OPC

Test item	Test conditions	Change in characteristics before and after test	
		Dark area voltage fluctuation	Light area voltage fluctuation
High temperature exposure	45 °C : 1,000 h	< ±5 %	< ±10 %
High temperature, high humidity exposure	35 °C, 90 %RH : 1,000 h	< ±5 %	< ±10 %
Heat cycle (10 cycles)	− 20 °C : 1h→ Normal room temperature and humidity : 0.5h→ 45 °C : 1h→ − 20 °C : 1h→ Normal room temperature and humidity : 0.5h→	< ±5 %	< ±10 %
Roller contamination test	Roller material : NBR, polyurethane rubber, silicone rubber	None	None
		No image faults	

of the light area voltage V_L and dark area voltage V_D. For all positive charge type OPCs, the dark area voltage and the light area voltage are stable and exhibit little environmental fluctuations in the temperature and humidity range from L/L (5 °C and 20%RH) to H/H (35 °C and 80%RH).

(3) High durability

As shown in Fig. 12, for all positive charge type OPCs, after exposure to ozone for 30 minutes at a concentration of 5 ppm, the charging potential initially drops, but then returns to the original charging potential after having been left to stand at room temperature for 24 hours. Type 11A and 11D OPCs have particularly high resistance to ozone, and therefore only experience slight drops in charging potential immediately after exposure.

In a printing duration evaluation using a two component development printer, the OPC type 11D exhibited stable light area voltage and dark area voltage with no observable image defects, and had a printing life of approximately 200,000 sheets.

(4) High reliability

Table 4 shows the changes in characteristics as a result of various reliability tests. Light area voltage fluctuations of less than 10% are considered to provide high reliability, and in all the tests, the fluctuation in dark area voltage did not exceed 5%.

In a roller contamination test, rollers formed from acrylonitrilebutadiene rubber (NBR), polyurethane rubber, silicon rubber and the like are pressed against each photoconductor, and even after the OPC was left standing in an environment of 50 °C and 90%RH for 250 hours, cracking did not occur in the photosensitive layer and the photoconductor characteristics did not change.

4. Postscript

The trends toward higher speed, greater multi-functionality, high image quality and lower cost will continue to advance for electrophotographic printers, and performance requirements for photoconductors will become more diverse. Fuji Electric intends to continue utilizing and developing chemical technology and photoconductor technology to provide a variety of high-function photoconductors suitable to meet the needs for information output, and in doing so, to make a positive contribution to society.

Organic Photoconductors for Digital Plain Paper Copiers

Takahito Miyamoto †
Shuichi Hamada †

1. Introduction

In recent years, the development of new analog products by copier manufacturers has essentially ceased, and electrophotographic copiers have entered an era of digital expansion and evolution. Accompanying this trend toward digitalization, copier technology is trending toward colorization, higher speeds, higher image quality, and better stability than conventional analog copiers. In order to increase added-value, each copier manufacturer is promoting solutions. In response to these market trends, photoconductors, which are the key imaging devices in electrophotographic machines, must be improved to attain higher sensitivity, higher durability, environmental stability and higher reliability.

Fuji Electric provides a type 9 series of organic photoconductors (OPCs) for use in analog copiers and a type 10 series for use in digital copiers. This paper presents an overview of the type 10 series of OPCs for use in digital plain paper copiers.

2. Product Overview

Copiers that use OPCs can be categorized according to their copying speed as low-speed copiers (up to 25 ppm), medium-speed copiers (25 to 50 ppm) and high-speed copiers (50 ppm and above). Fuji Electric continues to advance the development of materials and design of the photoconductive layer in order to provide OPCs that are compatible with these digital copiers and that satisfy customer specifications. A separated-function type multilayer OPC is formed by applying an undercoat layer (UCL) on a cylindrical conductive substrate typically made of aluminum or the like, and then by applying a charge generation layer (CGL) on top of the UCL, and finally by applying a charge transport layer (CTL) on the top surface.

Digital copier-use OPCs are used with a laser diode (LD) light source. The materials employed in laser printer-use OPCs (type 8 series) can shared, and the knowledge base of materials technology and coating technology acquired with the type 8 series can be applied to the type 10 series OPCs.

† Fuji Electric Device Technology Co., Ltd.

3. Product Features

With the present migration from analog to digital technology, copiers are advancing toward higher speeds, higher image quality and higher reliability. As such, increasingly diverse and more sophisticated levels of performance are being required of OPCs, and materials development is being advanced in response to these requirements.

Fuji Electric's copier-use OPCs can be installed in low-speed, medium-speed and high-speed copiers and are provided with the following characteristics.

(a) High sensitivity
(b) High responsivity
(c) High durability
(d) High environmental stability
(e) High reliability

3.1 High sensitivity

As with laser printers, digital copiers also use lasers or light emitting diodes (LEDs) as exposure sources, and therefore digital copier-use OPCs are required to be sensitive to wavelengths in the 650 to 800 nm range. To accommodate a variety of customer process designs, Fuji Electric provides the three types of digital copier-use OPCs listed in Table 1: low-sensitivity (type

Table 1 Basic characteristics

Type	Half decay exposure in applied sensitivity band ($\mu J/cm^2$)	Half decay exposure ($\mu J/cm^2$)	Dark decay ratio [after 5 sec] (%)	Residual potential (−V)	Applied range of printing speed (ppm)
10 A (low sensitivity)	0.20 to 0.60	0.38	98	50	< 30
10 B (medium sensitivity)	0.12 to 0.24	0.18	96	25	20 to 60
10 C (high sensitivity)	0.06 to 0.14	0.08	96	10	40 <

Fig.1 Spectral sensitivity characteristics

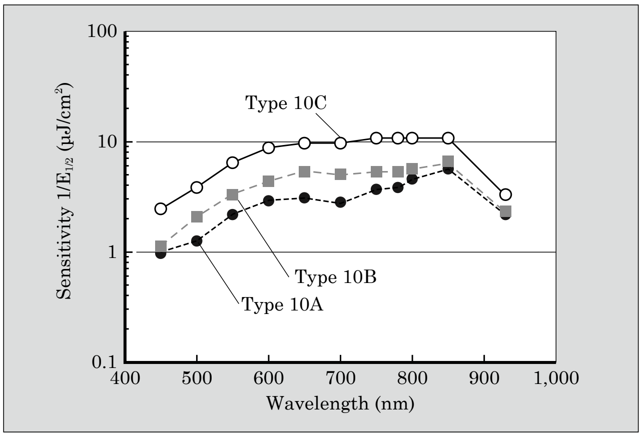
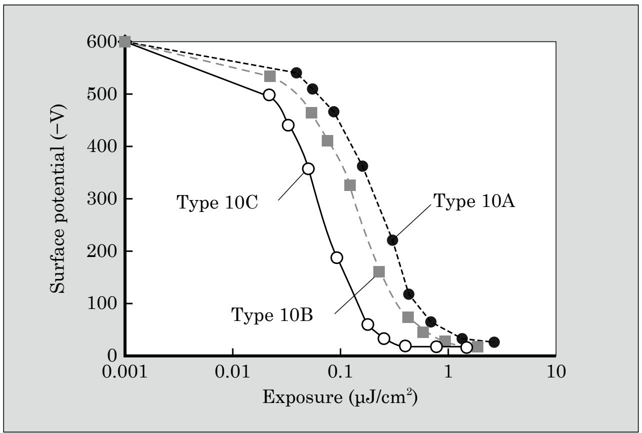


Fig.2 Photo-induced discharge characteristics



10A), medium-sensitivity (type 10B) and high-sensitivity (type 10C). Figure 1 shows the spectral sensitivity of each type.

Figure 2 shows the photo-induced discharge characteristics of each type. High-sensitivity OPC type 10C has higher sensitivity than types 10A or 10B by 50% and 30%, respectively. Moreover, each type exhibits a sharp reduction in the vicinity of the residual potential and this is advantageous for the design of the digital copying process in a copier.

3.2 High responsivity

Digital copier manufacturers offer a wide lineup of digital copiers, from low-speed machines for small offices/home offices (SOHOs) and for personal use to high-speed machines for business use. Within this lineup, higher responsivity is especially required of OPCs for super high-speed machines having greater than 100 ppm capacity and that target the on-demand copying market and high-volume printing applications such as in the advertising field.

The material mobility, consistency of the ionization potential among materials, and purity are key factors for enhancing responsivity. In order to realize high responsivity, Fuji Electric researched high mobility charge transport materials (CTMs) and developed a high mobility CTM having a mobility that is several times higher than that of the conventional material. Figure 3 shows the dependence of surface potential after exposure on the exposure-development time and Fig. 4 shows the development characteristics when installed in a copier. The surface potential after exposure of the high-responsivity type that uses high mobility CTM stabilizes in an exposure-development time of approximately 40 ms. This performance provides sufficient support for high-speed processes of 50 ppm and above in the case of an OPC having an external diameter of 30 mm and 120 ppm and above in the case of an OPC having an external diameter of 100 mm. Moreover, a comparison of the image density (black density) to that of the conventional type reveals a higher degree of reproducibility when using the high-responsivity type CTM.

Fig.3 Dependence on time from exposure to development (for surface potential after exposure)

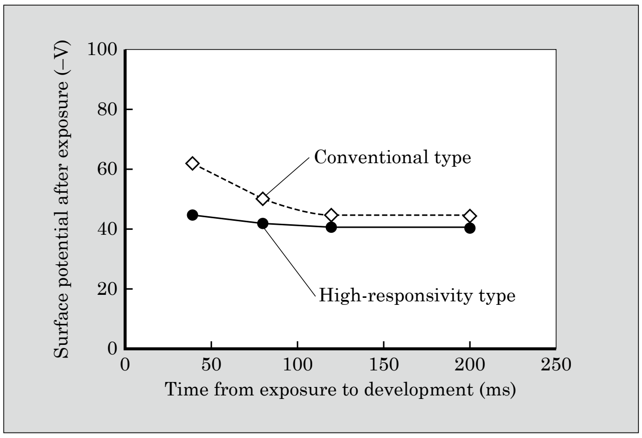
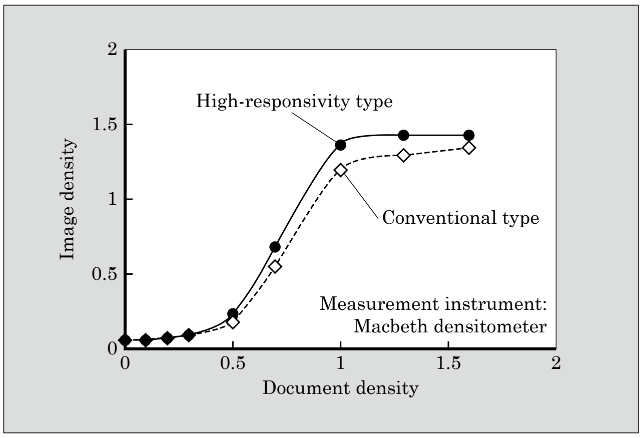


Fig.4 Developing characteristics



3.3 High durability

In consideration of the frequency of copier use and in order to simplify maintenance, OPCs for digital copiers are required to provide approximately 10 times higher durability than OPCs for laser printer-use.

(1) Improvement of electrical characteristics

The repeated exposure of the OPC to ozone gener-

Fig.5 Durability characteristics (electric potential in actual copier)

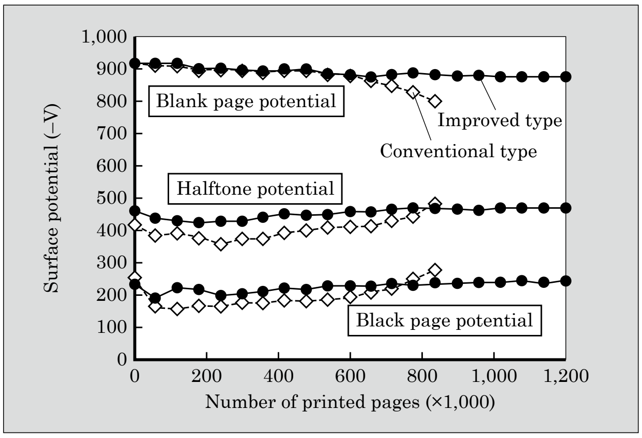
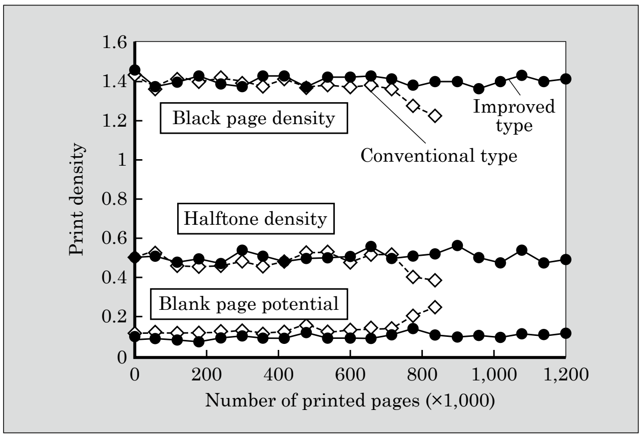


Fig.6 Durability characteristics (print density of actual copier)

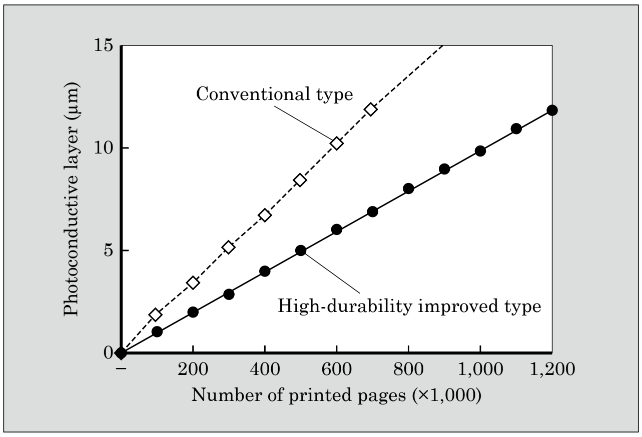


ated by corona discharge during the charging process and to light during the exposure process causes chemical changes in the functional material. The result is a deterioration in electrical characteristics such as, for example, a decrease in charging potential or an increase in residual potential, causing such image problems as low print density or fog.

To suppress this decrease in charging potential and increase in residual potential, Fuji Electric has developed a proprietary charge control agent that suppresses the occurrence of electrical defects in the photoconductive layer, and by maintaining a consistent ionization potential among the OPC layers, Fuji is able and to supply OPCs that operate stably in various machine processes.

Figures 5 and 6 show the change in surface potential and image density for OPCs evaluated in a digital copier in which a high degree of durability (a guaranteed OPC service life of 1.2 million pages) is required. With the conventional type, a large change in image density due to a decrease in charging potential and an increase in residual potential can be seen after copying approximately 800,000 pages, but the improved OPC exhibits little change in surface potential and image quality and excellent operating stability through the

Fig.7 Durability characteristics (wear)



end of its guaranteed service life of 1.2 million pages.

(2) Improvement of mechanical characteristics

Contact between the OPC and the charging roller, developing roller, toner, paper, transfer roller, cleaning blade and the like degrades the physical and mechanical characteristics of the OPC by causing wear and scratches on the photoconductive layer and by causing the adherence of toner or paper dust particles. The degree to which this degradation occurs varies according to the machine process, but is largely dependent on the properties of the binder, which is a component of the CTL, and on the combinational ratio of CTM and binder.

Fuji Electric has installed a durability tester capable of evaluating the binder performance within a short time, and has implemented an accelerated evaluation which has verified a dramatic improvement in the binder performance.

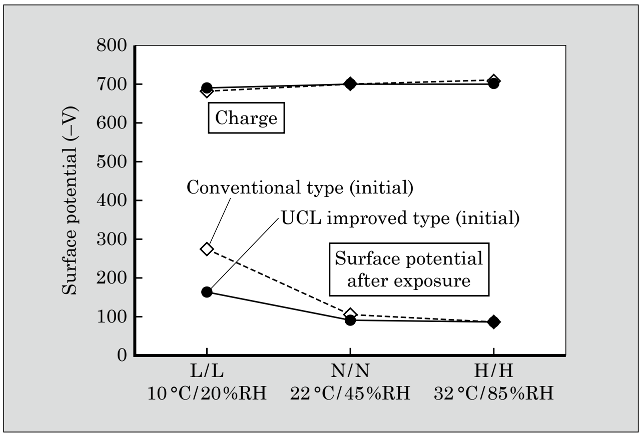
The binder material in the CTL is molecularly designed to have a polymeric molecular structure and have excellent lubricating properties, and this binder material increases the film hardness while reducing the frictional coefficient between the OPC and the cleaning blade. As is shown in Fig. 7, by reducing the friction with other contact parts, wear and scratching of the photoconductive layer have been reduced and the service life of the OPC has been increased by approximately 1.7 times as compared a conventional OPC. As a result, the improved OPC is suitable for use in the fields of high-speed and light printing.

3.4 High environmental stability

OPCs are desired to be environmentally stable so as to be compatible with a variety of copier environments.

Fuji Electric has optimized the UCL filler performance and binder and suppressed fluctuations in volume resistivity due to the environment in order to ensure stability in normal temperature and normal humidity (N/N), low temperature and low humidity (L/L) and high temperature and high humidity (H/H) environments. Figure 8 shows data from a process simula-

Fig.8 Environmental surface potential characteristics



tion of the environmental dependency of surface potential. The improved OPC exhibited minimal fluctuation and good characteristics in all environments.

3.5 High reliability

Fuji Electric carried out the reliability testing listed in Table 2 in order to verify the reliability of OPC products. Product development was advanced after confirming that the characteristics associated with each evaluation item were free from abnormalities.

4. Postscript

This paper has discussed OPCs for digital plain paper copiers.

In the copier market, nearly the entire installed base of machines has changed over from analog to digital technology. Moreover, digitalization is driving a trend toward multifunctional (MF) machines that combine printer, copier and facsimile capabilities into a single unit and is eliminating the distinction between printers and copiers in the low and medium-speed fields, and market demand is centered on MF machines. Fuji Electric is refining the technology needed to address these market trends. Moreover, in the high-speed copier field, higher operating stability in the range of approximately several to 10 times that of a laser printer is required, and further improvements in the OPC characteristics are required. Fuji Electric intends to continue to develop desirable OPCs by accurately assessing required characteristics in accordance with market needs.

Table 2 Reliability tests

Item	Condition
Ozone exposure test	100 ppm, 2 h
Light-induced fatigue test	1,000 lx, 5 min
High temperature exposure test	45 °C, 1,000 h
High humidity exposure test	40 °C, 90%RH, 1,000 h
Low temperature exposure test	−20 °C, 1,000 h
Cyclic test of temperature and humidity (5 cycles)	−20 °C, 1 h →Normal temperature, normal humidity, 0.5 h →45 °C, 1 h →Normal temperature, normal humidity, 0.5 h → −20 °C, 1 h

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