

Hitachi Chemical
**Technical
Report**

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Hitachi Chemical
Working On Wonders



HITACHI

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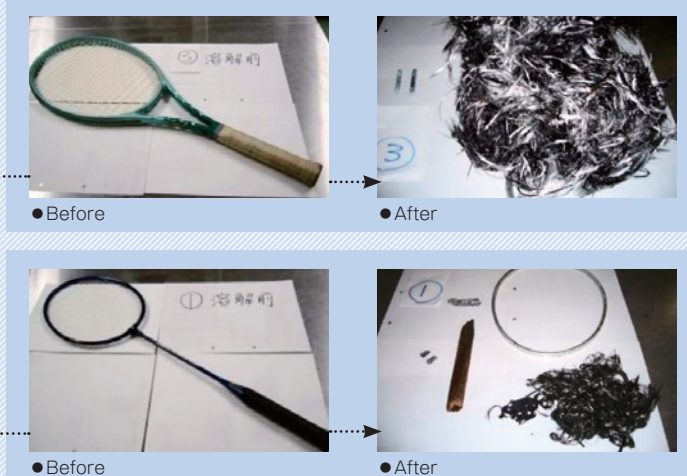
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Executive Officer
General Manager
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Misao Nakagawa

Implementation of material business to materialize infinite possibilities and contribute to society


Hitachi Chemical started manufacturing electrical insulating varnishes for domestic electric motors in 1912 as part of Hitachi Ltd., and has produced countless products in the 101 years since, using various properties of organic, inorganic and metallic materials. What we have pursued over all these years is “finding infinite possibilities of individual materials, giving them a concrete shape to meet customer needs, and ultimately helping society develop.” We celebrated our 50th anniversary and stepped toward the next half-century last year. In addition to the material and process technologies we have accumulated to date, we will optimally exploit our newly obtained wisdom and ingenuity to offer breathtaking, valuable products to our customers in the next 50 years. We believe this is how best to achieve our corporate slogan “Working On Wonders: WOW.”

This technical report presents challenges in the fields of telecommunication, display, the environment and energy.

[Improving the ability to propose solutions in the telecommunication and display fields]

Technological development and commercialization are very fast in these fields, as typically seen in the accelerated development of 3D packages in semiconductor products, or the rapid expansion of touch-panel application. Accordingly it is crucial for us to be ready to develop technologies at any time, and immediately propose solutions to our customers. We have made proposals to our customers for their material systems using our extensive product lineups; ranging from preprocessing materials such as CMP slurries and interlayer dielectrics for semiconductors, to postprocessing materials, including die attach films, encapsulation resins, and package substrate materials. Recently we also introduced a cutting-edge evaluation system in the Advanced Packaging Technology Center to enhance our ability to make proposals. We will launch the so-called “open laboratory” approach to invite our customers to evaluate various combinations of materials using our system. Through this approach, our proposals not only include combinations of materials but also extend to semiconductor and mounting processes.

In the display field, we have a high market share in the display circuit connection films and moisture-proof insulating materials. In addition, we have successfully marketed optical clear adhesive films that improve the durability and clearness of touch panels, and transparent conductive films with lower electric resistance and larger flexibility than the ITO electrode. We will increase the pace at which we create new products in this field, and improve our ability so that we offer total solutions in display materials in future.



In the telecommunication and display fields, where changes in products and technologies may accelerate in future, we will strive to play a major role in technological innovation in these fields by swiftly identifying customer needs and immediately proposing optimal solutions by combining our materials.

[Improving the ability to develop new products in the environment and energy fields]

Increased concern over environmental impacts such as climate change and a review of dependency on nuclear energy will spawn a steady expansion of environmental and energy markets in future. Although our business has centered on electronics to date, we must also focus on developing new technologies and products in these fields. In the renewable energy field, our products on the market range from solar battery materials such as electro-conductive films for connecting the tab and the solar battery electrode without solder, to heat-resistant insulating resin pastes. We will also develop sliding brushes for wind power generators and separators for fuel cells in future using inorganic material technologies.

In the field of lithium-ion batteries, mainly used in consumer products such as PCs and mobile equipment to date, and increasingly applied to automobiles and industrial products recently, we already boast a large share in the anode market, and will also promote the development of materials for lithium-ion batteries. We will concentrate our management resources in this field to accelerate product development and business expansion, and make it the second pillar of the Advanced Performance Materials Operational Headquarters.

[Improving resin materials and technologies]

We must improve fundamental resin technologies to develop new products in these two fields, in other words, present our new capabilities. Material technologies, including those in resin design for controlling resins at a particle level, and nanotechnology for applying nano-level particles, will become increasingly important. Hitachi Chemical provides all functional materials ranging from base polymers to applications. To capitalize on such corporate characteristics, we will promote innovations in fundamental resin technologies by strategically allocating development resources and through active collaboration with outside research organizations.

When global markets are expanding and dynamically changing, Hitachi Chemical Group will establish a foundation for production overseas to meet the needs of our global customers promptly, and R&D and business operations in proximity to our customers.

The catalyst for this comes in the form of the three genes inherited within Hitachi Chemical Group: “Spirits of Trail Blazer” to challenge new things unhesitatingly, “Flexibility” to respond to the changing era and market, and “Strong Customer Orientation.” Hitachi Chemical will reaffirm these genes before advancing into the new half-century, and continue to offer our customers values to realize our corporate vision “Contribution to Society through the Development of Superior Technologies and Products.”

CFRP Recycling Technology Using Depolymerization under Ordinary Pressure

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We have developed carbon fiber reinforced plastic (CFRP) recycling technology using depolymerization of cured epoxy resin (EP) under ordinary pressure. Carbon fiber (CF) was recovered from used tennis rackets by dissolving EP with tripotassium phosphate as a catalyst and benzyl alcohol as a solvent at 200 °C for 10 hours. We were able to produce non-woven fabrics with the recovered CF using a carding machine. With these fabrics we then produced recycled CFRPs, and measured their mechanical properties. Their properties were nearly equal to the CFRP using commercial fresh CF non-woven fabric. At the same time, the depolymerized EP cured with acid anhydride was analyzed with HPLC and NMR. Our results showed that the depolymerization was proceeded by a transesterification to produce diesters and bis-diols, which can be used for recycled EP.

1 Introduction

CFRP has been rapidly and extensively used in transportation equipment such as aircraft and automobiles due to their light weight that improves fuel efficiency. Manufacturing CF, however, involves prolonged and high-temperature heating process, and considerable energy. The results of a life cycle assessment (LCA) indicate that CFRP is not an environmentally friendly material. Fuel can be saved when CFRP is used to reduce the weight of a transportation system, but Takahashi et al. of Tokyo University implied in their estimate that this is a minor effect seen only in commercial transportation systems^{1), 2)}. They also suggested that the best option would be to reuse CF, recovered from used transportation systems, in equivalent transportation systems.

None of the recycling technologies used to recover CF from CFRP and reused in CFRP has yet come into commercial use, but technologies are under discussion as shown in **Table 1**.

Toray Industries, Inc., Teijin Ltd. and Mitsubishi Rayon Co., Ltd. are studying recycling technologies using a thermal decomposition technique in which resins are decomposed and removed at 500 °C to 700 °C^{3), 4)}. In 2010, they commissioned the recycling work to the recycling plant of Japan Coke & Engineering Co., Ltd., located in Ohmuta, Fukuoka prefecture, where 1,000 tons of recycled CFRP are produced annually. Here, a thermal decomposition technique is used, but preprocessing such as pulverization is omitted. Takayasu Co., Ltd. developed a technology to recover longer CFs⁵⁾. It also developed a technique to cut recovered CFs to any length, and produces high-quality non-woven fabric using both dry and wet methods. The facility has a capacity of 5 tons/month.

Okajima, et al. of Shizuoka University are carrying out a research project sponsored by NEDO to study CFRP recycling technologies using supercritical alcohol^{6), 7)}. EP, which is the CFRP matrix resin, is decomposed to recover CF using supercritical methanol. Remoldable thermosetting resin is produced by removing methanol from the decomposed resin and adding a curing agent.

Table 1 CFRP chemical recycling technologies in Japan

Item	Thermal decomposition		Supercritical fluid technique	Subcritical fluid technique	Depolymerization under ordinary pressure
Organization	Toray Industries, Teijin, Mitsubishi Rayon	Takayasu	Shizuoka University	Kumamoto University	Hitachi Chemical
Temperature	500–700 °C	Not known	250–350 °C	300–400 °C	200 °C
Pressure	Ordinary pressure	Ordinary pressure	5–10 MPa	1–4 MPa	Ordinary pressure
Solvent	None	None	Methanol	Benzyl alcohol	Benzyl alcohol
Catalyst	None	None	None	Alkali metal salt	Alkali metal salt
Preprocessing	Pulverization	None	Pulverization	None	None
Processing capacity	1,000 tons/year	60 tons/year	(5 L)	(0.5 L)	12 tons/year (200 L x 2 baths)

Goto, et al. of Kumamoto University are studying a method of recycling CFRP using subcritical alcohol^{8), 9)}. When high-boiling alcohol such as benzyl alcohol is heated at 300 °C to 400 °C to turn it subcritical, and used for CFRP treatment, the whole resin decomposes within an hour. No catalyst is needed for decomposition, but CF is less damaged when alkali metal salt is used as the catalyst. This method, using high-boiling alcohol, is characterized by a relatively low pressure of around 4 MPa, which may eliminate the cost required for the dissolution bath with supercritical fluid.

Depolymerization under ordinary pressure was developed to establish a recycling business profitable for the economy by recovering and reusing CFs and resins from CFRP at low cost and energy. CFRP recycling technology using the depolymerization under ordinary pressure is discussed in subsequent sections.

2 Outline of Depolymerization under Ordinary Pressure

Depolymerization under ordinary pressure is a technique to depolymerize and dissolve cured resins using a treatment liquid consisting of alcohol solvent and alkali metal salt as a catalyst. When this technique is applied to composite materials containing thermosetting resins such as unsaturated polyester resin (UP), the resins in the composite depolymerize and dissolve, and inorganic substances such as metal, glass fiber (GF) and CF can be separated and recovered¹⁰⁾⁻¹²⁾.

A treatment liquid consisting of tricalcium phosphate (K_3PO_4) as the catalyst and benzyl alcohol (BZA) as the solvent is used for CFRP treatment. Both K_3PO_4 and BZA are approved food ingredients, and their safety for the human body is unquestionably high. When CFRP is treated with this treatment liquid at around 200 °C under ordinary pressure, the cured EP immediately depolymerizes and dissolves, allowing the CF to be recovered intact. The treatment time depends on the CFRP thickness, but the whole EP dissolves in about 10 hours.

Compared with other chemical recycling techniques, this approach to depolymerization under ordinary pressure has three characteristics: Processing is under ordinary pressure, resins are recovered, and no preprocessing such as pulverization is necessary. All these features result from the discovery of an optimum combination of catalysts and solvents to selectively break the specific bond in resins. Treatment under ordinary pressure denotes low facility costs. Moreover, continuous processing facilitates more economical mass production. Recovered resins, when recomposed, can be reused as high value materials. Because this approach eliminates preprocessing, no fragmentation and pulverization costs are incurred, and applications of recovered materials may be increased. When resins are pulverized, the length of the recovered fiber tends to be short, less than 1 mm, hindering efforts to reuse them as reinforcing materials. In terms of safety, depolymerization under ordinary pressure eliminates the danger of dust explosions and pneumoconiosis caused by pulverization.

3 Dissolution of CFRP

Figures 1 and 2 show the results of depolymerization under ordinary pressure for processing used tennis and badminton rackets, typical sports equipment, using CFRP¹³⁾. All tennis rackets were made of FRP, and the material recovered was CF containing a little GF. Aluminum frames, wooden grips, and CF used for shafts were recovered from the badminton rackets in this experiment. As the strings of both tennis and badminton rackets dissolved during treatment, we estimated they were made of polymer esters. Recovering aluminum and wood intact is one of the characteristics of this approach as shown in the experimental results.

Figure 3 shows the SEM photographs of CFs recovered from a tennis racket and a molded part of transportation equipment using depolymerization under ordinary pressure, and **Table 2** the results of single fiber tensile tests¹⁴⁾. For comparison, CF recovered with pyrolysis and fresh CF are also presented. The surface profile of the CF recovered from the molded part using depolymerization under ordinary pressure is approximately equivalent to that of fresh CF. The regularity of vertical lines seen in CF recovered from the tennis racket indicate they are not caused by damage. The results of tensile tests on these CFs are equal or exceed those on the fresh CF, suggesting their high potential for use as reinforcing materials.

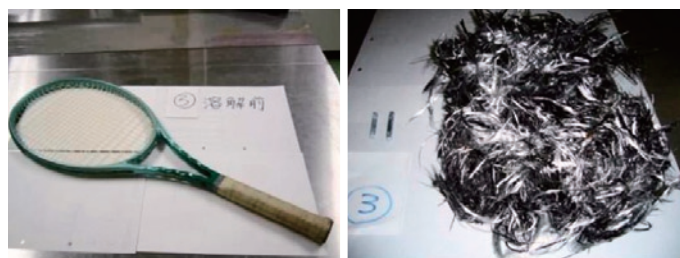


Figure 1 A treated CFRP tennis racket, before (left) and after (right)

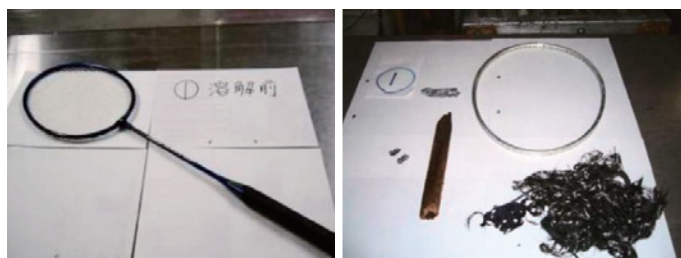


Figure 2 A treated CFRP badminton racket, before (left) and after (right)

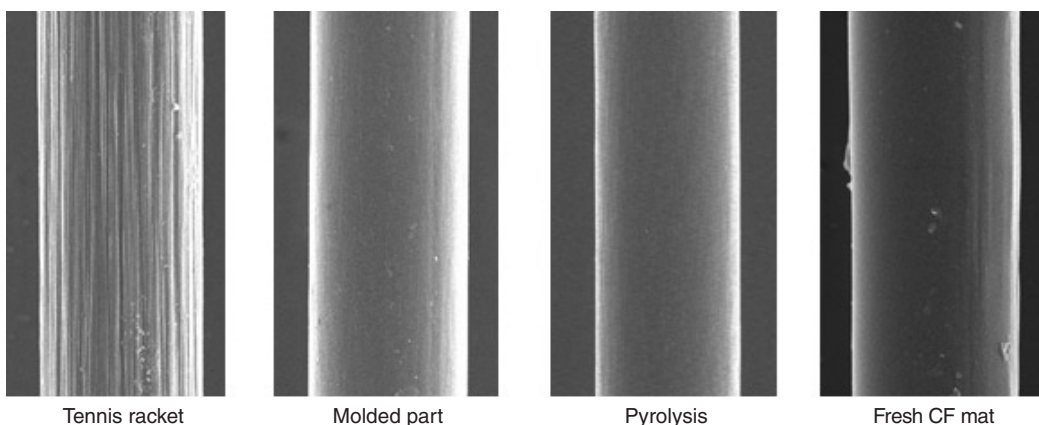


Figure 3 SEM photographs of Recovered CFs

Table 2 Results of single fiber tensile tests of recovered CFs

Item	Tennis racket	Molded part	Pyrolysis	Fresh CF mat
Tensile strength (MPa)	3,200	4,393	3,459	3,198
Tensile modulus (GPa)	188	303	301	152
Elongation (mm)	0.34	0.29	0.23	0.21

4 Development of Recovered CF Applications

CFs recovered from CFRP were flocculating, and we thought this would reduce the production efficiency of CFRP and inhibit the production of quality CFRP. To solve this problem, we examined how to produce non-woven fabric using recovered CF. Either a dry or wet method can be used to produce non-woven fabrics, and either was found to allow non-woven fabric to be produced from recovered CF¹⁴⁾. A carding machine was used in the dry method, and a paper pressing machine in the wet process to produce wadding from cotton, etc. As CF is conductive, the processing machine must be sufficiently insulated.

A carding machine was introduced to produce non-woven fabric from recovered CF in the dry process. Using this machine, CF was opened and carded, and several thin CF sheets, shown in **Figure 4**, were layered to produce non-woven fabric. **Figure 5** shows the non-woven fabric produced from the recovered CF. From this non-woven fabric, CFRP was experimentally produced



Figure 4 Production of recovered CF non-woven fabric with a carding machine



Figure 5 Recovered CF non-woven fabric



Figure 6 Recycled CFRP using recovered CF non-woven fabric

with the compression molding method. **Figure 6** shows the molded recycled CFRP. Similar to comparisons of single fibers, **Figures 7 and 8** show the results of tensile tests, and **9 and 10** the results of bending tests in comparison with non-woven fabric made of CF recovered with pyrolysis and CFRP using a fresh CF mat¹⁵⁾.

From these test results, no significant differences emerged between any of the recovered CFs and CFRP from a fresh CF mat, suggesting these CFs can be used for CFRP. All properties are reduced with CF content exceeding 25 %; probably due to imperfect carding, rather than defects in the machine or condition.

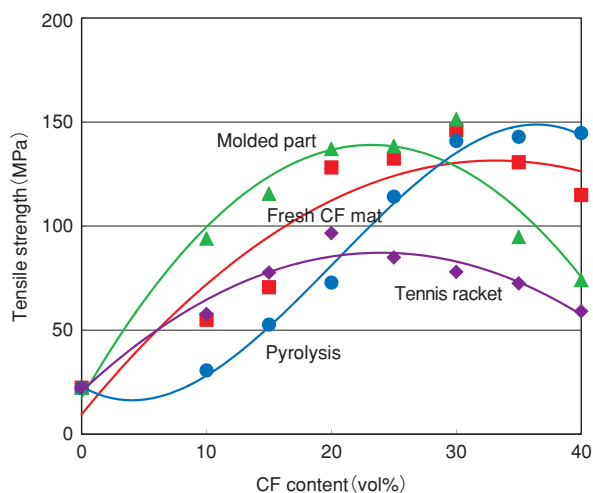


Figure 7 Tensile strength of recycled CFRPs

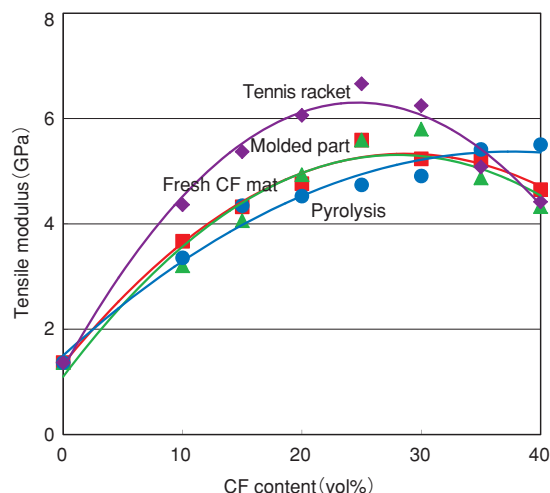


Figure 8 Tensile modulus of recycled CFRPs

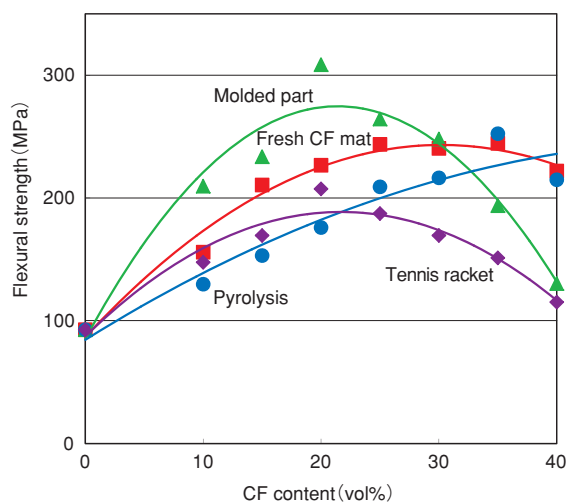


Figure 9 Flexural strength of recycled CFRPs

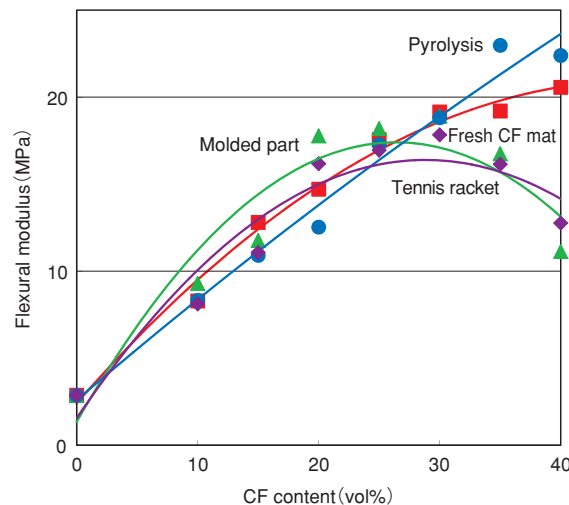


Figure 10 Flexural modulus of recycled CFRPs

5 Development of Recovered Resin Applications

EPs mainly used for CFRP include amine curing EP (EP/Am) and acid anhydride curing EP (EP/Ah) for which amine (Am) and acid anhydride (Ah) are used as hardener respectively. In depolymerization under normal pressure, a transesterification is used for depolymerization for exchanging ester bonds in the resin structure with solvent, i.e. mono alcohol. This technique was therefore applied only to CFRPs of EP/Ah, but we found that it could also be used for EP/Am through detailed settings on the depolymerization under ordinary pressure¹⁶⁾. The mechanism of depolymerization of EP/Am is under analysis, but this approach has become available for recycling almost all CFRPs with detail settings.

The depolymerization mechanism of EP/Ah has already been found. Depolymerization is triggered by a transesterification, and depolymerized products with benzyl ester or diol at the end of their chemical chains are generated¹⁷⁾. **Figure 11** shows the estimated depolymerization reaction formulas of EP/Ah.

EP prepolymer may be regenerated by degenerating these products.

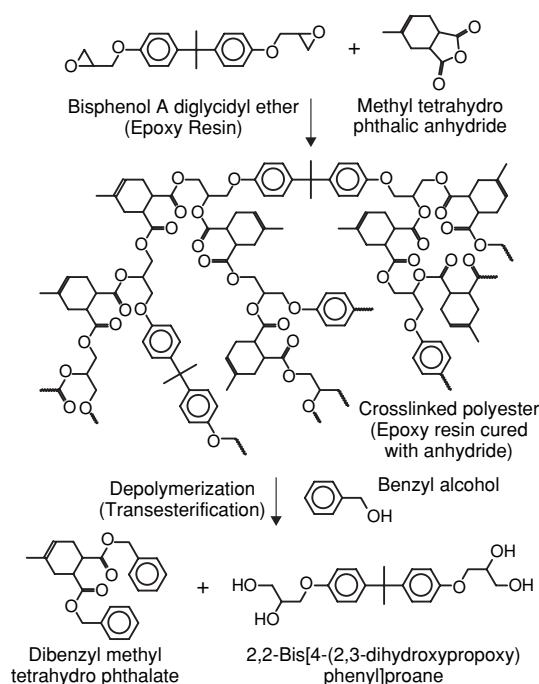


Figure 11 A estimated depolymerization reaction of EP/Ah

6 LCA of Recovered CFs

Tennis rackets made of CFRP having 50 wt% of CF content were used as samples subject to dissolution. After the samples had been treated with depolymerization under ordinary pressure, all the resins dissolved in 10 hours, whereupon EP-depolymerized products and CFs were recovered. Three categories of treatment, 1,000, 2,000 and 17,000 rackets/month were respectively defined. Facilities and processing conditions suitable for these categories were determined, and the required energy for dissolution, cleaning and drying processes was calculated and totaled to determine the overall energy required to recover CFs.

The energy required for 1,000, 2,000 and 17,000 rackets/month is 91, 78 and 63 MJ/kg, respectively (**Figure 12**). A breakdown of energy for 17,000 rackets/month revealed that the distillation energy was 38 MJ/kg, accounting for about 60 % of the total¹⁸⁾. To save more energy required to recover CFs, we plan to examine a new method of regenerating cleaning liquids.

Compared with the energy required to manufacture fresh CFs, i.e. 286 MJ/kg^{19), 20)}, the energy is smaller in all other categories, and about 1/4 or less in the category of 17,000 rackets/month (**Figure 13**).

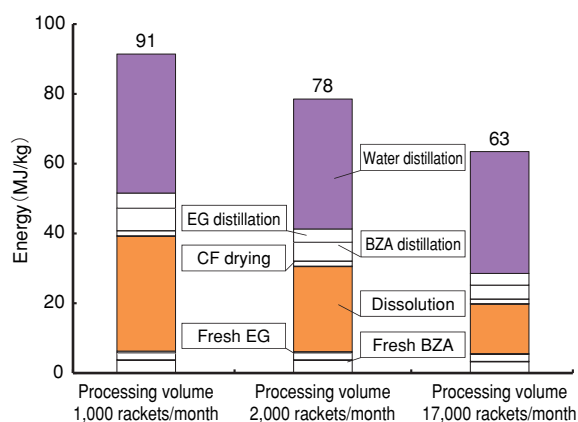


Figure 12 Energy of recovered CF by dissolving method under ordinary pressure

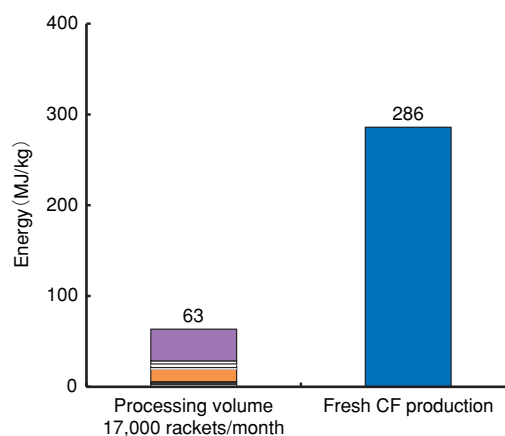


Figure 13 A comparison of energy of a recovered CF by dissolving method under ordinary pressure with a fresh CF on the market

Japanese companies have a substantial share of CF and CFRP markets, and related technologies are representative in Japan. Japan is also regarded as the most advanced nation for CFRP recycling technologies at present. Although papers on chemical recycling technologies for CFRP using, for example, supercritical propanol²¹⁾ have begun to appear overseas, almost all of them concern CF recovery technologies using pyrolysis. However, large projects targeting the development of recovered CF applications have been launched in Europe and the U.S., in which numerous researchers and engineers have participated.

Conversely, projects relating to the development of CFRP technologies do exist, but recycling technologies are merely one of objectives for these projects in Japan. There are no national projects solely targeting the development of CFRP recycling technologies. Hitachi Chemical started a business promotion project focusing on CFRP recycling in April 2012. Commercial operation is currently under discussion together with CF processing companies, CFRP manufacturers, CFRP users, and other stakeholders.

These technologies have been adopted and promoted in the 2005–2006 regional new industry creation technology development subsidy program sponsored by the Kanto Bureau of Economy, Trade and Industry.

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Photosensitive Film for HDI Optimized for DI

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1 Abstract

Direct imaging (DI) has been introduced into the patterning process of HDI instead of conventional mask contact exposure method. To achieve high throughput equivalent to conventional method, DI needs photosensitive films with high sensitivity. And recent increasing density of HDI requires properties of higher resolution and adhesion. We have been developing and marketing photosensitive films with these properties. In this report, we discuss the design concepts of our products for DI, and the new product (DL-3600 series) featuring less development sludge and smaller stripped flakes.

2 Product Features

- A product lineup for various types of DI exposure equipment contributes to increasing throughput.
- Rectangular resist profile has a large margin for resolution and adhesion and improves the yield.
- Less amount of development sludge helps to reduce the maintenance for the developing line.
- Smaller stripped flakes help to reduce the maintenance of the stripping line.

3 Background of Development

Layer alignment precision is a critical issue in the patterning process as HDI becomes denser and more multilayered in recent years. DI, which allows high-precision alignment with correction of exposure data based on the substrate dimensions, has been increasingly used. To produce a pattern of [line/space = 40/40 μm] with a high throughput equivalent to that of the mask contact exposure method, photosensitive DI films for HDI patterning must have resist film thickness of 20 to 30 μm , exposure energy quantity of 10 to 25 mJ/cm^2 , and resolution of 20 to 25 μm after development. At the same time, they should also meet the requirements for less development sludge and smaller stripped flakes, as conventional photosensitive films, to reduce the frequency of line maintenance.

4 Details of Technology

1. Optimizing the amount of photo initiator

When the amount of photo initiator is increased, sensitivity is improved. However, the absorbance of the film increases, resulting in an inverted trapezoidal resist which decreases adhesion (**Figure 1**). Our product provides excellent adhesion and high throughput by optimizing the type and amount of photo initiator according to the DI exposure equipment used.

2. Optimizing Tg and acid value of hydrophobic binder polymer

Hydrophobic binder polymers can effectively improve resolution and reduce the resist foot (**Figure 2**). Increases in the glass transition temperature (Tg) of hydrophobic binder polymer tend to improve resolution, but decrease the diffusion into the developer and increase the development sludge dose (**Figure 3**). Moreover, decreases in the acid value increase hydrophobicity and improve resolution, on the other hand, stripped flakes become bigger, which may entwine conveying rolls (**Figure 4**). Our new DL-3600 series uses hydrophobic binder polymers with optimized Tg and acid values to provide higher resolution and shorter resist foot while achieving less development sludge dose and smaller stripped flakes.

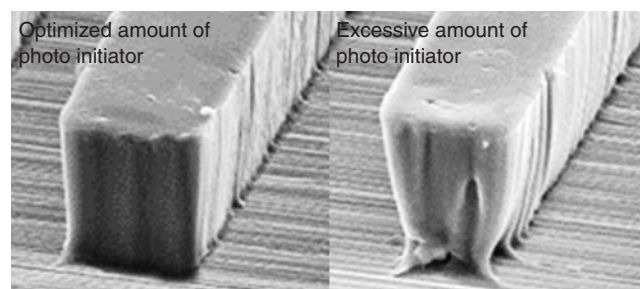


Figure 1 Relationship between amount of photo initiator and resist profile

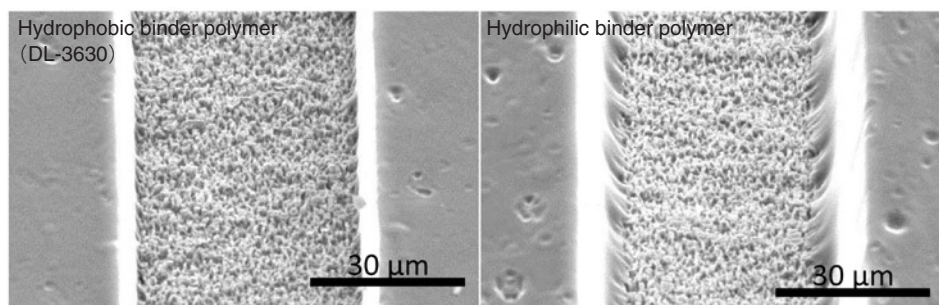


Figure 2 Relationship between hydrophobicity of binder polymer and resist foot length

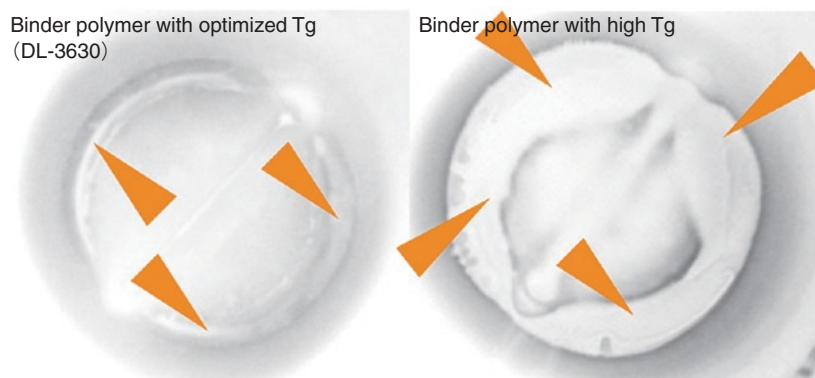


Figure 3 Relationship between Tg of binder polymer and development sludge dose (▶ sludge)

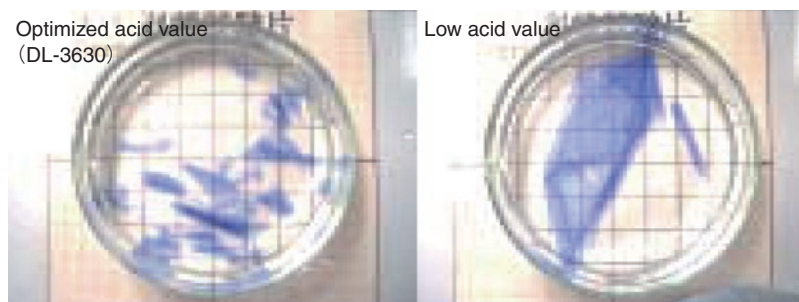


Figure 4 Relationship between acid value of binder polymer and stripped flake size

5 Future Developments

Development of DI photosensitive films for next-generation HDI (wiring pattern of line/space = 30/30 μm)

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New Material for Fine Patterning Package Substrates by Semi-additive Process“PF-EL”

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1 Abstract

The demand for miniaturization of electronic components and thinning has become stronger to achieve the miniaturization of high-performance electronic devices such as smartphone and tablet PC. Thus, the high-end package substrate is demanded to have higher stiffness and wiring density. We have developed new materials composed of the primer having high adhesion property with electrolessly plated copper and glass-fabric prepreg. It is PF-EL. Combining newly developed materials with glass-fabric prepreg, we finally obtained the build-up material for the higher wiring density and stiffness for the package substrate. The obtained build-up material may expand the capability of the next generation packaging.

2 PF-EL Features

- Fine line formation is possible in semi-additive process (SAP) using a roughened copper foil.
- High adhesion with copper plating is achieved.
- It can be used with prepreg to produce highly stiff, fine patterning substrates.

3 Background of Development

As recent electronic equipment becomes more functional and smaller, package substrates need to be denser and thinner. When the proportion of film materials used for build-up layer on these fine patterning package substrates increases, the coefficient of thermal expansion (CTE) tends to rise and stiffness is likely to decrease due to a thinner core layer. Accordingly, warpage increases, and chip cracks and other packaging defects are prone to occur. Finer line formation and stiffer structures are required for both core and build-up layers¹⁾.

Hence, we estimated that both fine line formation and high stiffness could be achieved by using an ultra-thin primer layer on the surface of low thermal expansion and ultra-thin glass-fabric prepreg, in place of the film material on the build-up layer, as shown in **Figure 1**. For starters, we developed copper foils coated with several μm of primer on which SAP is applicable.

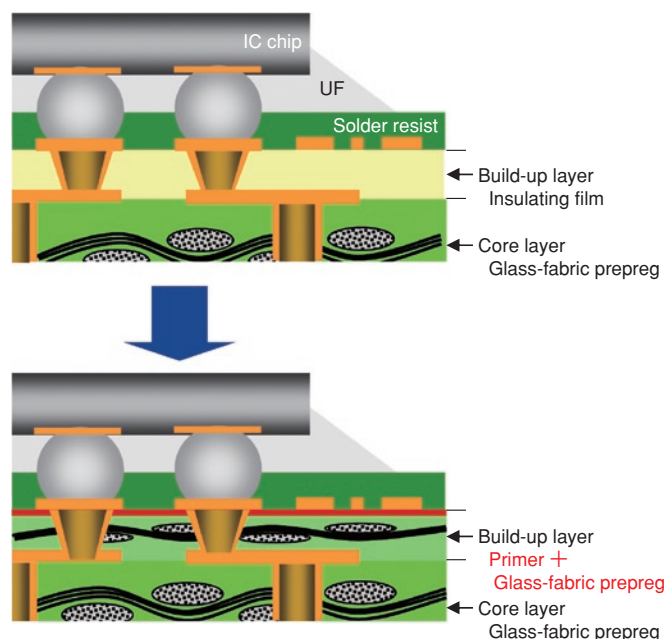


Figure 1 Package substrate using PF-EL

4 Details of Technology

1. PF-EL design concept

PF-EL is basically designed with glass-fabric prepreg coated with several μm of primer on which a roughened copper foil is transferred. The primer targets high adhesion with copper plating through the physical anchor effects of the primer surface, on which a roughened ultra-low profile copper foil is transferred, and the inclusion of a functional group, having high chemical interaction with copper, into the resin. With this primer, a fine line formation in SAP using a stable and microscopic roughened form (surface roughness Ra: 0.40 μm or less) by transferring roughened copper foil, and high peel strength against copper plating are achieved.

2. Adhesion between PF-EL and copper plating

Figure 2 shows the peel strength measurements of copper-plated PF-EL. The peel strength is 0.4 kN/m or less without primer, but increases to 0.7 kN/m or more and stabilizes after primer is applied. It was confirmed that the plating peel strength is improved by adding a more microscopic roughened form produced in the desmear process. Hence, it is proved that the physical and chemical interactions between the primer and copper plating can effectively improve and stabilize adhesion.

Sample		A	B	C	D	E
Primer		None	Used	Used	Used	Used
Desmear	Swelling	—	—	80°C/ 2 min	80°C/ 5 min	80°C/10 min
	Micro-etching	—	—	80°C/ 3 min	80°C/ 8 min	80°C/15 min
	Neutralization	—	—	40°C/ 5 min	40°C/ 5 min	40°C/ 5 min

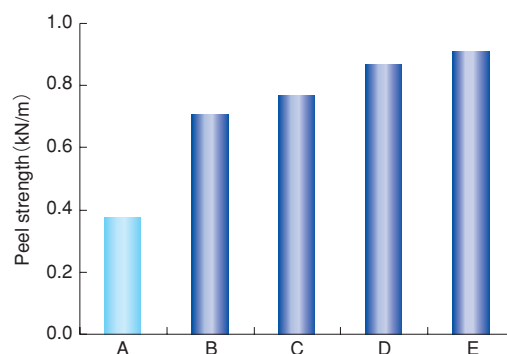


Figure 2 Peel strength between PF-EL and copper plating

3. Fine line formation of PF-EL

Figure 3 shows the fine line formation of PF-EL in SAP. We confirmed the fine line formation of a line/space = 10/10 μm level. **Figure 4** shows the results of highly accelerated life tests. A potential decrease in the reliability of interconnection insulation of PF-EL due to the migration of copper between narrow pitched wirings was a concern, but the insulating resistance did not deteriorate, even after 300 hours, proving that PF-EL has good insulation reliability.

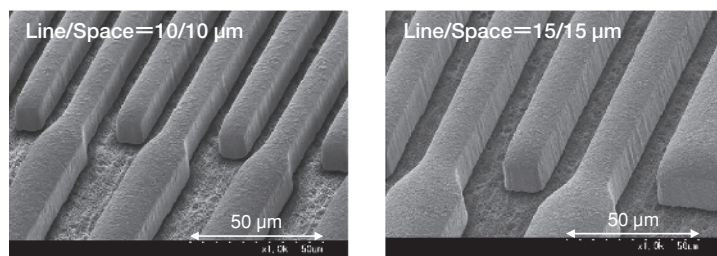


Figure 3 SEM image of fine line formation on PF-EL

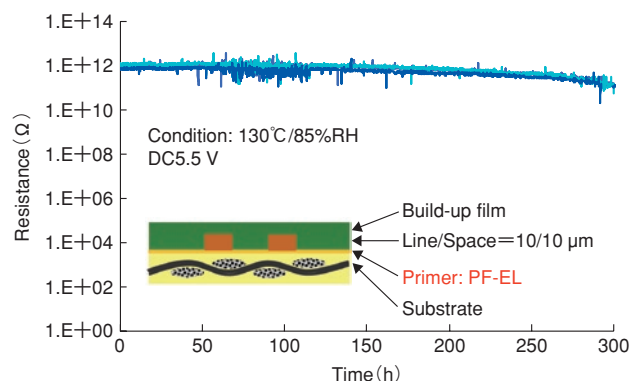


Figure 4 Result of HAST of PF-EL

5 Future Prospects

- Development of semi-additive fine line formation materials for next-generation equipment (development of Airfoil)
- R&D of the application of ultra-low roughened copper foil (Ra: 0.2 μm or less) and improvements in adhesion with copper plating

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Next Generation Molding Compound GE-110 Series for BGA

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1 Abstract

Regarding the HAST (Highly Accelerated temperature and humidity Stress Test) failure by Cl ion with Cu wire¹⁻³⁾, we established the method for ion mobility checking in molding compound by dielectric dispersion evaluation and then we confirmed the correlation between ion mobility and HAST failure. In addition, we can improve the HAST performance with using ion mobility control by resin structure optimization. And regarding the warpage control for thin package, we can improve the warpage to use the CTE (Coefficient of Thermal Expansion) control technique by installing new additive.

We developed the GE-110 series with using these ion mobility control technique and CTE control technique for Cu wire apply and thin package apply as new generation molding compound for BGA.

2 Product Features

- Prevention of corrosion caused by Cl ions produced in HAST by controlling the ion mobility in resin and applying this technique to copper wire packages
- Control of the coefficient of thermal expansion of resin by applying a material to control thermal expansion and decrease the warpage of thin packages

3 Background of Development

We developed a technique to reduce viscosity using polymer material and organic-inorganic composite technologies. This technique was applied to the GE-100 Series, and the excellent flow property of wire and good continuous formability they feature have contributed to a high market share for BGA molding compounds. However, it is difficult to apply the current GE-100 Series to the copper wire increasingly used recently in place of gold wire, and warpage of thinning molding packages.

The use of copper wire requires measures to prevent corrosion caused by Cl ions^{1,3)}. The current solution involves adding an ion trap material with high chlorine trapping capability⁴⁾, but this technique tends to hinder the flow property and formability. The issue is how to maintain the latter properties while applying this technique. To prevent warpage of thin packages, both at room temperature and during the reflow process, Coefficients of thermal expansion of resin CTE1 and CTE 2 need to be controlled separately, suggesting that the problem is not solved by simply adjusting the filler volume.

We developed a next-generation molding composite GE-110 Series for BGA using newly developed resin ion mobility control and thermal expansion control technologies and adapting to copper wire and warpage of thin packages.

4 Product Design

(1) Controlling the ion mobility in resin

Figure 1 shows the master curves obtained when measuring dielectric relaxation (reference temperature: 165°C), where the absolute dry condition at 165°C is equivalent to the iso-free volume fraction of a water absorption of 0.3 wt% at 130°C. In **Figure 1**, the peak in frequency range between 10^{-3} and 10^2 Hz is associated with the molecular motion in the side chain of the resin. It is assumed that ions move with this molecular motion in the side chain. In GE-110, the peak is seen in a lower frequency range than that in GE-100, and ion mobility is obviously slow as intended in the design. Ion mobility in the GE-110 Series is controlled by increasing the Tg (glass transition temperature) of resin and decreasing water absorption with a special additive.

(2) Controlling the thermal expansion of resin

The additive used to reduce water absorption was found to be capable of adjusting CTEs, increasing CTE1 and slightly decreasing CTE2 by forming a domain in resin. Accordingly, it proved effective for improving the mismatch of thermal expansions of substrate and resin, and suppressing warpage of thin packages. **Table 1** lists the properties of resins.

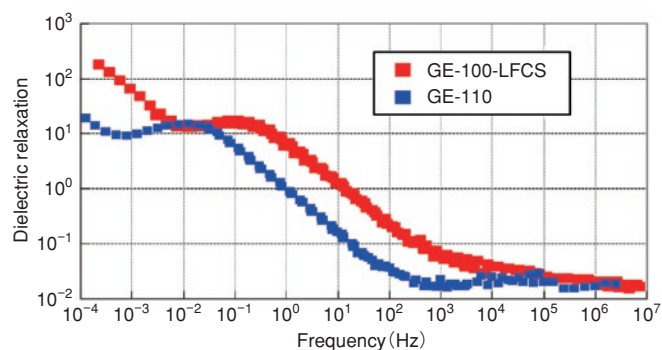


Figure 1 Dielectric dispersion 165°C

Table 1 Comparison of GE-100 series and GE-110 series

Item	GE-100-LFCS	GE-110-LS
Epoxy	Biphenyl	Biphenyl
Filler Content (wt%)	88.5	85.0
Additive for lowering moisture	None	Added
Spiral Flow (cm)@175°C	185	230
Gel Time (sec)@175°C	45	39
CTE1 (ppm)	9	11
CTE2 (ppm)	39	40
Tg (°C)	143	151
Moisture absorption (wt%) @130°C, 85%RH	0.31	0.3
pH	5.6	5.6
Cl ⁻ (ppm)	13	10

5 Future Prospects

- Global marketing of the GE-110 Series
- Application to compression corresponding and mold underfill materials

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- 2) H. J. Kim, J. Y. Lee, et al., Effects of Cu/Al Intermetallic Compound (IMC) on Copper Wire and Aluminum Pad Bondability, IEEE TRANSACTIONS ON COMPONENTS AND PACKAGING TECHNOLOGIES, Vol. 26, No. 2, JUNE 2003
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Doping Paste for Photovoltaic Solar Cell

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1 Abstract

In response to global trends such as environmental protection and abolition of nuclear power plants, renewable energy sources have attracted attention increasingly¹⁾. Especially photovoltaic (PV) related business has been expected as a growth industry. In the field of the crystalline silicon PV, the development of high performance cells of new structure such as the selective emitter cell, back-contact cell and bifacial cell has been progressing quickly. We paid our attention to the doping of phosphorus (P) or boron (B) indispensable to these cells. In this paper, we outlined the development of doping paste (DP) which can diffuse P or B into silicon uniformly and selectively.

2 Features of Developed Product

- Uniform diffusion of dopant (phosphorus or boron) under Si surface increases the uniformity of sheet resistance in the substrate.
- The performance of dopant diffusion on the area coated with this product (selective diffusion) is high.
- Solubility in hydrofluoric acid is high, and remnants of the hydrofluoric acid etching process are minimized.

3 Background of Development

Figure 1 shows a cross-sectional view of a conventional PV cell and the high-efficiency PV cell (SE and IBC cells). We analyzed PV cell structure trends, and noted that the n-type doping paste was suitable for forming the n^{++} layer of SE cell, and also applicable to the formation of p^{++} and n^{++} layers of IBC by combining p- and n-type doping pastes. In the feasibility study of doping paste, which started in the second half of 2009, we selected phosphorus and boron-mixed compounds, and after confirming the potential for dopant diffusion with these compounds in principle, started the full-scale development of doping paste.

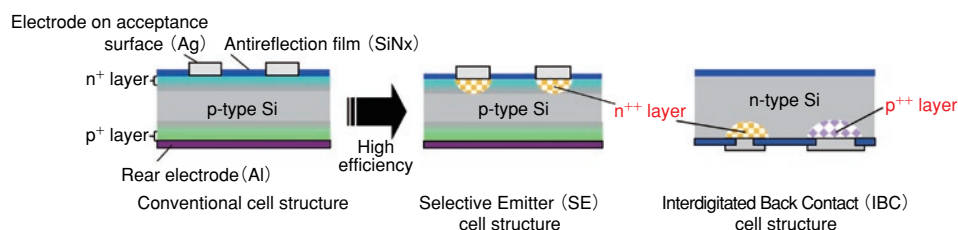


Figure 1 Cross sectional view of the conventional cell and the next generation cell

4 Details of Technology

(1) Material design concept

Figure 2 shows the process of forming the n^{++} layer using the developed n-type doping paste, which consists of phosphorus mixed compound, resin and solvent. When the paste is coated on the Si substrate, and the resin and solvent are removed in the drying and degreasing process, only phosphorus-mixed compound remains as particles. As the latter is designed to melt at a high temperature over 800°C , and follow the Si surface at the diffusion temperature ($\geq 800^{\circ}\text{C}$), phosphorus diffusion on the Si surface is uniform. The same design concept is used for p-type doping paste, namely, boron-mixed compound is used in material design to

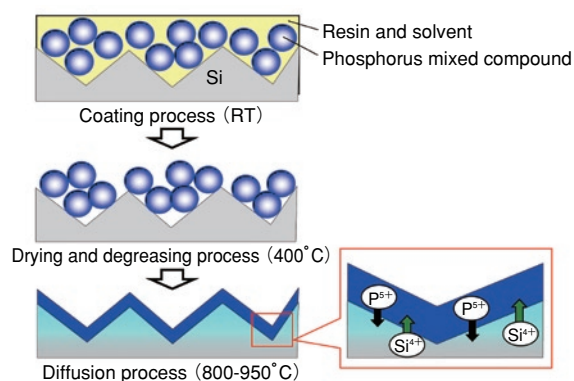


Figure 2 Concept of n^{++} layer forming on Si with n-type doping paste

facilitate the uniform diffusion of boron.

(2) Evaluation of p-type doping paste

According to the aforementioned material design concept, **Figure 3** shows the results of measurement and mapping of the sheet resistance of boron doped Si surface (156 mm x 156 mm, entire size) using the p-type doping paste containing boron-mixed compound. The colors indicating the sheet resistance values are homogeneous in the surface area, confirming the uniform diffusion of boron on the Si surface. **Figure 4** shows the SEM image of boron doped Si surface after etching with hydrofluoric acid, clearly showing no residual boron-mixed compound. Diffusion of gases such as BBr_3 is a typical way of boron doping, but this generates residual material due to the boron-rich layer (BRL) during diffusion, impairing efficiency.²⁾ The SEM observation of this product does not find any residual, and confirms repellency to indicate the absence of BRL. This means the p-type doping paste will be effective for forming the p layer of various high-efficient cells.

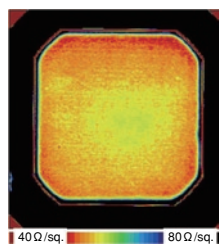


Figure 3 Sheet resistance mapping on the boron-doped Si surface with p-type doping paste

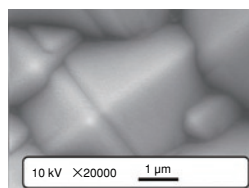


Figure 4 SEM image of the boron doped Si surface after etching with HF solution

(3) Evaluation of n-type doping paste

Figure 5 shows the result of SIMS analysis of phosphorus diffusion in dosed and non-dosed areas 2 mm apart from the dosed area, beneath the Si surface dosed and diffused with n-type doping paste in a pattern. The phosphorus concentration in the non-dosed area near the Si surface is significantly low, although high in the dosed area, indicating the area is sufficiently dosed and confirming a highly selective diffusion of phosphorus. Using this selective diffusion, we made the prototype SE cell shown in Figure 1, and evaluated its PV properties. **Table 1** shows the results. The SE cell using our n-type doping paste has greater short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) than those of conventional cells, resulting in an increase of 0.4% in conversion efficiency (Eff). This product was marketed as YT-2100-N in the first half of 2012, and is used by PV manufacturers for SE.

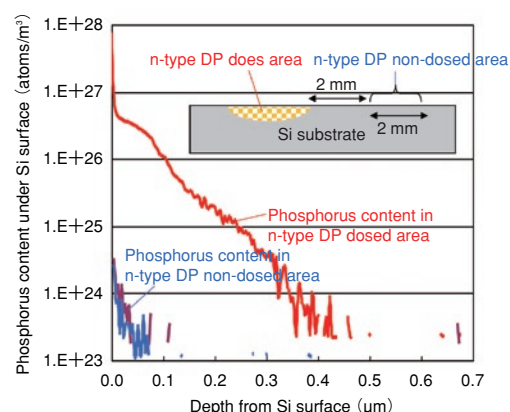


Figure 5 Concentration distribution of Phosphorus beneath Si surface doped with n-type doping paste [SIMS analysis]

Table 1 PV Properties of Selective Emitter Cell doped with n-type Doping Paste

Cell type (single crystal Si)	Short-circuit current density (J_{sc}) [mA/cm ²]	Open-circuit voltage (V_{oc}) [mV]	Fill factor (F.F.)	Conversion efficiency (Eff) [%]
Conventional cell	37.0	623	80.1	18.5
SE cell	37.4	634	79.7	18.9(+0.4)

5 Future Prospects

- Development of p-and n-type doping pastes for the IBC cell
- Identification of the doping paste composition available for simultaneous diffusion of phosphorus and boron

[References]

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- 2) M. A. Kessler et al.: Semiconductor Science and Technology, 25 (2010) 055001 (9pp)

[Related Patents]

Japan Patent Nos. 04868079, 04978759, 05176158, and 05176159

Tear Total IgE Detection Kit

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Medical Business Unit

1 Abstract

This product is an in vitro diagnostic kit and is used for auxiliary diagnosis of allergic conjunctival diseases. This product has been launched in medical institutions after its approval by MHLW in September 2008. The unique value of this product is that it is able to take the tear fluid directly from the patient's eye. The doctor can collect the specimen and test immediately, in person, at the medical practice. Therefore the development of this product to new markets is expected to be categorized as POCT (Point of care testing).

This product form is strip shape, which is suitable for testing small amounts of tear fluid. In certain cases, it had been reported in the medical field that tear fluid collection from a patient took too long due to the patient's inability to produce the necessary tear volume to conduct the test. We have developed a product, which improves the collection time of the tear fluid.

2 Features

- Improved sample absorbency by decreasing the void ratio of sample collection fabric, hydrophilic treatment of fabric and optimizing placement size
- Reduction of the sampling time and sample volume

3 Background of Development

Although the method of easily measuring a small quantity of IgE was not available before, we succeeded in commercializing this method by using high-efficiency antibodies and by an immunochromatographic technique used for influenza diagnostic products and pregnancy tests. This product form is strip shape. **Figure 1** shows the principle of reacting IgE in tear fluid on the strip.

The required tear fluid volume for measuring with this product is about 10 μ L. Samples are collected by applying the sample collection area, which is made of non-woven fabric, on the lower conjunctival fornix of the eye. When the collected tear fluid moves from the sample collection area to the test area made of nitrocellulose membrane via capillary action, the test area impregnated with reagent is immediately moistened with the tear fluid, whereupon reaction begins. The time taken for the test area to get wet was problematic at the medical practice. We examined the possible improvements in the tear fluid absorbency of the sample collection fabric, and the optimization of the connection between the collection areas and the test areas, and improved the product to shorten the time required to collect tear fluid.

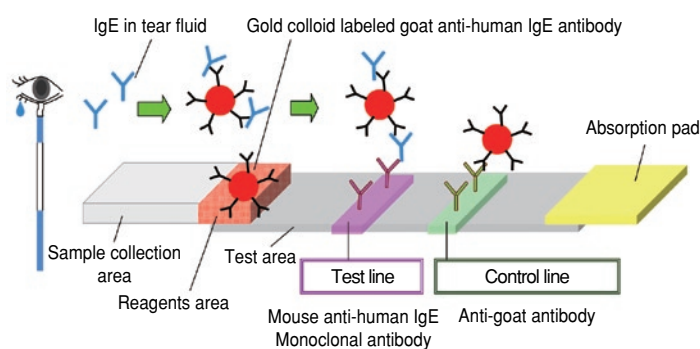
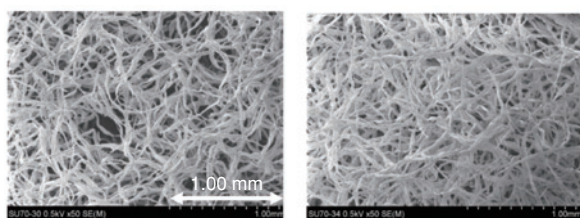


Figure 1 Principle of the assay

4 Details of Technology

(1) Design

The sample collection area is made of cellulose non-woven fabric, and contains voids between entangled fibers. As it was supposed that a smooth movement of the fluid to the test area would be interrupted if the fluid were trapped in these voids, the void ratio was reduced by compressing the non-woven fabric. **Figure 2** shows SEM images of conventional fabric in (a) and compressed fabric in (b). The product was improved by the hydrophilic treatment of fabric and by optimizing placement size (**Figure 3**).



(a) Conventional non-woven fabric (b) Compressed non-woven fabric

Figure 2 Non-woven fabric SEM image

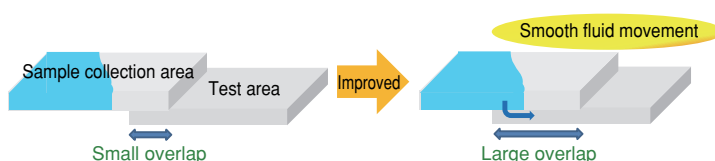


Figure 3 Optimization of placement

(2) Evaluation

1) Sample absorption time

With 10 μ L of control sample, the time taken for the test area to get wet was measured. The result is shown in **Figure 4**. Whereas the conventional product took about 30 seconds to start getting the test area wet from the start of absorbing the sample, the improved product took 10 to 15 seconds, it is nearly half the time of the conventional product. The time of the improved product for getting the entire test area wet is also shorter than the time of the conventional product by about 30 seconds.

2) Sample volume

The sample volume were divided into ten categories, and 10 strips were tested for each volume. The number of measurable strips and absorption time were also measured. **Figure 5** shows the results. Using 5 to 7.5 μ L that were less volume than the volume to be required by the conventional product, improved product strips were measurable. When the sample volume is small, the absorption time usually increases, however, with the improved product, a smaller volume was absorbed in shorter time than the time of the conventional product.

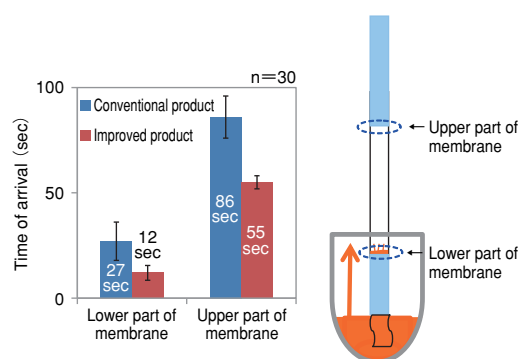


Figure 4 Sample absorption time

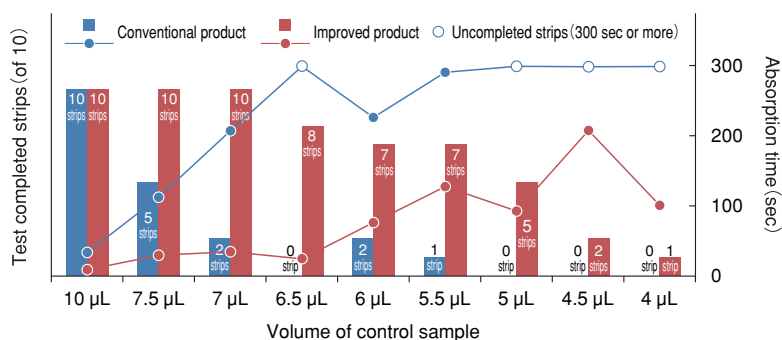


Figure 5 Study of sample volume

Regarding the basic reagent performance including sensitivity, precision and within-run reproducibility, the improved product has basic performance that is equivalent to conventional products and meets the required quality standard.

5 Future Prospects

- Development of test reagents for small amounts of body fluids except tear fluid (e.g. saliva, nasal discharge)
- Development of specific IgE test reagents

[References]

1) Hitachi Chemical Technical Report, No. 52 (2009-1)

[Patent]

Japan Patent No. 5218235

Editor's Note

Japan looks booming by Abenomics and its accompanying economic upturn. Abenomics is seeking recovery of economic cycle: money flow increases in the market, deflation ends, prices increase, companies' profits increase, salaries increase, consumers buy more, and then companies become strong. The theory sounds reasonable, but can the economic cycle really become better in such a short period?

Considering our research and development, however, it seems difficult to achieve good results in the short term. Material development usually takes at least several years for tangible consequences to be realized, even after a selection and concentration policy is established and resources are heavily allocated to critical themes. We must remain patient all the while, even though the next yard looks nice, or in the event of significant pressure from top management. Changing themes frequently in a short time will not make it big with hit products or new business.

The accomplishments presented in this report also reflect many twists and turns through the years. We thank all of the people who were engaged in these field, and hope the growth of resulting new products or new businesses.

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