Green photonics for laser-based manufacturing

— Photonics contributes to a sustainable society in the “photon century” —

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Green photonics is expected to reduce energy consumption and pollution associated with a broad range of manufacturing processes. This paper is a study on the development of laser-based methods and their applications. High precision surface processing of various materials is a key technology for practical industrial applications. Well-defined micro-fabrication with high-speed and high-quality treatment of materials was performed by laser irradiation. The technical challenges are particularly great in this area, but recent developments in laser processing have opened up new frontiers. Due to advances in laser processing systems, and greater understanding of the phenomenon of diverse excited states generated by laser irradiation, these methods can be considered mature and versatile techniques that present some key benefits over other more established fabrication techniques.

Keywords **:** High-power laser, laser-material interaction, photo-induced excitation, surface chemical reaction

1 Introduction

The clarification of interaction between photon and matter substances and photon (light) has been an important academic research topic since ancient times, and currently, research is promoted actively as an advanced topic in many countries. Looking at the process of photon absorption by substances, various excitation states are induced in substances (atoms and molecules) through photon absorption, followed by a relaxation process, chemical bond cleavage, and others. In the relaxation process from high-vibrational excitation, a high-temperature state occurs through the so-called photothermal process, and in the chemical bond cleavage from an electron excitation state, the chemical reactions such as dissociation of molecules and recombination of chemical bonds occur through the photochemical process. The main characteristic in practical use is that area-selective localized treatment to a specific area is possible by irradiating the base material with light focused into micro-patterns or micro-spotlights.

The main topic of this paper is the processing technology using lasers, and the localized laser treatment technology based on the characteristic photo-excitation process induced by irradiating high-power lasers to various advanced materials including polymers, glass and ceramic, metals, and composites is addressed. The goal is to use the laser excitation processing technology for cost reduction, increased efficiency, and environmental load reduction in industrial application, by promoting process and part saving in manufacturing. Particularly, we aim for widespread use in society by improving energy-saving characteristics of products, by providing novel members, parts, and products through the realization of high-precision, high-quality processing of difficult-to-process materials. By introducing the laser technology to the manufacturing process, we hope to achieve greening of the product and manufacturing processes.

The greening of the manufacturing process means the promotion of energy saving, material saving, and waste reduction throughout the whole process of new manufacturing methods compared to the conventional methods. Since the energy saving measures are thoroughly implemented in the Japanese factories, expectation is high for altering the process content such as process saving and reduction in the number of parts rather than simple renewal of a process. Greening of the products means that the production volume of energy-saving members and parts that are desired by the market are stabilized and used in products. Although the effect may be small for a single part, the ripple effect on society as a whole may be large if the amount used throughout the market is enormous. Particularly, if such parts are used as main parts of durable consumer goods, the energy-saving effect will be enhanced.

For the R&D of material processing technology using lasers in Japan, budgets are allotted heavily by the New Energy and Industrial Technology Development Organization (NEDO) of the Ministry of Economy, Trade and Industry (METI), and the Japan Science and Technology Agency (JST) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), for industry-academia collaboration toward industrial application. Overseas, the collaboration

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for photonic application technology is encouraged by the European Union and the European governments. In the United States, the National Additive Manufacturing Innovation Institute (NAMII) was established in 2012 as an industry-government-academia collaboration center, and research for 3D forming technology is being promoted.

In Chapter 2, the characteristics of the laser processing technology are compared with the competing technologies, and the capabilities as of present are overviewed and organized. In Chapter 3, what kind of elemental technologies were combined for the processing technology using lasers are presented by describing the specific case studies of actual research that we conducted. In Chapter 4, the significance of research results and the comparison and discussion with the future scenario are discussed.

The year 2015 when this paper is published was designated and declared as the “International Year of Light (IYL2015)” at the United Nation General Assembly (UNGA 68, Paris) (Fig. 1). Various educational activities are planned to feature the importance and attractiveness of the science and technology of light.[1]

2 Characteristics of the laser materials processing technology

2.1 Main properties of laser devices and their effects

Since the laser has higher temporal and spatial coherency compared to other light sources, it has the characteristics of: (1) monochromaticity (short wavelength, wavelength selectivity), (2) high directivity, and (3) high intensity. Table 1 shows a list of properties of the laser devices currently used in laser processing. Main properties are the five parameters: laser wavelength, average power, pulse width, pulse repetition rate, and beam quality. Wide ranges of property distribution have been achieved for each parameter. However,

Fig. 1 Official logo of the International Year or Light (IYL2015; color version)

Table 1. Specifications of laser equipment used in materials processing

Main property	Specifications
Laser wavelength	IR, Visible 800 nm, UV 400 nm, 200 nm, VUV 10 nm, X-ray (↔)
Average power	1 µW, 1 mW, 1 W, 1 kW, 100 kW (↔)
Pulse width (sec)	cw, ms, µs, ns, ps, fs (↔)
Pulse repetition rate	10 Hz, 1 kHz, 100 kHz, 1 MHz, 1 GHz (↔)
Beam quality	Multimode, Single-mode (↔)

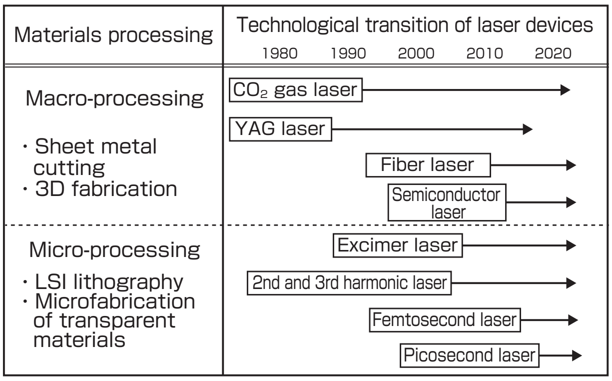
Note) Although the performance of laser equipment is evolving constantly, the specifications shown in the table have not been comprehensively or entirely realized between the main properties.

the characteristics of lasers that can be emitted from one laser device is limited, and the selection of the device appropriate for the use objective and the optimization of irradiation parameters are important tasks in conducting high-speed, high-quality laser processing. Another characteristic of laser irradiation is that the irradiation environment factors such as temperature and gas can be selected freely.[2]-[4]

In the fundamental step of laser processing, the absorption of photon energy to the target material without loss is important. By irradiating photons that possess wavelength (number of vibrations) that corresponds to the energy difference between the quantum state of substances, it is possible to shift to excitation level (it is also necessary to fulfill the selection principle). If the excitation can be achieved with the absorption of one photon, it is a one-photon absorption process (linear absorption process) that is a phenomenon that occurs commonly in nature. The absorption spectrum that is measured using an ordinary spectrometer shows wavelength dependency of photon absorption volume in one-photon absorption. Therefore, in order to infuse photon energy to the target material without loss through one-photon absorption, the basic procedure is to irradiate at the absorption band wavelength of the material.

On the other hand, if the density of light is increased, the phenomenon in which multiple photons are absorbed simultaneously to a substance is observed. This is called the multi-photon absorption process. Since it occurs in proportion to the power of light intensity (nonlinear absorption process), it is a phenomenon that occurs prominently in the irradiation of ultra-short pulse lasers with high peak power of femtosecond- or picosecond- pulsed light. The level excited by multi-photon absorption is the sum of photon energy that is absorbed simultaneously, and the excitation to levels higher than the one-photon absorption is possible. That is, with the multi-photon excitation of near-infrared region with wavelength of 1,000 nm, the excitation level can be shifted to the level equivalent to the energy of visible or ultraviolet energy. There are many organic polymer materials and glass materials that

Table 2. Historic transition of high-power laser equipment used in material processing



Note) Left end of a device sign corresponds to the "year when it was put to industrial practical use."

possess strong absorption bands in the ultraviolet to visible region but have no absorption bands in the near-infrared region. The irradiation method, where the multi-photon excitation is induced only in the area inside the base material where the light is focused by irradiation with near-infrared ultra-short pulse lasers, is being studied.[5]

Average power is the total sum of photon energy emitted by a light source device in one second. With pulse action oscillators, the average power is the product of photon energy and pulse repetition rate of a single pulse. The average power is the factor that determines the rate of the whole processing, and a light source device with large average power output is selected for the application fields that demand high-speed processing.

For beam quality, in the case where the energy intensity in the radial direction of the laser shows Gaussian distribution is called the single mode, and smaller focused beam diameter can be obtained compared to the multimode light. Therefore, in the case where irradiation is done by a single spotlight, high-speed scanning by the single mode is effective. However, for LSI (semiconductor) lithography where fine, complicated patterns are transferred to the photoresist, the multimode light with narrow-short bandwidth that is capable of controlling the speckle noise (spots of light and dark that can be seen in scattered light; a unique phenomenon that occurs when the laser is coherent) is used as the light source of the reduction optical system. It is effective to use lasers when one wishes to conduct site-selective processing or analysis of specific areas. Moreover, a pulsed laser device improves temporal control in addition to the aforementioned characteristics. Therefore, it becomes possible to precisely handle the two control factors, "space" and "time," and this enables material control technology in the micro- and nano-scale region.

Table 2 shows the historic transition of high-power laser equipment for material processing. In the recent progress of laser equipment, the improvement of high power, beam quality, and achievement of short pulses are points that are gathering attention. With fiber lasers that are being introduced to the market at speed similar to CO_2 gas lasers and YAG lasers that used to lead the microfabrication fields, the average power improved up to the 100 kW range, and the electricity-light conversion efficiency reaches 30 % for the plugin and thus have high energy-saving performance. This is mainly due to the high performance of the laser diode device, and the achievement of high power (several kW range) is also remarkable in the stacking laser diode device for direct irradiation. These laser devices have realized high-quality, high-speed processing in various material processing technologies including cutting, drilling, welding, joining, surface modification, and 3D fabrication. The short wavelength lasers and ultra-short pulse lasers are being introduced in the field of microfabrication.

2.2 Characteristic of the laser processing machine system

The industrial machine system for laser processing technology in manufacturing lines consists of four main elements: (1) the laser device, (2) the optical and beam delivery system, (3) the positioning and transfer system for materials (products), and (4) the processing procedure (including in-process monitoring technology). The core elemental technologies that determine the processing performance are (1) and (4). The elemental technologies that improve the productivity in manufacturing are (2) and (3). As actual machining tools, not only the 2D processing devices for flat base materials, but also the 3D processing systems that can handle 3D products is being developed for use in the manufacturing line. The technology that allows the precise reflection of digital design data to processed products is advancing and continues to evolve.

The progress in irradiation optical systems and transfer systems is contributing to the increased processing resolution and processing speed, as well as increased size of the products. As a characteristic example, laser processing is applied to the manufacturing process of liquid crystal display television (LCD-TV) and photovoltaic cells. In the LCD-TV, a repair machine system that saves the defective lot during panel manufacture by correcting the defect of the TFT array to increase the yield has been developed, and in the photovoltaic cells, the patterning machine system for various thin films such as transparent electrode films, semiconductor films, and metal films are used. As the size of mother-glass plates increases every year to several meter levels, the processing precision of micrometer level is demanded. The dynamic range may reach five to six digits, and state-of-art mechatronics technology is utilized.

Recently, the advanced technology for automatic control among various elements, where the sensors attached to various main elements described above possess internal communication functions to exchange information mutually, is being developed in conjunction to the progress in IT and robot technologies. It is expected to shorten the manufacturing tact time and increase the operation rate of the whole plant, and efforts such as IoT (Internet of Things) in the United States and Industry 4.0 of Germany are gaining attention.[6][7] In the IoT for manufacturing industry, it is expected that not only advancement and optimization of the manufacturing process but also a globally dense manufacturing system can be constructed by directly linking the customer demand and ordering information. Industry 4.0 is almost the same concept as IoT, and the name denotes the "Fourth Industrial Revolution" in human history.

2.3 Comparison with the competing processing technologies

2.3.1 Processing by physical mechanisms such as cutting and drilling processes

Compared to competing machining technologies, since laser processing is noncontact processing that does not employ cutting tools, there is no expendable parts by wear and degradation. Also, since there is no process reaction force, high-precision processing can be conducted on base materials with low stiffness. Transmission loss is small, and the light source device does not generate noise or vibration. Even with continuous wave lasers of kW range, transmission is possible from the light source device to the processing head using optical fiber delivery. The connection of the light source and the head is simple, and there are advancements in cutting and welding technologies by remote processing (method whereby the processor head and base materials are kept at a distance) that can be applied to high-speed processing in remote or tight areas. When conducting laser processing by physical mechanisms, the mechanism is often based on the generation of high-temperature conditions through the photothermal excitation. Therefore, a major characteristic is that the balance of light energy absorption and the rate of heat diffusion are optimized, assist gas is used, and this can be applied to the processing of metal materials with high melting points. In laser processing, effective processing can be done for target materials up to several centimeters, but currently, cutting of plates with thickness of 5 cm or more is difficult.

Laser processing technology is expanding application as a technology for medium to small volume production. In the processing using molds, work efficiency and profitability are expected for mass-production for lots in several tens or several hundreds of thousand units, while laser processing may be a cost reduction technology for production of several hundred to several thousand units in the prototype development stage. By conducting flexible processing by direct laser drawing, the necessity of mold fabrication and the risk factors such as mold management are removed, and it is being used widely as the production technology for high-precision processing that allows quick delivery (shortened delivery time) and flexible changes in specs for small to medium volume production of multiple product types.

2.3.2 Processing by chemical mechanisms such as photochemical surface modification

When chemical bond cleavage from an electron excitation state by photo-irradiation is applied, it is possible to induce chemical reactions such as molecule dissociation and chemical bond recombination with high efficiency and at high density. If micro-focused beam or micro-patterns of the light is irradiated onto target materials, the area-selective localized chemical treatment to specific areas can be done easily. Not only can the form of the target material be modified by physical laser processing, but also arbitrary changes in the chemical surface property can be done. The characteristics of surface modification using light are as follows:

- direct formation of modified layer on the material, micro-pattern modification,
- reduction of consumption of reagents, process without solvents, and
- treatment in air or under atmospheric pressure.

It is possible to induce photoreaction by using a lamp as a light source device. The merits of using lasers are that pattern forming treatment is possible and that active species can be generated at high density. For the surface modification of materials, there are four main methods of laser irradiation as shown in Fig. 2. Figure 2(a) is a method in which lasers are irradiated directly onto a material that one wishes to modify. If photoreactive molecules or functional groups are present in the substrate or surface layer, the molecules or functional groups in the surface layer are excited by laser irradiation, and this kicks off a surface reaction. By carefully selecting the type of photoreaction induced, it is possible to add a functional group to the surface, and set off polymerization or alter the surface polarity. By coating the substrate surface

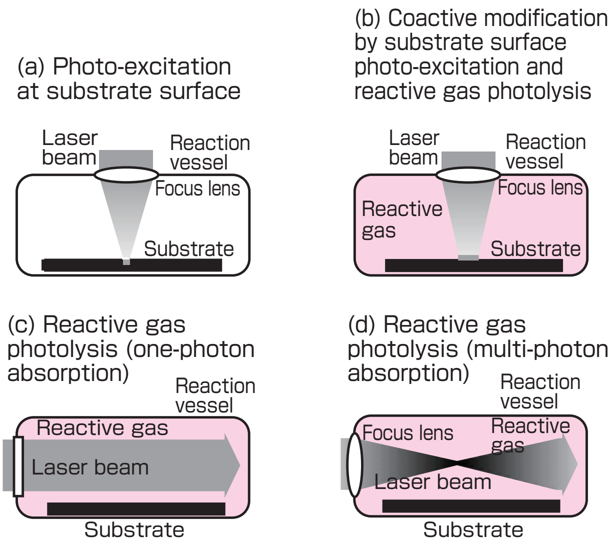


Fig. 2 Surface modification method by laser processing

Table 3. Industrial applications of surface modification achieved by photoreaction

Type of surface modification	Industrial application
Improvement of wettability	Improvement of affinity and adhesivity, printability, improvement of biocompatibility, water repellency, antifogging
Cross-linking, crystallization	Formation of hard surface layer, wear resistance
Removal of contaminated layer	Surface cleaning
Surface modification (grafting, coating)	Formation of highly lubricant layer, formation of colored layer, photo-reflective (prevention) film, liquid crystal oriented film, heat resistance, chemical resistance, gas barrier property, antistaticity, weather resistance, flame resistance

with a thin hydrophilic or hydrophobic layer, and then partially exposing the substrate by removing the film layer by laser processing, it is possible to form micro-patterns using the surface property.

Figure 2(b) is the derivative of Fig. 2(a), and reactive gas is used as the atmosphere for laser irradiation. Therefore, it is possible to accelerate the surface reaction, and to conduct a target surface reaction by selecting the optimal reactive gas type without intentionally introducing the photoreactive molecules to the substrate surface layer. In this method, it is also possible to photo-excite both the substrate and the reactive gas, and patterned surface modification can be done as in Fig. 2(a).

In Fig. 2(c) and 2(d), the characteristic is that surface modification properties are obtained without photo-excitation of the substrate, but by the deposition of the photoreactive product of reactive gas on the substrate surface. In the case where the reactive gas is dissolved by one-photon absorption, the normal incidence irradiation as in Fig. 2(c) is sufficient. In the case where the reactivity of gas molecules is low, or if multi-photon absorption is necessary, practical reaction efficiency can be increased by tightly focusing the lasers inside the reaction vessel.

Table 3 shows the major types of surface modification and application examples mainly for photoreaction. In order to fabricate a modified surface with low time degradation and with high durability, more often, it is better to modify not just the uppermost surface layer of the material of the reaction site but also the internal layer to a degree base material characteristics are not lost. Particularly, in systems where the main chain structures of molecules are flexible and subject to movement like in polymer materials, the surface hydrophilicity may gradually decrease after treatment since the hydrophilic group in the uppermost surface layer may diffuse into the internal layers. Therefore, highly durable modification can be achieved by adding hydrophilicity to the surface layer of about 1 μm thickness.

3 Specific case studies

In Chapter 3, three specific case studies are presented that aimed at further application and practical use of methods described in Chapter 2 using the current laser processing device system as base technology. All the cases are high-speed, high-quality processing that is difficult to achieve using ordinary laser processing methods or other competing processing technologies.

3.1 High-speed, high-quality processing of composite materials

Recently, CO_2 reduction and energy savings are promoted as measures against global warming, and weight reduction and decreased fuel consumption of transportation machines such as automobiles and aircraft are progressing. Carbon fiber reinforced plastic (CFRP) that has superior specific strength and specific elasticity compared to metals such as aluminum is given as a major candidate structural material for weight reduction. In the transportation equipment, the CO_2 reduction effect of automobiles and aircraft that use CFRP is drawing interest, and the wide diffusion of products developed using such materials will be an effective way to promote energy savings of society as a whole. However, CFRP is known as a dissimilar difficult-to-cut material, and the development of high-precision cutting and joining technologies are demanded as innovative manufacturing technology. Moreover, further shortening of the manufacturing tact time is an urgent issue. When considering application to industrial manufacturing processes, the target-processing rate can be set from the value of tact time resulting from the manufacturing lead time. Taking the example of mass-production of passenger vehicles, the tact time is approximately one minute. Therefore, the processing speed of about 6 m/min is necessary for the exterior trimming of roof and hood that are large parts, based on the processing area needed for the size of the individual parts. Therefore, we studied the industrial application of high-speed laser processing to CFRP materials (Fig. 3).[8]

To compare with laser processing, the processing speed

Fig. 3 Laser cutting of 30 cm square CFRP substrate

of water jet processing and mechanical machining that are positioned as competing technologies actually used in aircraft manufacturing were measured using the 2 mm thick CFRP material. The results were 0.1 m/min and 1 m/min, respectively. For the aforementioned objectives, these processing methods lack speed, and issues such as tool wear and parts degradation occur. In case of laser processing, if the demand is for improved speed only, the problem will be basically solved by increasing the average power of the oscillator, and the processing speed of several m/min can be achieved by large laser devices with kW range average power. As a technological issue to be overcome, the important point is to control the reduction of heat damaged area during the processing.

Carbon fiber is a material made of fibers of 5~10 micron diameter with high heat resistance and high thermal conductivity. In contrast, resin is a matrix material with low heat resistance and low thermal conductivity. CFRP has a structure that is composed of the two materials, and in the case where excess heat input is generated during high-power laser irradiation, there is a tendency for heat damage and delamination of the resin part. Particularly, in the case of continuous fiber CFRP materials, the carbon fiber bundles may act as heat conduction paths, and there is a possibility that the heat damage may spread to the resin area around the process site. If the degree of adhesion between the fiber surface and the resin interface decreases due to heat damage, the strength property of the structural material declines, and it is necessary to avoid as much as possible the spread of heat damage around the process site. For example, it was found that if a CO_2 gas laser (800 W, 20 kHz, 8 μs) is used in standard cutting conditions for sheet metal, the heat damage of the resin layer spreads over 1 mm in the cross section of a 2 mm thick sample. This is an inappropriate condition setting. Therefore, a high-speed sweep method was used to conduct multiple irradiation (multiline multipath irradiation) along the processing line, and the number of irradiation needed to completely cut a 3 mm thick base plate was greatly reduced. For the heat damage to the resin layer, it was found from the micro X-ray CT measurement that it was kept to about 0.1 mm (Fig. 4). The development of the domestic high-power fiber laser device was done as an industry-academia-government collaboration, and as of now, the processing speed of 6 m/min has been attained (Fig. 5).

3.2 Localized surface chemical reaction of the resin surface

For the surface modification of polymer materials, research for the improvement of wettability and adhesiveness is being done actively, and it involves important technologies in basic research as well as in wide-ranging fields of industrial application. In the polymer materials that mainly consist of hydrocarbon chains such as polyimide and polyester, hydrophilicity can be gained by replacing hydrogen with the hydrophilic group in the carbon-hydrogen (C-H) bond sites. Therefore, a photo-oxidation reaction is the general method of modification. The point of treatment to attain hydrophilicity in polymer materials is to introduce the hydrophilic group to the side chain structure site without breaking the main carbon chain structure. If the main carbon chain structure is broken by oxidation, the molecular chain becomes low-molecular weight, and this may cause elution, thus becoming a factor that lowers durability. In this subchapter, chemical surface modification using lasers is explained through the example of obtaining surface hydrophilicity in fluororesin.

Fluororesin represented by polytetrafluoroethylene (PTFE) is an excellent material with high chemical stability and heat resistance (Fig. 6). However, since it has very high hydrophobicity on the surface, adhesiveness and bonding property with different materials are extremely poor, and currently, the surface is made hydrophilic by defluorination through immersing the PTFE specimen in a metallic sodium organic solution. The organic solution of metallic sodium has the danger of ignition and degrades rapidly. Moreover, since the specimen is immersed in the solution, the whole surface is modified, and the development of a new method that is safe

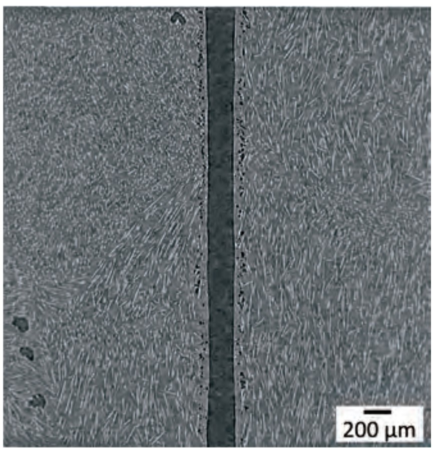


Fig. 4 Cross-sectional picture of micro-X-ray CT of CFRP sample after laser cutting[8]

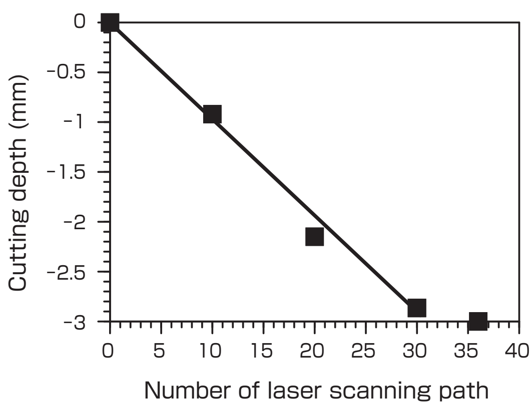


Fig. 5 Cutting depth of 3 mm thick CFRP sample using double-line multipath laser irradiation
(Laser beam scanning speed of 3.6 m/s)

and allows area-selective modification was awaited.

The characteristic of the surface modification of fluororesin is that the hydrophilicity is attained by breaking the carbon-fluorine (C-F) bond of the side chain and replacing the fluorine atoms with hydrophilic groups. However, since the C-F bond has higher chemical bond energy than the C-C bond of the main chain, the main chain C-C bond will be broken unless a reaction system that acts specifically on the C-F chain is selected, and surface etching will occur due to the detachment of the monomer unit and the decreased molecular weight of the polymer chain. In the aforementioned metallic sodium organic solution, the key reaction is the reaction of sodium atoms and fluorine atoms to specifically generate NaF. Similarly, the method of directly photo-exciting polymers by laser irradiation causes the break in the main chain C-C bonds, and it is difficult to change the surface to hydrophilicity efficiently. Therefore, it is necessary to use the reaction system that acts on the C-F bonds by introducing the reactive gas as in Fig. 2(b). Here, we describe a case study using hydrazine.[9]-[11]

Hydrazine (N_2H_4) molecules are known to dissolve at high quantum efficiency by ultraviolet light irradiation. In the photolysis process, hydrogen atoms, hydrazyl radicals, amino radicals, and others are produced at high efficiency (Fig. 7). First, the hydrogen atoms react with fluorine atoms to produce HF (exothermic reaction), and the carbon radicals produced by the desorption of fluorine atoms react with the hydrogen atoms or amino radicals, and as a result, a modified surface with partial replacements by the amino group consisting mainly of hydrocarbon chains is obtained. In an actual experiment, as seen in Fig. 8, the hydrazine was introduced into the decompressed reaction vessel as steam and irradiated with ArF excimer lasers (wavelength 193 nm). In the X-ray photoelectron spectroscopy (XPS) measurement, the fluorine signal decreased significantly after the laser treatment and the nitrogen and oxygen peaks occurred. The atomic ratio was C:F:N:O = 100:1.6:19:3.3, and the majority of fluorine atoms were removed from the surface.[10] The contact angle to water was 130º→25º, and the surface became hydrophilic. From the results of the static secondary ion mass spectrometry (SIMS) or positive ion observation, it was clearly shown that the change to hydrocarbon chains occurred while maintaining the main carbon chain structure after the laser treatment (Fig. 9). Similar active species can be generated by plasma treatment, but the laser method is superior from the perspective of generation concentration and pattern treatment.

When ordinary chemical plating is done to laser treated substrates, nickel plates adhere only to the hydrophilicized parts (Fig. 10),[12] and the adhesivity was maximum100 kgf/cm^2

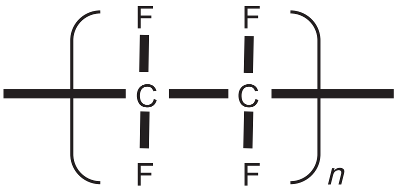


Fig. 6 Chemical structure of PTFE

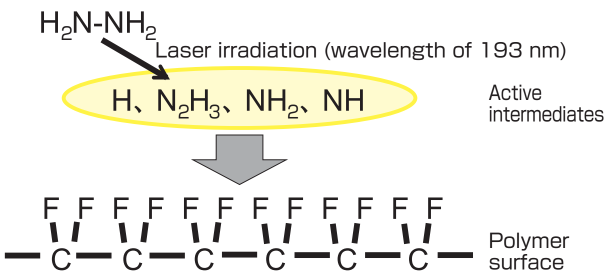


Fig. 7 Schematic diagram of the surface reaction

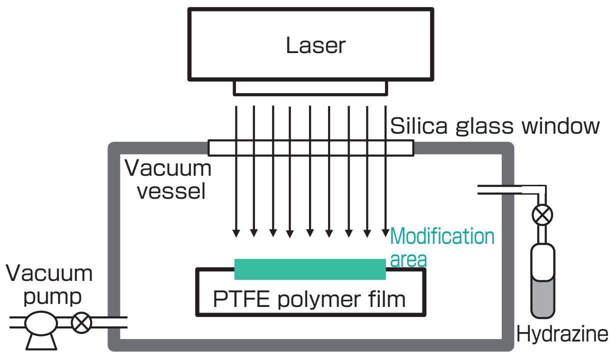


Fig. 8 Experimental apparatus

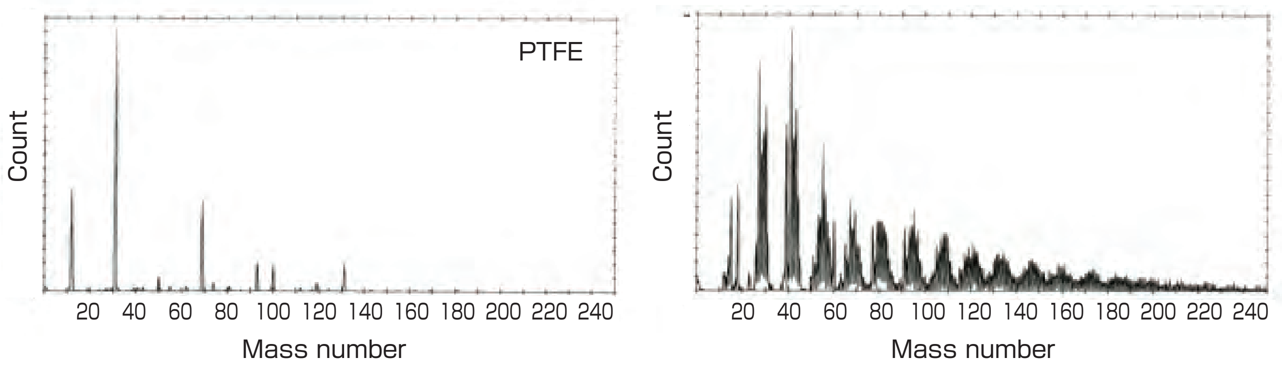


Fig. 9 SIMS spectrum of a polymer surface: left, before laser treatment; right, after laser treatment

in the pullout tension test.[10] When an iron rod and a fluororesin sample were joined using a cyanoacrylate adhesive, maximum 10 MPa tensile strength was obtained.[11] Considering that the tensile strength of fluororesin itself is about 10 MPa, it could be said that the modified layer adhered solidly to the base layer.

3.3 High-quality microfabrication of hard-brittle materials

In the case of base materials with extremely small or no laser absorption, the penetration length into the substrate becomes large since the excitation density is small. Therefore, damages such as cracks and chipping occur around the irradiated area during processing, and high-quality microfabrication becomes difficult in many cases. Such transparent materials include silica (quartz) glass and sapphire materials that have no absorption in the visible and ultraviolet ranges, and these are categorized as hard-brittle materials.

AIST developed its own laser processing method for indirectly microfabricating silica glass surfaces by ablation of dye solutions, where the ultraviolet lasers are irradiated, while a dye solution that readily absorbs ultraviolet light is placed in contact with the processing target.[13][14] Laser-induced backside wet etching (LIBWE) has two types: the excimer laser exposure projection-mask type that has high size precision, and the laser scanning irradiation type where the prototypes can be made easily (Fig. 11). In the LIBWE method, a highly concentrated dye solution is used, and lasers can penetrate only a few µm into the solution layer and is completely absorbed in this thin layer. Therefore, a high-density excitation state of dye molecules is formed locally near the silica interface, ablation of the solution occurs, and the silica glass surface layer is etched at depth of several tens of nm by excess high-temperature and high-pressure. The processing depth increases in proportion to the cumulative pulse number by conducting concurrent irradiation.[13] Compared to other methods, the photoresist protection layer formation and its removal, which were necessary in the conventional lithography process, as well as vacuum devices are not necessary, and the pretreatment and post-treatment are greatly simplified.

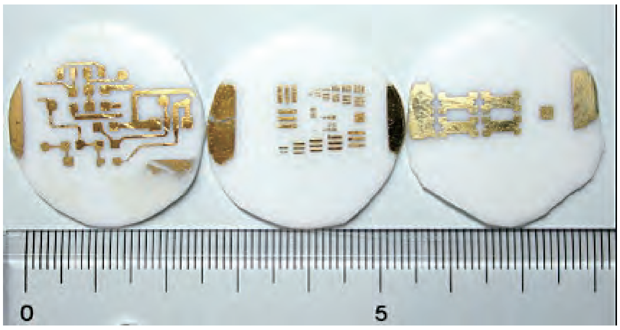


Fig. 10 Nickel chemical plating on PTFE (Topmost surface of plated film has been gold replaced.)[12]

The evenness of the processed surface is high, and adhesion of broken fragments that might occur during ablation and fine processing damages such as cracks were not observed. With the improvements of the projection-mask exposure optical system such as the installment of a beam homogenizer and a projection lens array, we succeeded in the lattice microfabrication with maximum of 1 µm resolution and microfabrication on large optical elements (Fig. 12).

The result of processing when aluminosilicate (SiO_2-Al_2O_3-Na_2O) glass was selected as the base material is shown in Fig. 13. Aluminosilicate glass has a thermal expansion property similar to silicon wafers, and since anodic bonding with little distortion can be formed with silicon, it is used widely as conjunction glass for micromachining to fabricate various sensors such as MEMS. Using the nanosecond pulse lasers with wavelength of 355 nm, laser beam scanning was done using the galvanometric optical scanner on the glass substrate in contact with the pyrene-toluene solution. The galvanometric optical scanner is an optical device that scans the laser at high speed and in a wide range using a motor and a reflective mirror, and it is appropriate for direct drawing along a designed diagram (vector mode scanning).

For three types of grooves of width 20 µm (single-line scanning), 50 µm (accumulation of four lines), and 80 µm (accumulation of eight lines), the depth of grooves

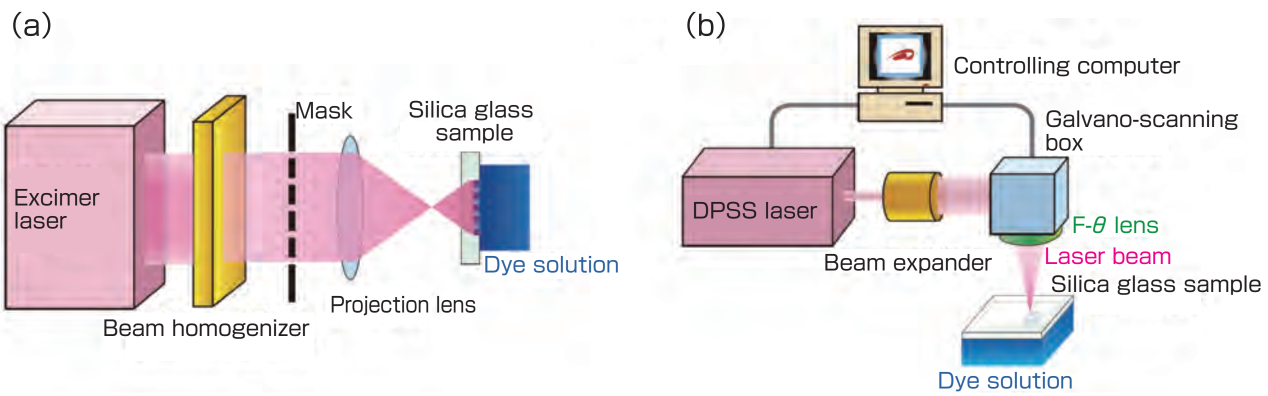


Fig. 11 Experimental apparatus for the LIBWE method
(a) Excimer laser exposure projection-mask type, (b) DPSS laser/ beam scanning irradiation type[14]

obtained by concurrent irradiation with increased number of processing paths was 150 μm or deeper for each groove. Figure 13 shows the deep groove structure with different depths and widths on one piece of glass substrate. In the LIBWE process, this can be fabricated in one batch, and this demonstrates the advantageous characteristic in reducing the number of processes.

4 Discussion: Meaning of the research result and comparison with the future scenario

Development progresses for innovative, lightweight, and high-strength materials that are aimed to achieve a sustainable and safe society. In considering clarification of research goals that one wishes to be realized in society, there is a need for a new processing technology that exceeds the conventional methods for the integration of materials and product realization. Achievement of high performance such as multiple functions, micro-sizing, and high speed is specifically demanded by companies. Therefore, the research goal here is to promote the greening of the manufacturing processes and products through material processing technology using lasers.

The future scenarios for the specific case studies presented in Chapter 3 for attaining this research goal and the means to achieve it are shown in Fig. 14. The overall diagram is shown in Fig. 15.

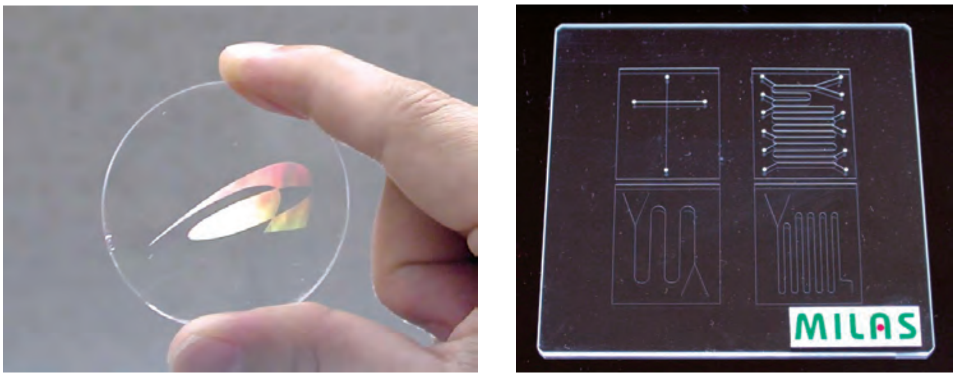


Fig. 12 Large surface area processing by LIBWE method onto silica glass: fabricated by laser scanning irradiation device (Colored area of the left figure is the scattering light from the transmission diffraction grating.)[14]

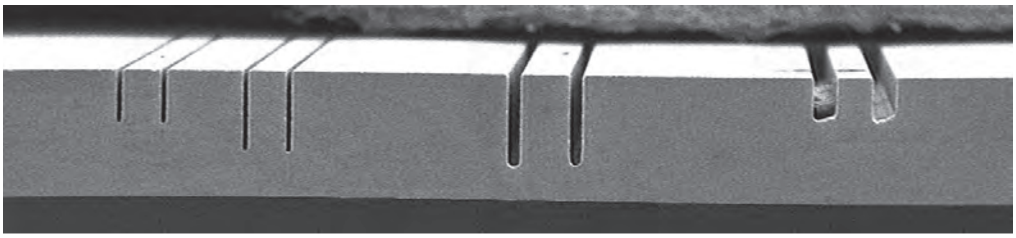


Fig. 13 Cross-sectional SEM photograph of deep groove processing by LIBWE method on aluminosilicate glass substrate (thickness of glass substrate: 0.5 mm). Groove width 20 μm (left), 50 μm (center), and 80 μm (right).

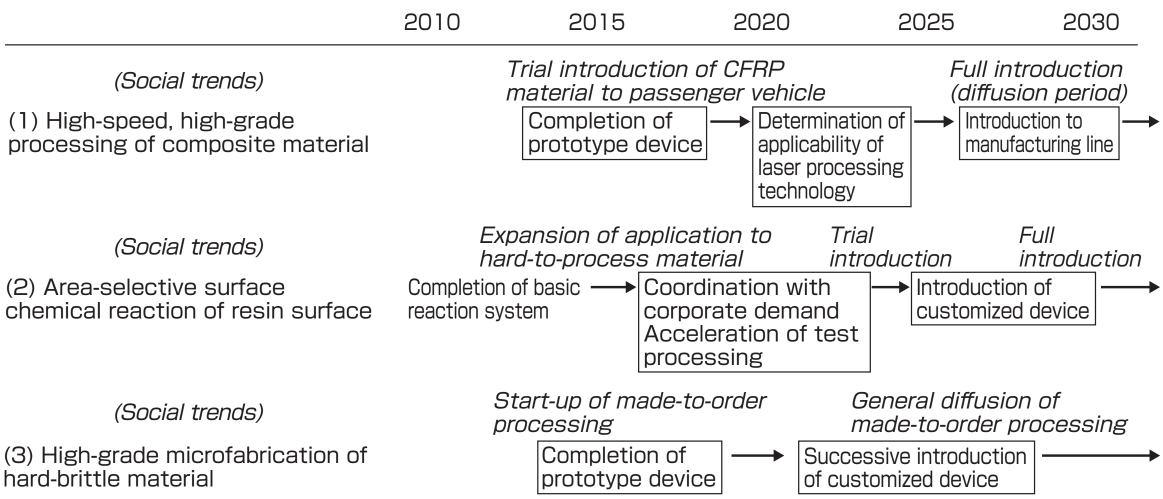


Fig. 14 Technology roadmap of specific case studies described in Chapter 3

Table 4. Social impact etc. of specific case studies described in Chapter 3

	Social impact	Expected new product group	Market size
Composite material processing	Improvement of fuel consumption by weight reduction of body	Ultra-lightweight passenger vehicle	25,000 tons (projection for international production of carbon fibers in 2020) 10 million cars (projection for international sales of eco-cars in 2020)
Surface chemical reaction	Expansion of application range of fluororesin	Surface modified fluororesin material for electrical and electronic application	10,000 tons (domestic sales of fluororesin in 2008)
Microfabrication of hard-brittle material	Shortened manufacturing lead time of customized micro-optical devices	Precision fabricated product using silica glass materials	2 trillion yen (domestic production of glass products in 2006) 73 billion yen (domestic production of silica glass in 2006)

To spread the results of laser application technology to society, first, prototypes of the processing device system are fabricated, and then, high-quality finished devices are shaped by repeated tests. The prototype devices have been completed for the CFRP process in Subchapter 3.1 and the glass microfabrication in Subchapter 3.3, and are currently in trial of whether they can perform and fulfill the on-site demands. The key point is close collaboration with the companies that may purchase the devices. Table 4 summarizes the social impact and others. The gaps between the future scenario and the current technological levels are as follows: (1) for composite material processing, it must be coordinated with the on-site production technology, (2) for surface chemical reaction, large surface area treatment technology must be established and the amount of chemicals used must be reduced, and (3) for microfabrication of hard-brittle materials, details of demand for custom items must be understood.

In general, in cases where laser processing technology is introduced, it is most appropriate for improving productivity in multi-variety variable quantity production. Current laser processing devices are successful in metal sheet processing (cutting and welding) and repair technology during manufacturing (yield is improved by conducting laser repair on defective products during manufacturing right in the manufacturing line; an example is correction of defects in LCD).

In material processing, maintenance of high-quality property and achievement of high-speed treatment often conflict, and by experience, it is known that the two are in tradeoff relationship, but in laser processing, both properties can be improved by carefully exercising process control. The specific examples presented in Chapter 3 are characterized by the addition of the viewpoint of material chemistry to surface treatment of hard-to-process materials. In the material processing where light is used, the processing target can be worked while maintaining balance of multiple factors. The Nobel Prize for Chemistry in 2014 was given to the development of the ultra-resolution fluorescent microscope.[15] By irradiating two lasers with different wavelengths (micro-spotlight and donuts pattern), the forced de-excitation phenomenon is induced in the fluorescent molecules, and the stimulated emission depletion (STED) allows microscopic observation at 10 nm scale that breaks past the diffraction barrier of 200 nm. Here, excellent results that surpass the conventional theory are presented when the roles of the two incident lights are clarified and are simultaneously irradiated. Currently, the microfabrication technology that uses this STED phenomenon is being studied at the fundamental research level.

Compared to other manufacturing technologies, the laser process may involve complex and expensive devices and systems, and this may lead to high costs. Therefore, in using lasers as part of production and analysis methods, the maintenance of economy that matches the market value is an important issue. Rather than using lasers for less expensive

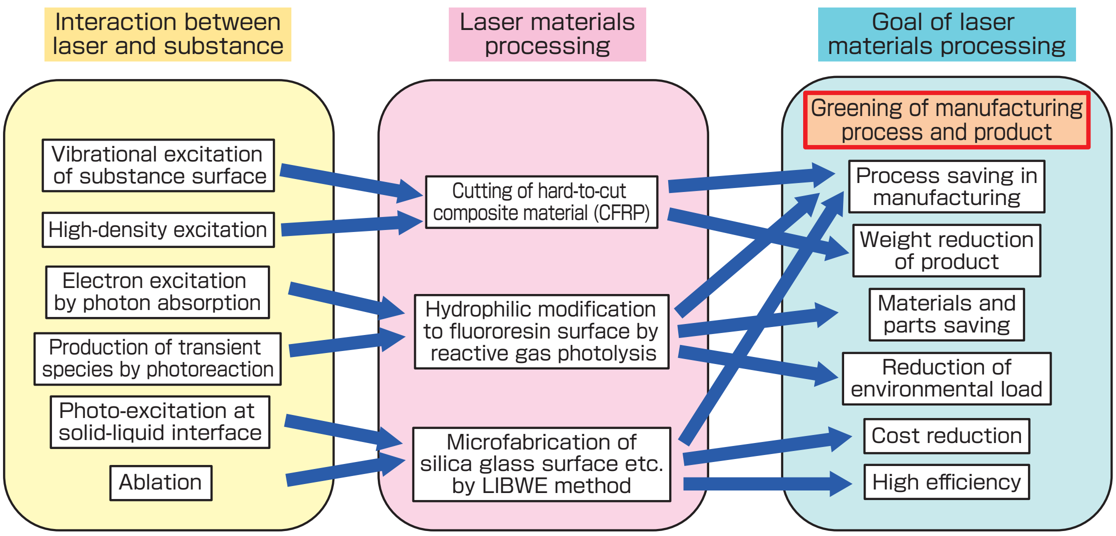


Fig. 15 Diagram of specific case studies described in Chapter 3

mass-production products, the main fields of application, in which the characteristic of laser treatment can be maximized, are substrate selective reaction by optimal wavelength and localized treatment to specific areas for which high added value is expected, or the processing control in ultra-short time from nano to femtoseconds. Since it can sufficiently handle 3D fabrication and digitized flexible production style, it is effective as a method to maintain traceability. As a future issue to fill in the gap with the scenario, further industry-academia collaborative efforts will be needed.

In this research, there are elements that depend on the performance of basic devices such as light sources and processing systems, and the results and performances demonstrated by the device used in trial has the potential of improving and accelerating the progress of the core device performance in the future. It is undeniable that the collaborative efforts for improving the device performance and advancing the process will be the main key for the future of processing technology. Therefore, the ability to widely grasp knowledge and to observe of the related technological fields, and serendipity are also important factors.

5 Summary and future issues

Through various applications of the material processing technology using high-power laser devices as described in this paper, more process saving and shorter time compared to conventional manufacturing processes will be achieved. Also, new elements, parts, and products can be supplied by realizing high-precision, high-quality microfabrication of hard-to-process materials, and the energy-saving property of the products may be improved further. In the progress of individual elements, attention is paid to the development of diffraction optical elements and spatial light modulators for irradiation optics. By actively utilizing the “duality of light” where light has both the properties of particles and waves, high-performance molecular beam and fine pattern making may be accomplished easily.

To promote further performance of the processing device system, breakthrough type innovation development is effective through the fusion of state-of-art Japanese technology with other areas (such as digitization of processing data, network transmission technology, or robotic technology). It is thought that the direction of innovation in manufacturing technology will be indicated through international competition.

Acknowledgement

The CFRP process is the result of research conducted under the New Energy and Industrial Technology Development Organization (NEDO) Project “Advanced Laser and Processing Technology for Next-generation Materials Project.” It was done jointly with the research institutions and companies that belong to the Advanced Laser and Process Technology Research Association (ALPROT). The high-quality microfabrication of hard-brittle materials by the LIBWE method is the result of research conducted with the members of the Laser Chemical Process Group (at the time), Research Institute for Innovation in Sustainable Chemistry, AIST.

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Discussions with Reviewers

1 Overall

Comment (Naoto Kobayashi, Center for Research Strategy, Waseda University)

This paper reveals the technology, along with its characteristic and usefulness, for high-precision, high-quality surface processing of substances and materials using lasers that the author has studied throughout the years. In the sense that it is a systematic description of the "laser processing technology," it is appropriate for *Synthesiology*. The technological content is of a high level. However, the first draft seemed merely a technological explanatory article, and not sufficient as a paper of "synthesiology." After you added the discussions based on our questions and comments, the paper has become more understandable.

Comment (Norimitsu Murayama, AIST)

This research is a synthesiological effort where new application of laser processing is sought by combining laser processing with other technologies. It is appropriate as a paper of *Synthesiology*.

2 Research objective and title of the paper

Comment (Naoto Kobayashi)

The title of the paper in the first draft is "Development of high-speed, high-quality laser processing technology." This gives an impression that the paper describes a general technological development. In *Synthesiology*, it is required that you state the objective of research to be realized in society, the scenario and the road taken to attain the objective, and the selection and integration of the elemental technologies. For the research objective, it is necessary to clarify (1) R&D for surface processing of materials to obtain a specific function, or (2) R&D for characteristic processing technology. Also, the title of the paper is recommended to be specific and appealing to the readers.

Answer (Hiroyuki Niino)

Thank you for your indication. I made revisions to discuss specifically and in depth the material processing technology using a high-power laser device in light of synthesiology. The first factor of synthesiology in this research is the background in which the development of innovative materials such as lightweight, high-strength materials and biocompatible materials progresses, and a new processing technology is demanded to go past the conventional method for integrating and realizing products. Specific corporate demands are increasing for high performance such as multiple function, micro-sizing, and high speed. By employing the material processing technology using light such as lasers, and by continuously promoting the advancement that is unique to this technology as shown by the temporal development from past to present, I clarified the research objective of this paper: "to promote the greening of the manufacturing processes and the products." Regarding the second factor of synthesiology, I described the scenario and the road taken to attain the goal by clarifying the specific research objectives through individual case studies. As for the third factor, I discussed the selection and integration of the elemental technologies. The developments by fusion and joining with technologies of other fields are also described where appropriate, in addition to the steady, solid, and ordinary development conducted in the manner of a linear model. The title was changed to "Green photonics for manufacturing and products by laser materials processing." Concerning "high-speed" and "high-quality," words originally included in the title, these qualities were explained in detail by adding specific property data to individual case studies.

3 Overall technological configuration

Comment (Naoto Kobayashi)

You had better state the research goal of what you wish to realize through high-speed, high-quality laser processing technology, the scenario to achieve the goal, and the integration of elemental technologies. Specifically, you can show the author's intention to the readers by showing an overview diagram of the technologies.

Comment (Norimitsu Murayama)

For the three case studies, please summarize in a diagram how you combined the laser technology with various kinds of technologies, and present them more clearly.

Answer (Hiroyuki Niino)

To clarify the overall concept, I described the three specific factors of synthesiology in this paper in Chapter 4, and added the overall diagram as Fig. 15, and provided discussions. Centering on the three case studies (hard-to-cut complex materials, reactive gas photolysis, and LIBWE method) shown in Chapter 3, "interaction of lasers and substances" (surface vibration excitation, high-density excitation, electron excitation by light, etc.) were presented as necessary factors, as well as the characteristics of laser processing that were featured in the case studies, particularly the greening of the manufacturing process and product.

4 New application

Comment (Norimitsu Murayama)

Please expand on the assumed scenario for the new applications of laser processing: (1) high-speed, high-quality processing of composite materials, (2) localized surface chemical reaction of the resin surface, and (3) high-quality microfabrication of hard-brittle materials. Please describe the social impact, new products, and the market size of these three new applications. Also, please include a time axis in the scenario. Add more detailed description about the gap between the scenario and current technologies, as well as the future issues to fill in the gap. I think it will be easier to understand if you illustrate the content with a figure.

Answer (Hiroyuki Niino)

In Chapter 4, I clarified the specific research objectives in individual case studies or the second factor of synthesiology, and described the scenario and the course for achieving the goal with the addition of a time axis. The gaps between the scenario and current technologies were listed, and the future issues to fill those gaps were described (Fig. 14). Specifically, the scenario assumed is as follows: (1) for high-speed, high-quality processing of composite materials, prototypes are expected to be completed around 2015, the applicability of laser processing devices will be determined after 2020, and it will be introduced to the manufacturing line between 2025 to 2030. Moreover, the social impact, expected new products, and market size were added (Table 4). For example, the social impact of complex material processing is expected to be "dramatic improvement of fuel consumption by weight reduction of the automobile body," the expected product group is "ultra-lightweight passenger vehicles," and the expected market size is 25,000 tons (projected international production of carbon fiber in 2020) and 10 million cars (projected international sales of eco-cars in 2020).

5 Issues for practical use

Question (Naoto Kobayashi)

As described in detail in this paper, there are many advantages in laser processing. Specifically, as seen in this paper, it is already partially used in the manufacturing process of flat-panel television and solar cells, but the diffusion seems slow. I think the cost is the greatest bottleneck. Including the CFRP processing and glass microfabrication as presented in this paper, which issues do you think must be overcome to achieve practical use (or commercialization)?

Answer (Hiroyuki Niino)

As issues toward practical use of the processing machine tool, price reduction, low electrical consumption, robustness, reliability, and others are important. From the perspective of those using the processing devices, the key is to be able to use it in the core system of highly flexible manufacturing that allows high degree of freedom for multi-variety appropriate-volume production. Therefore, it is desirable that the hardware of the processing device be customizable and the software and operation be freely changeable according to customer demand. The devices for sheet metal processing that is equipped with kilowatt level CO_2 gas lasers and fiber lasers belong in the macro-processing field dominated by a few worldwide companies, and products with performance that fulfill their demands are introduced whenever necessary. The world market for processing machine tools is one trillion yen per year, and the macro-processing field dominates about 60 %. On the other hand, in the micro-processing field, there are several hundred manufacturers around the world, and it is all out rivalry amongst the warlords. The individual case studies incorporate maximum utilization of laser properties, but the relatively small market scale is a major issue in maintaining and expanding the business. Like in the excimer laser exposure device in the LSI lithography process, if we succeed in improving the device performance steadily without delayed delivery in pace with the progress of exposure technology, we can gain the trust of the market for this product, even if it has the highest unit price among the laser devices.

6 Future trend

Question (Naoto Kobayashi)

In this paper, you mention the examples of IoT and Industry 4.0. Since the control by information and communication technology (ICT) can be done more easily for laser processing compared to other processing methods, fusion with ICT including remote processing will become extremely important in the future. Can you give us your opinion about the future trends of laser processing including incorporation of ICT, along with the situation of the current 3D printers?

Answer (Hiroyuki Niino)

As you indicated, machining tools equipped with lasers that can be remote controlled by ICT is being developed. The concepts described by IoT and Industry 4.0 are being studied in Japan, and some functions are already implemented in the actual machining systems. However, IoT and Industry 4.0 not only improve the performance of the machining system, but also are expected to build new business models that renew the relationship between the one who places the order and the one who receives the order. Also, since there will be global information unity of the manufacturing centers that are scattered around the world, it may provide global solutions to social and environmental issues.

For example, with the performance of the current 3D printers, days to weeks of work time are necessary to shape large objects of meter class dimensions. Therefore, it is impossible for a person to monitor the machines at all times. As the reliability and controllability of the devices improve and the performance can be sufficiently remote controlled, this technology has potential to affect the differentiation with competitors, geographical conditions of the factory location, as well as the organization of the company including work and employment style of the engineers.

7 International competition

Question (Norimitsu Murayama)

Your indication that Germany leads Japan in the R&D of laser processing technology arise from the background as follows: (1) Germany has continuously, without interruption, promoted this research as a major national project since the latter half of the 1980s, and (2) active employment of the laser processing technology (particularly for metal welding of automobile bodies) to actual manufacturing lines was done early in German automobile manufacturing companies. The lead by Germany in macro-processing field is significant. Also, major academic contributions by German scientists in the dawn of modern optics (19th century) set the starting point that continues today.

In Japan, with the foundation of the development of CO_2 gas laser equipment for manufacturing industry (project period; 1977~84) and the development of excimer laser equipment (1986~94), the sheet metal processing devices and the semiconductor lithography devices maintain worldwide share. However, we had a late start in the development of fiber laser equipment with kilowatt average power, and at this point, the presence of the Japanese fiber laser machine tools is not too high in the industrial trade shows for the latest laser processing devices.

The laser processing technology can be applied to a wide range of materials, and it is characterized by the fact that it can be applied to multitude of fields. Therefore, diverse R&D projects are promoted around the world, and Europe, North America, and Japan are the top runners in the world.

As the future development plan, the goal for light source development for industrial use should be the achievement of high power several tens to hundreds order higher than the current performance, and the following three are the candidate topics: (1) kilowatt level picosecond to femtosecond lasers, (2) fiber light-guided semiconductor lasers (high-power light-guided optical fiber in micron core diameter), and (3) deep ultraviolet range semiconductor lasers (gallium nitride system for ultra-small devices). The ranking corresponds to the degree of possibility of realization, and the core technology exists in Japan. Moreover, much high-level, basic academic research is being conducted in the optics field, and it is necessary to construct an organization that can quickly extract and develop the technologies that form the core of next-generation industrial application of such frontier research. I think the flexible setting of project scale, organization, and period according to individual topics, as well as scenario-driven collaboration among individual topics are effective. As explained in Subchapter 2.2, the laser processing device system is an accumulation of various high technologies, and at this point, the fusion with IT technology is promoted. The point is to lead the expansion of the market by discerning which and when a technological element should be developed heavily along the timeline. Therefore, it is important not to allow gaps in the joints of the multiple layers of technology and to increase affinity between the layers.

The majority of laser processing technology so far has been dominated by case studies utilizing the particle property of light. By employing the wave property of light, I think a new industrial application technology will develop in the future.