Japan Overview of Radiation Curing Market and Technology

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Abstract

Economy in Japan has been on the way of recovery from the serious recession triggered by Lehman Brothers' shock in 2008. Many new technologies have been proposed to make the next decade prosperous. Radiation curing is one of the key technologies that lead the new technologies become reality. This paper overviews the newly developed radiation curing technologies in Japan, in particular, its industrial applications and the market situation of the radiation curing applications which was surveyed by RadTech Japan in 2010.

1. Introduction

Industrial production and shipment data of Japan reported by Ministry of Economy, Trade and Industry (METI) of Japan had shown a steady growth of Japanese economy until the first half of 2008 since 2005.[1] The annual growth rate of year 2006 and 2007 were 5.2% and 3.0%, respectively. However, a drastic decline started on October 2008 and eventually the index went down to 70% compared to the previous year to hit the bottom on February 2009. This economic recession was symbolically triggered by a bankruptcy of Lehman Brothers and it has seriously affected the global economy and resulted in a recession for following years. Automobiles, semiconductors, electronic parts and devices, electric appliances, and IT related industries where the Japanese industries have played a major roll, have shown significant drop.

Through the economic recession, it has been clearly recognized that earth's resources are limited and rambunctious greenhouse gas emission might destroy the earth itself. On the way to recover from the economic recession, we will not reproduce the old industries as-is, but want to utilize new technologies to recover the industries. In the context of reduction of greenhouse gas one cannot move backward the technology trend such that from petrol-driven vehicle to hybrid-powered, electric-powered or fuel-cell-powered vehicle. A change of the energy source from fossil fuel to solar power generation is the trend which cannot be wound backward. Japanese government also strongly accelerates such changes by setting certain privileges.

The radiation curing technology has been recognized as an environment friendly technology by characteristic features such as energy savings, low environmental damage due to a reduction of VOC and high productivity. The radiation curing will become one of the key technologies to realize the efficient way of manufacturing. Although the radiation curing industries also impacted by the recession, many promising applications have been proposed to develop the new fields of industries as described in the following sections.

2. Market Overview

As shown in Figure 1, the industrial production and shipment data for the every five segment, automobiles, semiconductors, electronic parts and devices, electric appliances and IT related field, experienced significant recession in the Q4 of 2008 through the Q1 of 2009. These figures indicate the Japanese economy is now on the way of upturn. After this serious recession, RadTech Japan interviewed the current situation of radiation curing market in Japan with several leading companies who manufacture the radiation curing related materials and equipment. The results are summarized in Tables 1 and 2.

2.1. Raw Materials for Radiation Curing

The demand of raw materials for radiation curing in 2008 decreased 7% from that in 2007 as shown in Table 1. The demand in 2009 is estimated to be 8% down from that in 2008. The volume of the raw materials is almost same as that in 2004 or 2005 level. However Table 2 shows that the demand of formulated materials in 2008 was only 3% down from that in 2007 and also the demands in 2009 is estimated to be 5% down from the previous year. This suggests that some portion of the formulated materials is made by using the imported raw materials.

2.2. Formulated Materials for Major Application

Although the demand of formulated materials also shows the down turn in 2008 and 2009, some applications such as resists for LCD, photopolymer plate and optical disk coatings show the upturn among them. A demand of resists for LCD in 2008 was driven by the growth of LCD-TV and resulted in 20% up from 2007. The demand in 2009 is also expected to grow. Worldwide shipment value of large size FPD-TV (over 10") in Q3 2009 recorded 31.9% up compared with Q2 2009 and 9.2% up with Q2 2008, respectively. In Japan, the shipment value of FPD-TV in October 2009 was 39.9% up from the previous month and 67.7% up with the same month of 2008. Among the FPD-TV, the LCD-TV grew 43.4% up in shipment value and 71.7% up in shipment volume against 2008. A PDP-TV also showed a favorable growth.[2] The forecast of the sales volume of LCD-TV in 2010 is estimated to be 23% up.[3] The FPD-TV will continue to boost a growth of digital electronics market. Various kinds of UV curable materials, color resist, column spacer, sealing materials, insulation coatings, hard coatings, antireflection coatings, and so on are used to manufacture the FPD-TV.

World Semiconductor Trade Statistics reported that the semiconductor market in 2008 and 2009 were 2.8% down and 11.5% down from the previous year at dollar-basis, respectively.[4] However year 2010 is expected to turn to positive to be plus 12.2% and following 2011 will also show plus 9.3% growth. The Japanese semiconductor market is on the same track, thus the annual growth rate of 2009, 2010 and 2011 are minus 21.2%, plus 8.9% and plus 8.1%, respectively.[4] The photoresist for semiconductors shows the same trend as the semiconductors market.

The demand for UV curable materials for optical disk jumped up 3,500 tons in 2008 from 3,000 tons in 2007. The demand in 2009 decreased to 2,700 tons. This drastic decrease was caused by an outflow of manufacturing site abroad.

A world wide optical fiber demand for Q1 through Q3 of 2009 was about 113% to the same periods of 2008. Although North America, Europe and Japan slowed down during these periods, only China showed a significant growth to make the worldwide growth rate positive.[5] According to the Japanese Electric Wire and Cable Makers' Association,[6] the shipment of the fiber of Q1 through Q3 in 2009 decreased 4% comparing to that of previous year. Up-until Q2 of 2009, 16.5 million of households have introduced optical fiber to the individual home (FTTH) in Japan, 10.5 millions are the subscribers of ADSL and 4.2 millions are those of Cables. Remaining about 30 millions is the potential market for the FTTH. Optical fiber network is the infrastructure to support the coming new decade. The growth of the fiber network will accelerate the development of new technologies and services.

3. Technology Overview

3.1. Flat Panel Display Use

For the LCD-TV, technology challenges have been carried out to make the screen size wider, the response time faster and the contrast brighter to increase its performance. Further more, the technology challenges to make the LCD-TV environmental friendly by reducing power consumption both in manufacturing and in operation.

A significant movement in the LCD panel is the fact that newly developed LEDs take over conventional fluorescent tubes due to the better energy efficiency. The market share of the LCD-TV driven by LED back light is forecasted to be 25% in 2010 and growing more. The LED back light system is featured by the advantages; the contrast can be tunable by controlling individual LED's output, color reproducibility can be enhanced by using individual RGB LEDs, and energy consumption can be reduced by optimizing the output of individual LEDs. This new light source will strongly affect the performance of other materials used in LCD panels. In the back light unit of LCD a prism sheet is employed in. The design of the prism shape is modified suitable for the layout of LEDs to reduce the inhomogeneity of the light intensity. For the UV curable prism sheet, higher refractive index is preferable to higher the panel brightness.

Sharp Corporation, a leading company of LCD-TV manufacturing, announced that a new technology that makes the LCD with higher contrast and faster response time was developed and commercialized.[7] In the LCD panel, liquid crystalline molecules should be oriented along a particular direction on a polyimide alignment layer. This orientation is conventionally made by the mechanical rubbing by using fabrics. Photo induced alignment method has been proposed to make the orientation of liquid crystalline molecules for making the alignment finer and more uniform. The new technology enables us to increase the contrast 1.6 times high. Resulting from this, one can increase N.A. about 20% up. It is accordingly possible to reduce the energy consumption during operation. The progress of alignment technology impacted the design of the materials used in the LCD panels.

In order to increase the productivity of the LCD panel, the glass substrates have been getting wider and eventually the substrate called "G10" in size of 2950mm by 3400mm has been used in mass-production.[8] According to an increase of the substrate size, new process technologies and innovative materials development have been required and realized. The slit coating method overcame the conventional spin coating one to coat the color resists and spacer materials. An X-Y step exposure system has been predominantly employed instead of the conventional one-shot exposure. Changes in the manufacturing process need changes in the performance of the materials. The UV curable materials should have higher sensitivity to realize the faster processing. Non-uniformity of the panel took place by the inhomogeneous temperature distribution in the oven, the fluctuation of the intensity of exposure of curing, or the poor leveling performance of coating materials. And consequently the production yield might decrease. Permissible limits of dimension of each component should be controlled with an accuracy of nm-order. In response to this, the materials should have wider process windows to allow the fluctuation of the process.[9]

3.2. Photo-resist for Nano-fabrication in Semiconductors

Downsizing is an everlasting challenge for semiconductor device manufactures. A liquid immersion ArF process has become the technology to manufacture devices with 60nm hp and 45nm hp at the mass-production lines widely. Because the ArF immersion technology can achieve denser patterns without changing the infrastructure technology of existing state-of-the-art ArF dry lithography process.
In the liquid immersion process a resist layer is immersed in water during exposure. This immersion process might raise concerns such as leaching of resist components into water and consequently forming residuals affecting the post-processing or damaging exposure optics.[10] A method using a top-coat layer on the resist layer has been developed and employed in the mass production for better throughput.[11] The top coat is formulated with polymers having hydrophobic groups and alkaline developable groups, additives and solvent. The water repellent polymer is used as the components of the top coat. The top coat with a thickness of 90nm can suppress the leaching of photo acid generator from resist layer below 1/100 of that without top coat.

By eliminating top coat layer one can save the material cost as well as the machine time. Non-top coat resists thus have been developed to have the performance that can suppress leaching of the resist components and repel water at the surface.[12] As increasing water-repellant property of the surface, the solubility of the resists to developer tends to decrease and accordingly the defects might be generated during development. DLS (Dynamic Light Scattering) analysis revealed that the occurrence of defects was highly correlated with the size of the polymer cluster in developing solution.[13] It is considered that the polymer cluster in large size might be formed from the resist components having less solubility. By optimizing resist formulation, it is possible to reduce the generation of the cluster of large size and thus one can drastically reduce the defects formed during developing and rinsing.

The ArF water immersion technique will not be able to provide sufficient resolution for sub-30nm hp patterns. DP (Double Patterning) of ArF immersion and EUV (Extreme Ultra-Violet) processes have been proposed as the next generation photolithography. As the DP lithography, dual-trench (litho-etch-litho-etch, LELE) and dual-line (litho-litho-etch, LLE) processes were proposed.[14] The former technique requires dual lithography and dual etching after transferring the first litho pattern on an inorganic stack by etching. Thus the high throughput cannot be expected. On the other hand, in dual-line process the entire lithographic patterns are completed before transferring, it is thus the higher throughput can be expected. A freezing technique has been developed in order to protect the configuration of the first litho patterns.[15] After making the first litho patterns, a freezing agent comprised of resins, cross-linker and suitable solvent is coated on them. During the bake process, cross-linking takes place between the freezing agent and the first litho patterns to make them insoluble during the second litho process. It has been proven that the freezing technique could afford to provide sub-30nm hp patterns. Furthermore, a self-freezing resist has also developed. The self-freezing resist requires a single step bake process, thus the damages caused by the second litho process can be prevented. Promising performances for 28nm L/S pattern and 48nm hole/96nm pitch pattern were demonstrated. Much higher throughput can be expected than the LELE process.[16]

EUV lithography has been expected to realize the sub-30nm hp patterning by utilizing a light source having a wavelength of 13.5nm. There have been several difficulties to be overcome, such as development of light sources, masks and photo-resists, to realize the EUV process. Up to late 2009, a great progress had been reported in development of the light source which could be used for semi-commercial manufacturing of sub-30nm hp patterning.[17] For the material development big challenges are to achieve low Line-Width Roughness (LWR), high sensitivity, high resolution and low out-gas. For the finer pattern, sub-20nm, a 3σ of LWR should be controlled within 2nm. The dimension of the particles made of resist polymer cannot be negligible. In order to develop chemically amplified resist, it is important to establish the guiding principle to design the molecules which can work well in this nano-field. A low acid volatilization and a short acid diffusion length have been found to be necessary to suppress the deterioration of LWR, exposure latitude and linearity in the patterns in nm-size. In addition to this, incorporating hydrogen bond formation concepts to the acid bulkiness can further reduce the LWR deterioration by making the acid diffusion length short.[18] These new concepts accelerate the development of resists suitable for the sub-20nm hp generation and beyond.

3.3 Optical Fiber and Optical Waveguide Uses

Single mode optical fibers have been widely employed for the telecommunication network. The single mode optical fiber consists of a glass fiber having a diameter of 125μm and the dual layers of protective coatings. The dual layers, primary and secondary layers with a thickness of 60μm consist of UV curable polyurethane acrylates having soft and hard mechanical properties, respectively. One of the requirements on developing coating materials is to enhance the performance of anti-microbend properties of fibers,[19] and the other one is to provide the coatings which can enhance the productivity of the fiber. Considerable efforts have been made to realize these requirements and the results will be brought to the market soon.

Optical signal is delivered to individual subscribers' home through the optical fibers. Optical devices, splitter and multiplexer, are needed to divide or add the optical signals. These devices consisted of the optical wave guide have been used. The optical waveguide is manufactured by silicate through deposition and dry-etch process. The polymer optical wave guides which were made of UV curable materials through photolithography technique have been developed.[20]

A self-written waveguide formation was demonstrated by utilizing the phenomena that the refractive index changes upon polymerization. The refractive index change induced by the polymerization causes self-focusing and self-trapping of the optical beam inside the polymerized part.[21] The acrylic/epoxy hybrid resin is irradiated by UV light which induces radical polymerization of acrylic component. The irradiated UV light is confined within a high refractive index part where the polymerization takes place and the cured part, which eventually forms core part, gradually grows in the liquid form of the hybrid resin. After making core part, the remaining part is cured by irradiating UV light having different wave length of the first UV light. This second UV light induces cationic polymerization of the remaining part and then the clad is formed. Based on this technique, multi-mode waveguide having a propagation loss value 1.7dB/cm at 680nm was demonstrated [22] and the self written connections between 8-ports fiber array and 1x8 single mode fiber splitter were also demonstrated.[23]

3.4. UV Ink for Printing

The printing market in Japan is expected to grow at annual growth rate of 4.0% since 2006 to 2011.[24] Among many applications in printing, rapid development of UV-LED and increase of digital printing accelerate the expansion of the UV ink market.

A UV-LED light source has been developed and became available in 2009.[25] UV ink suitable for such new light source also has been developed.[26] By employing UV-LED as a light source, one can reduce the energy consumption up to 75% comparing to a conventional mercury UV lamp. The advantages of UV-LED are narrow UV spectrum, less heat emission, quick turn-on/-off property, long-life, and more. The narrow spectrum emission band means that no vacuum UV is emitted and accordingly no ozone generated as by-products during irradiation, and consequently no ventilation is necessary. The UV-LED emits no near-IR and IR radiation thus the no thermal effect takes place on the materials irradiated. The intensity of the UV-LED is still not enough because the emission spectra of the UV-LED do not match the absorption spectra of existing photo-initiators. It is thus the UV ink formulation carefully optimized to utilize the light energy.

The share of the digital printing in Japan is currently very small and was only 2% in 2008. It is however expected to grow to be 10% in 2012 due to the growth of the on-demand-printing. An ink-jet printing is a promising candidate to accelerate the growth of digital printing. Taking into account the processing speed, UV curable ink-jet system is preferable comparing to the water borne ink-jet one. For the digital printing, it is needed to balance among the three major performances, printing speed, printing area, and quality of printing, at high level. At the 14th DRUPA 2008 in Dusseldorf, many progresses in the ink-jet printing technology were demonstrated and these progresses have been translated into reality. High line head speed can be achieved by the development of not only the ink-jet head but also the UV ink. Considerable effort has been made to develop the UV ink system including cationic curable UV ink-jet ink [27] to enhance the wet-ability to the substrates. Good wet-ability to the various substrates can accelerate the development of the market of UV ink-jet ink.

4. New Technologies

4.1 Nano-imprinting

Considerable interest has been paid on the development of fabrication methods for microstructures with sub-micron or several ten-nm in size. Imprinting process to duplicate nano-structures has been demonstrated. Imprinting mold having nano-structures is made by using cutting, photolithography, or any other suitable methods on the substrates. The nano-structures are transferred to UV curable resins or thermo-set resins though imprinting process. This transferred nano-structure is used as the mold to reproduce the structure. UV curable materials were proposed for the nano-imprinting resist which satisfies various requirements such as viscosity, volatility, curing performance, release-ability from the template materials, and mechanical and chemical durability for multi-imprinting process.[28] The studies on vinyl ether resist formulations have been carried out to see correlation between the cured film roughness and the formulations to optimize the resist performance.[29]

One of the promising applications of the nano-structure is to fabricate moth eye patterns on a transparent film for reducing reflection at the surface. In order to utilize such moth eye pattern for commercial uses, a roll-to-roll imprinting process with a reasonable cost should be developed. The other application is expected to increase the luminance of LED. The luminance of LED can be enhanced by introducing photonic crystal structure on the semiconductor substrates of the diode. A well-designed photonic crystal structure with several-100nms of convexoconcave pattern can enhance the LED emission more than 50%.[30] This is done by the nano-imprinting process by utilizing UV curable resist.

4.2. Film Coatings for Surface Decoration

The attempt has been made to differentiate molded plastics products by adding an elaborated design on the surface. Hot stamping and insert injection molding have been used for making the decorative surface of the molded plastic parts. A new method has been demonstrated to provide the decorative surface to the molded products through vacuum transfer process by using a laminated dry film.[31] A five layered film is prepared by laminating, separate film, thermal adhesive layer as a primer, decorative base film composed of urethane and acrylic resins, UV curable resin layer as a clear coat and the protective film in sequence. After removing the separate film, the four layered film is introduced into a vacuum molding cavity and is stuck to the surface of the plastic part by the vacuum pressure under elevated temperature. By employing the materials having a good draw-ability as well as by utilizing the vacuum pressure, it is possible to make the 4-layered film to follow micro-structures such as grooves and overhangs on the surface of the plastic parts. After transferring the 4-layered film, the UV curable resin is cured by irradiating UV light trough the protective film. Then the final product having the decorative layer covered with the UV clear coat is obtained by removing the protective top film. The other layers having additional functionalities, such as color design, bright electro-plating feature and/or holographic design, can be inserted in between the primer layer and the UV curable resin layer to add the outstanding design for the molded plastic parts.

5. Summary

The radiation curing market and technology progresses in Japan are overviewed. In response to the world wide economical recession since the second half of 2008, the radiation curing market has been also shown drastic decline. In this circumstances the world around us are turning the direction toward the adoption of non-fossil fuel, reduction of the greenhouse gas emission and energy savings. Some of the particular market segments which are bound to this new trend showed favorable growth even in this economic situation. It is believed that the radiation curing technology is one of the key technologies to support and lead the new trend for the next decade.

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Table 1. Raw materials market overview

Ton/Year

Material	2004	2005	2006	2007	2008	2009 Estimate	Applications
Reactive Diluents	**20,200**	**20,900**	**22,040**	**23,240**	**21,400**	**20,050**	Not specified
Mono Acrylates	3,200	3,300	3,400	3,500	3,200	3,000	Coatings, OP varnishes
Di Acrylates	5,000	5,100	5,360	5,630	5,100	4,500	Coatings, OP varnishes
Multi Acrylates	7,400	7,500	7,880	8,280	7,800	7,500	inks, Hard coat, Resists
Methacrylates	700	800	900	1,010	900	850	Dry films
Others	1,000	1,100	1,200	1,310	1,200	1,200	Not specified
For synthesis	2,900	3,100	3,300	3,510	3,200	3,000	Oligomer synthesis
Oligomers	**16,320**	**17,200**	**18,300**	**19,560**	**18,300**	**16,400**	
Epoxy Acrylates	5,000	5,400	6,000	6,670	6,000	5,000	Solder resists
Urethane Acrylates	5,200	5,700	6,300	6,960	6,600	6,000	Optical fiber coatings
Polyester Acrylates	2,800	2,800	2,800	2,800	2,700	2,600	Wood coatings
Other Acrylates	920	1,000	1,100	1,210	1,200	1,200	Not specified
Unsat. Polyester	2,400	2,300	2,100	1,920	1,800	1,600	Wood coatings
Photoinitiators	**1,800**	**1,900**	**2,000**	**2,110**	**2,000**	**1,900**	
total	**38,320**	**40,000**	**42,340**	**44,910**	**41,700**	**38,350**	

Table 2. Application market overview

Ton/Year

		2004	2005	2006	2007	2008	2009 Estimate
Coatings		16,660	17,440	19,550	23,390	22,950	21,300
	Wood coatings	7,200	7,400	7,500	7,600	7,000	6,500
	PVC floor coatings	700	700	700	700	600	500
	Metal coatings	260	250	250	250	250	250
	Hard coatings(Film&Vac.Dep)	4,800	5,140	5,510	8,000	8,000	8,000
	Optical disk coatings	580	590	2,000	3,000	3,500	2,700
	Optical fiber coatings	1,130	1,260	1,380	1,510	1,400	1,500
	Ceramic coatings	1,700	1,800	1,900	2,010	1,900	1,600
	Release coatings	290	300	310	320	300	250
Inks		9,820	10,120	10,470	10,840	10,870	10,860
	Offset ink	6,800	7,000	7,200	7,410	7,450	7,450
	Gravure ink	1,450	1,500	1,600	1,710	1,760	1,800
	Metal coatings ink	800	800	800	800	750	750
	Silk screen ink	590	620	650	680	650	600
	Flexiso ink	180	200	220	240	260	260
Photoresists		18,580	20,970	22,620	24,300	22,300	21,100
	Dry film resist	2,500	3,000	4,000	5,000	4,500	4,300
	Liquid resist	6,200	6,400	6,600	6,810	5,400	4,900
	Electro-deposition resist	380	420	420	420	400	400
	Resist for LCD	2,400	2,700	2,900	3,110	3,850	3,900
	Barrier rib for PDP	2,100	3,200	3,200	3,200	3,000	2,500
	Semiconductor resist	3,000	3,200	3,400	3,610	2,950	3,100
	Photo polymer plate	2,000	2,050	2,100	2,150	2,200	2,000
Others		1,770	1,880	1,990	2,110	2,300	2,300
	Rapid prototyping	70	80	90	100	100	100
	Adhesives	1,700	1,800	1,900	2,010	2,200	2,200
Total		46,830	50,410	54,630	60,640	58,420	55,560

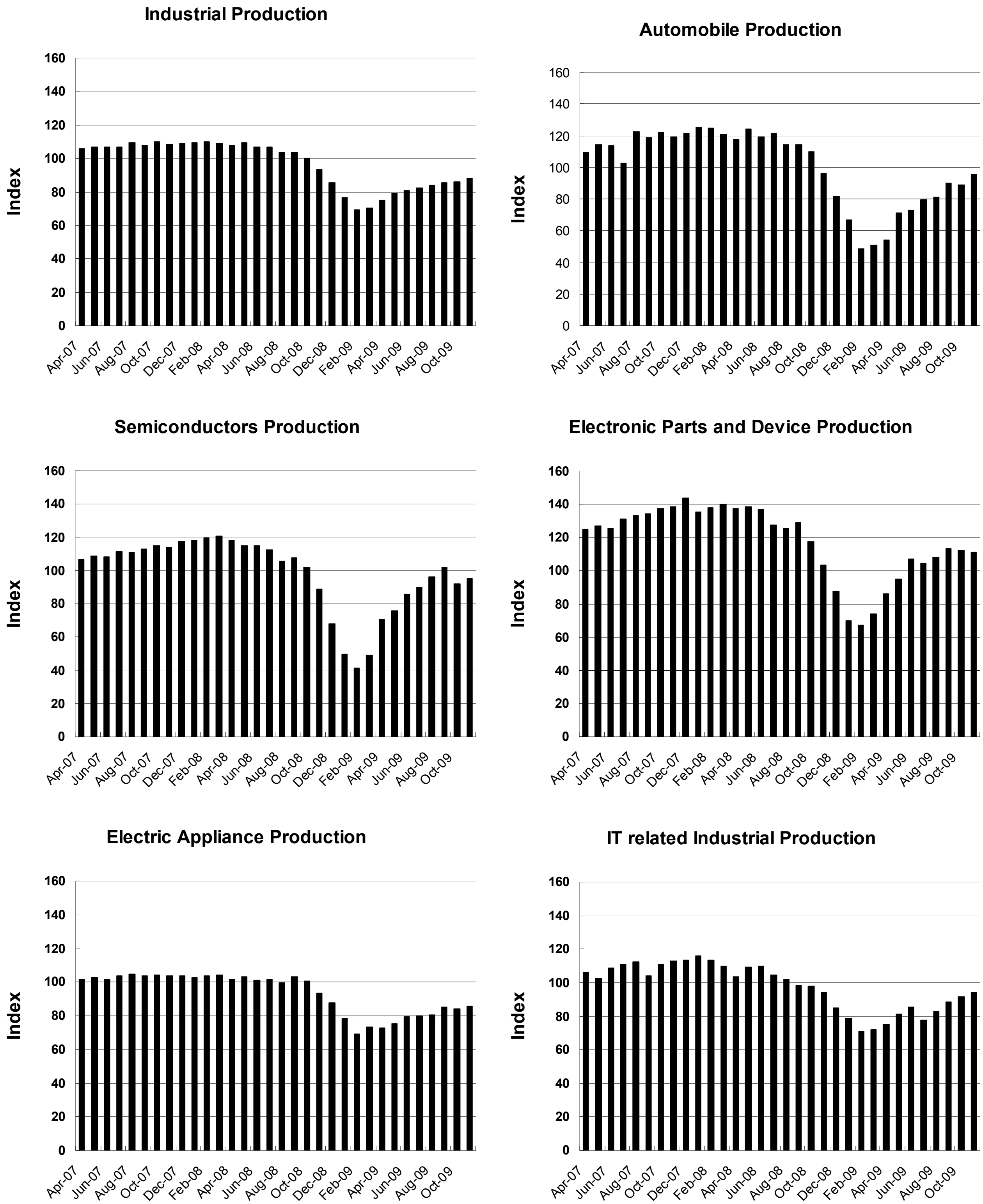

Figure 1. Industrial production data of Japan since 2007 April to 2009 October reported by MEITI of Japan.[1] Production indices of the total industry and other five major industrial segments are shown above.

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