Recent Advances in TASC (Thermal Activation of Semi-Conductors) Technology for Environmental Issues Focused on the Disassembly and Recycling of Solar Panels and Laminated Glass

—A New Technology Characterized by Radical Propagation in Giant Molecules—

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Thermal activation of semiconductors (TASC) is our novel technology characterized by radical propagation in giant molecules, allowing us to decompose any polymers, in an instant, into H2O and CO2. The present phenomenon has successfully been applied to complete decomposition of VOC (volatile organic compound), or to elimination of polymer matrix in composites in order to recover valuables, for example, decomposition and recovery of FRPs (fiber reinforced plastic), repair of partially damaged FRPs, reclaim of rare-earth powder from resin-bonded magnets, disassembly and recycling of solar panels and laminated glass. The TASC technology dates back to our accidental finding that significant oxidative properties appear in semiconductors when heated at about 350–500°C while quite inactive at room temperature. The oxidative effect (i.e. removal of bonded electrons) has been interpreted as arising from thermally generated defect electrons (“hole”) formed in the valence band of semiconductors. This triggers the decomposition of polymers by creating unstable radicals. Then, the radicals propagate, just like a domino phenomenon, throughout the polymer to make the whole polymer unstable, resulting in the fragmentation of the giant molecule into small pieces such as ethylene and propane. Finally, the fragmented molecules react with oxygen in air to give H2O and CO2 (i.e. complete combustion). This process caused by radical propagation is compared to the reverse reaction of “radical polymerization”. The present overview describes the recent advances in TASC technology with major focus on the disassembly and recycling of solar panels and laminated glass.

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1. Introduction

Thermal activation of semi-conductors (hereafter abbreviated to TASC) is a novel technology developed uniquely by us that decomposes any polymers, in an instant, into H2O and CO2.1,2,3,4 The main player here is free radicals caused by TASC which propagate throughout the polymer. The TASC technology is based on our accidental finding that significant oxidative properties appear in semiconductors when heated at elevated temperatures at about 350–500°C while quite inactive at room temperature.1) The significant oxidative property means a strong electron-capturing ability. The effect has been interpreted as arising from the formation of a vast number of thermally generated defect electrons (“hole”) in the valence band of semiconductors.2–4) This triggers the decomposition of giant molecules such as polymers as shown schematically in Fig. 1.

The initial TASC-process is to capture bonded electrons from the polymer to create unstable cation radicals (step 1). Then, the radicals propagate throughout the polymer to make the whole polymer unstable, resulting in the fragmentation of the giant molecule into small pieces such as ethylene and propane, just like a domino phenomenon (step 2).2–4) Then, the fragmented molecules react with oxygen in air to give H2O and CO2 (i.e. complete combustion: step 3). As a matter of course, smaller molecules such as VOC (volatile organic compound) can also be decomposed into H2O and CO2. The destruction mechanism is summarized. 1st step: creation of radicals by oxidation caused by TASC. 2nd step: fragmentation of giant molecules by radical splitting. 3rd step: reaction of fragments with oxygen in air to give H2O and CO2 (i.e. complete combustion). The present decomposition process of polymers played by radicals is compared to the reverse reaction of “radical polymerization”. Details on the TASC process are given in Appendix.

Since the TASC process is carried out in air (i.e. in an oxygen atmosphere) at high temperatures, oxide semiconductors come into consideration, and the metal oxides as those of Cr2O3, α-Fe2O3, NiO, TiO2 are the choice of semiconductors. These semiconductors are also called “catalysts” in the present paper. Among these, we are particularly interested in Cr2O3 because of its high stability (melting point: about 2200°C). In addition, its ecological

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safety is assured as shown by the fact that \( \text{Cr}_2\text{O}_3 \) is widely used as the green colorant for glass dyeing of whisky or wine bottles, etc. The materials to be decomposed are: all kinds of thermoplastic and thermosetting polymers, diesel exhaust which includes benzene, toluene, and PM (particulate matter), tar, tobacco smoke, VOC as well as offensive odor.

Up to now, the TASC-technology has successfully been applied to complete decomposition of VOC (volatile organic compound),\(^{4,17}\) or to elimination of polymer matrix to recover valuables, for example, decomposition and recovery of FRP (fiber reinforced plastic),\(^{18,19}\) repair of partially damaged FRPs,\(^{20}\) reclaim of rare-earth powder from resin-bonded magnets,\(^{21}\) disassembly and recycling of solar panels and laminated glass (i.e. this publication). During this period, there were three phases in technical development. Phase I was centered on the construction of a VOC elimination apparatus which features the following three crucial points: compact, high performance, and low cost. Our ultimate equipment developed is characterized by heater-embedded or heater-built-in honeycomb system.\(^{17}\) The task for phase II was aimed at entirely decomposing polymer matrix in composites such as FRP,\(^{18,19}\) bonded magnets\(^{21}\) in an attempt to reclaim glass or carbon fibers, and rare-earth powder, respectively. The most difficult issue here was how to cleanly decompose polymer matrix alone to recuperate valuables. For example, decomposition with a fluidized bed system based on powdered semiconductor was found to be of no use, because the targeted valuables were only recovered in mixtures with powdered semiconductor. At this moment, an innovative idea crossed our mind that makes use of spontaneous radical-multiplication in the TASC process. This required us to merely put an FRP plate on the catalyst-coated honeycomb, followed by heat treatment, so that the seed radicals can be formed at a few contact points between FRP and honeycomb, and these propagate throughout the polymer, ending up with polymer decomposition. On the basis of this idea, we could ultimately develop a clean system for decomposition of FRP wastes. In phase III, the most recent phase, we have been engaged in the disassembly and recycling of solar panels and laminated glass, utilizing basically the same technology as developed in phase II. However, we met here with a serious difficulty as to the size of an object having a large area. This requires us a long propagation length of free radicals within their lifetime. That is, the present task could only be achieved if the propagation length of free radicals could be sufficiently long. Then, we started our experiment to measure the propagation length of radicals in polymers, and finally found, to our great surprise, that the radicals are able to propagate over 120 mm or more during the TASC process. This led us to a successful disassembly of solar panels and laminated glass.

In the present overview, we first briefly present the summary of phases I and II, and then describe in detail the subject on the disassembly and recycling of solar panels and laminated glass by means of our TASC technology.

2. Summary of Phase I: Development of a VOC Elimination Equipment Using Catalyst-Coated Honeycombs Combined with Built-in Heaters\(^{17}\)

Previously, we worked mainly with a fluidized bed system based on powdered semiconductor for both VOC and polymer composites.\(^{4}\) On the one hand, the fluidized bed system is very efficient for decomposition of VOC because the collision frequency between semiconductor powder and VOC (or composites) is assumed to be quite high. On the other hand, the system is not appropriate for practical applications, because the recovered valuables, especially in the case of composites, are randomly mixed with powdered semiconductor. For this reason, we directed our attention toward an apparatus based on catalyst-coated honeycombs in combination with integrated heaters. After several trials, we developed an ultimate VOC elimination apparatus equipped with heater-embedded honeycombs as described below.\(^{17}\)

Figure 2 shows a \( \text{Cr}_2\text{O}_3 \)-coated honeycomb unit which includes a 300 W heater in a groove of the substrate. The dimension of the heater-embedded honeycomb is 130 mm × 200 mm × 30 mm. Eight pieces of the catalyst unit were stacked in pile and arranged horizontally to constitute a catalyst system as schematically shown in Fig. 3(a). Figure 3(b) is the external appearance of the apparatus. VOC is then made to flow through a series of the catalyst units, and the temperature was controlled with two thermocouples placed at the middle and the end of the honeycomb system near the outlet.

The present apparatus (model: MT-130-200) is designed for a process-volume of about 1.2 m\(^3\)/min for the flue-gas whose temperature is about 250–300°C. For room-temperature VOC, combination with a heat exchanger is highly recommended.

We have constructed various models of VOC elimination equipment in accordance with the VOC process-volume. These are presented at http://jintech.org which is the URL of our start-up company named JinTech Corporation.

One example of VOC decomposition is given in Fig. 4 which shows complete elimination of formaldehyde (so to speak formalin) for concentrations of 200 and 2000 ppm.\(^{16}\) The experiment was performed at 500°C in air. The reaction time was calculated to be about 20 ms. Formaldehyde is extremely toxic and is classified as a cancer-causing substance. Nevertheless, it is still widely used as a material for the preservation of internal organs, or as a cross-linker for phenol resins, for example, for button manufacturing industries.

Various VOCs were also tested: diesel exhaust, toluene, benzene and PM,\(^{8}\) methanol and methane,\(^{9}\) chloro-based...
organic solvents (dichloromethane and trichloroethene), and isopar L fluid (Exxon Mobile Chemical), as well as ammonia, isopropyl alcohol, and tetrahydrofuran. Regarding the decomposition selectivity of VOC species with TASC, it should be noted that our TASC system basically exhibits no selectivity, because our system functions by removing bonded electrons from VOC species to make VOC unstable due to radical formation (Fig. 1) which then triggers the fragmentation of the species, ending up with the formation of H_2O and CO_2. On the other hand, conventional chemical catalysts work through the formation of activated complex which depends variously on reaction species.

3. Summary of Phase II: Decomposition of FRPs and Recovery of Fiber Fabrics

3.1 FRPs of the plate form

The cost for FRP decomposition is a matter of primary importance for the recycling business of recovered fibers. As stated in Introduction, decomposition of FRPs with a fluidized bed system based on powdered semiconductor is obviously neither practical nor clean. For this reason, we looked closely again into the destruction mechanism and focused on the formation of free radicals and their propagation (Fig. 1). Then, we felt convinced that the free radicals multiply spontaneously (i.e. automatically) to induce the radical splitting, leading to the fragmentation of the giant molecule into small pieces such as ethylene, propane, etc. This suggested us to create, at least, one seed radical in FRP in the initiation process, and then all the rest (i.e. multiplication and propagation of radicals) proceeds automatically.

In practice, it is sufficient to make mechanical contacts between FRP and Cr_2O_3, so that radicals can be formed at the contact when heated at high temperatures. This has been achieved in the following way. Figure 5 shows a Cr_2O_3-coated honeycomb substrate colored green due to Cr_2O_3. We simply put a carbon fiber FRP (CFRP) plate (20 mm x 70 mm x 2 mm) on it and then sandwiched by another honeycomb, so that the FRP plate contacts Cr_2O_3 above and below the FRP plate, as shown in Fig. 6. At the time when the present experiment was carried, we believed that the radicals could travel only a short distance within their lifetime. For this reason, we performed our experiment with the sandwich structure in order to achieve a full propagation of radicals throughout the FRP plate. Then, the plate is heat-treated in air in a furnace at 400°C for 10 min. The temperature was adjusted to 400°C because the carbon fiber reacts with oxygen in air above 450°C to yield CO_2. The carbon fibers were perfectly recovered with the TASC technology as though these were virgin textiles.

Figure 7 shows CFRP plate before TASC treatment. Figure 7(b) is the plate after TASC treatment at 400°C for 10 min in air. Polymer matrix was entirely decomposed, giving rise to clean carbon-fiber textiles. Amazingly, no trace of carbonaceous deposits was recognized on the woven textiles.

Figures 8(a) and 8(b) show the SEM (scanning electron microscope) pictures for one single carbon fiber (i.e. one filament), before use and after recovery. No significant difference is recognized in appearance between them.

In view of the above positive result, we carried out additionally a number of decomposition experiments of FRPs as a function of thickness. We confirmed the complete

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**(Fig. 3)** VOC elimination system (model: MT-130-200): (a) schematic representation and (b) external appearance (240 mm x 300 mm x 560 mm; 20 kg).

**(Fig. 4)** Elimination of formaldehyde for concentrations of 100 and 2000 ppm.

**(Fig. 5)** Cr_2O_3-coated honeycomb substrate colored green due to Cr_2O_3: 100 mm x 100 mm x 2 mm.
decomposition of FRPs whose thickness is 4 mm. This thickness is said to be the maximum thickness used practically, even for aircraft wings.

3.2 Decomposition of polymer composites of any shape

The sandwich arrangement for FRPs is not applicable to composites of any shape, for example, a mold motor. We intend here to decompose the polymer matrix in order to recuperate an embedded motor. To achieve this, we applied the mold motor with a thin layer of Cr$_2$O$_3$ as a pre-treatment for the TASC process. A thin layer of Cr$_2$O$_3$ (about 5–10 µm in thickness) was coated on the mold motor by dipping it into a Cr$_2$O$_3$-containing suspension. When heat-treated, free radicals were formed at the interface between the mold motor and Cr$_2$O$_3$, and then self-multiplication and propagation followed just in the case of FRPs of the plate form.

Figure 9(a) is an example of the motor coils recovered from the mold motor that was embedded in a mold resin. The process was carried out at 400°C for 20 min in air. Figure 9(b) is a recovered glass-epoxy circuit board integrated in the motor. The encapsulating epoxy resin in IC chip has completely been decomposed, exposing a copper base plate. The circuit board was glass-fiber textile. Cu leads as well as trace of an IC chip are also seen in the picture.

On the basis of the above successful result, the radical propagation length was estimated to be over about 20 mm, since this value is the thickest part of the mold.

Similarly, a circuit board as shown in Fig. 10(a) was TASC-treated at 500°C for 30 min. Figure 10(b) shows the recovered electronic parts as well as a glass fiber fabric used as the base plate.

3.3 Similar TASC applications to repair of partially damaged FRPs and reclaim of rare-earth powder from resin-bonded magnets

Similarly, repair of partially damaged FRPs$^{20}$ and reclaim of rare-earth powder from resin-bonded magnets$^{21}$ have been carried out with success. Details are given in relevant references.


Disassembly and recycling of solar panels as well as those of laminated glass have been tackled in phase III with special attention to the propagation length of free radicals that play the major role in the TASC treatment. If the propagation length of radicals in composites is long enough, we will have great potential to disassemble and recycle the solar panels and laminated glass.

4.1 Background

Photovoltaic solar cells have recently attracted much
attention as one of the representative renewable energy sources as those of wind power, hydrogen power, solar energy, bio energy, and heat pump. This is especially accelerated because of the disaster of the Nuclear Power Plant caused by the Great East Japan Earthquake in 2011. The present movement is also consistent with the world trend towards increasing awareness of sustainability and the demand for renewable energy sources. At present, more and more photovoltaic (PV) solar cells are brought into the market as a clean energy source, as also assisted by Feed-in-Tarif. However, if the solar industry is to truly present a sustainable solution, the fate of the end-of-life PV panels must be addressed.

At the moment, crystalline Si solar cells account for more than 90% of worldwide PV production in 2013 and many solar panel manufacturers offer a warranty that guarantees electrical production for 10 years at 90% of rated power output and 25 years at 80%. This means that most solar panels installed in the early 1990s will come to end of their life in the next decades and appear as wastes. There is also another concern called the PID (potential-induced degradation) phenomenon which greatly reduces the operation life time of PV panels. PID is occurring in photovoltaic modules that results in the power loss of 30–50% or more. PID is said to occur mostly at negative voltage with respect to the ground potential and is accelerated by high system voltages, high temperatures, and high humidity. PID can obviously accelerate the increase in the disposal of solar panels. In order to tackle the problem of solar industry waste and recycling, it is imperative to develop innovative technologies that consider methods for recapturing material instead of sending them to landfills.

On the other hand, laminated glass has also a similar problem to that of solar panels. Laminated glass is a combination of two or more glass sheets with one or more resin interlayers. In case of breakage, the interlayer holds the fragments together and continues to provide resistance to the passage of persons or objects. As a resin for interlayers, polyvinyl butyral (PVB) is typically used at the moment. Laminated glass is normally used when there is a possibility of human impact or where the glass could fall if shattered: for example, automobile windshields, shop-fronts, etc. As for the disposal of laminated glass, waste disposal of laminated glass is no longer permitted in land fill in most European countries, as the end-of-life vehicle directive is implemented.

### 4.2 Structure and current disassembly-technologies of the solar panel and laminated glass

Figures 11 and 12 show the cross section of the solar panel and laminated glass, respectively.

In solar panels (Fig. 11), the basic building block is the solar cell itself. However, the cells occupy only about 4% of the total mass of the solar panel (1500 mm × 2000 mm × 50 mm; weighs about 20 kg). All the rest is the solar-cell supporting system in order to provide electrical insulation and protect against environmental corrosion. The active Si cells, which are wired together to form a module, are fully encased in a transparent material referred to as an encapsulant. The typical crystalline Si PV panel consists of four main components: the front cover (3 mm in thickness), encapsulate (1 mm), solar cells (0.25 mm), and the back sheet (1 mm), as shown in Fig. 11. The front cover is primarily made of glass. The encapsulant acts as an adhesive and connects the front cover and back sheet to the solar cells. Typically this is made of ethylene-vinyl acetate (EVA) which resists darkening or browning on ultraviolet (UV) irradiation and is stable against moisture, but polyvinyl butyral (PVB) can also be used. On the other hand, polyvinyl fluoride (PVF) is preferably used as a durable, weather-resistance back sheet for PV modules.

As judged from the structure of the solar panel, the difficulty for disassembly and recycling is obviously caused by polymer encapsulants such as EVA, PVB, and PVF which adhere closely between glass cover and solar cells, also between solar cells and back sheet.
At present, pyrolysis, which burns wastes at about 500°C in atmospheric pressure, or oxygen-depleted atmospheres is the most common method to separate composite material into its original constituents.\textsuperscript{24,25} Although many people still view pyrolysis as a means of recycling composite waste and many trials have been conducted, pyrolysis inevitably accompanies by-product ash such as carbonaceous deposits arising from imperfect combustion of polymers. In addition, unseparable parts often remain that are firmly fixed by polymer binders. These are randomly mixed with disassembled components of glass cullet, metal electrodes, Si wafers, and inorganic fillers. Furthermore, these components are often stuck together with carbonized decomposition products of polymers. Separation and sorting are costly, time-consuming, and labor-intense task. This is obviously one of the decisive drawbacks of the pyrolysis. In this sense, pyrolysis is not a clean system for dismantling the solar panels, as the European Commission also points out.\textsuperscript{26}

Thermal process in combination with mechanical one is also employed at the moment.\textsuperscript{27} The process flow begins with the disassembly of the Al frame, and then the panels are shredded and put into a hammer mill in order to break the glass down to several small pieces. Through a thermal process, plastic components are separated from the panel, while the remaining parts are manually removed. Once the components (glass, Al, etc.) are separated, they are sorted and placed into their respective established processes. Separation and sorting are again a big issue.

Another thermal process is the use of a fluidized bed reactor which operates at about 450°C.\textsuperscript{28} There is also a report on PV module recycling with organic solvent method.\textsuperscript{29} It requires, however, about 10 days to entirely remove EVA by soaking the panel in trichloroethylene at 80°C. In addition, the use of trichloroethylene can cause another environmental problem.

As seen from the above technical issues, the key to solving the question for PV recycling is to develop a novel technology that can effectively and cleanly remove the polymer matrix alone in PV panels. This is viable with our TASC technology.

On the other hand, the structure of laminated glass (Fig. 12) is quite simple. The dimension of laminated glass used typically in automobile is: two pieces of glass plate (one piece: about 2 mm in thickness) is bonded together with PVB using heat and pressure. The thickness of the interlayer is about 0.8 mm. A study shows that waste laminated glass is placed into a separating device such as rolling mill where the glass is fragmented and the larger cullet is mechanically detached from the inner film. The application of heat then melts the laminating plastic, usually PVB, enabling the glass to be recycled. However, it is questionable whether the resin may accompany carbonaceous deposits and/or harmful aldehyde-like odor during the heat treatment.

4.3 Key issue for the disassembly and recycling of the solar panel and laminated glass

When we prepare a module piece (120 mm × 120 mm × 5 mm) of the solar panel and try to disassemble it with the same sandwich method developed for FRP decomposition (section 4.1), we soon meet with a difficulty as caused by the presence of Si solar-cells in the solar panel that are spread over a large area closely and densely. The inorganic Si layer (not an organic compound) is likely to block the propagation of radicals arising from the back sheet which is in contact with a Cr\textsubscript{2}O\textsubscript{3}-coated honeycomb at the bottom. An alternative method is to apply a thin Cr\textsubscript{2}O\textsubscript{3}-layer at the side-edge of the panel piece and then let the radicals propagate horizontally throughout the plane, as shown in Fig. 13. In this case, again, we will have another difficulty regarding the propagation distance of radicals. However, these problems come down to the question how long the propagation distance is. If the propagation distance is long enough, the radical can travel horizontally to remove not only the EVA-layer, but also the back-sheet. Similarly, if the propagation distance is sufficiently long, the radical can also detour around the Si layer and propagate through openings between solar cells. To check up this possibility, an attempt was made to measure the propagation distance of radicals by using a module piece of the solar panel as shown in Fig. 13. At the side-edge of the module piece (120 mm × 120 mm × 50 mm), we applied a thin layer of Cr\textsubscript{2}O\textsubscript{3} by dipping, using a Cr\textsubscript{2}O\textsubscript{3}-containing suspension.

Four kinds of samples were prepared in regard to the number of edge-coating as shown in Fig. 14: (a) four cross-sections, (b) three cross-sections, (c) two cross-sections, and (d) one cross-section. The arrow denotes the direction of the radical propagation during the TASC process. This experiment aimed at determining the propagation distance of radicals from one corner of the module piece to another. Each sample was placed on a plain (i.e. uncoated) honeycomb substrate and heat-treated at 500°C for 20 min in the furnace. To our great surprise, all the sample gave the same result which show the complete elimination of polymer components. This experimentally indicates that the radical propagates or penetrates through a distance of over 120 mm. It appears then that the propagation of radicals is occurring in accordance
with the Huygens’ principle of the wave propagation: every wavefront serves as a source for the subsequent wave.

The above result motivated us to disassemble the module piece in the same way as we did for the FRP experiment (section 3.1). That is, we placed a module piece just on a Cr$_2$O$_3$-coated honeycomb in such a way that the underside of the back sheet contacts Cr$_2$O$_3$ and then heat treated in a furnace at 500°C for 20 min. In this case, radicals propagate from bottom (back sheet) to top (EVA-layer). The present experiment gave the same excellent result as that of the in-plane experiment mentioned above, indicating that the radical has propagated throughout the solar panel and detoured around the Si layer.

Finally, we could develop an excellent method to disassemble and recycle the solar panel.

### 4.4 Disassembly and recycling of solar panels

#### 4.4.1 Disassembly of the solar panel

A module piece of the solar panel (size: about 120 mm × 120 mm × 50 mm) was prepared by cutting from a solar panel of VLXA-125 from Next Energy and Resource Co. Ltd. The module was then placed on a Cr$_2$O$_3$-coated honeycomb as shown in Fig. 15 in manner that the underside of the back sheet contacts Cr$_2$O$_3$ and then heated in a furnace while introducing air. Radicals are first formed at the back sheet due to thermally-activated Cr$_2$O$_3$ and propagate, from bottom to top, throughout the polymer layers of EVA, PVB, and PVF in the module piece. This process ends up with the decomposition of all organic components into H$_2$O and CO$_2$.

Figure 16(a) shows the result of the TASC-treated module piece heated at 500°C in air for 20 min; whereas Fig. 16(b) is the result when the TASC-process was carried out with a α-Fe$_2$O$_3$-coated honeycomb in place of Cr$_2$O$_3$. In both cases, no trace of carbonaceous deposits due to incomplete combustion of polymers was observed. When the honeycomb with the TASC-treated module piece was held on slant and tapped with a finger, a number of glass cullet fell down. Then, with a little stronger tap, the solar cells with interconnectors were separated, leaving behind on the honeycomb substrate white residuals due to fillers such as CaCO$_3$ and TiO$_2$, as determined by our X-ray fluorescence analysis. The recovered cullet, solar cells and an interconnectors are shown in Fig. 17. The recovered glass cullet, solar cell, and electrode are extraordinary clean, showing the effectiveness of the TASC technology.

#### 4.4.2 Benefits of glass cullet, metal, and Si wafers

The outer glass cover (see Fig. 13) constitutes the largest share of the total mass of a PV module (about 65%). The glass is recovered in the form of clean cullet with no loss of purity or quality and can readily be accepted by glass manufacturing industry. Especially, the present glass cullet is a high-tech glass which is similar in morphology and composition to those glasses used in flat displays (for example, liquid crystal display) and automotive industry.

As for the metals, Al is primarily used as the frame. In solar cells are: Ag in the form of a grid on the front side of the cell, Al on the back, as well as interconnecting wires made of Cu and Sn which connect solar cells in series. These metals are said to occupy about 20% of the total cost.

Al frames are dismantled manually and can easily be recycled. Ribbons of Cu/Sn alloy (1.6 mm in width and 0.14 mm in thickness: see Fig. 17), used as the interconnector, were easily picked up with a pair of tweezers from the solar cells and can be used for recycling without further treatment. The Cu/Sn = 2/1 composition was identified by our X-ray fluorescence analysis. Ag grid-electrodes are usually prepared on the surface of a solar cell by screen printing technology. The reclaim of Ag from the solar-cell surface was carried out in the following way. First, 9.6 g of solar cells were immersed in 20 mL of concentrated HNO$_3$ in order to dissolve Ag pastes to give a pale yellow solution. Then, concentrated HCl was added to the solution to yield
0.3 g of the AgCl precipitate. Reduction of AgCl (0.3 g) with Na₂CO₃ (0.6 g) at 950°C gave about 0.2 g of pure Ag. In this way, nearly 95% of Ag was recovered from the Ag paste electrode. The Ag content in the solar cell is calculated to be about 2.4%. Another solar panel from Changzhou Trina Solar Energy Co. Ltd. gave about 1% of Ag content. Al paste electrode on the rear side of the solar cell was not recovered, since the recovered Al is of no practical value.

The Si wafers occupies about 4% of the total mass of a PV panel. The recovered Si wafers were mostly broken. The remaining wafers after Ag-recovery can either be used as materials for the production of Si crystals or as materials for glass through standard glass recovery/recycling processes.

4.4.3 Continuous equipment for the decommissioning of the solar panel

A continuous equipment for dismantling the solar panel has also been constructed, as shown in Fig. 18. The equipment is composed of a central furnace with “inlet/outlet” doors, together with two chain-conveyer systems for module-piece transfer. A minute amount of fresh air is introduced from the bottom of the furnace, and the exhaust gas is vented through an exhaust pipe above the furnace, leading to a VOC elimination apparatus (Fig. 3) located behind the furnace.

The dismantling process for the PV module piece is as follows. The furnace is pre-heated to a temperature of 300°C. A tray, which includes a module piece of 80 mm × 160 mm × 5 mm placed on a Cr₂O₃ or α-Fe₂O₃-coated honeycomb, is transferred to the inlet door of the furnace. Then, the door opens and the tray enters the furnace, followed by door closing. The furnace is then heated from 300 to 500°C and keeps this temperature for 20 min for the disassembly of the module piece. After that, the furnace is cooled down to 300°C. Then, the outlet door opens and TASC-treated tray is pulled out, followed by door closing. At this moment, the next tray will be supplied into the furnace for the second run.

The TASC-result of the module piece is shown in Fig. 19. The result is equivalent to that of the manual treatment shown in Fig. 16.

4.4.4 Dismount of the Al frame by TASC

As is well known, the dismantling of the Al frame in the solar panel is an extremely cumbersome task. At the moment, the mechanical disassembling by pulling the Al frame in four different directions seems to be the only way. For this difficult task, we challenged with TASC technology, utilizing the long propagation length of radicals. We made the solar block (with Al frame and terminal) contact Cr₂O₃-coated honeycombs as shown in Fig. 20. Or, an alternative method was to partly coat a thin layer of Cr₂O₃ by spraying or dip-coating. The experiment proceeded as we had expected. Figure 21 shows the recovered species: Si wafers, glass cullet, Al frame, and interconnector.

4.4.5 Disassembly of laminated glass

Similarly, a laminated glass (size: about 110 mm × 130 mm × 5 mm: Fig. 22(a)) was prepared by cutting an automobile windshield (TOYOTA: CROWN) and then its side-edge was coated with Cr₂O₃ and heat-treated at 500°C for 30 min. TASC treatment shows that the PVB interlayer was entirely removed to give two pieces of the glass plate, as shown in Fig. 22(b).

5. Concluding Remarks

TASC technology has been reviewed in the present overview from the accidental finding of the phenomenon to various applications in the environmental field. Apart from the main subject, two outstanding novel phenomena shown below were also observed and their mechanisms have been elucidated.

(1) The present technology is an entirely novel invention which has neither been reported in High-Tech semiconductor areas, nor in the area of industrial wastes. The formation and propagation of free radicals caused by TASC play the decisive role in the applications described in phases I, II, and III. This technology is
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Appendix

Outline of the TASC Theory

1. Optical Excitation versus Thermal Excitation: Origin of the Oxidative Properties

For discussions on optical and thermal excitations in semiconductors, it should be noted that these excitations are characterized by “surface” and “bulk” excitations, respectively. Furthermore, photons bring about directly electrons and holes in the conduction and valence bands, respectively; whereas the thermal excitation (i.e. higher temperature) induces an increase in the population of electrons at higher energy levels in accordance with the Fermi-Dirac distribution function. This means that there is a marked difference in the carrier formation mechanism between these excitations.

We first explain the optical excitation together with its subsequent photoconducting phenomenon [Fig. A1(a)] and then discuss the oxidative property of holes. In semiconductors, completely filled bands of electrons (called the valence band) are separated by forbidden energy gaps from the other bands completely empty of electrons (called the conduction band). When the semiconductor is excited by a photon whose energy is larger than the band gap, then an electron in the valence band is excited across the forbidden gap to the conduction band, leaving behind a positively-charged defect electron called hole in the valence band. Both electrons and holes are mobile and thus contribute to the increase in electrical conductivity. This is known as the photoconducting phenomenon.

We focus here on the property of holes. The hole is known to strongly attract an electron from the conduction band or from organic compounds adsorbed on the surface in order to bring back the semiconductor to the original stable state. In other words, the hole has strong oxidation ability. These oxidative holes are utilized in photocatalysts for decomposition of organic compounds adsorbed on the surface. However, the decomposition performance is known to be quite poor. Then, we try to excite the semiconductor with much higher light intensity in an attempt to construct a stronger oxidation system in anticipation of the increase in photoconductivity. However, this trial fails, because the electrons and holes created are immediately recombined after excitation in recombination centers due to lattice defects on the surface. In addition, the light irradiation impinges exactly on the surface filled with these recombination centers. Therefore, the increase in electrical conductivity is generally limited to, at most, one order of magnitude.

We then considered the thermal excitation [Fig. A1(b)] which is the bulk excitation rather than the surface one. The number of electrons and holes is known to increase in
accordance with an exponential function of temperature according to the semiconductor theory.31) The number of charge carriers is given by the product of the Fermi-Dirac distribution function and the density of state in the conduction band or valence band. So we estimate approximately a ratio of the number of charge carriers at room temperature (RT) and 350°C, using the Boltzmann distribution function. The electron and hole concentrations ($n_e$ and $n_h$, respectively) for intrinsic semiconductors are given by the following equation, where $E_g$, $k$, $T$, $m_e$, and $m_h$ denote the energy gap, temperature, Boltzmann constant, effective masses for electrons and holes, respectively.

\[
n_e = n_h = 2 \left( \frac{kT}{2\pi\hbar^2} \right)^{3/2} \left( m_e m_h \right)^{3/4} \exp\left(-\frac{E_g}{2kT}\right)
\]

The number of carriers at room temperature (RT) and 350°C gives a ratio of $n_{623K}/n_{RT} \approx 8.8 \times 10^{13}$ where $E_g = 3.2$ eV (band gap of titanium dioxide of the rutile phase). In fact, our experiment using a single crystal of TiO$_2$ showed that the resistivity is about $10^{11}$ Ω cm at RT. However, the resistivity is remarkably reduced to only 15 Ω cm at 500°C, although the electron-hole recombination is still occurring at the surface.2,3) This fact experimentally shows that the resistivity is reduced by ten orders magnitude, indicating the formation of a vast number of free charge carriers. That is, the appearance of significant oxidative properties due to TASC can now be interpreted as arising from the formation of a large number of holes in the valence band.2,3)

2. Example of a Polymer Decomposition by TASC

We will show below an example of the instantaneous, complete decomposition of polycarbonate (PC: substrate material for optical discs) by TASC together with its destruction mechanism.3) We carried out an experiment using two glass tubes, each of which contains PC chips in the presence or absence of TiO$_2$ used as a semiconductor (Fig. A2). These were heated in air at 500°C for 30 min.

The PC in the absence of TiO$_2$ melted at about 200°C and then boiled, ending up with the carbonization. This is the typical result when a plastic is roasted in air. On the other hand, no trace of PC was recognized in the presence of TiO$_2$. Here remain just white powder of TiO$_2$. Gas analysis of the decomposition product was made by mass spectrometer and the result is shown in Fig. A3(a).3) Since the experiment was performed in air, we see peaks of N$_2$ (28) and O$_2$ (32) that are components of air, as well as peaks of H$_2$O (18) and CO$_2$ (44). Furthermore, we observe a peak of Ca (40). This is due to a metallic soap of Ca used as a lubricant in PC. The present result indicates that PC (molecular weight: about 25,000) has entirely been decomposed into H$_2$O and CO$_2$ in an instance. This is an amazing effect. On the other hand, when the experiment was carried out under vacuum, we see a number of small fragments as shown in Fig. A3(b). However, these peaks disappear in an oxygen atmosphere, leaving only two
peaks of H$_2$O and CO$_2$. This clearly indicates that oxygen is absolutely necessary for the disappearance of fragment peaks.

On the basis of the above experiments as well as those by electron spin resonance (ESR) for radicals, we proposed the destruction mechanism as schematically shown in Fig. A4. The first process of the decomposition reaction is the capture of bonded electrons from polymers by defect electrons, leaving behind cation free radicals. The free radical is unstable and can propagate throughout the polymer chain at 350–500°C. This makes the whole polymer chain unstable and induces “radical splitting”. This results in the fragmentation of the giant molecule into ethylene, propane etc., in a fashion, just the reverse reaction of “radical polymerization”. The fragmented molecules then react with oxygen in air to give just H$_2$O and CO$_2$. To summarize the destruction mechanism, the process is composed of the three steps: (1) oxidation, i.e. creation of radicals, (2) radical splitting, i.e. fragmentation of the giant molecule, and (3) reaction with oxygen, i.e. complete combustion.

3. Conditions for the Reaction to Continuously Proceed

Thermal excitation brings about a vast number of electrons and holes. Among these, the holes are consumed at the edge of the valence band, leading to the formation of cation radicals in the polymer. Then, how about the fate of electrons (i.e. counter charge of holes) that are also supposed to be consumed somewhere in semiconductors in order to preserve the electrical neutrality. The neutrality is actually the critical condition for the reaction to continuously proceed. In general, in reactant systems of semiconducting particles, oxidation reaction occurs at the edge of the valence band while the reduction at the edge of the conduction band, so that the electrical neutrality is maintained. In the case of the TASC process, as shown in Fig. A4, the electron is consumed to reduce adsorbed oxygen in air to give an anion radical of O$_2^-$ at the edge of the conduction band: O$_2$ (gas) $\rightarrow$ O$_2$ (adsorbed) and then O$_2$ (adsorbed) + e$^-$ $\rightarrow$ O$_2^-$ (adsorbed). This means that the TASC reaction ceases in the absence of oxygen because the electrical neutrality is not maintained. The existence of the anion radical has been confirmed by ESR.

REFERENCES