

광을 이용한 해체용 접착소재의 최근 동향

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(2021년 06월 03일 접수, 2021년 06월 23일 수정, 2021년 06월 26일 채택)

Recent Trends of Light Induced Bonding-Debonding Adhesives

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(Received Jun 03, 2021; Revised Jun 23, 2021; Accepted Jun 26, 2021)

요약: 세계적으로 지속가능한 세상을 만들기 위한 노력이 제조업에서 많이 이루어지고 있다. 이를 위해서는 사용 후 제품을 쉽고 간단하게 해체할 수 있는 설계 개념 중요하다. 접합된 제품 해체 시 부품에 대한 피해가 없도록 접합부위가 분해되어 재활용이나 수리를 가능하게 하는 신기술이 최근 개발되고 있다. 본 총설에서는 조절가능한 접합-해체용 소재 기술, 특히 빛으로 해체하는 접착소재기술 동향을 정리하였다. 또한 반도체, 디스플레이 산업에 현재 활용되고 있는 빛 이용 임시 접합-해체용 필름에 대해 기술하였다.

Abstract: A variety of efforts are attempted to make the world sustainable in fabrication industries worldwide. To achieve the goals, a new design concept for products is one of crucial factors to be able to dismantle them after use in easy and simple ways. New debonding technologies have been developed in recent years for the recycle and/or repair of bonded structures, where the bonds are broken without the damage of the components and make recycling easier. Some representative technologies of controlled delamination materials (CDM) are reviewed with an emphasis on light induced debonding of adhesives. We also describe current applications of light induced CDMs as temporary bondable films in semiconductor and display industries.

Keywords: Adhesives, Dismantlable, Bonding, Delamination, Light

1. Introduction

The world is witnessing the damaging impact of industrial society on the environment and the ecosystem of the planet where we live, and which we depend upon. Resources are finite and the impact of society on the ecosystem depends upon the ways in which we use energy and materials. A variety of efforts are attempted to make the world sustainable in fabrication industries. A good design for products means taking into account

the need to be able to dismantle them in easy and simple ways. New debonding technologies have been developed in recent years for the processes for the recycle and/or repair of bonded structures, where the bonds are broken without damage of the components and make recycling easier. This is an environmental friendly disassembly of bonded structures. The adhesives of controlled delamination materials (CDM) are easy to disassemble the bonded structures and convenient to separate parts for reuse or recycling. The CDM can be applied to fast assembly-disassembly processing in the industries and for repair and maintenance to upgrade the parts [1]. There

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are growing market-inducing factors for CDMs. Producer responsibility legislation exists already in many industries which is forcing a change for the better. The producer (manufacturer) is responsible for the end of life of their products, which fosters a very different mindset for the design and the specification of assembly methods. Some examples of CDM include the removal of dental prosthetics, the repair of a bonded composite automotive structure, or the separation of the components of an aircraft [2]. The multitude of considerations on CDM are concentrated on followings, (1) the methods, effectiveness, triggers, and applications potential, (2) the short-term and long-term performance of joints, (3) the micro-mechanical effects of expansion within bondlines, and finally (4) the influence of the type and nature of externally applied loads technology. Debonding is achieved by weakening the bonded site with the help of applied stimuli such as mechanical stress, heat, electrical current, light, etc.

In this paper, we review the recent studies focusing on light induced CDM technologies along with industrial product developments. Some bonding materials are known to be transformed to materials with low adhesion strength due to chemical degradation, decrosslinking and chemical structural transformation under the light irradiation, resulting in debonding on demand.

2. CDM Technologies

2.1. Classifications of CDM

There is an increasing demand for recyclability, driven by economic as well as environmental reasons for sustainable society. For example, key technology drivers for End-of-Life Vehicles (ELVs) are rapid assembly and disassembly joining solutions. As for the electronic chip industry, several research teams started the research for disassembly on adhesive formulations to enable rapid removal of chips at end of life [3].

To meet those demands, researches are focused on the polymer design and the introduction of an additive in the designed adhesive. In the development of adhesives which can be used in the disassembly of products, it is important to ensure that the mechanical properties and adhesive strength. It is also necessary to study the applications of an external energy source like heat (thermal and induction), electrical, light, or magnetic flux during debonding processes. The preferred materials for

bonding and debonding processes should be easy to apply, environmentally friendly, cost effective and should not leave any adhesive residue on the substrate.

The CDM can be represented by the following categories, i.e.

The EDA technology among them was described elsewhere in detail by one of authors [4].

- Thermally expanding particles (microspheres, graphite, etc)
- Thermally induced separation of phases
- Chemical and physical foaming agents
- Electrically debonding adhesives (EDA)
- Photo-induced transformable materials in chemical or morphological structures and others

2.2. Conventional examples of CDM technologies

There are several CDMs as explained in the previous section. When some adhesion materials are heated, they are easily debonded because the adhesion strengths are decreased due to the particle expansion included, or phase separation in multicomponent materials, or foaming by foaming agents, etc. In other cases, they are delaminated upon applying electrical current or light irradiation.

Lu et al. compared various CDM techniques and rated them as in Table 1 [5]. Ionically conducting epoxy adhesive, chemical foaming agent, and thermally expandable microspheres can be applied to automotive industries and their overall ratings are good.

The early example of CDM technology is on the utilization of microcapsules for separating shoe soles [6]. Metallic inclusions were incorporated for the debonding process into the adhesive to efficiently absorb and emit heat energy when subjected to alternating electro-magnetic field to activate the release of micro-encapsulated solvents, which would further degrade the polymeric structure. An automotive company, Daimler-Chrysler [7] deployed microcapsule technology and patented the encapsulated solvents and organic amines or acids which can cleave an epoxide backbone. Microcapsules were recommended to be made of amino resins or metal halides. Nissan Motor Company [8] patented oxidizing agents (ammonium perchlorate, potassium permanganate, etc.) into the adhesive matrix which produced a self-burning reaction at elevated temperatures.

2x, with $x \approx 1$, where light-heat conversion is facilitated by the ultraviolet (UV) light-absorbing metal-ligand motifs, or (B) self-complementary hydrogen-bonding ureidopyrimidinone (Upy) motifs (Upy-PEB-Upy), where a UV absorber was added for light-heat conversion as in Fig. 2. Also shown are schematic representations of the stimuli-responsive assembly and disassembly of supramolecular polymers using light or heat.

Single lap joints were prepared by sandwiching films of the supramolecular polymers of a thickness of 80-100 μm between two substrates and bonded by exposure to either UV light (320-390 nm, 900 mW/cm^2) or heat (80 or 200°C) for UPy-PEB-Upy and the metallopolymers, respectively. UPy-PEB-Upy and $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ displayed a shear strength of 0.9-1.2 and 1.8-2.5 MPa, respectively, Table 2. When lap joints were placed under load and exposed to light or heat, the samples debonded within seconds. They could be rebonded through exposure to light or heat, and the original adhesive properties were recovered [9].

Heinzmann et al. also studied metallosupramolecular polymers in which defects can be healed upon exposure to ultraviolet (UV) light. The building blocks can be assembled into polymeric structures with approximately stoichiometric amounts of Zn^{2+} and La^{3+} salts. The metal-ligand motifs absorb incident UV light and convert it into heat, which causes the temporary dissociation of the metal-ligand motifs and transforms the material into a low-viscosity liquid. When the light is switched off, the metallopolymers re-assemble and their original properties are restored. A similar behavior was reported for nanocomposites consisting of either Mebip-PEB-Mebip-based metallopolymers [11] or UPy-PEB-Upy as the matrix and cellulose nanocrystals as a filler.

The principle of a repeatable adhesion is based on the

Table 2. Shear Test Results of Quartz Lap Joints Bonded with $[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$ or UPy-PEB-Upy [9].

	Shear stress (MPa)	
	$[\text{Zn}_{0.8}\text{Mebip-PEB-Mebip}](\text{NTf}_2)_{1.6}$	UPy-PEB-Upy
Thermally bonded	2.5 ± 0.2	0.9 ± 0.1
Thermally rebonded	2.5 ± 0.1	1.0 ± 0.1
UV bonded	1.8 ± 0.4	1.2 ± 0.1
UV rebonded	2.3 ± 1.0	1.6 ± 0.2

reversible change of the melting or softening point of the adhesive, which is associated with the reversible photoreaction. Consequently, the adhered substrates cannot be separated when the adhesive is solid, while they can be easily separated without any applied force when the adhesive becomes liquid.

Akiyama et al. [12] found that sugar alcohol derivatives with multi azobenzene arms are photochemically and isothermally liquefied from a powdered solid upon irradiation with ultraviolet light at room temperature, and then solidified on irradiation with visible light, where the transition between solid and liquid are reversible, Fig. 3. These compounds possess similar chemical structures to comb-like liquid crystalline oligomers. The adhesive materials used had 4-8 hexylazobenzene-oxyundecanoyl groups connected by a sugar alcohol scaffold or alkylazobenzene side chains of a polyacrylate main chain. The azobenzene moieties are trans-cis photoisomerisable and coloured units. However, due to the use of azobenzenes unit, the adhesives are colored yellow or orange.

Their photochemical and thermal phase transitions were investigated in detail and were compared with those of other sugar-alcohol derivatives. The adhesions were varied by alternately irradiating the compounds with ultraviolet and visible light to photoinduce phase transitions. The azobenzene hexyl tails, lengths of the

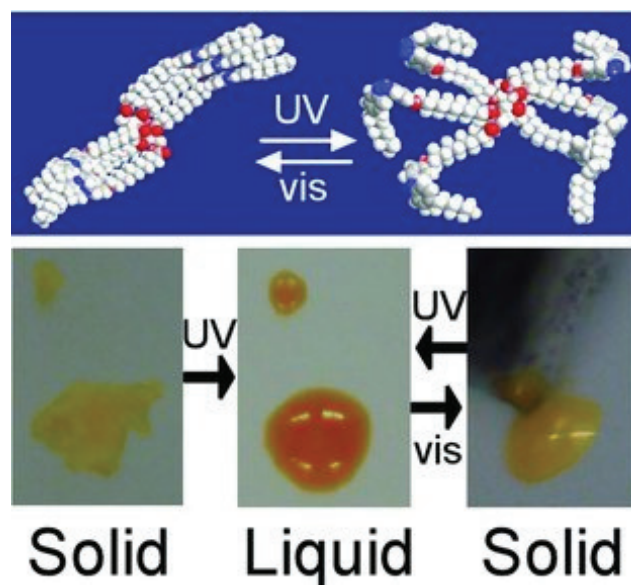


Figure 3. Liquefaction and solidification of sugar alcohol derivatives with multi azobenzene arms. Reprinted with permission from [12]. Copyright (2012) John Wiley and Sons.

methylene spacers, and differences in the sugar-alcohol structures affected the photoresponsive of the materials.

Akiyama also achieved a reversible isothermal phase transition between the liquid and solid states in response to light irradiation in side chain-type azobenzene polymers [13]. These materials can be used as adhesives that are detachable without applying any mechanical and thermal stress but also repeatedly reworkable because of their photoinduced liquefaction and solidification properties. The adhesive strength to glass plates was more than 3 MPa in single lap shear tests. This value is three times higher than previously reported and is sufficiently strong for glass substrates.

Akiyama et al. designed and synthesized polyvalent anthracene derivatives [14]. Core technologies are thought to be the synthesis of monomeric polyvalent anthracene derivatives that remain in a liquid state at ambient temperature. It was found that the substitution position at the anthracene was important to obtain liquid-phase compounds at room temperature. Importantly, the use of anthracene-terminated liquid compounds with hexamer structures ($2,500 \text{ g mol}^{-1}$) gave colorless adhesives. The photo-crosslinkable and thermo-degradable materials demonstrated reworkable adhesion of glass plates. Thus, the cured material was stable up to 120°C , but it returned to the original liquid state at room temperature after heating at 180°C , resulting in the detachment of the substrates without applying any strong force, Fig. 4. The

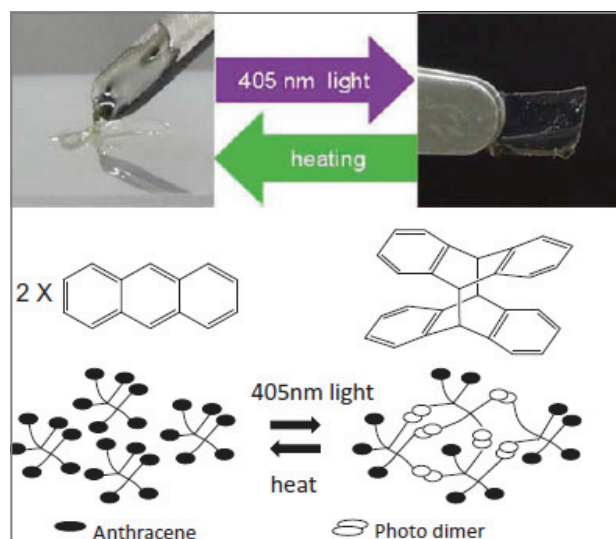


Figure 4. Reversible photocuring of a hexa-anthracene compounds with 25% of dibutyl phthalate on irradiation with 405 nm light and on heating 180°C [14].

cycles of the curing and liquefying processes was reproducible for at least five consecutive times.

Liquid crystal (LC) provides a suitable platform to exploit structural motions of molecules in a condensed phase. Amplification of the structural changes enables a variety of technologies not only in LC displays but also in other applications. Until very recently, however, a practical use of LCs for removable adhesives has not been explored, although a spontaneous disorganization of LC materials can be easily triggered by light-induced isomerization of photoactive components. The difficulty of such application derives from the requirements for simultaneous implementation of sufficient bonding strength and its rapid disappearance by photoirradiation.

Saito et al. reported a dynamic molecular LC material that meets these requirements [15]. They found that columnar-stacked V-shaped carbon frameworks display a sufficient bonding strength even during heating conditions, while its bonding ability is immediately lost by a light-induced self-melting function. Fig. 5 shows isothermal photoinduced melting of molecule 1 in the range of $70\text{--}135^\circ\text{C}$ (left to right), in which the columnar LC phase of 1 is photochemically transformed into a fluid mixture mainly composed of unreacted 1 and its photodimer product. Heating the melted mixture at 160°C

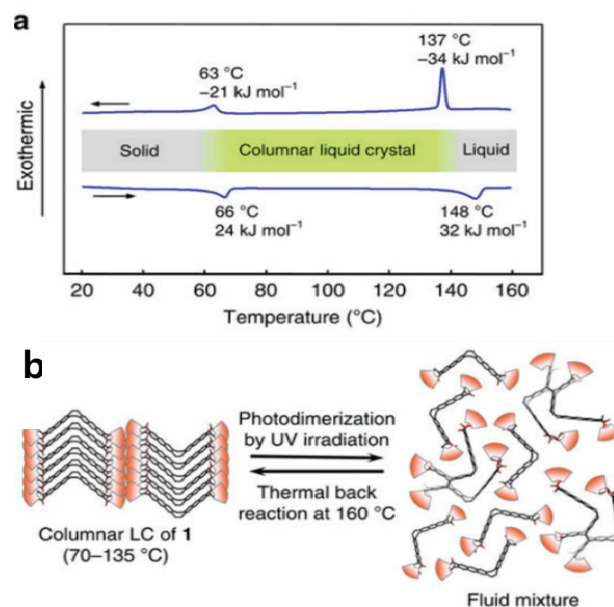


Figure 5. Photoinduced melting in a columnar LC phase [15]. DSC traces of 1 at 2°C min^{-1} rate of cooling and heating and (b) Isothermal photoinduced melting of 1 in the range of $70\text{--}135^\circ\text{C}$ (left to right).

induces a thermal back reaction of the photodimer into the monomer 1, which recovers the columnar LC phase when the temperature is set again in the range of 70–135°C (right to left).

The light-melt adhesive is reusable and its fluorescence color reversibly changes during the cycle, visualizing the bonding/nonbonding phases of the adhesive. The room-temperature shear strengths are plotted in Fig. 6 before and after 320 mJ cm⁻² ultraviolet exposure at 100°C in the recycling processes. The inset photographs show the fluorescent film in the corresponding stage.

2.4. Effect of wave lengths on debonding of adhesives

It is worthwhile to note the importance of the effect of wavelength on debonding mode for laser light induced debonding. A 248 nm UV laser tends to cause a delamination at the glass/adhesive interface whereas a

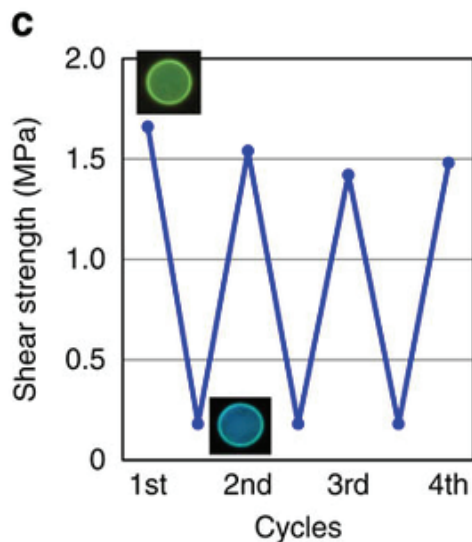


Figure 6. Reusability of an adhesive [15].

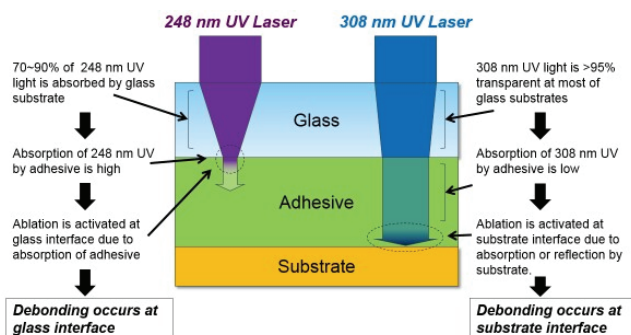


Figure 7. The effect of wavelength on the debonding mode [16].

308 nm UV laser tends to cause a delamination at the substrate adhesive interface due to differences where the light is absorbed, Fig. 7 [16]. When 248 nm UV laser is used, the laser energy is absorbed by the adhesive, resulting in the debonding at the glass/adhesive interface, which is far from being desirable. By contrast, when 308 nm UV laser is used, the laser energy absorbance by the adhesive is low, resulting in the debonding at the adhesive/substrate interface.

3. Industrial Applications of CDMs

3.1. Process films for semiconductor industries

The fabrication of electronic devices from ultrathin flat semiconductor wafers is becoming more important than ever. Special films with controllable bonding-debonding characteristics are needed for thin wafer handling and thin wafer backside processing.

For more than several decades, process films such as BG (back-grinding) tape, DC (dicing) tape, and DAF (die attach film or die bonding tape) have been used in the semiconductor industries.

A BG tape is used to protect the circuit surface from damage by foreign matter, chipping, cracking and contamination during back grinding process. The functions required to the BG tape are;

- Excellent adhesion to an uneven wafer surfaces, such as on the circuit side
- Effective control of particles
- Excellent grinding accuracy and good water-seepage control during back grinding
- Easy peeling, and effective control on adhesive deterioration with time [17].

DC tapes are used for semiconductor wafer dicing and for ceramic hybrid substrate sawing and are also useful for surface protection. These applications require an adhesive tape with relatively low adhesion, no adhesive transfer, and the ability to stretch without tearing. The tape is also used extensively for scribing and expanding. DC tape is investigated by various companies. For example, two R&D products of Higashiyama Film Co. in Japan are under evaluation, Fig. 8. The peel strength ranges from 2.39 to 7.6 N/25 mm when the products are applied. The peel strength is decreased down to, upon UV irradiation, from 0.10 to 0.43 MPa/25 mm.

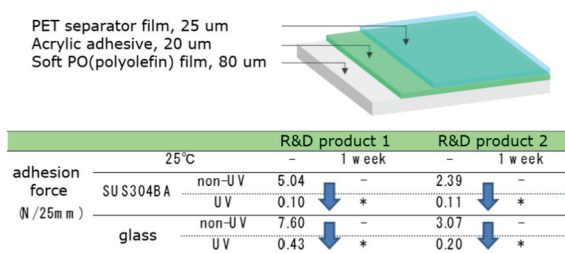
DAF and DDAF (dicing die attach film) have been

commercially available since 2000 AD. DAF and DDAF are epoxy adhesives which are film-based instead of paste-based and are attached to the back of the wafer prior to dicing. DAF is sold without a support dicing tape, whereas DDAF is sold on a stretchable support dicing tape which is partially sawn and subsequently poked by ejector needles during automated die pick [18]. Major DAF suppliers provide the circular DAF sheets in rolls for automatic machine lamination. The applications

of these films are well illustrated by Furukawa and Disco, as shown in Fig. 9.

One of the key challenges in Temporary Wafer Bonding (TWB) is high yield debonding at low forces. To enhance chipping property, Sumitomo Bakelite is producing tapes with higher adhesion strengths, say, 100-1650 N/25 mm, and lower adhesion strengths, say, 10-40 N/25 mm, Table 3 [21].

Ablation methods are also useful for TWB. One of the



Measurement

- For Non-UV : at 1h after lamination, 180 peel/300 mm/min
- For UV : right after UV irradiation, 180 peel/300 mm/min

Figure 8. The Peel Strength of DC Tapes of Higashiyama Film Co.

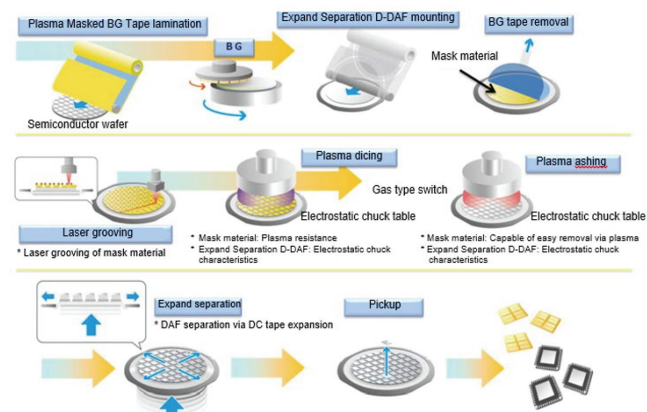


Figure 9. Applications of process films: BG tape, DC tape, and DAF [19,20].

Table 3. Sumitomo Bakelite's Sumilite FSL Tape with High Adhesion Strengths [21]

Use	Total thickness (μm)	Adhesion strength (N/25 mm, silicone)	Face material
General grade	90~100	Before UV : 300~350	PVC, PO
		After UV : 20~40	
For package & substrate sawing	165~220	Before UV : 1200~1650	PO
		After UV : 35	
For rectangular chip	90~110	Before UV : 100~250	PVC, PO
		After UV : 10~15	

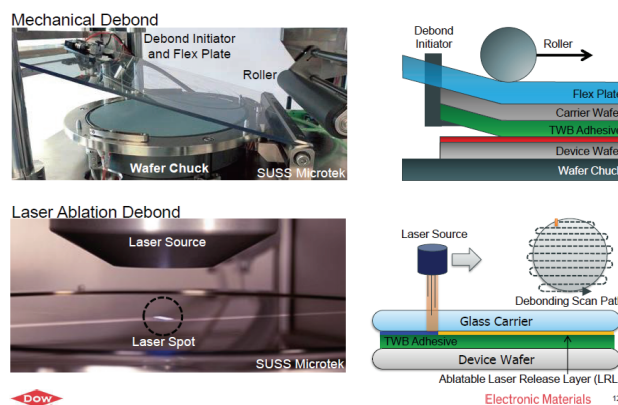


Figure 10. Comparison of debonding modes: mechanical debond vs. laser ablation debond [23].

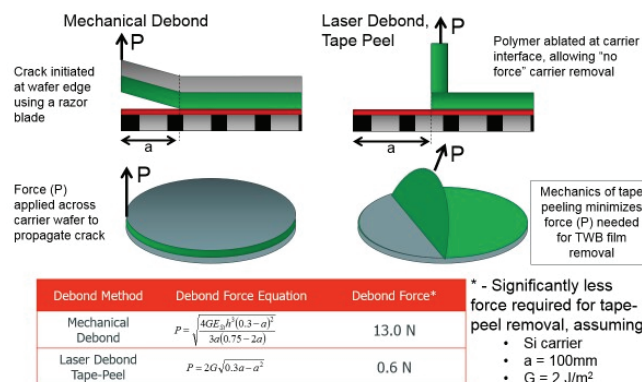


Figure 11. Debond forces in temporary wafer bonding [TWB] [16].

methods is Henkel's hot air ablation. Loctite 3382, a water-debondable epoxy adhesive, provides an excellent bond strength to both silicon and metal-mounting substrates used during the ingot sawing process, yet breaks down easily on exposure to hot air eliminating corrosive debonding solutions [22]. It also debonds with hot water. Dow Chemical investigated a laser ablation method, which was presented by Fleming et. al. [23], by a paper entitled "Thin wafer handling using mechanical- or laser-debondable temporary adhesives", illustrating debonding including mechanical or laser ablation modes (requiring bonding force as low as 0.6 N, though it could be more expensive to install and maintain), as shown in Fig. 10. Laser debond reveals a considerable lower debond force than mechanical debond as shown in Fig. 11 [16]. The debond force for mechanical debond is 13 N, whereas that of laser debond tape-peel is 0.6 N.

3.2. Laser lift-off(LLO) technology for flexible display fabrications

LLO technology can be best explained through an example of flexible OLED process, where a polyimide solution is coated onto glass substrates. The resulting PI film should be debonded from the glass substrate before making a flexible display. LG Display's patent [24] tells the process: a polyimide film is made on a carrier substrate, then the display TFTs are placed on the polyimide film. And upon irradiation of a laser beam, 200-400 nm, from the bottom of the carrier glass, some of the PI formulation is converted into gas which is able to delaminate the PI film from the carrier glass. When the PI/glass structure is subject to curling, a CTE (coefficient of thermal expansion) compensation film such as PET/SiO₂/SiNx is laminated [25] onto the other side of the carrier glass.

4. Conclusion

Future recycling concerns all necessitate the development of a new joining solution, which assists the rapid disassembly of components for repair and maintenance scenarios. Adhesive bonding outperforms conventional joining solutions, particularly where multi-material assemblies are concerned. However, one of their main limitations is their poor disassembly efficiency. Reviewing most of these current studies on CDM, we notice two approaches are prevailed in R&D

topics. One is to add the expandable or foaming additives/particles to adhesives. The other is to incorporate sensitive moieties to external fields of light, electric, or thermal to induce chemical/physical/morphological structural changes, in turn, to affect adhesion strengths at a joining area. The functional additives approach (such as chemical foaming agents, oxidising agents, thermally expandable microspheres) has generally received more attention because they can be introduced into existing adhesive products.

In this review, we describe recent studies of light induced CDMs together with their applications in semiconductors and flat panel displays. It is noted that none of the approaches mentioned create a system sufficiently effective for the disassembly of an adhesive application. In the development of adhesives which can be used in the disassembly of products, it is important to ensure both the mechanical properties and adhesive strength. It is also necessary to study the applications of an external energy source like heat (thermal and induction), electrical, light, or magnetic flux during debonding processes. The preferred materials for bonding and debonding processes should be easy to apply, environmentally friendly, cost effective and should not leave any adhesive residue on the substrate.

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