

박막 실리콘 웨이퍼용 UV 경화형 Debonding 아크릴 접착제의 두께별 접착 물성

이승우¹ · 박지원¹ · 이석호¹ · 이용주¹ · 배경렬¹ · 김현중^{1†} · 김경만² · 김형일³ · 유종민³

¹서울대학교 환경재료과학전공 바이오복합재료 및 접착과학 연구실, 농업생명과학연구원,

²한국 화학연구원 에너지소재연구센터, ³충남대학교 공업화학과, 유기재료 응용화학연구실

(2010년 7월 22일 접수, 2010년 9월 16일 수정, 2010년 9월 17일 채택)

Adhesion Performance of UV-curable Debonding Acrylic PSAs with Different Thickness in Thin Si-wafer Manufacture Process

Seung-Woo Lee¹, Ji-Won Park¹, Suk-Ho Lee¹, Yong-Ju Lee¹, Kyung-Rul Bae¹, Hyun-Joong Kim^{1†},
Kyoung-Mahn Kim², Hyung-il Kim³, and Jong-Min Ryu³

¹Laboratory of Adhesion & Bio-Composites, Program in Environmental Materials Science,
Research Institute for Agriculture & Life Science, Seoul National University, Seoul 151-921, Korea

²Energy Materials Research Center, Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea

³College of Engineering Chungnam National University, Daejeon 305-764, Korea

(Received July 22, 2010; Revised September 16, 2010; Accepted September 17, 2010)

Abstract: UV-curable acrylic Pressure-sensitive adhesives (Acrylic PSAs) are used in many different parts in the world. A wafer manufacture process which is based on semiconductor industry is one thing. We have used acrylic PSAs whose thickness is different from 20 μm to 30 μm in wafer manufacture process so far. But as wafers become more thinner, acrylic PSAs are supposed to satisfy the requirements such as proper adhesion performance. The main purpose of this research is studying proper adhesion performance and UV-curing behavior of UV-curable acrylic PSAs with very thin thickness and then determining optimized conditions to raise the efficiency of thin wafer production. Acrylic PSAs contain 2-Ethylhexyl Acrylate (2-EHA), Acrylic Acid (AA) and Butyl Acrylate (BA). Ethyl acetate (EtAc) is used as solvent. The acrylic PSAs are obtained using solvent polymerization. Thickness of UV-curable acrylic PSAs is different from 10~30 μm . By peel strength and probe tack, adhesion performance and UV curing behavior of acrylic PSA are concerned.

Keywords:

1. Introduction

“Multi-Chip Packages” or MCP refers to a packaging configuration containing at most five chips, connected via wirebonds to a multilayer circuit board, and protected by either a molded encapsulant or a low-cost ceramic package. It is as if all the chips were integrated into one single die and packaged as such, since the same form factor and footprint are kept to facilitate subsequent board assembly operations. Pressure-sensitive adhesives for MCP semiconductor at manufacture process have to satisfy the following conditions,

- Thin-film coating technology of UV-curable PSAs (coating thickness below about 10~20 μm)
- Not only outside but inside curing of PSAs

PSAs are branch of adhesives that attach to the substrate by low pressure contact, and also do not require any reaction processes like adhesives. PSAs can be peeled from the substrate without failure, so the expensive films which consist of the display can be recycled cleanly even if the defect is appeared. Therefore, PSAs should have fluidity for wetting and cohesion force for peel resistance. Those properties can be controlled by monomer components and crosslinking density[1-3].

UV-curing is rapid and practical to convert a fluidic

[†]Corresponding author: Hyun-Joong Kim (hjokim@snu.ac.kr)

monomer to solid polymer by exposure to radiation. This technology developed in the 1960's and reached to the latest market in many applications such as coating, ink, adhesives as well as electronic industries. UV-curing which can be divided into photoinitiated polymerization, photopolymerization or photocrosslinking is a polymerization reaction involving a functionalized oligomer leading to the formation of a solid crosslinked film[4,5]. UV curing is a fast, room temperature curing process indicating low energy consumption and requiring little space for the equipment. The energy content of a photon is defined by the equation.

$$E = h\nu = \frac{hc}{\lambda}$$

where ν is the frequency and λ is the wavelength (nm). This equation informs that the shorter wavelength of photon reveals the higher energy. UV light in the wavelength region of 300~400 nm should already be able to cleave C-C bonds. The high energy photons of e-beam and X-ray are enough to cleave C-C or C-H bonds, therefore, they do not need a distinctive photoinitiator for forming the expected radical species as initiators for polymerization. In the case of UV exposure, photoinitiators are commonly used because the direct splitting processes are not efficient[6].

Photoinitiator undergoes chemical modification leading to the formation of active species which initiate the curing process by UV radiation absorbance. Relying on the polymerization mechanism, UV-curing can be divided into two major class; free radical UV-curing, cationic UV-curing. Each of these mechanisms display separate benefits and limitations, so both are competitive but complimentary. The composition of free radical or cationic UV-curable formulations varies both in character of the oligomers and photoinitiators[7,8].

So, UV curing technology is many advantages in semiconductor wafer processing because of fast curing time and environment-friendliness and according as PSAs thickness is thinner, it is important to find proper requirements such as multifunctional monomer, photo-initiator and UV dose.

- Photoinitiator: Any chemical compound that decomposes into free radicals when exposed to light
- Functionalized oligomer or binder: Binder carries the polymerizable groups and composes the largest part

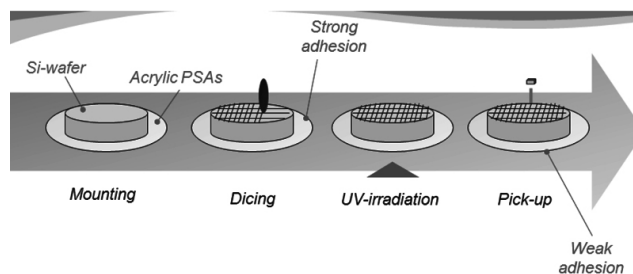


Figure 1. Scheme of dicing process on si-wafer.

of the formulation. This element constitutes the film backbone during crosslinking.

- Monomer as reactive diluent: It adjusts the viscosity of formulation. This element copolymerizes with the binder and is thus embodied into the polymer matrix during curing process.

Crosslinking of multifunctional acrylates increases their thermomechanical stability. When an adhesive is weakly crosslinked, it shows a fluid-like behavior, however in the case of more-crosslinked adhesive, creep resistance greatly increases[9-11].

2. Experimental

2.1. Materials

Acrylic monomers, 2-ethylhexyl acrylate (2-EHA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea), butyl acrylate (BA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea), and acrylic acid (AA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea) were commercially available and used without purification. Ethyl acetate (EAc, Samchun Pure Chemical Co., Ltd, South Korea) was used as solvent. 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemical, Japan) were used as thermal initiator and 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Miwon, Specialty Chemical, South Korea) was the photoinitiator. Dipentaerythritol hexaacrylate (DPHA, Miwon Specialty Chemical, South Korea) was used as the hexafunctional diluent monomer.

2.2. Methods

2.2.1. Synthesis of Debonding Acrylic PSAs

Acrylic monomers (2-EHA, BA and AA) were synthesized as 45 wt %, 45 wt % and 10 wt % respectively by solution polymerization (2-EHA/BA/AA = 45/45/10). For solvent, ethyl acetate (EtAc, Samchun Pure Chemical Co., Ltd,

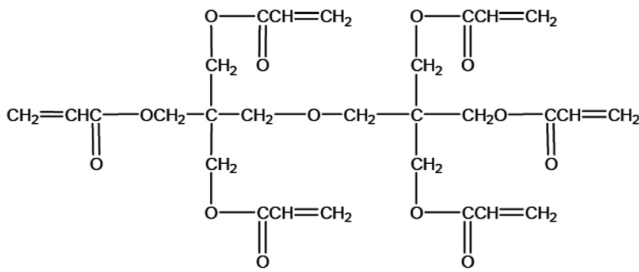


Figure 2. Hexa-functional monomer: dipentaerythritol hexaacrylate.

South Korea) were used, and 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemical, Japan) were used as thermal initiator without purification. The amount of AIBN was 0.2 phr in binders. This mixture in a 500 ml four-neck flask equipped with stirrer, condenser and thermometer was heated up to 70°C with mixing, and after the end of exothermic reaction, temperature was maintained for 30min and blend of EtAc and AIBN was added following 0.5 h, 2.5 h reaction. Finally polymerization was terminated and cooled down to room temperature.

2.2.2. Formation of PSAs Film

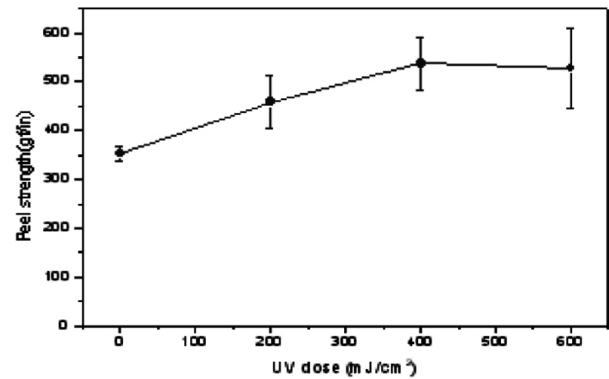
All acrylic PSAs were coated onto corona treated polyethylene terephthalate (PET, SK Chemical, S. Korea) film using coating bars and kept at room temperature for 1h and then dried in an oven at 80°C for 15 min. These dried films were kept at 22°C ± 2% RH for 24 h before performing the other tests.

2.2.3. Curing of Acrylic PSAs

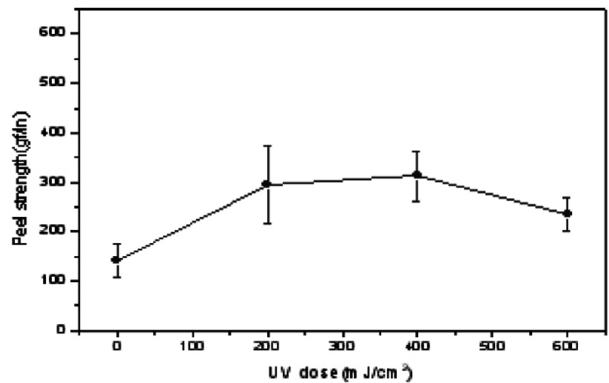
Using UV-curing system, UV-curable PSAs were prepared by blending of polymerized PSAs, a photoinitiator and hexa-functional acrylic monomer as shown in Figure 2. Among di-, tri-, hexa-functional acrylic monomers, hexa-functional acrylic monomer was second to none in that debonding force was the lowest (Figure 3). UV-curable PSAs were coated onto polyester (PET) films and cured using a conveyor belt type UV-curing equipment with a 100 W high pressure mercury lamp (main wavelength: 365 nm). UV doses were gauged by an IL 390 C Light Bug UV radiometer (International Light, USA).

2.2.4. Peel Strength

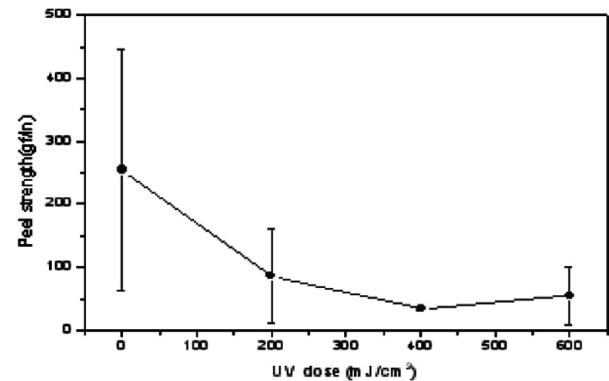
Peel strength was also measured by using Texture Analyzer (Micro Stable Systems, TA-XT2i). The specimens were prepared into 25 mm widths. The specimens were pressed onto the stainless steel substrate by 2 passes of 2 kg rub-



(a)



(b)



(c)

Figure 3. Peel strength of debonding acrylic PSA with (a) di-functional, (b) tri-functional, and (c) hexa-functional monomer.

ber roller and stored at room temperature over 12 h. The peel strength was executed at 180° angle with a cross-head speed of 300 mm/min at 20°C based on ASTM D3330. Peel strength was the average force on debonding process. The force was recorded in g unit during 5 different runs and the average force was reported in g/25 mm.

2.2.5. Probe Tack

Probe tack was measured by using Texture Analyzer (Micro Stable Systems, TA-XT2i) with a 5 mm diameter stainless steel cylinder probe at 20°C. The standard probe tack test was divided by three stages: approaching to the surface of PSAs, contact and detachment from the surface of PSAs. The speed of probe was 0.5 mm/s, contact time on PSAs surface was 1 s under 100 g/cm² constant force and separation rate was 10 mm/s. In the debonding process, the probe tack was obtained at the maximum debonding force.

2.2.6. Fourier Transform Infrared Spectroscopy (FT-IR)

IR spectra was measured by FT-IR-6100 (JASCO, Japan) equipped with attenuated total reflectance (ATR) accessory. The ATR crystal was zinc selenide (ZnSe) and its refractive index was 2.4 at 1,000 cm⁻¹. IR spectra was recorded from 650 to 4,000 cm⁻¹ wavelength ranges and scanned 15 times with the 4 cm⁻¹ resolution. All the obtained results were corrected with baseline correction, smoothing, noise elimination, CO₂ reduction and H₂O reduction. The curing behavior of cross-linking with UV dose was obtained using the FTIR-ATR method.

3. Results and Discussion

3.1. Adhesion Performance

By measuring peel strength and probe tack, the adhesion performance of the debonding acrylic PSAs was determined. The peel strength of all decreased with increasing UV dose, as shown in Figure 3. Especially, all samples but 10 μ m sample declined sharply from 0 mJ to 200 mJ. Interfacial failure, which means that there was no remainder, was showed on all the samples. These results were attributed to the networking formation of the debonding acrylic PSAs. Also, crosslinked structure resulted in the cohesion force within the debonding acrylic PSAs. The probe tack of all decreased steadily with increasing UV dose, as shown in Figure 4. The strain-stress curve of the debonding acrylic PSAs which was coated in 15 μ m thickness was shown in Figure 5. The area of the strain-stress curve decreased definitely with increasing UV dose. The result indicated that the fibrillation of the debonding acrylic PSAs was not only affected by UV dose but also decreased the area of the strain-stress curve.

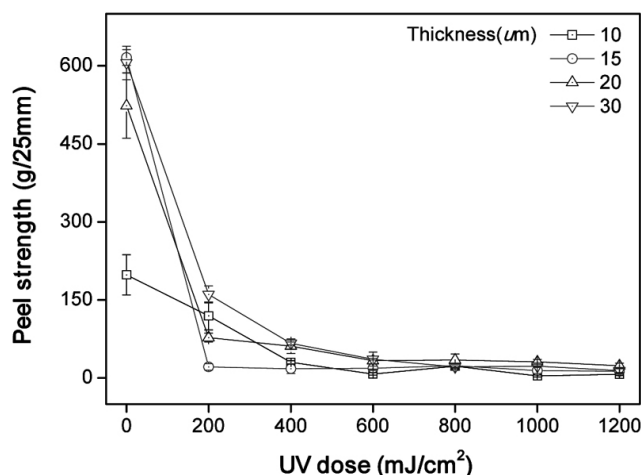


Figure 4. Peel strength at various different thickness for acrylic copolymer PSAs.

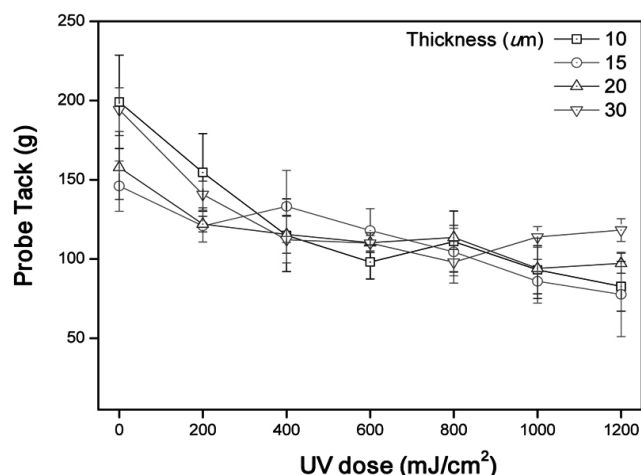


Figure 5. Probe tack at various different thickness for acrylic copolymer PSAs.

3.2. FTIR-ATR Spectroscopy

The curing behavior of cross-linking with UV dose was obtained using the FTIR-ATR method. FT-IR spectra of UV-curable mixture composed of 2-EHA/AA/BA copolymer (2-EHA/BA/AA = 45/45/10) and hexa-functional monomer (30 phr in binder) was shown in Figures 7, 8. The relative concentration of C=C bonds in the blends of all samples decreased sharply as the UV dose was increased, especially from zero to 200 mJ, because of hexa-functional monomer's fast reactivity. But in spite of the photoinitiator's role, the C=C bonds might have been unreacted at some degree. Because the C=C bonds were trapped in the cross-linked network.

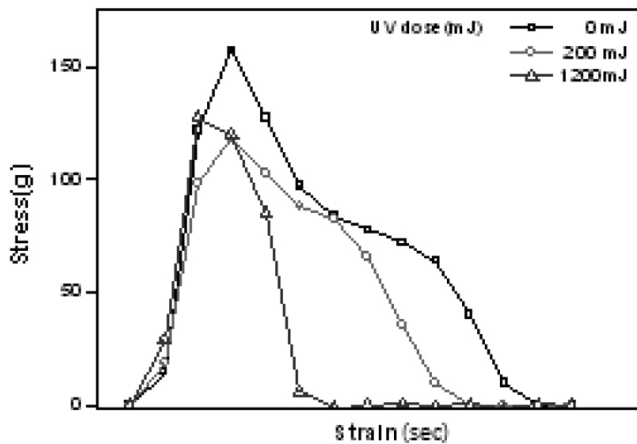


Figure 6. Strain-stress curve of the acrylic PSA on thickness 15 μm .

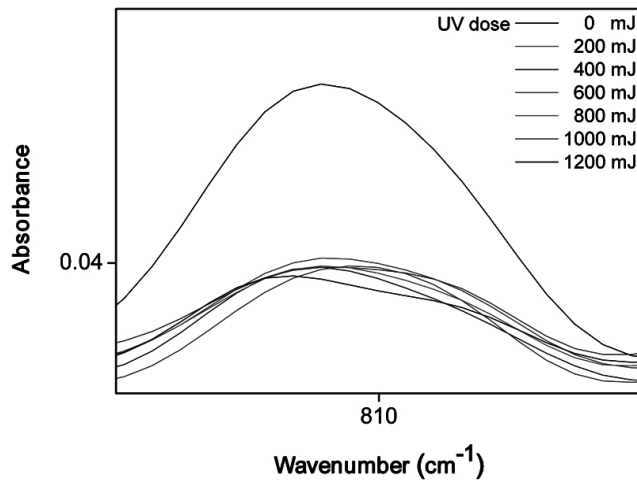


Figure 7. FT-IR spectra of UV-curable mixture composed of 2-EHA/AA/BA copolymer (2-EHA/BA/AA = 45/45/10) and hexa-functional monomer (30 phr in binder) at about 810 cm^{-1} as a function of UV dose.

4. Conclusion

In summary, the adhesion performance and curing behaviors were obtained by blending acrylic copolymer, a hexafunctional monomer, photoinitiator. The UV curable adhesives formed cross-linked structures after UV-curing. With increasing UV dose, peel strength of all samples goes to about zero sharply except 10 μm . The FTIR spectra showed a decrease of the specific peaks for C=C bond. Through strain-stress curve of the acrylic PSA, UV-curing behavior is concerned. But actually except for coating thickness of debonding acrylic PSAs, there are many factors affecting UV-curing behavior such as mono-

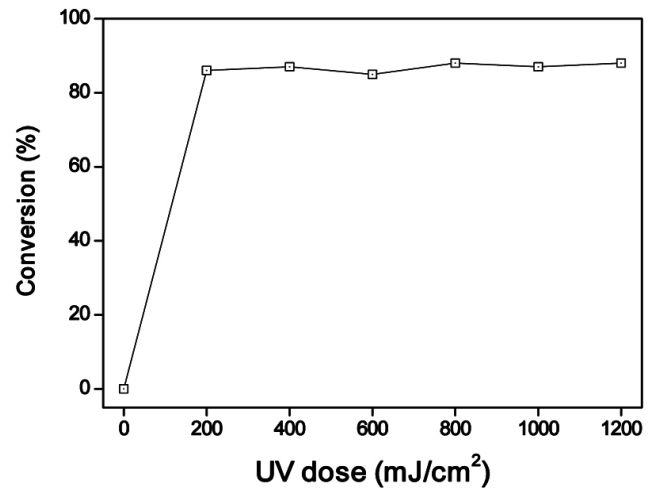


Figure 8. Conversion of C=C bonds as a function of UV dose at 810 cm^{-1} with thickness 15 μm .

mer types and ratio, photoinitiator, crosslinker, additives and so on. Therefore this study will be considered as one part of all.

Acknowledgements

This project was supported from a grants (090400-010-112,010311) programmed by the Ministry of Knowledge Economy and Korea Research Council for Industrial Science & Technology.

References

1. High-Density Packaging (MCM, MCP, SIP): Market Analysis and Technology Trends, The Information Network (2005).
2. D. Satas (Ed.), *Handbook of Pressure Sensitive Adhesive Technology*, Satas & Associates, Warwick, RI (1999).
3. H. J. Kim, D. J. Kim, and G. W. Cho, Chemistry and Application of Adhesion, *J. Adhesion and Interface*, Korea (2002).
4. J. W. Park, *J. Adhesion and Interface*, **10**, 127 (2009).
5. C. M. Ryu, *J. Adhesion and Interface*, **10**, 134 (2009).
6. H. S. Joo, *J. Adhesion and Interface*, **6**, 19 (2005).
7. A. Zosel, *Int. J. Adhes. Adhes.*, **18**, 265 (1998).
8. J. Kajtna, *Int. J. Adhes. Adhes.*, **29**, 186 (2009)
9. I. Benedek and L. J. Heymans, *Pressure Sensitive Adhesives Technology*, Maecel Decker, USA (1997).
10. K. Ebe, H. Seno, and K. Horigome, *J. Appl. Polym. Sci.*, **90**, 436 (2003).

11. Z. Czech, *Int. J. Adhes. Adhes.*, **27**, 49 (2007).
12. H. S. Do, *European Polymer Journal*, **44**, 3871 (2008).
13. Czech, Z., *European Polymer Journal*, **40**, 2221 (2004).
14. J. J. Park and J. H. Kim, Korean Patent, 10-2000-0035727.
15. H. S. Do and H. J. Kim, Korean Patent, 10-2004-094902.
16. K. Horigome, *J. Appl. Polym. Sci.*, **93**, 2889 (2004).
17. I. Kim, *Korean Chem. Eng. Res.*, **46**, 76 (2008).
18. Z. Czech, *Int. J. Adhes. Adhes.*, **24** 533 (2004).