UV Curable Pressure-Sensitive Adhesives for Fabricating Semiconductors. I. Development of Easily Peelable Dicing Tapes

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ABSTRACT: In order to develop easily peelable dicing tapes from diced wafers, UV curing of various pressure-sensitive adhesives (PSAs) was studied. After UV irradiation, the adhesive strength of a PSA composition including a diacrylourethane oligomer (UDA) decreased drastically compared with other compositions. Because of network formation via UV irradiation, this composition had a greater volume contraction that might yield microvoids at the interface between the adhesive and the wafer, resulting in the loose adhesion. Its storage modulus increased up to about 1000 times that before UV curing, which was due to the

crosslinking of the UDA component. It was suggested that the increased crosslinking density and the high internal coagulant energy of the UDA backbone structure caused a remarkable decrease of the adhesive strength. Furthermore, it was ascertained that the UV-irradiated UDA adhesives left few residual deposits on the wafer released from the tape. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 436–441, 2003

Key words: pressure-sensitive adhesives; UV curing; silicon wafer; dicing tape; adhesive deposit

INTRODUCTION

Adhesive tapes have been commonly adopted to tightly hold silicon wafers during dicing for the fabrication of semiconductor chips. Such adhesive tapes are called dicing tapes. With the recent rapid development in integrated semiconductor technology, higher reliability is required for the manufacturing process of electronic devices. In conventional dicing tapes this requirement has induced a serious problem in the successive die-bonding process: the picking up of diced chips becomes increasingly difficult because of their holding strength. The purpose of the present work was to resolve such an antimony or self-contradiction.

Ebe noted that an excessive degree of crosslinking resulted in poor adhesive strength in pressure-sensitive adhesives (PSAs) prepared from unsaturated polyester resins by electron beam irradiation.¹ This observation led us to establish a novel dicing process that is illustrated in Figure 1. At stage 1 in Figure 1 a piece of silicone wafer is tightly held by dicing tape with a strong adhesion strength, which enables rapid and smooth dicing of the wafer. This procedure is followed by stage 2, wherein the adhesive layer is irradiated with UV light through the front side of the backing substrate. Stage 2 decreases the adhesion strength to a level where it easily picks up diced chips at stage 3 for a further die-bonding process. Dicing tapes developed with this process have been reported elsewhere,^{2,3} and similar ideas have been suggested.^{4,5} Quite recently, Ozawa et al.⁶ reported on the reduction of the peel strength of a PSA system comprising acrylate copolymer and UV curable urethane acrylate oligomer, although the practical performance was not described. In this work, various PSA compositions consisting of an acrylic copolymer and UV-curable oligomers were investigated to find out the most suitable system for stages 1, 2, and 3 and further procedures.

EXPERIMENTAL

Materials and preparation of tapes

Adhesive compositions were prepared by mixing the commercially obtained materials shown in Table I. A viscous composition was coated onto a polyolefin film to a thickness of $10 \pm 2 \mu m$ after air drying at 100°C for 1 min in order to crosslink the acrylic copolymer and vaporize the organic solvent. The dried sample was subsequently kept standing for 1 week at 23°C and 65% relative humidity for aging. UV irradiation was performed under a nitrogen atmosphere with a high-pressure mercury lamp with a nominal power of 80 W/cm. The distance between the lamp and the PSA tape was 12 cm and the illuminant energy at 365 nm was 200 mW/cm.

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Figure 1 A schematic diagram of the dicing process using UV-curable PSA.

Measurements and testing

The adhesive strength (180° peel strength) was measured according to JIS Z 0237. The conversion of the double bonds by UV irradiation was determined with IR spectroscopy. The volume contraction of the adhesives caused by UV irradiation was calculated from the ratio of the specific gravity before and after irradiation as measured with an electrical hydrometer in pure water at 23°C. The viscoelastic properties were measured by using a Rheovibron (DDV-II-EP) instrument at a 3.5-Hz frequency and 23°C.

The process performance during the dicing of the silicon wafer was observed using a dicing machine (DAD 2H/6T, Disco Corp.), wherein the adhesive layer was cut to a depth of approximately 30 μ m with a 50.8-mm diameter blade (NBC ZH 27 HECC 205 O). The force for picking up various size chips from the dicing tapes was measured with a push-pull gauge with one needle (Aikoh Engineering Corp.) in order to evaluate the ability to be handled with a fully automatic die bonder (PA-10.2, Shinkawa Corp.).

The residual adhesives contamination on the surface of a released wafer was evaluated by counting the number of fragments measured with a laser surface inspector (LS-5000, Hitachi Electrical Engineering Co., Ltd.). The contaminating fragments were further analyzed by X-ray photoelectron spectroscopy. The spectrometer (PHI Quantum 2000, ULVAC-PHI, Inc.) was operated at 102.3 W, 20 kV, and 5.1 mA under a photon energy of 1486.6 eV and a pass energy of 23.50 eV. The take-off angles (the angle between the sample plane and the axis of the analyzer) were 17, 30, 45, and 90° and the measurement area was $1500 \times 100 \ \mu m$.

RESULTS AND DISCUSSION

Reduction of peel strength through UV irradiation

To survey the effect of the oligomer structure on the lowering of the adhesive strength, five varieties of adhesive compositions, which consisted of the base acrylic copolymer and different oligomers shown in Table I at a mixing ratio of 0.25 mmol oligomer/g copolymer, were irradiated with UV light at an irradiant energy of 200 W cm⁻² for 2 s. The results are shown in Figure 2. As can be seen in the figure, the adhesive strength of the compositions containing dia-

Materials Used for UV Curable Formulations			
Copolymer			
Oligomer	Abbreviation	M_w	Supplier
Poly(oxyethylene) diacrylate	PEGDA	500	Toagosei Co. Ltd.
Oligoester diacrylate	OEDA	450	Toagosei Co. Ltd.
Oligoester tetraacrylate	OETA	570	Toagosei Co. Ltd.
Epoxy diacrylate	EPDA ^a	480	Toagosei Co. Ltd.
Diacrylourethane ^b	UDA	4900	Dainichi-Seika Color & Chemicals Mfg. Co. Ltd.
Photoinitiator	1-Hydroxy cyclohexyl-phenylketone (4 wt % oligomer)		
Crosslinker	Aromatic triisocyanate (5 wt % copolymer)		

TABLE I

The copolymer is copoly(butyl acrylate-acrylic acid) with acrylic acid content of 9 wt % and $M_w = 8 \times 10^5$.

^a Bisphenol A type.

^b Synthesized from poly(ethylene glycol) ($M_w = 200$), methylene diisocyanate, and hydroxylethyl acrylate.

10.0

7.5

5.0

2.5

0

PEGA

Adhesion, N/25mm

Figure 2 The effect of oligomer content on the reduction of the adhesion strength. Oligomer content: 0.25×10^{-3} mol/g oligomer; UV exposure: 2 s at 200 mW/cm². Abbreviations of oligomers are shown in Table I.

UDA

Oligomer in the composition

OEDA

OETA

EPDA

Before UV irradiation After UV irradiation

crylourethane oligomer (UDA) and oligoester triacrylate (OETA) decreases drastically upon UV irradiation, while those of other compositions decrease only slightly or even increase. The results being as such, those factors that might affect the change in the adhesion strength were further investigated with the use of the UDA and oligoester diacrylate (OEDA) compositions that contain oligomers with the same functionality but different tendencies in the adhesion changes.

Figure 3 illustrates the relationship between the oligomer contents and the adhesive strengths before and after UV irradiation. As for the OEDA compositions, the adhesive strength gradually decreases with increasing oligomer content before or after UV curing;



Figure 3 The effect of the oligomer content on the reduction of the adhesion strength (\bigcirc, \triangle) before UV irradiation and $(\bullet, \blacktriangle)$ after UV irradiation.



Figure 4 The conversion of double bonds by UV irradiation.

its reduction with UV irradiation is less within the whole range studied. By contrast, the UDA compositions have almost the same level of adhesive strength, regardless of the oligomer content before UV irradiation, whereas the strength is reduced to almost zero at more than 0.5 mmol/g copolymer of UDA content when irradiated. These facts may be due to the difference in the interaction between the acrylic copolymer and oligomers because the UDA oligomer has highly polar urethane units.⁷

The conversion curves of the double bonds in the compositions containing UDA and OEDA are shown in Figure 4. The double bonds in the former disappear completely within 1 s, but the curing of the latter is incomplete even after irradiation for 2 s. It is expected⁷ that the cohesion energy in the molecules of the UDA composition is larger than that of the OEDA composition. Hence, the entanglement and/or orientation of UDA around the acrylic copolymer might induce a rapid radical chain reaction, resulting in high conversion of UDA.

Speculated mechanism of reduction in adhesion

Figure 5 shows the effect of the oligomer content on the volume contraction with UV irradiation. It is clearly observed in this figure that, although the volume contraction of the OEDA compositions are almost the same as that of neat OEDA, those for the UDA compositions are about twofold that of neat UDA. Such a high degree of contraction may induce more microdefects at the interface between the adhesive layer and wafer, resulting in poor adhesion, which is under investigation. Thus, it is concluded that the greater the volume contraction, the larger the decrease of the adhesive strength.

The storage modulus (E') and loss tangent (tan δ) of the UDA composite and neat UDA are plotted against



Figure 5 The volume contraction at fully cured states by UV irradiation.

the temperature in Figure 6(a,b), respectively. When irradiated with UV light, the UDA composition shows the same level of E' at room temperature as that of neat UDA (10³ MPa). As for the tan δ , the peak at around -15° C in the unirradiated sample disappears with UV irradiation and a new peak appears near 60°C instead. Because the cured sample from the neat UDA oligomer also has a peak at a similar temperature, it can be considered that UDA is crosslinked into such a network structure because it is sufficiently entangled with acrylic copolymer chains.

The relationship between the storage modulus and the oligomer content of the UDA compositions is shown in Figure 7. The storage modulus of the UDA composition after UV irradiation was steeply increased with increasing content of UDA and then levels off. Further, although we were unable to measure the storage modulus for the neat UDA before UV irradiation because of its low viscosity, it should be noted that the neat UDA gives a lower storage modulus after UV irradiation than the UDA composition.

The above facts may account for the mechanism of the drastic decrement of the adhesion strength in the present radiation-curable composition. The high cohesion energy of UDA⁷ that has a polar backbone structure seems to contribute to the above specific phenomenon in such a way as to tightly bind the polymeric chains of the copolymer. With the entanglement of the crosslinked UDA network around the copolymer chains, the mobility of the copolymer may be remarkably decreased to such a level that the original peak in the storage modulus disappears.

Practical performance of UV-curable dicing tapes

Based on the above results, UV-curable dicing tapes were prepared by using the UDA compositions (UDA tapes) to evaluate their practical properties. The limit of the adhesive strength required for a tape to hold all the diced chips during the dicing of a silicon wafer was estimated by using samples with different adhesion strengths. The results are shown in Figure 8. In the figure all the diced chips, except the scrap corner chips, adhered during the procedure in the tight zone whereas any object chips flying off the tape were in the loose zone. A marginal region, where corner chips fly off, exists between these two zones. It





(b)

Figure 6 Thermograms of (a) the storage modulus (E') and (b) the loss tangent (tan δ) of the UDA composition.



Figure 7 The relationship between the storage modulus at 23°C and the oligomer content in the UDA compositions. The storage modulus before UV is calculated from the equation E' = 3G'.

is clearly demonstrated that the smaller the chip size, the larger the required peel strength. As shown in Figures 2 and 3, the adhesive strengths of the UDA tapes are far over the limit of the tight zone or are usable even for such a small chip size as 1 mm².

The procedure of dicing into chips and UV irradiation is followed by processing with a die bonder, which picks up chips from the UV-irradiated tape and then bonds them on a circuit board. Accordingly, diced chips should be easily picked up with a die bonder. Therefore, the workability of a die bonder was investigated by measuring the force to pick up various sizes of chips with a push–pull gauge. The pick-up forces of the UV-cured UDA tape and a conventional removable tape are plotted against the surface area of a chip in Figure 9. In the upper region beyond the



Figure 9 Plots of the force for picking up a chip versus the chip's surface area.

dotted line, picking up a chip is almost impossible with the die bonder used in this work, as is the case for the conventional removable tape. As can be expected from the results shown in Figure 2, however, it was ascertained that the UV-cured UDA tapes show such low forces as for below the border. Thus, it was proved that the die bonder could fulfill its function when using the UV-curable dicing tapes developed here.

In the manufacturing procedure of integrated semiconductors, chips should not be contaminated by dicing tapes in order to achieve reliability. Therefore, the degree of contamination for the UV-curable dicing tapes was checked with a laser surface analyzer that



Figure 8 Plots of the adhesion level capable of holding chips versus the chip-surface area.



Figure 10 A surface observation of wafers contacted with dicing tapes with the particles on the control wafer of <40 and a particle size of $>0.27 \ \mu$ m.



Figure 11 Plots of the carbon/silicon ratio versus the the take-off angle (a) of XPS of the (\bullet) control wafer (mirror) and (\blacktriangle) the wafer released from the PSA tape (UDA composition).

detects contaminating particles larger than 0.27 μ m. As shown in Figure 10, the contamination level remaining on a wafer with the use of the adhesive tape prepared from the UDA composition (UDA-PSA) is clearly much less than those with a commercial removable tape (PSA) or tapes from OEDA and OETA compositions. We believe that the higher crosslinking density of UV-cured UDA-PSA achieves lower contamination.

It should also be noted that the contamination level shown in the UDA composition in Figure 10 is apparently even less than that on the unused control sample. This result indicates that the tape takes away the original contaminating particles and the particles released from the tapes and left on the wafer may differ in nature from those on the control wafer. Therefore, these particles were further characterized with ESCA. The results shown in Figure 11 clearly reveal that the contaminants left by the PSA tape contain more organic compounds, which are residual deposits of PSA. The fact that the C/Si ratio of the wafer released from PSA remarkably increases with a decreasing take-off angle (α) indicates that there are smaller size residual deposits than those detected (Fig. 10) with the laser surface analyzer used in this work. A further study is underway on the effects of these microparticles on the performance of fabricated semiconductors.

CONCLUSIONS

In this study on UV curing of PSA dicing tapes, the following conclusions were made:

- 1. By 2-s UV irradiation of the PSA tape comprising a poly(butyl acrylate-*co*-acrylic acid) and a UDA oligomer (UDA-PSA tape), the adhesive strength of the PSA tape was drastically reduced from 10.0 to 0.3 N/25 mm.
- This drastic reduction of the adhesive strength can be attributed to the increase in the volume contraction and the storage modulus by UV curing.
- The adhesive residue contamination of the released surface of the wafer was remarkably reduced with the use of the UDA-PSA tape compared to conventional tapes.

Thus, such dicing tapes, which are easily peelable and suitable for further processing, were successfully developed.

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