



Wettability and adhesion characteristics of photo-crosslinkable adhesives for thin silicon wafer

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ABSTRACT

Acrylic pressure-sensitive adhesives (PSAs) have many applications in the processes of electronic industry. As the silicon wafers become thinner, the acrylic PSAs need to show proper adhesion and better wettability on the thin wafer. The acrylic copolymers were synthesized by solution polymerization of 2-ethylhexyl acrylate, ethyl acrylate, and acrylic acid with AIBN as an initiator. Photo-crosslinkable PSAs were synthesized by reaction of the acrylic copolymers with glycidyl methacrylate (GMA) and lauryl glycidyl ether (LGE). The adhesion performance of acrylic photo-crosslinkable PSAs was investigated based on wettability, probe tack, peel strength, cohesiveness, and viscoelastic properties. The adhesion characteristics varied significantly depending on the ratio of GMA to LGE in the photo-crosslinkable PSAs.

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1. Introduction

Pressure sensitive adhesives (PSAs) are polymeric materials that form strong adhesive joints with substrates of various chemical natures under application of a slight external pressure (1–10 Pa) over a short period (several seconds) [1–3]. Dicing tape is a kind of PSA tape which is commonly adopted to tightly hold the silicon wafers during the fabrication of semiconductor chips. With the rapid development of integrated semiconductor technology, a higher reliability is needed for the manufacture of electronic devices [4]. In previous papers [5–8], the effects of various factors on peel strength of the crosslinked acrylic PSAs were explored. It has been revealed that the surface structure of multi-component polymeric systems is different from that in the bulk. The component having lower surface free energy is generally enriched in the surface region in order to minimize the interfacial free energy between air and the polymer. This phenomenon is called surface segregation or interface segregation, which is reviewed elsewhere [9–13]. In order to avoid these segregation problems, chemical crosslinking is needed for PSAs. PSAs generally turn into less tacky materials with decreased tack and peel strength as the crosslinking of PSAs proceeds [14]. Therefore, the degree of crosslinking should be controlled carefully. Ultraviolet (UV) radiation has already been used to produce

interpenetrating polymer networks (IPNs) or semi-IPNs by photo-polymerization of acrylate monomers in various applications of adhesives and coatings. However, the effect of photo-crosslinking of acrylic copolymers on the wetting and adhesion properties has not been studied so far. Both the kind of side chains and the content of reactive groups in acrylic copolymers can give the significant variation in the polymer network structures of acrylic copolymer upon photo-crosslinking, resulting in the subsequent variation in adhesion performances. In this study, acrylic copolymer was post-reacted with both glycidyl methacrylate (GMA) and lauryl glycidyl ether (LGE) to give the photo-crosslinkable PSAs having various contents of photo-reactive groups and long side chains, respectively, via the reaction between carboxyl and epoxy groups. The adhesion properties of the photo-crosslinked PSAs were evaluated by investigating the variations in wettability, peel strength, probe tack, cohesiveness, and viscoelastic properties at various UV doses.

2. Experimental

2.1. Materials

2-Ethylhexyl acrylate (EHA), ethyl acrylate (EA), and acrylic acid (AA) were used to synthesize the acrylic copolymers and were purchased from Samchun Pure Chemical, Korea. Ethyl acetate (Junsei Chemicals, Japan) and 2,2'-azobisisobutyronitrile (AIBN, Daejung Chemicals, Korea) were used as the solvent and

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initiator for the synthesis of acrylic copolymers, respectively. GMA (Misubishi Rayon, Japan) and LGE (Miwon Chemical, South Korea) were used to introduce the photo-reactive groups and the long side chains to the acrylic copolymers, respectively, in a solution of toluene (Samchun Pure Chemical, Korea). 2-Hydroxy-2-methyl-1-phenylpropane-1-one (Miwon Chemical, Korea) and triphenyl phosphite (TPP, Sigma Aldrich, USA) were used as the photo-initiator and the catalyst for reaction between epoxy and carboxyl groups, respectively.

2.2. Synthesis of acrylic copolymer

The acrylic copolymer was synthesized with fixed compositions of EHA, EA, and AA in 41.7, 41.7, and 16.6 wt%, respectively. The acrylic copolymer was synthesized by solution radical polymerization with 1.5 wt% AIBN in ethyl acetate at a solid content of 32.5 wt% in a 500-ml, four-necked, round-bottomed flask equipped with a thermometer, condenser, dropping funnel, and mechanical stirrer. The flask was charged with 50% of the monomer and solvent mixture, and then polymerization was carried out at 80 °C for 0.5 h followed by the addition of the remaining 50% of the monomer and solvent mixture over 1.5 h and the further reaction was carried out at 80 °C for 3 h.

2.3. Synthesis of photo-crosslinkable acrylic copolymers

The photo-crosslinkable acrylic copolymers were synthesized in toluene solution of 30 wt% solid content at 70 °C for 10 h. Various molar ratios of GMA:LGE such as 0.9:0.1, 0.7:0.3, and 0.5:0.5 were employed for the preparation of photo-crosslinkable acrylic copolymers containing various contents of carbon double bonds and lauryl side chains.

2.4. Preparation of photo-crosslinkable acrylic PSA samples

All the photo-crosslinkable acrylic copolymers were coated on the corona-treated poly(ethylene terephthalate) (PET, SK Chemical, Korea) film using coating bars. The photo-crosslinkable acrylic copolymer coated PET films were kept at room temperature for 1 h and then dried in an oven at 110 °C for 3 min. The dried films were kept at 22 ± 2 °C and $60 \pm 5\%$ RH for 24 h before performing the adhesion tests. In order to avoid any heating effects from the high pressure mercury lamp, a cold mirror was used as a reflector during the UV irradiation. The photo-crosslinking of acrylic PSAs was performed with a HM-1500UV conveyor system (UMC Korea, South Korea) at various UV doses (0, 200, 500, 1000 and 2000 mJ/cm²) with main wavelength of 365 nm.

2.5. Wettability

Wettability was measured as the time required for contacting the thin silicon wafer completely with PSA film. PSA films were put on thin silicon wafer of 5×5 cm² for the measurement of wettability as shown in Fig. 1.

2.6. Probe tack

Probe tack was measured by a texture analyzer (Stable Micro Systems, TA-XT2i, UK) at 20 °C. A polished stainless steel cylinder with a diameter of 5 mm was used as the probe. The probe moved at a rate of 0.5 mm/s and stayed on the contacting surface of PSA for 1 s under a constant force of 100 gf/cm² followed by debonding at a separating rate of 10 mm/s. Probe tack was obtained as the maximum debonding force during the debonding process.

2.7. Peel strength

The specimen for peel strength test was cut into 1 in. width. PSA film was attached to stainless steel substrate and then a 2 kg rubber roller was passed 2 times. The peel strength was measured using a texture analyzer (Stable Micro Systems, TA-XT2i, UK). The measurements were carried out at a crosshead speed of 300 mm/min at 20 °C based on ASTM D3330.

2.8. Gel content

The gel contents of the photo-crosslinked PSAs were measured gravimetrically. The initial weight of sample (W_1) was measured before the immersion of sample in toluene at room temperature. The sample was filtered through a 200 mesh wire net after immersion for 24 h in toluene followed by drying at 70 °C for 24 h and measuring the weight (W_2) at room temperature. The gel contents of photo-crosslinked PSAs were calculated using the following equation [15–17]:

$$\text{gel content(\%)} = \left(\frac{W_2}{W_1} \right) \times 100$$

2.9. Shear adhesion failure temperature (SAFT)

A specimen for SAFT was prepared by attaching PSA film to a stainless steel substrate with a bonding area of 1 in² and pressing once with a 2 kg rubber roller. SAFT specimens were hung with a weight of 2 kg connected at the end of each sample in the heating oven. The oven was heated over the range from 25 °C to 200 °C at a heating rate of 0.4 °C/min. SAFT was measured as the temperature at which the separation of PSA film from SAFT specimen occurred.

2.10. Advanced rheometric expansion system (ARES) analysis

The viscoelastic properties of the acrylic PSAs were determined using an ARES (Rheometric Scientific, UK) equipped with an 8 mm parallel plate mode. The typical temperature scan range was -60 to 200 °C and the heating rate was 5 °C/min. The frequency was 1 Hz and the gap between the plates was 1 mm.

3. Results and discussion

3.1. Variations in gel content of photo-crosslinked PSAs

The gel content of photo-crosslinked PSA is a function of molecular entanglement and degree of crosslinking. Only the insoluble crosslinked polymeric parts are swollen in contact with the solvent. However, other parts such as linear or branched polymers are soluble in the solvent. The content of insoluble parts varied depending on the extent of crosslinking. The extent of crosslinking was controlled by varying both the content of crosslinkable groups and the UV doses at the fixed content of photo-initiator. Fig. 2 presents the effect of both the content of crosslinkable groups and the UV doses on the gel content of photo-crosslinked PSAs. A higher gel content was generally obtained for the photo-crosslinked PSAs having higher content of carbon double bonds originated from GMA, which resulted in the higher extent of crosslinking. Once the PSAs were irradiated with UV, the gel content of photo-crosslinked PSAs was not varied significantly depending on UV doses because even a lower UV dose of 200 mJ/cm² was enough for the photo-crosslinking in this system.

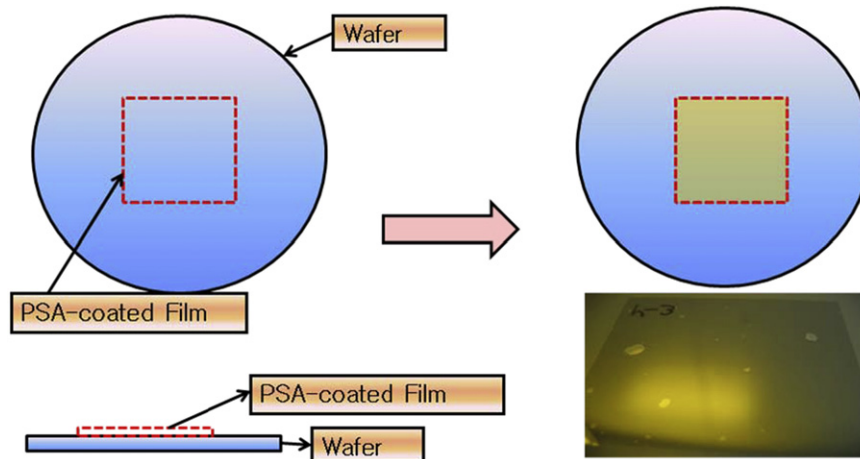


Fig. 1. Schematic presentation of wettability measurement on silicon wafer surface.

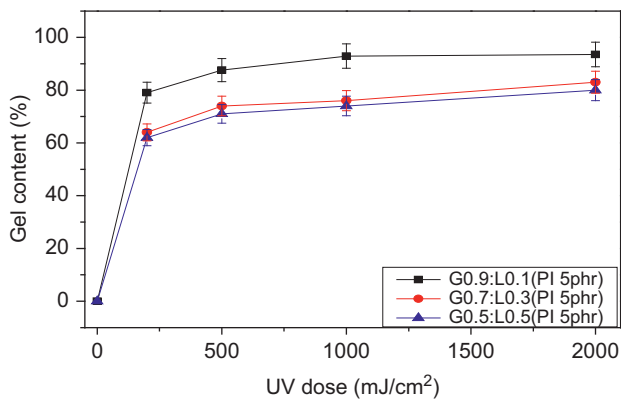


Fig. 2. Variation of gel contents of acrylic PSAs containing 5 phr photo-initiator depending on molar ratio of GMA/LGE and UV dose.

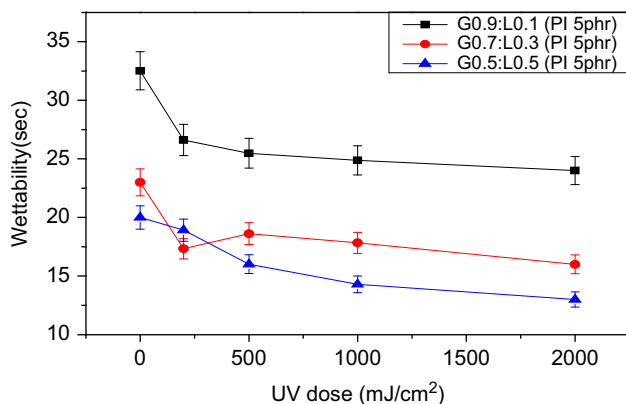


Fig. 3. Variation of wettability of acrylic PSAs containing 5 phr photo-initiator depending on molar ratio of GMA/LGE and UV dose.

3.2. Variations in wettability of photo-crosslinked PSAs

Faster wetting of acrylic PSA on silicon wafer was possible as the content of lauryl side chain increased in acrylic copolymer because both hydrophobicity and flexibility of acrylic PSA increased efficiently by introducing the long aliphatic side chains as shown in Fig. 3. The long lauryl side chains were expected to lower the surface energy of PSA, which would facilitate the wetting and sorption of PSA on the surface of silicon wafer.

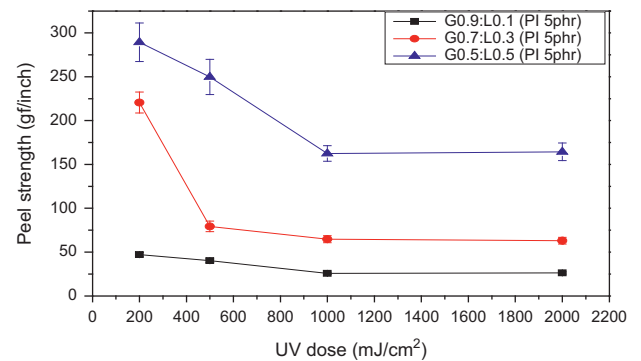


Fig. 4. Variation of peel strength of acrylic PSAs containing 5 phr photo-initiator depending on molar ratio of GMA/LGE and UV dose.

3.3. Variations in adhesion characteristics of photo-crosslinked PSAs

The effects of molar ratio of GMA/LGE and UV dose on the adhesion performance of acrylic PSAs are shown in Figs. 4–6. The peel strength of acrylic PSAs varied significantly depending on molar ratio of GMA/LGE and UV dose as shown in Fig. 4. Peel strength of PSA decreased significantly by increasing the content of GMA as well as increasing UV dose. The decrease of peel strength is attributed to the increased extent of crosslinking by photo-polymerization of carbon double bonds upon UV irradiation [16,18–21]. Interfacial failure, which meant no adhesive remainder on the silicon wafer substrate, was found for all the PSA samples after peeling. The decrease of peel strength was likely due to the contribution of crosslinking which hindered the efficient chain mobility and anchoring at the interface.

Probe tack tests are intended to measure the tackiness of PSA. Since the tackiness indicates the ability of adhesive to adhere to substrate at low pressure, it is highly dependent on the mobility of polymer chains and the extent of crosslinking. The variations in probe tack of acrylic PSAs are shown in Fig. 5. Probe tack decreased rapidly as molar ratio of GMA/LGE and UV dose increased because the increased extent of crosslinking induced severe hindrance in chain mobility of acrylic copolymer similarly as in the case of peel strength variation.

Cohesiveness increased significantly as the extent of crosslinking increased due to the improved thermal stability [4,22–24]. The variations in cohesiveness of acrylic PSAs are shown in Fig. 6.

Cohesiveness increased significantly as molar ratio of GMA/LGE and UV dose increased because the increased extent of crosslinking improved the thermal stability of acrylic copolymer matrix.

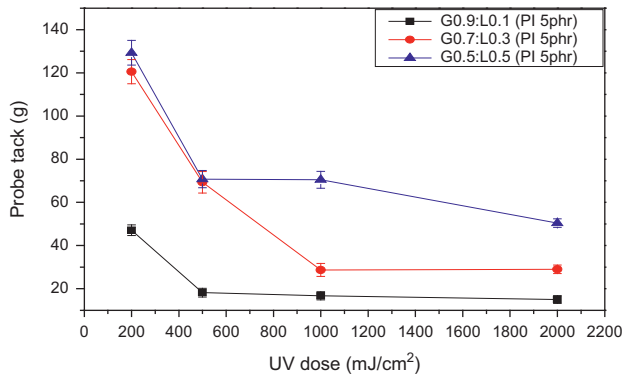


Fig. 5. Variation of probe tack of acrylic PSAs containing 5 phr photo-initiator depending on molar ratio of GMA/LGE and UV dose.

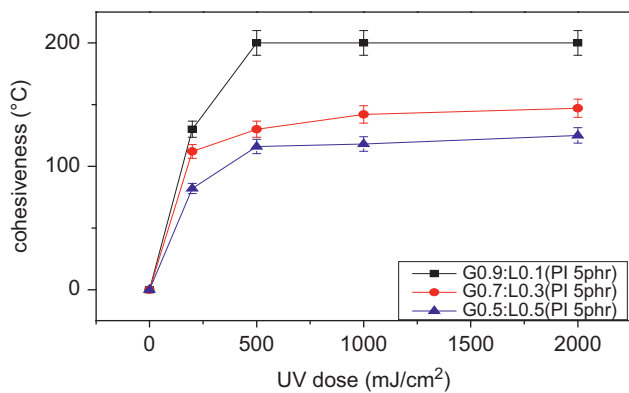


Fig. 6. Variation of cohesiveness of acrylic PSAs containing 5 phr photo-initiator depending on molar ratio of GMA/LGE and UV dose.

The viscoelastic properties usually play an important role in the adhesion performance of PSAs [25]. The viscoelastic properties of acrylic PSAs were measured with ARES as shown in Fig. 7. The storage modulus (G') and the loss modulus (G'') are associated with the elastic nature and the energy absorption of adhesive, respectively; $\tan \delta$ is determined by the following equation:

$$\tan \delta = G'' / G'$$

Both storage modulus and loss modulus of acrylic PSAs showed significantly different behaviors depending on the photo-initiator content. The glassy plateau region increased with high temperature as the photo-initiator content increased upto 5 phr because the photo-initiator content affected the crosslinking reaction to some extent. The abrupt change in the storage modulus is related to the glass transition of acrylic PSAs which also has a close relation with the chain mobility. Therefore, the photo-initiator content was fixed at 5 phr for all the photo-crosslinking of acrylic PSAs in this study in order to eliminate the factors which might affect the photo-crosslinking concomitantly as far as possible.

4. Conclusions

The gel content of acrylic PSAs increased significantly with increasing content of GMA and the UV dose resulting from the increased extent of crosslinking. The wettability of acrylic PSAs was improved by increasing the content of lauryl side chain due to both the decreased surface energy and the increased flexibility of acrylic copolymer. Both probe tack and peel strength of acrylic PSAs decreased rapidly as both the content of GMA and the UV dose increased due to the hindrance in chain mobility induced from the increased extent of crosslinking. Cohesiveness of acrylic PSAs increased significantly with increasing the content of GMA and the UV dose due to the increased extent of crosslinking.

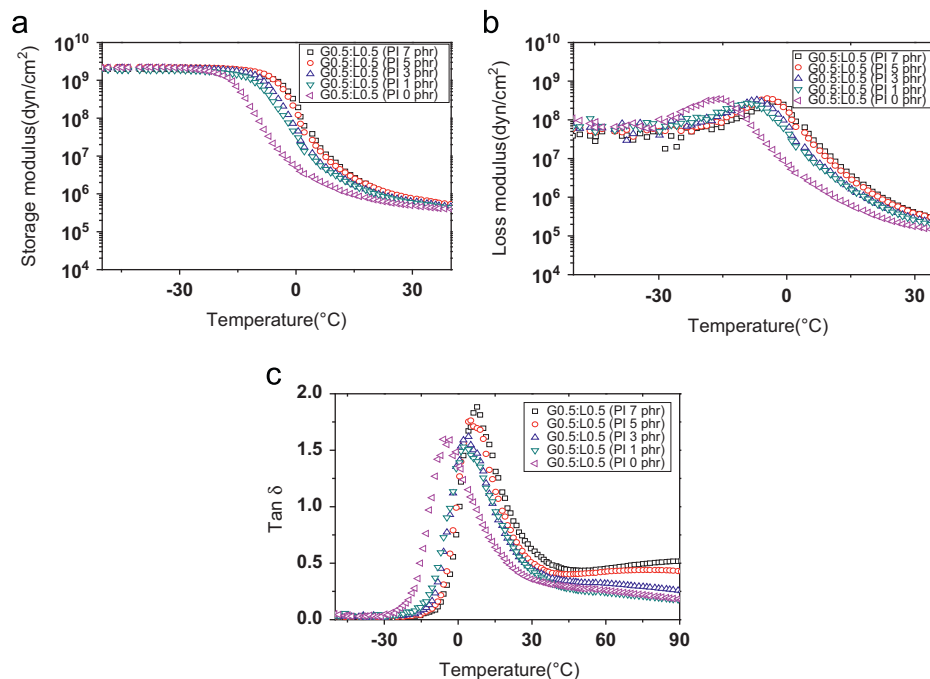


Fig. 7. Variation of (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$ of acrylic PSAs containing same molar content of GMA and LGE depending on the content of photo-initiator. (photo-crosslinking at UV dose of 200 mJ/m^2).

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