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Electroconductive Adhesives: Comparison of Three Different Polymer Matrices. Epoxy, Polyimide and Silicone

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Electrically conductive organic adhesives are used in the microelectronics manufacturing industry for the attachment of silicon dies. These adhesives are composite materials which owe their conductivity to the incorporation of silver flakes. Several polymers have been formulated into electricallyconductive adhesives to meet different applications in the microelectronics industry; these are an epoxy resin, a polyimide and a silicone polymer. The purpose of this paper is to examine properties of these die-bonding adhesives in order to determine the advantages or disadvantages of these materials. This study offers a comparison of hardening chemistry, chemical purity, processing, electrical, thermal, and mechanical properties of three conductive adhesives based on an epoxy, a polyimide and a silicone polymer. We discuss correlation of composite properties with the structure of each matrix. The results indicate that the choice of the matrix is dictated by the application for which the electronic grade conductive adhesive is to be used and the desired properties for best reliability and performance.

KEY WORDS Microelectronic adhesive; electroconductive composite; epoxy; polyimide; silicone.

INTRODUCTION

For twenty years now, silver-filled conductive adhesives have been designed for bonding integrated circuits and semiconductors where electrical and thermal conductivity are required. Figures 1 and 2 show a plastic encapsulated integrated circuit. Such a plastic package is one of the most widely used methods to encapsulate integrated circuits. As shown in Figures 1 and 2, the adhesive is placed between the die and the lead frame. Three methods of bonding are currently used: solders, organic adhesives and inorganic adhesives.¹

Gold solder systems were the microelectronics industry standard a few years ago and are still used in hermetic packages. The method is based on the reaction

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FIGURE 1 Encapsulated integrated circuit, showing gold wire, die, lead frame and molded package.

of the silicon from the back of the die with gold solder at high temperature (over 350°C). The bonding is achieved with formation of a gold-silicon eutectic.

The organic die-attachment materials offer important cost savings over the previously-discussed gold solders. Moreover, the use of organic adhesives permits lowering of the stresses in the silicon die. The higher flexibility of organic adhesives reduces problems of large dies cracking during thermal shocks. The inorganic solders also have the disadvantage of higher processing temperatures.

The high-temperature sealing (>400°C) of ceramic packages requires very stable adhesives. The limited thermal stability of standard organic adhesives is well established and a new approach of using inorganic adhesives has recently emerged.² These materials contain silver, low-temperature glasses, solvent, and a low level of organic polymer ($\approx 1\%$). The disadvantage of using inorganic glass adhesives is due to the special processing used; high temperatures (>400°C) and



FIGURE 2 Cross-section of encapsulated integrated circuit, showing lead frame, die, molded package, gold wire, and conductive adhesive.

oxidizing atmospheres are required to remove the organic portion. After processing, the adhesive is a completely inorganic material (silver and glass) which offers excellent thermal stability.

A new US military specification, Method 5011, MIL STD 883C, which imposes minimum requirements for organic adhesives, was prepared in 1986.^{3,4} These adhesives are being extensively used in microelectronic packaging. However, specifications and controls of materials have not yet been standardized, though the need is apparent. The objective of Method 5011, MIL STD 883C, is to establish improved qualification requirements and to become a standard for the selection and use of polymer adhesives in microelectronic applications. Suppliers must provide adhesives with high thermal stability (low outgassing at 300°C) and low levels of water-extractable mobile ions to avoid failure in service.

The aim of the present work is to evaluate and compare the properties of three new organic die-bonding materials. Performance of these adhesives based on an epoxy resin, a polyimide and a silicone will be described and discussed.

EXPERIMENTAL

Materials

Epoxy adhesive The matrix was a liquid phenol epoxy novolac resin of electronic grade (Quatex of Dow Chemical) diluted with a few percent of high purity butanedioldiglycidylether (Ciba–Geigy) which is a very efficient reactive diluent in formulations requiring high filler loadings. The matrix solution was prepared by heating (at 40°C) and mixing the resin, the reactive diluent and the solvent 2-butoxyethanol (Prolabo) used to control the formulation viscosity. Reactive diluent and solvent were distilled before use (butanedioldiglycidylether: bp 115°C under 2 mm; 2-butoxyethanol: bp 54°C under 7 mm). Matrix:



The silver flakes (Demetron D35 of Degussa) were used as received and mixed with the hardener (1%), the azine derivative of an imidazole (Curezol 2E4MZ-azine of Shikoku), which is a latent curing agent providing a long shelf life at low temperature and fast curing time at high temperatures. This powder blend (83% by weight) was mixed with the resin solution (17%) and the mixture was degassed under vacuum.

Polyimide adhesive The matrix was a high purity polyimideamide (PIA),

(Nolimid of Rhone-Poulenc). As this material was a solid, it had to be first dissolved in a polar solvent for use as an adhesive. The mixture used was a solution of the PIA in *N*-methylpyrrolidone (concentration: 35% by weight).



The silver flakes (DM of Comptoir Lyon-Alemand-Louyot) (70% by weight) were mixed with the polymer solution (30% by weight) and the mixture was degassed under vacuum.

Silicone adhesive The matrix used was a thermoplastic elastomer, a multiblock silicone polymer. The synthesis of this polymer is described in Reference 5. The polymer was dissolved in toluene at 85°C. The solution (45% by weight) was mixed with silver flakes (Demetron D35 of Degussa) (55% by weight). The hot solution was spread on a Teflon sheet and the film obtained was dried at 100°C for one hour under vacuum (20 mm). Flexible films 50 to 100 μ m thick were obtained.



Characterization

lonic purity An analysis was carried out on each adhesive to determine the content of water-extractable ions. Water-extraction analyses were performed on the solid adhesives to determine the total ion content, sodium ion, potassium ion, ammonium ion, chloride ion and hydrogen ion (pH) contents. For the analysis, epoxy and polyimide adhesives were cured, as described below, on Teflon films. The cured adhesive films were ground to a powder, except for the thermoplastic silicone film which was cut into small pieces. One gram of the adhesive was placed in a Teflon Parr bomb with 15 ml of electronic grade deionized water. The bomb was heated in an oven at 105°C for 20 hours.

The extractable sodium and potassium analyses were performed using atomic absorption (Perkin-Elmer 5000). The hydrolyzable chloride analysis was conducted using ion chromatography (Dionex 10). The extractable ammonium content was measured using an ion specific electrode. The pH of the water extract was determined using a pH meter with a standard combination electrode. A conductivity meter (Tacussel CD 810) was used to measure the total ionic content which corresponds to the specific electrical conductivity of the aqueous extract.

Thermal properties

Thermal stability The thermal stability of the adhesives was determined as a function of temperature in nitrogen atmosphere. In order to evaluate degradation temperature and outgassing at 300°C (percent weight loss) a thermobalance (Perkin-Elmer TGS 2) was used. The samples were cured as described below and heated from 30°C to 700°C at a heating rate of 10°C/min.

Transition temperatures A DuPont TMA 943 thermomechanical analyser was used to determine the glass transition temperature (T_g) of the epoxy and the polyimide adhesive. The cured samples were heated at 10°C/min. The thermomechanical system senses the change in the coefficient of thermal expansion that occurs at the softening point which permits the measurement of the glass transition temperature. The melting point of the silicone adhesive was determined using differential scanning calorimetry at a heating rate of 10°C/min.

Thermal expansion The coefficients of linear thermal expansion were measured during the T_g determination. The cured samples were subjected to thermomechanical evaluation as described above over the temperature range of -65° C to $+150^{\circ}$ C.

Electrical Properties

The electrical volume resistivity was measured on strips of adhesive. The silicone film adhesive was simply cut in a strip 3 mm wide. The paste adhesives were spread, using a razor blade, between two parallel strips of transparent adhesive tape (3M) on an insulating substrate. The tape strips were then removed and the adhesive cured as described below.

The resistances of the strips were then measured using an ohm-meter and the resistivity was determined by the following formula:

$$r = ewR/L \tag{1}$$

where r: resistivity, e: thickness, w: width, R: resistance and L: length.

Mechanical Properties

We used several methods for determining bond strength. The die shear test was carried out using 2 mm square gold-plated silicon bonded to an alumina substrate on a Dage BT 22 microtester.

The lap shear test was made using aluminum plates (alloy 2024, dimensions: 2.54 cm \times 7.62 cm \times 0.15 cm; overlapping 10 mm). The aluminium was etched in a cleaning solution (150 g K₂Cr₂O₇, 900 ml H₂O, 125 ml H₂SO₄) at 60°C for 30 min, rinsed with deionized water and air dried before use. The adhesives were applied and spread on the plate to a sufficient length in the area across the end of the metal sheets so that the adhesive covered a length of approximately 10 mm. In

order to avoid entrapped solvent bubbles which could decrease bond strength, the adhesives were dried at 70°C for 30 minutes. After drying, the plates were assembled in pairs so that the overlap length was 10 mm. Clamps were used to hold the pieces together under uniform pressure. The thickness was set at $25 \,\mu\text{m}$ with an aluminium film between the plates. The adhesives were cured as described below. The test was performed on an Instron 1185 at a speed of 0.5 mm/min according to ASTM-D 1002 to determine the load at failure.

RESULTS AND DISCUSSION

Processing

Epoxy adhesive The adhesive is a thermosetting product which has the consistency of a smooth paste. The novolac epoxy matrix has to be crosslinked by a curing agent which polymerizes it to a tough, hard solid.

In the latent curing agent, a substituted imidazole, the secondary amine functional group on the imidazole ring of the original type was exchanged for an inactive diaminotriazine radical. This functional group is inactive at low temperature due to the blocking action of the radical. However, the radical will separate from the imidazole above 100°C and these compounds can form adducts with the epoxy allowing the resin to cure in a short time. The adhesive can be applied by printing, stamping or positive displacement and cured according to one of the following: 15 min at 180°C (best overall results), 20 min at 160°C, 30 min at 140°C, 90 min at 120°C. Kinetics data obtained from a DSC study show that at 180°C the conversion is 95% within 6 minutes. However, it is necessary to dry the composite completely in order to avoid outgassing due to entrapped solvent.

Before packaging, the evaporation of volatiles during cure causes no reliability problems since they can escape to the surrounding oven atmosphere. However, when the integrated circuit is encapsulated there should be no outgassing in the package. The drying is achieved in 15 min at 180°C.

Polyimide adhesive The polyimideamide matrix is a thermoplastic polymer which does not require a final imidization step, unlike polyamic acids, the classical polyimide precursors. Moreover, during the imidization step, polyamic acids give off water vapor:



TAB	LE	Ι
Processing	con	ditions

Adhesive	Operation	Temperature	Time
ероху	crosslinking + drying	180°C	15 min
polyimide	drying	60°C	60 min
		+150°C	30 min
		+350°C	30 min
silicone	melting	200°C	≈10 s

The polyimideamide adhesive only needs a drying step to bond the silicon dies. Actually, the large amounts of solvent used to dissolve the polymer could cause voids under the die. In order to avoid this problem, a three-step cure is used. Step 1: 1 h at 80°C; step 2: 30 min at 150°C, and finally step 3: 30 min at 350°C to drive off the last traces of N-methylpyrrolidone. Printing, stamping or positive displacement are also used to apply this adhesive.

Silicone adhesive This silicone film is a new type of conductive adhesive which may be shaped into preforms. The processing conditions require the film to be heated above the melting point of the polymer matrix (180°C) and the substrate to be applied to the melted surface of the adhesive for a few seconds. Curing and drying operations are not needed. The wafer is normally sawed into individual dies. Table I recapitulates processing conditions for the three adhesives.

The new thermoplastic silicone film approach offers potential for increased automation.⁶ This film has the major advantage over the paste adhesives of very short processing time resulting in higher productivity. The fast cure and low processing temperature features of the epoxy adhesive are useful when increased productivity is desired with standard dispensers or when it is necessary to keep to a minimum the time and temperature exposure of the bonded parts. The complex multistep and high temperature cure required with the polyimide adhesive rules out many automation possibilities.

Electrical conductivity

Silver-filled composites are electroconductive materials.⁷ Silver conductive particles are scattered in an insulating polymer. They form a network within the matrix and electrons can flow across particle contact points. Percolation theory describes the mechanism of current flow through the adhesive.^{8,9}

Models calculate a loading of 30% (volume) as the threshold for conductivity. The establishment of current-flow paths requires uninterrupted contacts. For volume loadings below the critical volume fraction, the resistivity is very high. As loading increases, the conductivity begins to be greater than zero when the number of contacts per particle becomes greater than one. The conductivity will appreciably increase at higher and higher loadings until every particle has two

TABLE II Resistivities of conductive composites				
Silver Adhesive % (weight) Resistivity (Ω				
ероху	87	2.5×10^{-6}		
polyimide	83	3×10^{-6}		
silicone	83	3.5×10^{-6}		

contacts with other particles. For more than two contacts, the conductivity will not perceptibly increase.

The percolation threshold is obtained for smaller critical volume fractions when the surface area of the particle is increased. Flakes of irregular shapes give higher numbers of contact points and produce higher conductivities than regularlyshaped powders.

As current flow only occurs over the small area of the contact point, the resistivity of the adhesive is higher than the resistivity of the metal:

silver:	$1.6 \times 10^{-8} \Omega \mathrm{m}$
silver-filled adhesive:	$2 \times 10^{-6} \Omega m$
epoxy resin:	$10^{16} - 10^{17} \Omega m$

The adhesive can be described as containing two types of regions: one in which the silver flakes are in continuous contact through the sample and another in which there is insulating resin between the silver flakes. Schoch and Bennett¹⁰ have compared this situation to an equivalent circuit: a resistance, representing the part where the particles are in contact, in parallel with a resistance and a capacitance in series, representing the part with an insulating layer between particles.

As predicted by this circuit, they have shown that the resistance of some tested adhesives is constant at low frequencies (the current flows through the resistance) and decreases at higher frequencies (the current flows through the capacitance resistance combination).

Silver is a relatively expensive filler but other, cheaper, metals cannot be used since there is a growth of insulating oxide on the particle surfaces. The three conductive materials investigated have the same resistivity values (Table II). We have found that the nature of the matrix does not play a significant part in the value of the resistivity.

Purity

An important reliability problem for integrated circuits is the contamination and the corrosion caused by aqueous-extractable ionic impurities in the dieattachment adhesives.¹¹⁻¹³ Few corrosive failures occur in hermetic ceramic packages but the plastic packages are permeable to water vapor and extractable ions can induce corrosion of the metallization or of the aluminium pad areas. Serious failure problems have been observed, particularly with integrated circuits operating at elevated temperatures where the ion mobility in electric fields is increased.

It becomes obvious that electronic manufacturers need extremely clean die-attachment adhesives containing very low levels of extractable sodium, potassium and other ionic impurities to make highly reliable circuits. The adhesives shown in Table III are among the cleanest die-attach adhesive materials currently available.

Epoxy novolac resins are normally synthesized from a novolac (polyphenol) and epichlorhydrin (1-chloro-2,3-epoxypropane) using sodium hydroxide as the reaction catalyst:



Generally these materials contain high levels of chlorides and other ionic impurities. However, electronic grade resins are distinguished from standard epoxy resins by their very low hydrolyzable-ion content. The enhanced purity of these resins makes them especially suitable for electronic-related applications where maximum performance is desired. To avoid large amounts of ionic impurities, resin suppliers have extended the reaction time. Purification techniques (extraction, recrystallization, distillation...) can be used to remove the last traces.

Until quite recently, high-purity epoxy adhesives were not available and polyimide adhesives were relatively widely used in many high-reliability, plasticencapsulated, integrated circuits because of the low levels of extractable-ionic

Extractable ionic content						
Material	Cl⁻ ppm	Na⁺ ppm	K⁺ ppm	NH₄ ppm	рН	Total ionic content (conductivity of water extract) S m ⁻¹
epoxy	n	2	1	20	()	2.0 × 10=3
polvimide	2	2	1	28	0.0	3.0 × 10
adhesive	1	1	1	4	6.2	1.1×10^{-3}
silicone						
adhesive	8	2	1	23		
(Decussa)	1	5	1	30		36×10^{-3}
silver	1	5	1	50		50 × 10
(C.L.A.L.)	1	4	2	1		1.7×10^{-3}

TABLE III

impurities in polyimide matrices. The polyimide synthesis is a very clean reaction which does not involve contaminating ions.

The polymer is produced through the polycondensation of trimellitic anhydride with 4,4'diisocyanatodiphenylmethane in N-methylpyrrolidone at elevated temperatures but without catalyst. The use of the acid anhydride leads to a polyimideamide:



As the process does not introduce ionic impurities it is easy to obtain a very high degree of ionic purity by using purified starting materials (monomers and solvent).

The thermoplastic silicone matrix is a high molecular weight, semicrystalline $(AB)_n$ -type, multiblock copolymer synthesized by polycondensation of rigid and flexible chains using the hydrosilylation reaction:¹⁴



rigid a, w divinyl polydimethylvinylsilylbenzene



flexible α, ω dihydrogenopolydimethylsiloxane



The initial telechelic polysiloxane is synthesized by the following process: hydrolysis of dichlorodimethylsilane, cracking of reaction product over potassium hydroxide, purification, cationic polymerization of obtained cyclic oligomers with dihydrogenotetramethyldisiloxane and devolatilization of low molecular weight oligomers.

The initial telechelic rigid chain is prepared from polyaddition of bisdimethylvinylsilyl-1,4 benzene and bisdimethylhydrogenosilyl-1,4 benzene by a hydrosilylation reaction:



Most of the traces of chloride coming from initial polymers or from the hydrosilylation catalyst (chloroplatinic acid) are eliminated through precipitation and washing with ethanol.

In fact, very pure polymer matrices are available even for epoxies and silicones. Die-mount systems can be designed which are free of water-leachable ionic contaminants. The differences observed in the three adhesives come from the filler. Silver is a major source of ionic contamination. It is known that individual silver particles of commercial conductive flakes are commonly coated with a thin organic layer in order to maximize dispersion, which is essential for low ultimate resistivity.

It is, therefore, possible that this dispersion agent may contain contaminating ions coming from the processing of the metal flakes. The polyimide adhesive is purer than epoxy and silicone adhesives because the silver used for its preparation is the purest of the powders used. The silver flakes used for the epoxy and silicone adhesives contain ammonium ion (30 ppm) which is found again in the adhesive by water extraction. Formulation of the epoxy resin with the clean silver showed low levels of ammonium ion similar to the polyimide adhesive proving that the silver flakes were the contaminating agent.

Thermal properties

Thermal analysis is a method of investigating thermal characteristics such as the variations of mass and dimensions of the specimen with temperature and glass transition temperature.

Thermal stability The use of organic adhesives in high reliability packages has

been slow to be accepted because of their low thermal stability and because of outgassing of entrapped solvents which are a serious problem in hermeticallysealed packages.¹⁵ Evolution of volatiles must be avoided within most aerospace and other high-reliability integrated circuits. After the adhesive cure, any further release of volatile material is potentially dangerous. Gaseous decomposition products causing pressure buildup contributes to failure during lid sealing of ceramic-dip packages. After curing and packaging, volatiles may contaminate or corrode the integrated circuit.

Thermogravimetric analysis in nitrogen on the three formulated die-attach materials is shown in Figures 3, 4 and 5. Results are summarized in Table IV.

This study permits the conclusion that these particular epoxy and silicone adhesives present comparable stabilities (lower outgassing for epoxy but degradation takes place sooner).

This particular polyimide adhesive shows a very high stability without weight loss at 250°C and 300°C and a degradation temperature of 500°C (weight loss 0.36% at 500°C). Even in air, we found that this adhesive had a high degradation temperature—the same as the pure polymer. This result is somewhat surprising since classical polyimide + silver systems have low degradation temperatures,¹⁶ close to the degradation temperatures of epoxy-silver systems. This astonishing



FIGURE 3 Thermogravimetric analysis of epoxy composite.



FIGURE 5 Thermogravimetric analysis of silicone composite.

TABLE IV Thermogravimetric analysis			
Degradatie % weight loss temperatu			
Adhesive	250°C	300°C	°C
epoxy	0.10	0.34	390
polyimide	0.00	0.00	500
silicone	0.22	0.38	460

phenomenon by itself (because of the high thermal stability of polyimides) has been explained by the effect of the silver filler.¹⁷

The unfilled polyimideamide normally has a degradation temperature well over 400°C but with silver-filled systems the degradation temperature in air becomes lower than 400°C, while it remains the same with gold filler (over 400°C). It is clear that the surface of the silver has an influence on the stability of the polyimideamide. The epoxy-silver systems show the same decomposition temperature as the pure epoxy resin. In fact, it is the thin coating of silver oxide which is likely to accelerate the degradation. The oxide is strongly basic¹⁷ and the basic surface of the silver flakes catalyses the decomposition of the polyimide chain at high temperatures.

Glass transition temperature and thermal expansion As die sizes increase, the problems of thermal stresses become more and more important. Thermal stresses are generated between the silicon die and substrate during cooling after bonding. They may cause cracking or distortion of the die. During the bonding operation, the adhesive is in a liquid state and the die is in the zero-stress condition. Stresses appear during cooling when the material passes through its glass transition temperature. These stresses are due to the thermal coefficient of expansion mismatch between silicon and die-attachment material.

It has been proposed¹⁷ that thermal stresses are proportional to the following expression:

$$S = \Delta \alpha \, \Delta T (E_{a}E_{s})^{1/2} (L/x)^{1/2}$$
⁽²⁾

where $\Delta \alpha$: difference between expansion coefficients of the two joined materials, ΔT : difference between test temperature and glass transition temperature, E_a : adhesive tensile modulus, E_s : substrate tensile modulus, L: die length and x: adhesive thickness.

Table V gives the characteristics of the three processed adhesives. The glass transition temperature has an important impact on the coefficient of thermal expansion. At temperatures above T_g , the rapid expansion of the epoxy adhesive gives a coefficient of thermal expansion 2.5 times larger than at temperatures below T_g . Although the difference between thermal expansion coefficients of epoxy-silver adhesive and silicon ($\alpha_{si} = 3 \times 10^{-60} C^{-1}$) is large, the rapid thermal expansion above T_g is not a major problem since the adhesive is more compliant above the T_g .

TADLE M

Glass transition temperatures and coefficients of linear thermal expansion			
Adhesive	T _g ℃	below T_g	above T_{g}^{α}
ероху	50	30×10^{-6}	80×10^{-6}
polyimide	250	60×10^{-6}	
silicone	-120		

The silicone adhesive is an elastomeric material with a T_g of -120° C. Polyimides have rather low thermal expansion coefficients compared with other polymers. This is due to the linearity and the rigidity of their skeletons. However, their T_g is much higher and Eq. (2) predicts high thermal stresses.¹⁸ The polyimide adhesive is more rigid than the other adhesives and the probability of large dies cracking is increased.

Mechanical properties

One of the functions of conductive adhesives is to join the surfaces of the silicon and of the substrate and to provide adequate mechanical strength across the joint. Die-bonding adhesives must generally develop high strength after a short cure period in order to resist the displacement during packaging and subsequent exposure to sequential test environments (high temperature storage, temperature cycling, mechanical shock and constant acceleration). Sufficient strength is also required at high temperature to resist displacement during the wire bonding operation or during the sealing of ceramic packages. Table VI shows the comparative data for the three adhesives. At room temperature, the epoxy composite has the best shear strength. At 150°C the epoxy composite is above T_g and the lap shear strength is substantially reduced.¹⁹

The lower value for the polyimide at room temperature is easily explained by the fact that this composite contains large amounts of solvent which creates voids during cure, thus reducing the area of contact between the adhesive and the substrates.²⁰ However, the high Tg of the material allows exposure to high temperature before the softening point is reached and shear strength decreases.

Being an elastomer at room temperature, the silicone adhesive exhibits a low shear strength compared to the other, more rigid materials. However, the

TABLE VI Die shear and lap shear strengths					
Die shear strength Lap shear strength Adhesive 20°C MPa 25°C MPa 150°C M					
ероху	19	13	8		
polyimide	13	10	8		
silicone	2				

mechanical behavior of these semicrystalline multiblock polymers can vary widely depending on their composition. Properties ranging from flexible to rigid were obtained by varying the polysiloxane content. Higher shear strength values have been obtained (2-5 MPa) by increasing the amount of crystallizable hard segments in the main polymer chain.

CONCLUSIONS

From this study it has become obvious that the choice of a matrix for a die-attachment adhesive is dictated by the application for which the adhesive is to be used, the performance requirements needed for high-speed, high-yield production, and the reliability requirements needed to ensure no failures of the encapsulated integrated circuit.

By comparing the three prepared adhesives we found that the formulated epoxy adhesive is superior for general bonding of integrated circuits in dieattachment applications because it offers good processing characteristics and high strength. The fast-cure feature is useful when increased productivity is desired or when it is necessary to keep to a minimum the time and temperature exposure of the bonded parts.

Since the material based on the polyimideamide matrix gives lower bond strength and is more difficult to cure and process, we think this particular adhesive is better suited for speciality die attachment applications. It is particularly useful for applications that require subsequent exposure to extremely high temperatures. The high thermal stability of the polyimide and the absence of outgassing at high temperatures allow the product to resist lid-sealing operations for hermetic packages at temperatures in excess of 460°C for 8 minutes.

We believe that the material based on the block silicone copolymer we synthesized is best suited for applications requiring stress-accommodating properties. It is less rigid than the polyimide and the epoxy. Thus, the silicone conductive adhesive is ideally suited for bonding large dies where thermal stresses could cause die bending and cracking. Moreover, the unique properties of this silicone thermoplastic matrix contribute to higher productivity since this polymer requires no curing operations and preforms can be used.

References

- 1. R. K. Shukla and N. P. Mencinger, Solid State Technol. 28, 67 (1985).
- 2. F. K. Moghadam, ibid. 27, 149 (1984).
- 3. J. C. Bolger and C. T. Mooney, Natl. SAMPE Tech. Conf. 17, 543 (1985).
- R. H. Estes, "Adhesives for microelectronics MIL-A-87172 and beyond" Epoxy Technology, Inc. (Billerica, MA, U.S.A.), Techn. Memo. (1985).
- C. Prud'homme, Fr. Patent Appl. 86/14581 (Oct. 20, 1986) to Rhone-Poulenc Multi-Techniques.
 A. Glosecki, Solid State Technol. 29, 75 (1986).
- 7. J. C. Bolger and S. L. Morano, Adhesives Age 27, 17 (1984).
- 8. A. J. Lovinger, J. Adhesion 10, 1 (1979).
- 9. R. L. Opila and J. D. Sinclair, Ann. Proc. Reliab. Phys. Symp. 23, 164 (1985).

- 10. K. F. Schoch and A. L. Bennet, Proc. Electr./Electron. Insul. Conf. 17, 291 (1985).
- 11. C. T. Mooney, Proc. Electron. Compon. Conf. 35, 326 (1985).
- D. M. Barnes and C. N. Robinson, *ibid.* 34, 68 (1984).
 K. E. Manchester, D. W. Bird and H. Charest, *Proc. Int. Reliab. Phys. Symp.* 20, 272 (1982).
- 14. M. Bargain and C. Prud'homme, U.S. Patent 4,233,427 (Nov. 11, 1980) to Rhone-Poulenc Industries.
- J. C. Bolger and C. T. Mooney, Proc. Electron. Compon. Conf. 33, 227 (1983).
 R. H. Estes and F. W. Kulesza, Int. J. Hybrid Microelectron. 5, 336 (1982).
- 17. J. C. Bolger, in Polyimides 2, K. L. Mittal Ed., (Plenum Press, New York, 1984), p. 871.
- 18. J. C. Bolger and C. T. Mooney, IEEE Trans. Compon. Hybrids Manuf. Technol. CHMT 7, 394 (1984).
- 19. F. W. Kulesza and T. F. Saunders, Proc. Int. Microelectron. Symp. (1979), p. 360.
- 20. R. H. Estes, Solid State Technol. 27, 191 (1984).