Chapter 10
Electrically Conductive Adhesives (ECAs)

Daniel Lu and C.P. Wong

Abstract Conductive adhesives consist of conductive particles and polymeric matrix, and can provide both electrical and mechanical connections. Much advance on conductive adhesive technology has been made over the years. This chapter provides a comprehensive overview on the basic aspects, key applications in electronic packaging, and latest advances of both anisotropically conductive adhesives (ACAs) and isotropically conductive adhesives (ICAs).

10.1 Introduction

Electrically conductive adhesives (ECAs) are composed of polymeric matrices and conductive fillers. The conductive fillers provide the electrical properties while the polymeric matrix provides mechanical properties. Therefore, electrical and mechanical properties are provided by different components, which are different from metallic solders that provide both the electrical and mechanical properties [1–3]. There are two types of conductive adhesives: anisotropically conductive adhesives/films (ACAs/ACFs) and isotropically conductive adhesives (ICAs).

10.2 Description of Anisotropically Conductive Adhesives

10.2.1 Overview

Anisotropically conductive adhesives (ACAs) provide electrical conductivity only in the vertical or *Z*-axis. This directional conductivity is achieved by using a relatively low volume loading of conductive filler (5–20 vol.%) [4–6]. The low volume loading is insufficient for inter-particle contact and prevents conductivity in

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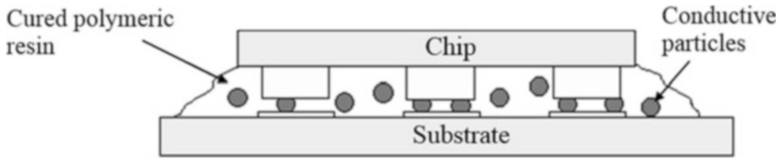

Fig. 10.1 A schematic of an ACA joint

the *X*–*Y* plane of the adhesive. The *Z*-axis adhesive, in film or paste form, is interposed between the two surfaces to be connected. Application of heat and pressure to this stack-up causes conductive particles to be trapped between mating bonding pads on the two components. Once electrical continuity is achieved, the dielectric polymer matrix is hardened by chemical reaction (thermosets) or by cooling (thermoplastics). The hardened dielectric polymer matrix holds the two components together and helps maintain the contact pressure between component surfaces and conductive particles. A sketch in Fig. 10.1 illustrates an ACA joint between a chap and substrate. Anisotropically conductive adhesives have been developed for use in electrical interconnection, and various designs, formulations and processes have been patented in Europe, Japan, and the USA [6].

10.2.2 Adhesive Matrix

Both thermosetting and thermoplastic materials are used as the matrix of ACAs. Thermoplastic adhesives are rigid materials at temperatures below the glass transition temperature (T_g) of a polymer. Above the T_g, polymers exhibit flow characteristics. Thus, the T_g must be sufficiently high to avoid polymer flow during the application conditions, but the T_g must be low enough to prevent thermal damage to the electronic devices during assembly. The primary advantage of thermoplastic adhesives is the relative ease with which interconnections can be disassembled for repair or rework operations [7, 8]. However, thermoplastic ACAs suffer from many disadvantages. One of the most serious issues is that adhesion is insufficient to hold the conductive particles in position, causing the contact resistance to increase after thermal shocks [7, 8]. Moreover, a phenomenon called "spring back" increases the contact resistance while the adhesive layer recovers from the stress caused by pressing of an ACA onto the components during bonding. This phenomenon, a creep characteristic exhibited by thermoplastic elastomers, occurs much after an ACA film has been heated to create the electrical joints. The contact resistance sometimes increases to more than three times the initial resistance during spring back (i.e., unloading) [7].

Thermosetting adhesives, such as epoxies, form a three-dimensional cross-linked structure when cured under specific conditions. The thermosetting ACAs are stable at elevated temperatures and, more importantly, provide a low contact resistance, which results from a compressive force that holds the conductive

particles in intimate contact with bonding pads after the cure. The ability to maintain strength at high temperature and robust adhesive bonds are the principal advantages of these materials. However, because the cure reaction is not reversible, rework or repair of interconnections is not an option [7, 8].

10.2.3 Conductive Fillers

10.2.3.1 Solid Metal Particles

Conductive fillers are used to provide the adhesive with electrical conductivity. The simplest fillers are metal particles such as gold, silver, nickel, indium, copper, and lead-free solders (SnBi) [6, 7, 9–11]. The particles are usually spherical and range 3–15 μm in size for ACA applications [12].

10.2.3.2 Non-Metal Particles with Metal Coating

Some ACA systems employ non-conductive particles with a thin metal coat. The core material is either plastic or glass with a metal coating consisting of gold, silver, or nickel. The basic particle shape of these systems is also spherical. Plastic-cored particles deform when compressed between opposing contact surfaces, and thus provide a large contact area. Polystyrene (PS) is often selected as the core material because the coefficient of thermal expansion of metal-coated PS beads is very close thermoset adhesives. The combination of epoxy resin and metal-plated PS beads results in a large improvement in thermal stability [7]. In addition, glass can also be selected as the core material. Glass-cored particles coated with metal lead to a controlled bond-line thickness because the glass core is not deformable. Since the conductive particle size is known, the conductivity of the joint can be predicted.

10.2.3.3 Metal Particles with Insulating Coating

To achieve fine pitch connections, metal spheres or metal-coated plastic spheres coated with insulating resin fillers were developed. The insulating resin layer is only broken under pressure to expose the underlying conductive surfaces, referred to as a microcapsule filler (MCF). Higher filler loading can be achieved with MCFs for fine pitch applications to avoid creating electrical short circuit conditions between printed circuit features [7, 12]. A typical cross section of an ACA interconnection with microcapsule filler material is illustrated in Fig. 10.2.

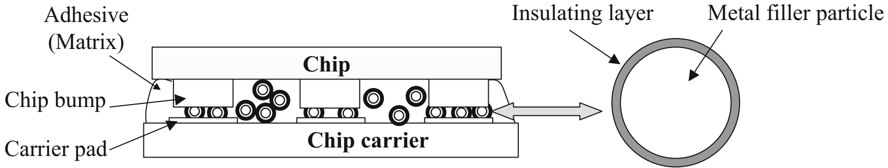

Fig. 10.2 Schematic depicting the cross section of an interconnection using a MCF-filled ACA

10.2.3.4 Nanoparticles

To meet the requirements for future fine pitch and high-performance interconnects in advanced packaging, conductive adhesives with nanomaterial or nanotechnology attract more and more interests due to the specific electrical, mechanical, optical, magnetic, and chemical properties.

Nano-Ag particles can be incorporated into polymeric matrix by externally addition or in situ formulation [13]. Self-assembled monolayer (SAM) was introduced onto the nano-Ag particle surfaces to further enhance the current carrying capability of ACA joints [13].

ACF using nickel nanoparticles with a straight-chain-like structure as conductive fillers was developed [14] by mixing nickel nanoparticles and solvent in a mixture of epoxy resin on a substrate film, and orienting the particles toward the vertical direction of the film surface and being fixed in the resin by evaporating the solvent. The ACF showed superior insulation reliability.

Nanowires exhibit high possibilities due to the small size and extremely high aspect ratio. Nanowires could be applied in FET sensor for gas detection, magnetic hard-disk, nanoelectrodes for electrochemical sensor, thermal-electric device for thermal dissipation and temperature control, etc. [15–17]. To prepare nanowires, it is important to define nanostructures on photoresist. Many expensive methods such as e-beam, X-ray, or scanning probe lithography have been used but the length of nanowires cannot be achieved to micrometer. Another less expensive alternative is electrodeposition of metal into nanoporous template such as anodic aluminum oxide (AAO) [18] or block-copolymer self-assembly template [19]. The disadvantages of block-copolymer template include thin thickness (that means short nanowires), non-uniform distribution and poor parallelism of nanopores. However, AAO has the benefits of higher thickness (>10 μm), uniform pore size and density, larger size, and very parallel pores. As an example, bi-metallic Ag/Co nanowires were fabricated using AAO approach and then impregnated with a polyimide resin [20]. The Ag/Co nanowires/polyimide composite films could be obtained with diameter of nanowire about 200 nm and maximum film thickness up to 50 μm. The *X*–*Y* insulation resistance achieved was 4–6 GΩ and *Z*-direction resistance including the trace resistance (3 mm length) is less than 0.2 Ω.

10.2.3.5 Self-Aligned Magnetic Particles

A novel anisotropic conductive adhesive (ACA) was investigated for high-frequency applications. In the presence of a direct current (DC) magnetic field, columns for interconnecting between a chip and substrate were created by the self-alignment of ferromagnetic particles into conductive columns within an epoxy matrix. A very low transmission loss (<0.5 dB per transition) was demonstrated in the frequency up to 30 GHz [21].

10.2.3.6 Nanofiber/Solder

The polyvinylidene difluoride (PVDF) nanofiber/Sn58Bi solder ACF was prepared first by fabricating PVDF nanofibers through electrospinning technique [22]. It was observed that PVDF nanofiber completely covers the Sn58Bi solder ball, and successfully suppressed the conductive solder ball movement and acted as an insulating layer around the solder balls. PVDF nanofiber/Sn58Bi solder ACFs showed better reliability compared to those of conventional Ni particle filled ACFs primarily because PVDF nanofiber/Sn58Bi solder ACFs contain stable metallurgical solder joints along with the high contact area.

10.3 Flip Chip Applications Using Anisotropically Conductive Adhesives

In traditional flip chip packages, solder bumps provide electrical connections between a chip and chip carrier (or substrate). To achieve high reliability, organic underfill materials are usually required to fill the gap between the chip and chip carrier. The cured underfill creates a monolithic structure that evenly distributes the stress over all the material in the gap, not just on the solder connections. In the past several years, much research has been conducted to develop flip chip packages using ACAs in place of solder bumps. The primary advantages of ACA over lead-bearing solder for flip chips include ACAs' fine pitch capability, lead-free, low processing temperature, absence of flux residue, and generally lower cost. Also, ACA flip chip technology does not require an additional underfilling process because the ACA resin acts as an underfill.

ACA flip-chip technology has been employed in many applications where flip chips are bonded to rigid chip carriers [23]. This includes bare chip assembly of ASICs in transistor radios, personal digital assistants (PDAs), sensor chips in digital cameras, and memory chips in laptop computers. In all the applications, the common feature is that ACA flip-chip technology is used to assemble bare chips where the pitch is extremely fine, normally less than 120 μm. For those fine

applications, it is apparent that the use of ACA flip-chips instead of soldering is more cost-effective.

ACA flip-chip bonding exhibits better reliability on flexible chip carriers because the ability of flex provides compliance to relieve stresses. For example, the internal stress generated during resin curing can be absorbed by the deformation of the chip carrier. ACA joint stress analysis conducted by Wu et al. indicated that the residual stress is larger on rigid substrates than on flexible substrates after bonding [24].

10.3.1 ACA Flip Chip for Bumped Dies

10.3.1.1 Two Filler Systems

Y. Kishimoto et al. reported [25] anisotropic conductive adhesive pastes using two different fillers: Au-coated rubber particles (soft) and nickel particles (hard). The ACAs were used to bond a flip chip with Au-plated bumps to a board with copper metallization. With the application of pressure, the soft particles were brought into contact with surface pads and were deformed which lowered this contact resistance. The hard particles, however, deformed the bumps and pads, thus were also in intimate contact with the surfaces to help reduce this contact resistance. The study showed that their choice of both hard and soft fillers in ACA materials had similar voltage–current behavior, and both exhibited stable contact resistance values after 1000 cycles of thermal cycling and 1200 h of 85 °C/85%RH aging conditions [25].

10.3.1.2 Coated Plastic Filler

Casio developed an advanced anisotropic conductive adhesive film called the Microconnector (Fig. 10.3) [26–28]. This adhesive contains conductive particles made by coating plastic spheres with a thin layer of metal, followed by an additional 10 nm-thick layer of insulating polymeric material. The insulating layer consists of a large number of insulating micro powder particles that electrically insulate the outer surface of the spheres. The thin insulation layer is formed by causing insulating micro powder particles to adhere to the surface of the metal layer via electrostatic attraction. The base adhesive resin is thermoplastic or thermosetting, producing compressive force when cured. When heat and pressure are applied during bonding, the insulating layer, which is in contact with the bump surface of an IC, is broken. However, the insulating layer remains intact on conductive particles not crushed by the bonding pads, thereby producing only *Z*-axis electrical interconnections and preventing lateral short circuit conditions. With an additional insulating layer, a fine pitch and low contact resistance can be achieved without the

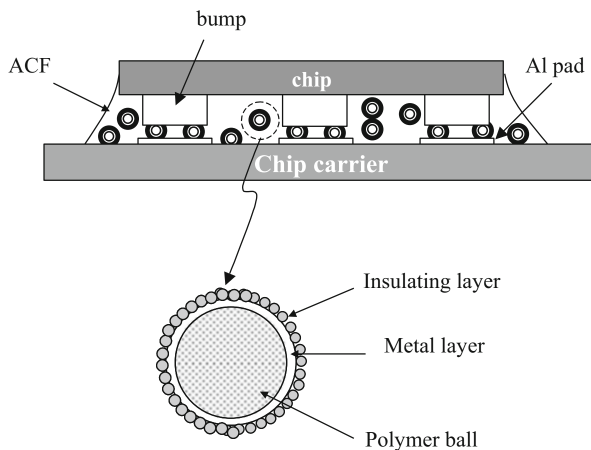

Fig. 10.3 Schematic depicting Casio's ACF technology—microconnector

risk of lateral short-circuiting by increasing the filler percentage (i.e., amount of particles per unit volume base adhesive resin or film). Casio is manufacturing pocket TV's with a liquid crystal using this material [28].

10.3.1.3 Solder Filler Systems

Unlike most commercial ACAs, where the electrical conductivity is based on the degree of mechanical contact achieved by pressing conductive particles to contact pads on board and chip bumps, solder-filled ACAs establish microscopic metallurgical interconnections. The advantage of these joints is that the metallurgical bonds that are established prevent electrical discontinuities from occurring should the adhesive polymeric matrix undergo relaxation during the operational lifetime. Therefore, solder-filled ACAs combine the benefits of both soldering and adhesive joining resulting in more reliable ACA joints. Furthermore, better electrical performance is achieved due to lower contact resistance established through the metallurgical bonds [29].

Joints made with SnBi-filled and Bi-filled ACAs experience brittle intermetallic compound formation and have problems with typical conductor and coating materials such as copper, nickel, gold, and palladium [30]. Bi and SnBi are, however, compatible with tin, lead, zinc, and aluminum. Because Zn and Al are easily oxidized, only Sn and Pb are suitable surface finish materials for SnBi- and Bi-filled ACA applications. High-quality interconnections were formed by metallurgically bonding SnPb-bumped chips on SnPb-coated substrates utilizing a Bi particle-filled ACA [31]. The joints once formed at a relatively low temperature could withstand a high temperature. The joint formation process is illustrated in Fig. 10.4. At the bonding temperature, 160 °C, as the Bi particles have locally penetrated thin oxide layers on both SnPb surfaces, the liquid lentil formation occurs immediately. After the Bi particles have dissolved completely into the liquid

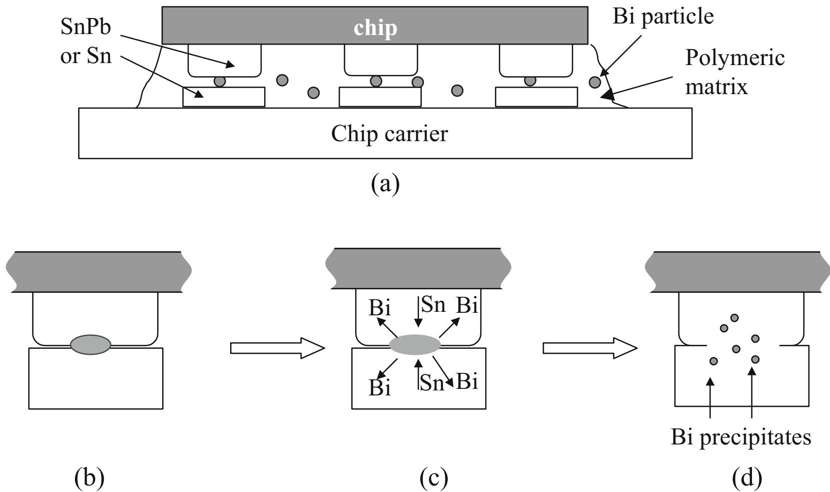

Fig. 10.4 Schematic illustration of the formation of electrical interconnects between a bumped chip and a mating carrier using a Bi-filled ACA. (**a**) The chip is aligned and placed on a chip carrier. (**b**) The Bi-particle is deformed between a chip bump and a carrier pad when a bonding pressure is applied. (**c**) The Bi-particle dissolves into the liquid lentils upon exposure of heat. (**d**) Bi diffuses into the Sn-Pb matrix and form fine solid precipitates

lentils between the solid SnPb bumps and coating, more Sn and Pb will dissolve into the liquid lentils until the liquid has reached its equilibrium composition at the bonding temperature. After solidification, the dissolved Bi will precipitate out as very fine particles from the saturated solution. Since the melting is transient, the re-melting of the solid lentils will happen at higher temperatures than the first melting. The re-melting point of the solid lentils can be controlled by the concentration of Bi present in the joint. The formed ACA joints exhibited a stable resistance after 2000 h of 85 °C/85%RH aging or after 1000 h of temperature cycle testing (−40 to 125 °C). Even though this work is still preliminary, it demonstrates an interesting idea and concept. For lead-free applications, different materials such as pure Sn can be used for chip bumps and surface finish on the substrate [31].

10.3.1.4 Ni Filler

Toshiba Hino Works developed a flip chip bonding technology using an anisotropically conductive film (ACF) filled with nickel spheres and LSI chips with gold ball bumps for mobile communications terminals. A resin sealing process at the sides of the LSI chip was added to improve mechanical strength. An FR-5 glass epoxy chip carrier was utilized to improve heat resistance. The assembled pager sets passed qualification consisting of drop, vibration, bending, torsion, and high temperature

testing. The process has been demonstrated capable of mass production utilizing full automation of the flip-chip bonding method capable of producing 30,000 pager modules per month [32].

10.3.2 ACA Bumped Flip Chips on Glass Chip Carriers

ACAs are probably the most common approach for flip chip on glass applications. The ACA flip chip on glass technology not only provides assemblies with a higher interconnection density and a thinner and smaller size but also has fewer processes and lower costs as compared with TAB (tape automated bonding) technology. Also, bonding IC chips directly to the glass of the LCD panel using ACAs is a better choice when the pitch becomes less than 70–100 μm. Small size and high-resolution LCDs such as viewfinders, video-game equipment displays, or light valves for liquid-crystal projectors use flip-chip on glass technology for the IC connections.

10.3.2.1 Selective Tacky Adhesive Method

Sharp developed a flip-chip bonding approach that utilizes ACA technology depicted in Fig. 10.5 [33, 34]. The novel feature of the Sharp technology is the method of attaching electrical conductive particles onto IC termination pads. This "bumping" procedure consists of coating the wafer with a 1–3 μm thick UV curable adhesive. Coated wafers are irradiated with UV light in a standard

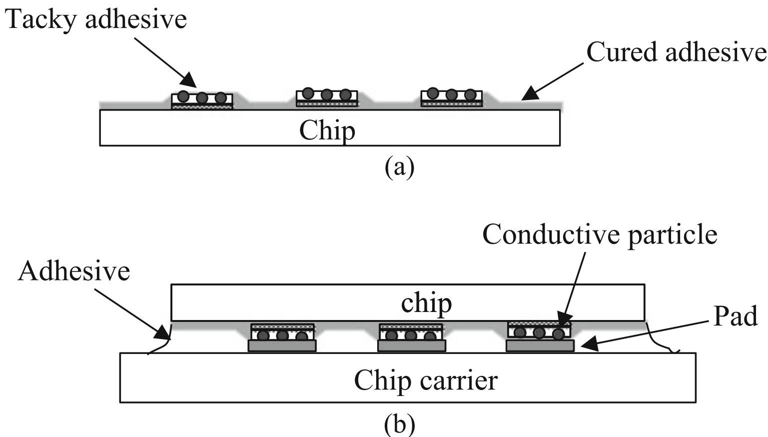

Fig. 10.5 Schematic depicting an ACA flip-chip technology scheme utilized by Sharp. (**a**) Conductive particles adhere to uncured tacky adhesive on pad areas of a chip. (**b**) Chip remains in contact with the glass chip carrier since the adhesive exerts a compressive force after it is cured with light (UV)

photolithographic process while the Al pads on the IC are optically masked. As a result of this process, the thin adhesive film above the Al pads remains uncured and tacky, whereas the adhesive on other chip areas is cured. Due to the tackiness of the adhesive on the Al pads, conductive particles only easily adhere to these sites. The conductive particles utilized by Sharp are gold-coated polymer spheres. UV-curable adhesive is dispensed on LSI chips before being aligned with a glass carrier. While still applying pressure to maintain contact between the LSI chip and glass carrier, a light-setting adhesive is irradiated with UV light. Even upon releasing the pressure, the chip terminations remain electrically connected to their mating carrier pads. This is due to the deformed conductive particles which remain in contact with these termination pads as a result of the compressive force exerted by the cured adhesive. This process has several advantages, among them is that no bump plating is required; and the bonding process can be done by irradiating with UV light at room temperature, thus other materials are not damaged due to the effects of heat. This packaging concept can potentially achieve a high throughput.

10.3.2.2 The MAPLE Method

Seiko Epson Corporation developed a flip-chip on glass technology called the "MAPLE" (Metal-Insulator-Metal Active Panel LSI Mount Engineering) method. The MAPLE method is to bond ICs directly to a glass panel substrate using a thermosetting anisotropic conductive film containing uniformly distributed conductive Au particles. While typical flip-chip on glass technologies require several alignment steps, this bonding process is very simple. First an ACA sheet is placed on a glass panel. After aligning the IC bumps with mating glass panel pads and temporarily bonding, proper IC interconnections are established by permanently bonding at high temperature and pressure. It is necessary for the bonding press-tool surface to be flat and parallel to the IC [35]. Comparing Metal-Insulator-Metal (MIM) panel modules made with TAB, MIM panel modules utilizing the MAPLE approach had smaller panel fringe size, thinner panel thickness, fewer assembled sides, fewer processes, and simpler module structure. The panel modules utilizing MAPLE passed all the required reliability tests. The MAPLE approach was used in mass production of MIM panel modules.

10.3.3 ACA Bumped Flip Chips for High Frequency Applications

In many low frequency applications, conductive adhesive joining has proved to be a cost-effective and reliable solution. The high frequency behavior of ACA interconnections has attracted much attention in the past several years. The high frequency behavior of ACAs in flip chip packages has been reported by several investigators.

Rolf Sihlbom et al. demonstrated that ACA-bonded flip chips can provide performance equivalent to solder flip chips in the frequency range of 45 MHz–2 GHz on FR4 chip carriers and 1–21 GHz on a high-frequency Telfon-based chip carrier. The different particle sizes and materials in the conductive adhesives gave little difference in high frequency behavior of ACA joints [36, 37].

Myung-Jin Yim et al. developed a microwave frequency model for ACF-based flip chip joints based on microwave network analysis and S-parameter measurements. By using this model, high frequency behavior of ACF flip chip interconnections with two filler particles, Ni and Au-coated polymer particles, was simulated. It was predicted that Au-coated polymer-particle-filled ACF flip-chip interconnections exhibited comparable transfer and loss characteristics to solder bumped flip chips up to about 13 GHz, but Ni-filled ACF joints can only be used for up to 8 GHz because the Ni particle has a higher inductance compared to the Au-coated particle. Polymeric resins with a low dielectric constant and conductive particles with low inductance are desirable for high-resonance frequency applications [38].

10.3.4 ACA for Unbumped Flip Chips

Although ACAs are typically utilized with flip-chip bumped die, they are also used for unbumped flip chips in some cases. For unbumped flip chips, a pressure-engaged contact must be established by bringing the particles to the aluminum chip pads rather than a bump. The pressure must be sufficient to break the oxide on the aluminum pads. A sufficient quantity of particles must be trapped in the contact pad area and remain in place during bonding and curing to achieve a reliable interconnection. In addition to maximizing the number of particles in the contact area, the number of particles located between adjacent pads must be minimized to prevent electrical shorts. An additional factor that must be considered in the case of unbumped flip chips is adhesive flow during bonding and curing. It is essential to control the temperature heating rate to be sufficiently slow when the polymeric resin is curing so the conductive filler particles can migrate from the chip carrier side to the chip side pad [39].

10.3.4.1 Gold-Coated Nickel Filler

An application utilizing gold-coated nickel particles has been reported to provide reliable connection to unbumped flip chips [40]. Another study showed ACAs containing larger particles could accommodate planarity issues due to surface roughness, non-flat or non-parallel pads, compared to ACAs containing smaller particles. It was very difficult to obtain 100 % consistency in conduction with unbumped flip-chip dice using ACAs with small diameter balls [41].

10.3.4.2 Ni/Au-Coated Silver Filler

A flip-chip technology developed by Toshiba Corporation utilized an ACF to attach bare unbumped chips (with Al pads) onto a PCB with bumps formed from a silver paste screen printed on the PCB [42]. After curing, Ag bumps were formed (70 μm diameter, 20 μm height) which were subsequently over plated with Ni/Au. It was determined that an ACF with a low CTE (28 ppm/°C), low water absorption rate (1.3 %), and utilizing a Au-plated plastic ball worked best. It was also found that Ni/Au plated Ag paste-formed bumps exhibited a lower initial connection resistance and a lower connection resistance increase as compared to Ag paste-formed bumps which were not over-plated with Ni/Au.

10.3.4.3 Metal Pillar ACF

Nitto Denko Corporation developed a novel ACF which can connect a bump-less chip and a high density Printed Wiring Board (PWB) [43]. This ACF is composed of micrometer size metal pillars (not small conductive particles) and thermoplastic polymer resin. These pillars are coated with the insulating resin of a high T_g polymer (such as polyimide) for completely separating one pillar from another. The combination of adhesive and this insulation coating make the interconnection very robust and free from any electrical short. Ni, Au, Sn/Pb, or other solder materials are plated on the both top and bottom of the metal pillars to ensure a good connection. Figure 10.6 shows the cross-sectional image of flip chip interconnection using metal pillar ACF. Superfine interconnection pitch (25 μm) was successfully demonstrated using this ACF. This flip chip interconnection with the ACF between bump-less pads of a chip and Ni/Au pads (100 μm pitch) on a FR-4 PWB shows good reliability in various environmental tests.

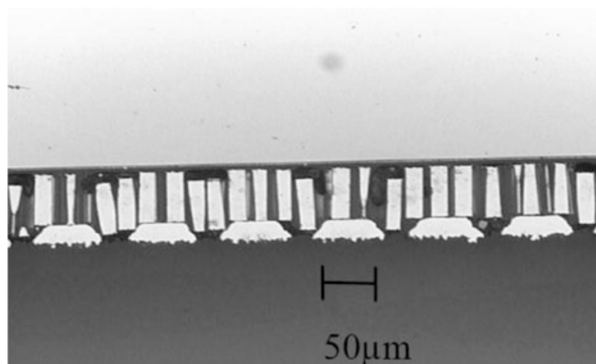

Fig. 10.6 Cross-sectional image of 100 μm pitch flip-chip interconnection formed using metal pillar-filled ACF [43]

10.3.5 ACAs for CSP and BGA Applications

Aiming at the CSP application market, Merix Corporation and Auburn University collaborated to develop anisotropic conductive adhesives called Area Bonding Conductive (ABC) adhesives. ABC adhesives are two-region thermoset adhesives with electrically conductive adhesive pads surrounded by a continuous oxide filled dielectric adhesive to form a total area bond. Both regions are solvent-free, B-staged, non-tacky epoxies supplied on a Mylar carrier release film. In contrast to conventional ACAs, conductive areas of ABC adhesive are only at bond pad locations. The ABC adhesives potentially can provide a reliable, low cost, low temperature, low pressure process for flip chip and CSP applications [44].

10.3.5.1 Double-Layered ACF Film

Motorola developed a low-cost and low-profile flip chip on flex CSP package using ACFs [45]. The package has the flexibility to utilize the existing wire-bonding pad configuration without adding prohibitive redistribution and wafer solder bumping costs, and eliminated the need for under-chip encapsulation. Two types of ACF film were studied: double layer films with the second layer loaded with Ni-Au plated polystyrene-divinylbenzene (PS-DVB) spheres, and solid Ni particles. The film structure, consisting of a non-filled and a conducting particles-filled adhesive layers, is illustrated in Fig. 10.7. The double-layer design reduces the particle density in *x*–*y* spacing of interconnection pads, which serve to enhance the *x*–*y* plane insulation characteristics. At the same time, the double-layer film provides more adhesive volume that helps to entrap more particles on the bonding interconnection pads. Both calculated and observed values show that the number of conducting particles trapped is much higher than those in single-layer ACF. This indicates that even though particle density in a double-layer ACF is low, conducting particles to effect electrical contact with both interconnection pads are trapped more effectively between interconnection pads in the double-layer ACF. The die has Ni/Au plated bonding pads and the chip carrier is flexible polyimide, which can provide adequate compensation for the planarity differences. Its compliant nature under compressive bonding operation allows the copper traces at the bonding area to deform and compensate for non-planarity or irregularity that exists. The ACF adhesive system provided the system with stable contact resistance after 500 cycles of the liquid to liquid temperature shock (LLTS) aging (−55 to 125 °C).

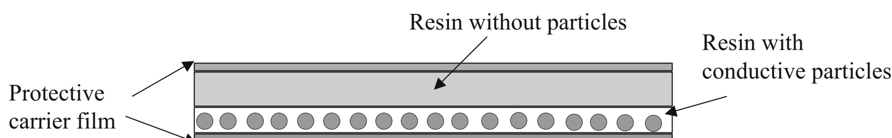

Fig. 10.7 A schematic of a double layer ACF

10.3.5.2 Ceramic Chip Carriers vs. Organic Chip Carriers

A ceramic chip carrier and an organic chip carrier, whose configuration is equivalent to that of micro-ball grid array (μBGA) style chip scale package (CSP) and broadly representative of BGA and flip-chip devices, were evaluated using ACAs with conducting particles of various sizes [46]. The ceramic chip carrier has AgPd thick film bonding pads and the organic chip carrier is a conventional PCB (1 oz Cu clad FR5 laminate) with sub-micron Au-coated Cu pads. It was determined that uniform conductivity and high yield were more readily achieved with organic chip carrier rather than ceramic chip carriers. This is because bonding pads on the FR5 chip carrier have better coplanarity compared to the thick-film ceramic chip carrier. It was demonstrated that the optimum process conditions and adhesive material choice were very different for organic and ceramic chip carriers. ACAs with finer particles exhibited worse overall performance on both chip carriers, while ACAs with larger and polymer-cored particles exhibited better performance because the deformable polymer-cored particles compensated the gap variations between the chip bumps and the chip carriers.

10.3.6 Failure Mechanism

Since the adhesive matrix is a non-conductive material, interconnection joints rely to some extent on pressure to assure contact for conventional ACAs. Adhesive interconnections therefore exhibit different failure mechanisms compared to soldered connections, where the formation of intermetallic compounds and coarsening of grains are associated with the main mechanisms. Basically there are two main failure mechanisms that can affect the contacts. The first is the formation of an insulating film on either the contact areas or conductive particle surfaces. The second is the loss of mechanical contact between the conductive elements due to either a loss of adherence, or relaxation of the compressive force.

10.3.6.1 Oxidation of Non-Noble Metals

Electrochemical corrosion of non-noble metal bumps, pads, and conductive particles results in the formation of insulating metal oxides and significant increase in contact resistance. Electrochemical corrosion only occurs in the presence of moisture and metals that possess different electrochemical potentials. Humidity generally accelerates oxide formation and so too the increase in contact resistance. Reliability test results for flip chip on flex (FCOF) using gold bumps and ACFs filled with Ni particles indicated that the connection resistance increased with time under elevated temperature and humidity storage conditions [47, 48]. In this case, the gold bump acts as cathode and the Ni particle as an anode. A nickel oxide, which is electrically insulating, eventually forms on the surface of the Ni particles.

10.3.6.2 Loss of Compressive Force

The compressive forces acting to maintain contact among the conductive components are partly due to curing shrinkage achieved when curing the polymeric matrix of ACAs. Both the cohesive strength of the adhesive matrix and the interfacial adhesion strength between the adhesive matrix and the chip and chip carrier must be sufficient to maintain the compressive force. However, the thermal expansion of adhesives, their swelling due to moisture adsorption, and mechanical stresses due to applied loads tend to diminish this compressive force created as a result of curing. Moreover, water not only diffuses into the adhesive layer but also penetrates to the interface between adhesive and chip/chip carrier causing a reduction in adhesion strength. As a result, the contact resistance increases and can even result in a complete loss of electrical contact [49].

10.4 Description of Isotropic Conductive Adhesives (ICAS)

10.4.1 Percolation Theory of Conduction

Isotropic conductive adhesives (ICAs) are composites of polymer resin and conductive fillers. The conductive fillers provide the composite with electrical conductivity through contact between the conductive particles. With increasing filler concentrations, the electrical properties of an ICA transform it from an insulator to a conductor. Percolation theory has been used to explain the electrical properties of ICA composites. At low filler concentrations, the resistivities of ICAs decrease gradually with increasing filler concentration. However, the resistivity drops dramatically above a critical filler concentration, Vc, called the percolation threshold. It is believed that at this concentration, all the conductive particles contact each other and form a three-dimensional network. The resistivity decreases only slightly with further increases in the filler concentrations [50–52]. A schematic explanation of resistivity change of ICAs based on percolation theory is shown in Fig. 10.8. In order to achieve conductivity, the volume fraction of conductive filler in an ICA must be equal to or slightly higher than the critical volume fraction. Similar to solders, ICAs provide the dual functions of electrical connection and mechanical bond in an interconnection joint. In an ICA joint, the polymer resin provides mechanical stability and the conductive filler provides electrical conductivity. Filler loading levels that are too high cause the mechanical integrity of adhesive joints to deteriorate. Therefore, the challenge in formulating an ICA is to maximize conductive filler content to achieve a high electrical conductivity without adversely affecting the mechanical properties. In a typical ICA formulation, the volume fraction of the conductive filler is about 25–30 % [4, 5].

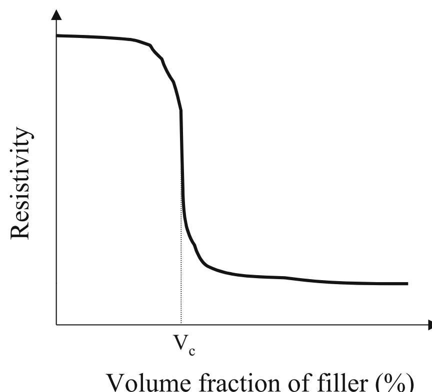

Fig. 10.8 Effect of filler volume fraction on the resistivity of ICA systems

10.4.2 Adhesive Matrix

Polymer matrices of isotropic conductive adhesives are similar to anisotropically conductive adhesives. An ideal matrix for ICAs should exhibit a long shelf life (good room temperature latency), fast cure, relatively high glass transition temperature (T_g), low moisture pickup, and good adhesion [53].

Most commercial ICAs must be kept and shipped under a very low temperature, usually −40 °C, to prevent the ICAs from curing. Pot life is a very important factor for users of the ICAs. In order to achieve desirable latency at room temperature, epoxy hardeners must be carefully selected. In some commercial ICAs, solid curing agents are used, which do not dissolve in the epoxy resin at room temperature. However, these curing agents can dissolve in the epoxy at a higher temperature (curing temperature) and react with the epoxy resin. Another approach to achieve latency is to employ an encapsulated imidazole as a curing agent or catalyst. An imidazole is encapsulated inside a very fine polymer sphere. At room temperature, the polymer sphere does not dissolve or react with the epoxy resin. But at a higher temperature, after the polymer shell is broken, the imidazole is released from the sphere to cure the epoxy or catalyze the cure reaction. Fast cure is another attractive property of a desirable ICA. Shorter cure times increase throughput resulting in lower processing cost. In epoxy-based ICA formulations, proper hardeners and catalysts such as imidazoles and tertiary amines can be used to achieve rapid cure.

10.4.3 Conductive Fillers

Because polymer matrices are dielectric materials, conductive fillers in ICA formulations provide the material with electrical conductivity. In order to achieve high conductivity, the filler concentration must be at least equal or higher than the critical concentration predicted by percolation theory.

10.4.3.1 Silver Particles

Silver (Ag) is by far the most popular conductive filler, although gold (Au), nickel (Ni), copper (Cu), and carbon are also used in ICA formulations. Silver is unique among all of the cost-effective metals by nature of its conductive oxide (Ag_2O). Oxides of most common metals are good electrical insulators and copper powder, for example, becomes a poor conductor after aging. Nickel and copper-based conductive adhesives generally do not have good conductivity stability because they are easily oxidized. [4]. The most common morphology of conductive fillers used for ICAs is flake because flakes tend to have a large surface area, and more contact spots and thus more electrical paths than spherical fillers. The particle size of ICA fillers generally ranges from 1 to 20 μm. Larger particles tend to provide the material with a higher electrical conductivity and lower viscosity [54]. In addition, short carbon fibers have been used as conductive fillers in conductive adhesive formulations [50, 55]. However, carbon-based conductive adhesives show much lower electrical conductivity than silver-filled ones.

10.4.3.2 Silver-Coated Copper Particles

One critical obstacle for preparing highly reliable ICAs filled with Cu particles is the oxidation and corrosion of Cu fillers, which cause the degradation of electrical properties of the ICAs at elevated temperatures and relative humidity (RH) during long-term reliability tests. Various organic compounds could be used for corrosion prevention of the surface of Cu fillers, however, with poor thermal stability at elevated temperatures. Combination of adding silver coating on Cu particles and incorporating an amine curing agent for in situ oxidation/corrosion prevention was demonstrated to be an effective approach to obtain ICAs with stable resistance [56]. The coordination of the amine curing agent to the exposed Cu surface of Ag-coated Cu particles prevents the oxidation of the exposed Cu during the ICA curing at 150 °C. After curing, the formed ample secondary and tertiary amine groups could further protect the exposed Cu surface from oxidation/corrosion effectively in harsh environments. Ho et al. [57] also studied the ICAs filled with silver-coated copper particles which are either spinous or spherical in shape. They found that the conductive adhesive filled with spherical silver-coated copper showed much more stable electrical resistance than the ICA filled with spinous silver-coated copper presumably due to the better silver coating coverage on spherical copper particles.

10.4.3.3 Low-Melt Fillers

In order to improve electrical and mechanical properties, low-melting-point alloy fillers have been used in ICA formulations. A conductive filler powder is coated with a low-melting-point metal. The conductive powder is selected from the group

consisting of Au, Cu, Ag, Al, Pd, and Pt. The low-melting-point metal is selected from the group of fusible metals, such as Bi, In, Sn, Sb, and Zn. The filler particles are coated with the low-melting-point metal, which can be fused to achieve metallurgical bonding between adjacent particles and between the particles and the bond pads that are joined using the adhesive material [58, 59].

10.4.3.4 Nanoparticles

Silver Nanowires

It was reported in the literature that ICAs filled with silver nanowires can achieve similar level electrical conductivity at the much lower filler loading than traditional ICAs filled with micron-sized silver particles. The better electrical conductivity of the ICA filled nanowires was contributed to the fewer number contact (lower contact resistance) between nanowires, more stable conductive network, and more significant contribution from the tunneling effects among the nanowires [60]. The ICAs filled with Ag nanowires tend to have better mechanical properties (e.g., shear strength) due to the lower filler loading.

Several researchers [61–63] reported adding Ag nanoparticles into ICAs filled with micron-sized Ag particles had negative impact to the electrical conductivity of the ICA presumably due to the additional contact resistance resulted from the nanoparticles. However, it was observed that heating the ICA to a higher temperature can reduce the resistivity quite significantly. This is likely due to the high activity of nano-sized particles. For micro-sized paste, this temperature effect was considered negligible. The inter-diffusion of silver atoms among nano-sized particles helped to reduce the contact resistance and resistivity significantly [61, 64, 65].

Carbon Nanotubes (CNTs)

Carbon nanotubes are a new form of carbon, which was first identified in 1991 by Sumio Iijima of NEC, Japan [66]. Nanotubes are sheets of graphite rolled into seamless cylinders. Besides growing single wall nanotubes (SWNTs), nanotubes can also have multiple walls (MWNTs)—cylinders inside the other cylinders. CNTs are chiral structures with a degree of twist in the way that the graphite rings join into cylinders. The chirality determines whether a nanotube will conduct in a metallic or semiconducting manner. Carbon nanotubes possess many unique and remarkable properties. The measured electrical conductivity of metallic carbon nanotubes is in the order of 104 S/cm [66]. Since carbon nanotubes have very low density and long aspect ratios, they have the potential of reaching the percolation threshold at very low weight percent loading in the polymer matrix.

It was reported in the literature that adding CNT to silver-filled ICAs could enhance the electrical conductivity of the conductive adhesives greatly when the silver filler loading was still below percolation threshold [67]. Therefore, it is

possible to achieve the same level of electrical conductivity by adding a small amount of CNT to replace the silver fillers. Although CNTs have exceptional physical properties, incorporating them into other materials has been quite a challenge due to the surface chemistry of carbon. Problems such as phase separation, aggregation, poor dispersion within a matrix, and poor adhesion to the host must be overcome. A proper surface treatment could enhance the interaction between CNTs and the host matrix which could greatly improve CNT dispersibility in the matrix, and mechanical and electrical properties of the ICA [68, 69]. Mantena et al.'s research also showed that CNT-filled ICAs had higher bulk resistivity and contact resistance than traditional ICAs filled with silver flakes [70].

Copper Nanoparticles

Inoue et al. [71] investigated the development of conduction paths in a copper microrod-loaded ICA composed of an epoxy-based binder and aliphatic amine hardener during curing in air. The ICA exhibited a low electrical resistivity of ~10^{-4} Ωcm even after curing in air. The development of conduction paths in the adhesive occurs during curing by two different elementary steps including microstructure formation of a filler network and evolution of electrical conductivity between filler particles. The electrical conductivity between filler particles evolves regardless of the cross-linking reaction of the binder. A Cu-amine complex that forms in the adhesive paste can be reduced in the temperature range where conduction paths develop in the adhesive during curing in air.

Ho et al. [72] synthesized copper nanoparticles coated with an organic protection layer to prevent copper nanoparticle from oxidation, and evaluated the performance of ICAs filled with this particles (with 80 wt% filler loading). It was found that the bulk resistivity of ICA with organic-coated copper filler was more stable than that of ICA with pure copper filler under high temperature aging, but less stable than traditional Ag-filled ICAs.

AgNPs/Reduced Graphene Oxide (rGO)

Zeng et al. [73] synthesized Ag nanoparticles with the size from 15 to 20 nm and narrow size distribution, which were successfully grown on both sides of the reduced graphene oxide (rGO) nanosheets. The ECAs were prepared by mixing AgNPs/rGO, silver flakes, and epoxy. The results showed that, when the total amount of the conductive filler was maintained at 70 wt%, the mass fraction of AgNPs/rGO reached 0.2 wt%, and the bulk resistivity (8.76×10^{-5} Ω cm) was lower than that of filled pure silver flake (1.11×10^{-4} Ω cm).

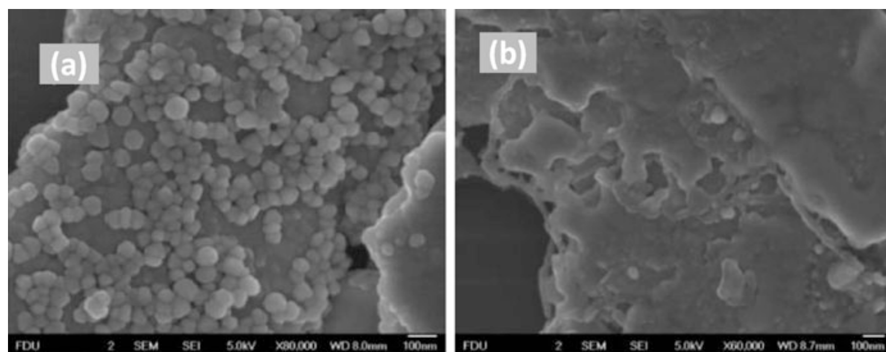

Fig. 10.9 (**a**) Ag nanoparticles formed on Ag flakes; (**b**) sintering of nanoparticles between Ag flakes at 180 °C [74]

In Situ NanoAg-Coated Silver Flakes

Jin et al. [74] developed a new approach for preparing interconnected micron-sized silver flakes, enabling the wide use of high conductive and flexible adhesives. First, a thin layer poly(dopamine) was coated on the silver flake surface by dopamine oxidative self-polymerization, which acted as the chemisorption sites of silver ions and enabled the reduced silver nanoparticles deposition. Then Ag nanoparticles were produced by one-step reduction and fixation on the surfaces of poly(dopamine)-coated silver flakes, which made the preferred uniform dispersion of nanoparticles in the silver flake-filled adhesives. They were able to produce a dense layer of silver nanoparticles with an average diameter less than 50 nm completely covered the silver flake surfaces (Fig. 10.9a), and the morphology studies showed the interconnection generated among flakes by sintering of silver nanoparticles (Fig. 10.9b). Furthermore, the electrical measurements suggested that both the coverage density of nanoparticles on the flake surfaces and the thickness of the coated poly(dopamine) layer played a role in the silver nanoparticles sintering, and hence of the electrical resistivity of the resultant adhesives.

10.5 Flip Chip Applications Using Isotropic Conductive Adhesives

A key factor in achieving a low-cost, flip chip technology is the use of isotropic conductive adhesives. In comparison to the classical flip chip (FC) technologies, the use of ICAs for the bumping and joining provide many advantages (Table 10.1).

Table 10.1 Advantages of flip-chip technologies utilizing ICAs

Advantages
Process simplification and reduction of indexing steps by eliminating activation and purification processes
A smaller temperature load on elements and wiring carriers
The availability of a large spectrum of material combinations
A broad range of applicable adhesive systems allows a selection of processing parameters and joining characteristics
Few requirements for under bump metallization (UBM) since alloy phase formation does not have to be considered

10.5.1 Polymer Bump Flip Chip

The polymer bumping method is a low-cost and efficient process conducted at the wafer-level and suitable for large-scale production. Data of joint resistance stability under accelerated aging conditions such as 85 °C/85 % relative humidity and temperature cycling demonstrates polymer flip chip interconnections are capable of long-term stability. The polymer flip chip assembly is compatible to a large range of rigid carriers, and heat-sensitive, flexible chip carriers.

Several flip-chip bumping and joining techniques have been reported in the literature. Flip chips using ICAs are often called polymer flip chips (PFC). The PFC process is a stencil printing technology in which an ICA is printed through a metal stencil to form polymer bumps on bond pads of IC devices subsequent to the under bump metallization deposition on aluminum termination pads. The sequential processes to achieve PFC interconnects are UBM deposition, stencil printing an ICA, bump formation (ICA solidification), flip chip attach to achieve electrical connections, and underfill for enhanced mechanical and environmental integrity [75–77]

10.5.2 Metal-Bumped Flip Chip Joints

ICAs can also be used to form electrical interconnections with chips that have metal bumps. In order for the ICAs to be used for flip-chip applications, they must be selectively applied to only those areas that are to be electrically interconnected. Also, the materials are not to spread during placement or curing to avoid creating electrical shorts between circuit features. Screen or stencil printing is most commonly used to precisely deposit the ICA pastes. However, to satisfy the scale and accuracy required for flip-chip, bonding requires very accurate pattern alignment. To overcome this difficult requirement, Matsushita developed a transfer method [78].

Raised studs or pillars are required on either the die or chip carrier. Matsushita uses a conventional ball bonder to form Au-stud bumps. Bumping is significantly

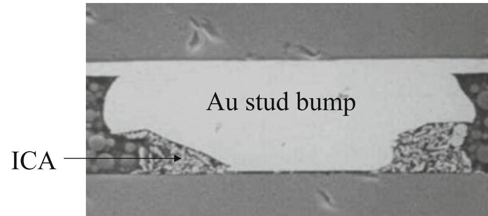

Fig. 10.10 A cross-sectional image of ICA flip-chip interconnect

faster than creating complete wire bonds. A ball bumping process eliminates the need for traditional sputtering and plating processes used for standard bump formation. To prevent the bond area from becoming too large, the bumps are formed in a conical shape. The bumps are pressed level by a flat surface, which adjusts both height and planarity. The ICA is selectively transferred on the bump tips by contacting the face of the die to a flat thin layer of the ICA which is produced by screen printing and whose transfer thickness is controlled by changing the printed layer thickness. Then the die is picked, aligned, and placed on a chip carrier. The whole assembly is exposed to heat to cure the ICA and form connections between the die and chip carrier. Finally, an underfill (an insulating adhesive) is introduced between the die and the chip carrier and cured. This method offers the options of oven curing an assembly since bonding pressure is not required. A specially formulated ICA is used to avoid silver migration, containing 20 % palladium in a silver palladium alloy. A cross-sectional image of flip chip interconnect formed with Au stud bump and ICA paste is shown in Fig. 10.10.

Another process for bonding a flip chip with metal bumps consists of screen-printing an ICA on a chip carrier, aligning and placing the chip, curing the ICA to form bonds, and underfilling. By using this approach, SINTEF Electronics conducted a comparison study between an ICA-bonded and solder-bonded flip chips on FR4 chip carrier with Ni/Au metallization. The number of thermal cycles (−55 to 125 °C) to failure for both solder and ICA flip chip circuits was compared. The study showed that stable contacts could be maintained for at least 1000–2000 cycles for ICA flip chip joints. This is comparable to the lifetime for solder flip chip joints. However, the variation among ICA samples was very high and optimization of assembly processes is needed in order to achieve more reproducible joint resistance [79].

10.5.3 ICA Process for Unbumped Chips

Another polymer flip-chip bumping process is known as micromachined bumping [80, 81]. Initially, Cr/Au contact metal pads for conductive-polymer bumps are deposited on Si wafers, followed by patterning a thick photoresist to create bump holes. A high aspect ratio and straight sidewall patterns are very important in shaping the conductive-polymer bumps. After the lithography, thermoplastic

conductive polymer materials, usually thermoplastic paste filled with Ag flake, is applied by either dispensing or screen printing the paste into the bump-hole patterns. The wafer is heated in a convection oven to remove the solvent. Due to the difference in curing conditions between the thick photoresist and conductive-polymer, the photoresist can be carefully stripped to expose the dried polymer bumps. Finally, the wafer is diced into individual chips.

Chips with thermoplastic bumps are placed on chip carriers and preheated to approximately 20 °C above the melting point of the polymer causing the bumps to reflow onto the matching chip carrier pads. Mechanical and electrical bonds are established as the chip carrier cools below the polymer melting temperature. To enhance the mechanical bonding strength, a small amount of pressure can be applied by placing a weight on the chip.

This flip-chip bonding technique has high potential to replace conventional solder flip-chip techniques for sensor and actuator systems, optical micro electro-mechanical systems (MEMS), optoelectronic multichip modules (OE-MCMs), and electronic system applications [81].

10.6 Surface Mount Applications

Tin-lead solders (Sn-Pb) have been the standard interconnect materials for surface mount technology (SMT) for many years. Recently, electronics industry is moving to lead-free. Among the lead-free interconnect materials are electrically conductive adhesives (ECAs) and lead-free solders [82–84]. Compared to soldering technology, ECA technology can offer numerous advantages such as fewer processing steps which reduces processing cost, lower processing temperature, which makes the use of heat-sensitive and low-cost chip carriers possible, and fine-pitch capability [85].

A study of conductive adhesive joining technology on printed circuit boards (PCB) was conducted by RÖRGREN et al. [86]. Six different isotropically conductive, silver-loaded epoxies were evaluated for the surface mount process. These adhesives were used to attach electrically and mechanically 160-lead, 25-mil pitch, quad flat pack-age (QFP) and 0805 chip components on PCBs with flash gold, passivated copper, and tin/lead metallization. The reliability of the conductive adhesive joints was evaluated in two types of environmental test: constant humidity at 60 °C and 90 %RH for 1000 h, and temperature cycling for 1000 h from −40 to 85 °C. Under these conditions, both the electrical performance, in terms of contact resistance, surface insulation resistance (SIR), and the mechanical strength of the adhesive bonds were evaluated. The results show that reliable conductive adhesive joining can be achieved for both chip components and QFP components on PCBs with all three metallizations tested. Under well-controlled conditions, and with the right choice of adhesive for the application in mind, no significant increase or variation in electrical resistance during the temperature cycling test was encountered. The humidity exposure test was found to have a minor impact on both contact

resistance and adhesion strength of most adhesives tested. In general, there was little difference between the different PCB metallizations used (except for SIR measurements). No evidence of silver migration could be observed after the humidity exposure for any of the adhesives tested.

Radio frequency identification (RFID) is quickly gaining a foothold in the identification and security industry. It is used in areas of healthcare, cashless ticketing system, inventory management, and security identification. Passive RFID tag is made up of a RFID chip, a coil antenna and the substrate where the chip is attached to the coil antenna. The tag is powered up only when the coil antenna captures the signal from a reader. To produce a RFID tag, the process starts from the foundry processing where a RFID wafer consisting of thousands of complex circuits is produced. This is followed by the tag assembly which consists of the following processes. First the wafer is thinned down where excess silicon is removed using the back grinding process, a mechanical-chemical polishing technique. Next the RFID dies are singulated from the wafer using mechanical dicing process where a diamond-grit coated blade is used. Once the chips are singulated, the die is attached to the antenna using one of the established assembly methods such as wire bonding or flip chip. Finally, it would be pack-aged to form a complete RFID tag.

However, one critical roadblock that prevents companies in adopting RFID technologies is the manufacturing cost with assembly cost as the main contributing factor. One approach to reduce the assembly cost is using surface mount technology. Currently, anisotropic conductive adhesives (ACA) and non-conductive adhesives (NCA) are being used for RFID flip chip assembly. However, these two approaches only permit series assembly which results in longer assembly time as compared to Surface Mount Device using ICA which allows batch screen printing. Isotropic conductive adhesives (ICA) joints however are more sensitive to moisture and mechanical stress. Lim et al. [87] utilized an ultraviolet (UV) curable epoxy to encapsulate the chip that had been surface mounted onto the substrate so as to increase the mechanical strength of the ICA and also to reduce the exposure to moisture which degrades the joints. The assembled RFID packages performed well in all the reliability tests including thermal cycling (-40 to 125 °C) and 30 °C/60% RH, and active tests on detection distance.

10.7 ICAs for CSP Applications

Matsushita Electric Industrial Co., Ltd. developed solderless joining technologies using nickel-filled isotropic conductive adhesives to mount a ceramic chip scale package (CSP-C) onto a FR4 board [88]. Nickel was selected instead of Ag because, unlike Ag, nickel does not migrate. A significant coefficient of thermal expansion (CTE) mismatch existed between the CSP-C ceramic chip carrier (CTE = 7 ppm/K) and the FR4 organic chip carrier (CTE = 16 ppm/K). This CTE mismatch resulted in large stress to be generated within the solder joints during

accelerated thermal cycle (ATC) testing which led to early failure due to solder fatigue. ICAs usually exhibit better thermo-mechanical properties than solders. In addition, metal-migration between joints is a great concern because the joints in a CSP area array package are arranged with a fine pitch.

The packaging process was as follows: (1) the ICA was screen-printed on the area array lands of the FR4 motherboard; (2) the CSP-C was mounted; (3) and the ICA was cured to form bonds. The Ni-filled conductive adhesive demonstrated a much higher resistance to metal migration compared to Ag-filled ICAs, and equivalent to solder joints. Also, the thermal fatigue life of the Ni-filled ICA joints was five times greater than comparable solder joints.

10.8 ICAs for Advanced Packaging Applications

10.8.1 Solar Cell

Thin solar cells are difficult to interconnect with standard soldering techniques. High temperature during soldering introduces stress on the joints and cells. This can cause warping and possible breakage of cells. Substituting soldering for a low temperature joining technique would avoid building up of mechanical stress, thus increasing process yield and reliability.

A promising alternative technique is interconnection with conductive adhesives because the processing temperature is much lower, depending on the applied adhesive. D.W.K. Eikelboom et al. [89] studied rear-contacted solar cells interconnected with conductive adhesives. The stress on thin cells and joints between traditional soldering and conductive adhesives was compared.

Solar cells generate high currents, requiring low resistances. Long-term stability in outdoor conditions requires excellent optical and mechanical properties. High volume production demands screen printable adhesives. Contacts made on silver-plated substrates with silver-plated tabs show excellent electrical properties. Contact resistances are in the milliohm range like soldered contacts.

Samples have been damp/heat tested along with soldered references. No degradation was observed after 2500 h at 85 °C/85 %RH and 200 temperature cycles (−40°C/+80°C).

10.8.2 3D Stacking

Wirebonding process applies significant mechanical force [90, 91] in order to produce a reliable friction welded connection, often creating latent defects within a conic region of the silicon underneath bonds in die thinned below 75 μm. Wirebond-induced defects can also extend beyond the bonded die itself through

underlying die attach materials and into die beneath the originally bonded die within the stack. Reverse loop bonding processes have been developed [92] to mitigate this problem in stacked die packages somewhat, although the same reliability issues often reemerge as die are further thinned below 50 μm. Wirebonding to extremely thin die presents a significant challenge, and an electrical interconnect process that dramatically reduces applied force during application will result in both enhanced yields and superior product reliability over traditional electrical interconnect methodologies.

Andrews et al. [93] demonstrated forming electrical interconnections along the edges of stacked integrated circuits by an extrusion process that utilizes automated needle dispense equipment to form local deposits of conductive adhesive paste. This vertical interconnect process was designed to form three-dimensional circuits without the imposition of significant mechanical forces that are known to cause mechanical damage to thin die or fragile substrate materials. The process was demonstrated with productivity rates that exceed 100 interconnections per minute. Figure 10.11 shows an image of a stack die package with conductive adhesive vertical interconnections. The paste extrusion process utilizes automated needle dispense equipment to produce electrically conductive structures from die-to-die, or die-to-substrate, without imposing any significant mechanical forces. The paste vertical interconnect process is insensitive to die type, die count (up to 128 vertical die have been demonstrated), stacking configuration or final packaging requirement (e.g., QFN, BGA, WL-CSP, etc.).

Significant processing cost advantages were achieved by cycle-time reduction vs. traditional wirebond stacked-die interconnect, because serial die attach/wirebond process steps are eliminated in favor of a single staging at each process tool regardless of die-count. Additional cost advantages were also found due to the elimination of gold (by eliminating the wirebonding process and reducing the gold thickness upon bondable surfaces). Further cost reduction could be achieved by adopting gang vertical interconnect methods, including but not limited to multi-needle dispense and print based methods [93].

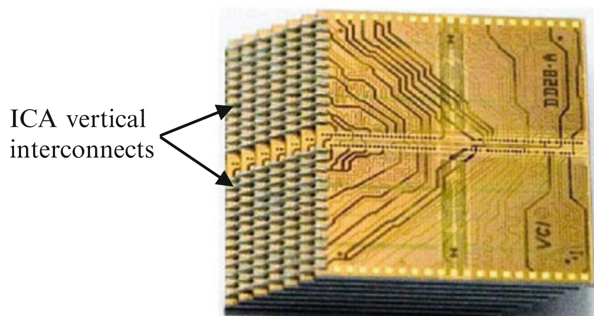

Fig. 10.11 Vertical interconnection formed by a conductive adhesive on stack die package

10.8.3 Microspring

Micromachined springs are attracting attentions in microsystem packaging for low-stress interconnection, high density and low-damage probing for device testing. For instance, new probe cards consisting of micro-machined springs are in practical use [94] and essential for high-performance device testing, because their dimensions can easily be smaller than a few hundred micrometers. They are therefore applicable to higher pad-density and smaller pad pitch chips, and capable of being effective in a test using high speed signals above 1 GHz. Curl-up micro-cantilever spring probes [95] and s-type microspring probes using multilayer electroplating [96] for the probe card applications were reported in the literature.

On the other hand, microsprings may also be required for microelectronic packaging. Flip-chip packages, which are utilized for high-performance microsystems, are carried out using the standard interconnect technologies, such as solder balls, gold bumps, and conductive adhesives. However, since their interconnect structures have very limited compliance, thermal expansion mismatches within the packages between the silicon integrated circuit (IC) and the package substrate can cause problems such as failures during thermal cycle testing and damages in low-k dielectrics. To overcome these, Chow et al. experimentally demonstrated that a compliant, low force (10 mgf), pressure contact using thin film microsprings [97] could make reliable electrical contact to a gold pad [98]. Furthermore, in 0-level MEMS packaging, a commonly applicable cap wafer may need through-hole interconnect vias and microsprings to interconnect the device electrodes.

Aiming to fabricate microspring probes without photolithography steps, T. Itohl et al. utilized an ultra-precise dispenser with three-axis stage system to develop a new three-dimensional microstructure forming method utilizing a continuously repeated dispensing of conductive adhesive pastes [99, 100]. The inner diameter of the nozzle used is 22 μm and the minimum dispense dot size was as small as 22 μm in diameter. High aspect ratio structures were realized by dispensing the paste dots repeatedly. By heating the substrate over 350 K, the organic solvent in the paste dispensed on the substrate vaporizes and the viscosity of the paste increases. Taking advantage of this process, overhanging structures such as cantilever shapes were formed when the nozzle was moved in lateral direction as shown in Fig. 10.12a. For example, in the case of the cantilever shown in Fig. 10.12b, 20 times dispensing for the post part and 40 times dispensing for the lever part were carried out. The shapes of cantilevers did not change after curing at 423–523 K for 30 min. It was found that fabricated micro cantilevers have probing resistance lower than 1 Ω with a low contact force of 1 mN. More complicated shapes such as spiral structure shown in Fig. 10.13 were successfully realized by controlling the dispense conditions and the substrate temperature.

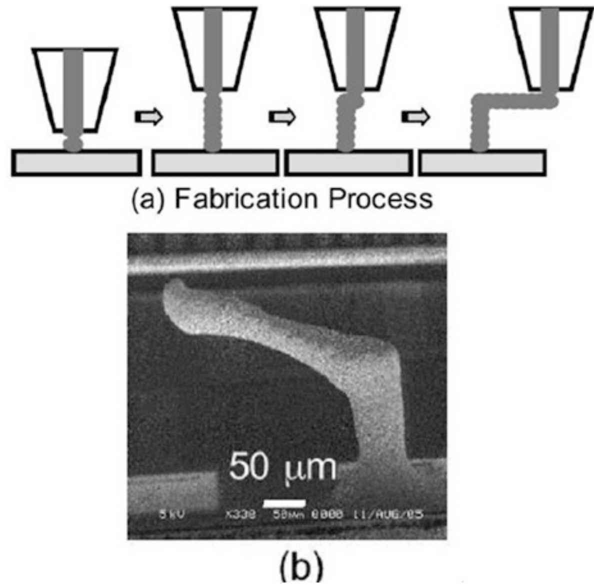

Fig. 10.12 (**a**) A schematic description of the fabrication process; (**b**) microcantilever springs fabricated using conductive paste continuous dispensing

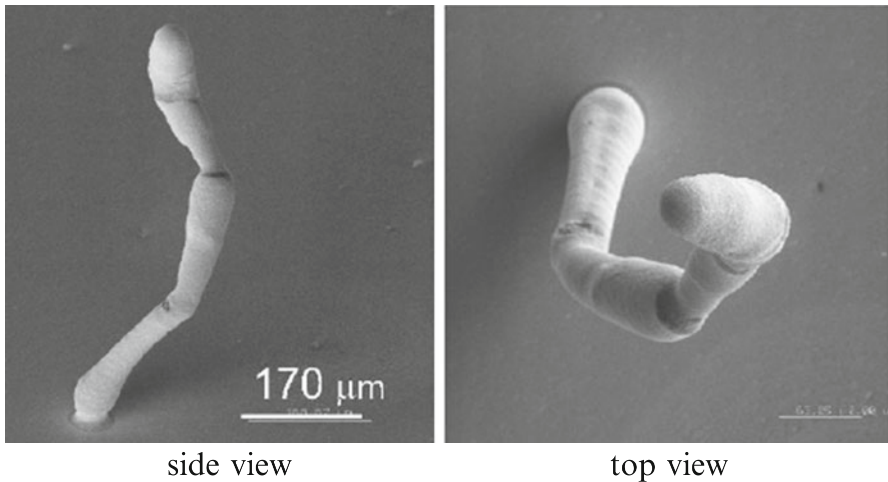

Fig. 10.13 A spiral structure fabricated using conductive adhesive dispensing

10.8.4 ICAs for Printed Circuit Board Applications

The electronics assembly industry has great interest in high-density PCBs (Printed Circuit Boards) with acceptable costs. One of the key problems for more efficient use of conventionally PCBs is plated through holes (PTH), because they consume a large fraction of PCB surface area. One of the solutions that can save the PCB

surface area is to use blind and buried vias in the design. Currently, many expensive plating and sequential lamination steps are needed to create most blind/buried vias. Recently, several new manufacturing technologies of PCBs have been introduced, e.g., ALIVH (Any Layer Inner Via Hole) which eliminates steps mentioned above [101, 102]. Any layer interstitial via hole structure enables interconnections between any two wiring layers of the board, and thus offers benefits of downsizing, shorter wiring length for high frequency circuit applications and ease of automatic designing. Moreover, components can be attached under the land, because via holes are filled with conductive paste. This fabrication process uses laminate-based substrates, where holes are filled with conductive adhesive material to make reliable multilayer interconnects. This technique allows highly space-efficient circuit design and production, but requires using the laminates with special properties, adhesives and advanced printing technologies. It will be very useful to implement the advantages of ALIVH technology into conventional double-sided PCBs. The idea of such process is based on applying electrically conductive adhesives for hole filling [103, 104]. The filling of plated through holes has been practiced for many years in order to improve the thermal performance of PCBs, particularly with BGA packages [105]. Other applications of hole filling procedure include filling vias in inner layers and blind vias in outside layers of PCBs made by SBU (sequential build-up) technology [106]. The main requirements of electrically conductive adhesives for the via filling applications are as follows [105, 107]:

1. Low viscosity to facilitate filling high aspect ratio vias
2. Stable enough to have a reasonable shelf life
3. Low electrical resistance: no higher than tens of milliohms electrical resistance per via (via depth 0.6 mm, aspect ratio 2:1)
4. Adhere well to the walls of through holes
5. Survive reliability tests including soldering shock test, 1000 thermal cycles of −55 to +125 °C, and dump heat tests 85 °C/85%RH
6. Have stable contact resistance in combination with non-noble metals including pure Sn or Sn/Pb alloys

Suzuki et al. [108] utilized a conductive adhesive with spherical copper powder (with an average particle size of 3–6 μm) to fill the via holes in an ALIVH. Low resistance and good reliability were achieved. Calculation and SEM image suggested the existence of metallic bond between copper particles and between copper particle and copper foil.

Kisiel et al. demonstrated filling mechanically drilled through holes with silver-filled isotropic conductive adhesives [103]. The average filling resistance of holes with a diameter of 0.6 mm and aspect ratio of 2.7:1 was about 150 mΩ. The resistance was stable after five times soldering. By changing the type of adhesives, the fill resistance was decreasing to below 100 mΩ, for the holes diameter 0.5 mm and aspect ratio 2:1 [104]. The additional advantage of applied adhesive in the holes (with a diameter of 0.5 mm) was good average fill resistance stability after 1000 thermal cycles (−40 to +125 °C); resistance changes do not exceed 20 %. Unfortunately, the average fill resistance after dump heat test 85 °C/85%RH significantly

exceeds 100 % [109]. However, the resistance of the holes of double-sided PCBs with Au metallization filled by conductive adhesives are in the range or below 50 mΩ per hole and showed stable resistance after dump heat test [110, 111]. Such resistance values can be acceptable by consumer electronic applications.

10.9 High-Frequency Performance of ICA Joints

Only limited work has been conducted to investigate the high frequency behaviors of ICA joints. J. Felba et al. [112] investigated a formulation of ICA that performed well as a solder replacement in microwave applications. The study involved in various different adhesive base materials and several types of main (silver flakes, nickel, and graphite) and additional (soot and silver semiflake powder) filler materials. In order to assess the usefulness of a given adhesive formulation, an additional gap in the gold strip of a standard microstrip bandpass filter was made and bridged by an adhesive bonded silver jumper. Both the quality factor (Q-factor) and loss factor (L) of the filter with the bonded jumper were measured at a frequency of 3.5 GHz in a preliminary experiment and at 3.5 and 14 GHz in a final experiment. It was determined that silver flake powders are the best filler materials for ICA for microwave applications because ICAs filled with the silver flake powders exhibit the highest Q-factor and lowest loss factor. Also, addition of soot should be avoided since it decreases the quality factor [112].

A study at Georgia Tech was reported where a flip-chip test vehicle was mounted on a FR4 chip carrier with a gold-plated copper transmission line [113]. The performance of eutectic Sn-Pb and ICAs were evaluated and compared using this test device. Both ICAs and eutectic Sn-Pb solder were determined to exhibit almost the same behavior at a frequency range of 45 MHz–2 GHz and the measured transmission losses for both materials were minimal. It was also found that the S_{11} characteristics of both Sn-Pb and ICAs after exposure to 85 °C/85 % relative humidity aging for 150 h did not vary from the signals prior to aging, but S_{12} value of the Sn-Pb joints deviated more than that of ICA joints after the aging.

Recently, Kaoru Hashimoto et al. [114] studied feasibility of the conductive adhesive joints for high-speed signal transmission, both transmission characteristics and power supply ability at the conductive adhesive joints using specially designed interconnection models which consisted of a high speed CMOS driver LSI, a model BGA package and a model circuit board. It was found that differential pulse signals could transmit without degradation at 12 Gbps through the eight conductive adhesive joints in daisy chain configuration, and the conductive adhesive joint exhibits waveform degradation in the case of long transition time. This was considered to be caused by its DC resistance which is about ten times higher than that of the solder joint. However, it showed less waveform degradation in the case of short transition time. This is probably caused by the capacitive coupling interference effect due to proximity arrangement of Ag flakes in the conductive adhesive.

10.10 Reliability of ICA Joints

To date, quite some work has been published demonstrating the usefulness and limitations of isotropic adhesives to bond a variety of surface mount compounds (e.g., QFP) and passive components (R and C) under different aging conditions using various circuit and component-metallizations [115]. Most of the isotropic conductive adhesives require noble metallizations (e.g., Au or AgPd) to survive harsh environmental conditions as for instance 85 °C/85%RH and temperature cycling from−40 to +125 °C. Most of the adhesives give poor results on SnPb surfaces, a few special types show better results in 85 C/85%RH. Deterioration of the electrical properties is due to an increase in the contact resistance. The bulk resistance of the adhesive, although considerably higher than that of solder, usually remains quite stable. On passivated Cu substrates reasonable good results were obtained.

Jon B. Nysæther et al. [116] compared the failure of flip chip on board (FCOB) with solder or ICA joints and with underfill under thermal cycling. The measurements of solder bump lifetime were compared to a lifetime model based on analytical calculations of solder strain. For two filled types of underfill with CTE nearly matched to that of solder, the measured average lifetimes vary from around 2700 to 5500 cycles. Measurements of the lifetime of FCOBs with ICA connections were carried out for two different material systems. The obtained lifetimes vary between approximately 500 and 4000 cycles. The lifetime seems to be dependent on the properties of the bump on the chip pad. Delamination, for instance at the ICA/bump interface, was found to be an important failure mechanism. The best results (>4000 cycles) were obtained for 5 μm high Ni/Au bumps.

Aiming to understand the performance of ICA interconnects under fracture and fatigue loading, J. Constable et al. [117] investigated performance of ICA interconnects under fracture and fatigue loading by monitoring resistance changes (micro-ohm sensitivity) of ICA joints during pull and fatigue testing (cyclic loading up to 1000 cycles). Observation of the fracture surface suggested that the ICA joint life depended upon the adhesive failure of the bond to the metal surface. It was observed that fracture strains for the ICAs were in the range of 20–38 %, and resistance remained approximately constant in the elastic region, but the resistance started to increase rapidly as soon as the pull-force departed from linear elastic behavior. For fatigue tests, linear displacement was ramped up the pre-programmed maximum displacement and ramped back to the starting position. It was observed that the shear strain for ICA joints surviving 1000 cyclic loading was typically 10 %, which is about an order of magnitude greater than solders. This suggests that using conductive adhesives may be advantageous for some flip chip applications. It is believed that since silver filler particles of ICAs cannot accommodate this large strain, the silver filler particles must move relative to one another as the epoxy matrix is strained. The most common pattern of resistance change was only increased to a point corresponding to about a 70 % loss in interface contact

resistance before sudden failure. This was an indication that the interface crack slightly propagated into the adhesive [117].

In an effort to gain a fundamental understanding of the fatigue degradation of ICAs, R. Gomatam et al. [118] studied the behavior of ICA joints under temperature and humidity conditions. The fatigue life decreased at elevated temperature and high humidity conditions. It was also observed that the fatigue life of the ICA joints decreased considerably as the temperature cycle frequency was decreased. This effect was attributed to the fact that as the frequency was decreased, the propagating crack was exposed to higher loads for longer periods of time, effectively resulting in high creep loading [118].

M. Yamashita et al. [119] investigated the interfacial degradation mechanism between Ag-filled ICA and SnPb surface finish at elevated temperatures. It was found that, at 150 °C, the interface degradation was caused by the preferential diffusion of Sn from the plated SnPb layer into the Ag filler in the ICA. Due to this diffusion, Ag-Sn intermetallic compounds were formed on the Ag fillers adjacent to the plating layer, and many large Kirkendall voids were formed in the SnPb plating layer. Also, an interfacial debonding was observed between the ICA and the SnPb plating layer after the heat exposure.

Xu et al. [120] investigated the mechanical behavior of electrically conductive adhesive (ECA) joints exposed to elevated temperature and relative humidity conditions and failure mechanisms of conductive adhesive joints. Three silver-filled, epoxy-based adhesives were used in conjunction with printed circuit board (PCB) substrates with metallizations of Cu/Ni/Au and Cu. Double cantilever beam (DCB) tests were adopted to investigate the effects of environmental aging on ECA joints. This study revealed that conductive adhesives as well as substrate metallizations both play important roles in the durability of conductive adhesive joints. The rate of water attack on the interface of conductive adhesive joints with Cu-plated PCB substrates is faster than for those with Au/Ni/Cu metallization. A possible explanation of this phenomenon was based on considerations of surface free energy and interfacial free energy. The fracture energy of all three ICAs decreased with time under the aging condition. Following drying of the aged conductive adhesive joints, the fracture energy recovered to some extent. This recovery in the fracture energy could be attributed to the reversible effect of plasticization of the bulk adhesives, as well as the regaining of bond strength between the adhesive and the substrate during drying at 150 °C. However, the fracture energy of the adhesive joints showed little recovery after the metal surface was oxidized. For ECA/Cu joints, water attack on the adhesive joint may be divided into three phases: displacing the adhesive from the substrate, oxidizing copper, and weakening the copper oxide. At the end of aging, the three ECA/Cu joints exhibited different modes of failure. ECA1/Cu joints failed interfacially along the adhesive/ copper oxide interface, while ECA2/Cu joints exhibited the locus of failure within the copper oxide layer. For ECA3/Cu joints, the failure occurred within the secondary layer of the adhesive, which is adjacent to the interface and is a

silver-depleted layer. XPS analysis of DCB failure surfaces suggested that diffusion of Cu to the Au surface might have occurred on the Au/Ni/ Cu-plated PCB substrates during aging. Copper oxide was detected on the substrate surface upon exposure of the conductive adhesive joints to the hot/wet environment [120].

S. Kuusiluoma et al. [121] compared the reliability of isotropically conductive adhesive (ICA) attachments on liquid crystal polymer (LCP) substrate to the reliability of lead-free solder (SnAgCu) attachments on same substrate material. The assembled components were similar surface mount components and the reliability was assessed through real-time measurements of contact resistance of each connection. The devices were subjected to two environmental stress tests: a thermal cycle test and a sinusoidal vibration. Results showed that when using LCP as a substrate material, the reliability of the device under thermal cyclic stress is somewhat inferior to the reliability of SnAgCu solder. No significant differences could however be observed from the vibration test results since none of the assemblies failed in the test. The failure analysis revealed that most failures occurred at the interface between component lead and the attachment material in both cases, but the test methods need to be developed to make further conclusions.

Ales Duraj et al. [122] investigated the influence of dynamic mechanical load (bending of testing boards) on resistance of the adhesive joints. The load was induced by a definite deflection of testing boards (fiberglass-laminated PCB assembled with 1206 SMD resistors). It was found that the applied dynamic load caused changes of basic electrical parameters of the bonds. The more the deflections applied the more changes of resistance were observed. The increase of joint resistance was not linear and was not same for all tested adhesives.

J. Lee et al. [123] studied the junction resistance variation of Ag epoxy-filled ICAs on Cu and immersion-Ag finished PWB during the 85° C/85 %RH aging. It was found that the junction resistances of immersion-Ag PWB are lower than those of Cu-finished PWB, and the junction resistance shift on the immersion Ag PWB was much smaller than those of Cu-finished PWB during the aging.

10.11 Recent Advances on ICAS

10.11.1 Improvement of Electrical Conductivity

Electrical conductivity of ICAs is inferior to solders. Even though the conductivity of ICAs is adequate for most applications, a higher electrical conductivity of ICAs is still needed. To develop a novel ICA for modern electronic interconnect applications, a thorough understanding of the materials is required.

10.11.2 Eliminate Lubrication Layer

An ICA is generally composed of a polymer binder and Ag-flake filler material. A thin layer of organic lubricant is present on the surface of the Ag flakes. This lubricant layer plays an important role in the performance of ICAs, including the dispersion of Ag flakes in adhesives, and the rheology of the adhesive formulations [124–127]. The organic layer consist of a Ag salt formed between the Ag surface and the lubricant, which typically is a fatty acid such as stearic acid [127, 128]. This lubricant layer affects the conductivity of an ICA because it is electrically insulating. To improve conductivity, the organic lubricant layer must be partially or fully removed through the use of chemical substances that can dissolve the organic lubricant layer [127–129]. However, the viscosity of an ICA paste may increase if the lubricant layer is removed. An ideal chemical substance (or lubricant remover) should be latent (does not remove the lubricant layer) at room temperature, but become active (capable of removing the lubricant layer) at a temperature slightly below the cure temperature of the polymer binder. The lubricant remover can be a solid short-chain acid, a high-boiling-point ether such as diethylene glycol monobutyl ether or diethylene glycol monoethyl ether acetate, and a polyethylene glycol with a low molecular weight [127–129]. These chemical substances can improve electrical conductivity of ICAs by removing the lubricant layer on the Ag-flake surfaces and providing an intimate flake–flake contact [127–129].

10.11.3 Increase Shrinkage

In general, ICA pastes exhibit low electrical conductivity before cure, but the conductivity increases dramatically after they are cured. ICAs achieve electrical conductivity during the cure process, mainly through a more intimate contact between Ag flakes caused by the shrinkage of polymer binder [130]. Accordingly, ICAs with high cure shrinkage generally exhibit the best conductivity. Therefore, increasing the cure shrinkage of a polymer binder is another method for improving electrical conductivity. For ICAs based on epoxy resins, a small amount of a multifunctional epoxy resin can be added into the formulation to increase cross-linking density, shrinkage, and thus increase conductivity [130].

10.11.4 Transient Liquid Phase Fillers

Another approach for improving electrical conductivity is to incorporate transient liquid-phase sintering metallic fillers into ICA formulations. The filler used is a mixture of a high melting-point metal powder (such as Cu) and a low-melting-point alloy powder (such as Sn-Pb). During the sintering process, the mixture is heated to

just above the liquidus temperature of the lowest melting-point component. The liquid phase has solubility in the solid phase particles and is absorbed. As the heating progresses, the composition of the liquid phase changes until it isothermally solidifies. The electrical conductivity is established through a plurality of metallurgical connections formed in situ from these two powders in a polymer binder. The polymer binder fluxes both the metal powders and the metals to be joined and facilitates the transient liquid bonding of the powders to form a stable metallurgical network for electrical conduction, and also forms an interpenetrating polymer network providing adhesion. High electrical and thermal conductivity can be achieved using this method [131–135]. The ICA joints formed include metallurgical alloying to the junctions as well as within the adhesive itself. This provides a stable electrical connection during elevated temperature and humidity aging. In addition, the ICA joints showed good impact strength due to the metallurgical interconnection between the conductive adhesive and the components. One critical limitation of this technology is that the numbers of combinations of low melt and high melt fillers are limited. Only certain combinations of metallic fillers that are mutually soluble exist to form this type of metallurgical interconnections. In addition, the bonding substrate surfaces need to be properly metallized in order for this type of adhesive to work and work metallurgical connection between the ICA and bonding substrate surfaces.

10.11.4.1 Incorporation of Intrinsic Conducting Polymers

Gumfekar et al. conducted some interesting study on incorporating intrinsic conducting polymer polyaniline (PANI) in the silver flake-filled ICAs [136]. It was reported that adding the PANI facilitates the formation of a continuous network of conductive fillers, and results in a reduced percolation threshold. From results, it is worth mentioning that a percolation threshold was reached at lower concentration of the Ag flakes, when PANI was added to the Ag-epoxy composite. It was explained that the added polyaniline acted as charge carrier medium in the insulating region between Ag flakes, and reduce the tunneling resistance and constriction resistance at mesoscale contact area between Ag particles. Polyaniline seemed to decrease the constriction resistance by establishment of contact between two Ag particles.

10.11.4.2 Polymer Resin Alloy

Inoue et al. studied how polymer alloying effects can affect electrical conductivity in conductive adhesives containing Ag flakes and micro-particles [137]. They reported that necking (partial sintering) between the Ag micro-fillers was induced by specific polymeric matrix composition during curing and post-annealing in these adhesives. Low resistivities (10^{-5} Ω cm) were achieved after curing at 150 °C in Ag

flake-loaded adhesives. Because the Ag micro-filler sintering behavior can be controlled by the matrix composition, matrix-chemistry-based material design will be important for the development of ECAs.

10.11.5 Improvement of Contact Resistance Stability

Contact resistance between an ICA (generally a Ag-flake-filled epoxy) and non-noble metal finished components increases dramatically during elevated temperature and humidity aging, especially at 85 °C/85 %RH.

10.11.5.1 Causes for Resistance Increase

Two main mechanisms, simple oxidation and corrosion of the non-noble metal surfaces, have been proposed in the literature as the possible causes for the increase in contact resistance of ICA joints during elevated temperature and humidity aging. Simple oxidation of the non-noble metal surface is claimed as the main reasons for the observed increased resistance. Corrosion is claimed as the possible mechanism for resistance increase only by several investigators [138–140]. One study strongly indicates that galvanic corrosion rather than simple oxidation of the non-noble metal at the interface between an ICA and non-noble metal is the main reason for the shift in contact resistance of ICAs (Fig. 10.14) [141, 142]. The non-noble acts as the anode, and is reduced to a metal ion ($M-ne = M^{n+}$) due to the loss of electrons. The noble metal acts as a cathode, and its reaction generally is $2H_2O+O_2+4e=4OH^-$. Then M^{n+} combines with OH- to form a metal hydroxide or metal oxide. As a result of this electrochemical (corrosion) process, a layer of metal hydroxide or metal oxide is formed at the interface that is electrically insulating, causing the contact resistance to increase dramatically [141, 142].

10.11.5.2 Approaches to Stabilize Contact Resistance

Reduce Moisture Absorption

Galvanic corrosion requires the presence of moisture. An electrolyte solution must be formed at the interface before galvanic corrosion can occur. Therefore, one way to prevent galvanic corrosion at the interface between an ICA and the non-noble metal surface is to lower the moisture absorption of the ICA. ICAs that have low moisture absorption generally exhibit more stable contact resistance on non-noble surfaces compared with those with high moisture absorption [143, 144]. Without an electrolyte, galvanic corrosion rate is very low. The electrolyte in this case is mainly from the impurity of the polymer binder (generally epoxy resins). Therefore, ICAs formulated with high purity resins should perform better.

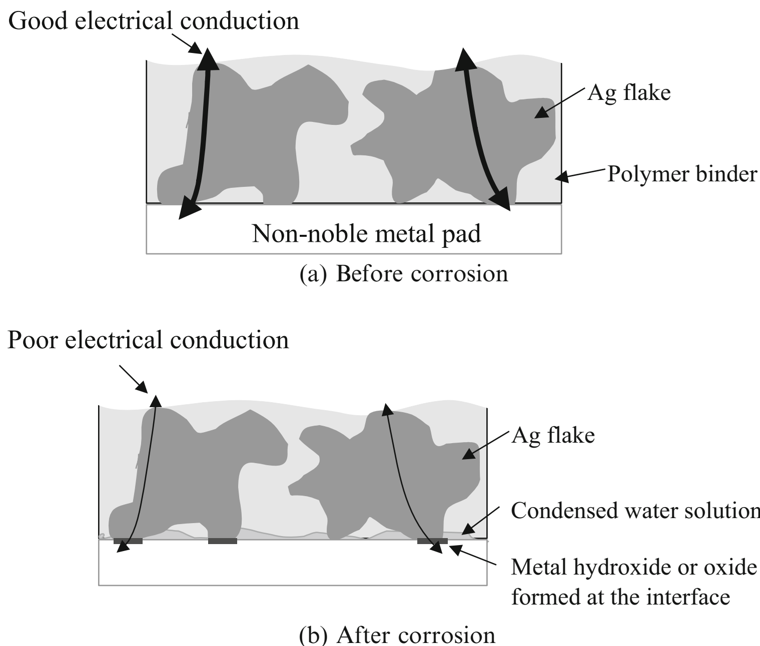

Fig. 10.14 Schematic depicting the effect of galvanic corrosion of a non-noble metal pad on electrical conduction of a silver-filled ICA. (**a**) Good electrical conduction before corrosion. (**b**) Poor electrical conduction due to the formation of a metal hydroxide or oxide formation as a result of galvanic corrosion

Use of Corrosion Inhibitors

Another method of preventing galvanic corrosion is to introduce organic corrosion inhibitors into ICA formulations [142–145]. In general, organic corrosion inhibitors act as a barrier layer between the metal and environment forming a film over the metal surfaces [146–149]. Some chelating compounds are especially effective in preventing metal corrosion [148]. Most organic corrosion inhibitors react with the epoxy resin at a specific temperature. Therefore, if an ICA is epoxy-based, the corrosion inhibitors must not react with the epoxy resin during curing which would cause them to be consumed and lose their effect. Organic corrosion inhibitors are thoroughly discussed in the literature [147, 149]. Figure 10.15 shows the effect of a chelating corrosion inhibitor on the contact resistance between an ICA and a Sn/Pb surface. It can be seen that this corrosion inhibitor is very effective in stabilizing the contact resistance.

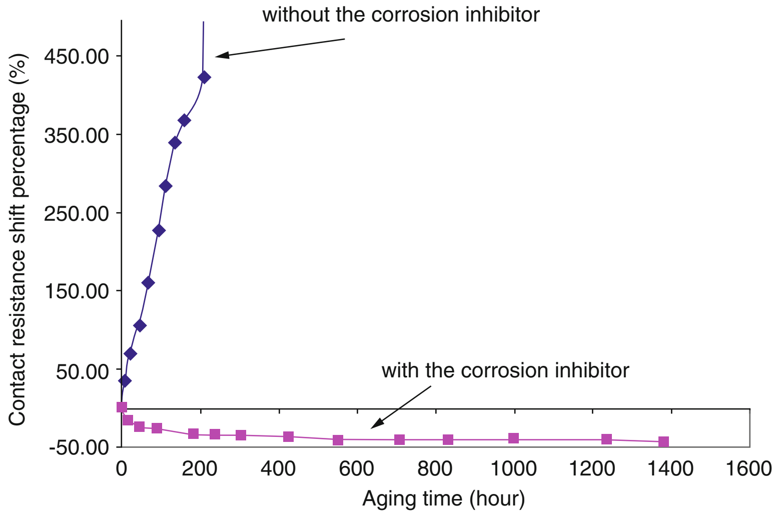

Fig. 10.15 Effect of a corrosion inhibitor on contact resistance between an ICA and a Sn-Pb surface with time, aging condition: 85 °C/85 %RH

Use of Oxygen Scavengers

Since oxygen accelerates galvanic corrosion, oxygen scavengers can be added into ICA formulations to slow down the corrosion rate [149]. When oxygen molecules diffuse through the polymer binder, they react with the oxygen scavenger and are consumed. However, when the oxygen scavenger is completely depleted, then oxygen can again diffuse into the interface and accelerate the corrosion process. Therefore, oxygen scavengers only delay the galvanic corrosion process. Similar to corrosion inhibitors, the oxygen scavengers used must not react with the epoxy resin at its cure temperature [146, 150–153].

Sharp-Edge Filler Particles

Another approach of improving contact resistance stability during aging is to incorporate some electrically conductive particles, which have sharp edges and referred as oxide-penetrating fillers, into the ICA formulations. Force must be provided to drive the oxide-penetrating particles through the oxide layer of adjoining particles and metal pads, and keep them in position. This can be accomplished by employing polymer binders that show high shrinkage when cured as discussed in Sect. 10.11.3 [154]. This concept is used in Poly-Solder (a silver-loaded ICA material patented by Poly-Flex Circuits), which has good contact resistance stability with standard surface-mounted devices (SMDs) on both solder-coated and bare circuit boards [154].

10.11.6 Improvement of Impact Performance

Impact performance is a critical property of solder replacement ICAs. There has been continuing efforts in developing ICAs that have better impact strength to pass the drop test, a standard test used to evaluate the impact strength of ICAs.

Nano-sized metal particles were used in ICAs to improve the electrical conduction and mechanical strength. Using nano-sized particles, agglomerates are formed due to surface tension effect [155]. Another approach is simply to decrease the filler loading to improve the impact strength [156]. However, such a process reduces the electrical properties of the conductive adhesives. A recent development was reported where conductive adhesives were developed using resins of low modulus so that this class of conductive adhesives could absorb the impact energy developed during the drop test [157]. However, the electrical properties of these materials were not mentioned in the paper. Conformal coating of the surface-mounted devices was used to improve mechanical strength. It was demonstrated that conformal coating could improve the impact strength of conductive adhesives joints [158].

Rao et al. study indicated that the impact performance of an ICA is highly dependent on its damping property (loss factor, tan δ) [159].

More recently, Xu et al. [160] designed a novel falling wedge test to quantitatively characterize the impact resistance of electrically conductive adhesives. The viscoelastic energy, which is a result of the internal friction created by chain motions within the adhesive material, has played an important role in the fracture behavior of the conductive adhesives. As a measure of the internal friction, the loss factor was found to be an indicator of an adhesive's ability to dissipate the mechanical energy through heat. By quantitatively relating the impact fracture energy of the adhesive joints to the loss factors of the ICAs, the author demonstrated that the impact fracture energy tends to exhibit a logarithmic relationship with the corresponding loss factor, as the increased loss factor at the test conditions consistently results in the improved impact performance. This finding suggests that the impact performance of a conductive adhesive may be improved by formulating the adhesive with good damping ability under impact conditions that may be encountered in the service.

Aiming at formulating ICAs with high damping property, D. Lu et al. developed a class of conductive adhesives which is based on an epoxide-terminated polyurethane (ETPU) [161–163]. This class of conductive adhesives has the properties of polyurethane materials, such as high toughness and good adhesion. The modulus and glass transition temperature of the ICAs can be adjusted by incorporating some epoxy resins such as bisphenol-F epoxy resin. Conductive adhesives based on the ETPU showed a broad loss factor (tan δ) peak with temperature and a high tan δ value at room temperature. The tan δ value of a material is a good indication of the damping property and impact performance of the material. In general, the higher the tan δ value, the better the damping property (impact strength) of the material. As an example, changes in tan δ and modulus with temperature of an ETPU-based ICA

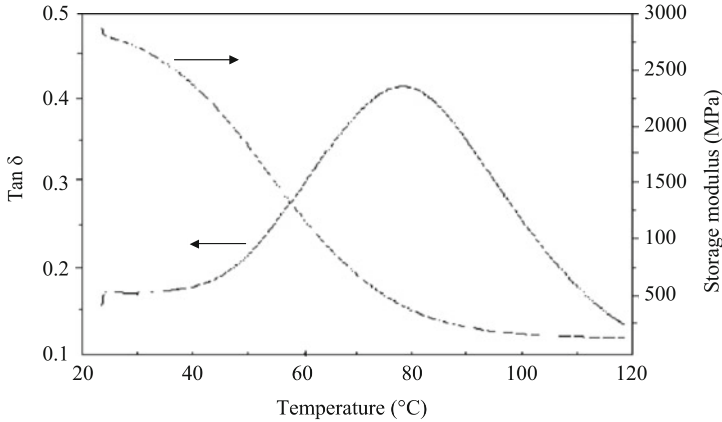

Fig. 10.16 Changes of tan δ and storage modulus with temperature of an ETPU-based conductive adhesive

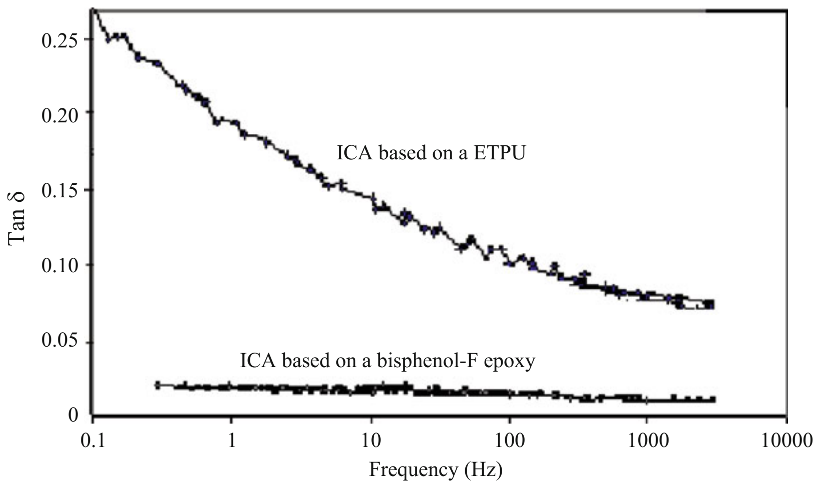

Fig. 10.17 Loss factor (tan δ) vs. frequency of two ICAs

which were measured by a Dynamic Mechanical Analyzer (DMA) are shown in Fig. 10.16. ICA based on ETPU resin also showed much higher loss factor (tan δ) in a wide frequency range than the ICA based on bisphenol-F epoxy resin (Fig. 10.17). This indicated that the ICAs based on ETPU resin should exhibit good damping property and improved impact performance in different electronic packages. This class of conductive adhesives showed superior impact performance and substantially stable contact resistance with non-noble metal surfaces, such as Sn/Pb, Sn, and Cu [161–163].

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