Nano-conductive Adhesives for Nano-electronics Interconnection

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Abstract With the phasing out of lead-bearing solders, electrically conductive adhesives (ECAs) have been identified as one of the environmentally friendly alternatives to tin/lead (Sn/Pb) solders in electronics packaging applications. In particular, with the requirements for fine-pitch and high-performance interconnects in advanced packaging, nanoconductive adhesives are becoming more and more important due to the special electrical, mechanical, optical, magnetic, and chemical properties that nano-sized materials can possess. There has been extensive research for the last few years on materials and process improvement of ECAs, as well as the advances of nanoconductive adhesives that contain nano-filler such as nanoparticles, nanowires, or carbon nanotubes and nanomonolayer graphenes. In this chapter, recent research trends on electrically conductive adhesives (ECAs) and their related nanotechnologies are discussed, with the particular emphasis on the emerging nanotechnology, including materials development and characterizations, processing optimization, reliability improvement, and future challenges/opportunities identification. The state of the art on nanoisotropic/anisotropic conductive adhesives incorporated with nanosilver, carbon nanotubes, and nanonickel, and their recent studies on those for flexible nano/bioelectronics, transparent electrodes, and jettable processes are addressed in this chapter. Future studies on nanointerconnect materials are discussed as well.

Keywords Electrically conductive adhesives (ECAs) · Isotropically conductive adhesives (ICA) · Percolation threshold · Nanotechnology · Carbon nanotubes (CNT) · Self-assembled monolayer (SAM) · Thermo-compression bonding (TCB) · Sintering · Current-carrying capability · Anisotropic conductive adhesives (ACAs) · Fine-pitch interconnection · Nanoconductive fillers · Transparent electrodes

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1 Introduction

Miniaturization of electronic and photonic devices is a demanding trend in current and future technologies including consumer products, military, biomedical, and space applications. In order to achieve this miniaturization, new packaging technologies have emerged such as embedded active and passive components and 3D packaging, where new packaging designs and materials are required.

Fine-pitch interconnection is one of the most important technologies for the device miniaturizations. Metal solders including eutectic tin/lead solder and lead-free alloys are the most common interconnect materials in the electronic/photonic packaging areas.

Conventional eutectic tin/lead solder or lead-free solders cannot meet the requirements for fine-pitch assembly due to their stencil printing resolution limit and bridging issues of solders in fine-pitch bonding, which is an intrinsic characteristic of metal solders.

Recently, polymer-based nanomaterials have been intensively studied to replace the metal-based interconnect materials, and many research efforts to enhance material properties of the electrically conductive adhesives (ECAs) are on going. Furthermore, incorporating nanotechnology into the ECA systems not only enables the ultra-fine-pitch capability but also enhances the electrical properties such as reducing the percolation threshold and improving the electrical conductivity.

In this chapter, recent research and study trends on ECAs and their related nanotechnologies are discussed, and the future of the nanomaterial-based polymer composites for fine-pitch interconnection is reviewed.

Electrically conductive adhesives (ECAs) are composites of polymeric matrices and electrically conductive fillers. The polymeric resin, such as an epoxy, a silicone, or a polyimide, provides physical and mechanical properties such as adhesion, mechanical strength, impact strength, and the metal filler (such as, silver, gold, nickel, or copper) conducts electricity. Metal-filled thermoset polymers were first patented as electrically conductive adhesives in the 1950s [1–3]. Recently, ECA materials have been identified as one of the major alternatives for lead-containing solders for microelectronics packaging applications. ECAs offer numerous advantages over conventional solder technology, such as environmental friendliness, mild processing conditions (enabling the use of heat-sensitive and low-cost components and substrates), fewer processing steps (reducing processing cost), low stress on the substrates, and fine-pitch interconnect capability (enabling the miniaturization of electronic devices) [4–9]. Therefore, conductive adhesives have been used in flat panel displays such as LCD (liquid crystal display), and smart card applications as an interconnect material and in flip-chip assembly, CSP (chip-scale package) and BGA (ball grid array) applications in replacement of the solder. However, no currently commercialized ECAs can replace tin-lead metal solders in all applications due to some challenging issues such as lower electrical conductivity, conductivity fatigue (decreased conductivity at elevated temperature and humidity aging or normal use condition) in reliability testing, limited current-carrying capability, and poor impact strength. Table 1 gives a general comparison between tin-lead solder and a generic commercial ECA [6].
Depending on the conductive filler loading level, ECAs are divided into isotropically conductive adhesives (ICAs), anisotropically conductive adhesives (ACAs) and nonconductive adhesives (NCAs). For ICAs, the electrical conductivity in all $x$-, $y$-, and $z$-directions is provided due to high filler content exceeding the percolation threshold. For ACAs or NCAs, the electrical conductivity is provided only in $z$-direction between the electrodes of the assembly. Figure 1 shows the schematics of the interconnect structures and typical cross-sectional images of flip-chip joints by ICA, ACA, and NCA materials illustrating the bonding mechanism for all three adhesives.

Isotropic conductive adhesives, also called as “polymer solder,” are composites of polymer resin and conductive fillers. The adhesive matrix is used to form a mechanical bond for the interconnects. Both thermosetting and thermoplastic materials are used as the polymer matrix. Epoxy, cyanate ester, silicone, polyurethane, etc., are widely used thermosets, and phenolic epoxy, maleimide acrylic preimidized...
polyimide, etc., are the commonly used thermoplastics. An attractive advantage of thermoplastic ICAs is that they are reworkable, i.e., can easily be repaired. A major drawback of thermoplastic ICAs, however, is the degradation of adhesion at high temperature. A drawback of polyimide-based ICAs is that they generally contain solvents. During heating, voids are formed when the solvent evaporates. Most of commercial ICAs are based on thermosetting resins. Thermoset epoxies are by far the most common binders due to the superior balanced properties, such as excellent adhesive strength, good chemical and corrosion resistances, and low cost, while thermoplastics are usually added to allow toughening and rework under moderate heat. The conductive fillers provide the composite with electrical conductivity through physical contact between the conductive particles. The possible conductive fillers include silver (Ag), gold (Au), nickel (Ni), copper (Cu), and carbon in various forms (graphites, carbon nanotubes, etc.), sizes, and shapes. Among different metal particles, silver flakes are the most commonly used conductive fillers for current commercial ICAs because of the high conductivity and the maximum contact between flakes. In addition, silver is unique among all the cost-effective metals by nature of its conductive oxide. Oxides of most common metals are good electrical insulators. Copper powder, for example, becomes a poor conductor after oxidation/aging. Nickel and copper-based conductive adhesives generally do not have good resistance stability. As such, electrical reliability issues of ECA joints, in particular on non-noble metal finishes at elevated temperature and high relative humidity are of critical concern for implementing ECAs into the high-performance device interconnects. Intensive studies on this ECA joint failure led to understanding of the failure mechanisms, that corrosion at the ECA joints was the underlying mechanism rather than a simple oxidation process of the non-noble metal used [10, 11] (Fig. 2). Under the elevated temperature/humidity (for example, 85°C/85%RH), the non-noble metal acts as an anode, and is oxidized by losing electrons, and then turns into metal ion (M−ne− = Mn+n). The noble metal acts as a cathode, and its reaction generally is 2H2O + O2 + 4e− = 4OH−. Then Mn+ combines with OH− to form a metal hydroxide, which further oxidizes to metal oxide. After corrosion, a layer of metal hydroxide or metal oxide is formed at the interface. Because this layer is electrically insulating, the contact resistance increases dramatically.

Since this underlying mechanism was reported, many research activities for reliable ECAs have been intensively conducted via various approaches, such as using low moisture absorption resins, incorporating corrosion inhibitors or oxygen scavengers, using sacrificial anode materials and oxide-penetrating sharp particles [10, 12–15]. In addition, many approaches to improve the electrical conductivity of ECAs have been reported, such as increasing the cure shrinkage of the matrix resin, replacing a lubricant of Ag flake with a shorter chain length carboxylic acid, adding an in-situ reducing agent for preventing the Ag flake-surface oxidation and adding low melting point alloys (LMA) for enhancing conductivity [16–21]. With the help of those intensive researches on enhancing the ECA performance, recently, ICAs
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Fig. 2 Metal hydroxide or oxide formation after galvanic corrosion

have also been considered as an alternative to tin/lead solders in surface mount technology (SMT) [22, 23], flip chip, [24] and other applications.

Anisotropic conductive adhesives (ACAs) or anisotropic conductive films (ACFs) provide uni-directional electrical conductivity in the vertical or Z-axis. This directional conductivity is achieved by using a relatively low-volume loading of conductive fillers (5–20 vol.%). The low-volume loading is insufficient for inter-particle contact and prevents conductivity in the X–Y plane of the adhesives. The Z-axis adhesive, in film or paste form, is interposed between the surfaces to be connected. Heat and pressure are simultaneously applied to this stack-up until the particles bridge the two conductor surfaces.

The ACF-bonding process is a thermo-compression bonding as shown in Fig. 3. In case of tape-carrier packages (TCP) bonding, the ACF material is attached on a glass substrate and pre-attached. Final bonding is established by the thermal cure of the ACF resin, typically at 150–220°C, 3–20 s, and 100–200 MPa, and the conductive particle deformation between the electrodes of TCP and the glass substrate by applied bonding pressure.

Interconnection technologies using ACFs are major packaging methods for flat panel display modules to be of high resolution, light weight, thin profile,
and low power consumption [25], and are already successfully implemented in
the forms of outer lead bonding (OLB), flex to PCB bonding (FPCB), reli-
able direct chip attach such as chip-on-glass (COG), chip-on-film (COF) for flat
panel display modules [26–29], including liquid crystal display (LCD), plasma
display panel (PDP), and organic light-emitting diode display (OLED). As for
the small and fine-pitched bump of driver ICs to be packaged, fine-pitch capa-
bility of ACF interconnection is much more desired for COG, COF, and even
OLB assemblies. There have been advances in development works for improved
material system and design rule for ACF materials to meet fine-pitch capa-
bility and better adhesion characteristics of ACF interconnection for flat panel
displays.

In addition to the LCD industry, ACA/ACF is now finding various applica-
tions in flex circuits and surface mount technology (SMT) for chip-scale package
(CSP), application-specific integrated circuit (ASIC), and flip-chip attachment for
cell phones, radios, personal digital assistants (PDAs), sensor chip in digital cam-
ers, and memory chip in lap-top computers. In spite of the wide applications
of ACA/ACF, there are some key issues that hinder their implementations as
high-power devices. The ACA/ACF joints generally have lower electrical con-
ductivity, poor current-carrying capability, and electrical failure during thermal
cycling.

To meet the requirements for future fine-pitch and high-performance intercon-
nects in advanced packaging, ECAs with nanomaterial or nanotechnology attract
more and more interests due to the specific electrical, mechanical, optical, magnetic,
and chemical properties. There has been extensive research on nanoconductive
adhesives, which contain nano-filler such as nanoconductive particles, nanowires,
or carbon nano tube (CNT). This chapter will provide a comprehensive review of
most recent research results on nanoconductive adhesives.
Recent Advances on Nanoisotropic Conductive Adhesive (Nano-ICA)

2.1 ICAs with Silver Nanowires

Wire-type nano1D materials (such as silver nanowires and CNT) have been addressed for their interconnect applications because of the flexibility and lowering the percolation threshold in composites. Those advantages bring stress absorbing as well as light-weight interconnections. Silver nanowires are one of the important 1D materials for interconnect due to their high electrical conductivity. An ICA filled with nanosilver wires has been reported and compared to two other ICAs filled with micrometer-sized (roughly 1 μm and 100 nm, respectively) silver particles for the electrical and mechanical properties [30]. It was found that, at a low filler loading (e.g., 56 wt%), the bulk resistivity of ICA filled with the Ag nanowires was significantly lower than the ICAs filled with 1 μm or 100 nm silver particles. The better electrical conductivity of the ICA-filled nanowires was contributed to the fewer number of contact (lower contact resistance) between nanowires, more stable conductive network, and more significant contribution from the tunneling effects among the nanowires.

It was also found that, at the same filler loading (e.g., 56 wt%), the ICAs filled with Ag nanowires showed similar shear strength to those of the ICAs filled with 1 μm and 100 nm, respectively. However, to achieve the same level of electrical conductivity, the filler loading must be increased to at least 75 wt% for the ICA filled with micro-sized Ag particles, and the shear strength of these ICAs is then decreased (lower than that of the ICA filled with 56 wt% nanowires) due to the higher filler loading.

Chen et al. reported synthetic routes of Ag nanowires for conductive adhesive applications and demonstrated that the electrical conductance of a multicomponent system (mixture of different geometry fillers) was better than that of a single-component system (e.g., sphere or flake themselves). A possible mechanism was described in the report as these nanowires act as bridges to establish perfect linkage among particles, and the probability of contact and contact area becomes more than the cases without wires [31].

2.2 Effect of Nano-sized Silver Particles to the Conductivity of ICAs

Nano-sized fillers are being introduced into the ECA to replace the micro-sized silver flakes in recent research. Lee et al. studied the effects of nano-sized filler to the conductivity of conductive adhesives by substituting micro-sized Ag particles with nano-sized Ag colloids either in part or as a whole to a polymeric system (polyvinyl acetate - PVAc) [32]. It was found that, when nano-sized silver particles were added into the system at 2.5 wt% each increment, the resistivity
increased in almost all the cases, except when the quantity of micro-sized silver was slightly lower than the threshold value. At that point, the addition of about 2.5 wt% brought a significant decrease in resistivity. Near the percolation threshold, when the micro-sized silver particles were still not connected, the addition of a small amount of nano-sized silver particles helped to build the conductive network and lowers the resistivity of the composite. However, when the filler loading was above the percolation threshold and all the micro-sized particles were connected, the addition of nano-particles seemed only to signify the relative contribution of contact resistance between the particles. Due to its small size, for a fixed amount of addition, the nano-sized silver colloid contained a larger number of particles when compared with micro-sized particles. This large number of particles should be beneficial to the connection between particles. However, it also inevitably increased the contact resistance. As a result, the overall effect was an increase in resistivity upon the addition of nano-sized silver colloids. They also studied the effects of temperature on the conductivity of ICAs. Heating the composite to a higher temperature could reduce the resistivity significantly. This is likely due to the high surface activity of nano-sized particles. For micro-sized paste, this temperature effect was considered negligible. The interdiffusion of silver atoms among nano-sized particles helped to reduce the contact resistance quite significantly and the resistivity reached $5 \times 10^{-5}$ $\Omega$ cm after treatment at 190°C for 30 min.

Ye et al. reported that the addition of nanoparticles showed a negative effect on electrical conductivity [33]. They proposed two types of contact resistance, i.e., restriction resistance due to small contact area and tunneling resistance when nanoparticles are included in the system. It was believed that the conductivity of micro-sized Ag particle-filled adhesives could be dominated by constriction resistance, while the nanoparticle containing conductive adhesives is controlled by tunneling and even thermionic emission. Fan et al. also observed a similar phenomenon (adding nano-size particles reduced both electrical and thermal conductivities) [34].

The overall resistance ($R_{\text{total}}$) of the isotropic conductive adhesive (ICA) formulation is the sum of the resistance of fillers ($R_{\text{fillers}}$), the resistance between fillers ($R_{\text{btw fillers}}$), and the resistance between filler and pads ($R_{\text{filler to bond pad}}$) (Equation 1). In order to decrease the overall contact resistance, the reduction of the number of contact points between the particles may be obviously effective. Incorporation of nano-fillers increases the contact resistance and reduces the electrical performance of the ICAs. The number of contacts between the small particles is larger than that between the large particles as shown in Fig. 4a, b. A recent study by Jiang et al. showed that nano-silver particles could exhibit sintering behavior at curing temperature of ICAs [35, 36]. If nanoparticles are sintered together, then the contact between fillers will be fewer. This will lead to smaller contact resistance (Fig. 4c). By using effective surfactants for the dispersion and effective capping those nano-sized silver fillers in ECAs, obvious sintering behavior of the nano-fillers can be achieved. The sintering of nano-silver fillers improved the interfacial properties of conductive fillers and polymer matrices and reduced the contact resistance between
fillers. The dispersion and interdiffusion of silver atoms among nano-sized particles could be facilitated and the resistivity of ICA could be reduced to $5 \times 10^{-6} \ \Omega \ \text{cm}$.

$$R_{\text{total}} = R_{\text{btw fillers}} + R_{\text{filler to bond pad}} + R_{\text{fillers}}$$ (1)

### 2.3 ICA Filled with Aggregates of Nano-sized Ag Particles

To improve the mechanical properties under thermal cycling conditions while still maintaining an acceptably high level of electric conductivity, Kotthaus et al. studied an ICA material system filled with aggregates of nano-sized Ag particles [37]. The idea was to develop a new filler material which did not sacrifice the mechanical property of the polymer matrix to such a great extent. A highly porous Ag powder was attempted to fulfill these requirements. The Ag powder was produced by the inert gas condensation method. The powders consist of sintered networks of ultra-fine particles in the size range 50–150 nm. The mean diameter of these aggregates could be adjusted down to some microns. The as-sieved powders were characterized by low level of impurity content, an internal porosity of about 60%, a good ability for resin infiltration.

Using Ag IGC instead of Ag flakes is more likely to retain the properties of the resin matrix because of the infiltration of the resin into the pores. Measurements of the shear stress–strain behavior indicated that the thermo-mechanical properties of bonded joints may be improved by a factor up to two, independent of the chosen resin matrix.

Resistance measurements on filled adhesives were performed within a temperature range from 10 to 325 K. The specific resistance of a Ag IGC-filled adhesive is about $10^{-2} \ \Omega \ \text{cm}$ and did not achieve the typical value of commercially available adhesives of about $10^{-4} \ \Omega \ \text{cm}$. The reason may be that Ag IGC particles are more or less spherical whereas Ag flakes are flat. So, the decrease of the percolation threshold because of the porosity of Ag IGC is overcompensated by the disadvantageous shape and the intrinsically lower specific conductivity. For certain applications where mechanical stress plays an important role, this conductivity may be sufficient and therefore the porous Ag could be suitable as a new filler material for conductive adhesives.
2.4 Nano-Ni Particle-Filled ICA

Sumitomo Electric Industries, Ltd. (SEI) has developed a new liquid-phase deposition process using plating technology. This new nanoparticle fabrication process achieves purity greater than 99.9% and allows easy control of particle diameter and shape. The particles’ crystallite size calculated from the result of X-ray diffraction measurement is 1.7 nm, which leads to an assumption that the particle size of primary particles is extremely small. When the particle size of nickel and other magnetic metals becomes smaller than 100 nm, they are changed from the multidomain particles to the single-domain particles, and their magnetic properties change. That is, if the diameter of nickel particles is around 50 nm, each particle acts like a magnet that has only a pair of magnetism, and magnetically connects with each other to form the chain-like clusters. When the chain-like clusters are applied to conductive paste, electrical conduction of the paste is expected to be better than the existing paste. The developed chain-like nickel particles were mixed with pre-defined amount of polyvinylidene difluoride (PVdF) that acts as an adhesive. Then, N-methyl-2-pyrrolidone was added to this mixture to make conductive paste. This paste was applied on a polyimide film and then dried to make a conductive sheet. Specific volume resistivity of the fabricated conductive sheet was measured by the quadruple method. The same measurement was also conducted on the conductive sheet that used the paste made of conventional spherical nickel particles. Measurement of the sheet resistance immediately after paste application defined that the developed chain-like nickel powders had low resistance of about one-eighth of that of the conventionally available spherical nickel particles. This result showed that, when the newly developed chain-like nickel particles were applied as conductive paste, high conductivity can be achieved without pressing the sheet.

2.5 Nano-conductive Adhesives for Via-Filling Applications in Organic Substrates

The demand of higher density organic substrates is increasing recently. Traditionally, greater wiring densities are achieved by reducing the dimensions of vias, lines, and spaces, increasing the number of wiring layers, and utilizing blind and buried vias. However, each of these approaches possess inherent limitations, for example, those related to drilling and plating of high aspect ratio vias, reduced conductance of narrow circuit lines, and increased cost of fabrication related to additional wiring layers. One method of extending wiring density beyond the limits imposed by these approaches is to form more metal-to-metal Z-axis interconnection of sub-composites during lamination to form a composite structure. Conductive joints can be formed during lamination using an electrically conductive adhesive. As a result, one is able to fabricate structures with vertically terminated vias of arbitrary depth. Replacement of conventional plated through holes with vertically terminated
vias opens up additional wiring channels on layers above and below the terminated vias and eliminates via stubs, which cause reflective signal loss.

Conductive adhesives usually have high filler loading that weaken the overall mechanical strength. Therefore, reliability of the conductive joint formed between the conductive adhesive and the metal surface to which it is mated is of prime importance. Conductive adhesives can have broad particle size distributions. Larger particles can be a problem when filling smaller holes (e.g., diameter of 60 μm or less), resulting in voids.

Das et al. developed conductive adhesives using controlled-sized particles, ranging from nanometer scale to micrometer scale, and used them to fill small diameter holes to fabricate Z-axis interconnections in laminates for interconnect applications [38]. A variety of metals, including Cu, Ag, and low melting point (LMP) alloys with particle sizes ranging from 80 nm to 15 μm were used to make the epoxy-based conductive adhesives. Among all, silver-based adhesives showed the lowest volume resistivity and highest mechanical strength. It was found that with increasing curing temperature, the volume resistivity of the silver-filled paste decreased due to sintering of metal particles. Sinterability of silver adhesive was further evaluated using high-temperature/pressure lamination and shows a continuous metallic network when laminated at 365°C.

As a case study, they used a silver-filled conductive adhesive as a Z-axis interconnecting construction for a flip-chip plastic ball grid array package with a 150 μm die pad pitch. High aspect ratio, small diameter (∼55 μm) holes were successfully filled. Silver-filled adhesives were electrically and mechanically better than Cu and LMP-filled adhesives. All adhesives maintained high tensile strength even after 1000 cycles thermal cycling (−55 to 120°C). Conductive joints were stable after three times reflowing, 1000 cycles thermal cycling, pressure cooker test (PCT), and solder shock. The adhesive-filled joining cores were laminated with circuitized subcomposites to produce a composite structure. High-temperature/pressure lamination was used to cure the adhesive in the composite and provide stable, reliable Z-interconnections among the circuitized subcomposites.

2.6 Nano-ICAs Filled with CNT

2.6.1 Electrical and Mechanical Characterization of CNT-Filled ICAs

Carbon nanotubes are a new form of carbon, which was first identified in 1991 by Sumio Iijima of NEC, Japan [39]. 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, which act as multichannel transport of electrical and thermal for thermal interface materials (TIMs) applications. The carbon nanotube can be 1–50 nm in diameter and 10–100 μm or up to a few centimeters in length, with each end “capped” with half of a fullerene dome consisting of five- and six-member rings. Along the sidewalls and cap, additional molecules can be attached to functionalize the
nanotube to adjust its properties. CNTs are chiral structures with a degree of twist in the way that the graphite rings join into cylinders. The SWCNT 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. The thermal conductivity of carbon nanotubes at room temperature can be as high as 6600 W/m K [40]. The Young’s modulus of carbon nanotube is about 1 TPa. The maximum tensile strength of carbon nanotube is close to 30 GPa, some reported at TPa [41]. 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.

Epoxy-based conductive adhesives filled with MWNTs have been recently developed [42]. It was found that ultrasonic mixing process helped disperse CNTs in the epoxy more uniformly and made them contact better, and thus lower electrical resistance was achieved. The contact resistance and volume resistivity of the conductive adhesive decreased with increasing CNT loading. The percolation threshold for the MWNTs used was less than 3 wt%. With 3 wt% loading, the average contact resistance was comparable with solder joints. It was also found that the performance of CNTs-filled conductive adhesive was comparable with solder joints in high frequency. By replacing metal particle fillers with CNTs in the conductive adhesive, a higher percentage of mechanical strength was retained. For example, with 0.8 wt% of CNT content, the 80% of shear strength of the polymer matrix was retained, while conventional metal-filled conductive adhesives only retain less than 28% of shear strength of the polymer matrix.

Experiments conducted by Qian et al. [43] show 36–42% and 25% increases in elastic modulus and tensile strength, respectively, in polystyrene (PS)/CNT composites. The TEM observations in their experiments showed that cracks propagated along weak CNT–polymer interfaces or relatively low CNT density regions and caused failure. If the outer layer of MWNTs can be functionalized to form strong chemical bonds with the polymer matrix, the CNT/polymer composites can be further reinforced in mechanical strength and have controllable thermal and electrical properties.

### 2.6.2 Effect of Adding CNT to the Electrical Properties of ICAs

Effect of adding CNT to the electrical conductivity of silver-filled conductive adhesive with various CNT loadings were reported [44]. It was found that the CNT could enhance the electrical conductivity of the conductive adhesives greatly when the silver filler loading was still below percolation threshold. For example, 66.5 wt% silver-filled conductive adhesive without CNT had a resistivity of $10^4 \ \Omega \text{cm}$, but showed a resistivity of $10^{-3} \ \Omega \text{cm}$ after adding 0.27 wt% CNT. Therefore, it is possible to achieve the same level of electrical conductivity by adding a small amount of CNT to replace the silver fillers.
2.6.3 Composites Filled with Surface-Treated CNTs

Although CNTs have exceptional physical properties, incorporating CNTs into other materials has been inhibited by 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. Zyvex claimed that they have overcome these restrictions by developing a new surface treatment technology that optimizes the interaction between CNTs and the host matrix [45]. A multifunctional bridge was created between the CNT sidewalls and the host material or solvent. The power of this bridge was demonstrated by comparing the fracture behavior of the composites filled with untreated and surface-treated nanotubes. It was observed that the untreated nanotubes interacted poorly with the polymer matrix, and thus left behind voids in the matrix after fracture. However, for composite filled with treated nanotubes, the nanotube remained in the matrix even after the fracture, indicating strong CNT interaction with the matrix. Due to their superior dispersion in the polymer matrix, the treated nanotubes achieved the same level of electrical conductivity at much lower loadings than the untreated nanotubes [45].

2.7 Inkjet Printable Nano-ICAs and Inks

Areas for printing very fine-pitch matrix (e.g., very fine-pitch paths, antennas) are very attractive. But there are special requirements for inkjet printing materials, namely the most important ones are low viscosity and very homogenous structure (such as molecular fluid) to avoid sedimentation and separation during the process. Additionally, for electrical conductivity of printed structure, the liquid has to contain conductive particles, with nano-sized dimension to avoid the printing nozzle blocking and prevent sedimentation phenomenon. The nano-sized silver seems to be one of the best candidates for this purpose, especially when its particle size dimensions will be less than 10 nm.

Inkjetting is an accepted technology for dispensing small volumes of material (50–500 pl). Currently, traditional metal-filled conductive adhesives cannot be processed by inkjetting (due to their relatively high viscosity and the size of filler material particles). Smallest droplet size achievable by traditional dispensing techniques is in the range of 150 μm, yielding proportionally larger adhesive dots on the substrate. Electrically conductive inks are available on the market with metal particles (gold or silver) <20 nm suspended in a solvent at 30–50 wt%. After deposition, the solvent is evaporated and electrical conductivity is enabled by a high metal ratio in the residue. Some applications include a sintering step [46, 47].

There are many requirements for an inkjettable, Ag particle-filled conductive adhesive. The silver particles must not exceed a maximum size determined by the diameter of the injection needle used. At room temperature, the adhesive should resist sedimentation for at least 8, preferably 24 hours. A further requirement by the end user on the adhesive’s properties was a two-stage curing mechanism. In the
first curing step, the adhesive surface is dried. In this state, the product may be stored for several weeks. The second curing step involves glueing the components with the previously applied adhesive. By heating and applying pressure the adhesive is cured. Thus, the processing operation is similar to that required for soldering. A conductivity in the range of $10^{-4} \, \Omega \cdot \text{cm}$ in the bulk material is required. An adhesive less prone to sedimentation was formulated by using suitable additives. Furthermore, the formation of filler agglomerations during deflocculation and storage was reduced. This effect was achieved by making the additives adhere to the filler particle surfaces. This requires a very sensitive balance. If the insulation between individual silver particles becomes very strong, overall electrical conductivity is significantly reduced.

Jana Kolbe et al. demonstrated feasibility of an inkjettable, isotropically conductive adhesive in the form of a silver-loaded resin with a two-step curing mechanism [48, 49]. In the first step, the adhesive was dispensed (jetted) and precured leaving a “dry” surface. The second step consisted of assembly (wetting of the second part) and final curing. The attainable droplet sizes were in the range of 130 $\mu$m, but could be further reduced by using smaller (such as 50 $\mu$m) and more advanced nozzle shapes.

Nano-Ag particles for nano-ink applications are coated with capping agents for dispersion, which should be removed before the solidification process such as sintering. Otherwise, the particles cannot fuse or sinter each other. The capping agent removal usually requires heating the printed pattern to evaporate solvent and induce sintering. Wakuda et al. recently demonstrated room temperature sintering Ag nanoparticles that are protected by a dispersant in an air atmosphere, where the dodecylamine dispersant was removed in methanol and the Ag nanoparticles were densely sintered. The sintered Ag wires showed low resistivity of $7.3 \times 10^{-5} \, \Omega \cdot \text{cm}$, which can be used for inkjet printing [50].

3 Recent Advances of Nano-ACA/ACF

3.1 Low-Temperature Sintering of Nano-Ag-Filled ACA/ACF

One of the concerns for ACA/ACF is the higher joint resistance since interconnection using ACA/ACF relies on mechanical contact, unlike the eutectic solder, which forms the metallurgical bonding during reflow. An approach to minimize the joint resistance of ACA/ACF is to make the conductive fillers fuse each other and form metallic joints such as metal solder joints. However, to fuse metal fillers in polymers does not appear feasible, since a typical organic printed circuit board ($T_g \sim 125^\circ\text{C}$), on which the metal filled polymer is applied, cannot withstand such a high temperature; the melting temperature ($T_m$) of Ag, for example, is around 960$^\circ\text{C}$. Studies have showed that $T_m$ and sintering temperatures of materials could be dramatically reduced by decreasing the size of the materials [51–53]. It has been reported that the surface premelting could be a primary mechanism of the $T_m$ depression of
the fine nanoparticles (<50 nm). For nano-sized particles, sintering behavior could occur at much lower temperatures, as such, the use of the fine metal particles in ACAs would be promising for high electrical performance of ACA joints by eliminating the interface between metal fillers. The application of nano-sized particles can also increase the number of conductive fillers on each bond pad and result in more contact area between fillers and bond pads as illustrated in Fig. 5. For the sintering reaction in a certain material system, temperature and duration are the most important parameters, in particular, the sintering temperature.

![Fig. 5 Schematic illustrations of ACA/ACF with (a) micro-sized conductive fillers and (b) nano-sized conductive fillers](image)

Current–resistance ($I$–$R$) relationship of the nano-Ag-filled ACA joint is shown in Fig. 6. As can be seen from the figure, with increasing curing temperatures, the resistance of the ACA joints decreased significantly, from $10^{-3}$ to $5\times10^{-5} \, \Omega$. Also, ACAs cured at higher temperature exhibited higher current-carrying capability than ACAs cured at low temperature. This phenomenon suggested that more sintering of nano-Ag particles and subsequently superior interfacial properties between fillers and metal bond pads were achieved at higher temperatures [53], yet the $x$–$y$ direction of the ACF maintains an excellent insulation property for electrical insulation.

### 3.2 Self-Assembled Molecular Wires for Nano-ACA/ACF

To enhance the electrical performance of ACA/ACF materials, self-assembled molecular wires (SAMW) have been introduced into the interface between metal fillers and metal-finished bond pad of ACAs [54, 55]. These organic molecules adhere to the metal surface and form physico-chemical bonds, which allow electrons to flow, as such, it reduces electrical resistance and enables a high current flow. The unique electrical properties are due to their tuning of metal work functions by those organic monolayers. The metal surfaces can be chemically modified...
by the organic monolayer and the reduced work functions can be achieved by using suitable organic monolayer coatings. An important consideration when examining the advantages of organic monolayers pertains to the affinity of organic compounds to specific metal surfaces. Table 2 gives the examples of molecules preferred for maximum interactions with specific metal finishes; although only molecules with symmetrical functionalities for both head and tail groups are shown, molecules and derivatives with different head and tail functional groups are possible for interfaces concerning different metal surfaces.

Different organic molecular wires, dicarboxylic acid, and dithiol have been introduced into ACA/ACF joints. For SAM-incorporated ACA with micron-sized gold/polymer or gold/nickel fillers, lower joint resistance and higher maximum allowable current (highest current applied without inducing joint failure) was achieved for low-temperature curable ACA (<100°C). For high curing temperature ACA (150°C), however, the improvement was not as significant as low curing temperature ACAs, due to the partial desorption/degradation of organic monolayer coating at the relatively high temperature [56]. However, when dicarboxylic acid or dithiol was introduced into the interface of nano-silver-filled ACAs, significantly improved electrical properties could be achieved at high-temperature curable ACA/ACF, suggesting the coated molecular wires did not suffer degradation on silver nanoparticles at the curing temperature (Fig. 7). The enhanced bonding could attribute to the larger surface area and higher surface energy of nanoparticles, which enabled the monolayers to be more readily coated and relatively thermally stable on the metal surfaces [57].
Table 2  Potential organic monolayer interfacial modifiers for different metal finishes

<table>
<thead>
<tr>
<th>Formula</th>
<th>Compound</th>
<th>Metal finishes</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-S-H</td>
<td>Thiols</td>
<td>Au, Ag, Cu, Pt, Zn</td>
</tr>
<tr>
<td>R-COOH</td>
<td>Carboxylates</td>
<td>Fe/Fe$_3$O$_4$, Ti/TiO$_2$, Ni, Al, Ag</td>
</tr>
<tr>
<td>R-C≡N</td>
<td>Cyanides</td>
<td>Au, Ag, Pt</td>
</tr>
<tr>
<td>R-N=C=O</td>
<td>Isocyanates</td>
<td>Pt, Pd, Rh, Ru</td>
</tr>
<tr>
<td>R-SiOH</td>
<td>Imidazole and triazole derivatives</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>Organosilane derivatives</td>
<td>SiO$_2$, Al$_2$O$_3$, quartz, glass, mica, GeO$_2$, etc.</td>
</tr>
</tbody>
</table>

R denotes alky and aromatic groups

Fig. 7  Electrical properties of nano-Ag-filled ACA with dithiol or dicarboxylic acid [57]

3.3 Silver Migration Control in Nano-silver-Filled ACA

Silver is the most widely used conductive fillers in ICAs and exhibits exciting potentials in nano-ACA/ACF due to many unique advantages of silver. Silver has the highest room temperature electrical and thermal conductivity among all the conductive metals. Silver is also unique among all the cost-effective metals by nature of its conductive oxide (Ag$_2$O). In addition, silver nanoparticles are relatively easy to be formed into different sizes (a few nanometers to 100 nm) and shapes (such as spheres, rods, wires, disks, flakes) and well dispersed in a variety of polymeric matrix materials. Also the low-temperature sintering makes silver one of the promising candidate as conductive fillers in nano-ACA/ACF. However, silver migration has long been a reliability concern in electronic industry. Metal migration is an
electrochemical process, whereby, metal (e.g., silver), in contact with an insulating material, in a humid environment and under an applied electric field, leaves its initial location in ionic form and deposits at another location [58]. It is considered that a threshold voltage exists above which the migration starts. Such migration may lead to a reduction in electrical spacing or cause a short circuit between interconnections. The migration process begins when a thin continuous film of water forms on an insulating material between oppositely charged electrodes. When a potential is applied across the electrodes, a chemical reaction takes place at the positively biased electrode where positive metal ions are formed. These ions, through ionic conduction, migrate toward the negatively charged cathode and over time, they accumulate to form metallic dendrites. As the dendrite growth increases, a reduction of electrical spacing occurs. Eventually, the dendrite silver growth reaches the anode and creates a metal bridge between the electrodes, resulting in an electrical short circuit [59].

Although other metals may also migrate under specific environment, silver is more susceptible to migration, mainly due to the high solubility of silver ion, low activation energy for silver migration, high tendency to form dendrite shape, and low possibility to form a stable passivation oxide layer [60–62]. The rate of silver migration is increased by (1) an increase in the applied potential; (2) an increase in the time of the applied potentials; (3) an increase in the level of relative humidity; (4) an increase in the presence of ionic and hydroscopic contaminants on the surface of the substrate; and (5) a decrease in the distance between electrodes of the opposite polarity.

To reduce silver migration and improve the reliability, several methods have been reported. The methods include (1) alloying the silver with an anodically stable metal such as palladium [61] or platinum [63] or even tin [64]; (2) using hydrophobic coating over the PWB to shield its surface from humidity and ionic contamination [65], since water and contaminates can act as a transport medium and increase the rate of migration; (3) plating of silver with metals such as tin, nickel, or gold, to protect the silver filler and reduce migration; (4) coating the substrate with polymer [66]; (5) applying benzotriazole (BTA) and its derivatives [67]; (6) employing siloxane epoxy polymers as diffusion barriers due to the excellent adhesion of siloxane epoxy polymers to conductive metals [68]; (7) chelating silver fillers in ECAs with molecular monolayers [69]. As an example shown in Fig. 8 [70], with carboxylic acids and forming chelating compounds with silver ions, the silver migration behavior (leakage current) could be significantly reduced and controlled.

3.4 ACF with Straight-Chain-Like Nickel Nanoparticles

Sumitomo Electric recently developed a new concept ACF using nickel nanoparticles with a straight-chain-like structure as conductive fillers [72]. They applied the formulated straight-chain-like nickel nanoparticles and solvent in a mixture of epoxy resin on a substrate film. Then the particles were made to orient toward the vertical direction of the film surface and fixed in a resin by evaporating the solvent, and this approach is similar to the elastomeric conductive polymer interconnects (ECPI), dispersed Ni-coated glass spheres in a silicone matrix, which has
been developed by AT&T Bell Laboratory [73]. In the estimation using 30 μm-pitch IC chips and glass substrates (the area of Au bumps was 2000 μm², the distance of space between neighboring bumps was 10 μm), the new ACF showed excellent reliability of electrical connection after high-temperature, high-humidity (60°C/90%RH) test and thermal cycle test (between –40 and 85°C). The samples were also exposed to high-temperature, high-humidity (60°C/90%RH) for insulation ability estimation. Although the distance between two electrodes was only 10 μm, ion migration did not occur and insulation resistance has been maintained at over 1 GΩ for 500 h. This result showed that the new ACF has superior insulation reliability and has potential to be applied in very fine interconnections.
3.5 Nanowire ACF for Ultra-fine-pitch Flip-Chip Interconnection

To satisfy the reduced I/O pitch and avoid electric shorting, a possible solution is to use high-aspect-ratio metal post. Nanowires exhibit high possibilities due to the small size and extremely high aspect ratio. In literature, nanowires could be applied in FET (field effective transistor) sensor for gas detection, magnetic hard-disk, nanoelectrodes for electrochemical sensor, thermal-electric device for thermal dissipation and temperature control, etc. [71,74,75]. To prepare nanowires, it is important to define nanostructures on the 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 micro-meter size. A less expensive alternative is electrodeposition of metal into nano-porous template such as anodic aluminum oxide (AAO) [76] or block-copolymer self-assembly template. The disadvantages of block-copolymer template include thin thickness (that means short nanowires), nonuniform distribution and poor parallelism of nano-pores. However, AAO has benefits of higher thickness (>10 μm), uniform pore size and density, larger size, and very parallel pores. Lin et al. [77] developed a new ACF with nanowires. They used AAO templates to obtain silver and cobalt nanowires array by electrodeposition. And then low viscous polyimide (PI) was spread over and filled into the gaps of nanowires array after surface treatment. The bi-metallic Ag/Co nanowires could remain parallel during fabrication by magnetic interaction between cobalt and applied magnetic field. The silver and cobalt nanowires/polyimide composite films could be obtained with a diameter of about 200 nm for nanowire and maximum film thickness up to 50 μm. The X–Y insulation resistance is about 4–6 GΩ and Z-direction resistance including the trace resistance (3 mm length) is less than 0.2 Ω. They also demonstrated the evaluation of this nanowire composite film by stress simulation. They found that the most important factor for designing nanowire ACF was the volume ratio of nanowires. However, actually the ratio of nanowires cannot be too small to influence the electric conductance. They concluded that it is important to get a balance between electric conductance and thermal-mechanical performance by increasing film thickness or decreasing modulus of polymer matrix.

3.6 An In Situ Formation of Nano-conductive Fillers in ACA/ACF

One of the challenging issues in the formation of nano-filler ACA/ACF is the dispersion of nano-conductive fillers in ACA/ACF. A lot of research has been going on in recent years to address the dispersion issue of nano-composite because nano-fillers due to their high surface reactivity and high electrostatic force tend to agglomerate. For the fine-pitch electronic interconnects using nano-ACA/ACF, the dispersion issues need to be solved. The efforts usually include the physical approaches such as sonication and chemical approaches such as surfactants. Recently, a novel ACA/ACF incorporated with in-situ formed nano-conductive particles is proposed for the next generation high-performance fine-pitch electronic packaging applications [78, 79]. This novel interconnect adhesive combines
the electrical conduction along the $z$-direction (ACA-like) and the ultra fine-pitch (<100 nm) capability. Instead of adding the nano-conductive fillers in the resin, the nanoparticles can be in situ formed during the curing/assembly process. By using in situ formation via chemical reduction of nanoparticles, during the polymer curing process, the filler concentration and dispersion could be controlled and the drawback of surface oxidation of the nano-fillers could be easily overcome [80].

3.7 CNT-Based Conductive Nanocomposites for Transparent, Conductive, and Flexible Electronics

The electrically conductive and optically transparent coating is an upcoming potential for various applications such as transistors [81–84], diodes [85], sensors [86, 87], optical modulators [88] or as conductive backbone for electrochemical polymer coating [89], smart windows [90], photovoltaics [91], solar cells [92,93] and organic light-emitting diode (OLED) [94, 95].

With the popularity of flex circuits or substrates, in particular for large-scale flexible flat panel displays, there are demands for flexible interconnect materials, especially under highly mechanical bending conditions of printed electronics. ITO (indium tin oxide), fluorine tin oxide (FTO), and conductive polymers such as polyaniline (PANI) have been de facto options as transparent and conductive coating materials. However, those materials have no flexibility in nature, which is critical for flexible devices such as bendable displays and sensors. Thus, materials with mechanical flexibility as well as electrical conductivity and transparency can find various applications. The CNT incorporated polymer composite is one of the candidates because its tremendously high aspect ratio can provide a significantly low percolation threshold in electrical conduction. Its tiny size (<10 nm in diameter (SWCNT), smaller than $1/4\lambda$ of visible light) lets light pass through and the polymer matrix renders flexibility. Therefore, intensive efforts to materialize transparent, conductive, and flexible CNT-based polymer composite have been dedicated.

Kaempgen et al. found that single wall CNTs (SWCNTs) are more suitable for transparent conductive coatings than multi wall CNTs (MWCNTs) [96]. This is likely due to a significantly higher diameter of each MWCNT, which increases the light absorption (Fig. 9). The longer CNTs increase the conductivity for the same transparency with the decreased number of contacts because the electrical transport is dominated by contact resistances between the CNTs [97–101]. The uniform dispersion is a key factor to manufacture reproducible coatings or composite films.

Some CNT-based polymer composites already met the requirements for various applications. Figure 10 compares the resistivity (1 kΩ/sq) of the CNT coating with 90% light transmittance to those of various target applications [96], where it can be seen that currently 90% transparent CNT coating can meet the requirements for many applications such as touch screen and electrostatic discharge, although
only shielding of electromagnetic interference (EMI) is out of reach at least for transparent coatings. There are trade-off values between transparency and surface resistance of the CNT composites with regard to their applications. Recently, a CNT film on polymer or glass with 80% light transmittance exhibited a resistance of 20 Ω/sq [102]. With extensive research and development of CNT nanocomposite, more reliable conductive and transparent adhesives will find versatile applications in microelectronics.
4 Concluding Remarks

In this chapter, recent advances in nano-electrically conductive adhesives (ECAs) were reviewed and in particular, innovative approaches by using cutting-edge nanotechnologies were presented. The nanotechnology-based ECAs will be playing a very important role in future nanoelectronics, nanophotonics, nano-biomedical devices etc.

Although Ag filler is known as one of best conductive materials for ECA, its high cost and intrinsic propensity for silver migration are of concern for low-cost consumer products or high-performance device-packaging interconnects. As such, copper will be a silver alternative as ECA filler, as copper is the second highest electrically conductive element after silver and has less migration tendency. However, copper is very vulnerable to oxygen and corrosion, and unlike Ag, its oxide is a poor electrical conductor. Therefore, in order to achieve all the benefits from copper, much research effort on preventing copper from oxidation/corrosion is needed and the use of SAM/surfactant as mentioned in Table 2 may provide some solutions.

Tremendous evolution in display technologies has been demonstrated over the past decades, and future display technologies need very flexible and high-performance interconnect materials for nano- or bio-medical device packaging. In general, bending or physical deformation of ECAs can degrade the electrical conductivity. Therefore, novel flexible electrically conductive materials to respond to repeated bending or high elongations will be required for future flexible display technologies. In addition, transparent conductive adhesive is needed for some applications such as organic LED (OLED) application. Ouyang et al. [103] have demonstrated a transparent conducting polymer glue and the feasibility of fabricating organic electronic devices through a lamination process by using the PEDOT:PSS electric glue. By combining this technology with the large-area continuous coating process of organic films, it is possible to fabricate large-area organic electronic devices through a continuous roll-to-roll coating process. This electric glue made from a conducting polymer provides new applications for conducting polymers; it will revolutionize the fabrication process of flexible electronic devices.

Although some researches on enhancing current-carrying capability of ECAs have been carried out, there is no commercial ECA material to replace metallic solders yet. Thus, increasing current-delivering capability of the ECA will be a continuing research effort. Employing molecular wires in the ECA joints or conductive elements and manipulating conductive joint work functions with high thermal stability, are some of the promising approaches for the high-current ECA challenges.

With particle size of ECAs becoming smaller in particular for nano-ACAs, there is serious implication from the point of view of the manufacturing process. When ACAs are used to attach the metal pads on two mating surfaces, the warpage and coplanarity of these surfaces need to be carefully controlled to ensure all the metal pads on the mating surfaces are making contact to the conductive spheres in the ACA simultaneously. Large and compliant (deformable) conductive particles will ease the manufacturing process because these particles can accommodate the warpage and
noncoplanarity. With conductive particles becoming even smaller in nano-ACAs, the manufacturing will become more challenging.

The ECAs will be continuing to evolve to meet future technological needs, as such, much attention is needed on the breakthrough technology developments by engineers and scientists including materials scientists, chemists and physicists, etc. We all should bear in mind that high-performance interconnection materials for advanced nanoelectronics, photonics, bio-medical devices, and systems packaging are the key for future microelectronics.

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