Anisotropic conductive adhesive for micro joining in semiconductor interconnects application (solder alternative for fine pitch & environment friendly IC packaging)

Goh, Chin Foo

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**Anisotropic Conductive Adhesive For Micro Joining In Semiconductor
Interconnects Application (Solder Alternative For Fine Pitch &
Environment Friendly IC Packaging)**

Goh Chin Foo

**Nanyang Technological University
School of Materials Engineering**

**A thesis submitted to the Nanyang Technological University in
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ABSTRACT

Microelectronic packaging has been accelerating towards adoption of novel solutions that offer lower cost, higher electrical performance, and better reliability. Flip chip technology lends itself excellently to these goals. The development of anisotropic and isotropic conductive adhesives (ACA & ICA respectively) as an alternative to solder bumps has received extensive attention in flip chip packaging as it offers an array of advantages like finer pitch interconnects, green processes, low cost, and low temperature processing. The Anisotropic Conductive Adhesive (ACA) is one promising candidates which also shows potential for future pitch reduction. However, the main concern with anisotropic conductive adhesive interconnection is its long-term reliability. The degree of spread of the conductive particles between the 50 μ m bump pitch and substrate pad, determined by the amount of pressure applied during the bonding process, has a great influence on the contact resistance of the ACA joints. As a result, nanosized conductive particles are preferably used in the finer pitch ACA application (5 μ m bump pitch) to enhance reliability and performance. Therefore, the main objectives of this project are to develop nanosized hollow silica microspheres and encapsulate nickel with these microspheres. By using these encapsulated nickel particles as fillers in ACA interconnection, long-term reliability of ACA joints can be improved.

In this study, one of the objectives was the development and synthesis of sub-micron nickel powders. Nickel was the conductive filler taken into consideration because of

the many advantages it offered. Hydrothermal reduction of nickel sulphate using hydrazine was the main synthesis route. The nickel salt concentrations were varied to investigate their influence on nickel sizes. It was found that reducing the salt concentration resulted in size reduction; however, the trend was non-linear. Spiky spherical nickel particles were produced ranging from 300 nm to 1 micron. The spiky morphology may have a detrimental effect on the conductivity of the ICA & ACA flip chip interconnect due to its smaller contact surface and propensity towards oxidation. The morphology of the nickel surface can be changed by annealing the particles between 270°C and 360°C for 4 to 12 hours. A smoothening effect leading to more or less smooth spherical particles along with an increase in conductivity was observed after annealing at 360°C for up to 12 hours. An analytical model considering surface diffusion is established here to describe the temperature activated and energy minimization driven smoothening of the Ni particles.

An interfacial synthesis method was used to synthesize thermally stable hollow silica microspheres. The structure was synthesised at room temperature from a vortexed mixture of water and droplets of tetraethoxysilane (TEOS) containing aminopropyltriethoxysilane (APTES): droplets were stabilized with the surfactant cetyltrimethylammonium bromide (CTABr) to produce silica shells. The results showed that the process parameter (stirring speed) and surfactant/chemical chemistry have great effects on size of the hollow particles. The sizes of hollow silica were observed to decrease with increasing stirring speed. When the percentage of APTES

was increased from 10mol% to 15mol% of the total ethoxysilane used, the results gave an approximately hundred-fold decrease in the size of hollow spheres. Final experiment of this study also showed a successfully encapsulation of nickel particle with hollow silica spheres. This material would be favourably to be used as filler in ACA flip chip interconnections.

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Introduction

1.1. Background information

Along with demands for cheaper, smaller and higher performance devices, microelectronics technology is also moving towards lower cost, finer pitch, higher electrical performance, and better reliability. Flip chip technology is the main candidate that meets all these demands [1]. Lead-based solder materials have been used for interconnections of electronics component on printed circuit boards (PCBs) for many decades. However, as public environmental awareness increases, the toxicity of lead has become increasingly important, and the pressure to eliminate or reduce the industrial use of lead is growing. Legislation and policies have been proposed in Europe to ban or limit the use of lead in solder, and the United States is likely to follow this trend. Following this tendency, great efforts have been made in the industry to develop lead-free and environmentally friendly soldering materials to replace lead-based solders. One alternative to lead-bearing solders is lead free, low melting temperature metals and metal alloys. Some applications have been found in this area. However, some limitations still exist in lead-free solder technology, including the relatively high cost or limited availability of some metals alloys [2].

Moreover, compared with lead-bearing solders, joint embrittlement and fatigue are also serious concerns in lead-free solder applications as embrittlement of solder joints after reflow and fatigue cracks induced by temperature cycling are among the major causes of lead-free solder joint failure [3].

Solder alternative for flip chip interconnection are fast emerging due to the drive for environmental friendly processes. Two main classes of materials have been reported, the lead free solders and electrically conductive adhesives. Among the electrically conductive adhesives, the anisotropic conductive adhesive (ACA) is a promising candidate that shows potential for further pitch reduction. Electrically conductive adhesives (ECAs) are playing an increasing important role in the design and production of electronic packages. Their advantages over the solder connection technology include fewer and cleaner processing steps and lower curing temperatures. [4, 5, 6] It consists of a polymeric matrix with conductive fillers. ACA has conductivity in one directions [7]. Choices for fillers in ACA include silver, copper, nickel or gold. Electrically conductive adhesives (ECAs) provide an environmental friendly solution for interconnections in electronics applications [8,9,10]. Moreover, ECAs also offer several potential advantages over conventional solder interconnection technology including finer pitch printing, lower temperature processing [11,12]. In addition, compared with lead-free solders, conductive adhesive systems exhibit greater flexibility, creep resistance, and energy damping [13], which can reduce the possibility of failure that occur in lead-free solder interconnections. Therefore, electrically conductive adhesives are perceived as the next generation interconnection material for electronic packaging [14]. As a relatively new interconnection technology, however, conductive adhesive technology does have some limitations and drawbacks. Some reliability issues including limited impact resistance [15,16] are several major

obstacles currently preventing ECAs from becoming a general replacement for solders in electronic applications.

1.2. Objectives and Significance of This Study

This PhD work aims to synthesis an anisotropic conducting particles suitable for fine pitch application. There are three main objectives in this study:

1. Synthesis the sub-micron conductive particles
2. Study the mechanism of the as synthesis particle during annealing.
3. Develop a methodology to encapsulate the sub-micron conductive particles use for fine pitch application.

The first objective is to synthesis electrical conductive particle suitable for fine pitch application, Nickel is an ideal candidate because of the numerous advantages it possesses. It shows chemical stability and oxidizes relatively slower compared to copper. Although it has a higher electrical resistance compared to silver (about 25% of silver), silver is much more cost prohibitive.[4]

The second objective is to study the mechanism of the as synthesis sub-micron particles during annealing. Temperature has a most profound influence on the coefficients and diffusion rates. Annealing provides an effective approach to modify the morphology and/or phase of the microstructures, thus tuning the materials' properties. One of the key factors leading to the morphology change of a particle is

surface diffusion. Surface diffusion, or atom and molecular dynamics at surfaces, is a subject of considerable importance in surface and nano sciences since many surface phenomena involves mass transport and dynamic fluctuations of atoms, cluster and molecules [17]. These phenomena include surface reconstruction, crystal growth and thin films epitaxy, shape-change and sintering, adsorption and desorption, and surface promoted chemical reactions.

The third objective is to synthesize sub-micron composite particle use for future flip chip application. The purpose is to produce conductive particle that is suitable for 5 μ m pitch application. It is developing a coating technology for the finer Ni particle use in fine pitch applications. Particles with a thin insulated layer on top of the metal layer allow very closely spaced conductive particles. This represents another interesting development trend [18]. The purpose is to increase packaging density without getting shorts. By using the insulating layer, the particles can have physical contact with one other in the horizontal layer without causing short circuiting. In vertical direction, however, the insulating layer is broken when the particle is squeezed between the pads.

Literature review

1.3. Introduction to Flip Chip

The primary reason for adding metal particles to polymer is to enhance the electrical and/thermal conductance of the polymer. In general, such important polymer properties as low density, strength, and impact resistance are reduced by the addition of metallic particles. The thermal conductivity of such a composite of metal particles may increase to 10 times that of the matrix polymer by the addition of metal particles. [19]

Flip-chip joining is not a new technology, it has been around for more than 35 years since C4 (controlled collapse chip connection) process was invented. However, it is gaining popularity only recently. One of the reasons is the increasing demands for miniaturization, high electrical performance, high I/O pin count etc. Another reason is the increase in availability of the lower-cost bonding and encapsulation materials, substrate, bump bare dies, and equipment. [20, 21, 22, 23, 24, 25] The technology has been driven by IBM for mainframe computer applications. Many millions of flip chips have been processed by IBM on ceramic substrates since the end of 60's. At the beginning of 70's the automotive industry also began to use flip chips on ceramics. Today flip-chips are widely used for watches, mobile phones, portable communicators, disk drives, hearing aids, LCD displays, automotive engine controllers as well as the main frame computers. The number of flip chips assembled

was over 500 million in year 1995 and close to 600 million flip chips were consumed 1997 [26,27].

This technology has been strongly pushed due to the fact that the materials used in LCDs are not compatible with solder temperature. Nor does solder wet the indium tin oxide (ITO) metallization used for creating transparent conductors on the glass. Only in recent years have efforts been made to develop this technology on low-cost flip chip techniques for printed circuit boards. Today it is possible to buy, off-the self, conductive adhesives that are tailored for a specific electronic packaging process. New high strength and high-reliability thermosetting-type anisotropic conductive adhesives (ACAs) have also been developed for flip chip and die-attach applications offer the unique advantage of die repair. ACAs are used for flip chip assembly with down to 70 μ m pitch on glass substrate [28]. Parallel to this, a great deal of research work is currently under way to develop process and technologies for conductive adhesive joining [29], as well as to understand the failure mechanics associated with the used of adhesives. Figure 1 showed the comparison of number of I/O vs. chip size between area array and perimeter array pad arrangement for pitches of 0.2 mm and 0.4mm.

Potentially flip chip technology is cheaper than wire bonding because bonding of all connections takes place simultaneously whereas with wire bonding one bond is made at a time. In practice, however, the price benefit is not always achieved due to

immature processes, e.g. the cost of die bumping with current processes can be significant, especially in low volumes.

1.3.1. General benefits/disadvantages

The conductivity of any material is related to its atomic or molecular structure [30].

The electrons of an atom exist in different energy states corresponding to different orbits around the nucleus.

In general, flip chips are smaller in size, e.g. smaller IC footprint (only about 5% of that of packaged IC e.g. quad flat pack), reduced height and weight.

The use of flip chips allow an increase in the number of I/O. I/O is not limited to the perimeter of the chip as in wire bonding. An area array pad layout enables more signal, power and ground connections in less space. A flip chip can easily handle more than 400 pads. Short interconnect delivers low inductance, resistance and capacitance, small electrical delays, good high frequency characteristics, thermal path from the back side of the die.

Epoxy underfill in large chips ensures high reliability. Flip-chips can reduce the number connections per pin from three to one. Because flip chips are not encapsulated, the back side of the chip can be used for efficient cooling.

Batch bumping process, cost of bumping decreases, cost reductions in the underfill-process.

Figure 1. Comparison of the number of I/O vs. chip size between area array and perimeter array pad arrangement for pitches of 0.2 mm and 0.4 mm.

The Disadvantages of Flip Chip are as follows:

- a) Difficult testing of bare dies.
- b) Limited availability of bumped chips.
- c) Challenge for PCB technology as pitches become very fine and bump counts are high.
- d) For inspection of hidden joints an X-ray equipment is needed.
- e) Weak process compatibility with SMT.
- f) Handling of bare chips is difficult.
- g) High assembly accuracy needed.
- h) With present day materials underfilling process with a considerable curing time is needed.
- i) Low reliability for some substrates.
- j) Repairing is difficult or impossible.

1.3.2. Relative cost comparison

The cost of flip chip technology can be divided into bumping cost and assembly process cost. Die bumping costs are dependent on wafer size, number of dies per wafer, wafer yield and volume. The assembly processes for the most common flip chip technology include pick and place together with flux application, reflow and cleaning as well as underfill process and its curing. The cost of the necessary equipment and floor space, the capacity of the equipment and its compatibility with other manufacturing processes are also important factors having influence on the economy of the technology for particular product. The substrate has also an important impact on the packaging costs. The cost of substrate depends e.g. on via sizes, layer count, line width and spaces, die pad pitch, flatness requirements, material type, panelization optimisation and the fabrication process.

In the case of manufacturing of 300 - 400 I/O BGA packages in the volume of 1 million per month the capital cost of flip chip process is less than half of the corresponding cost for wire bonding technology and the floor space needed is also only about one half of that for wire bonding technology

The cost of bumping with solder bumps using common batch processes is practically independent of the wafer size. The costs per die are therefore strongly dependent on the number of good dies obtained from one wafer. An order of magnitude for wafer bumping in high volume production is \$85 per wafer. For the case of 10 mm die on 8 inch wafer and yield of 90% the bumping cost per die is \$0.37.

The cost of wire bonding process increases with increasing number of I/O's while the cost of flip chip process is practically independent of the I/O count. For very high I/O numbers the flip chip process is the only choice.

Wire bonding, which is a mature technology, costs about \$0.03 per pin, based on a 500 I/O device. The cost to bump a 200 mm with the evaporative process is around \$200, sputtering and plating comes in at around \$100, and electroless nickel bumping cost projections are below \$50 [13].

1.3.3. Availability of components

A precondition for using flip chip technique is availability of bumped chips or alternatively known good bare dies when bumping is done separately. The use of solder bumping is the most common process alternative. Many chip houses already deliver solder bumped dies. Solder bumping which is a wafer level process, needs big and expensive facilities. Therefore it is not convenient to have in house processing facilities for solder bumping. There are also specialized companies making services of solder bumping.

The situation with the availability of solder bumped and tested chips for flip chip bonding is still not satisfactory. Flip chip bonding knowledge is spreading slowly and as an additional production step in wafer manufacturing the known good die (KGD) issue is still causing a certain degree of uncertainty on the user side [31].

Although flip chip technology has been used already for about 30 years, it is still in quite limited use. It has many technical variations which have very different levels of

maturity and fairly restricted availability. The flip chip technology using solder joining is already in a fairly mature state. The limitations are at least partly related to the limited availability of bumped components and limited compatibility with available SMD processing equipment

1.3.4. Description of each flip chip process

There are many different alternative processes used for flip-chip joining. A common feature of the joined structures is that the chip is lying face down to the substrate and the connections between the chip and the substrate are made using bumps of electrically conducting material. Cross sections of flip chip joints without and with underfill material are shown in Figure 2. Examples of the different types of flip chip joints are schematically shown in Figure 3.

Figure 2. Cross sections of flip chip joints without and with underfill material

Figure 3. Examples of different types of flip chip joints.

1.3.5. Flip chip process by solder joining

In flip chip soldering process solder bumped chips are soldered onto the circuit board. Solder is usually, but not always, deposited also on to the substrate pad areas. For fine pitch applications, solder can be deposited e.g. by electroplating, solder ink jet or solid solder deposition. Tacky flux is applied to the solder contact areas either by dipping the chip into a flux reservoir or by dispensing flux onto the substrate. For coarse pitch applications (>0.4 mm) solder paste is deposited on the substrate by stencil printing. The bumps of chips are placed into the tacky paste and they are

reflowed in an oven. After the reflow process cleaning of the flux is preferred. The underfill material is applied by dispensing along one or two sides of the chip, from where the low viscosity epoxy is drawn by capillary forces into the space between the chip and substrate. Finally the underfill is cured by heat. Repairing of the flip chip joint is usually impossible after the underfill process. Therefore testing must be done after reflow and before the underfill application. The steps of flip chip soldering process are:

- 1 Die preparing (testing, bumping, dicing)
- 2 Substrate preparing (flux application r solder paste printing)
- 3 Pick, alignment and place
- 4 Reflow soldering
- 5 Cleaning of flux residues (optional)
- 6 Underfill dispensation
- 7 Underfill curing

Figure 4.Flip Chip solder process

Figure 5.The underfill application by dispensing

1.3.6. Adhesive

Two types of adhesives in general have been used for flip-chip applications. One of these is the anisotropic conductive adhesive (ACA). ACAs are composed of an adhesive polymer matrix and a conductive filler, with fillers that are metallic particles or metal-coated polymer balls. As opposed to the isotropic conductive adhesives (ICAs), the amount of conductive filler is below the percolation threshold. This means that component is attached to the substrate, some of the particles are trapped between the die pads and the pads of the substrate. The purpose of the particles is to create conductive paths between the corresponding contact pads [32] Anisotropic conductive adhesives are often purchased in a film format, called anisotropic conductive film (ACF). Table 1 shows major ACA materials available in market today. In addition to this, Hereaus Namics; Three Bond and Hitachi Chemicals have also developed anisotropic Conductive pastes. A clear trend towards smaller and more uniform particle sizes is observed.

Adhesives	Particles type and size
Hitachi Chemicals, ACF-c48a, 25 μ m thick	Ni, 3 μ m
Hitachi Chemicals, Double Layer, 40 μ m thick	Ni, 3 μ m
Loctite, ACA paste, LID 3169	Sn-Bi-ally, 7 μ m
Loctite, ACA paste, LID 3316	Ni/Au plastic balls, 5 μ m
Loctite, ACA paste, LID 3334	Ni/Au plastic balls, 7 μ m
Loctite, ACA paste, LID 3333	Ni/Au plastic balls, 11.5 μ m
Sony Chemicals, H05-1-11, 50 μ m thick	Non-Conductive
Sony Chemicals, H05-1-11 (BCx4), 50 μ m thick	Au Plated plastic balls with insulating layer
Toshiba Chemicals XAP0017	Au-coated polymer particles, 3 μ m

Table 1. Some of the major ACA materials available today for flip-chip joining on rigid and flexible substrates

1.3.7. Conducting Particles

The contact between the bump and the substrate is made from a very thin layer of Au. This may not sufficiently reduce the contact resistance between the bump and the substrate. For anisotropic conductive adhesive, electrical conduction in the z-direction is achieved by electrical contact between conducting particles and bonding electrodes, increasing the contact area between them is very important to decrease the interconnection resistance. The ideal metallurgy for the conductive particles should be ductile, and resistant to corrosion or oxidation.

Figure 6. Schematic drawing showing the formation of interconnection between bump and substrate pad with conducting particle

Silver

Silver is commonly used as conductive filler for anisotropic conductive adhesives because of its high electrical conductivity, chemical stability, and lower cost compared to gold [33]. Unlike many other metals such as copper, that become non-conductive after being oxidized due to exposure to heat and humidity, silver oxides also show high conductivity. The other important attribute is that silver can be easily

precipitated into a wide range of controllable sizes and shapes. The silver fillers are typically fabricated into flakes and pretreated with organic lubricants to ensure the proper rheology of the ECAs [34]. The organic lubricant on the surface of silver flakes can greatly affect the performance of ECAs, including the dispersity of the Ag flakes in the ECA, rheology, and electrical conductivity of the ECA. A mixture of silver flakes and particles with broad size distribution can offer improved conductance over narrow size distribution [35]. Flakes can provide improved conductivity by allowing the flake-like particles to overlap one another. On the other hand, the voids caused by the overlapping can be filled with the small particles.

Nickel

The ability to resist oxidation allows nickel to be used as stable conductive fillers. However, as a hard, poorly malleable metal, nickel cannot be easily fabricated into optimized geometries. Generally, nickels show both higher filler resistance and contact resistance than silver based products. However, nickel has found use in anisotropic conductive adhesives where spherical particles are commonly used.

1.4. Synthesis of Nano particles

Much work has been done on the synthesis and characterization of nanoscale metal nanocrystals due to their unusual chemical and physical properties, and technological applications [36, 37, 38, 39, 40, 41]. Nanoparticles are being used widely in conducting paints [42], rechargeable batteries [43] and [44], chemical catalysts [45], optoelectronics [46], magnetic recording media [47], ferro-fluids [48], magnetic resonance imaging contrast enhancement and drug delivery [49, 50, 51] and so on. To cater to the requirement of magnetic nanocrystals with tuning properties, a great many methods have been developed to synthesize particles with controlled size and shape. The most popular methods are photolytic reduction, [52] radiolytic reduction [53], sonochemical method [54], solvent extraction reduction [55], microemulsion technique [56, 57] and, polyol process [58], and alcohol reduction [59]. Recently, the use of organometallic precursors has recently been proven interesting since it leads to particles with controlled size, surface coordination, and crystallinity that are monodisperse to ± 1 atomic shell [60].

Among the transition metal magnetic nanoparticles, nickel nanocrystals are difficult to be prepared because they are easily oxidized. To obtain pure nickel nanocrystals, many methods were performed in organic media to avoid the formation of oxide or hydroxide. Organometallic precursors, such as $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{Cp})_2$, have been used for the synthesis of nickel nanoparticles [60], and $\text{Ni}(\text{COD})_2$ was also used to

synthesize nickel particles by spontaneous decomposition in CH_2Cl_2 in the presence of poly(vinylpyrrolidone) [61, 62]. More interesting, trigonal nickel nanoparticles could be prepared through the reaction of $\text{Ni}(\text{COD})_2$ in tetrahydrofuran with tetra-*n*-octylammonium carboxylates as reducing and stabilizing [63]. Especially the newly developed high-temperature solution-phase method, which can form particle samples that are uniform in size, composition, shape, internal structure, and surface chemistry, allowing the properties of nanoscale magnetic materials to be mapped. The nickel nanocrystals with diameters of 20–100 nm were rarely synthesized until now.

1.5. Metal-coated particles

Most ACA filler materials to-date are made from polymer coated spheres. Typically, a polymer sphere is coated a metallic layer which is further insulated from other particles with a secondary polymeric coating. (Figure 7)

The limitations of commercially available materials are:

- ❖ These filler particles are 10-20 μm in size and are not suitable for fine pitch bonding (of less than 50 μm) that will require smaller particles.
- ❖ These materials are polymer based and provide no additional functionality to the ACA material. (ie they do not enhance mechanical or thermal properties of the materials)

Figure 7. Typical ACA particles

Solid and hollow particle technology spans a wide range of industries, including the materials, agriculture, medicine, engineering, and food sciences [64,65]. Of interest to this particular research is the synthesis and application of “core-shell” particles—microcapsules “composed of an excipient matrix (or wall or coat) and an incipient component referred to as a core substance [66].” This may include any type of particle containing a solid, liquid, or gaseous core and a shell of a second material. These systems are also commonly referred to as “shells,” “microballons,” “hollow

microspheres,” “ vesicles,” or “microcapsules [64,65].” Table 2 lists the common applications and functions of core-shell structures.

Applications	Functions
Electrical circuit boards Fiber-optic microsensors Light weight composites Refractory thermal insulation Casting molds Encapsulation/Microencapsulation: Medical (e.g. drug release) Carbonless copy paper Adhesives, perfumes, cosmetics Agricultural products Gas/Chemical storage Fire retards, explosives shock absorbing armor plates	Containment of solids/liquid and gases Creation of composites with desirable properties: Electrical Mechanical Optical Thermal Density Bearing and support surfaces Free flowing materials Metering

Table 2. Common applications and functions of core-shell particles structures [64]

In some applications, metal-plated conductive particles have been used, especially in anisotropic conductive adhesives. Although the original intent of using plated particles was to reduce cost, various types of plated particles have been specially designed for specific characteristics and end uses. Silver, nickel and gold plating on non-metals such as glass and plastic are among the most common types of filler product [67]. Besides the conductive fillers described above, other fillers such as gold and carbon particles are also used in special applications. Due to the high cost, gold filler is mainly used for highly demanding military and space applications. Because of their poor conductivity, carbon-based adhesives are only used for low conductivity

applications such as keyboards or shielding. Two types of adhesives in general have been used for flip-chip applications. One of these is the anisotropic conductive adhesive (ACA). ACAs are composed of an adhesive polymer.

1.5.1. Methods for Synthesizing of Hollow Silica Microspheres -fabrication of Core-Shell Particles

Fabrication of core-shell systems has been accomplished with a variety of materials. The shell portion of the particle has been synthesized from polymeric, metallic, and ceramic materials, and the core can contain solid metal or polymeric substances, oily or aqueous liquid environments, or gaseous phase cores. For the purposes of microencapsulation, drug delivery, and drug detoxification, the systems of most interest are the hollow and fluid-filled core-shell particles. There are several general methods of fabricating core-shell particles, including nozzle-reactor systems, sacrificial cores, and emulsion/phase separation. The first two yield coarse hollow particles in the micrometer to millimeter diameter range, while the latter generally allows formation of hollow or fluid-filled nanometer to micrometer sized particulates. Nozzle reactor systems afford the fabrication of microspheres with well controlled wall thickness and diameter, and have used spray drying or pyrolysis to produce hollow polymer-, metal-, oxide-, and ceramic-shell composite microspheres. These include hollow silica [68], thin-shell titanium dioxide [69], and glass spheres [70].

Sacrificial core methods involve the coating of a core with the material of interest by surface reaction or deposition of molecular precursors. This is followed by the removal of the core via thermal or chemical means. The result is a hollow particle with a shell of the desired material [71, 72]. This method has been used to form ceramic and oxide shell particles based on polystyrene latex and other polymer cores [73, 74, 75].

A third method used to produce core-shell particles is via emulsion and phase separation mediated chemistry. Here, oil-in-water (O/W), water-in-oil (W/O), and water-in-oil-in-water (W/O/W) emulsions droplets; reverse micelles; or emulsion foams are used as a template for shell deposition or as a reactor vessel in which the contained reaction yields a shell at the droplet interface [76]. Using emulsion or interfacial polymerization, hollow micron scale polymeric particles have been synthesized from polyvinyl alcohol (PVA) [77], poly(N-isopropylacrylamide)[78], and latex [79, 80]. In addition, ceramic and ceramic oxide particles have been synthesized by emulsion and phase separation means. For example, micron scale hollow silica spheres and oil-filled silica nanospheres were prepared using emulsion templates [81, 82, 83]; and Al_2O_3 , SiO_2 , and mullite hollow particles were formed using liquid-liquid extraction [84]. Chitosan-coated alginate microspheres have also been prepared by an emulsification/internal gelation technique [85].

1.5.1.1. Interfacial Synthesis of Hollow Silica Microspheres

Interfacial synthesis of hollow silica spheres does not require any addition of auxiliary cosurfactants or cosolvents, substrates, stringent conditions and/or specialised equipment, and the products are structurally and morphologically well defined and stable upon calcination. Christabel E *et al.* [86, 87] reported that the structures were synthesised at room temperature by hydrolysis and condensation of tetraethoxysilane (TEOS) in an aqueous solution of cetyltrimethylammonium bromide (CTABr), which was subjected to rapid quenching by dilution followed by pH neutralisation after an induction period. The size of the hollow silica sphere was 900nm. The process flow is shown in Figure 8.

Figure 8. Process flow of interfacial synthesis of hollow silica sphere

Formation of hollow spheres was sensitive to the stirring condition, induction time, and time delays between the dilution and the neutralisation steps of the synthesis procedure. For the condition used, TEOS is only partially hydrolysed prior to dilution so droplets of the reactant form in the reaction mixture. These are probably stabilized to some extent by CTABr molecules that partition at the TEOS/water interface [86]. Moreover, as the pH was lowered significantly on dilution and neutralisation, slow hydrolysis and condensation of TEOS at the droplet/water interface is curtailed so that mesostructured spherical shells only 20nm in thickness are produced.

The size of the hollow silica sphere can be further reduced to 360nm by using a mixture of TEOS and aminopropyltriethoxysilane (APTES) in water containing CTABr. The bromide counterion $[\text{CTA}^+\text{Br}^-]$ of CTABr was replaced with the large cobalticarborene $([\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-)$ anion [87]. Silica is deposited preferentially at the TEOS/water interface; hollow spheres are formed in situ. This method therefore eliminates the need for any template extraction techniques and as the diameter of the shells depends on the droplet size; this can be controlled to some extent by varying the surfactant counterion.

Christabel E *et al.* [87] reported that the formation of well-defined, non-aggregated silica shells was dependent on the concentration of APTES and CTABr used in the reaction mixture. These components are partitioned at the TEOS droplet surface,

where they markedly influenced the rate of TEOS hydrolysis specially at the droplet/water interface under mildly alkaline conditions. The mean diameter of the hollow silica spheres could be changed by adjusting the size of the TEOS/APTES droplets whilst maintaining their interface stability.

The final product was yellow in colour and showed the presence of cobalt, indicating surface adsorption on or intercalation of $\text{CTA}^+ [\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$ within the silica hollow shells. In conclusion, by controlling the rate of the TEOS hydrolysis specially at the droplet/water interface, intact microspheres with uniform wall thickness and thermal stability can be routinely synthesized.

Figure 9. SEM micrograph of as-synthesized hollow silica microspheres

1.5.1.2. Sol-gel Processing

(i) Preparation of hollow silica microspheres in W/O emulsions with polymers

Micrometer-sized hollow silica particles were synthesized by sol-gel reaction in water-in-oil (W/O) emulsion. An emulsion is defined as a heterogeneous system, consisting of at least two immiscible liquids or phases. Emulsions are prepared by dispersing one liquid into another in the presence of surface-active materials such as surfactant or polymers. Emulsions are thermodynamically unstable. Rearrangement from the droplet form into the two bulk liquids will occur with a net reduction in interfacial area, and this is energetically favourable.

To obtain hollow structures in silica particles, the viscosity of water droplets in W/O emulsion was controlled with polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP). Hydroxypropyl cellulose (HPC) was added to the oil phase to stabilize the emulsion structure. Without HPC, the particles have an irregular shape and hardly have a particulate form. As the concentration of HPC increased from 0.8 to 1.4 wt%, the size of silica particles decreased from 10 to 1 μm . But above 1.4 wt%, the solution was very viscous, so that it was difficult to handle [88]. PEG or PVP in the water phase was very importance because they not only stabilized the W/O emulsion structure, but also influenced the formation of hollow structure. The hollow silica particles were formed when the molar ratio of water to TEOS was 4 and the

concentration of PEG and HPC were 6 and 1.4 wt% respectively. Weight ratio of water phase to oil phase = 1:9. The process flow is shown in Figure 10.

Figure 10. Process flow of preparation of hollow silica microspheres in W/O emulsions with polymers

1.5.1.3. W/O emulsion with PEG

In the case of using PEG in the inner phase, the adsorption of PEG on the silica surfaces had an influence on the formation of hollow particles. First, the ether oxygen of PEG interacts with the isolated silanol (SiOH) by hydrogen bonding so that absorption of silica particles occurred and the absorbed silica did not penetrate into inner phase. Second, because hydrophobic interaction existed among the siloxane (Si-O-Si) surface, hydrophobic group of external phase such as 1-octanol and

HPC, the primary silica particles are accumulated only at the surface [88]. By using PEG, both the surface of silica particle and the inside have the mesoporous structure (Figure 11a). The yield of hollow silica particles with mesoporous shell was below 10% [89].

Figure 11.(a) TEM images of silica particles produced from W/O emulsions containing PEG (b) PVP

1.5.1.4. W/O emulsion with PVP

The particles prepared using PVP showed a yield different from that using PEG in that they evidently have hollow structure (Figure 11b). The molecular behaviour of PVP is different from that of PEG [25]. The PVP polymer has a specific character of partially amphiphilic property. The hydrophilic part in PVP is arranged toward the aqueous layer in droplet and the hydrophobic part in PVP is arranged towards inner oil phase in aqueous droplet. The particles prepared using PVP have hollow structure more than 80% [89].

(ii) Synthesis of hollow silica microspheres with mesoporous shell in non-ionic W/O emulsion

Wenjiang *et al.* reported a method to synthesis hollow silica microspheres by sol-gel process of TEOS in non-ionic W/O emulsion containing kerosene, Span 80 and water. The microspheres synthesized show no agglomeration and do not collapse even after calcination at 700°C for 8 hours. Furthermore the shell of the hollow sphere is mesoporous with pore size in the nm range. The method includes the following steps:

- (1) Prehydrolysis of TEOS
- (2) Self-assembly of the silicon source with the surfactant (Span 80)

The prehydrolysis process was a crucial step to produce hollow silica microspheres.

Figure 12.SEM images of crushed hollow silica spherical particles

Figure 12 indicates clearly the smooth internal structure of hollow silica microspheres. This could be the result of rapid gelation of silica pieces in the water surrounding the oil droplets. Moreover, the kerosene phase outside the water region also provided a complete isolation condition, which avoided the agglomeration among spheres.

(iii) Preparation of monodisperse hollow silica particles without using templates

Monodisperse hollow silica particles without using templates via a two-step method based on the sol-gel process in aqueous solution, were controlled in size and hollow diameter, and were selectively soluble in organic solvent [90]. The process steps are:

- (1) Hydrolysis of phenyltrimethoxysilane (PTMS) under acidic conditions
- (2) Condensation of the silane under basic conditions

The resultant particles were collected with a membrane filter and washed with water and ethanol several times. The particles were dried for 2 hours in a vacuum oven at 80 °C.

The hydrolysis time plays an important role in the formation of the hollow particles. The hydrolysis time used in this study for preparation of hollow particles was in the range of 0.5-4.0 minutes, in which all the resultant particles were observed as hollow particles (Figure 13). Outside this range no hollow silica particles were obtained. The particle size and hollow diameter of the particles were controlled by the hydrolysis

time. The particle size decreased with increasing hydrolysis time. In addition the particle size and hollow diameter of the particles can also be controlled by PTMS concentration, reaction temperature and so on [90].

Figure 13. TEM micrograph of monodisperse hollow silica particles

Mechanism of formation of hollow structure

When PTMS is added to the acidic solution in the first step, PTMS is immiscible with the aqueous solution and phase separation (silane-water) occurs in the mixture solution. Under stirring conditions, droplets of PTMS are formed and become smaller gradually due to miscibility of hydrolyzed PTMS with the aqueous solution as the hydrolysis progresses. In the second step, NH_4OH solution is added to the resultant homogeneous solution and then the condensation is commenced immediately. After a second to a minute, the turbidity of the mixture solution increases rapidly and monodisperse hollow silica particles are prepared ultimately. The production of methanol caused by hydrolysis has an effect on the solubility of

the unhydrolyzed PTMS, existent in the interior of droplets, in the aqueous solution. The release of the unhydrolyzed PTMS with methanol from the droplets coincides with the formation of silica particles. In general, hydrolysis occurs continuously in basic as well as in acidic conditions, although the rate of condensation is faster than that of hydrolysis in basic conditions. The released PTMS monomers are used for growth of particles [90].

1.5.1.5. Employment of Sacrificial Core of Making Hollow Silica

Microspheres

(i) Versatile synthesis of nanometer sized hollow silica spheres

Jeroen *et al.* [91] reported that the used of controlled precipitation of silica from sodium silicate solution at the preset pH on functionalized polystyrene latexes, nanometer sized silica-coated spheres could be prepared and subsequently modified to allow dispersion in non-aqueous solvents; removal of the interior polymer by calcination resulted in the formation of hollow silica spheres. The pH of the sodium silicate solution was kept at 9.7. The process steps are as follow:

- (1) Precipitation of silicic acid on functionalized polystyrene latexes
- (2) Removal of the majority unreacted silicic acid by dialysis
- (3) Calcination of the interior (polystyrene) matrix

Usage of polystyrene latexes with either an amine functionalized or zwitterionic surface, the latter consisting of amine and carboxylate groups (approx. 30 mol% of the latter), could be used to template the deposition of silica (Figure 14). Thickness of the shell is determined by the ratio of template to silicic acid; however, if the relative amounts of silicic acid become too high, silica particles without an organic core also formed.

Figure 14. Representation of the synthesis of silica coated latex particles

I. Tissot *et al.* [92] reported more details on the surface properties of the formation of the functionalized latex particles and on the formation of a silica layer at the polymer particle surface through hydrolysis and condensation of TEOS in aqueous ammoniacal alcoholic suspensions. Hollow silica nanoparticles were obtained in a subsequent step by thermal degradation of the polymeric latex core as depicted in Figure 15.

Figure 15.Representation of the different steps involved in the coating reaction of SiOH-functionalized latex particles with silica and formation of hollow silica beads

(ii) Fabrication of hollow silica microspheres from colloidal core-nanocomposite multiplayer shell particles.

Here report on the fabrication of hollow silica microspheres through the colloid templated electrostatics layer-by-layer (LbL) self-assembly of silica nanoparticle (SiO₂)-polymer multilayers, followed by removal of the templated core and optionally, the polymer (Figure 16) [93,94].

Figure 16. Illustration of procedures for preparing inorganic and hybrid hollow spheres. The scheme is shown for PS latex particles

It was reported that the colloid-templated multiplayer assembly process, which proceeds primarily as a result of electrostatic interactions between the charged species deposited, is relatively straightforward and versatile, allowing high degree of control to be exerted over the wall (i.e. shell) thickness (in the nanometer range) and composition of the resulting microspheres [93].

The number of SiO₂-PDADMAC multilayers assembled on the PS lattices before calcinations was found to influence the morphology of the resulting hollow spheres [95]. Calcination of PS lattices coated with one SiO₂-PDADMAC layer pair resulted in hollow spheres composed of silica. Both broken spheres and complete hollow spheres were obtained and shown in Figure 16. This may indicate that the silica wall

thickness was not invariably sufficient to maintain the initial spherical structure of the PS latex particle upon its removal.

Figure 17.(a) SEM and (b) TEM micrograph of hollow silica spheres produced by calcinations of PS lattices coated with one SiO_2 -PDADMAC multilayer

Complete hollow spheres were obtained when the number of multilayers on the colloid was two or more and the samples were calcined. TEM and SEM micrographs (Figure 17a and b) of hollow silica spheres, formed by calcining of PS lattices coated with three SiO_2 -PDADMAC multilayers, show that the sphericity of the templated particles was preserved. Some of the hollow spheres were deliberately broken to confirm that the spheres were hollow.

Figure 18.(a) SEM and (b) TEM micrograph of hollow silica spheres produced by calcinations of PS lattices coated with three SiO₂-PDADMAC multiplayer

1.5.1.6. Comparison of Hollow Silica Synthesizing Methods

Method	2.8.1 Interfacial Synthesis	2.8.2 Sol-Gel Processing (i), (ii), (iii)	2.8.3 Employment of Sacrificial Core (i), (ii)
Size	Nanosized particle	Microsized particle	Nanosized particle
Process condition/ parameter	<ul style="list-style-type: none"> Ambient condition Stirring time affects particle size Concentration of CTABr / APTES affect particle size Molar composition: 0.044CTABr :0.9TEOS: 0.1APTES: 180water 	<p>(i)</p> <ul style="list-style-type: none"> Concentration of HPC affects particle size Weight ratio water phase to oil phase = 1:9 <p>(ii)</p> <ul style="list-style-type: none"> Prehydrolysis process is crucial step for the formation of hollow structure TEOS: Span: HNO₃: EtOH = 1: 4: 0.01: 3 <p>(iii)</p> <ul style="list-style-type: none"> Hydrolysis time is crucial for the formation of hollow particles Reaction temperature affects particle size 	<p>(i)</p> <ul style="list-style-type: none"> Template: Fuctionalized polystyrene latex Ratio of template to silicic acid determines the shell thickness PH of sodium silicate solution = 9.7 <p>(ii)</p> <ul style="list-style-type: none"> Template: Polystyrene latex Comonomer: MPS Amount of MPS affects particle size
Advantages	<ul style="list-style-type: none"> Simple method: Does not require any addition of auxiliary cosurfactants or cosolvents, substrate and stringent conditions No need to wash the final products 	<p>(i)</p> <ul style="list-style-type: none"> Uniform particle size <p>(ii)</p> <ul style="list-style-type: none"> No agglomeration of hollow sphere <p>(iii)</p> <ul style="list-style-type: none"> Uniform and smooth surface 	<p>(i)</p> <ul style="list-style-type: none"> Easy to coat latex particles by slow precipitation of silica from a sodium silicate solution <p>(ii)</p> <ul style="list-style-type: none"> Hollow silica can be obtained easily

	<ul style="list-style-type: none"> • Short process time • Eliminate the template-removing procedure 	texture	by thermal degradation of polymeric latex core
Disadvantages	<ul style="list-style-type: none"> • Low yield of hollow silica spheres 	<p>(i)</p> <ul style="list-style-type: none"> • Long process time • Final product needs to be washed in ethanol • Complicated process: need to prepare external oil phase and water phase separately <p>(ii)</p> <ul style="list-style-type: none"> • Final product needs to be filtrated and washed in hexane, acetone and water <p>(iii)</p> <ul style="list-style-type: none"> • Final product needs to be washed in water and ethanol several times 	<p>(i)</p> <ul style="list-style-type: none"> • Holes formed in the shell due to exhausting of volatile products during calcinations • Need to remove template <p>(ii)</p> <ul style="list-style-type: none"> • Need to remove template

1.5.2. Chemistry in Sol-Gel processing

A process that has, in the past years, gained much notoriety in the glass and ceramic fields is the sol-gel reaction. This chemistry produces a variety of inorganic networks from silicon or metal alkoxide monomer precursors. Although first discovered in the late 1800s and extensively studied since the early 1930s, a renewed interest [96,97] surfaced in the early 1970s when monolithic inorganic gels were formed at low temperatures and converted to glasses without a high temperature melting process.[98] Through this process, homogeneous inorganic oxide materials with desirable properties of hardness, optical transparency, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperatures, as opposed to the much higher melting temperatures required in the production of conventional inorganic glasses. [98,99,100] The specific uses of these sol-gel produced glasses and ceramics are derived from the various material shapes generated in the gel state, i.e., monoliths, films, fibers, and monosized powders. Many specific applications include optics, protective and porous films, optical coatings, window insulators, dielectric and electronic coatings, high temperature superconductors, reinforcement fibers, fillers, and catalysts.[99]

The sol-gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). [16] The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by

various reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process, often mixed with TEOS.

At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. This general reaction scheme can be seen in Figure 19. However, the characteristics and properties of a particular sol-gel inorganic network are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as, pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, H₂O/Si molar ratio (R), aging temperature and time, and drying. [101,102] Of the factors listed above, pH, nature and concentration of catalyst, H₂O/Si molar ratio (R), and temperature have been identified as most important. Thus, by controlling these factors, it is possible to vary the structure and properties of the sol-gel-derived inorganic network over wide ranges. [22] For example, Sakka et al. observed that the hydrolysis of TEOS utilizing R values of 1-2 and 0.01 M HCl as a catalyst yields a viscous, spinnable solution. It was further shown, that these solutions exhibited a strong concentration dependence on the intrinsic viscosity and a power law dependence of the reduced viscosity on the number average molecular weight:

$$[\eta] = k(M_n)^a(1)$$

Values for α ranged from 0.5 to 1.0, which indicates a linear or lightly branched molecule or chain.

In contrast, when R values greater than two (2) and/or base catalysts were utilized, solutions were produced which were not spinnable at equivalent viscosities. [103,104]

Values of α in eq. 1 ranged from 0.1 to 0.5, indicating spherical or disk shaped particles. These results are consistent with the structures which emerge under the conditions employed by the Ströber process [105] for preparing SiO_2 powders. It was further shown that with hydrolysis under basic conditions and R values ranging from seven (7) to twenty-five (25), monodisperse, spherical particles could be produced.

Figure 19. General Reaction of sol-gel process: hydrolysis, alcohol condensation, and water condensation

Generally speaking, the hydrolysis reaction (Eq. 2), through the addition of water, replaces alkoxide groups (OR) with hydroxyl groups (OH). Subsequent condensation reactions (Eqs. 3 and 4) involving the silanol groups (Si-OH) produce siloxane bonds (Si-O-Si) plus the by-products water or alcohol. Under most conditions,

condensation commences before hydrolysis is complete. However, conditions such as, pH, H₂O/Si molar ratio (R), and catalyst can force completion of hydrolysis before condensation begins. [20] Additionally, because water and alkoxides are immiscible, a mutual solvent such as an alcohol is utilized. With the presence of this homogenizing agent, alcohol, hydrolysis is facilitated [21] due to the miscibility of the alkoxide and water. As the number of siloxane bonds increases, the individual molecules are bridged and jointly aggregate in the sol. When the sol particles aggregate, or inter-knit into a network, a gel is formed. Upon drying, trapped volatiles (water, alcohol, etc.) are driven off and the network shrinks as further condensation can occur. It should be emphasized, however, that the addition of solvents and certain reaction conditions may promote esterification and depolymerization reactions according to the reverse of equations (2), (3), and (4). [20,22]

In the following sections, specific factors that influence the hydrolysis and condensation reactions of the sol-gel process will be discussed. It has been established that certain reaction parameters are more important than others. [16,17,19,20-24] Hereinafter, we will primarily focus on the following influences: pH, nature and concentration of catalyst, and H₂O/Si molar ratio (R).

1.5.2.1. Hydrolysis

1.5.2.2. pH

Iler [106] divides this polymerization process into three pH domains: < pH 2, pH 2-7, and > pH 7. However, regardless of pH, hydrolysis occurs by the nucleophilic attack

of the oxygen contained in water on the silicon atom as evidenced by the reaction of isotopically labeled water with TEOS that produces only unlabelled alcohol in both acid- and base-catalyzed systems: [22]

It can be seen in Figure 20 how pH affects the hydrolysis rate.

Figure 20. pH Rate Profile for Hydrolysis in Aqueous Solution.

1.5.2.3. Nature and Concentration of Catalyst

Although hydrolysis can occur without addition of an external catalyst, it is most rapid and complete when they are employed. Mineral acids (HCl) and ammonia are most generally used, however, other catalysts are acetic acid, KOH, amines, KF, and HF. [18] Additionally, it has been observed that the rate and extent of the hydrolysis reaction is most influenced by the strength and concentration of the acid- or base catalyst. [107]

Aelion et al. found that all strong acids behave similarly, whereas weaker acids require longer reaction times to achieve the same extent of reaction. [27] From a plot of the logarithm of the hydrolysis rate constant versus acid concentration, a slope of one was obtained. They concluded that the reaction was first-order in acid concentration.

Under basic conditions, the hydrolysis reaction was found to be first-order in base concentration. However, as the TEOS concentration was increased the reaction deviated from a simple first-order to a more complicated second-order reaction. With weaker bases such as, ammonium hydroxide and pyridine, measurable speeds of reaction were produced only if large concentrations were present. Therefore, compared to acidic conditions, base hydrolysis kinetics is more strongly affected by the nature of the solvent. [27]

1.5.2.4. Acid-Catalyzed Mechanism

Under acidic conditions, it is likely that an alkoxide group is protonated in a rapid first step. Electron density is withdrawn from the silicon atom, making it more

electrophilic and thus more susceptible to attack from water. This results in the formation of a penta-coordinate transition state with significant S_N2 -type character. [18] The transition state decays by displacement of an alcohol and inversion of the silicon tetrahedron, as seen in Figure 21.

Figure 21. Acid-Catalyzed Hydrolysis

1.5.2.5. Based-Catalyzed Mechanism

Base-catalyzed hydrolysis of silicon alkoxides proceeds much more slowly than acid-catalyzed hydrolysis at an equivalent catalyst concentration. [27] Basic alkoxide oxygens tend to repel the nucleophile, -OH . However, once an initial hydrolysis has occurred, following reactions proceed stepwise, with each subsequent alkoxide group more easily removed from the monomer than the previous one. [108] Therefore, more highly hydrolyzed silicones are more prone to attack. Additionally, hydrolysis of the forming polymer is more sterically hindered than the hydrolysis of a monomer. Although hydrolysis in alkaline environments is slow, it still tends to be complete and irreversible. [20]

Thus, under basic conditions, it is likely that water dissociates to produce hydroxyl anions in a rapid first step. The hydroxyl anion then attacks the silicon atom. Again, an $\text{S}_{\text{N}}2$ -type mechanism has been proposed in which the -OH displaces -OR with inversion of the silicon tetrahedron. This is seen in Figure 22.

Figure 22. Base-Catalyzed Hydrolysis

1.5.2.6. H₂O/Si Molar Ratio (R)

As stated previously, the hydrolysis reaction has been performed with R values ranging from less than 1 to over 50, depending on the desired polysilicate product. From equation 2, an increased value of R is expected to promote the hydrolysis reaction. Aelion et al. found the acid-catalyzed hydrolysis of TEOS to be first-order in water concentration; however, they observed an apparent zero-order dependence of the water concentration under basic conditions. ²⁶ This is probably due to the production of monomers by siloxane bond hydrolysis and redistribution reactions (i.e., reverse reactions 3 and 4). Nonetheless, the most obvious effect of the increased value of R is the acceleration of the hydrolysis reaction. Additionally, higher values of R caused more complete hydrolysis of monomers before significant condensation occurs. Differing extents of monomer hydrolysis should affect the relative rates of the alcohol- or water-producing condensation reactions. Generally, with understoichiometric additions of water ($R \ll 2$), the alcohol producing-condensation mechanism is favored, whereas, the water-forming condensation reaction is favored when $R \geq 2$.²⁸

Although increased values of R generally promote hydrolysis, when R is increased while maintaining a constant solvent: silicate ratio, the silicate concentration is reduced. This in turn reduces the hydrolysis and condensation rates, resulting in longer gel times. This effect is evident in Figure 23 which shows gel times for acid-catalyzed TEOS systems as a function of R and the initial alcohol: TEOS molar ratio. [109]

Finally, since water is the by-product of the condensation reaction (Eq. 3), large values of R promote siloxane bond hydrolysis (reverse of Eq. 3).

Figure 23. Gel Times as a function of H₂O: TEOS Ratio, R .

1.5.3. Condensation

1.5.3.1. pH

Polymerization to form siloxane bonds occurs by either an alcohol-producing or a water-producing condensation reaction. It has been shown by Engelhardt et al. that a

typical sequence of condensation products is monomer, dimer, linear trimer, cyclic trimer, cyclic tetramer, and higher order rings. [110] This sequence of condensation requires both depolymerization (ring opening) and the availability of monomers which are in solution equilibrium with the oligomeric species and/or are generated by depolymerization (reverse of Eqs. 3 and 4). [18]

The rate of these ring opening polymerizations and monomer addition reactions is dependent upon the environmental pH. In polymerizations below pH 2, the condensation rates are proportional to the $[H^+]$ concentration. Because the solubility (see Figure 24) of silica is quite low below pH 2, formation and aggregation of primary silica particles occur together and ripening (i.e., growth of a network) contributes little to growth after particles exceed 2nm in diameter. Thus, developing gel networks are composed of exceedingly small primary particles. [18]

It is generally agreed that between pH 2 and pH 6 condensation rates are proportional to $[-OH]$ concentrations. Condensation preferentially occurs between more highly condensed species and those less highly condensed and somewhat neutral. This suggests that the rate of dimerization is low, however, once dimers form, they react preferentially with monomers to form trimers, which in turn react with monomers to form tetramers. Cyclization occurs because of the proximity of the chain ends and the substantial depletion of the monomer population. Further growth occurs by addition of lower molecular weight species to more highly condensed species and aggregation of the condensed species to form chains and

networks. The solubility of silica in this pH range is again low and particle growth stops when the particles reach 2-4 nm in diameter. [20]

Above pH 7, polymerization occurs the same as in the pH 2 to pH 6 range. However, in this pH range, condensed species are ionized and therefore, mutually repulsive. Growth occurs primarily through the addition of monomers to the more highly condensed particles rather than by particle aggregation. Due to the greater solubility of silica and the greater size dependence of solubility above pH 7, particles grow in size and decrease in number as highly soluble small particles dissolve and reprecipitate on larger, less soluble particles. Growth stops when the difference in solubility between the smallest and largest particles becomes indistinguishable. This process is referred to as Ostwald ripening. Particle size, is therefore, mainly temperature dependent, in that higher temperatures produce larger particles. Additionally, in this pH range, the growth rate depends upon the particle size distribution. [18]

Figure 24. Dissolution rate and relative gel time as a function of pH.

1.5.3.2. Nature and Concentration of Catalyst

As with hydrolysis, condensation can proceed without catalyst, however, their use in organosiloxanes is highly helpful. Furthermore, the same type catalysts are employed: generally those compounds which exhibit acidic or basic characteristics.

It has been shown that condensation reactions are acid and base specific. [11] In addition, Iler has shown that under more basic conditions, gel times are observed to increase. [26] Condensation reactions continue to proceed, however, gelation does not occur. Again, catalysts which dictate a specific pH, can and do drive the type of silica particle produced as seen in the previous discussion on pH.

1.5.3.3. Acid-Catalyzed Mechanism

It is generally believed that the acid-catalyzed condensation mechanism involves a protonated silanol species. Protonation of the silanol makes the silicon more electrophilic and thus susceptible to nucleophilic attack. The most basic silanol species (silanols contained in monomers or weakly branched oligomers) are the most likely to be protonated. Therefore, condensation reactions may occur preferentially between neutral species and protonated silanols situated on monomers, end groups of chains, etc. [18]

1.5.3.4. Base-Catalyzed Mechanism

The most widely accepted mechanism for the base-catalyzed condensation reaction involves the attack of a nucleophilic deprotonated silanol on a neutral silicic acid: [26]

Figure 25. Nucleophilic Attack to Form Siloxane Bond

Furthermore, it is generally believed that the base-catalyzed condensation mechanism involves penta- or hexa-coordinated silicon intermediates or transition states, similar to that of a S_N2 type mechanism. [18]

Methodology

1.6. Synthesis of Nickel

A number of physical and chemical techniques can be used to produce metal particles in the nanosized regime. Some examples include photolytic reduction, radiolytic reduction, solvent extraction reduction, hydrothermal reduction and microemulsion technique.^[112, 113, 114] Among the chemical methods, the reduction of a metal salt or oxide by an appropriate reducing agent is frequently employed. Properties of the product are strongly influenced by the reactants which include the metallic precursor, the reducing agent and the solvent medium. Properties of the reaction medium such as basicity, polarity, viscosity and boiling point will also affect the reaction to a great extent. ^[115]

Hydrothermal reduction was the selected method for this study as it allows for better removal of solvent (water) after synthesis. In this study to obtain pure nickel particles, aqueous nickel sulphate had to be reduced using aqueous hydrazine solution at a specific pH and range of concentrations. In the literature, 0.05M of nickel sulphate was used; nickel particles of about 700 nm were obtained.^[116]

1.6.1. Materials

Table 4 shows all the reagents used as obtained from the following suppliers.

Table 4. Chemicals for nickel synthesis

Chemicals	Purity	Suppliers
Nickel Sulphate	99%	Merck
Hydrazine	98%	Aldrich Chemical Co.
Sodium Hydroxide	98%	Aldrich Chemical Co.

1.6.2. Methodology

25ml of 10M-hydrazine solution was added to 500ml of 0.05M NiSO₄ solution. The pH was kept at 11 by adding sodium hydroxide to the resulting solution. Reduction was carried out in an autoclave that was kept in the range of 90-95°C for one and the half hours with stirring.

In order to obtain particles of different sizes, their dependence on the salt concentration was investigated. 4 other concentrations ranging from 0.01M to 0.1M were used. The amount of hydrazine and sodium hydroxide added were changed accordingly. Table 5 shows the amounts of reactants added.

Table 5.: Amounts of reactants for different salt concentrations

Nickel Sulphate	Hydrazine	Sodium Hydroxide
200 ml of 0.1M	20 ml of 10M	5 ml of 2M
200 ml of 0.075M	15 ml of 10M	5 ml of 2M
200 ml of 0.05M	10 ml of 10M	5 ml of 2M
200 ml of 0.025M	5 ml of 10M	7 ml of 2M
200 ml of 0.01M	5 ml of 10M	10 ml of 2M

All the products were washed with deionized water.

The after washed nickel particle was left in a dry incubator at room temperature with vacuum to drive off all moisture. Oven drying is not suitable, as the higher temperatures will cause agglomeration of nickel particles.

1.6.2.1. Characterization Tests

X-ray diffraction patterns for the synthesis nickel particle were obtained using Rigaku D/max-rA X-ray diffractometer. The X-ray diffraction pattern allows for the identification of samples with their characteristic peaks.

Particle morphology characterization was done with field emission scanning electron microscope (FESEM) from JOEL JSM-6340F.

Zeta Potential Particle Sizer from Brookhaven Instruments Corporation was used to evaluate the particle sizes. Based on the principles of Dynamic Light Scattering (DLS), particle sizes ranging from 3 nm to 3 μ m can be measured. In DLS, random intensity fluctuations arising from the Brownian Motion of colloidal particles are analyzed to give either a simple mean size and polydispersity (distribution width) or a more complete distribution data such as multimodal distribution. Hence, particle size distribution can also be obtained.

1.7. *Heat Treatment of Nickel Particles*

Genetically, although nickel exhibits good electrical conductivity, the synthesized nickel particles show high resistivity to electrical current according to electrical tests conducted. As observed in the FESEM micrographs, the nickel particles show an overall spherical structure but spiked morphology. It was speculated that the spikes contributed to the electrical resistance of the nickel particles. Other factors such as internal strains and microscopic defects of the synthesized nickel may also have caused the poor conductivity. Similar morphology and electrical conductivity were observed in the acquired commercially produced nickel particles.

To improve electrical conductivity, both the synthesized and commercial polycrystalline nickel particles were sent for heat treatment.

1.7.1. Methodology

The polycrystalline nickel powders were heat treated in air at four different temperatures and duration. Table 6 shows the details of the three batches of nickel powder sent for annealing.

Table 6.: Batches of nickel powder for heat treatment

	Type	Supplier	Size
(1)	Commercial	Novamet	300 – 700nm
(2)	Commercial	Johnson Matthey Electronics	3 – 7 μ m
(3)	Synthesized	-	~ 700nm

The synthesized nickel powder used in this experiment was produced in-house using hydrothermal reduction of 0.5M of nickel sulphate with hydrazine as the reducing agent. Details of the experiment can be found in Section 3.1.1.

1.7.2. Annealing Flow Chart

The annealing experiments were proceeded as follows:

1.7.3. Characterization Techniques

After annealing, the morphology, grain size, electrical conductivity and oxidation characteristics were of interest in this study.

1.7.3.1. Particle size and morphology

As the primary purpose of annealing the nickel powders was to find out whether the heat treatment would lead to any changes in the morphology of the particles, the Field Emission Scanning Electron Microscope (FESEM) was used, with accelerating voltage set at 5keV. Any change in the particle sizes was also observed.

1.7.3.2. Oxidation and Grain Size

XRD tests were conducted to find out whether oxidation of the nickel particles had occurred since annealing was done in air. As higher temperatures and durations will definitely enhance the effects of annealing, it was of interest to find the maximum temperature and time the heat treatment could be done without the oxidation of the nickel particles.

Grain size changes in the polycrystalline powder were also of interest. With this observation, the extent of the effects of annealing could be analyzed. The Debye-Scherrer equation,

$$t = \frac{0.9\lambda}{B \cos(\theta)} \text{ where } B \text{ is a constant,}$$

was used to compute changes in the grain size.

1.7.3.3. Temperature of onset of oxidation

Thermogravimetric Analysis (TGA) runs were conducted to find out the effects of annealing on the onset of oxidation of the annealed nickel particles.

TGA measures minute weight change as a function of temperature thereby providing the onset of heat-induced changes of the sample. A highly sensitive electronic balance is used for the weight measurement. Two high temperature resisting sample dishes are used, one for the sample and the other one for a reference material.

In our study, heat was supplied to the annealed samples at 10°C per minute until temperature reaches 600°C. A steady flow of air was supplied to the setup during heating. Oxidation that occurred in the sample will be observed as an increase in the mass of the sample.

1.8. Epoxy Formulations

A thermoset epoxy system is the choice for the adhesive matrix in this study. The study includes finding out the curing time as well as the pot life for different catalyst amounts.

Materials

The components of this system are as shown in Table 7.

Table 7. Components of epoxy system

Chemicals	Type	Suppliers
Diglycidylether bisphenol-A	Epoxy Resin	Sigma Aldrich
Methyl hexahydrophthalic anhydride	Hardener	Sigma Aldrich
Benzyl dimethyl amine	Catalyst	Sigma Aldrich
3-glycidoxypropyl trimethoxy silane	Diluent	Sigma Aldrich

Methodology

Catalyst amount is measured by x parts to 100 parts of resin. The resin to hardener ratio is fixed. Table 8 gives the various proportions of catalyst tested. Diluent was not added in this study as it does not significantly affect the curing time.

Table 8.: Different proportions of catalyst

Type	Trial 1 (Ratio)	Trial 2 (Ratio)	Trial 3 (Ratio)	Trial 4 (Ratio)
Epoxy Resin	170	170	170	170
Hardener	166	166	166	166
Catalyst	0	0.425	0.85	1.7
x parts catalyst	0 parts	2.5 parts	5 parts	10 parts

Characterization Tests

Differential Scanning Calorimeter was used to evaluate the curing time with different proportions of the catalyst added. Pot life was evaluated by leaving the mixture at room temperature. The mixture was stirred to find out the time it takes to gel.

3.1 Cure Kinetics

Materials

The nickel particles used were obtained from Novamet of sizes 0.3 – 0.7 μ m.

Methodology

Nickel particles were mixed into the epoxy system (2.5 parts of catalyst) as decided from the results of experiment done in Section 3.2. Table 9 shows the samples of different nickel weight% used in this study.

Table 9.: Samples for cure kinetics

Sample	Loading
Sample 1a	0 wt%
Sample 1b	32.25 wt%
Sample 1c	75 wt%

Characterization Tests

Differential Scanning Calorimeter (DSC) from TA Instruments was used to evaluate the curing time with different proportions of the nickel added. The Differential Scanning Calorimetry (DSC) detects the occurrence of any thermal transition by monitoring the heat flow between a reference and the sample. Should an exothermic

reaction such as curing occur, the heat released by the sample would cause the baseline to deviate. The area under the peak indicates the enthalpy heat for the curing reaction. Isothermal runs were done at 130°C, 140°C and 150°C respectively.

1.9. Thermal Impedance Measurements

This study was done with the aim of evaluating the trend of different particle sizes in epoxy on thermal conductivity.

Materials

Three different sizes of nickel particles were used. Two of the nickel samples were obtained commercially. The third sample was synthesized with the method as described in Section 3.1, using the nickel sulphate concentration of 0.05M. Table 10 shows the different batches of nickel used.

Table 10.: Nickel particles used for thermal impedance measurements

Size	Supplier
3 μm – 7 μm	Johnson Matthey Electronics
~780 nm	—
0.3 μm – 0.7 μm	Novamet

Methodology

The particles were annealed at 310°C for 4 hours and mixed in the epoxy system. For each batch of nickel particles, four different loadings were made. A sample of epoxy

with no nickel loading was also made to serve as a comparison. The samples used for testings are as shown in Table 11.

Table 11.: Samples used for thermal impedance measurements

Sample	Nickel Size	Loadings
Sample 2	—	0 wt%
Sample 3a-d	Annealed Distribution 0.3 μ m – 0.7 μ m	16.25wt%, 32.5wt%, 56.25wt%, 75wt%
Sample 4a-d	Unannealed Distribution 0.3 μ m – 0.7 μ m	16.25wt%, 32.5wt%, 56.25wt%, 75wt%
Sample 5a-d	Annealed Distribution ~780 nm	16.25wt%, 32.5wt%, 56.25wt%, 75wt%
Sample 6a-d	Annealed Distribution 3 μ m – 7 μ m	16.25wt%, 32.5wt%, 56.25wt%, 75wt%

The samples were cast in Teflon moulds of thickness 5 mm and cured in an oven at a temperature of 140°C. They were subsequently trimmed into discs of 1 inch diameter for the thermal impedance measurement.

Equipment

Bulk thermal conductivity can be measured using thermal impedance measuring equipment following the ASTM D5470 standard. This involves measuring the

thermal impedance of the material in a standard test fixture with a specified clamping pressure and constant heat flow. (Refer to Figure 26) Thermal impedance is defined as the total opposition that an assembly material and material interface presents to the flow of heat.

In this setup, the sample is sandwiched between two pieces of thermal interface material and positioned in between two heating blocks and two cooling blocks. A load cell is used to control the amount of pressure exerted on to the blocks and the pressure is shown on the pressure controller. A heater is embedded in the first heating block which is kept insulated by a round Teflon block. This heater is connected via the thermocouple to the temperature controller. On the other hand, the lower cooling block is connected to a chiller which maintains it at a low temperature of approximately 3°C. The lower heating blocks and the upper cooling blocks each has three holes drilled in them. Temperature at these 6 points are read during the experiment with thermocouples and used to calculate the thermal impedance.

Thermal impedance is measured based on the amount of heat passing through the thermal interface material. (Equation 3-1) This heat, Q is dependent on the contact area, A of the sample, the temperature difference, ΔT across the sample and the thickness of the sample.

$$\text{Thermal impedance} = \Delta T.A/Q \text{ -----(3-1)}$$

Figure 26. Thermal impedance measurement setup ASTM D 5470 standard

The measurement is carried out using the software Labview and each testing takes approximately 10 to 15 minutes.

1.9.1.1. Electrical Resistance

Synthesis nickel powder was used to study the effects of annealing on electrical resistance of nickel particles.

According to the XRD readings, it was found that nickel powders that were annealed at 410°C were mostly oxidized. Thus, this temperature was deemed unsuitable for annealing nickel particles in air. The powders annealed at 270°C, 310°C and 360°C for durations of 4hrs, 8hrs and 12 hrs were sent for testing. The synthesized nickel powder which had not undergone annealing was also tested for its resistance.

Since the annealed nickel powder was purposed for use as conductive fillers in ECAs applications, electrical resistance were measured after the nickel powder was incorporated into a thermoset epoxy system as the adhesive matrix in this study. The test specimens were formulated with the components as shown in Table 12.

Table 12.: Components of the Epoxy System

Chemicals	Type	Suppliers
Diglycidylether bisphenol-A	Epoxy Resin	Sigma Aldrich
Methyl hexahydrophthalic anhydride	Hardener	Sigma Aldrich
Benzyl dimethyl amine	Catalyst	Sigma Aldrich

Catalyst amount is measured by 2.5 parts to 100 parts of resin. The resin to hardener ratio is fixed according to previous research, and 75 weight% of annealed (1) commercial nickel powder was used. Table 13 gives the amount of components that were used in the systems. Diluent was not added in this study as it does not significantly affect the curing time.

Table 13.: Amount of Components of the Epoxy System

Component	Amount /mg
Epoxy Resin	1010.6
Hardener	986.8
Catalyst	2.52
Nickel	6000

After the nickel powder was mixed with the epoxy system, the samples were cast in Teflon moulds of thickness 5 mm and cured in the oven for about 30 min at 140°C. When the curing was completed, the mobility of the nickel particles was lost. They were subsequently trimmed into square pieces of 1 by 1 inch for electrical resistance measurement with the experimental set up shown in Figure 27.

Figure 27. Schematic diagram – Experimental Setup for Resistance Measurements

1.10. Coating of Sub-micron Nickel Particle

The coating of nickel particles provides a method to extend the conventional ACAs to fine pitch application by increasing particle loading higher than percolation threshold using insulated conductive particles. During the bonding process, with the applied load, the coated insulation layer of conductive particles between the bump and pad could be broken and form the electrical interconnection between the electrodes, while other particles are still insulated each other. With the increase of particle density, the contact resistance could reduce due to the increased contact area between the electrodes. Moreover, the CTE of ACAs could be reduced due to the increased particles and the reliability could be improved due to the lower CTE mismatch compared with the conventional ACAs with lower particle loading. Based on our previous research [117], the modulus of adhesive plays a very important role in the adhesion strength of the adhesive with chip or substrate. Therefore, the modulus of ACAs may also increase with the increase of particles and lead to higher adhesion strength between the interface of chip and adhesive or substrate and adhesive. The thermal conductivity will also be improved due to the higher particles loading. With the increase of the contact area, the current crowding which induces the electromigration issues could be suppressed.

Initial effort was focused on coating a layer of silica on the commercial available Nickel powder with dimension in a range of 300 to 500 μm . These particles were

stabilized by adding surfactants such as oleic acid to the Nickel powder suspended in solution.

These Nickel powder could be directly coated with amorphous silica, produced via hydrolysis of sol-gel precursor. Because the Nickel has a strong affinity towards silica, no primer was required to promote the deposition and adhesion of silica. In a typical procedure, 50mg of Nickel powder was suspend in 4ml de-ionized water (DI) and 20ml 2-propanol. Under continue mechanical stirring, 0.5ml ammonia solution and 10ml of tetraethyl orthosilicate (TEOS) were consecutively added to the reaction mixture. The reaction was allowed to proceed at room temperature for 3 hr under continue stirring. The growth of silica shells on Nickel particle involved the base-catalyzed hydrolysis of TEOS and subsequent condensation of silica onto the surfaces of Nickel particle. The coated particle could be separated the reaction medium by centrifuging at about 4000rpm and then redispersed into DI water. Due to the presence of negative charges on the surfaces of silica shells, these particles could form very stable dispersions in water without adding other surfactants.

Hydrolysis and condensation of droplets of a mixture of tetraethoxysilane (TEOS) and aminopropyltriethoxysilane (APTES) formed by vortexing the reaction mixture in water containing cetyltrimethylammonium bromide (CTABr). Silica is deposited preferentially at the TEOS/water interface; hollow microspheres are formed in situ. This method therefore eliminates the need for any template extraction techniques and

as the diameter of the shells depends on the droplet size; this can be controlled to some extent by varying the molar composition of APTES.

The chemicals required are:

- Tetraethoxysilane (TEOS)
- Cetyltrimethylammonium bromide (CTABr)
- Aminopropyltriethoxysilane (APTES)
- Conductive particle
- Deionized (DI) water

Solution to prepare

i. 0.02g CTABr in 4.0g of deionised water

ii. 1.70g TEOS

(Volume: $1.70\text{g} / 0.934\text{g/ml} = 1.82\text{ml}$)

iii. 0.20g APTES

(Volume: $0.20\text{g} / 0.946\text{g/ml} = 0.21\text{ml}$)

iv. 0.01g Conductive particle

Encapsulated hollow silica microspheres were synthesised at room temperature. This method consisted of the following steps:

1. 0.02g of CTABr was dissolved in 4.0g of deionised water under continuous stirring. CTABr helps to improve the stability of the ethoxysilane/water interface and is critical for the production of well-defined silica microspheres.

2. 0.25ml of a mixture of TEOS (1.82ml), APTES (0.21ml) and 0.01gm conductive particle was added drop wise into CTABr solution while stirring for 3 minutes.
3. The pH of the entire mixture was initially increased to 11 and then decreased to 10.
1. The entire mixture was left unstirred under ambient conditions, a white layer of product was formed at the air/water interface.

When the pH of the mixture dropped to 9.5 after 30 minutes, the white layer of product disappeared and the mixture turned into cloudy

Figure 28. Flow Chart of the Synthesis Process

Results and Discussion

1.11. Synthesis of Nickel Particle

Hydrothermal reduction was the chosen synthesis route. Hydrazine was added to nickel sulphate to produce nickel particles.

Addition of hydrazine to nickel sulphate forms a complex $[\text{Ni}(\text{N}_2\text{H}_4)_3]^{2+}$ which is very stable at room temperature when kept in an alkaline environment (by addition of sodium hydroxide). At higher temperatures, stability of the complex decreases. When a critical temperature is reached, the complex decomposes to form the pure metal, nickel. No inert gas is needed for the synthesis as nitrogen is produced during reaction. The reduction reaction is as follows:

When the temperature and pH were kept at the 90-95°C and 11 respectively, pure nickel particles were obtained.

1.11.1. Particle Sizer

The average size obtained from Brookhaven ZetaPlus Particle Sizer is calculated using multimodal size distribution. In this distribution, a numerical algorithm, including Mie theory, is used. Figure 29 shows the distribution obtained for the reduction of nickel sulphate at 0.05M.

Table 14 gives the results for other nickel sulphate concentrations obtained from this characterization test. Figure 30 shows a graph of salt concentration vs particle sizes with their maximum and minimum values.

It can be seen that lowering concentrations resulted in a decrease in particle sizes and the distribution of sizes measured showed the range of sizes for each concentration is $\pm 5\%$.

It is also observed that the mean arithmetic diameter increased linearly with nickel salt concentration from 0.01M to 0.08M. An increase of salt concentration to 0.1M does not significantly increase the particle size

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
761.8	0	0	781.5	78	33	801.0	0	100
763.6	0	0	783.1	89	44	802.9	0	100
765.3	0	0	784.8	97	56	804.7	0	100
767.0	0	0	786.4	100	68	806.5	0	100
768.8	0	0	788.0	97	80	808.4	0	100
770.6	0	0	789.7	89	91	810.2	0	100
773.3	17	2	791.3	78	100	812.1	0	100
775.0	25	5	793.8	0	100	813.9	0	100
776.6	37	10	795.6	0	100	815.8	0	100
778.2	50	16	797.4	0	100	817.7	0	100
779.8	64	23	799.2	0	100	819.5	0	100

Figure 29.Multimodal size distribution

Table 14. Sizes obtained with different salt concentrations

Nickel Sulphate Concentration	Average Particle Sizer (nm)
0.1M	988.4
0.075M	939.7
0.05M	784.3
0.025M	567.4
0.01M	485.7

Figure 30. Graph from particle sizer

1.11.2. X-Ray Diffraction

Figure 31 shows the diffraction pattern observed for the nickel synthesized using the hydrothermal reduction method. From the peaks identified, it can be concluded that pure f.c.c nickel particles were obtained using this method of synthesis.

Figure 31. XRD pattern for the synthesized Ni particles

1.11.3. Field Emission Scanning Electron Microscope (FESEM)

Hydrothermal reduction using hydrazine on nickel sulphate produces nickel particles with spiky surfaces as seen in Figures 32 – 34. This surface phenomenon could be due to the preferential growth of nickel in a particular direction during synthesis.

Figures 32 – 34 gives the pictures taken for concentrations of 0.05M, 0.025M and 0.01M respectively.

Figure 32. Nickel particle obtained from 0.05M

Figure 33. Nickel particle obtained from 0.025M

Figure 34. Nickel particle obtained from 0.01M

1.12. Annealing of Nickel particle

1.12.1. Oxidation

The temperature which oxidation of the nickel powder occurs is also of interest in this study as the results will be able to provide insights to the maximum time and temperature that can be used for annealing nickel powder in air.

TGA was used to find the onset temperature of oxidation of the nickel powders. Since the mass of the nickel powder do not show a sharp increase, the onset oxidation temperature was found by using tangents to the curve, shown in an example in Figure 35.

Figure 35. Schematic diagram – Obtaining Oxidation Onset Temperature

1.12.2. Annealing

Spiky surface of the nickel particle was observed after the synthesis. This surface phenomenon could be due to preferential growth of nickel in a particular direction during synthesis.

Nickel particles were heat treated at 270°C, 310°C and 360°C for duration of 4, 8, and 12 hours.

Figure 36 to 39 showed a change of this spiky morphology.

Temperature has a most profound influence on the coefficients and diffusion rates. Annealing provides an effective approach to modify the morphology and/or phase of the microstructures, thus tuning the materials' properties. One of the key factors leading to the morphology change of a particle is surface diffusion. Surface diffusion, or atom and molecular dynamics at surfaces, is a subject of considerable importance in surface and nano sciences since many surface phenomena involves mass transport and dynamic fluctuations of atoms, cluster and molecules [118]. These phenomena include surface reconstruction, crystal growth and thin films epitaxy, shape-change and sintering, adsorption and desorption, and surface promoted chemical reactions.

Figure 36. Synthesis nickel particle (3500X)

Figure 37. Annealed at 360°C for 4hr (3500X)

Figure 38. Annealed at 360°C for 8hr (3500X)

Figure 39. Annealed at 360°C for 12hr (3500X)**1.12.3. Modeling of the annealed nickel particles**

In order to understand the underlying mechanism for the smoothening effect of nickel particles during annealing, an analytical model is established considering surface diffusion. From thermodynamics point of view, smoothening is favorable due to the decrease of surface energy through surface diffusion. This surface diffusion is locally generated by the gradient of curvature. Namely, local input of Laplace tension in the Gibbs energy per atom (i.e., chemical potential) is expressed as:

$$\Delta\mu = \Omega \cdot \frac{\gamma}{R}. \quad (1)$$

Where $\Delta\mu$ is the potential energy (J), Ω is the atomic volume ($1.09 \times 10^{-29} \text{ m}^3$), γ is the surface energy (1.7 J/m^2) and R is the curvature ($0.6 \mu\text{m}$). Thus, force per atom (N),

$$\text{arising from the change of curvature } 1/R, \text{ is equal to } F_s = -\frac{\partial}{\partial s} \left(\Omega \cdot \frac{\gamma}{R} \right). \quad (2)$$

Where ∂s is the change of curvature.

So, the surface diffusion flux density (J_s) is

$$J_s = \frac{C_s D_s}{k_B T} F_s = -\frac{C_s D_s}{k_B T} \frac{\partial}{\partial s} \left(\Omega \cdot \frac{\gamma}{R} \right) \quad (3)$$

Where C_s is the concentration (8.908 kg/m^3), D_s is the diffusion coefficient ($3.5 \times 10^{-24} \text{ m}^2/\text{s}$), k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$), T is the temperature (633 K)

Shape evolution of the surface is determined by the local divergence of surface fluxes. Namely, the divergence of surface flux density is proportional to velocity, which is normal to the profile.

$$V_n = -\Omega \frac{\partial J_s}{\partial s} \quad (4)$$

Combining eqs (4) and (3), we obtain:

$$V_n = -\Omega \frac{\partial J_s}{\partial s} = \frac{\Omega C_s D_s}{k_B T} \frac{\partial^2}{\partial s^2} \left(\Omega \cdot \frac{\gamma}{R} \right) \quad (5)$$

If we use Cartesian coordinates, curvature (k , i.e., the inverse of radius) is

$$\frac{1}{R} = \frac{\frac{d^2 y}{dx^2}}{\left[1 + \left(\frac{dy}{dx} \right)^2 \right]^{3/2}} \quad (6)$$

Cartesian components of the local velocity are:

$$V_{nx} = -V_n \cdot \sin \theta = -V_n \frac{dy/dx}{[1 + (dy/dx)^2]^{1/2}}, \quad (7)$$

$$V_{ny} = V_n \cdot \cos \theta = V_n \frac{1}{[1 + (dy/dx)^2]^{1/2}} \quad (8)$$

Commercial software MATLAB combined with finite difference method is used to model the change of morphology of the nickel particle. The expression in finite differences for Eq. (6) is:

$$\begin{aligned}
k_i &= \frac{1}{R_i} = \frac{\frac{\frac{y_{i+1} - y_i}{x_{i+1} - x_i} - \frac{y_i - y_{i-1}}{x_i - x_{i-1}}}{\left(\frac{x_{i+1} + x_i}{2} - \frac{x_i + x_{i-1}}{2}\right)}}{\left[1 + \left(\frac{y_{i+1} - y_{i-1}}{x_{i+1} - x_{i-1}}\right)^2\right]^{3/2}} = \\
&= \frac{2 \cdot (x_{i+1} - x_{i-1})^2 \cdot [(y_{i+1} - y_i)(x_i - x_{i-1}) - (y_i - y_{i-1})(x_{i+1} - x_i)]}{(x_{i+1} - x_i)(x_i - x_{i-1}) \left[(x_{i+1} - x_{i-1})^2 + (y_{i+1} - y_{i-1})^2 \right]^{3/2}}
\end{aligned} \tag{9}$$

Derivative of the function k along the profile is

$$\left. \frac{\partial k}{\partial s} \right|_{i+1/2} \cong \frac{k_{i+1} - k_i}{\left[(y_{i+1} - y_i)^2 + (x_{i+1} - x_i)^2 \right]^{1/2}}. \tag{10}$$

and the second derivative may be written as

$$\begin{aligned}
\left. \frac{\partial^2 k}{\partial s^2} \right|_i &\cong \frac{\left. \frac{\partial k}{\partial s} \right|_{i+1/2} - \left. \frac{\partial k}{\partial s} \right|_{i-1/2}}{\frac{1}{2} \left[(y_{i+1} - y_{i-1})^2 + (x_{i+1} - x_{i-1})^2 \right]^{1/2}} = \\
&= 2 \frac{\frac{k_{i+1} - k_i}{\left[(y_{i+1} - y_i)^2 + (x_{i+1} - x_i)^2 \right]^{1/2}} - \frac{k_i - k_{i-1}}{\left[(y_i - y_{i-1})^2 + (x_i - x_{i-1})^2 \right]^{1/2}}}{\left[(y_{i+1} - y_{i-1})^2 + (x_{i+1} - x_{i-1})^2 \right]^{1/2}}
\end{aligned} \tag{11}$$

Numerically the set of differential equations for arrays $x[i]$ and $y[i]$:

$$\frac{dx[i]}{dt} = -Vn[i] \cdot \frac{(y[i+1] - y[i-1])}{[(x[i+1] - x[i-1])^2 + (y[i+1] - y[i-1])^2]^{1/2}}, \tag{12}$$

$$\frac{dy[i]}{dt} = Vn[i] \cdot \frac{(x[i+1] - x[i-1])}{[(x[i+1] - x[i-1])^2 + (y[i+1] - y[i-1])^2]^{1/2}} \tag{13}$$

With

$$Vn[i] = \left. \frac{\partial^2 k}{\partial s^2} \right|_i$$

$$= 2 \frac{\frac{k[i+1] - k[i]}{\left[(y[i+1] - y[i])^2 + (x[i+1] - x[i])^2 \right]^{1/2}} - \frac{k[i] - k[i-1]}{\left[(y[i] - y[i-1])^2 + (x[i] - x[i-1])^2 \right]^{1/2}}}{\left[(y[i+1] - y[i-1])^2 + (x[i+1] - x[i-1])^2 \right]^{1/2}}$$

The above equation is solved by commercial MATLAB using non-dimensional time of 1e06 iteration. Figure 40 showed the results of the iteration.

The modeled particle with spiky surfaces showed toning down of the spikes with progressive annealing time (Figure 40). The modeling results compare favorably with the SEM images presented in Figure 39. It is observed that the spikes go through a smoothening process until they more or less disappear after a 12 hour anneal at 360°C. It is also observed, that in agreement with the experimental data, the overall size of the Ni particles does not change. Similar methodologies may be applied to other material systems and also to planar surfaces to simulate the morphological changes that may occur driven by diffusion and minimization of energy considerations. [119, 120]

Figure 40. Modeling of particles at 360° C, at different annealing times of (a) 0 hr, (b) 4 hr, (c) 8 hr, (d) 12hr

1.12.4. Surface Area of the anneal nickel particles

The surface area of the nickel particles was measured by the BET technique using Micromeritics ASAP 2000 analyser and the particle size was measured using Fritsch particle sizer analysttee 22 compact. Figure 41 showed the BET surface area of the annealed particles. It was observed that in general surface area reduces when spikes are toning down.

Figure 41. BET of the annealed particles

1.12.5. Particles size of the annealed particles

The particles size of the nickel particles was measured by using Fritsch particle sizer analysttee 22 compact. After annealing, the particle size showed no much different, which mean that the particles are not agglomerated.

Figure 42 showed the particle size of the annealed nickel particles

Figure 42. Particle size of the annealed nickel particles

1.13. Encapsulation process

Encapsulation is formed by hydrolysis and condensation of droplets of a mixture of tetraethoxysilane (TEOS) and aminopropyltriethoxysilane (APTES) formed by vortexing the reaction mixture in water containing cetyltrimethylammonium bromide (CTABr). Silica is deposited preferentially at the TEOS/water interface; hollow microspheres are formed in situ. (Figure 43)

CTABr, which acts as surfactant consists of two parts: a water-attracting (hydrophilic) portion and a water-resistant (hydrophobic) portion. Hence it is known as amphiphilic molecules. In a system of water and CTABr, the CTABr hydrophilic end will attract the water molecules to form aggregated structures. When TEOS is added, the TEOS molecules will be attracted to the other hydrophobic end of the CTAB. As a result, mesostructured silica with intact shells can be formed.

Figure 44 and 45 showed the TEM images of the encapsulated Ni Particles.

Focus Ion Beam is used to slice the encapsulated particle, Figure 45 showed the image of the internal morphology of the particle. We can observe that a particle was found inside the hollow shell. EDS (Figure 47) was performed on the particle and it was confirmed to be nickel particle.

Figure 43. Mechanism for the formation of mesostructured silica shells

Figure 44. TEM image of the silica encapsulated Ag particle

Figure 45.TEM image of the silica encapsulated Ni particle

Figure 46.FIB cut on the encapsulated particle

Figure 47.EDS on Figure 42

1.13.1. Modeling of the encapsulated hollow sphere

Commercial software ANSYS 8.0 was employed to carry out the stress distribution on the shell of synthesis hollow sphere when it is used in flip chip application. 3D finite element model with fixed boundary condition on both the top and bottom were built to simulate the force acting on the hollow sphere.

SOLID187 element was used to in this simulation. SOLID187 has a quadratic displacement behavior and is well suited to modeling irregular meshes. The element is defined by 10 nodes having three degrees of freedom at each node: translations in the nodal x, y, and z directions. The element has plasticity, hyperelasticity, creep, stress stiffening, large deflection, and large strain capabilities.

The dimension of the flip chip package used in analysis is shown in Table 15 and the properties of the materials are shown in Table 16. 1 μ m hollow sphere is used for this simulation.

Flip Chip Components	Length (μ m)	Width (μ m)	Thickness (μ m)
Silicon	10	10	1
Substrate	10	10	3
CuNiAu	5	5	0.3
eNiAu	5	5	0.3

Table 15. Package construction used in FEA modeling

Parameter	Silicon	Substrate	CuNiAu	eNiAu	Silica
Modulus (Pa)	131e9	18e9	207e9	150e9	73e9
Poisson's	0.25	0.3	0.3	0.3	0.17
Density (Kg/m ³)	2230	1200	2000	2000	2200

Table 16. Package material properties used in FEA modeling

Figure 48.The model used for the simulation

Figure 49.3D image of the model used for simulation.

Figure 50.Meshing of the model.

Figure 48 and Figure 49 showed the model used for the simulation. Figure 50 showed the meshing of the simulated model. The model has a total of 2500 element and 10000 nodes. A force of 100gm is applied on the surface of the silicon. This is to simulate the force at some stage in chip under compressive stress during bonding. The constraint is fixed at the bottom of the FR4 substrate.

It can be seemed from Figure 51 that forces are being built up at the shell particle. Figure 52 and 53 shows the maximum stress occurs at the hollow shell. The stress is greater than the modulus of silica, which mean the hollow sphere will crack under the load, thus provide a conductive path for the particles inside the hollow sphere.

Figure 51.FEA results for the model.

Figure 52.FEA results on the cross section of the model

Figure 53.FEA results on the hollow shell particle

1.14. Epoxy Formulations

DSC was used to investigate the curing time for each proportion of catalyst at 140°C. Figure 54 and 55 shows the isothermal runs for 2.5 parts catalyst and 10 parts catalyst respectively.

The time taken to cure shows a decreasing trend as catalyst parts increase. 10 parts catalyst gives the shortest curing time. However, its pot life is also significantly shorter. This means that it cannot be stored for long periods of time before it starts to gel. This is undesirable for the carrying out of investigative work. In the case where no catalyst is added, the curing time (greater than 2 hours) is too long for characterization work to be done efficiently.

Hence, a good balance between the two parameters is obtained with 2.5 parts catalyst. In this case, the curing time is 20 minutes and pot life is 7 hours. This is the formulation used for further investigative work of cure kinetics and thermal resistance measurements.

Figure 54. DSC graph for 2.5 parts catalyst **Figure 55.** DSC graph for 10 parts catalyst

For the different proportions of catalysts investigated, the results are as obtained in Table 16.

Table 17.: Results for curing time and pot life

Catalyst Parts	Curing Time (min)	Pot Life (days)
0 parts	> 120	> 10
2.5 parts	20.48	7
5.0 parts	14.85	5
7.5 parts	12.17	3
10 parts	9.95	3

Results from Table 16 are plotted in Figure 56 and 57.

Figure 56. Curing time for different parts of catalyst at 140°C

Figure 57. Pot life for different parts of catalyst at 140°C

1.15. Cure Kinetics

Isothermal runs were done for 3 different loadings as reported in Section 3.3. For each loading, runs were carried out at 130°C, 140°C and 150°C. The DSC graphs for 32.5 weight % nickel loading obtained as shown in Figure 58 to 60.

The use of DSC for studying the isothermal curing kinetics of thermosetting resins assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of cure (or the extent of reaction) of the sample at a given time.

The degree of cure, α is given by Equation 12.

$$\alpha(t) = H(t) / H_R \quad (12)$$

where $H(t)$ is the transient heat generated,

H_R is the total heat generated

From Figure 60 to 62, the following observations are made.

For sample 1a (0 weight % nickel), it can be seen that the rate of cure is fastest at the highest temperature of 150°C, which is followed by 140°C and finally 130°C. The same trend is observed in samples 1b (32.5 weight% nickel) and 1c (75 weight % nickel) also. (Figure 61)

This can be explained by the fact that higher temperature indicates an increase in the amount of heat transferred to the samples for a given time. This enhances the rate of

reaction and hence increases the curing rate, independent of the presence of nickel or its loadings.

An interesting phenomenon noted for Samples 1b and 1c is that the degree of cure is the same for an initial period of time for the three temperatures. From Figure 62, Sample 1b shows the trend until about 8% curing has occurred. In the case, of Sample 1c (refer to Figure 63), this trend is extended for longer periods of time till about 17% curing of the sample.

Since this phenomenon is not experienced by the epoxy with no nickel loadings, a possible explanation can be that initially, nickel absorbs most of the heat supplied at a very fast rate. The rate is so high that the amount of heat absorbed is about the same regardless of the temperature difference. Hence, the epoxy wetting the nickel particles get heated up fastest and cure first compared to the remaining epoxy in the system.

This also explains why the trend is only seen to a lower degree of cure for lower nickel loadings. At higher loadings, more epoxy will be wetting the nickel; hence, the trend is extended to about 17% curing in Sample 1c.

Figure 64 to 66 compare the degrees of cure in another angle. In these cases, the response of different nickel loadings at the same temperature will be discussed.

From Figure 64, the sample with 75 weight% nickel loading gives the fastest curing rate at 130°C. The blank sample, that is, with 0 weight% nickel loading reaches 100% degree of cure subsequently, followed by the sample with 32.5 weight% nickel loading.

A similar trend is observed in the case of isothermal curing at 140°C in Figure 65. However, in this case, the rates of cure for sample 1a and sample 1c for the initial

part were similar until about 70% curing were achieved in both samples. Subsequently, sample 1c shows an increase in the curing rate and hence cured the fastest.

At 150°C as shown by Figure 66, the order of speed of cure for the 3 samples is still the same as in the first two cases of 140°C and 130°C. However, it should be noted that it is sample 1a that shows a slightly faster rate of cure than sample 1c initially. This occurs until about 60 % degree of cure before sample 1a slows down its curing rate compared to sample 1c.

Two possible explanations can explain why sample 1c cures fastest but yet sample 1b that also contains filler loadings cure slower than sample 1a without nickel.

At each temperature, the heat energy supplied is needed to initiate and maintain the curing reaction. At the same time, part of the heat is absorbed by the nickel particles in the case of samples 1b and 1c. Hence, sample 1a should cure fastest since it contains no nickel and all the heat will go towards the curing reaction.

However, in the case of sample 1c, the nickel filler loading is so high that the epoxy content required being cure is only 25 weight % of sample 1a. Hence, it cures the fastest. Another reason could be due to the nickel particles acting as barriers between the crosslinked epoxy chains. As a result, the cured chains are much shorter than those in sample 1a and requires less time to crosslink.

As for Sample 1b, the two contradicting factors contribute to its curing process. Hence, it cures the slowest.

Figure 58. Isothermal runs at 130°C for 32.5 weight% **Figure 59.** Isothermal runs at 140°C for 32.5 weight%

Figure 60. Isothermal runs at 150°C for 32.5 weight%

Results obtained from DSC were used to model the degree of cure vs time. Figure 58 to 60 give the comparison for the degrees of cure of the same nickel loadings at the 3 different curing temperatures.

Figure 61. Degree of cure for 0 wt% nickel loading

Figure 63. Degree of cure for 75 wt% nickel loading

Figure 64 to 66 compare the degrees of cure in another angle. In these cases, the responses of different nickel loadings at the same temperature are plotted.

Figure 64. Degree of cure for isothermal runs at 130°C

Figure 65. Degree of cure for isothermal runs at 140°C

Figure 66. Degree of cure for isothermal runs at 150°C

1.16. Thermal Impedance Measurements

Samples 3, 5 and 6 contain annealed nickel particles. The particles subjected to annealing were kept in the furnace at 310°C for four hours. Figure 67 shows the annealed particles from Novamet (0.3µm to 0.7µm).

Due to the spiky nature of the synthesized nickel, the thermal conductivity will be affected. Hence, annealing is done to study the effect of temperature on surface morphology of the particles. It is found that annealing reduces the spikiness, and hence a smoother surface is obtained. (Refer to Figure 67) Samples 3a-d, Samples 5a-d and Samples 6a-d contained annealed nickel particles of different sizes as given in Table 12.

One batch of the samples (Samples 4a-d) is studied without annealing of the nickel particles. This is used to compare to Samples 3a-d for the effect of annealing on thermal properties, which contains the same batch of nickel particles that are annealed.

Results from the thermal impedance measurements are plotted in Figure 68 and 69.

From Figure 68, it can be seen that a common trend exhibit by all the 4 batches of samples is that thermal impedance decreases with increasing filler loadings. This can be understood since nickel is a very good conductor of heat compared to epoxy.

Increasing its content will help to improve heat conduction and bring down the thermal resistance. A slight inconsistency is seen in Sample 5d, where the 75 weight% loading shows higher thermal resistance than Sample 5c of 56.25 weight% loading. This can be attributed to experimental error.

Samples 3a-d and Samples 4a-d compare the effect of annealing nickel particles and those without from the same batch (distribution 0.3 to 0.7 microns). The annealed samples show decrease in thermal resistance for every loading. Annealing tones down the spikes on the surfaces of the particles which in turn increases the contact between them. As a result, better heat transfer and improved thermal conductivity is possible.

This annealing effect is more pronounced when the loadings are 32.5 weight% and above. At 16.25 weight%, the conductivities are similar. This could be due to the low loading and particles are not in contact with each other. Hence, surface morphology does not have such a big effect on influencing heat transfer yet.

Other observations include at higher loadings (56.25 weight% and 75 weight%), the thermal resistance of unannealed 0.3 – 0.7 microns nickel is always the highest. This is because the nickel fillers are unannealed and have higher contact resistances. It can

be concluded that the effect of annealing becomes pronounced after 44 weight% nickel loading as seen in Figure 69.

From Figure 69, it can be seen that the correlation of impedance vs. sizes for the lower and higher loadings are not the same. At the smallest loading of 16.25 weight%, the impedance shows a large jump with an increase in nickel size to 3 - 7 microns nickel fillers. However, the thermal impedances for the two smaller size nickel loadings are approximately the same. A similar phenomenon is observed for 32.5 weight%.

At higher loadings, the trend is reverse. For 56.25 weight%, the smallest size nickel fillers (0.3 – 0.7 microns) shows the highest thermal impedance, with the other two sizes showing approximately the same resistance values that is significantly lower. In the case of 75 weight%, without taking into account the sample with experimental error, (Sample 5d) a decreasing trend with increasing sizes is also observed.

This is because at lower loadings, for the same weight% nickel, the distance between particles is larger for the bigger size particles. With a shorter inter-particle distance, the epoxy system with smaller size nickel can conduct heat better since there are more nickel particles present to distribute and conduct the heat throughout the system.

At higher loadings, contact resistance is dominant since particles are in contact with one another. For the bigger particles, the contact resistance is lower. Hence, the thermal conductivity of the epoxy system with distribution 0.3 - 0.7 microns is better compared to those systems with smaller particle sizes.

Figure 67. Novamet nickel after annealing

Tables 18 to 21 give the thermal impedance measurements obtained from the thermal impedance tester following ASTM D5740 for the different sizes of nickel fillers.

Table 18. Thermal impedance results for 0.3 μ m to 0.7 μ m (anneal)

Nickel Loading (weight %)	Thermal Impedance (C.cm²/W)
0 (Sample 2)	73.785
16.25 (Sample 3a)	38.147
32.5 (Sample 3b)	27.060
56.25 (Sample 3c)	23.059
75 (Sample 3d)	13.997

Table 19. Thermal impedance results for 0.3 μ m to 0.7 μ m (not anneal)

Nickel Loading (weight %)	Thermal Impedance (C.cm²/W)
0 (Sample 2)	73.785
16.25 (Sample 4a)	39.520
32.5 (Sample 4b)	36.350
56.25 (Sample 4c)	30.746
75 (Sample 4d)	28.090

Table 20. Thermal impedance results for 780 nm (anneal)

Nickel Loading (weight %)	Thermal Impedance (C.cm²/W)
0 (Sample 2)	73.785
16.25 (Sample 5a)	38.949
32.5 (Sample 5b)	26.462
56.25 (Sample 5c)	16.386
75 (Sample 5d)	20.274

Table 21. Thermal impedance results for 3μm to 7μm (anneal)

Nickel Loading (weight %)	Thermal Impedance (C.cm²/W)
0 (Sample 2)	73.785
16.25 (Sample 6a)	47.251
32.5 (Sample 6b)	45.392
56.25 (Sample 6c)	18.076
75 (Sample 6d)	6.167

Figure 68. Thermal impedance vs. filler loadings for different nickel sizes

Figure 69. Thermal impedance vs. annealed nickel sizes for different filler loadings

1.17. Electrical Resistance

Table 22 shows the readings of the resistance measurements.

Table 22. Resistance of Nickel Powder Annealed at different Temperature and Duration

Temperature (°C)	Duration (Hr)	Readings(Ω)			
		1	2	3	Average
Not Annealed		Open	Open	Open	-
270	4	Open	Open	Open	-
	8	14.0	13.9	14.1	14.00
	12	12.8	12.7	12.4	12.63
310	4	37.5	40.2	39.6	39.10
	8	2.7	2.8	2.7	2.73
	12	3.9	4.1	3.6	3.87
360	4	5.2	5.3	5.3	5.27
	8	4.8	4.9	4.9	4.87
	12	4.2	4.3	4.8	4.43

The resistance readings showed open circuit for the sample with unannealed nickel powder and powder annealed for 4 hours at 270°C. In this experiment, unannealed nickel powder was not suitable for use in electrical interconnect applications. This may be due to insufficient thermal energy supplied to the powder for any significant

change in the morphology or microstructure of the particles, resulting in no change in the electrical conductivity. For the other two samples with nickel powders annealed at 270°C for 8 and 12 hours, the resistance readings show better electrical conductivity.

The lowest resistance record was measured from sample incorporated with nickel powder annealed for 8 hours at 310°C. For nickel powder annealed at the same temperature but for a longer duration of 12 hours, resistance readings show an increase. This may be due to trace amounts of oxide present in the nickel powder identified by XRD after annealing for a longer duration.

Resistance readings from samples with nickel powders annealed at 360°C for different durations showed reasonable conductivity. However, none of the samples annealed at this temperature had better conductivity than the nickel powder sample annealed for 8 hours at 310°C. This may again be due to slight oxidation of the nickel particles when annealed at a higher temperature.

Figure 70 shows the plot of electrical resistance of the nickel powder against annealing duration for annealing at the three temperatures.

Figure 70. Graph – Effects of annealing on Electrical Resistance of Nickel Powder

The graph generally showed a decrease in electrical resistance for nickel powders after annealing. With sufficient thermal energy supplied to the nickel particles, microstructural changes such as dislocation movements and defects elimination can occur, thus improving electrical conductivity. Macrostructural change in the morphology such as the diminishing spikes on the surface of the nickel.

Conclusion

Hydrothermal reduction allows for efficient synthesis of pure nickel particles. The average sizes of particles and their distribution were evaluated from the multimodal distribution using a particle sizer. As the concentration of nickel sulphate decreases, the particle size also decreases but in a non-linear fashion. Distributions of sizes were within a narrow range of $\pm 5\%$.

Nickel particles annealed at different temperatures showed toning down of the spiky surface. It was concluded that the changes brought about by heat treatment had contributed to the improved electrical conductivity of the nickel powders. Initially of uncharacteristically high electrical resistance, conductivity improved a great extent after the powders had undergone annealing. The relief of internal strains and defects in the microstructure also led to better electrical conductivity. An analytical model considering surface diffusion was established to account for the temperature activated and energy minimization driven smoothening of the Ni particles.

Silica encapsulated nickel was produced. Silica is deposited preferentially at the TEOS/water interface; hollow microspheres are formed in situ. This method therefore eliminates the need for any template extraction techniques. Finite Element Analysis was conducted and found that when the hollow was subjected to bonding force, the hollow shell will crack and thus provide the conductive path between the chip and the substrate.

In the cure kinetics study, three samples with 0 weight%, 32.5 weight% and 75 weight% nickel loadings in the formulated epoxy system were studied. It was concluded that the higher curing temperature, the lower the time taken to cure

However, for samples with high nickel loadings, the time taken to cure a low percentage of the epoxy is independent of the temperature. A possible explanation can be because the nickel absorbs heat initially at a very fast rate that is almost independent of temperature. Hence, epoxy wetting the nickel gets heated up first and cured at the same rate. This also explains why this trend is seen up to a higher degree of cure in 75 weight% than 32.5 weight%

In thermal impedance measurements it can also be concluded that an increase in loadings increases thermal conductivity for all the samples. This is expected since nickel is a much better conductor of heat than epoxy

This morphology has a very detrimental effect on electrical conductivity and a surface modification was therefore pursued by an annealing treatment at 270°C to 360°C for 4 to 12 hours. Its resistance from 5×10^3 ohms to under 2 ohms. The change in morphology did not lead to agglomeration or increase in particle sizes as confirmed by BET and particle size measurements.

Future Work

- ✿ The reliability tests such temperature cycling, pressure cooker tests are to be conducted as future work to investigate the thermal and mechanical behavior of conductive adhesive under accelerated test. By conducting conditions and correctly apply the accelerated tests results to extrapolate the behavior of the adhesives through their service life.
- ✿ Another problem to study in this system is electromigration. When the adhesive is subjected to the high current density, its effect on the particles will be interesting angle to pursue.
- ✿ One of the most promising technologies of today's chip-level interconnection is flip-chip technology, which has emerged as high density, and high performance interconnection method for integrated-circuit chips. A potential revolutionary technology of attracting devices by flip chip without solder bumps/balls and underfill epoxy is to use anisotropic conductive adhesives (ACAs). It is the belief that ECAs would offer the most advantages in flip chip application over solder among all applications in electronics. ACAs could provide most of the needs for flip chip technology by themselves; create electrical path vertically, ensure good horizontal gap insulation, reduce joint stress and provide strong mechanical adhesion. Furthermore, no cleaning/flux is required, secondary underfill is not necessary, and placement of adhesives is not critical. Thus, thorough research and development of ACAs, such as for improved current handling capability, better thermal performance, tight

controlling of filler particle sizes, optimized filler concentration, is critically important. Also an optimized flip chip process using ACAs need to be developed.

❁ Rework or repair is very important in electronic applications. Repair is estimated to be much more difficult and costly with ECAs than with solder. Once formed, adhesively bonded joints are not easily taken apart. One of the approaches to break adhesive bonds is to use high temperatures. However, for electronic packaging applications the semi conductor devices could be seriously damaged during high temperature debonding. Low temperature rework ability is an important research and development area for future ECAs. One direct direction for developing reworkable ECAs is to develop some kind of ECAs whose bond strength have strong temperature dependence, and thus they have high strength at room temperature (such as 200°C or lower). These will allow removal of the chips and the mounted components very easily with little force. Once the ECA comes down to ambient temperature, the bonding strength will increase back to original values. Another possible approach is to develop ECAs that can be easily half cured. In this case, the devices can be tested, and the die be removed from substrate or carriers in the event of device failure. The final full cure then can be done on the tested known good devices.

❁ The state of surfaces to be bond is extremely important. Many low surface energy materials are not well wetted by the ECAs, leading to low strength

bonds being formed. Proper surface pretreatment is a key factor in both the initial strength of the bonds joint and its long-term environmental resistance. Currently, the surface of the substrates and the component terminals are mostly lead-tin, copper, nickel or gold, it is worthwhile to evaluate other metallization schemes such as silver, palladium and titanium. Alternative metallization of substrate as well as component terminals could not only improve the bonding strength and durability, but also reduce contact resistance and maintain its stability.

List of Publication & Conference

1. C. F. Goh, H. Yu, S.S. Yong, S.G. Mhaisakar, F.Y.C. Boey and P.S. Teo, “Synthesis and cure kinetics of isotropic conductive adhesives comprising sub-micrometer sized nickel particles,” *Materials Science and Engineering B*, Vol 117, Issue 2, 15 March 2005, pp 153-158
2. C. F. Goh, H. Yu, S.S. Yong, S.G. Mhaisakar, F.Y.C. Boey and P.S. Teo, “The effect of annealing on the morphologies and conductivities of sub-micrometer sized nickel particles used for electrically conductive adhesive,” *Thin Solid Films*, Vol 504, Issue 1-2, 10 May 2006
3. C.F. Goh¹, A.M. Gusak², Z.H. Gan¹, S.G. Mhaisalkar¹, F.Y.C. Boey¹, P. S. Teo³ “Modeling of Smoothing Effect on Morphologies of Annealed Sub Micron Nickel Particles used for Electrically Conductive Adhesives” *J. Appl. Phys.* 100, (2006)
4. Mary Teo, S. G. Mhaisalkar, E. H. Wong, Poi-Siong Teo, C. C. Wong, Kristine Ong, & Chin Foo Goh, “Correlation of Material Properties To Reliability Performance of Anisotropic Conductive Adhesive Flip Chip Packages”, *IEEE Trans. Components, Packaging, & Manufacturing Technology*, 28 (1): 157-164, 2005.
5. C.F. Goh, S.S. Yong¹, X.Q. Ng, S. G. Mhaisalkar, F.Y.C. Boey¹, P. S. Teo, “Processing of Sub Micron Nickel Particles use for Electrically Conductive Adhesives”, 2nd International Conference of Materials for Advances Technologies, 2003
6. C.F. Goh “The Effect of Annealing on the Morphology and Conductivities of Sub-Micrometer Nickel Particle Used for Electrical Conductive Adhesive”, 3rd International Conference of Materials for Advances Technologies, 2005
7. C.F. Goh “Synthesis of Nickel nano-particles and the reliability of it in the application of Anisotropic Conductive Adhesives (ACA) by using the Surface Insulation Resistance (SIR) Test”, 3rd International Conference of Materials for Advances Technologies, 2005

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