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Review Article

Carbon Nanotube Composites for Electronic Packaging Applications: A Review

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Composite engineering comprises of metal matrix composites. They have high strength-weight ratio, better stiffness, economical production, and ease of availability of raw materials. The discovery of carbon nanotubes has opened new possibilities to face challenges better. Carbon Nanotubes are known for their high mechanical strength, excellent thermal and electrical properties. Recent research has made progress in fabricating carbon nanotube metal matrix and polymer-based composites. The methods of fabrication of these composites, their properties and possible applications restricted to the field of electronic packaging have been discussed in this paper. Experimental and theoretical calculations have shown improved mechanical and physical properties like tensile stress, toughness, and improved electrical and thermal properties. They have also demonstrated the ease of production of the composites and their adaptability as one can tailor their properties as per the requirement. This paper reviews work reported on fabricating and characterizing carbon- nanotube-based metal matrix and polymer composites. The focus of this paper is mainly to review the importance of these composites in the field of electronics packaging.

1. Introduction

Metal matrix composites of various combinations of metals have been used in engineering for various applications. Aerospace [1], automobile [2], and electronics applications [3] have seen the maximum usage of these composites mainly because of the light weight to mass ratio, stiffness, and ductility provided by the reinforcement [4]. Qualities like low coefficient of thermal expansion, high thermal conductivity, enhancement of electrical conductivity, and adjustable mechanical properties have made such composites very popular. Carbon-based research has gained boost with the introduction of carbon fibres in carbon-based composites. High strength and light weight made these composites a good choice for aerospace structures, rocket nozzle exit cones, re-entry heat shields, sporting goods, and structural reinforcement [5]. Over the past decades, there have been endless efforts to find suitable application for CNTs. Their extraordinary electrical, mechanical, thermal, and electrochemical properties [6] seem to have several possible applications: field emission devices [7], electronic circuits, devices, and interconnects [8], super capacitors and batteries [9], separation membranes [10], nanoscale sensors [11], drug delivery systems [12], and composite materials—both polymeric and metal matrix filled [13, 14]. However, the biggest obstacle is industrial or large-scale manufacturing of the material.

Copper is the conventional material used for interconnects because of its low electrical resistance and low cost of production. However, as we scale down and increase the packaging density the properties of copper will experience certain limitations. One of the major issues is huge CTE mismatch with silicon, which leads to thermomechanical stress that finally decreases the reliability of the devices. Better materials or composites which could overcome current limitations and also exhibit compatibility for future downscaling are required. CNTs are promising materials with extra ordinary electrical, mechanical, and thermal properties [15, 16] and are considered suitable for electronic packaging either in its pure form or as fillers for composites. CNTs have been praised as a very promising evasion of most of the current packaging challenges. Instead of waiting for them to mature from the laboratory stage the CNTs direct application for packaging as filler material in adhesives has been investigated. The fabrication of CNT-epoxy composites has been studied concerning their screen printing performance [17], and the selected formulations have then been compared with conventional Ag-filled conductive adhesives in terms of their mechanical, electrical, and thermal properties [18]. Besides, early reliability tests have been performed. The described studies show the potential and problems of implementing nanomaterials into electronic packaging. CNTs were tested with solders as well, and result was a decrease in creep behaviour [19]. Another attempt was made by the Wang et al. at Chalmers university where they synthesized vertically aligned carbon nanotubes in TSVs and analysed the required densification for CNT bundles to compete with copper in terms of its electrical characteristics [20]. Copper-CNT composites in the TSVs are also made possible through an electrodeposition process [21]. This work describes in detail the application of carbon nanotubes in electronic packaging. The first part analyzes all work done to explore the potential implementation of nanotubes with copper or as an individual material. The second part deals with current attempts in our laboratory to fabricate a copper-CNT composite film. Our work is attempting to fabricate a Cu-CNT composite film, and the potential improvement of the Cu-CNT is also being evaluated in comparison to other materials used.

2. CNTs as Filler Materials

Recently, CNTs are currently known as promising materials to work with or replace copper in the electronic packaging applications. Ongoing research is dedicated to analyze if CNTs can be coupled with solders, epoxy composites, and solder joints for various packaging applications to test their influence on reliability. In the back end processing, where the TSV dimensions are of a few microns, it is predicted that CNTs could replace copper in the near future [22]. The effective potential of CNTs in interconnected applications strongly depends on the density of nanotubes in the area, their chirality, the interaction between copper and CNTs, a good wetting in the matrix, and orientation of the nanotubes in the matrix [23]. There could be significant increase in the electromigration resistance of copper without having to compromise with its conductivity. The matrix or CNTs themselves have the potential to reduce the thermal mismatch in CMOS technology thereby improving the efficiency and performance significantly. Considerable research has been attempted to synthesize nanotubes in the VIAs with the catalyst or couple them with copper and fabricate composites. In the following sections all the work related to the electronic packaging has been reviewed.

2.1. CNT Epoxy Composites for Electrically Conductive Adhesives. Industrial applications like transportation, aerospace, automotive, energy, sportive goods, and so forth have known to use polymers and their composites [6]. They are known for their properties like conductivity, elasticity, strength, and durability. These properties can be further enhanced by adding carbon nanotubes. Dispersing the nanotubes in homogeneous manner will have improved the electrical and mechanical properties considerably [24].

Heimann et al. experimented with adhesives which were filled with CNTs and this polymer composite was tested for possible application in electronics packaging. It was found that there was improvement in the performance with the thermal conductivity of nearly 4.4 percent more with CNTs in the matrix when compared with the composite without CNTs. The mechanical properties also showed an improvement also when the storage modulus increased for CNTs filled resins. In the same study the nanotubes were chemically modified for better dispersion, which was an additional advantage in improving the mechanical performance [25].

In another work done by the same group they compared the CNT filled adhesives to conventional Ag-filled adhesives. The filler volumes were 3 wt.% and 82 vol.%, respectively. There was a 75% stiffness increase with the new filler material compared to the conventional one. Thermal characteristics also improvised with the new filler material. Reliability tests through temperature cycles and high humidity proved that the CNT composite has better performance than the Ag filled [18].

2.2. Solder Joints. In a detailed work done by Nai et al. from the National University of Singapore, the shear strength and the electrical resistivity of lead free solder when coupled with nanotubes were investigated. The composition of the weight percentages of nanotubes was varied in the composite, and the observed electrical performance did not change much. However, the shear strength of the composites showed improvement. This can be achieved only when there was homogenous dispersion of the nanotubes. This work has revealed that it is possible to achieve improvement in thermal and mechanical properties without affecting the electrical properties [26]. In another recent study by Han et al., they vary the ratio of Ni-coated CNTs that were incorporated into the solder matrix Sn–Ag–Cu (SAC) and formed solder composites. The thermomechanical testing showed improved thermal stability in the composite solders. The reinforced solder joint grew less significantly than the conventional solder joints. Ultimate shear strength of the composites proved to be better than conventional solders.

3. On Site Synthesis of CNTs

As mentioned earlier the use of CNTs is being tested for back end processing, through silicon VIAs (TSVs), interposers, and so forth, in the packaging industry. The widely used metal in the industry was aluminum; however, with shrinking dimensions Al failed to perform and was replaced with copper. As predicted by Moores law, the feature size has been decreasing and will continue to decrease; there will be an effective need to find materials which would replace copper or composite materials with copper.

With the current TSV dimensions (in microns) for back end processing, there has been an effort to synthesize nanotubes in the TSV itself. It has been calculated that to compete with the resistivity of copper, the density factor of conducting CNTs should be 10^{13} cm^{-2}. This is made possible by using different coatings. The fundamental work involves deposition of silicon dioxide on silicon wafer. Al_2O_3 layer or a TiN layer was then coated. The porosity of the layer permits more carbon atoms (from the feedstock gas) to dissolve into the catalyst particles, therefore there is better yield and higher density [27]. The catalyst layer like Fe, Co, or Ni is deposited. There could be a copper or Ti contact layer for future electrical characterization. For the barrier layer, Ta was also used. Using Thermal Chemical Vapor Deposition (TCVD) methods, controlled growth has been achieved. For achieving better quality CNTs, vapor deposition methods demand high-temperature requirements (more than 400°C) which are not in accordance with CMOS technology.

At Infineon Munich, Germany, Kreupl et al. achieved the integration of CNTs in TSVs. The nanotubes were synthesized through the buried catalyst technique, where in thin metal layers of Fe and Ta were used as catalyst. Electron beam lithography in combination with a hard mask technique was used to define the vias. Temperature between 450–700°C was used to synthesize the nanotubes using a chemical vapor deposition. For a 20 nm node, they achieved a current density of ($5 * 10^8$ A/cm^2) and a resistance of 7.8 kΩ for a single multiwalled vertical interconnect [28].

A good comparison of TCVD and low-pressure CVD grown CNTs was done by Wang et al. from Chalmers University, Sweden. I-V characteristics also reveal that the low-pressure CNTs have a lower resistance than TCVD grown [20].

In a recent work done by Esconjauregui et al. from Cambridge University, researchers achieved a nanotubes density of 10^{13} cm^{-2} by cyclic deposition and annealing the catalyst films [29].

One of the effective solutions to incorporate CNTs in the CMOS technology will be to synthesize them and transfer them efficiently to the required site. This was demonstrated by Chai from Hong Kong University, as they were able to transfer the CNTs from one area to another by liftoff transfer technique [30].

4. Electrochemical Deposition of CNT-Cu Composites

4.1. Randomly Oriented CNTs in Copper Matrix. Electrochemical deposition facilitates the codeposition of CNTs with any metal at room temperatures. This technology is believed to be ideal to fill the TSVs with Cu-CNT composite for its cost cutting and low technology handling issues.

CNTs are hydrophobic in nature. They do not form a uniform dispersion in water-based solution due to strong van der Waals forces. Hence, it is required to add surfactants to reduce the surface energy when dispersed in water solutions. There are two kinds of surfactants: cationic and anionic. Cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), octadecyltrimethylammonium bromide (OTAB), and so forth belong to the family of cationic surfactants, where they introduce a positive charge on the nanotubes and also help in preventing flocculation (floc or flakes are formed when the colloids come out of the suspension). When dispersed in a copper sulphate bath for electrochemical deposition, the metal ions which are positively charged and the nanotubes are electrochemically reduced which aids in the overall reaction [23]. On the other hand anionic surfactants like Nafion introduce a negative charge to the nanotubes, and thus they repel the positively charged metal ions. This also facilitates uniform deposition.

The other method for electroplating nanotubes with copper is chemical functionalization of the nanotubes with –OH or –COOH groups. A combination of acids with different ratios can be used to open the caps of the tubes and attach the functional group to the nanotubes. Functionalization not only breaks the strong van der Waals forces between the nanotubes, thereby preventing agglomeration but also improves the covalent bonds between filler and matrix. The effects of different additives on Cu-MWCNT composite plating were presented by Arai et al. [31].

In a work done by Chowdhury et al., they demonstrated the electrochemical deposition of CNTs with Nafion and CTAB. In this study the relation between resistivity and annealing temperature showed that the pure copper bath had the least resistivity change when compared to CTAB and CNT and Nafion and CNT. It was observed in this work that the increase in copper exchange current density and the decrease in equilibrium potential value are due to the addition of CNTs to the copper baths [32].

CNTs, when acid treated and ultrasonicated, get functionalized with –OH and –COOH groups. These were then electroplated in a normal copper bath. The work done by Liu et al. revealed that with a combination of electrophoresis and electroplating, it is possible to integrate functionalized nanotubes into the copper matrix [33].

A completely new approach was given to electroplating by patent filed from University of Central Florida by Chen [23]. The concept is called electro codeposition, where in the SWCNT the copper was deposited with an external magnetic field to orient the nanotubes as they deposit. It has been evaluated that nanotubes exhibit very good thermal and electrical properties along the radial direction of orientation and very good mechanical properties along the axial direction. Cationic surfactants were added to the bath and thickness of about 22 μm was achieved. The effective CTE of the composite was estimated between ($3–6 * 10^{-6}$/K) in the temperature range of 25°C to 120°C, with a volume portion of 18% of SWCNTs. The CTE value of the composite is about 4 times smaller than CTE of pure copper ($17 * 10^{-6}$/K), thus proving it to be a solution to the CTE mismatch in semiconductors. The thermal conductivity of the composite is about 640 W/mK, 66% higher than pure copper. There is at least a 40% decrease in the electrical resistivity of the composite ($1.22 * 10^{-6}$ Ω cm) when compared with pure copper ($1.72 * 10^{-6}$ Ω cm). The tensile strength of the composite has proved to be better. It is certainly a promising composite when the ratio of the CNTs to metal or the direction of orientation is under control.

Electromigration resilience of the composite also increases. Carbon-carbon bonds in the nanotubes are very strong since they comprise sp^2 bonds and require about 7 eV per

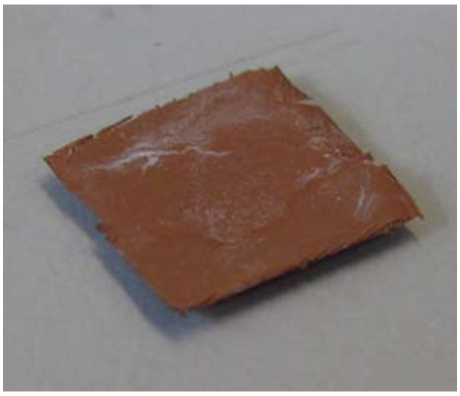

Figure 1: Thin foil of Copper-CNT composite prepared by electrodeposition [34].

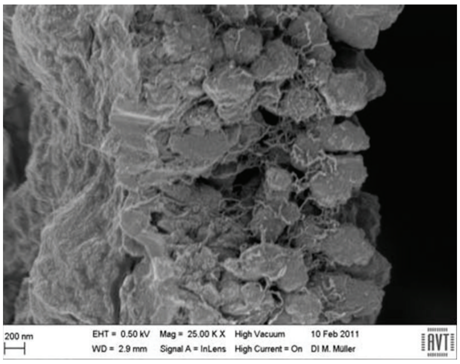

Figure 2: SEM Image of thin foil of the copper-CNT composite [34].

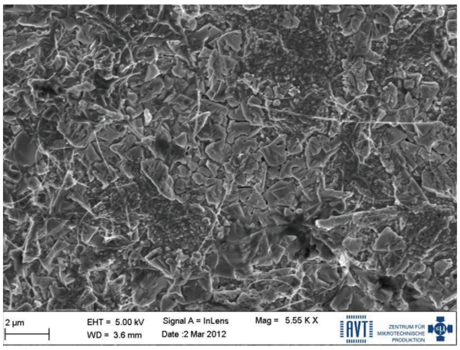

Figure 3: SEM Image depicting randomly oriented CNT in Cu matrix.

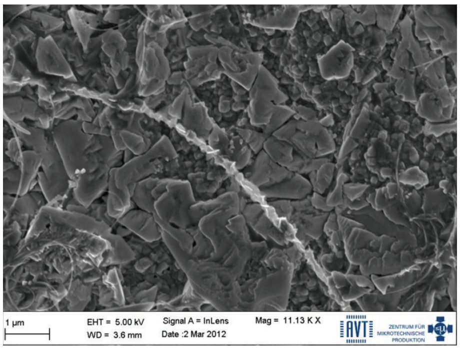

Figure 4: SEM Image of copper grains adhered to a carbon nanotube.

atom to be displaced. The nanotubes are also too large to migrate making electromigration almost nonexistent [23].

5. Results

In this section we discuss the fabrication method of the metal matrix composite comprising of copper and CNTs. The fabrication includes both vertically aligned CNTs and randomly oriented CNTs in copper matrix.

The copper-vertically aligned CNT (VACNT) samples were prepared successfully using an electro-deposition process at Fraunhofer IKTS, Dresden, by Dr. Endler and his group. The vertically aligned nanotubes were synthesized in a thermal CVD at 700°C on silicon substrate. A three-electrode configuration (Sensortechnik Meinsberg GmbH) was used to electrodeposit copper with Ag/AgCl as reference electrode, carbon foil (SGL Group Sigraflex) as the counter electrode, and silicon substrate with multiwalled nanotubes was the working electrode. The current density was $50\,\mathrm{mA/cm^2}$ for about 4.5 minutes; the thickness of the layer was 5 microns. The silicon substrate was now removed and copper was electro-codeposited on the reverse. The results are depicted in Figure 1 [34]. The SEM image in Figure 2 depicts the successful implementation of nanotubes in a random fashion into the copper matrix. The image is the side of the sample, and the copper grains with nanotubes can be seen there. The nanotubes are not aligned here; the possible reason for losing the alignment is during the electrodeposition process.

There are certain advantages to electrodepositing copper with CNTs. In the ongoing research at our laboratory, multiwalled nanotubes are electro-codeposited with copper. This is done using sodium dodecyl sulfate (SDS) as the surfactant. A certain amount of the nanotubes was dissolved in deionized water with SDS, a homogenous solution was formed, and later this was mixed with a copper sulphate bath in a certain volume ratio. The electrodeposition was then carried out at different current densities using pulsed reverse deposition varying the current as a function of time. Figures 3 and 4 depict the SEM images of the electrodeposited sample. It is noticeable that there is a good distribution of nanotubes in the copper matrix. In a thermal chemical vapor deposition method the yield of the nanotubes is always mixed; however with the electrodeposition process, one can determine exactly the type of the nanotubes required: single walled, double walled, and multiwalled. The main advantage of this method is selective electroplating of nanotubes, and one can thus determine exactly the requirement of each, specific to the application.

6. Conclusions

Carbon nanotubes are promising materials that seem to improve the overall performance. There are several challenges that certainly have to be overcome in order to prepare a homogenous composite, one being the uniform dispersion of the tubes, prevention of agglomeration of the tubes in the dispersion and in the composite itself, using better quality nanotubes. The most important factor is the ratio of the nanotubes in the composite which certainly influences the properties, making optimization necessary. Proper fabrication methods have to be designed in order to have a strong and good bonding between the metal/CNT interface. The efficient use of the composite can thus be implemented when these challenges are overcome. When using these composites for electronics, proper bonding could lead to better electron transfer and interaction between the two materials. Mechanical strength is also greatly improved with strong bonding.

Carbon nanotubes are desirable materials to modify the material properties required for packaging. For back end processing technology the most economical method is electroplating to reduce the CTE mismatch between the materials. Optimizing the ratio of copper to the amount of CNTs, while manufacturing the composite, can influence the resistivity of the composite,which can be tailored accordingly to compete with copper. The mechanical properties also improve considerably. However, onsite synthesis of CNTs in the aspect of temperature requiremen, is still a challenge. On the other hand, the achievement of a desired density to beat the current density of copper is easier with thin film and CVD growth technology. Future plans and possibilities within this field include investigating the CTE and Youngs modulus of the composite and a comparison of its performance with bulk copper.

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