FABRICATION AND CHARACTERIZATION OF Ag-Al DIE ATTACH MATERIAL FOR SiC-BASED HIGH TEMPERATURE DEVICE

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FABRICATION AND CHARACTERIZATION OF Ag-Al DIE ATTACH MATERIAL FOR SiC-BASED HIGH TEMPERATURE DEVICE

by

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PENGISYTIHARAN / *DECLARATION*

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam tesis ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya.

I declare that the contents presented in this thesis are my own work which was done at Universiti Sains Malaysia unless stated otherwise. The thesis has not been previously submitted for any other degree.

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SELECTED LIST OF ABBREVIATIONS

AFM	:	Atomic Force Microscopy
SEM	:	Scanning electron microscopy
EDX	:	Energy dispersive X-ray
TEM	:	Transmission electron microscopy
XRD	:	X-ray Diffraction
TGA	:	Thermogravimetric analysis
DSC	:	Differential Scanning Calorimetry
TMA	:	Thermomechanical analysis
CSAM	:	Confocal scanning acoustic microscopy
SPA	:	Semiconductor Parameter Analyzer
I-V	:	Current-Voltage
DBC	:	Direct-Bonded-Copper
DOE	:	Design of experiment
ANOVA	:	Analysis of variance
EG	:	Ethylene glycol
JCPDS	:	Joint Committee on Powder Diffraction Standards
CTE	:	Coefficient of thermal expansion
MOSFET	:	Metal-Oxide-Semiconductor field effect transistor
DRAM	:	Dynamic random-access memory
HCP	:	Hexagonal-close-packed
RMS	:	Root-mean-square

SELECTED LIST OF SYMBOLS

ΔH_r	:	Latent heat of melting
ΔH_∞	:	Bulk latent heat of melting
ρ_s	:	Solid phase density
σ_{sl}	:	Solid-liquid interfacial energy
D_l	:	Lattice diffusivity
D_b	:	Grain boundary diffusivity
D_s	:	Surface diffusivity
Δp	:	Vapour pressure difference
r	:	Particle radius
H_o	:	Null hypothesis
H_1	:	Alternative hypothesis
$P_{\max}$	:	Maximum indentation load
h_c	:	Contact depth
A	:	Contact area
E	:	Young's modulus of elasticity
S	:	Stiffness
H	:	Hardness
v	:	Poisson's ratio
E^*	:	Reduced Young's modulus of elasticity
T_m	:	Melting point (°C)
T_o	:	Operational temperature (°C)
T_h	:	Homologue temperature ratio (°C)

LIST OF PUBLICATIONS

International Peer-Reviewed Journals (ISI Indexed):

1. V.R. Manikam and K.Y. Cheong, "Die Attach Materials for High Temperature Applications: A Review," *IEEE Transactions on Components, Packaging and Manufacturing Technology*, vol.1, no.4, pp.457- 478, 2011.

2. V.R. Manikam, K.Y. Cheong and K.A. Razak, "Chemical reduction methods for synthesizing Ag and Al nanoparticles and their respective nanoalloys," *Materials Science and Engineering B*, vol. 176, no. 3, pp. 187-203, 2011.

3. V.R. Manikam, K.A. Razak and K.Y. Cheong, "Sintering of silver-aluminium nanopaste with varying aluminium weight percent for use as a high temperature die attach material," *IEEE Transactions on Components, Packaging and Manufacturing Technology*, 2012, 10.1109/TCPMT.2012.2209425.

4. V.R. Manikam, K.A. Razak and K.Y. Cheong, "Physical and electrical attributes of sintered Ag_{80}-Al_{20} high temperature die attach material with different organic additives content," *Journal of Materials Science: Materials in Electronics*, 2012, 10.1007/s10854-012-0801-y.

5. V.R. Manikam, K.A. Razak and K.Y. Cheong, "Reliability of sintered Ag80-Al20 die attach nanopaste for high temperature applications on SiC power devices", *Microelectronics Reliability*, 2012, http:// dx.doi.org / 10.1016 / j.microrel.2012.10.007.

6. V.R. Manikam, K.A. Razak, and K.Y. Cheong, "Effect of Sintering Time on Silver-Aluminium Nanopaste for High Temperature Die Attach Applications, *Advanced Materials Research*, Vol. 576 (2012), pp. 199-202, Trans Tech Publications, Switzerland.

7. V.R. Manikam, K.A. Razak and K.Y. Cheong, "Effects of varying organic additives weight percent content in the formulation of an Ag_{80}-Al_{20} nanopaste for use as a high temperature die attach material and its resulting post-sintering characteristics," *Metallurgical and Materials Transactions A*, 2012. (Manuscript under review).

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2. V.R. Manikam, K.A. Razak and K.Y. Cheong, "Effect of sintering time on Silver-Aluminium nanopaste for high temperature die attach applications," *International Conference on Advances in Manufacturing and Materials Engineering 2012*, Kuala Lumpur, Malaysia, 3rd – 5th July 2012. (Manuscript accepted)

3. V.R. Manikam, K.A. Razak and K.Y. Cheong, "Sintering of Ag_{80}-Al_{20} nanoalloy for high temperature die attach applications on silicon carbide-based power devices: The effects of ramp rate and dwell time," *35th International Electronics Manufacturing Technology Conference (IEMT) 2012*, Kinta River Front Hotel Ipoh, Perak, Malaysia, 6th – 8th November 2012. (*Won Outstanding Student paper, T.W. Chen Award*)

FABRIKASI DAN PENCIRIAN BAHAN KEPIL DAI Ag-Al BAGI PERANTI SiC UNTUK KEGUNAAN PADA SUHU TINGGI

ABSTRAK

Pembangunan bahan kepil dai Ag-Al bagi kegunaan suhu tinggi pada peranti silikon karbida telah dikaji secara sistematik. Kajian ke atas bahan kepil dai Ag-Al dijalankan dengan mengubah peratusan berat serbuk nano Al dalam matriks Ag serta kandungan bahan tambah organik. Bahan perekat nano Ag-Al disinter dalam relau pada suhu 380°C selama 30 minit. Ini membolehkan partikel nano Ag dan Al menjalani "keadaan gabungan pepejal". Seterusnya, pencirian fizikal, terma, elektrikal dan mekanikal dijalankan. Pembelauan sinar-X mendapati sebatian Ag_2Al dan Ag_3Al terbentuk selepas proses pensinteran. Sampel Ag-Al dengan kandungan 80% Ag-20% Al serta 13% berat bahan organik memberikan keputusan elektrikal dan terma yang terbaik antara semua sampel. Suhu peleburannya ditentukan pada 518 ± 1°C. Berdasarkan nisbah suhu homolog antara 0.67-0.85, bahan kepil dai Ag_{80}-Al_{20} boleh digunakan pada suhu 258.59°C hingga 400.18°C. Kekonduksian elektrikal serta terma bahan lampir dai Ag_{80}-Al_{20} lebih tinggi berbanding pateri aloi dan epoksi konduktif pada nilai 1.01×10^5 (ohm-cm)$^{-1}$ dan 123 W/m-K. Pekali pengembangan terma ditentukan pada nilai 7.74×10^{-6}/°C, di mana didapati nilai ini dekat dengan nilai silikon karbida. Ini bermakna, soal ketidak-seragaman terma dapat dikurangan. Nilai keliangan dan ketumpatan ditentukan pada 19% dan 6.42 g/cm^3. Kandungan bahan organik di dalam bahan kepil dai Ag-Al menentukan sifatnya. Ini termasuk sifat mekanikalnya seperti modulus keanjalan, kekerasan dan kekakuan bahan. Kajian ke atas jenis logam sebagai lapik bahagian belakang dai silikon karbida mendapati Ag dan Au memberikan nilai kekuatan lekatan yang terbaik antara 28.9-38.1 MPa. Secara lazimnya, didapati dengan mengurangkan kandungan peratusan berat bahan organik, prestasi bahan kepil dai Ag-Al bertambah baik.

FABRICATION AND CHARACTERIZATION OF Ag-Al DIE ATTACH MATERIAL FOR SiC-BASED HIGH TEMPERATURE DEVICE

ABSTRACT

An Ag-Al nanopaste for high temperature die attach applications on SiC power devices has been developed. The Ag-Al nanopaste was studied by varying the Al weight percent in the Ag matrix as well as the organic additives content. The Ag-Al nanopaste was sintered in open air at 380°C for 30 minutes to burn off the organic additives, causing Ag and Al nanoparticles to undergo solid-state fusion. The sintered Ag-Al die attach material's physical, thermal, electrical and mechanical attributes were examined. X-ray diffraction studies revealed the formation of Ag_2Al and Ag_3Al compounds in the post-sintered nanopaste. The sample with 80% Ag and 20% Al weight percent content having a total nanoparticle content of 87.0% demonstrated the best electrical and thermal characteristics. Its melting point was 518 ± 1°C. Based on homologue temperature ratios of 0.67-0.85, the Ag_{80}-Al_{20} die attach material can be used between 258.59°C to 400.18°C. It's electrical and thermal conductivities were higher than those of solder alloys and conductive epoxies at 1.01 x 10^5 $(ohm\text{-}cm)^{-1}$ and 123 W/m-K, respectively. The coefficient of thermal expansion was 7.74 x 10^{-6}/°C, which is close to that of SiC and can help minimize thermal mismatch. The Ag_{80}-Al_{20} sample also had the lowest porosity percentage at 19% amongst all samples and a density value of 6.42 g/cm^3. The organic additives used in the nanopaste affected the creation of a dense die attach material as well as the mechanical attributes of the die attach material, i.e. the modulus of elasticity, hardness and stiffness. SiC die back metallization tests concluded that Ag and Au coatings gave the best joint adhesion strength between 28.9 – 38.1 MPa for high temperature power device applications. In essence lower organic additives content improved the attributes of the die attach nanopaste.

CHAPTER 1

INTRODUCTION

1.1 Theoretical Background

Silicon carbide (SiC), alongside with other wide band gap semiconductors has demonstrated the ability to function under extreme conditions; high temperature, high power or radioactive environments (Neudeck, 1994; Chin *et al.*, 2011). Wide band gap semiconductors have higher achievable junction temperatures and thinner drift regions, which result in much lower on-resistance as compared to that of silicon based-devices (Neudeck, 1994). Thus, it is no surprise that SiC has become a favoured choice for device fabrication that can be applied to automobile, well-logging, aerospace or military ([a]Manikam and Cheong, 2011). For such demanding applications, the development of devices and selection of materials still centres around cost considerations (Neudeck, 1994; Werner and Fahrner, 2001). SiC-based device fabrication concerns have gained high focus and research momentum but there are still many issues which plague the selection of materials from a reliability stand point for packaging of the device, for example melting points and degradation aspects when subjected to high temperatures or harsh environments (Neudeck, 1994).

A power device electronic package must be able to distribute signal and power effectively as well as have good thermal properties for heat dissipation from the device. In addition, it must provide protection to the device from mechanical and environmental damage as well as ensuring continued reliable device operation capabilities (Ning, *et al*., 2010; Rebbereh *et al*., 2003; Chang *et al*., 2003; Funaki *et al*., 2007). The main development areas which need focusing for power device electronic packaging include die attach, substrates, encapsulation, case, heat spreader and heat sink (Coppola *et al*., 2007). Die attach for power device technology is of particular interest as it forms an integral part of the electronic package, i.e. it provides a mechanical, thermal and electrical interface between the device and the substrate (Kisiel and Szczepa´nski, 2009). A die attach material for power devices should ideally provide good thermal and electrical conductivity, low coefficient of thermal expansion (CTE) between the die and substrate, excellent adhesion to the die and substrate, i.e good wettability and acceptable fatigue resistance (Li *et al*., 2012; Knoerr *et al*., 2010; Siow, 2012). Figure 1.1 illustrates the main components in a typical semiconductor electronic package.

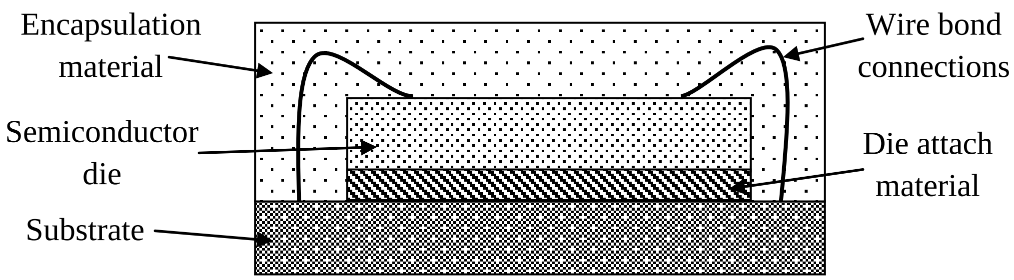

Figure 1.1: An illustration of components in a typical semiconductor electronic package.

1.2 Problem Statement

High temperature die attach materials have rather stringent requirements. Among the general requirements are good corrosion resistance, good ductility, solidus points ≥ 260°C, liquidus points ≥ 400°C, thermal conductivity > 0.2–0.3 W/cm-K, thermal shock reliability, good thermo-mechanical fatigue resistance, low toxicity, electrical volume resistivity < 100 μΩ-cm, reasonable costs, and compliant CTE mismatch between the die and substrate (Lalena *et al*., 2002; Hartnett and Buerki, 2009; Coppola *et al*., 2007). The main points of concern are the solidus and liquidus temperatures, as well as the electrical and thermal conductivity characteristics.

Over the years, many die attach materials have been introduced for high-temperature electronic packaging, such as the traditional leaded (Pb) solders ((Neudeck, 1994; Suganuma, 2004; Plumbridge *et al*., 2004; Abtew and Selvaduray, 2000) gold (Au)-based solders (Neudeck, 1994; Rebbereh *et al*., 2003), high-temperature conductive epoxies with metallic flakes (Neudeck, 1994; Rebbereh *et al*., 2003; Krishnamurthy et al., 1992), zinc (Zn)-based solders (Neudeck, 1994; Kim *et al*., 2009; Lee *et al*., 2007; Wang *et al*., 2010; Islam *et al*., 2005), germanium (Ge)-doped solders (Neudeck, 1994; Johnson *et al*., 2001), and silver (Ag)-based die attach pastes (Neudeck, 1994; Lalena *et al*., 2002; Zhang and Lu, 2002). Most of these die attach materials fall into the low- to medium-operational temperature range (Neudeck, 1994), which is below 400°C. There are exceptions though, for example Au-thick films (Neudeck, 1994; Rebbereh *et al*., 2003), but Au is costly for long-term manufacturing considerations. A solution was to use Ag based powders via sintering with pressures at around 40 MPa to create dense structures, which also lowers the processing temperature (Zhang and Lu, 2002; Knoerr *et al*., 2010; Schwarzbauer and Kuhnert, 1991). The concern for this application however surrounds the pressure being used, as the slightest irregularities during pressure application can cause damage to both the die and the substrate (Knoerr *et al*., 2010). The use of pressure also complicates the manufacturing process.

Through this approach, the use of Ag nanoparticles was introduced and proven to be a suitable candidate for high operational temperatures up to approximately 600°C under conditions with significantly lower processing temperatures up to 300°C (Coppola *et al*., 2007; [a-b]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004; Wakuda *et al*., 2007; Wakuda *et al*., 2008). A myriad of successful method has been used to fuse these Ag nanoparticles in order to create dense and reliable connections between the die and substrate for high power SiC devices ([a-c]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004; Wakuda *et al*., 2007; Wakuda *et al*., 2008; Hu *et al*., 2010; Wakuda *et al*., 2010; Knoerr and Schletz, 2010; Maekawa *et al*., 2010).

Nanoparticles have high surface energies which enable them to undergo particle coalescence at much lower processing temperatures as compared to the bulk materials ([a-c]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004; Wakuda *et al*., 2007; Wakuda *et al*., 2008; Hu *et al*., 2010; Wakuda *et al*., 2010; Knoerr and Schletz, 2010; Maekawa *et al*., 2010; Powen and Carry, 2000). Also, the need for external pressure can be removed, though in some cases a small amount of pressure up to 2 MPa is still applied (Schwarzbauer and Kuhnert, 1991; Knoerr and Schletz, 2010). By controlling the use of organic additives such as surfactants and dispersants, the nanoparticles undergo solid-state reactions instead of a liquidus state during sintering ([a-c]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004; Wakuda *et al*., 2007; Wakuda *et al*., 2008; Hu *et al*., 2010; Wakuda *et al*., 2010; Knoerr and Schletz, 2010; German, 1996). The controlled burn out of organic additives is able to promote coalescence between the nanoparticles ([a-c]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004; Wakuda *et al*., 2007; Wakuda *et al*., 2008; Hu *et al*., 2010; Wakuda *et al*., 2010; Knoerr and Schletz, 2010). Therefore, concerns of die floating or shifting do not surface in such applications ([a-c]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004). The lowered density as compared to a bulk material helps provide a much lower Young's modulus which is important for stress relieve during thermal mismatch between the die and substrate whereby values as low as 9 GPa have been recorded for sintered Ag nanopastes ([a-c]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004; Siow, 2012). As far as reliability is concerned, the use of Ag nanoparticles via sintering has been proven to be robust for high temperature applications and can help eliminate voiding which is typically found in solder alloys during reflow due to the presence of liquidus states during reflow (Kisiel and Szczepa´nski, 2009; [a-c]Bai *et al*., 2007; Bai *et al*., 2006; Lu *et al*., 2007; Lu *et al*., 2004; Knoerr and Schletz, 2010; Chen *et al*., 2012; Masson *et al*., 2011).

The ultimate aim of any die attach material technology is to have lowered costs, good thermal and electrical performance and ease of application for mass manufacturing. Therefore, based on the positive review of Ag nanopastes, this research work has been carried out to introduce sintered Ag and aluminium (Al) nanopastes for high temperature SiC power device applications. Al has the fourth best electrical conductivity value amongst the metals, good thermal conductivity and is relatively cheaper than both Au and Ag (Callister, 2000). In the past, nanoscale reactions have been researched between different metallic elements, but only at the alloy synthesis scale, for example using chemical reduction methods (Yamauchi *et al*., 2002).

Up to date, there has not been a similar method reported utilizing solid-state reactions and different element nanoparticles, in this case Ag and Al, to create a die attach joint structure for high temperature use. Nanoscale materials for high temperature die attach bring about new characteristics, which can be tailored to certain applications in the high temperature electronics field. This work discusses sintering for creating an Ag-Al high temperature die attach material. By varying the organic additives and Al weight percent content in the Ag-Al nanopaste, followed by sintering, it has been found that the sintered Ag-Al nanopaste provides good thermal, electrical and mechanical properties for such applications. Investigating the attributes and characteristics of the Ag-Al die attach nanopaste as well as its reliability issues is crucial for high temperature applications. With these considerations in mind, we seek to address the following problem statements by fabricating and characterizing:

1.) A high temperature die attach material which is suitable for SiC-based devices with operational temperatures between 300-400˚C.

2.) A die attach material with much cheaper material costs than existing Ag and Au-based solutions.

3.) A reliable die attach material with acceptable thermal, electrical and mechanical properties.

1.3 Research Objectives

The primary aim of this research work is to develop a high temperature die attach material using Ag and Al nanoparticles in a nanopaste form, which is sintered to create joints with SiC dies for power applications. The die attach material should demonstrate acceptable electrical, thermal, physical and mechanical properties at high temperatures. With this primary aim in mind, the following objectives were laid out:

1. To formulate an Ag-Al die attach nanopaste system utilizing metallic nanoparticles and organic additives.
2. To design an effective sintering profile which can promote coalescence of the nanoparticles during sintering with organic additives burn off from the Ag-Al nanopaste to form an Ag-Al nanoalloy.
3. To investigate the physical, electrical and thermal characteristics of the Ag-Al nanopaste having varying Al weight percent content (20-80%) and nanoparticles versus organic additives weight percent content (84.7-87.0%).
4. To assess the reliability of the sintered Ag-Al die attach nanopaste material for high temperature applications.

1.4 Scope of Study

In this research work, the Ag-Al nanopaste was first formulated using Ag and Al nanoparticles as well as organic additives. The Al and organic additives weight percent content was varied to obtain the optimum electrical, thermal, physical and electrical characteristics of the post-sintered Ag-Al nanopaste. The organic additives burn off from the nanopaste during sintering was studied using thermogravimetric analysis (TGA) to design the sintering profile. The sintered Ag-Al nanopaste's thermal properties were measured using a differential scanning calorimeter (DSC) and laser flash system. The electrical properties were determined using a semiconductor parameter analyzer (SPA).

The morphology and microstructure of the post-sintered Ag-Al nanopastes were observed using an atomic force microscope (AFM) and scanning electron microscope (SEM). The compounds formed in the post-sintered Ag-Al nanopaste were detected using an x-ray diffractometer (XRD). As for the mechanical characteristics of the post-sintered Ag-Al nanopaste, the attributes were obtained with thermo-mechanical analysis (TMA) and nanoindentation, whilst the bonding strength was tested using lap shear joints on an Instron system. The quality of the Ag-Al die attach material's bonding with SiC die back metalized dies after sintering and thermal aging were scanned using a confocal scanning acoustic microscope (CSAM).

1.5 Thesis Outline

This thesis is organized into 5 chapters. Chapter 1 develops an overview of high temperature electronic packaging for SiC power devices, the issues and challenges being faced for high temperature die attach material development, research objectives and scope of this research. Chapter 2 provides the literature review associated with high temperature die attach materials as well as findings and problems encountered. Chapter 3 lists the systematic methodology which was employed in this research work, as well as the materials and equipments used. Chapter 4 discusses the findings and results from this research work. In the final chapter which is Chapter 5, a summary, conclusion and future recommendations are delivered to the reader.

1.6 Important terms in the thesis

To help the reader understand this thesis much better, several major terms being used throughout is addressed here (German, 1996; Siow, 2012):

(i) Alloying: Alloying is done by combining one metal with one or more other metals or non-metals that often enhance its properties

(ii) Doping: Doping is generally the practice of adding impurities to something.

(ii) Solid-state sintering: Sintering without the presence of a liquidus state.

(v.) Solid-solution: A solid solution is a solid-state solution of one or more solutes in a solvent.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The need for high power density and high temperature capabilities in today's electronic devices continues to grow. More robust devices with reliable and stable functioning capabilities are needed, for example in aerospace and automotive industries as well as sensor technology. These devices need to perform under extreme temperature conditions, and not show any deterioration in terms of switching speeds, junction temperatures, and power density (Baliga, 1989; Coppola *et al*., 2007; Bhatnagar and Baliga, 1993). While the bulk of research is performed to source and manufacture these high temperature devices, the device die attach technology remains under high focus for packaging. The die attach material has to withstand high temperatures generated during device functioning and also cope with external conditions which will directly determine how well the device performs in the field. Chapter 2 reviews the numerous research works thus far for high temperature die attach materials on wide band gap materials, in particular silicon carbide (SiC), as well as document their successes, concerns and application possibilities, all of which are essential for high temperature reliability. The fundamentals of nanoscale sintering and use of statistics in this work will also be discussed.

2.2 High temperature demands for electronics and wide band gap semiconductors

Over the past decade, there have been numerous breakthroughs in silicon (Si) technology for semiconductors. Miniaturization efforts have led to denser devices and a wider field of application possibilities, encompassing multifunction capabilities. These requests need devices to function much faster, perform more functions, and more importantly, withstand extreme conditions and temperature conditions without failure (Baliga, 1989; Coppola *et al*., 2007; Bhatnagar and Baliga, 1993; Holz *et al*., 2007; Powell and Rowland, 2002). This includes microelectromechanical systems (MEMS) devices for sensor applications, which need to sustain their sensitivity levels even at such high temperatures. The new devices need to have higher breakdown voltages, possess lower switching losses, be capable of higher current densities and can operate at higher temperatures (Buttay *et al*., 2009).

The materials which possess such behaviour are wide band gap materials which include SiC, gallium nitride (GaN), and diamond. Such stringent and demanding requests have led to wide scaled sourcing efforts for new materials, both at the device and packaging levels. At the interconnect level between die and substrate, new high temperature die attach materials have been widely sourced, as they form a crucial element in packaging. These new die attach materials need to perform well in order to sustain the reliability of the package's die to substrate interconnection in extreme conditions and high temperatures. The requirements and tests for these high temperature application die attach materials are stringent.

Technologies such as SiC enable the creation of high temperature devices. This technology has the potential to improve upon many of the current limitations associated with Si electronics, in particular, the limitations of Si device switching speeds, junction temperatures, and power density (Hornberger *et al*., 2004). SiC, for example, has demonstrated the ability to function under extreme high-temperature, high-power, and/or high-radiation conditions and is expected to enable significant improvements to a far ranging variety of applications and systems. SiC based power electronics and MEMS devices have some excellent electrical characteristics, compared with conventional Si-based devices, namely high withstanding voltage, low on-state resistance, high operational temperature, and so on. The on-state resistance of power electronics device is an essential parameter related to the operational loss in the device itself (Matsukawa *et al*., 2004). In the particularly attractive area of power devices, a literature work indicated that SiC power MOSFETs and Schottky diode rectifiers can operate over higher voltage and temperature ranges, have superior switching characteristics, and yet have die sizes nearly 20 times smaller than correspondingly rated Si-based devices (Bhatnagar and Baliga, 1993). Table 2.1 summarizes and compares these wide band gap material properties.

Table 2.1: Characteristics of wide band gap semiconductors at 300K (Hudgins *et al*., 2003; Werner and Fahrner, 2001; Roccaforte *et al*., 2012).

Semiconductor material	Band gap, eV	Electron mobility, cm^2/Vs	Hole mobility, cm^2/Vs	Density, g/cm^3	Thermal conductivity, W/cm-K	CTE, ppm/K	Maximum operating temperature, °C	Process maturity	Key issues
Si	1.1	1400	450	2.33	1.3	2.6	150	Very high	Not suitable for aggressive environments
GaAs	1.43	8500	400	5.32	0.55	5.73	350	High	Contact stability at high temperatures, Not suitable for aggressive environments
3C-SiC	2.39	300-900	10-30	3.17	7	2.77	600	Low	Not available as bulk material
6H-SiC	3.02	330-900	75	3.21	7	5.12	700	Medium	Bulk material quality, Ohmic contact to p-type material
4H-SiC	3.26	700	-	-	7	5.12	750	Medium	Bulk material quality, Ohmic contact to p-type material
GaN	3.44	900	10	6.1	1.1	5.4-7.2	>700	Very low	Material quality and reproducibility, Ohmic contacts
Diamond	5.48	2200	1800	3.52	6-20	0.8	1100	Very low	N-type doping only polycrystalline material available

2.2.1 High temperature electronic packaging materials

Currently, a great deal of work is spent on the development of highly effective cooling systems for heat removal in power electronics, optoelectronics, and telecommunication systems. However, electronic components and microsystems capable of high-temperature operation would allow designers to eliminate, or at least minimize, the expensive and bulky cooling systems currently required to protect electronics from extreme environments (Werner *et al*., 2001). Thus, packaging plays an important role. In packaging, many processes are affected by the transition to high temperature power devices. These materials must be able to withstand the high operating temperatures and provide reliable support and protection to the chip or device inside the packaging. To achieve this, a careful selection of materials to minimize mismatch is critical, due to the significant temperature range of operation and the stiffness of die attach materials that are capable of withstanding such temperatures (Hagler *et al*., 2011).

Categories which need focusing on include die attach, substrate, interconnects, encapsulation, case, heat spreader and heat sink (Hagler *et al*., 2011). The criterion for selection depends on maximizing the density and lightness of the system, and providing long-term reliable assemblies. This literature work will concentrate on the die level interconnect technology, commonly termed as die attach for wide band gap devices and power devices. The requirements for these high temperature materials and characteristic for selecting a high temperature die attach material depending on device properties will be reviewed. Overall, there are 4 main concerns for high temperature material development, which are the die attach material, substrates, wire bond material and encapsulation material. Figure 2.1 depicts 3 levels of a typical electronic packaging system. Die attach materials fall into the first category, i.e. first level packaging which covers both single chip and multichip modules (Tummala, 2001). The structure of an electronic package incorporating a die attach layer was presented earlier in Figure 1.1 from Chapter 1.

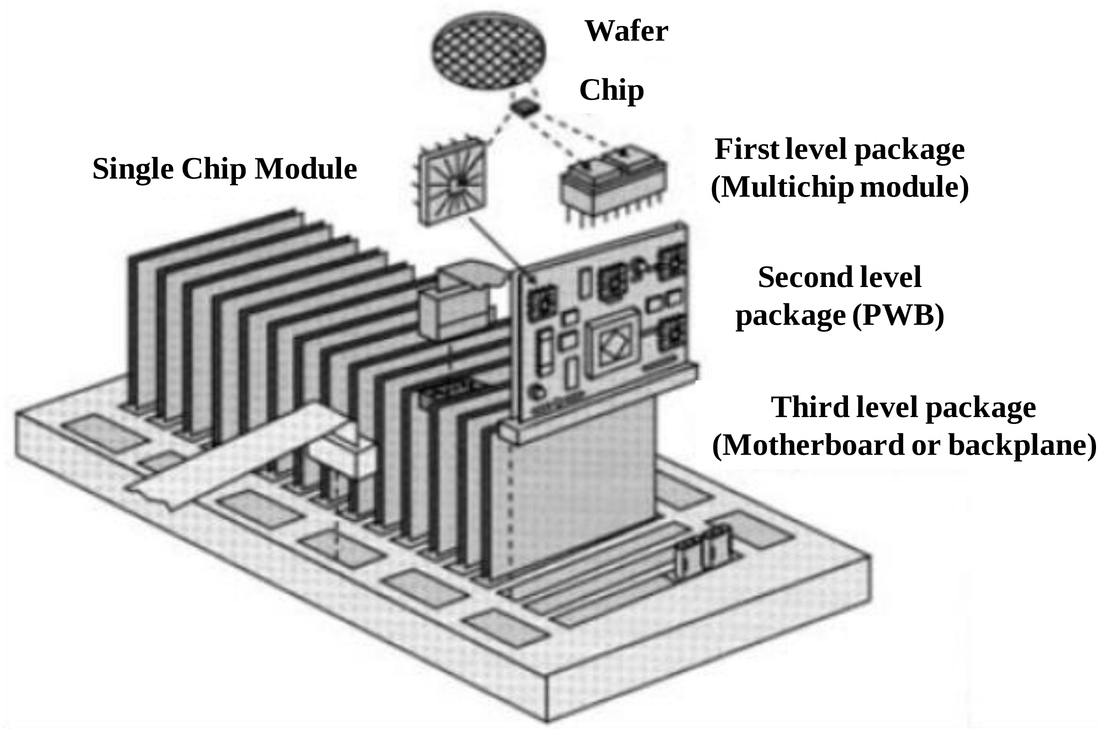

Figure 2.1: Schematic illustration covering three levels of electronic packaging (Tummala, 2001).

2.3 High temperature die attach materials

In this section, an overview will be provided on the SiC device technology for high temperature applications and how it affects the requirements for die attach materials selection subsequently. Concerns for utilizing these high temperature die attach materials in mass manufacturing environments are also presented.

2.3.1 Requirements for high temperature die attach materials

Die attach materials for power device technology is of particular interest as it forms an integral part of the electronic package, i.e. it provides a mechanical, thermal and electrical interface between the device and the substrate (Baliga, 1989). A die attach material which is intended for use on a power device should ideally provide high thermal and electrical conductivity, a low CTE between the die and the substrate, good wettability and adhesion to the die and to the substrate, acceptable mechanical properties with stress relaxation behaviour, excellent fatigue and corrosion resistance, ease of being reworked and reliable at high temperature conditions (Chin *et al*., 2011). Table 2.2 lists the operating temperatures of various device technologies by applications. It is quickly noticeable how the SiC Digital Logic devices can withstand up to 700°C approximately. Thus, the die attach material should be able to cope with such high temperatures. For the existing silicon technology, the maximum temperature is seen in the digital logic devices category at 400°C, still considerably high.

Table 2.2: Operating temperatures for various devices by application (Oppermann, 2009).

Devices by application	Current operating temperature, °C	Projected operating temperature, °C
Si microwave	150	200
Si digital logic	300	400
Si small signal	250	350
Si power	200	NA
Si DRAM	150	NA
SiC power	300	400
SiC digital logic	100	700
SiC small signal	400	NA
SiC power N-C MODSFET	600	NA
SiC DRAM	600	NA
Nitrides (n-type)	NA	700
Nitrides microwave	NA	700

Figure 2.2 categorizes a culmination of existing die attach materials and solders for high temperature use, ranging between 200°C to more than 500°C. The bulk of the die attach materials fall into the middle category for high lead. Not all high temperature solder alloys depicted in Figure 2.2 can or have been used as die attach materials. The reported die attach materials in literature works will be discussed accordingly by categories.

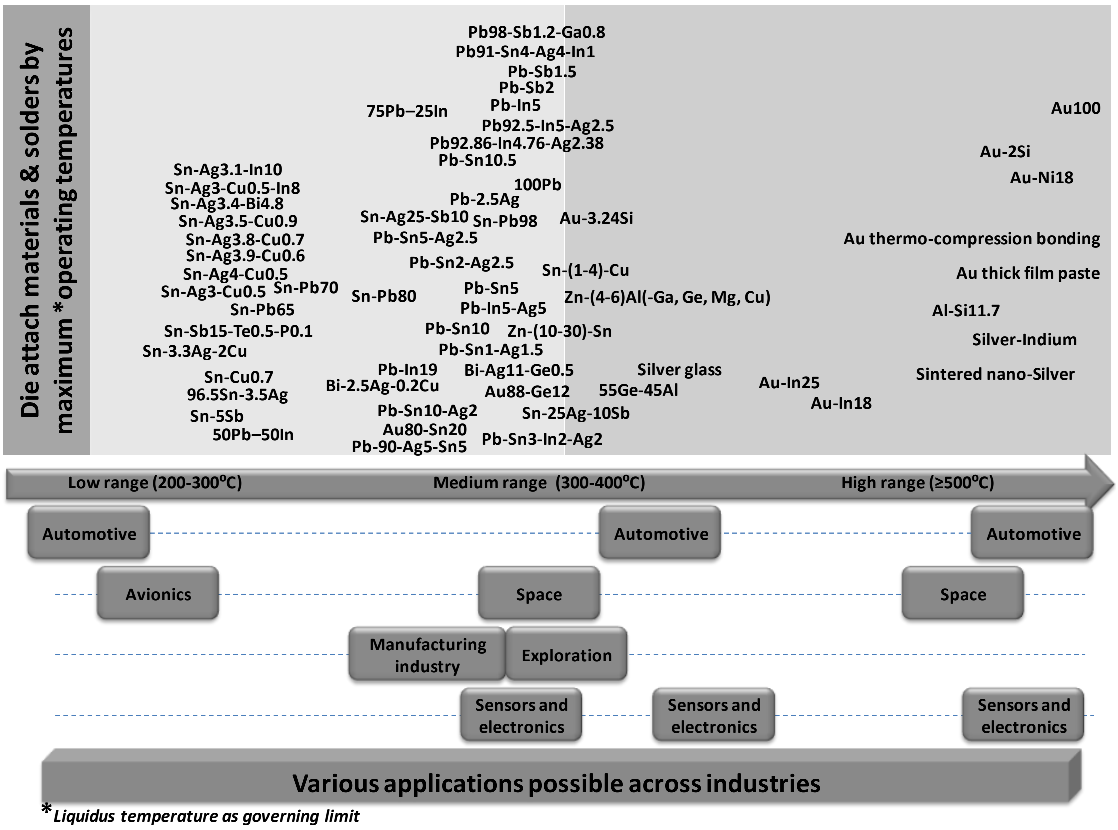

Figure 2.2: Various die attach materials and solders, their operating range and application possibilities (Manikam and Cheong, 2011).

When mass manufacturing plans for high temperature die attach materials come into play, certain points need to be noted; Young's modulus of elasticity (E), and processing temperatures, long-term chemical stability of the die attach material, voiding during die attach, the die attach dispense method and choice of material for wafer back metallization. Young's modulus and processing temperatures during the die attach process have been known to be among the main control points to avoid high stresses on the die. These stresses are mostly related to CTE mismatch issues. For applications in high temperature packaging, the thermal mechanical properties of die attach material such as CTE, Young's modulus, fatigue/creep properties, and their temperature dependences are very much of concern since the die attaching material is an intimate contact both electrically and mechanically, with the die and the substrate (Chen *et al*., 2000). Long-term chemical stability of the die attach material is also of a concern for high temperature use. If the die-attach is expected to be electrically conductive, the electronic properties of its interface with the die would also become critically important (Chen *et al*., 2000). This may degrade with time from the manufacturing date of the package. The effects of voiding on the thermal resistance of chip level packages were investigated and the results showed that for small, random voids, the thermal resistance increases linearly with void volume percentage (Fleischer *et al*., 2006). For wideband gap semiconductors this is a major concern toward the die's performance. There needs to be good control on the die attach dispense method during manufacturing so as not to cause excessive voiding when the die is attached.

Based on the understanding of void formation during die attach, the methods of dispense is crucial. An interesting research utilizing nano Ag in paste form showcased the good flowability and easy storage in a syringe. It can be dispensed to accurate locations on the substrate for die bonding, or even with stencil prints (Bai *et al*., 2007; Bai *et al*., 2007; Bai *et al*., 2007; Bai *et al*., 2006). This suits the current conventional die attach methods and equipments at large. Another interesting approach to die attach which is being considered is wafer backside coating of the die attach material (Winster *et al*., 2008). The die attach material can be applied and dried before further processing. It is said to be able to reduce the cost by as much as 20–30% compared to the conventional methods, and has better control on bond line thickness and achieves higher output. The authors created a novel resin system which maintains high modulus at temperatures up to 300°C and higher (Winster *et al*., 2008). The resin system is said to have good Ag loading for conductivity purposes.

However, the adhesion strength dropped at 280°C when the Ag content increased. For high temperature die attach materials, the challenge would be to have good adhesion and also high content of a particular element, in this case Ag, as extremely high thermal and electrical conductivity is needed.

Wafer back metallization is important for power devices. The choice of metallization type on wafers depends very much on the surface of the substrate and the die attach material itself. For example, the nanoscale Ag die attach material was attached to direct bonded copper substrates (DBC) which had Ag coatings electroplated onto them (Bai *et al*., 2007; Bai *et al*., 2007; Bai *et al*., 2007; Bai *et al*., 2006). The SiC dies had Ag metallization to create a good and reliable adhesion. Metallization of the dies prior to substrate and die attach bond creation is an essential point and needs proper analysis so as to avoid any unwanted failures particularly delamination. The effects of die back metallization on die attach failures were also studied using silicon dies having a Cr/Ni/Au wafer back metallization, which were attached to gold films with a thickness of approximately 500 Å (Radhakrishnan, 1997). The studies on the failed devices showed that the formation of nickel oxide causes poor die attachment even for an Au film thickness of 500 Å. Therefore careful selection of the die back metallization is crucial; it should take into account the metal being incorporated into the die attach material as well.

2.4 Types of high temperature die attach materials

In this section, major die attach systems for high temperature applications will be reviewed. They are divided into 6 groups; leaded solders, gold based systems, zinc based systems, bismuth based systems, Ag glass systems and finally Ag nanopaste systems.

2.4.1 Lead-Tin and other lead based systems

Based on Figure 2.2, it is seen that there is substantial use of leaded solders for die attach purposes. The majority of these devices fall into the medium range. Lead-tin (Pb-Sn) remains an important die attach material for high temperature applications, particularly for large size die. The driving force of this material is a combination of high ductility and acceptable thermal conductivity for most applications (Suganuma, 2004). Sn and Pb have melting points at 323°C and 232°C, respectively, and their alloys have lower melting points, with a minimum of 183°C occurring at the eutectic composition (37Pb–63Sn) (Plumbridge *et al*., 2004). High lead solders have been used for die-attach applications for many years within the power sector. These solders offer acceptable cost, processibility, and performance (Phillip, 2002).

Pb solder alloys for die attach have been around for quite some time, and are acknowledged as mature products. A relatively well-established knowledge base about the physical metallurgy, mechanical properties, flux chemistries, manufacturing processes, and reliability of eutectic Pb-Sn solders exists (Abtew and Selvaduray, 2000). Figure 2.2 depicts at least 26 types of Pb category high temperature solders, though not all of them have been proven to be suitable as die attach materials. The use of Pb die attach materials on large dies is due to the characteristics of the leaded solder alloys itself, as shown in Figure 2.3, which creates lower stress concentration points on the die and its edges due to its good ductility (Yamada *et al*., 2006). Currently, there are no other alternative lead-free die attach materials that will work effectively for large, high-power die. For Pb-free solders, unfortunately, a limited number of alloying systems are available (Suganuma *et al*., 2009). Therefore, the plan currently is to qualify smaller power device dies with developmental Pb-free solder solutions for die attach.

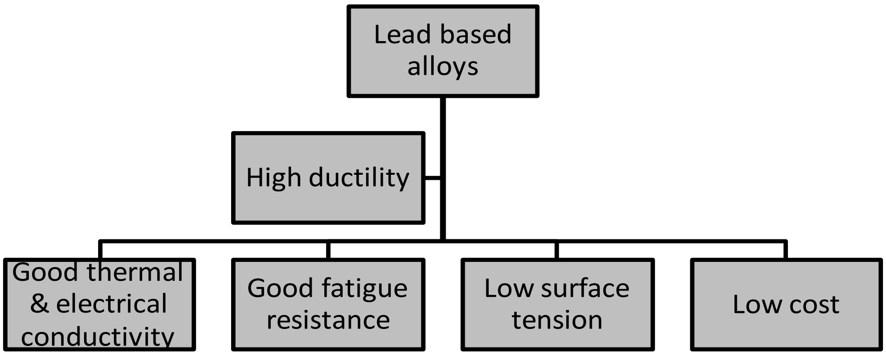

Figure 2.3: General characteristics of leaded solder alloys (Yamada *et al*., 2006).

Based on Figure 2.4 as the Pb content increases, the liquidus points also increase. The solder alloys in Figure 2.4 have been arranged according to individual increasing lead content. Generally, the Pb-Sn solder systems have high liquidus points and they have been popular for high temperature die attach materials thus far. However, the higher the Pb content, the slower the throughput in automated die attach machines, due to the time required for the Pb-Sn liquid to re-solidify after the die attach operation is completed, causing voiding in between the die and substrates' crevice. For larger dies, which require more die attach material coverage, the voiding issue will be more pronounced.

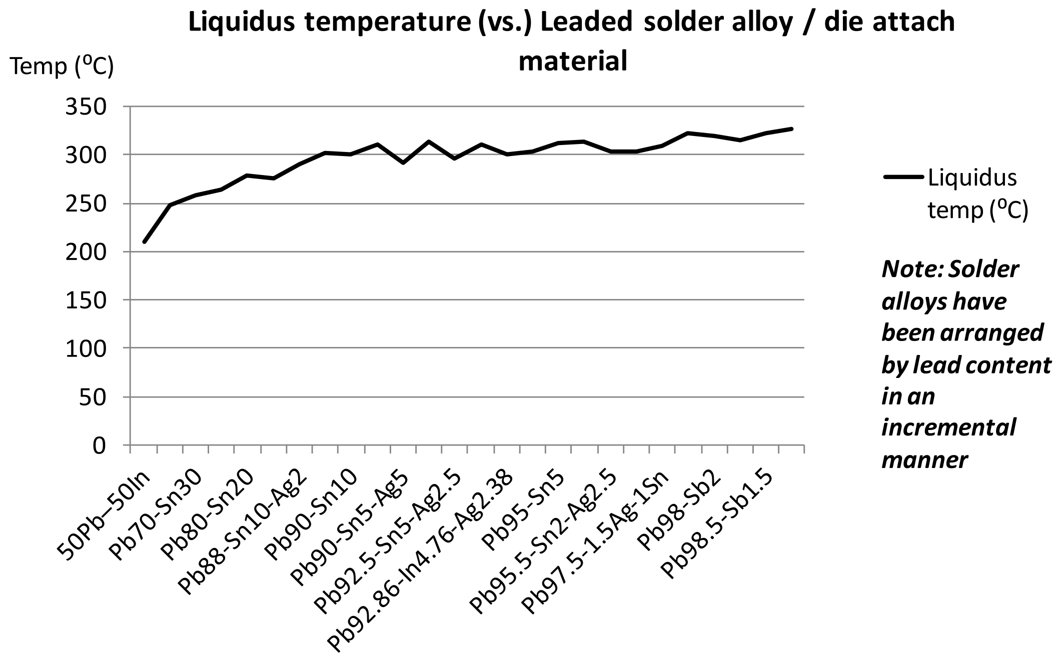

Figure 2.4: Liquidus temperature increment by lead content for leaded solder alloys (Manikam and Cheong, 2011).

However, lead (Pb) compounds have been cited by the Environmental Protection Agency (EPA) as one of the top 17 chemicals posing the greatest threat to human life and the environment (Wood and Nimmo, 1994). The concern about the use of Pb in the electronics industry stems from occupational exposure, Pb waste derived from the manufacturing process, and the disposal of electronic assemblies. Although the consumption of Pb by the electronics industry appears to be minimal, the potential for Pb exposure cannot be ignored (Wood and Nimmo, 1994). The European nations issued a directive on "Waste from Electrical and Electronic

Equipment" on the 1st of January 2004 (Abtew and Selvaduray, 2000). This directive required that the use of the use of lead, mercury, cadmium, hexavalent chromium and halogenated flame retardants' be phased out. It affects both domestic and foreign manufacturers in Europe (Abtew and Selvaduray, 2000).

2.4.2 Gold based systems

Gold (Au) based die attach systems have been widely accepted in the industry due to their excellent properties. One particular Au based die attach system is the gold-tin (Au-Sn) system, which is used for high thermal applications such as microwave devices, laser diodes, and RF power amplifiers (Hartnett and Buerki, 2009). The main factors which make the Au-Sn solder system so favourable for high temperature use are die attach processing temperatures below 320°C, thermal conductivity which is equal to or greater than 0.57 W/cm-K and the possibility of having fluxless applications (Hartnett and Buerki, 2009). The Au-Sn solder, with its combination of good thermal and electrical conductivities, is particularly attractive for "flip-chip" bonding, where the active area of the device is next to the sub-mount (Ivey, 1998). It is also reported that the Au-Sn20 solder is the most common composition utilized; it has a relatively high melting temperature (280°C), good creep behaviour and good corrosion resistance (Ivey, 1998). The solidified Au-Sn eutectic solder consists of two phases, ξ and δ. The ξ phase or Au5Sn has a HCP crystal structure and a composition ranging from 9.1 at% Sn at 521°C to 17.6 at% Sn at the eutectic temperature. The δ phase or Au- Sn is a $B8_1$-type (hexagonal) intermetallic compound with a melting temperature of 419.3°C (Ivey, 1998).