Direct Manufacturing of Diamond Composite Coatings onto Silicon Wafers and Heat Transfer Performance

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Abstract

This paper reveals new insights on how to achieve direct deposition of functional materials onto silicon wafers for cooling purposes. Manufacturing heat spreaders directly onto a microprocessor will negate the need for Thermal Interface Materials (TIMs) which often account for the highest resistances in a typical CPU thermal circuit.

In this work we demonstrate that Cold Spray can be tailored to directly print, on a silicon wafer, a layered structure of aluminum, copper and diamond. The thermal performance of the copper/diamond coating was also separately measured using an in-house testing apparatus showing heat-transfer enhancements in agreement with theoretical predictions.

Keywords: Direct Printing, Diamond Coating, Cold Spray

1. Introduction

The deposition of metals onto silicon (in the form of wafers or chemical compounds) is of great interest for a number of industries such as solar PV [1], development of anti-microbial coatings [2], and now the 3D printing of microprocessor heat sinks and heat spreaders. For the latter, direct bonding onto the microprocessor die could eliminate the need for a thermal interface material (TIM) between the die and the Integrated Heat Spreader (IHS) thus eliminating a significant thermal resistance from the overall thermal budget. However, differential thermal expansion between semiconductor dies and the metallic (e.g. Cu) IHS induces stresses that compromise long term reliability. Thus, the ideal IHS will have a high thermal conductivity and its CTE close to the semiconductor material. To this purpose, Cu-diamond composites have been considered, since the low CTE and high thermal conductivity of diamond can result in an ideal IHS material, compared with other offerings such as Copper-Tungsten composites which do offer low CTE, though with a compromised thermal conductivity.

Cold Spray (CS) is a process by which powders in the range of 5-60 μm are accelerated to supersonic speeds before impacting onto a substrate in "cold" state. The kinetic energy on impact results in large amounts of plastic deformation which allows bonding through mechanical interlocking and adiabatic shear stresses [3]; although a full understanding of the bonding mechanisms of cold spray is yet to be developed. Localized melting due to adiabatic shear stress has been shown to occur, promoting bonding to the substrate and surrounding particles. The particle melting (due to the severe strain rates) is not over a sufficient time period to induce microstructural changes and hence the feedstock properties and phase are maintained.

CS has been successfully applied for the deposition of a variety of materials for various applications including Ti and its alloys, typically onto steel components or polymers [4,5]. Coatings can exhibit excellent properties, good bond strength with the substrate, low porosity (high density) and are free from measurable oxides. For successful bonding during the CS process, there need to be adequate plastic deformation of both the particle and the substrate; however with brittle materials, such as ceramics, little deformation can occur and the particle or substrates will typically crack or shatter upon impact. There has been successful work in depositing ceramic-metal (cermet) or diamond matrices by pre-mixing with ductile metals so that deposition can occur [6-8]. Depositing onto brittle substrates (specifically silicon) with CS is a difficult operation that has shown some promise, unfortunately the studies available are limited [9,10] and critical questions, such as the particle bonding mechanism, remain open. In [9] the authors have successfully consolidated metals onto Si-wafers, however when using a very small particulate size range hence at a cost about 10 times the standard. Using techniques such as PVD or CVD it is possible to manufacture thin layers of metals onto wafers, however there is no potential for building 3D structures and over large areas. In recent times CS has been suggested as a method of 3D printing near net shape components [11].

Thus, this work aims to explore the deposition of functional materials onto silicon wafers with CS, using particulates standard size ranges, that would be able to dissipate unwanted heat in a more efficient manner; hence provide a new base for the manufacturing of next generation heat spreaders. Insights into the metal/silicon bonding mechanism are presented, alongside thermal performance tests of the produced deposits.

2. Experimental method

2.1. Materials selection and substrate preparation

The coatings were manufactured using the in-house CS system at Trinity College Dublin. The system consists of a de Laval nozzle (converging-diverging 180mm long), gas heater, CNC system, powder feeder, computer monitoring and control system, and a nitrogen supply. Nitrogen was used as the process gas for all the experiments undertaken. The heated gas (gas hating is applied to achieve higher gas and particle velocity at the nozzle exit) is injected into the nozzle head and the powder is fed into the nozzle through the feedstock inlet using a high pressure powder feeder. The aim of this work is to explore parameters so that metal layers can be deposited directly onto the wafer with efficient heat conduction. Materials were therefore being selected accordingly, being commercially pure aluminum and copper the best compromise between heat transfer coefficient levels, relatively high melting temperature and suitability for CS processing. At the same time, diamond is an ideal material for heat transfer applications with a very high thermal conductivity combined with low CTE; it is however not possible to be processed directly with CS as being brittle. In order to overcome to this, a composite mix can be produced having diamond powder blended with a metal using a specific ratio before being sprayed. When processed with CS, the metal phase would act as "glue", incorporating the diamond grit within the matrix in the coating. This strategy represents the best compromise between an ideal but not-processable pure diamond layer, and a metal layer.

It can be therefore concluded that, from the thermal point of view, the most efficient (yet feasible) solution is represented by a blend of copper and diamond deposited directly onto a silicon wafer. Despite this compromise, CS processing can still avoid the implementation of a TIM material which is a significant barrier to achieve efficient cooling.

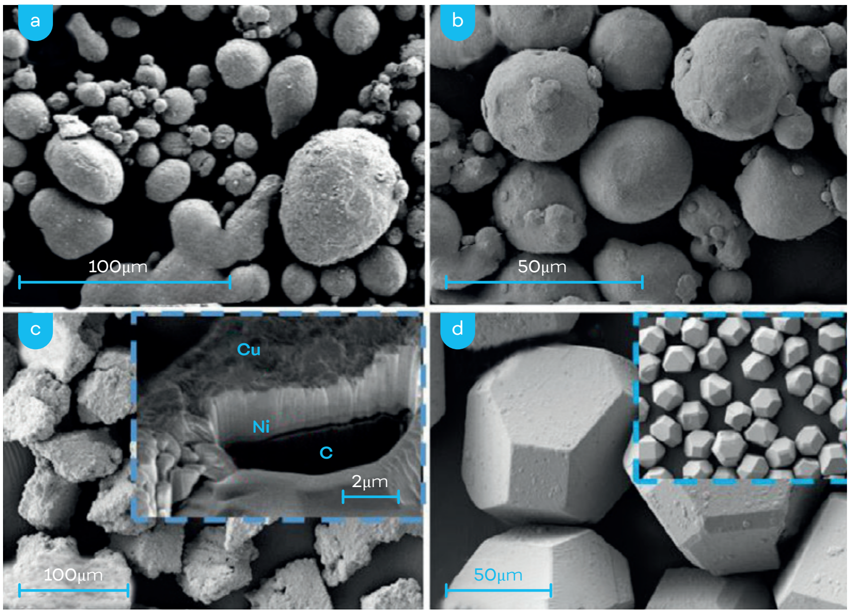


Fig 1. SEM images of powders (a) Aluminium (b) Copper (c) Copper cladded diamond with FIB section (d) Synthetic un-cladded diamond.

Also, recent work has suggested that if the diamond grit is copper cladded, CS processing is more efficient in maintaining the diamond fraction from the feedstock to the deposit [6].

Figure 1. therefore shows a SEM image of the relevant powder feedstock materials. Pure copper (-38+15 µm in size, > 99.9% purity, Safina, Czech Republic) and copper-clad diamond (-53+45 µm in size, PDA C50 grade, Element-Six, Ireland), and Commercially Pure Aluminium (-58 µm+15 µm in size, H-30 grade, >99.7% purity, Valimet Inc., California) were used in the experiments. Figure 1.(c) shows a Focused Ion Beam (FIB) section of the cladded material, revealing the thickness of the actual copper layer (2-4 µm) around the diamond particle; a thin layer of Ni is firstly used as bond coat.

The aluminium powder will be used as a seed layer for subsequent deposition as explained in section 3. Figure 1.(d) shows a SEM image of a synthetic diamond grade (Iljin Diamond, Korea) which is not cladded and uniform in size distribution. Whilst the work in [6] has shown the deposition behaviour will improve when using the cladded material, when referring to thermal characteristics the diamond in Figure 1.(d) is of higher purity, has a very uniform size distribution and will perform better.

The substrates (silicon wafers flat samples of 0.7mm thickness, measuring approximately 25x25mm in length and width) were used in two conditions. As delivered and without any post processing, and prepared with a grit blasting process in order to roughen the area and remove the oxide layers from the surface. The grit blasting process was carried out in a grit blasting apparatus at 0.9 MPa with Al_2O_3 grit and a mean diameter of 60 µm. Figure 2. shows the difference in surface preparation from silicon as delivered, and roughened. The corresponding surface roughness, S_a, was measured to be 0.016 µm and 4.19 µm using an omniscan microxam white light interferometer.

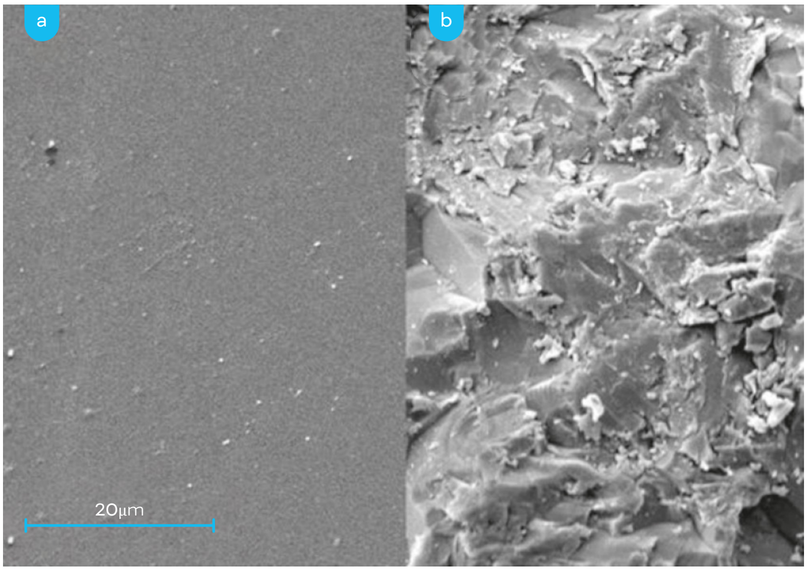


Fig. 2. (a) SEM surface image of a silicon wafer as received, (b) and after grit-blasting

2.2. Diamond composite coatings fabrication

A parametric study was therefore carried out. Copper and diamond clad powders were pre-mixed using a 50% volume ratio before being processed with CS, in the attempt to form a deposition layer onto the wafer substrate. Independently of the used spray parameters and wafer surface state (refer to Figure 2.), it was possible to identify two regimes. In the first one no deposition occurs, meaning all the particle bounce off the wafer substrate. In the second one, occurring when CS parameters are pushed to the upper limit and particle velocities upon impact are high, severe cracking of the wafer is predominant. It was not possible to identify a transition window whereby a coating would form without triggering severe wafer damage.

It is therefore concluded the impact energy necessary to achieve deposition with a mix of copper and diamond is above the cracking thresholds of a silicon wafer. This is certainly a plausible statement, considering the very brittle nature of the substrate. In order to overcome to this and avoid the substrate damage, a layered strategy was attempted in a second experiment: pure copper or aluminium would be deposited first, with the copper/diamond mix thereafter. The rationale of the idea is to use powder materials characterized by a lower critical speed for CS deposition as buffer layer, allowing for both silicon integrity and successful diamond coatings thereafter.

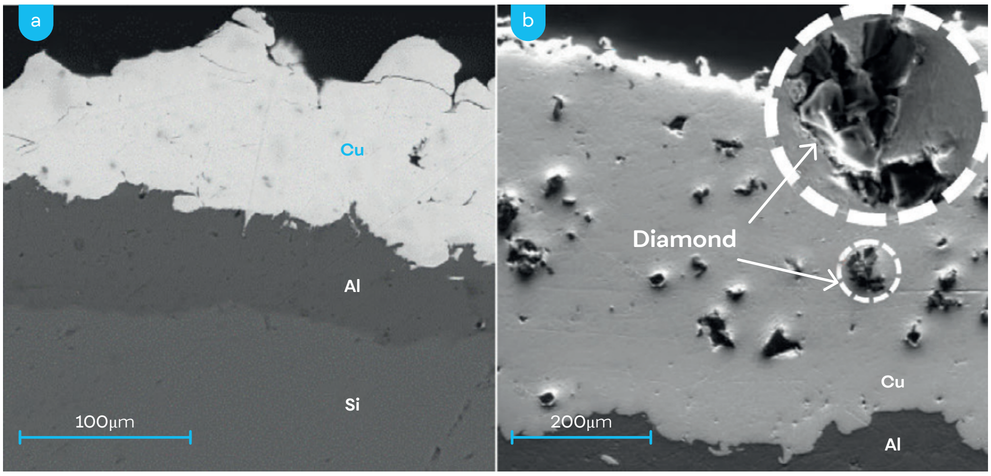


Fig. 3. Cross-section SEM images of (a) the silicon wafer after the initial cold spraying of an aluminium layer followed by a copper layer. (b) Section view of follow on deposition of diamond clad/copper mix.

Using pure copper as first interlayer with a smooth or roughened wafer resulted in good deposition levels but with very low bond strength; meaning the deposit would very easily peel off from the wafer surface. However, when using an aluminium seed layer, the above strategy was proved successful. Figure 3. shows a SEM image of a sample cross-section obtained with a nozzle pressure of 30bar, standoff distance of 40mm and transverse speed of 100mm/s. The full processing time was <1 minute, hence relatively fast.

Figure 3. shows an aluminium, copper and copper clad diamond layers of various thicknesses deposited onto a roughened Si wafer. Notably, successful deposition with aluminium layers of sub 50 µm are possible (Figure 3.(a)) Figure 3.(b) shows a zoom-in of a diamond particle, demonstrating very good wetting of the copper around it, hence without visible empty spaces. The porosity of the coating is low (<2% from an image analysis) in all sections, and the interfaces between materials are irregular (this is a typical finding in CS), however well consolidated and defined. The cross-section shows a diamond volume fraction in the coating certainly lower to the initial feedstock ratio. There is no doubt a portion of diamond grit bounced off the coating area during processing and did not embed into the matrix (despite the use of cladded diamond). Additionally, the size of the diamond particles in the coating is comparable to the original feedstock size range (refer to image in Figure 1.(c)), meaning no substantial diamond fracturing has occurred during processing.

In relation to the end scope of this work (the direct manufacturing of heat spreader onto wafers), having aluminium as interlayer may appear not to be ideal due to its TC of approximately half that of copper (~200 W/mK). However, that implies that a seed layer of 50 µm thickness (Figure 3.) will represent an equivalent thickness of copper of 100 µm; this is negligible for IHS of any significant thickness (>5mm). Thus, aluminium can be used as a seed layer allowing further building of the heat spreader with more preferential materials. Also, when TIMs are used thermal grease is typically employed as interlayer generating a much higher theoretical thermal resistance than aluminium. All considered, the author's choice would still represent a considerable improvement to the state of the art.

Figure 4. shows the roughness profile of the top surface of the coating, hence alongside the copper/diamond zone. This was measured using a white light interferometer, resulting in an Sa value of 8 µm.

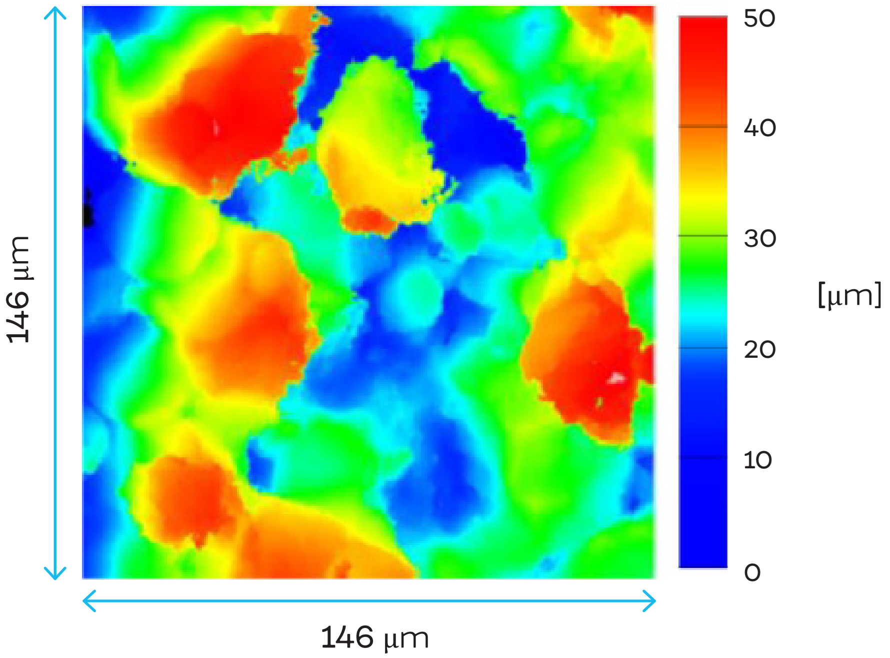


Fig. 4. Coating surface roughness.

3. The bonding mechanism

The deposition mechanism, based on the experimental evidence described above, is explained in Figure 5. and discussed by the following:

1. A smooth silicon surface will not allow bonding to occur efficiently. The particles (Cu or Al in the case of this wok) will impinge upon the surface, and because the surface is a relatively flat brittle material, deformation of the particle will occur but the particle will have no surface features to attach to or promote strong mechanical interlocking.
2. A roughened Si surface will allow thin layers of copper to be built; there are now features particles can possibly deform around upon impact. However, thick layers will delaminate and second passes will remove the initial layer. This is thought to be due to the formation of micro-cracks on the surface of the silicon as a consequence of the large kinetic energy associated with the momentum of the dense, hence relatively heavy, copper particles.
3. A roughened silicon surface will allow the building of (thin or thick) aluminium layers which are well bonded to the silicon. This layer can be successfully built upon with other materials such as copper, and copper diamond mixtures, potentially allowing a thermal heat spreader to be directly printed. At this stage it is possible to opt for a copper mix with cladded diamond, as used in Figure 3., to maximise deposition; or with the diamond in Figure 1.(d) to maximise thermal characteristics. The process mechanics will not change. The aluminium bonds well to the surface due to its lower density and hence lower kinetic energy on impact. This allows the deformation of the aluminium particles onto the Si surface features without the cracking of the rough substrate.

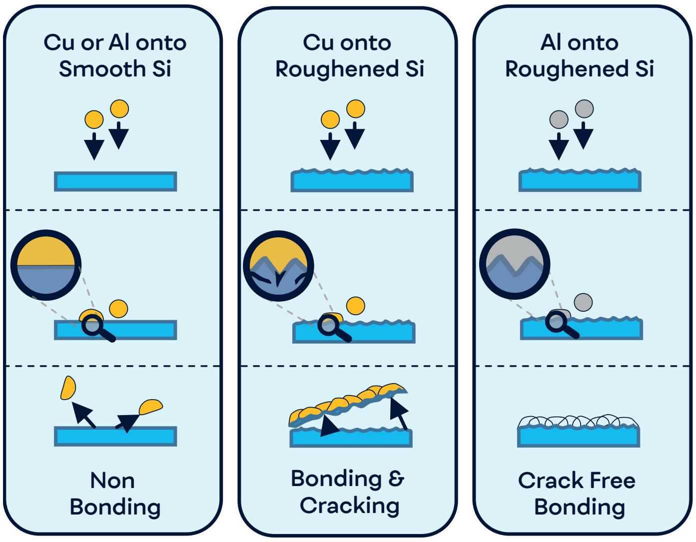


Fig. 5. Bonding mechanism illustration of copper and aluminium onto a smooth and roughened silicon wafer.

Since one of the main bonding mechanisms of CS is mechanical interlocking, bonding is difficult on a flat ceramic-like surface. With a metal-on-metal impact the powder will induce deformation on a flat substrate, i.e. the process is self-roughening once the particle velocity is sufficiently large. As there can be little to no plastic deformation on a brittle material, in this case the surface is in the need to be pre-roughened to initiate and facilitate the bonding process.

4. Heat transfer behaviour of the Cu/diamond composite

The critical characteristic for an IHS is the TC of the copper- diamond matrix as this section represents the largest thermal resistance. In order to measure the TC value, a separate diamond composite coating was manufactured using the same parameters as reported for Figure 3.
The coating was deposited onto a substrate, then removed from it and machined to form a block measuring 41 × 11.3 × 2.5 mm in dimensions. In this experiment the diamond shown in Figure 1.(d) was used, with a 30% pre-mix with copper. The TC of the copper-diamond composite was determined using the Fourier's law in Eq. (1).

$$q''=-TC(dt/dx) \tag{1}$$

A temperature gradient (dt/dx) is applied through a heat flux (q'') across the 41 mm long rectangular section of the block (so as to reproduce 1D flow) using a miniature cartridge heater and a liquid based heat sink. Temperature measurements were taken at points distant dx along the length of the section, which were used to calculate the actual temperature gradient and subsequent TC from Eq. (1).
For comparison purposes, the same experiment was repeated using a copper block manufactured with CS, but without the diamond inclusion. Figure 6. shows a summary of results. In the first place it is possible to use Maxwell's relationship [12], represented in Eq. (2), for a theoretical estimation of what TC should be measuring in a composite material:

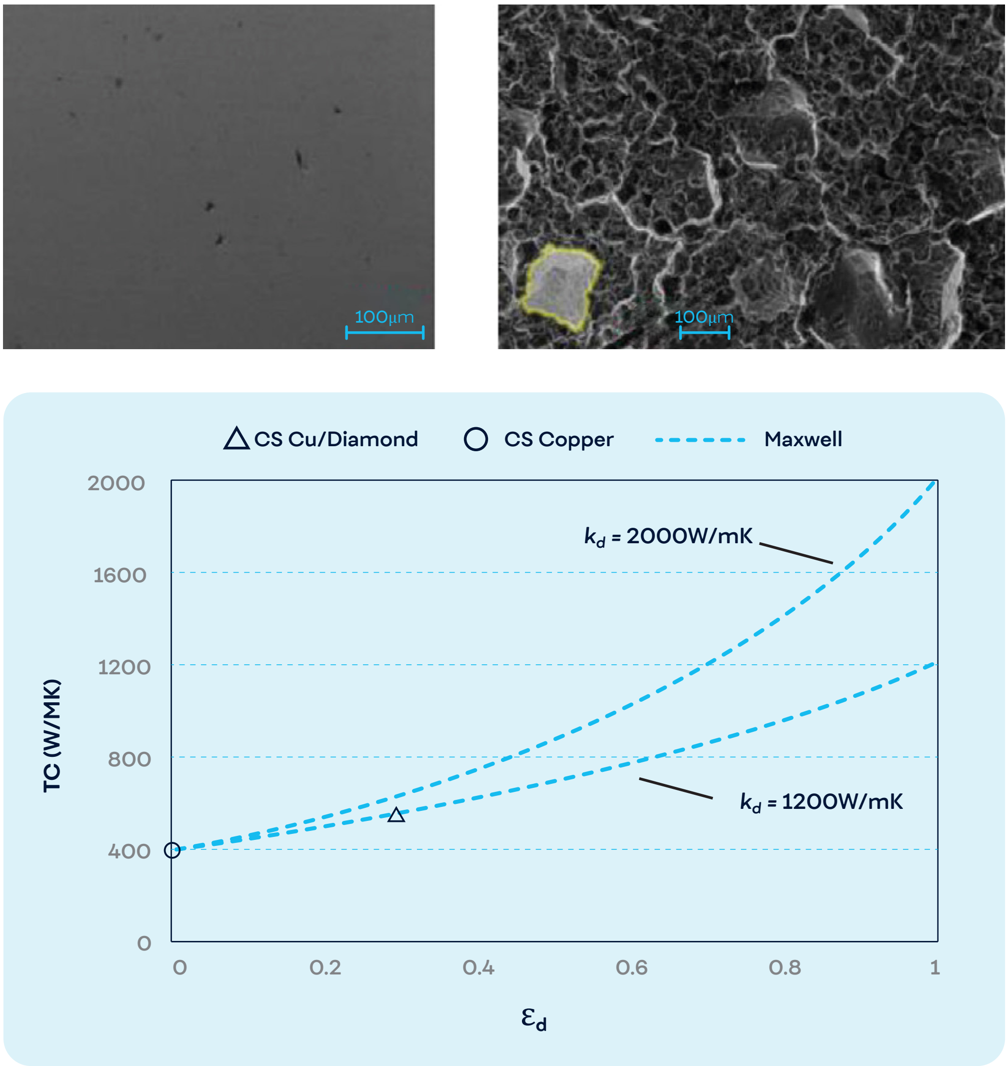
$$TC=k_m\left(2\left(\frac{k_d}{k_m}-1\right)\varepsilon_d+\frac{k_d}{k_m}+2\right)\left(\left(1-\frac{k_d}{k_m}\right)\varepsilon_d+\frac{k_d}{k_m}+2\right)^{-1} \tag{2}$$

where k_m is the conductivity of the matrix material, k_d is that of the dispersions and ε_d is the volume fraction of the dispersed phase, that is equal to zero for pure copper and to 1 for pure diamond. The k_d of synthetic diamond is in the 1200-2000 W/mK range, represented by the two Maxwell distributions in Figure 6. The figure also includes a surface image of the pure copper sample made with CS, and the diamond composite. From this image it is clearly possible to observe the diamond grit (one of them has been highlighted) well embedded within the matrix.

The thermal conductivity measurements not only verify that the diamond particles are present and participating positively with regard to thermal conductivity of the composite, but the close agreement with Maxwell's theory strongly suggests that the CS fabrication technique forms a composite with a low Cu-Diamond interfacial thermal barrier. In the first place, the TC of the copper CS sample was measured to be in the 400 W/mK region (experimental uncertainty determined by the Monte Carlo method). This is well in agreement with the TC of bulk copper, demonstrating the material is well consolidated and relatively pore-free; TC would be critically affected if that was not the case.

Most importantly, the incorporation of diamond has resulted in a higher TC level, 580 W/mK (10.5% error), approximately 33% more. In [12,13] it has been shown that interfacial thermal resistance can reduce the thermal conductivity to well below Maxwell's prediction for sintered Cu-Diamond; even to the extent that for moderate ε_d and small particle sizes (~20-30 µm) the composite material effective thermal conductivity is below that of Copper, by almost half. The cause for this phenomenon is poor wetting of diamond by the Cu-melt during sintering, which is not the case here.

Thus, from a materials fabrication standpoint this is a very exciting result in itself, before considering the fact that this has been fabricated using a 3D printing technique.


CS - Copper

CS - Copper/Diamond

Fig. 6. Surface SEM images of test samples and TC measurement for CS-Copper and CS-Copper/diamond (30% fraction), including Maxwell's relationship prediction for k_d = 1200 W/mK and k_d = 2000 W/mK.

5. Conclusions

The dissipation of unwanted heat is becoming of vital importance in the ICT industry. In this work the authors have demonstrated how to manufacture (3D print) structures with CS, directly onto Si-wafers, that are diamond based and will efficiently dissipate heat. The bonding mechanism onto the wafer can be categorized into 3 possible scenarios, providing novel and conclusive insights in the matter.

The Cu/diamond composite made with CS was separately tested in order to measure its TC, and results compared against Maxwell prediction. A 30% diamond ratio resulted in 33% increase in TC when compared to pure copper; this is in agreement with the theory. The presence of diamond within the matrix (with pore-free interfaces) has resulted in positive outcomes, that not always being the case for melt-driven processes. In conclusion, CS is a valid process to print spreaders directly on wafers, offering levels of materials flexibility, performance and scale up potential not yet seen in alternatives.

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