Abstract

This Thesis is about tuning three-dimensional graphene (3D-C) and three-dimensional hexagonal-boron nitride (3D-BN) into their hybrid 3D-BNC for various applications ranging from thermal management, to flexible electronics, space shielding and thermo-mechanical actuation in shape memory polymer (SMP). Through the ability to specifically control the compositions of C and BN, a highly tunable electrical conductivity (0 – 0.6 Scm^{-1}), controllable EMI shielding properties (0 – ~50 dB), while maintaining a high and stable thermal conductivity (0.84 – 1.2 $Wm^{-1}K^{-1}$) is obtained. The interconnected structure of these 3D porous, foam-like materials also prevents inhomogeneous distribution and aggregation commonly faced when using typical nanofillers in different matrices, which is why in this Thesis, they have been further developed in their bare state, as well as in conjunction with other matrices, such as polymers.

The advancement of semiconductor technology in the era of “more-than-Moore” has led to an increasing challenge in thermal management. Integrated circuits (ICs) are so densely packed that they heat up within milliseconds, resulting in an extreme increase of generated heat. In order to mitigate this problem, the two opposing extremes of foam, 3D-C and 3D-BN are used to cater for all types of application (electrically conducting, such as interconnects, and insulating, such as high voltage devices). Through compression of the foams, a high cross-plane thermal conductivity of 62 – 86 $Wm^{-1}K^{-1}$, as well as excellent surface conformity is demonstrated, which are characteristics essential for thermal management needs. These values of thermal conductivity are among the highest cross-plane conductivities of free-standing graphene or h-BN structures, and in the same range of eutectic metal foils. Evaluation of the thermal extraction efficiency on a state-of-the-art 2.5D electronic platform along with state-of-the-art thermal interface materials (TIMs) reveals 3D-foam’s improved performance of cooling by 20 – 30%, which means a temperature decrease by ΔT of 44 –

24°C. This is colder than any of the commercially available TIMs tested on the same platform (i.e. Sn/Au) and among the highest temperature decrease of hot spots on actual chips reported so far (e.g. highest values for alternative heat spreaders currently under research range around $\Delta T \sim 13°C$ for a CVD-graphene heat spreader and $\Delta T \sim 20°C$ for exfoliated few-layer graphene). This is a significant decrease, since it is known that the decrease of hot spot temperature on chips by 20°C extends the transistors lifetime by one order of magnitude.

One of the most pressing and difficult challenges faced in the field of flexible electronics deals with creating a base substrate that can support flexible devices and components. Many have considered polyimides (PIs) as the flexible platform for such applications; however, due to their poor thermal conductivity being orders of magnitude smaller than standard substrate materials of conventional electronics, a thermal control problem arises, which limits their use as flexible materials in electronics. By hybridizing 3D-C and 3D-BN with PI an improved thermal dissipation by 25-times (5 – 6 $Wm^{-1}K^{-1}$) is obtained, while preserving full flexibility and toughness of the PI. It is shown that these hybrid films can be directly used as printable substrates and can dissipate heat more efficiently from hot spots, which in turn allows increasing the maximum power applicable by at least 23%.

PIs have also been praised for their high temperature and UV stability and toughness, which currently makes them the standard choice for space shielding. However, their completely electrically insulating characteristics have caused other limitations, such as spacecraft electrostatic charging. Since the hybrid of 3D-C with PI has an electrical sheet resistance of 3 Ω/□, which fulfills the antistatic-criterion to dissipate the build-up of electrostatic charge, it is further developed for this application and space-qualified according to European Space Standards. It is shown that it withstands and keeps a stable performance throughout various thermal cycles (from -100°C to +160°C), as well as the oxidative and aggressive environment of ground-based simulated space environments (Gamma ray doses equivalent to 15 years in geosynchronous equatorial orbit, GEO, and atomic oxygen exposure equivalent to 8 months exposure in low Earth orbit, LEO).

Due to its easiness in shaping, ultra-light weight and customizability, SMPs have much potential in applications that require mechanical actuation, most commonly triggered by heat. However, the major drawback for SMP is its poor thermal conductivity, which often leads to a large thermal gradient across the material which results in non-uniform transformation of shapes and sometimes even results in cracks, due to the built up stress. To target this issue, 3D-BNC foams of varying concentrations are infused with SMPs. Thanks to the homogeneous distribution of the foam within the polymer, a uniform spread of heat is obtained, thus leading to an even transformation of shape. It is demonstrated that through this technique, bigger sample sizes are attainable (maximum sizes without 3D-foam infusion are 3 cm in length, while with the 3D-foam infusion up to 7 cm in length are demonstrated to transform without any cracking). It is shown that the 3D-foams speed up the transformation process by three times, reduce the required energy to initiate the transformation process by 20% and in addition, thanks to the tunability of electrical conductivity of 3D-BNC, a self-heating and timed actuation can be incorporated to the polymer.