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Boron Nitride Coated Three-Dimensional Graphene as an Electrically Insulating Electromagnetic Interference Shield

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Abstract — We demonstrate the potential of a novel hybrid nanostructure three-dimensional graphene (3D-C) coated with boron nitride (BN) as an electromagnetic interference (EMI) shield. BN, deposited by sputtering, encapsulates 3D-C to form a light-weight graphene based EM shield that has an electrically insulating exterior. The BN deposited on 3D-C was homogeneously distributed with even coverage on the struts of 3D-C. EMI shielding results have shown that the hybrid material has a total shielding effectiveness (SE_T) of 53dB and 58dB in the X band and Ku band respectively.

Keywords — three-dimensional graphene (3D-C), boron nitride (BN), hybrid material, electromagnetic interference (EMI) shielding.

I. INTRODUCTION

The demand to compact more electrical components within a miniaturised integrated circuit (IC) has been continuously increasing over the years. The densely packed ICs produce severe electromagnetic interference (EMI) which could potentially cause detriment or even failure to the device if they are not well shielded [1]. To reduce the EMI, EMI shields are added into ICs to reduce and eliminate the disruption caused by electromagnetic (EM) radiation. Current EMI shield solutions include the use of metals such as metallic coatings on plastics [2, 3] and metal walls [3, 4]. However, the use of metal brings about additional design considerations, such as the need to prevent the metals from corroding and oxidising. The use of metal solutions also undesirably increases in the size and weight of the IC.

Ever since the discovery of highly electrically conductive graphene [5] and carbon nanotubes (CNTs) [6], a lot of research has been done to design different forms of graphene to use them as EMI shields. Different forms of carbon, namely carbon black [7], graphene [8], CNTs [9] and three-dimensional graphene (3D-C) [10, 11] have been added to polymers as flexible, light-weight EMI shields as alternatives to heavy metal solution [12, 13]. However, these solutions are fully electrically conductive materials [14]. Components which are placed in contact with the carbon infused polymers could lead to components short

circuiting and hence device failure. This results in a limitation of reducing the space between electrical components in ICs.

3D-C is a material with high electrical conductivity [11]; while boron nitride (BN) is a compound which is highly electrically insulating [15, 16] and transparent to EM [17]. By coating an electrically conductive material with an electrically insulating material, not only will 3D-C be able to function as an EMI shield, electrical components can also be brought in contact with the EMI shield without having to be concerned about the circuit shorting, hence allowing ICs to have smaller footprints. In this paper, we present the potential to use BN coated 3D-C as an effective yet electrically insulating EMI shielding material for closely packed electrical components in ICs.

II. EXPERIMENT

A. Sample Preparation

3D-C was synthesized via thermal chemical vapor deposition (TCVD) [11]. The nickel template, which served as the catalytic template, was first annealed at 1000°C with argon and hydrogen flow before the carbon precursor, methane gas, is passed into the quartz tube. After growth of carbon onto the nickel template has been completed, the lid of the split-tube furnace is opened to air cool the system. The 3D-C coated nickel foam is then soaked in hydrochloric acid at 85°C to chemically etch the sacrificial nickel foam.

BN was then deposited onto the free-standing 3D-C with lanthanum hexaboride (LaB6) target as a precursor via a Hipster I pulsed power supply (Ionautics) combined with a high power impulse magnetron sputtering (HiPIMS) system (Mantis Deposition Ltd) [18]. The chamber was first evacuated to a low base pressure of 10^{-6} millibar before deposition. The deposition was then done on the grounded 3D-C foam by striking the LaB6 target at a pulse rate of 8kHz, pulse width of 20μs, pulse voltage of 330V, with a pulse intensity of 12A and an average power of 250W in an environment consisting of a gas ratio of 1:4 nitrogen: argon to reactively sputter the target.

The 3D-C and BN-coated 3D-C were drip-coated with polyvinylidene fluoride (PVDF) to retain the structure of the samples while being compressed between the waveguides. PVDF, an electrically insulating polymer, was synthesised via evaporating the solvent after complete dissolving in the solvent, N, N-dimethylformamide (DMF). The PVDF pellets were added to DMF and stirred at high speeds of 1200rpm at 60°C for 6 hours till the solution turned clear. Post dissolution of pelletised PVDF in DMF, the clear solution is then dripped onto the samples to coat them and heated at 135°C for 2 hours till all DMF has evaporated. The samples are then peeled from the glass piece. The clear solution was also separately dripped onto another glass piece and heated at 135°C for 2 hours till all DMF has evaporated [19]. The PVDF piece was then peeled from the glass piece to obtain a free-standing sheet.

B. Sample Characterisation

Scanning electron microscopy (SEM, JEOL JSM-IT100) was performed on 3D-C before and after deposition on BN to observe the materials' microstructure, followed by SEM/energy-dispersive X-ray spectroscopy (EDX, FEI Nova NanoLab™ 600 DualBeam, Oxford XMAX Detector) to analyse the materials' chemical composition and the dispersion of the La and BN particles on 3D-C.

C. Electrical Characterisation

With the aid of the Van-der-Pauw's method, the direct-current (DC) resistivities of the samples were measured with the use of a 4-point probe (Karl SUSS200 Micro-Prober).

D. EMI Shielding Effectiveness

The scattering parameters, S11 and S21 in the X-band (8.2-12.4GHz) and Ku band (12.4-18GHz) were measured with the use of 2 separate sets of waveguides connected to a Fieldfox handheld microwave analyser (Keysight N9917A). The microwave analyser was first calibrated using the Thru-Reflect-Line method at the corresponding frequency bands. After calibration, the samples were sandwiched between the cavities of the waveguides and the measurements were taken.

After obtaining the scattering parameters, the reflected power (R) and transmitted power (T) can be obtained using the equations (1) and (2) respectively [7].

$$R = |S_{11}|^2 \quad (1)$$

$$T = |S_{21}|^2 \quad (2)$$

The reflection loss (SE_R), absorption loss (SE_A) and total EMI shielding effectiveness (SE_T) can be calculated using equations (3), (4) and (5) respectively. [5].

$$SE_R = 10\log\left(\frac{1}{1-R}\right) \quad (3)$$

$$SE_A = 10\log\left(\frac{1-R}{T}\right) \quad (4)$$

$$SE_T = SE_R + SE_A \quad (5)$$

III. RESULTS & DISCUSSION

A. Sample Characterisation

Figure 1 shows SEM micrographs of 3D-C before and after BN deposition. Comparing Figures 1a and 1b, the coating of BN onto 3D-C did not result in any visible changes. Further analysis on a strut of BN coated 3D-C as circled in red in Figure 1b using SEM-EDX mapping shows that 3D-C has been homogeneously coated with BN, as seen in Figure 2.

Fig. 1. Morphologies of 3D-C and 3D-C coated with BN. a. SEM micrograph of 3D-C before BN deposition; b. SEM micrograph of BN coated 3D-C.

Fig. 2. SEM-EDX mapping of a strut of BN coated 3D-C.

B. Electrical Characterisation

To determine if the samples of 2mm thickness had an electrically insulating exterior and an electrically conductive interior, the samples were probed at 2 different depths: the surface of the sample, to determine if the sample has an electrically insulating exterior, as well as at a depth of 1mm from the surface of the sample, to determine if the sample had an electrically conductive interior. The obtained values were tabulated in Table 1.

Table 1. DC resistivities of samples at the surface and 1mm below the surface.

Sample	Height from surface of sample (mm)	DC Resistivity ($\Omega/\square$)
BN coated 3D-C	0	Beyond equipment range
BN coated 3D-C	1	0.45-5.83
3D-C	0	0.24-5.20
3D-C	1	0.23-4.82

Due to the low amount of electrically conductive La deposited on the surface of 3D-C (5 at%), the La particles are not connected and have electrically insulating BN particles in between them, resulting in an electrically insulating coating on 3D-C. As a result, at the surface of the sample, the high DC resistivity of the electrically insulating coating prevents a current from passing from the probes through the sample to obtain a resistivity value. However, once the probes have penetrated the electrically insulating coating, the probe was able to obtain a low value of resistivity, similar to that of 3D-C [17]. This shows that the interior of the sample still consists of highly electrically conductive 3D-C and that the electrical properties of 3D-C remain unchanged.

C. EMI Shielding Effectiveness

After 3D-C and BN coated 3D-C have been obtained, the samples are drip-coated with PVDF to ensure that the samples

of the samples while they were compressed between the waveguides. 2 different sets of waveguides were used for the X band and Ku band. Figure 3 shows the SE_T of 3D-C coated with PVDF, BN coated 3D-C coated with PVDF and electrically insulating PVDF polymer.

Fig. 3. SE_T of PVDF coated 3D-C, BN coated 3D-C coated with PVDF and PVDF polymer across the X band and Ku band.

A discontinuity was observed at the frequency linking the X band and Ku band as a different set of waveguides was used to measure the SE_T of the samples at the different frequency bands.

BN coated 3D-C has a SE_T of 53dB and 58dB in the X band and Ku band respectively, which is lower than the SE_T values of 3D-C of 68-71dB in the X and Ku bands. The 18-25% decrease in the SE_T is expected due to the presence of electrically insulating BN reducing the EMI shielding properties of the material. Nevertheless, substantial EMI shielding is provided by the electrically conductive interior of the material, as compared to an electrically insulating material such as PVDF, which has a SE_T of 0.01-0.05dB in the X band and Ku band. This is due to PVDF's electrically insulating nature, rendering it transparent to EM and would not be able to function as an EMI shield [17].

IV. CONCLUSION

3D-C was coated with BN via HiPIMS. SEM has shown that the BN layer does not result in a visible change in 3D-C. SEM-EDX analysis showed that BN and La are evenly distributed on the 3D-C struts. The results from van-der-Pauw's testing of the samples at its surface and probed into the samples showed the samples' electrically insulating exterior and electrically conductive interior. SE_T of BN coated 3D-C coated with PVDF is 53dB and 58dB at the X and Ku band respectively, which is comparable with the SE_T demonstrated by 3D-C coated with PVDF, CNTs [9] and graphene [12]. The properties of the BN coated 3D-C hence allow it to function as an electrically insulating EMI shield.

These results suggest that a novel hybrid material which is not only capable of functioning as an EMI shield, but also as an electrically insulating wall has been discovered.

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