Supplementary Material of

Enhanced Bonding Performance Between Vertical-aligned Carbon Fiber Thermal Interface Materials and Heat spreader through Silane Coupling Agent Insertion for FCBGA package

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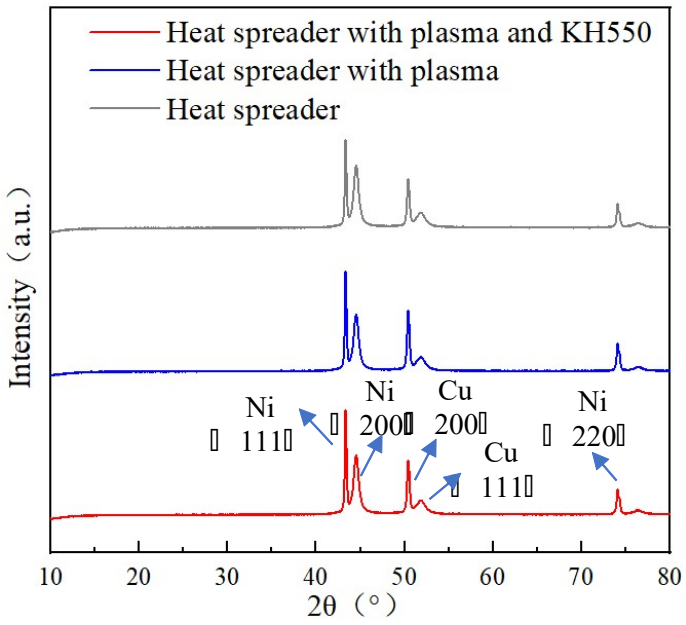

Fig. S1 XRD spectra of heat spreader.

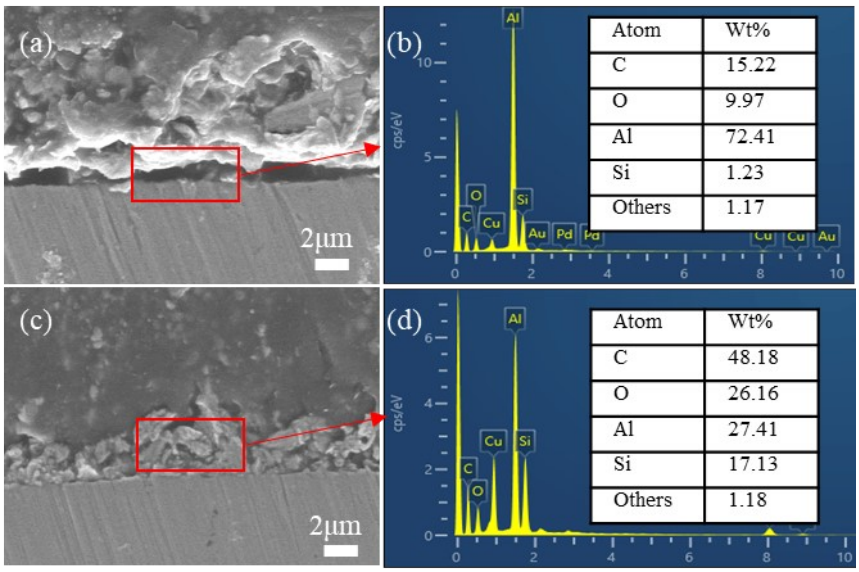

Fig. S2 SEM images and EDS spectra of the TIM/HS interface: a-b) correspond to samples without KH550 grafting, while c-d) correspond to samples with KH550 grafting.

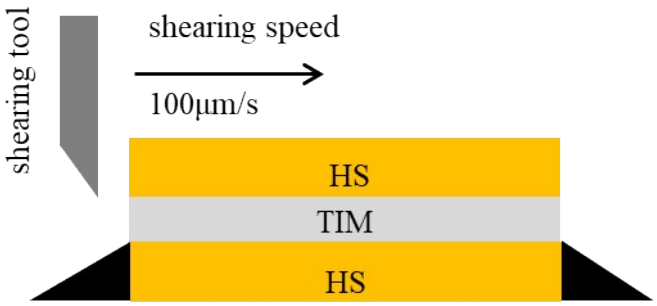

Fig. S3 Schematic of bonding strength test.

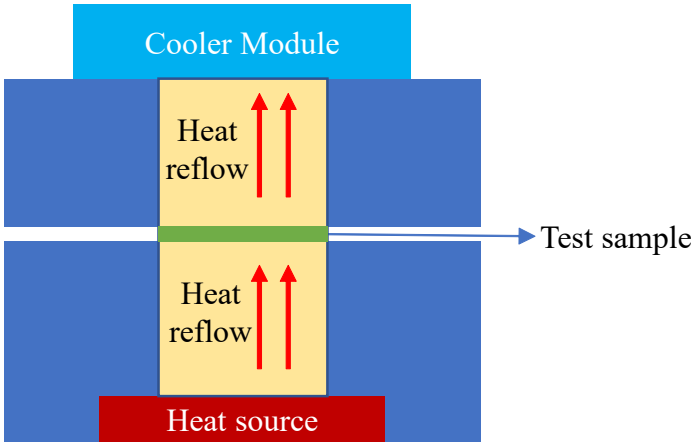

Fig. S4 Schematic of thermal test.

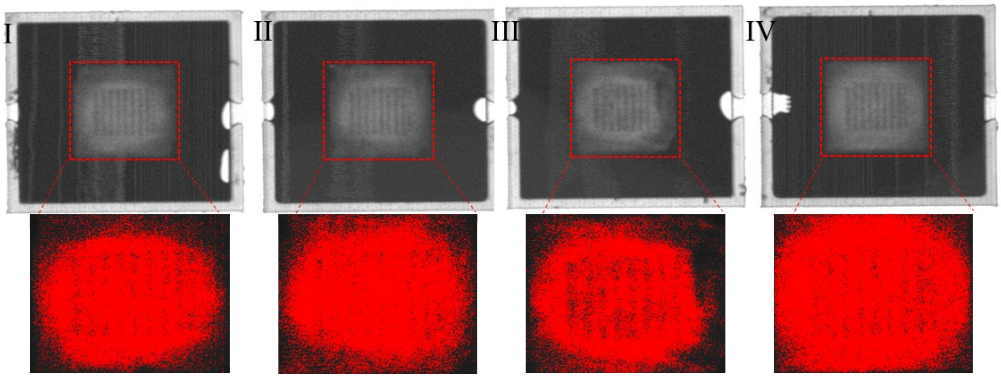

Fig. S5 T-scan and stained images of FCBGA packaging, I and II represent unmodified and 20%KH550 modified samples at a pressure of 0.1MPa, and III and IV represent unmodified and 20%KH550 modified samples at a pressure of 0.3MPa.

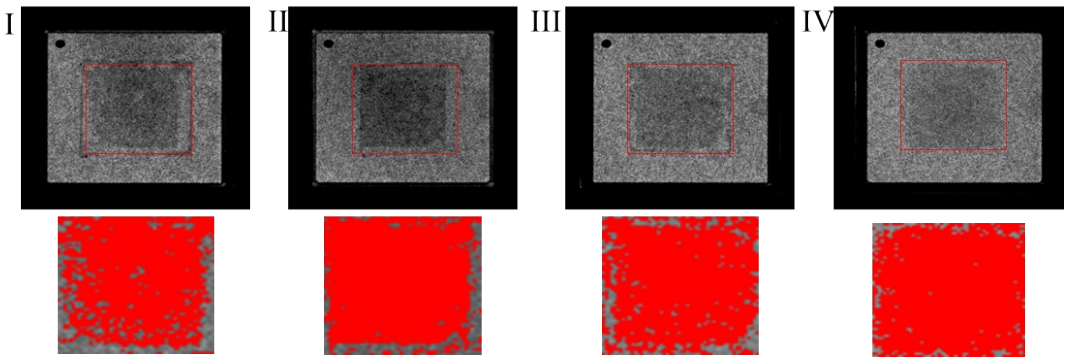

Fig. S6 C-scan and stained images of FCBGA packaging, I and II represent unmodified and 20%KH550 modified samples at a pressure of 0.1MPa, and III and IV represent unmodified and 20%KH550 modified samples at a pressure of 0.3MPa.

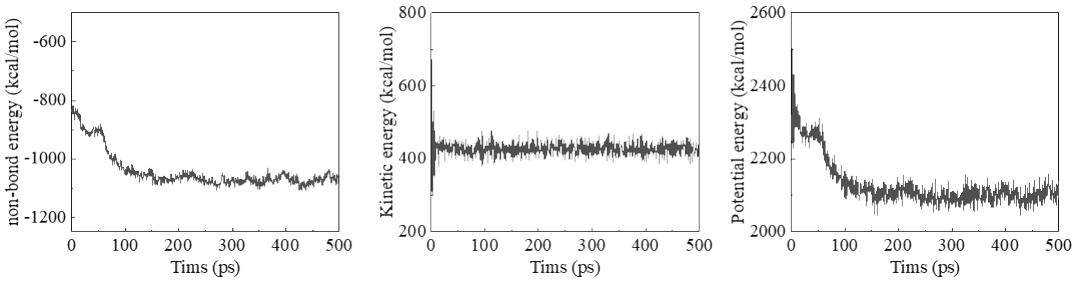

Fig. S7 Energy variation curves during molecular dynamics from 0 to 500 ps. a) Potential energy variation curve; b) Mechanical energy variation curve; c) Non-bonded energy (van der Waals and electrostatic energies) variation curve.

Bonding Strength Test Details:

In the bonding strength test, the sample was securely mounted at the center of the fixture to prevent any potential movement or vibration. The shear tester was then employed to apply a controlled force through the heat spreader (HS) at the upper extremity of the sample at a constant displacement rate of 100 μm/s, as illustrated in Fig. S3. Upon complete delamination of the sample, indicated by a shear force reduction to zero, the maximum stress recorded during the test is designated as the shear fracture stress. The shear strength is subsequently calculated by dividing the shear fracture stress by the effective shear area of the sample.

Thermal Test Details:

The lamination pressure and time for the thermal properties test samples were 0.3 MPa and 24 hours, respectively. The thermal resistance values include the TIM thermal resistance (R_{TIM}), the thermal resistance of the sandwich sample (R_{sample}), and the baseline thermal resistance (R_{basic}), which are all directly measured values. The data for R_{sample}, R_{tim} and R_{basic} were obtained by testing the pure TIM and pure HS using a steady-state thermal conductivity instrument.

As shown in Fig. S4, the test sample is placed in the center of the steady-state thermal conductivity instrument. To account for thermal contact resistance between the sample and the instrument, a silicone-based thermal grease was applied at all interfaces. The heat source applies a constant heat flux upward, and two temperature sensors is used to measure the temperature at both sides of the test sample. When the heat flux reaches a steady state (the temperature does not change with time), the temperature and heat flux at this time are recorded, and the overall thermal resistance of the sample is calculated using Fourier's law as follows:

$$R=(\Delta T)/(q\cdot A)$$

where $\triangle$T is the temperature difference between the two sides of sample, R is the thermal resistance, q is the heat flux, A is the contact area.

The interface thermal resistance (R_c) and the junction-to-shell thermal resistance

(θ_{Jc}) are calculated values. The formula used to calculate the interface thermal resistance is as follows:

$$R_c=R_{sample}-R_{TIM}-R_{basic}$$

The calculation formula for the junction-to-case thermal resistance θ_{Jc} is as follows, where the contact area S is 400 mm^2

$$\theta_{Jc}=R_{sample}/S$$

The packaging process of TIM in FCBGA:

The heat spreader was bonded to the TIM using a process involving plasma treatment, impregnation, and lamination. Unlike the bonding method for the Lid/TIM/Lid sandwich sample mentioned in the article, this process included covering one side of the TIM with a release film during lamination. After lamination, the release film was carefully removed to prevent damage to the TIM.

Next, the heat spreader with the attached TIM was interconnected with the chip through the Lid-attach process. This step utilized FCBGA Lid Attach equipment manufactured by Taiwan Hon Teng Technology Co., Ltd. First, adhesive was applied in a circular pattern around the substrate containing the chip via a dispensing process, using 200 mg of adhesive. The heat spreader with TIM was then attached to the substrate using the equipment's suction nozzle.

Subsequently, a pressure of 0.1 MPa was applied to the FCBGA at 150°C for 300 seconds to achieve adhesive pre-curing. The assembly was then placed in an oven at 150°C for 24 hours to complete adhesive curing. Finally, the packaged FCBGA product underwent a reflow process in a reflow oven, with a peak reflow temperature of 245°C. The reflow temperature are based on J-STD-020F in JEDEC.

Stained images of SAT and calculation of coverage:

As shown in Fig. S5 and Fig. S6, the red areas represent the intact interface coverage, while the black areas indicate delamination. The coverage is the area of the red area divided by the sum of the red and black areas.

Details of model construction and molecular dynamics:

The model construction steps are as follows:

1. Construct TIM interface: Create PDMS monomer molecules, designating the hydrogen atom adjacent to silicon as the head atom and the hydrogen atom connected to oxygen as the tail atom. Construct a homopolymer model with a chain length of 10 repeating units and a cross-linking degree of 3 repeating units.
2. Construct KH550 interface: Draw hydrolyzed KH550 monomer molecules and utilize the Amorphous Cell module to construct an amorphous KH550 model, setting the density to 1 g/cm^3 and the dimensions to 10 x 10 x 10 Å. This configuration results in 20 KH550 molecules.
3. Construct HS interface: Import NiO crystals from the Biovia database and use the supercell feature to build a crystal model of dimensions 10 x 10 x 10 Å. To facilitate subsequent calculations, retain only three molecular layers at the interface.
4. Construct three-layer interface modeling: Perform surface cleavage treatment on the

three interfaces, ensuring that all crystal planes are (1 0 0) planes. Utilize the build layer feature to stack the TIM, KH550, and HS layers, creating a sandwich structure with an interlayer spacing of 20 Å.

After constructing the model, the Forcite module of molecular dynamics is employed, divided into three steps:

1. Geometry Optimization: To relax the structure and minimize the system's energy for subsequent calculations, first optimize the system's structure using the Geometry Optimization module. The COMPASSII force field is applied, with a maximum of 50,000 iterations.
2. Molecular Dynamics Calculations: Use the Dynamics module to conduct molecular dynamics simulations on the optimized system. To accurately observe the motion trajectories of KH550 molecules, constrain (fix Cartesian coordinates) the TIM and HS layers before the calculation. Maintain constant volume and temperature (NVT) during the simulation, setting the temperature to 298.0 K. The total simulation time is 500 ps, with a timestep of 1.0 fs, and the COMPASSII force field is used.
3. Energy Calculations: After completing the molecular dynamics run, extract the last frame from the system's stable state and use the Energy module to calculate the various energy components. Subsequently, compute the energies of the TIM layer, HS layer, and KH550 layer. The final interface adsorption energy is calculated as follows

$$E_{int}=E_{system}-E_{tim}-E_{NiO}-E_{KH550}$$

Where E_{int} represents the interface adsorption energy, E_{system} is the total energy of the system, E_{tim} is the energy of the TIM layer, E_{NiO} is the energy of the HS layer, and E_{KH550} is the energy of the KH550 layer.

As illustrated in Fig. S7, all energy values stabilize after 200 ps, indicating that the total simulation time of 500 ps is adequate for the analysis.