Thermal Conductance of Epoxy/Alumina Interfaces

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Abstract. The interfacial thermal conductance (ITC) between filler and polymer matrix is considered as one of the important factors that limits the thermal conductivity of thermally conductive polymer composites. The effect of two different surface treatments (piranha solution and plasma) on ITC of epoxy/alumina was investigated using Time-domain thermoreflectance method (TDTR). The TDTR results show that compared with non-treated samples, the ITC of samples treated by piranha solution and plasma increased 2.9 times and 3.4 times, respectively. This study provides guidance for improving the thermal conductivity of thermally conductive polymer composites.

1. Introduction
In order to meet the increasing demand for high performance and convenience of electronic devices, the development of electronic devices begin to develop towards integration and miniaturization, which not only bring challenges in design and manufacture, but also put forward high requirements for the heat dissipation performance of electronic devices. Thus, the thermal management of electronics is receiving more and more attention [1-6]. Compared with traditional thermally conductive materials, polymer composites have the advantages of light weight, excellent dielectric properties, ease process and low cost[7,8], which can make up for the shortcomings of traditional thermally conductive materials (such as, metals and ceramics) in some fields. Especially in the application of electronic packaging, thermally conductive polymer materials play an important role. However, to date, the thermal conductivity of polymer composites cannot be effectively improved [9]. Strong interfacial phonon scattering has been commonly considered as the biggest bottleneck limiting the thermal transport in composites [10].

To improve the low efficiency of heat transfer between the interfaces of polymers/fillers, experimental and simulation works have been carried out on the ITC of organic/inorganic. For instance, Sun et al.[11] found that the ITC between gold and paraffin wax can be increased by functioning gold with self-assembled monolayers (SAMs) with different carbon chain lengths because SAMs act as a “bridge” to improve the vibrational densities match of gold and paraffin. Liu et al.[12] reported the ITC of atactic polystyrene (aPS) film and Si can be increased two times when the thickness of aPS film is less than or equal to the rotation radius of aPS body material. For simulation works, molecular dynamics (MD) simulation investigated the effects of various surface modification methods on ITC in epoxy/graphene composites, including covalent, non-covalent functionalization, isotope doping and acetylene linkage, the simulation result shows that acetylene linkage, the covalent and noncovalent functionalization techniques could considerably increase the ITC, and the ITC is insensitive to the
carbon isotope doping in graphene [13]. By using the same method, Zhang et al. [9] found that the ITC of graphene and the matrix of poly(methyl methacrylate) (PMMA) can be significantly improved by decorating the interface with SAMs under high coverage density. Fan et al. [14] found the ITC between functionalized gold (Au) and pentacene can be significantly improved because phonon vibration coupling and stronger interfacial interaction by non-equilibrium molecular dynamics method (NEMD). So far, there are few studies on manipulating the ITC of epoxy/inorganic filler through experiments. However, understanding the heat transport mechanism of epoxy/inorganic interface is of great significance to guide the manufacture of conductive composites with improved thermal conductivity.

In this work, we studied the relationship between the ITC of epoxy/alumina interfaces and the surface treatments of alumina. Our study shows that the ITC is significantly improved after alumina being treated by using piranha solution and plasma, which primarily attribute to the hydrophilic groups forming chemical bond between epoxy and alumina, and thus weakening the phonon scattering at the interface.

2. Experiment

2.1 Material
Alumina (0001) wafers (1 cm × 1 cm × 400 μm) with a root square roughness (Rq) ≤0.4 nm) were purchased from Hefei Kejing Materials Technology CO., LTD. The Epoxy resin (E20: epoxy value (eq/100g) 0.18~0.23) was purchased from Sinopec Baling Petrochemical Co. LTD. Tris(dimethylaminomethyl)phenol and Tetrahydromethylphthalic anhydride were purchased from Shanghai Liyi Technology Development Co., LTD.

2.2. Sample Preparation
First, the alumina wafers were cleaned by ultrasonication for 10 min in acetone, ethanol, and high-purity Milli-Q water in sequence. Afterwards, the wafers were dried by N2 flow. Some of them were immersed into the piranha solution (7H2SO4/3H2O2 by volume) at 90 °C for 1 hour to remove organic contamination on the surface. The rest of them were put into plasma generator for a 5 min (200W).

Second, E20 was dissolved in anisol to prepare a solution with a mass fraction of 4 wt%, Tetrahydromethylphthalic anhydride and Tris(dimethylaminomethyl)phenol were added into E20 solution in a mass ratio of 100:40:0.2. Epoxy nano films were prepared by spin-coating epoxy solution on alumina wafers with a typical rotation speed of 2000 rpm for 1 min and then were cured at 80 °C for 12 hours and 120 °C for 6 hours. Finally, 100 nm aluminum film was deposited onto the epoxy film as a transducer layer for TDTR.

To manipulate the ITC between epoxy and alumina, a series of Al/epoxy/Al2O3 sandwich samples were prepared. Figure 1 schematically shows the sample preparation process.

Figure 1 Schematic of sample preparation for interfacial thermal measurement
Table 1 The thickness of epoxy interlayer

|                        | Non-treated | Plasma   | Piranha solution |
|------------------------|-------------|----------|------------------|
| epoxy interlayer       | 134.2nm     | 136.1nm  | 136.3nm          |

2.3 Characterization

Water Contact Angle Measurement. The OCA25 contact angle system (DataPhysics Instruments GmbH, Germany) was used to record the contact angles. The static water droplet was recorded by the digital camera and analyzed with the software provided by CmbH for sessile contact angle information.

Thickness Measurement. The thickness of epoxy films was measured by a spectroscopic ellipsometer (M-2000V, J. A. Woollam). The incidence angle was set at 70°, and the wavelength scan was fixed at a range from 370.1 to 999.1 nm.

3. ITC measurement

ITC of the samples was measured by Time-domain thermoreflectance (TDTR) method. TDTR is a powerful, general-purpose tool and widely utilized in measuring the thermal transport properties of materials. Due to its high time resolution and relatively small thermal penetration depth, TDTR is quite suitable for interfacial thermal transport measurement. Thermal property determination by TDTR is typically accomplished by adjusting free parameters in a thermal model to minimize the difference between the predicted and measured thermal response of the sample. In our samples, the thermal model involves the thicknesses, the thermal conductivities and the volumetric heat capacities of the aluminum transducer, the epoxy interlayer and the alumina substrate, and the interfacial thermal conductance between them. All the other parameters except the epoxy/alumina interface must be determined first. Table 2 shows the value of all the other parameters and the data source, the thermal conductivity of epoxy and alumina were measured by TDTR with other reference samples.

Table 2 The properties of the samples

|                        | Thickness | Thermal conductivity | Heat capacities |
|------------------------|-----------|----------------------|-----------------|
|                        | nm        | W/(m·K)              | J/(cm³·K)       |
| Al transducer          | 100       | 237                  | 2.42            |
|                        | (ellipsometry) |              | Ref. [15]       |
| Epoxy interlayer       | See table 1| 0.19                 | 1.38            |
|                        | (ellipsometry) | (TDTR measurement) | Ref. [15]       |
| Al₂O₃ substrate        | Semi-infinite | 39                  | 3.03            |
|                        | (TDTR measurement) |              | Ref. [15]       |

Figure 2 shows one of the TDTR phase signal and the best fit curve. Figure 2 also shows the calculated curves with interfacial thermal conductance changed by 20% to demonstrate the sensitivity of the signal.
Since the properties of the samples are the same except the thicknesses of epoxy interlayers, the error of those properties will not influence the trend we observed. The thicknesses of epoxy interlayers are measured by ellipsometry, and the accuracy of the equipment used is less than 1 nm. Based on this accuracy, the error of the ITC we obtained from TDTR measurement is about 10%.

4. Results and Discussion

Figure 3 shows the contact angle of alumina surface after different treatment method and the ITC of the epoxy/alumina interfaces measured by TDTR experiment. The contact angle on the alumina surface without any treatment is 55°, while after plasma treating for 5 min and piranha solution treating for 60 min, the contact angle dropped to less than 10°.

The ITC of non-treated epoxy/alumina interface is about 8 MW/m²·K, while the ITCs of plasma and piranha solution treated interfaces are about 23 and 27 MW/m²·K. The wettability result means both treatments will significantly increase the force between alumina and epoxy, thus reduce the phonon scattering at the interface and increase and interfacial thermal conductance.

5. Conclusion

This paper presents an approach to enhance the ITC of epoxy/alumina. After piranha solution and plasma treatment, the ITC increased from 8 MW/m²·K to 27 MW/m²·K and 23 MW/m²·K, respectively, mainly due to the presence of hydroxyl groups that enhance the interfacial adhesion force between alumina and epoxy. This research provides a strategy for improving the thermal conductivity of other polymer/inorganic composites.
Acknowledgments
This work was supported by Science and Technology Project of State Grid Corporation of China (5500-202058317A-0-0-00).

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