Materials Letters 293 (2021) 129710

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Plasma-enhanced Si-SiC low-temperature bonding based on graphene composite slurry interlayer

Ximing Ye [a], Jiankun Wan [a], Xiang Yin [a], Wenhua Yang [a,b,*], Chao Xie [a], Chunyan Wu [a], Li Wang [a], Linbao Luo [a,*]

[a] School of Electronic Science and Applied Physics, Hefei University of Technology, Hefei 230009, China
[b] School of Electronic and Information Engineering, Anhui University, Hefei 230601, China

ARTICLE INFO

Article history:
Received 23 December 2020
Received in revised form 10 February 2021
Accepted 11 March 2021
Available online 18 March 2021

Keywords:
Graphene composite slurry
Low-temperature bonding
Sintering
Surfaces
Plasma treatment

ABSTRACT

Recently, silicon carbide (SiC) has replaced silicon (Si) as a potential material for next-generation power devices. In this study, a Si-SiC low-temperature bonding method based on graphene composite slurry as an interlayer was developed. Ar plasma was used to treat the surfaces of Si and SiC to improve surface hydrophilicity for higher strength bonding. With the increase of discharge power, the root-mean - square (RMS) surface roughness of Si and SiC has obviously increased and the bonding quality was also greatly improved. For 70 W discharge power, the RMS surface roughness values of Si and SiC were 3.22 nm and 1.67 nm respectively, and the bonding strength reached approximately 10 MPa. Through SEM interface analysis, it can be found that a seamless bonding interface was obtained using this bonding process.

1. Introduction

Silicon carbide (SiC) has been emerging as a material to solve silicon limitations in many applications due to its excellent band gap, high breakdown electric field, high thermal stability, and high chemical inertness [1,2]. It has been reported that the combination of SiC with Si can greatly improve the limiting power and the operating temperatures of Si-based devices [3]. However, the fabrication of SiC on traditional Si-based materials is still a huge challenge on account of the lattice mismatch between Si and SiC. Although Si/SiC bonding strategies such as surface activation bonding, vacuum ultraviolet surface radiation bonding, hydrogen–oxygen catalytic bonding have appeared in recent years, these strategies have their own disadvantages such as high bonding temperature, high cost, and complex process [4–6]. As a result, it is urgent to find a new bonding method with low temperature, low cost and simple process.

Graphene is considered a revolutionary material known to have excellent optical, electrical, thermal conductivity and mechanical properties [7,8]. Takenori Naito et al. used a wafer bonding method to prepare a Si-graphene-Si planar double heterostructure, but the interfacial bonding strength is only about 30 KPa, and the graphene film need to be transferred during the bonding process, which is difficult for mass-production and applications [9]. Graphene composite slurry made of graphene nano-powders is widely used as a conductive agent for lithium ion batteries because of good thermal and electrical conductivity [10]. Here, a facile Si-SiC bonding method using graphene composite slurry as an interlayer was proposed at low temperature. Thanks to excellent thermal conductivity and good electrical conductivity of graphene slurry, it may be applied for heat-spreader in power management integrated circuits (PMIC) [11] or as a potential conductive material for carbon-based device or ICs [12]. In this study, the morphological features, thermal and electrical conductivity of graphene composite slurry were analyzed. The effect of different discharge powers of plasma for surface treatment on the mechanical properties and the bonding interface were investigated. Additionally, the fracture positions of many bonded samples were observed after the shear test, and the reason of the fracture has been analyzed.

2. Experimental section

The single-side polished Si chips (10 mm × 10 mm) and double-side polished 4H-SiC chips (6 mm × 6 mm) were used in the experiments. Graphene composite slurry was prepared by mixing graphene powder (1%), polyvinylidene fluoride (PVDF, 1%), N-methylpyrrolidone (NMP, 95%), conductive carbon black (2%) and

---

* Corresponding authors at: School of Electronic Science and Applied Physics, Hefei University of Technology, Hefei 230009, China.

E-mail addresses: yang.wenhua@hfut.edu.cn (W. Yang), luolb@hfut.edu.cn (L. Luo).

https://doi.org/10.1016/j.matlet.2021.129710

dispersant (PVP, 1%). The bonding process is shown as follows. First, Ar plasma was used to treat the surfaces of Si and SiC chips, which can remove contaminants on the chip surfaces and lead to rougher and hydrophilic surfaces. Then, graphene composite slurry films ($\simeq$ 20 μm thickness) were spin-coated on the surfaces of Si and SiC by spin-coater (EZ4 SPIN COATER) at low speed (800 rad/s), respectively. Next, two pieces of chips to be bonded were put into the chamber of the thermo-compression bonding machine for low temperature sintering. Finally, an external pressure of $\simeq$ 600 N was applied to the two substrates at 200 °C for 30 min during bonding.

3. Results and discussion

The morphologies, thermal conductivity and the resistivity of graphene composite slurry film formed at different sintering temperatures (125 °C, 150 °C, 175 °C, and 200 °C) were studied, shown in Fig. 1. For lower sintering temperature, the film structure of the graphene composite slurry is loose and there are relatively large holes, as shown in Fig. 1(a), which is caused by the fact that a large amount of organic solvents in the film have not been volatilized. As the sintering temperature increases from 125 °C to 200 °C, the solvent begins to volatilize gradually, and the holes in the film structure of the graphene composite slurry become smaller and smaller. Therefore, a relatively dense graphene composite slurry film was formed at 200 °C. Moreover, the tightness of the graphene slurry film structure has greatly influence on the thermal conductivity and resistivity. Fig. 1(b) shows the thermal conductivity and resistivity of graphene slurry at different sintering temperatures measured by four probe tester (Keithley 4200-SCS) and thermal conductivity tester (LFA 467). It can be seen that as the sintering temperature increases to 200 °C, the resistivity of the film decreases to 0.05 Ω.m, and the thermal conductivity increases to 118 W/m.K, which is higher than that of SiC (83.6 W/m.K).

To improve bonding quality, the surfaces of Si and SiC chips were treated by Ar plasma to improve surface hydrophilicity. The RMS surface roughness of Si and SiC and the shear strength were measured by atomic force microscope (AFM) and shear strength tester (MFM 1200), respectively, as shown in Fig. 2(a)–(b). As the discharge power increases, the RMS surface roughness of the Si and SiC increases. In addition, owing to the hardness of SiC is greater than that of Si, the surface of Si is rougher than that of SiC at the same conditions. Meanwhile, the shear strength is improved with the increase of discharge power since the increase of roughness makes the chip surface more hydrophilic. For 70 W discharge power, the RMS surface roughness of Si and SiC are

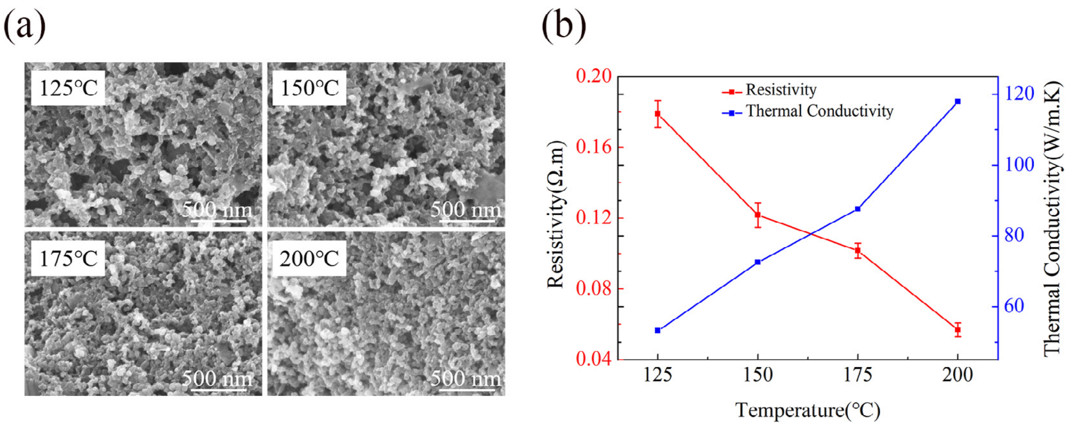

Fig. 1. (a) The morphologies of graphene composite slurry at different sintering temperatures and (b) The effect of different sintering temperatures on thermal conductivity and resistivity.

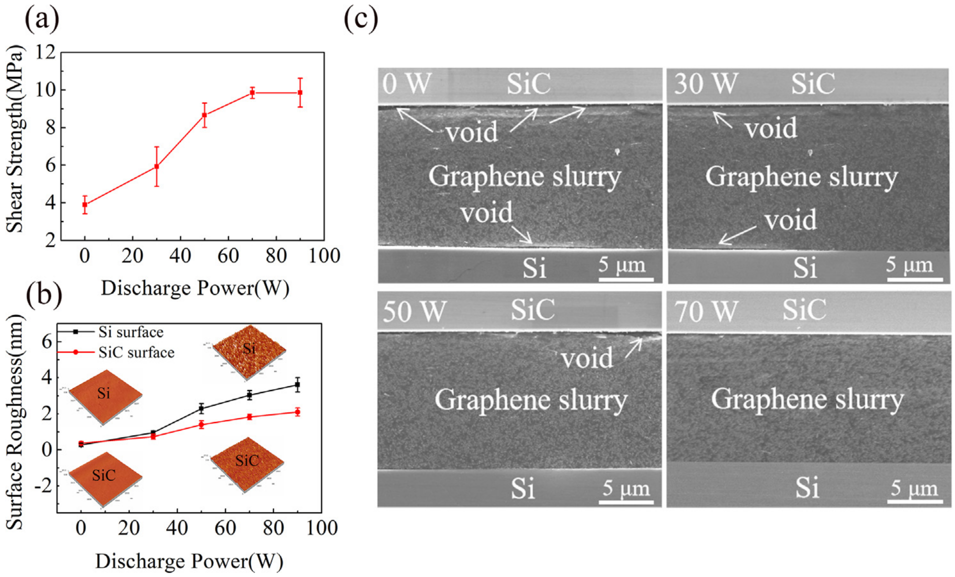

Fig. 2. The effect of different discharge powers of plasma on (a) The RMS surface roughness of Si and SiC, (b) The shear strength, and (c) The bonding interface.

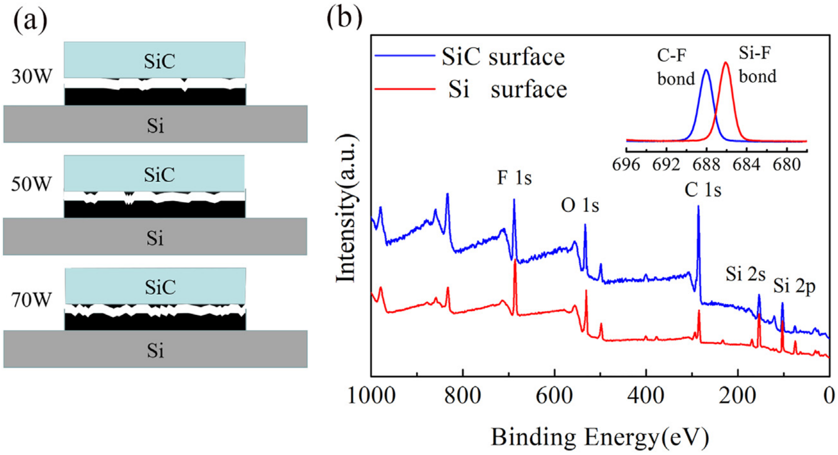

Fig. 3. (a) The fracture sketch of Si/graphene slurry/SiC bonding interfaces with plasma surface treatment at different discharge powers, (b) XPS analysis spectra from SiC and Si surface after shear test respectively, the inset shows the spectra of the F 1s core level.

respectively 3.22 nm and 1.67 nm, and shear strength of Si-SiC reaches approximately 10 MPa. Compared with the 30 KPa bond strength obtained by Takenori Naito et al. [9], the bond strength of Si-SiC was improved greatly in this study.

To study the bonding interface of the bonded samples before and after the Ar plasma treatment, cross-sectional SEM analyses of bonding interface treated with different discharge powers are performed, as shown in Fig. 2(c). It is clearly found that there are more gaps at the bonding interface before Ar plasma treatment, especially between the slurry and the SiC interface. The gaps between the slurry and Si interface are much smaller and less than the interface between the slurry and SiC, which means that the bonding strength between the slurry and Si is better than that between the slurry and SiC. With the discharge power of Ar plasma treatment increase from 30 W to 70 W, fewer or no gaps were found at interface, and a seamless bonding interface was formed with 70 W discharge power. The effect of bonding temperature on the interfacial resistivity also was studied (see Fig. S1 in supplementary material). It can be found that the interfacial resistivity decreases with the bonding temperature increase.

Fig. 3(a) shows the fracture sketch of bonding interfaces with plasma surface treatment at different discharge powers. Through fracture positions observation of many bonded samples after shear test, it can be found that most fractures of the bonded samples occur at the interface of the graphene slurry and SiC due to the weak bonding between the graphene slurry and SiC. With the increase of discharge power, the residual slurry on the SiC surface increases gradually, which indicates the bonding strength between SiC and slurry also increases gradually. There are two reasons for the fracture position at the interface of SiC and graphene slurry. One of the reasons is that the surface of Si is more hydrophilic than that of SiC surface after Ar plasma treatment for Si and SiC surfaces. The second reason may be the effect of fluorine contained in the PVDF in the graphene composite slurry. The fluorine ions may etch the Si surface to enhance the bonding strength, which has been reported by Chenxi Wang and Tadatomo Suga et al. [13–15]. To verify whether fluoride ions have an etching effect on the surfaces of Si and SiC, XPS analysis was performed for the bonded surface of Si and SiC after removing graphene slurry layer, as shown in Fig. 3(b). The F 1s peaks from Si and SiC surfaces show feature at 686.1 eV and 688.2 eV respectively, which are corresponding to Si-F bond and C-F bond reported previously [13]. It can be confirmed that Si-F bonds were formed at Si surface, which indicates that fluoride ions have an etching effect on the Si surface. However, there are only C-F bonds and no Si-F bonds to be found on the SiC surface, which indicates that the Si-C bond is not broken, and the C-F bonds maybe from the PVDF in graphene composite slurry. It can be confirmed that fluoride ions have almost no etching effect on the SiC surface. As a result, the bonding strength of graphene slurry/Si is greater than that of graphene slurry/SiC, and the fractures of the bonded samples usually occur at the interface of graphene slurry/SiC after shear test.

4. Conclusions

In this study, a low-temperature Si-SiC bonding process using graphene composite slurry as an interlayer was investigated. Ar plasma was used to treat the surface of Si and SiC before bonding to increase the hydrophilicity of the surface, which improved the bonding quality of Si/SiC. With the increase of the discharge power, the bonding strength also continues to increase, and reaches approximately 10 MPa when discharge power is 70 W. Meanwhile, the thermal conductivity of graphene slurry film reaches to 118 W/m.K at 200 °C, which is higher than that of SiC (83.6 W/m.K). Compared with traditional bonding, this bonding technology does not require high temperature, high cost and complicated process, which can be used for the fabrication of heat-spreaders for high performance power devices.

CRediT authorship contribution statement

Ximing Ye: Investigation, Writing - original draft. **Jiankun Wan:** Methodology. **Xiang Yin:** Visualization. **Wenhua Yang:** Conceptualization, Writing - review & editing, Supervision. **Chao Xie:** Resources. **Chunyan Wu:** Data curation. **Li Wang:** Data curation. **Linbao Luo:** Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 61404042) and the Fundamental Research Founds for the Central Universities of China (No. JZ2018YYPY0291).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2021.129710.

References

[1] H. Cheng, M. Yang, Y. Lai, M. Hu, Q. Li, R. Tu, S. Zhang, M. Han, T. Goto, L. Zhang, J. Eur. Ceram. Soc. 38 (2018) 3057–3063.
[2] J. Liang, S. Nishida, M. Arai, N. Shigekawa, J. Appl. Phys. 120 (2016) 034504.
[3] H. Shinohara, H. Kinoshita, M. Yoshimoto, Appl. Phys. Lett. 93 (2008) 122110.
[4] F. Mu, K. Iguchi, H. Nakazawa, Y. Takahashi, M. Fujino, T. Suga, ECS J. Solid State Sci. Technol. 5 (2016) P451–P456.
[5] J. Xu, C. Wang, D. Li, J. Cheng, Y. Wang, C. Hang, Y. Tian, Ceram. Int. 45 (2019) 4094–4098.
[6] A.A. van Veggel, D.V.D. Ende, J. Bogenstahl, S. Rowan, W. Cunningham, G.H.M. Gubbels, J. Eur. Ceram. Soc. 28 (2018) 303–310.
[7] M.K. Punith Kumar, M.P. Singh, C. Srivastava, RSC Adv. 5 (2015) 25603-25608.
[8] Y.B. Zhang, Y.W. Tan, H.L. Stormer, P. Kim, Nature 438 (2005) 201–204.
[9] T. Naito, K. Tanabe, Nanomaterials 8 (2018) 1048.
[10] Y. WU, R. Tang, W. LI, Y. Wang, L. Huang, L. Ouyang, J. Alloy. Compd. 830 (2020) 154575.
[11] S. Huang, Y. Zhang, S. Sun, X. Fan, L. Wang, Y. Fu, Y. Zhang, J. Liu, Proceedings of the 2013 IEEE 15th Electronics Packaging Technology Conference (EPTC), Singapore, 2013.
[12] L. Zhang, X.S. Zhao, Chem. Soc. Rev. 38 (2009) 2520–2531.
[13] C. Wang, T. Suga, J. Electrochem. Soc. 158 (2011) H525–H529.
[14] C. Wang, Y. Wang, Y. Tian, T. Suga, Appl. Phys. Lett. 110 (2017) 221602.
[15] C. Wang, Y. Liu, Y. Li, Y. Tian, T. Suga, ECS J. Solid State Sci. Technol. 6 (2017) P373–P378.