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Bonding Technique for Power Semiconductors Using Ni Nanoparticles

Norie MATSUBARA* Tomohiro UNO
Masayuki CHIBA Takayuki SHIMIZU

Abstract

The die-attach technique using Ni nanoparticles with diameters of 50–100 nm for high temperature electronics such as SiC power semiconductors was investigated. Basic knowledge about shear strength and sinterability of Ni nanoparticles was obtained. Under the optimum condition of Ni nanoparticle paste and a joining process, the sintered-Ni die-attach layer had a superior reliability in the thermal cycle test and in the high temperature storage test.

1. Introduction

Electric drive of transportation vehicles has greatly expanded over the last few years, and consequently, electric power conversion has become a key technology in related fields of industry. Power semiconductors form a mainstay for power conversion, and the change of the semiconductor material from Si to SiC is expected to produce an energy saving effect amounting to roughly 55 million kl–crude oil per year by 2030.[1)] Because SiC has desirable properties such as a high breakdown field intensity, a wide band gap, and a low on-resistance, SiC power devices can be made smaller and to have high breakdown resistance, low power loss, and high working temperature.[2)] Conventional Si power devices, in which heat arises from its own operation, are used generally at their working temperature of 398 K or below, and their packaging methods that allow a working temperature of 423 or 448 K have been studied recently. Since the physical properties of SiC allow working at higher temperatures, in contrast, SiC devices are promising for operation at 473 K or higher.

Figure 1 schematically shows a section of a typical power module. A power semiconductor device (a chip or a die) is fixed onto a ceramic substrate coated with a Cu layer with a die-attach layer in between, and the substrate is soldered onto a metal base plate serving also as a heat sink. The semiconductor chip and the substrate are connected to each other with bonding wires, and all these are encap-

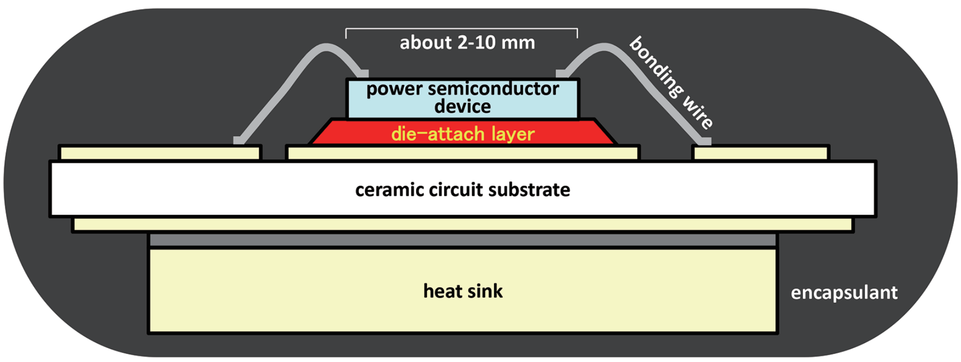

Fig. 1 Schematic cross-sectional illustration of a typical power module

* Researcher, Dr. Eng., Basic Technology Integration Center, Research & Development Division, Nippon Steel & Sumikin Chemical Co., Ltd.
(Former Researcher, Materials Research Lab., Advanced Technology Research Laboratories)
1-1 Tsukiji, Kisarazu City, Chiba Pref. 299-0835

sulated by a gel or resin to form an integrated piece.[3,4] Such a power module is formed not solely based on the device technology but through a combination of packaging technologies covering die-attach materials, insulating and heat radiating circuit substrates, bonding wires, sealing resins, and so forth. Semiconductor packaging for a working temperature of 473 K or higher requires not only stable operation at the target temperature but also resistance to the stress due to the heat resulting from repetitive on/off switching of the device, and for this reason, every package material must have both good heat resistance and high bond reliability.[5]

In semiconductor packaging for high working temperatures, a Si chip having a coefficient of thermal expansion (CTE) of 3 to 5 ppm/K, and a Cu substrate having a CTE of 17 ppm/K are bonded together. It is necessary for the die-attach layer between the two to withstand the heat arising from the chip operation as well as the thermal stress resulting from the CTE difference between them. In addition, it is desirable that the temperature of die-attaching during packaging is below the limit temperature in order to prevent adversely affecting the semiconductor die, which means that low-temperature bonding at 573 K or lower, resistance to a temperature of 473 K or higher and a high reliability of bonded joints against thermal stress are indispensable for die attaching.

Figure 2 shows the relationship between the bonding temperature and the heat resistance of common adhesives used for die attach. Firstly, with die attach using thermosetting resin, wherein metal fillers are made to contact each other by the hardening of the resin, and by this, electric conduction is established between the chip and the substrate, heat resistance is insufficient because the resin is organic. In addition, the existence of organic substances, not resistant to high temperature by nature, is undesirable for the operation of the package at high temperatures. Secondly, with solder die-attach, which employs a bonding mechanism whereby solder is melted when heated to its melting point, which is supposed to be between its solidus and liquidus lines, to form intermetallic compounds with the joining objects, the bonding temperature is naturally higher than the melting point of the solder, and accordingly, it is difficult to realize both bonding at low temperature and resistance to high temperature. In consideration of the above, sintering of metal nanoparticles is attracting attention as a third method of die attach.

By the die attach through sintering metal particles 20 to 100 nm in size, it is possible to realize both low-temperature bonding and obtain resistance to high temperature. **Figure 3** schematically illustrates the bonding process by the method. Particles, several tens of nanometers in size, surface-modified by an organic substance to prevent agglomeration, are mixed with a solvent and an additive into a paste, the paste is printed on the substrate, and a semiconductor chip is fitted onto the printed area of the substrate. Then, through heating, the solvent and the surface modifier decompose or oxidize, and evaporate from the paste, and thus the metal surfaces of the particles are exposed. Then, as a consequence of diffusion between the particles, bonds form between the particles as well as between the particles and the objects to be joined. After the particles are sintered, the melting point rises to that of the bulk metal, making them heat resistant.

The size range of 20 to 100 nm is selected in consideration of both good handling and sintering behavior at low temperatures. If the particle size is from several hundreds of nanometers (submicron particles) to several micrometers or more (micron particles), the temperature necessary for sintering them is usually 973 K or higher, but with nanoparticles several tens of nanometers in size, the sintering temperature can be as low as 573 K or lower. This is, we suspect, because there are atoms, on the surface of particles of this size

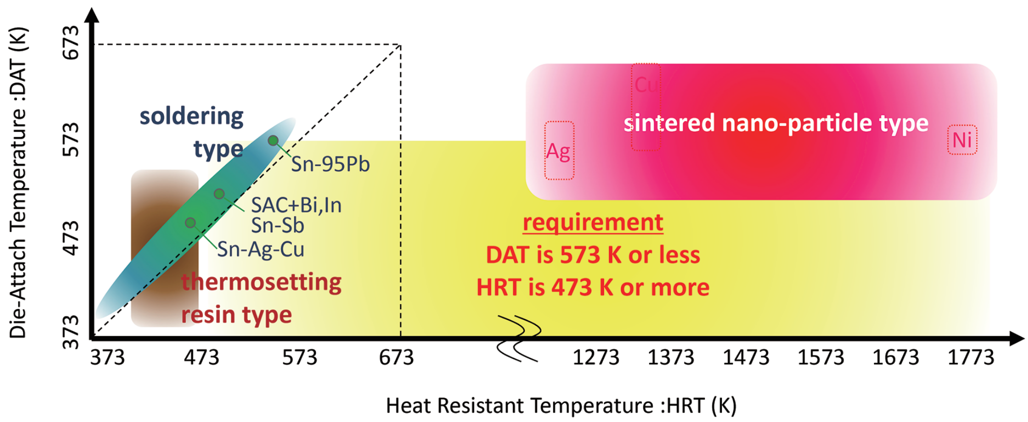

Fig. 2 Relationship between heat resistant temperature and die-attach temperature

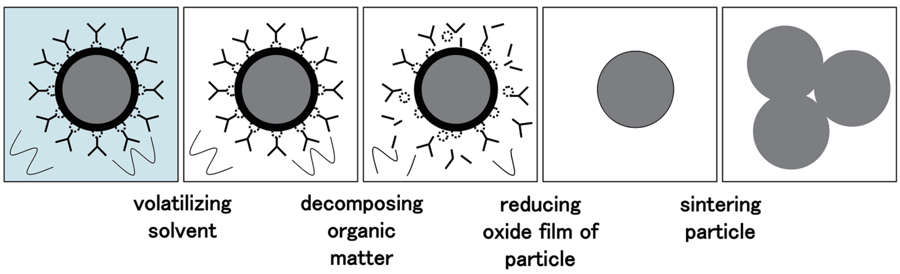

Fig. 3 Schematic illustration of the die-attach process using nano-particles

range, having a diffusion coefficient nearly as high as that in a liquid phase even at temperatures below the melting point, and these atoms act as the driving force for the adhesion of particles.[6] When the particle size is in the order of single nanometers, naturally, the particles melt because, owing to the size effect, their melting point falls to far below that of the bulk metal,[7] and bonding takes place during solidification. Since particles several nanometers in size are highly reactive, however, they are difficult to handle as they are, and for this reason, they are treated with a macromolecular organic surface modifier having dispersive effects to prevent their agglomeration. Unluckily, however, such organic modifier hinders the sintering of the particles, and they are likely to remain as residual carbon after the sintering process in the die-attach layer by a significant amount because of the large specific surface area of small particles. In consideration of this, a particle size range of several tens of nanometers, rather than single-digit nanometers, is preferred for this application.

Various attempts to commercialize a new method of die attach have been made over the last few years by sintering nanoparticles of Ag[8] or Cu[9]. Ag is characterized by the ease of sintering under more relaxed conditions than for Cu, and the highest thermal conductivity of all metal elements. In the temperature range of the bonding work and the operation of power devices, on the other hand, the sintering of Ag nanoparticles is feared to overshoot beyond necking, the grains grow too large and large voids form. This makes the die-attach layer brittle and lowers the bond strength, which is likely to lead to cracking of the die-attach layer and falling off of the chip. There have been reports of low die-attach strength due to the change of the die-attach layer structure.[10] Cu, in contrast, is characterized by lower cost than Ag, and by being the same element as the material of the circuits to be joined. The problem with Cu is, however, that it is easily oxidized and the bonding condition tends to be demanding.

Of the metal nanoparticles usable for sintered die attach, we focused attention on Ni particles and conducted development studies along this route.[11] As shown in **Fig. 4**, the CTE of Ni is 13 ppm/K, between those of the bonding objects, Si or SiC devices and Cu circuits. A die-attach agent having a CTE between those of the bonding objects is advantageous for lowering the thermal stress arising in the package,[12] and consequently, Ni is promising for enhancing bond reliability in the temperature range where the packages are likely to be under thermal stress. Figure 4 also shows the ratio of the operating temperature of the device (which is assumed here to be 523 K) to the melting point of the bulk metal (T_m). The ratio of Ni is far lower than those of Ag and Cu, and thus Ni is presumably less prone to structural change at high temperatures, and is promising for high bond reliability.

In the present study, the bond strength of sintered die attach using Ni nanoparticles was investigated as a basic study on the bonding method, and then the sintering behavior of Ni nanoparticles after heating was examined. Thereafter, in view of commercial use of the bonding method, the bond reliability was evaluated through the thermal cycle test and high-temperature storage test.

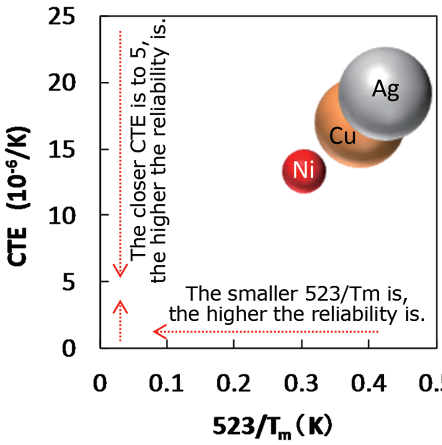

Fig. 4 Thermal properties of Ag, Cu and Ni

2. Body

2.1 Test method

2.1.1 Specimen paste

Paste was prepared for the present test by mixing the following two types of Ni particles with a solvent and an additive: Ni nanoparticles, 50 to 90 nm in average size, produced through the liquid-phase reduction process (newly developed and manufactured by Nippon Steel & Sumikin Chemical Co., Ltd.[13]), and Ni micro-particles, less than 10 micrometers in average size, available in the market.

2.1.2 Objects to be joined

The bonding objects, or the chips and substrates, listed in **Table 1** were procured in consideration of the methods of evaluation.

2.1.3 Methods of test piece preparation

Test pieces of semiconductor packages were prepared in accordance with the methods of evaluation. Those for the evaluation of shear strength (to be explained in 2.1.4) and observation of the sintered bond (2.1.5) were prepared in the following steps: the Ni paste was printed on the substrates using a metal mask 100 μm in thickness; the substrates were put into a reflow furnace (Model RSS-450-110 of Uni Temp GmbH make) and preheated at 373 K for 600 s in a reducing atmosphere of 3%H_2 + 97%N_2; then the Ni paste was printed a second time on the preheated paste on the substrates using the same metal mask; using a flip chip bonder (Model MCP-F100 of Sony), a chip was fitted onto each of the substrates at room temperature under a load of 5 MPa; and finally, the chips were bonded to the substrates, respectively, by holding at different peak temperatures of 533, 553, 573 and 628 K in the same reducing atmosphere for 3 600 s without applying load. The test pieces for the thermal cycle test (2.1.6) and high-temperature holding test (2.1.7) were prepared in

Table 1 Components of test pieces for different tests and observation

		2.1.4 Shear strength	2.1.5 TEM observation	2.1.6 TCT	2.1.7 HTST
Chip	Material (backmetal)	Cu(Ni/Au)	Si(Ti/Ni/Au)	Si(Ti/Ni/Au)	Si(Ti/Ni/Au)
	Area (mm^2) × Height (mm)	4 × 0.5	4 × 0.45	36 × 0.4	36 × 0.4
Substrate	Material (plating)	Cu(Ni/Au)	Cu(Ni/Au)	Cu/Si_3N_4/Cu	Cu(Ni)
	Area (mm^2) × Height (mm)	225 × 1	225 × 1	About 225 × 0.9	400 × 1

consideration of commercial packaging work as follows: the Ni paste was printed on the substrates using a metal mask 100 μm in thickness; the substrates were put into the reflow furnace and preheated at 363 K for 300 s in the same reducing atmosphere as the above; a chip was mounted on each of the substrates; and then the sets of the chips and the substrates were bonded together by holding at 573 K for 1800 s at the longest in the same reducing atmosphere and under an applied load of 5 MPa.

2.1.4 Measurement of shear strength

To measure the bond strength, we conducted the shear strength test at room temperature using a bond tester (Series 4000 of DAGE). The test pieces were as follows: those bonded at 533 to 628 K without applying load: and those bonded at 573 K under a load of 5 MPa and then subjected to the thermal cycle test described in 2.1.6 below. In the case where the bonded area of the chip was 4 mm^2, the tool width was set at 6 mm, its height from the substrate at 50 μm, and the upper limit of the load for measurement at 40 MPa (≈ 16 kgf), twice the shear strength (20 MPa) of common solder bond. On the other hand, in the case where the bonded area was 36 mm^2, the tool width was set at 10 mm, its height at 100 μm, and the upper limit of the load for measurement at 20 MPa (≈ 73 kgf) in consideration of the limitation of the tester. In either case, the tool speed during measurement was set at 100 μm/s.

2.1.5 Observation of sintered bond

The chip-substrate sets bonded at 628 K without applying load were embedded in epoxy resin, polished at section surfaces, cut into thin films by the focused ion beam (FIB) method, and the film specimens were observed through a 200-kV field-emission transmission electron microscope (FE-TEM, Model JEM-2100F of JEOL).

2.1.6 Thermal cycle test

As a method for evaluating the bond reliability under fluctuating temperature conditions, the thermal cycle test (TCT) was conducted, using a gas-type thermal shock tester (Model TSA-72-ES-W of Espec), wherein the specimens were subjected to 300 cycles of cooling (to 233 K) and heating (to 473 K) repeating at 3600 s/cycle. The bond reliability was evaluated using scanning acoustic tomograph (SAT) images of the bond interface obtained before and after the TCT using an ultrasonic imaging device (Model FineSAT III Advance of Hitachi Power Solutions). Here, the SAT images were obtained in the following manner: an ultrasonic beam of 200 MHz was projected onto the bonded specimen from the chip side, focused roughly on the interface between the chip and the die-attach layer so as to cover an area of 49 mm^2 to cover the entire chip bottom area of 36 mm^2. As an additional evaluation of the bond strength after the TCT, the shear strength of the specimens was measured by the method explained in 2.1.4 above.

2.1.7 High-temperature storage test

For the purpose of examining the structural change of the Ni die-attach layer during storage at high temperature, the specimens were held in a furnace maintained at 523 K for 900000 s (250 h) (hereinafter referred to as high-temperature storage test (HTST)), extracted from the furnace, their bond interfaces examined to obtain SAT images, embedded in epoxy resin, cut sectionally, and polished at section surfaces. Each section surface was observed in three fields through an optical microscope (Model Miniscope TM3000 of Hitachi High-Technologies) at 5000 times magnification, and through processing of the sectional images, the void ratio of the die-attach layer was calculated.

2.2 Test results and discussion

2.2.1 Bond strength of sintered die attach of Ni nanoparticles[10)]

Figure 5 shows the shear strength of the bonds of the specimens sintered at 533 to 628 K without applying load. Although it is recommendable to measure shear strength using several tens of test pieces because its reading often fluctuates significantly, to save on labor for the test piece preparation, two to three test pieces were prepared for each group of specimens for the present study, and the mean value of their readings was plotted in the graph. The shear strength of the specimens bonded at 573 and 628 K was 40 MPa or higher, and that of the specimens bonded at 533 and 553 K exceeded 20 MPa, the shear strength of common solder bonds.

Both the two bonding objects for the present study were made of Cu and there was no difference in the thermal expansion coefficient between them, and for this reason, it was possible to evaluate the shear strength of the die-attach layer without being affected by the thermal stress due to the difference in thermal expansion. The shear strength increased with higher bonding temperature presumably because the sintering of Ni nanoparticles advanced and the rate of necking increased. Sintering of the particles is expected to advance as the reducibility of the oxide film on the particle surface increases, Ni atoms diffuse more, and more organic matter, which hinders sintering, is removed; these three are accelerated at higher bonding temperature. This explains the above result of the present test.

2.2.2 State of sintered Ni nanoparticles[10)]

Oxide films form on the Ni particle surface during manufacturing, and during heating for sintering, the particles are presumed to bond with each other after the oxide films disappear. For this reason, they are sintered in a reducing atmosphere of 3%H_2 + 97%N_2 to remove the oxide film. The higher the H_2 concentration, the more easily the oxide films are reduced, but since H_2 is inflammable, it is industrially undesirable to use H_2 in a concentration higher than the lower explosion limit (4 volume %). Its use in a concentration above the higher explosion limit (94 volume%) is also undesirable because it is diluted and the concentration will fall within the explosion range. The fact that the oxide film can be reduced even when the H_2 concentration is below the lower explosion limit is therefore significant; the H_2 concentration of 3% was selected exactly for this reason.

Part (a) of **Fig. 6** shows a FE-TEM image of the bond interface

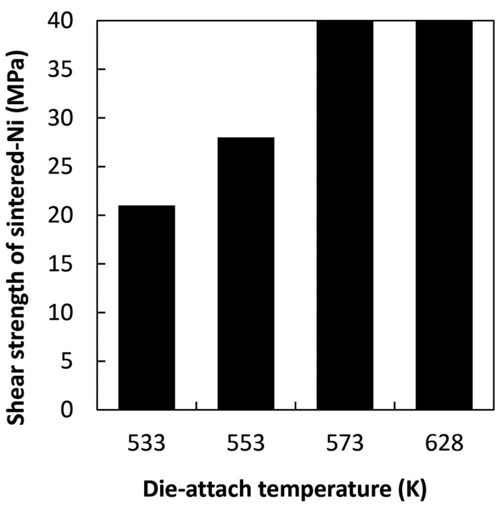

Fig. 5 Shear strength of sintered-Ni layer after heating at 533, 553, 573 and 628 K

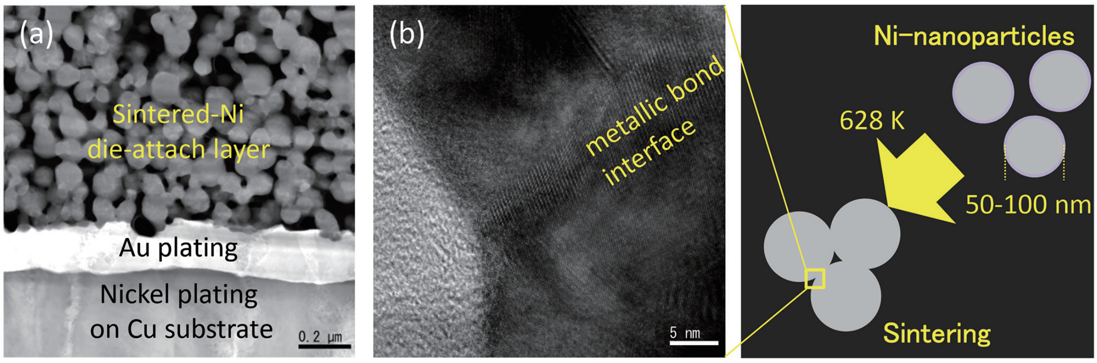

Fig. 6 Cross sectional TEM images of (a) Joint of Ni nanoparticle layer and Ni/Au plated substrate, (b) Ni nanoparticle layer, after heating at 628 K

on the substrate side of the die-attach layer, and part (b) another of a bond between Ni nanoparticles. Necking of the Ni nanoparticles is clearly seen in part (a), and at the interface between the particles and the substrate, we confirmed, diffusion of Au, which had been plated on the substrate surface, into Ni. Part (b), on the other hand, shows a joint between two particles, where a lattice structure can be seen. This indicates that the oxide film on the Ni nanoparticle surface is easily removed, and the metal surface is exposed even when the H_2 concentration is as low as 3%, which leads to the diffusion of Ni atoms to produce good bonding.

2.2.3 Bond reliability at thermal cycle test

From the test results of the shear strength of sintered Ni nanoparticles described in 2.2.1 and that of their sintering properties described in 2.2.2, the sintered die attach using Ni nanoparticles proved to have a sufficiently high bond strength. This bonding method, however, has problems such as poor handling properties of the Ni paste, complicated bonding processes, unstable bonding of large areas, and many voids in the die-attach layer. To solve these problems, we reviewed the grain size of the Ni particles, the mixing ratio and the solvent for the paste preparation, etc. Then, after confirming the thermophysical and mechanical properties of the improved Ni paste, we studied the bonding conditions such as the temperature profile for heating, pressing, and holding time. As a result of these studies from the viewpoints of paste composition and the bonding process, high-strength bonding with a Ni die-attach layer of a low void ratio has been enabled stably through fewer process steps, even when the bonding area is large.

Then, we investigated the bond reliability of the improved die-attach at cyclic temperature change through TCT. A SAT image of a specimen before the TCT and another after 200 cycles of 233/473 K are given in **Fig. 7**. The construction of the specimens is such that, usually, the thermal stress is largest at an edge of the joint between the chip and the die attach in the X/Y-Z section at a chip corner on the X-Y plane; flaking or cracking of a chip is likely to originate from this point, and the chip may peel off or a crack propagates from it. If there is a void containing air in the bond interface or the die-attach layer as a result of such peeling off or cracking, an ultrasonic beam is reflected almost entirely at the interface between the air and Si or Ni, and the void is shown in white in SAT images. There were no such portion in either part (a) or (b) of Fig. 7, which means that the bond remained sound in the entire chip area even after the 200 cycles of TCT.

In addition, to confirm the bond strength after 200 cycles of TCT, we measured the shear strength of specimens after the test. During the measurement, the shear load increased monotonously to the value equivalent to a shear strength of 20 MPa, confirming a bond strength equal to or higher than that of soldering.

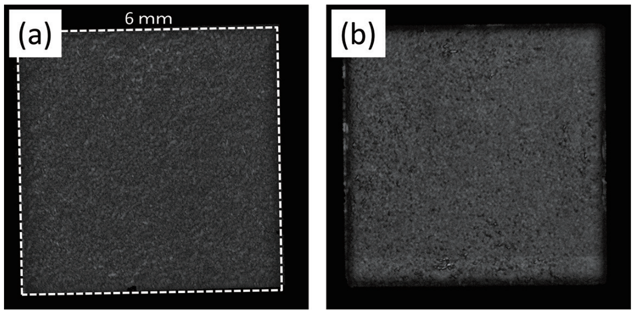

Fig. 7 SAT images of sintered-Ni die-attach samples (a) Before and (b) After 200 cycles of 233/273 K TCT The dotted square is the periphery of the Si chip.

As stated above, the thermal stress on the specimens, which arises from their components and structure, was minimized by using Ni having a CTE between those of the two objects to be joined, the Ni die-attach layer maintained a strong bond as a consequence, and presumably for this reason, there was no change to the structural integrity of the specimens before and after the TCT. In conclusion, the sintered die attach using Ni nanoparticles is considered to have high bond reliability at TCT from 233 to 473 K.

2.2.4 Bond reliability at high-temperature storage test

As stated earlier in Section 1, during sintering of Ag nanoparticles, the grains in the die-attach layer tend to grow prolifically during holding at high temperatures, and voids become coarse, making the structure brittle and fragile. It can be presumed from this that the porosity of the die-attach layer serves as an indicator of the decrease in bond strength. Based on this, to confirm the change in the structure of the die-attach layer during holding at high temperatures, we observed specimens after holding at 523 K for 250 h using SAT images and at sections. Sound bond without flaking was confirmed at SAT examination. **Figure 8** shows the change in the void ratio of the die-attach layers before and after the holding at 523 K; no significant change in the void ratio before and after the high-temperature holding was observed. This is presumably because the melting point of Ni was sufficiently higher than the holding temperature 523 K, the sintering that accelerates necking did not advance, and no structural change took place. This indicates that the sintered die attach using Ni nanoparticles is capable of withstanding the high-temperature holding at 523 K, maintaining high bond reliability.

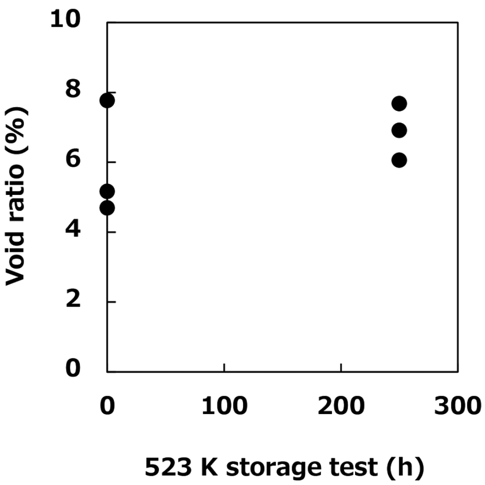

Fig. 8 Change in void ratio of die-attach layer of sintered Ni particles after storage at 523 K

3. Summary

For efficient use of energy, increasingly higher performance is required of energy conversion devices, and against this background, SiC semiconductors are used for next-generation power devices. With the aim of devising a new packaging method suitable for high-temperature operation of SiC semiconductors to make the most of the material properties to save energy, we have endeavored to develop a method for sintered die attach using Ni nanoparticles. In the present study, we examined the bond strength of the Ni die attach through shear tests, observed the sintering behavior of Ni particles through a sectional FE-TEM, and obtained fundamental findings on the Ni-sintered die attach from the viewpoints of shear strength and the state of sintered Ni particles. Then, in view of the commercial use of power semiconductor packages, we prepared specimens by bonding Si chips onto substrates of Si_3N_4 coated with Cu by the die attach of Ni particles, and by subjecting them to 200 cycles of TCT at 233 and 473 K, investigated the reliability of the bond under repetitive heating and cooling. They also studied the bond reliability against high temperature through HTST at 523 K for 250 h. The following results were obtained.

- Ni nanoparticles were sintered sufficiently strongly at 628 K or lower in a reducing atmosphere of a low H_2 concentration. Here, as a result of the progress of sintering from the nanoparticles, a good bond stronger than that by soldering was obtained.
- The die-attach bond remained sound through 200 cycles of TCT at 233/473 K and HTST at 523 K for 250 h, and no tangible difference was detected in it before and after these tests, which verifies the high reliability of sintered die attach of Ni nanoparticles.

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Norie MATSUBARA
Researcher, Dr. Eng.
Basic Technology Integration Center
Research & Development Div.
Nippon Steel & Sumikin Chemical Co., Ltd.
1-1 Tsukiji, Kisarazu City, Chiba Pref. 299-0835
(Former Researcher, Materials Research Lab.
Advanced Technology Research Laboratories)


Masayuki CHIBA
Nippon Steel & Sumikin Chemical Co., Ltd.


Tomohiro UNO
Chief Researcher, Dr. Eng.
Materials Research Lab.
Advanced Technology Research Laboratories


Takayuki SHIMIZU
Researcher
Nippon Steel & Sumikin Chemical Co., Ltd.