

HEAT-TRANSFER FLUIDS FOR THE MANUFACTURING OF SEMICONDUCTOR COMPONENTS

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DESCRIPTION

FIELD OF THE INVENTION

The present application relates to the use of a heat-transfer fluid based on an aliphatic diester in the manufacturing of semiconductor components.

BACKGROUND

Nowadays, heat dissipation is a relevant topic in the design and manufacturing of semiconductor components.

In this context, heat-transfer fluids (HTFs) play a critical role significantly impacting both the efficiency and quality of semiconductor components. These specialized fluids are indeed essential for maintaining precise temperature control, which is crucial for various processes involved in semiconductor fabrication.

Semiconductor manufacturing indeed involves numerous processes, such as lithography, etching, doping, and deposition, all of which require precise temperature control. Heat-transfer fluids ensure that these processes occur at optimal temperatures, minimizing thermal fluctuations that can lead to defects in the microelectronic structures.

Maintaining stable temperatures is therefore vital for consistent performance of semiconductor devices and heat-transfer fluids help in avoiding overheating or overcooling, which can affect the electrical properties and performance reliability of the components.

It is therefore strongly felt the need of identifying and developing new and improved heat-transfer fluids capable to meet the stringent requirements of semiconductor components' manufacturing.

Today, fluids for liquid cooling known in semiconductor manufacturing operations are specialized fluids, among which those containing PFAS (per- and polyfluorinated substances) have found wide application.

SUMMARY OF INVENTION

The Applicant noted, however, that even if specialized fluids such as those containing PFAS have satisfying properties that support the semiconductor manufacturing performance

properties, such as a wide range of operational temperatures from boiling point to pour point associated with low kinematic viscosity, high dielectric constant, and high volume resistivity in such a wide range of operational temperatures, these fluids have recently shown technical and application limitations.

PFAS, indeed, tend to have a high volatility and this results in a partial loss of these fluids due to their evaporation when exposed to high temperature components. This high volatility and partial loss of PFAS requires their refilling into the heat exchange system, at the same time increasing the exposition to said fluids for operators.

At the same time, PFAS have also raised relevant concerns for their environmental impact, rendering particularly critical their use and requiring also the adoption of complex and expensive containment systems for avoiding any spread and/or contact with the external environment during operation, transport, maintenance operations of the systems and devices using them.

An object of the present invention is therefore to provide a new heat-transfer fluid capable of meeting the performance requirements for semiconductor components' manufacturing while at the same time overcoming the environmental limits of the heat-transfer fluids currently employed and the Applicant surprisingly found out that a heat-transfer fluid based on a specific class of aliphatic diesters may effectively be used for such purpose.

Particularly, the present invention relates, in a first aspect, to the use of a heat-transfer fluid comprising at least one diester of at least one C₂-C₉ aliphatic diol with at least one linear or branched C₂-C₇ aliphatic monocarboxylic acid, in at least one manufacturing step of a semiconductor component, to exchange heat with such semiconductor component.

Surprisingly, the Applicant has indeed found out that such diesters show suitable rheological and fluid dynamic properties, thermal and chemical stability properties, as well as thermal capacity properties rendering the same effectively suitable to exchange heat with such semiconductor component during its manufacturing operations therefore ensuring that these operations occur at optimal temperatures, minimizing thermal fluctuations that can lead to defects in the microelectronic structures.

Advantageously, said diesters may also offer a more environmentally sustainable solution to PFAS-based specialized fluids, rendering the operation, transport, and maintenance operations of the cooling system, less critical.

In a further aspect, the present invention relates also to a method of manufacturing a semiconductor component, said method including at least one step wherein said semiconductor component exchanges heat with a heat transfer fluid, said heat transfer fluid comprising a diester as defined in the first aspect of the invention.

The advantages of the method according to this aspect of the present invention have been already disclosed in relation to the use according to the first aspect of the present invention and are not herewith repeated.

DETAILED DESCRIPTION OF INVENTION

The present invention relates, in a first aspect, to the use of a heat-transfer fluid comprising at least one diester of at least one C₂-C₉ aliphatic diol with at least one linear or branched C₂-C₇ aliphatic monocarboxylic acid, in at least one manufacturing step of a semiconductor component. Said heat-transfer fluid is apt to exchange heat with such semiconductor component, thereby ensuring that said manufacturing step occur at optimal temperatures, minimizing thermal fluctuations that can lead to defects in the semiconductor component's microelectronic structures.

Surprisingly, the Applicant has indeed found out that such diesters show suitable rheological and fluid dynamic properties, thermal and chemical stability properties, thermal capacity properties rendering the same effectively suitable to exchange heat with such semiconductor component during its manufacturing operations therefore ensuring that these operations occur at optimal temperatures, minimizing thermal fluctuations that can lead to defects in the microelectronic structures.

Advantageously, said diesters may also offer a more environmentally sustainable solution to PFAS-based specialized fluids, rendering less critical the operation, transport, maintenance operations of the cooling system.

Notably, said diesters offer excellent alternatives to PFAS-based fluids, particularly due to their remarkable low dynamic viscosity at extremely low temperatures. This exceptional property enables efficient pumpability and circulation of heat transfer fluids even in the harshest cold environments. Moreover, these esters boast a high flash point and low volatility, ensuring both safety and effective cooling of electronics at elevated temperatures. Their unique combination of low viscosity, high flash point, and low volatility make these diesters ideal choices for various types of cooling systems for semiconductor-based

components, providing efficient thermal management of their manufacturing by offering reliable and efficient heat transfer capabilities while prioritizing safety and performance.

These fluids, with their low viscosity, facilitate the effective transfer of heat away from semiconductor component during their manufacturing. The high flash point and low volatility of these esters ensure indeed at the same time safe operation and minimize the risk of fire or failure also in such operations.

For example, such diesters can be used as working fluids in heat pipes or in narrow channels or conduits, which are widely employed for indirect cooling during manufacturing of semiconductor components. These diesters enable efficient heat transfer in such conditions, allowing heat to be absorbed from the source and dissipated at the sink. The low viscosity of the fluids at the operational temperature ensures indeed optimal circulation through narrow channels or conduits and so even with a limited contact time and heat transfer surface area, enhancing the overall cooling performance.

In cooling systems with closed-loops customarily used in semiconductor cooling operations, for example, such diesters may therefore advantageously serve as the heat transfer fluids. As these fluids have low dynamic viscosity at the working temperature, they can easily flow through narrow channels and intricate cooling structures, efficiently carrying heat away from semiconductor components. The high flash point and low volatility enhance the safety and reliability of the cooling system.

Said diesters can also effectively be used in cold plate cooling systems, where they may advantageously flow through metal plates which are in turn in direct contact with semiconductor components. The low viscosity of these fluids allows for efficient heat transfer from metal plates, enabling effective cooling of high-power electronic devices. The high flash point and low volatility of the esters ensure safe operation and minimize the risk of fluid leakage or system damage.

Within the framework of the present description and in the subsequent claims, except where otherwise indicated, all the numerical entities expressing amounts, parameters, percentages, and so forth, are to be understood as being preceded in all instances by the term "about". As used herein, the term "about" will be understood by persons of ordinary skill in the art and will vary to some extent on the context in which it is used. As used herein when referring to a measurable value such as an amount, a temporal duration, and the like, the term "about" is meant to encompass variations of $\pm 20\%$ or $\pm 10\%$, including $\pm 5\%$, $\pm 1\%$,

and $\pm 0.1\%$ from the specified value, as such variations are appropriate to perform the disclosed methods.

Also, all ranges of numerical entities include all the possible combinations of the maximum and minimum values and include all the possible intermediate ranges, in addition to those specifically indicated herein below.

Unless defined otherwise, all technical and scientific terms used herein generally have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

As used herein, the articles "a" and "an" refer to one or to more than one (i.e. to at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

The present invention may present in one or more of the above aspects one or more of the characteristics disclosed hereinafter.

According to the present invention, the heat-transfer fluid comprises at least one diester of at least one C₂-C₉ aliphatic diol with at least one linear or branched C₂-C₇ aliphatic monocarboxylic acid.

Preferably, said C₂-C₉ aliphatic diol is selected from the group consisting of: ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, di-ethylene glycol, tri-ethylene glycol, di-propylene glycol, neopentyl glycol, 2-methyl-1,3-propanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol and mixtures thereof.

Preferably, the aliphatic diol of the diester according to the invention is a C₃-C₆ aliphatic diol, more preferably selected from the group consisting of: 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, di-ethylene glycol, tri-ethylene glycol, di-propylene glycol, neopentyl glycol, 2-methyl-1,3-propanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol and mixtures thereof. Even more preferably, the aliphatic diol of the diester according to the invention is a C₃-C₅ aliphatic diol, still even more preferably selected from the group consisting of: 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, di-ethylene glycol, neopentyl glycol, 2-methyl-1,3-propanediol, 1,5-pentanediol, and mixtures thereof.

In a preferred embodiment, the aliphatic diol of the diester according to the invention is selected from the group consisting of 1,2- propanediol, 1,3- propanediol, neopentyl glycol,

and mixtures thereof, preferably selected from the group consisting of 1,2- propanediol, 1,3- propanediol and mixtures thereof.

In an embodiment of the invention, the linear or branched C₂-C₇ aliphatic monocarboxylic acid of the diester according to the invention is a C₃-C₅ aliphatic monocarboxylic acid, more preferably selected from the group consisting of: propanoic acid, butyric acid, isobutyric acid, 2-methylbutyric acid, 3-methylbutyric acid, valeric acid, and mixtures thereof; more preferably is selected from the group consisting of: 2-methylbutyric acid, 3-methylbutyric acid, valeric acid, and mixtures thereof.

In another embodiment of the invention, the linear or branched C₂-C₇ aliphatic monocarboxylic acid of the diester according to the invention is a C₅-C₇ aliphatic monocarboxylic acid; preferably in such embodiment at least one of the monocarboxylic acids of the diester according to the invention is a C₅ acid. More preferably in such embodiment the aliphatic monocarboxylic acid of the diester according to the invention is a C₅ acid, optimally valeric acid.

In a preferred embodiment of the present invention, said diester is selected from the group consisting of: neopentyl glycol divalate, 1,2-propanediyl divalate, 1,3-propanediyl divalate, 2-methyl-1,3-propanediyl divalate, and mixtures thereof, more preferably 1,2-propanediyl divalate, 1,3-propanediyl divalate, and mixtures thereof.

Diols, monocarboxylic acids, and diesters as above defined have indeed surprisingly shown a combination of properties, such as a low dynamic viscosity at temperatures up to – 55 °C combined with a flash point higher than 125 °C, and a high volume resistivity, rendering them particularly suitable and operatively efficient in indirect electronic cooling systems in a broad temperature range window from - 55 °C to 125 °C, and so particularly efficient as components of heat-transfer fluids for use in the manufacturing of semiconductor components.

In addition to the diester, the heat-transfer fluid according to the invention may advantageously contains one or more other components, among which for example a synthetic or natural ester, a mineral oil, a polyether such as a polyalkylene glycol, a polyolefin, an additive.

In an embodiment, the heat-transfer fluid according to the invention comprises at least one diester as defined above and at least one monoester of at least one C₆-C₁₂ aliphatic mono-

alcohol with at least one linear or branched C₂-C₁₂ aliphatic monocarboxylic acid, for example a monoester such as 2-propylheptanyl valerate, 2-ethylhexanyl heptanoate.

Preferably, the heat-transfer fluid according to the invention comprises at least one an additive selected from the group consisting of: an antioxidant, a pour-point-depressant additive, an antifoam, an anticorrosion agent, a viscosity modifier, a wear-resistance and/or extreme-pressure additive, a friction modifier, a detergent, a dispersant, and mixtures thereof.

Advantageously, the heat-transfer fluid according to the invention shows one or more of the following features:

- a dynamic viscosity at – 30 °C of less than 50 mPa*s;
- a flash point higher than 125 °C;
- a volume resistivity at 25 °C higher than 0.1 tera ohm-centimeter (TΩ*cm).

Additionally, the heat-transfer fluid according to the invention shows suitable heat capacity and thermal conductivity properties for cooling semiconductor components during their manufacturing.

Preferably, the heat-transfer fluid according to the present invention is in liquid state when used in the manufacturing of semiconductor components.

In the manufacturing of a semiconductor component, the heat-transfer fluid according to the invention may be used in a direct liquid cooling system or in an indirect liquid cooling system.

As used herein, with the expression “indirect liquid cooling system” is meant a cooling system wherein the heat-transfer fluid is (or is kept) in liquid state, or predominantly in liquid state, during the operation of the system and wherein said heat-transfer fluid does not come into direct contact with the component that has to be cooled- while being apt to cool the same. In particular, when referred to an electronic component, an indirect liquid cooling system is a cooling system wherein the heat-transfer fluid does not come into direct contact with such electronic component, for example by interposition of a different element thermally coupled with the electronic component and made of a thermally conductive material, such as copper or other metals, that is interposed between the electronic components and the heat-transfer fluid. This thermally conductive element prevents the direct contact of the fluid with the electronic component and has the function of transferring the heat. In indirect cooling systems such different elements interposed between the electronic components and

the heat-transfer fluid may have different shapes and configurations (heat sinks, a wall in a tube, or a plate) depending on the design of the system.

In indirect cooling heat transfer involves both conduction and convection, as the fluid exchanges heat with a material thermally coupled with the component to be cooled and the heat exchange is predominantly influenced by the difference of temperature between the component to be cooled and the heat transfer fluid. Another well-known factor influencing the heat exchange is the quantity of the heat exchange fluid used, which in turn is limited by the design of the cooling system.

In a preferred embodiment, the heat-transfer fluid according to the invention is used in an indirect cooling system in at least one step of the manufacturing of a semiconductor component.

According to the present invention, the indirect liquid cooling system is not particularly limited and may be any type of indirect liquid cooling system known to the skilled person in the relevant technical field for indirectly cooling a semiconductor component during its manufacturing.

Preferably, the indirect liquid cooling system according to the present invention comprises at least one thermally conductive element thermally coupled to said semiconductor component, and said thermally conductive element is apt to transfer heat from said semiconductor component to said heat-transfer fluid. More preferably, said thermally conductive element is selected from the group consisting of: a wall, a layer, a heat sink, a cold plate, a heat pipe, and a vapour chamber.

Preferably, said indirect liquid cooling system comprises:

- a liquid cooling loop apt to circulate said heat-transfer fluid;
- a pump apt to pump said heat-transfer fluid throughout said liquid cooling loop;
- an heat exchanger apt to cool said heat-transfer fluid; and
- optionally, a reservoir apt to contain said heat-transfer fluid.

According to the present invention, the semiconductor component may be of any kind and is preferably selected from the group consisting of: a microprocessor, a semiconductor wafer, a power control semiconductor, and a semiconductor integrated circuit.

Thanks to its combination of properties, the heat transfer fluid according to the present invention may be effectively used in any manufacturing step of a semiconductor component.

Said step may be any step known to the skilled person in the relevant technical field.

Preferably, said manufacturing step is selected from the group consisting of: wafer fabrication, polishing, oxidation, photoresist coating, photolithography, etching, preferably dry etching, deposition, ion implantation, annealing, metal wiring, and testing.

In a further aspect, therefore, the present invention relates also to a method of manufacturing a semiconductor component, said method including at least one step wherein said semiconductor component exchanges heat with a heat transfer fluid, said heat transfer fluid comprising at least one diester of at least one C₂-C₉ aliphatic diol with at least one linear or branched C₂-C₇ aliphatic monocarboxylic acid, as above defined in the first aspect of the invention.

Advantages and preferred features of this method have been already defined above with respect to the first aspect of the invention, and are therefore not herewith repeated.

In the method according to this aspect of the invention, an heat-transfer fluid as defined in the first aspect of the invention is used. Preferred features of this heat-transfer fluid have been therefore already defined above with respect to the same component in the first aspect of the invention, and are therefore not herewith repeated.

Preferred features of the cooling system, of the semiconductor component and of the manufacturing steps of the method according to the present invention have also been already defined above with respect to the same respective components in the first aspect of the invention, and are therefore not herewith repeated.

Further features and advantages of the invention will appear more clearly from the following description of some preferred embodiments thereof, made hereinafter by way of the following non-limiting examples.

EXPERIMENTAL PART

Example 1 – preparation of neopentyl glycol divalerate

400 g (3.84 moles) of neopentyl glycol were charged in multi neck reaction flask equipped with anchor stirrer, Vigreux column, condenser and distillate vessel. 980 g (9.6 moles) of valeric acid and 3 g of sodium hypophosphite monohydrate were added to the flask. The stirring was started and the system was purged with nitrogen, then the temperature was raised up to the boiling of the reaction mixture. The reaction was then left to run until a quantity of water corresponding to 100 % of the stoichiometric amount for a 100%

esterification yield was evaporated. After that, the unreacted valeric acid was removed by vacuum distillation, until an acid value of less than 5 mg KOH/g was obtained. A sodium hydroxide aqueous solution at 4 wt% in stoichiometric excess with respect to the quantity needed to neutralize said acid value was added to the esterified product and stirred for 30 minutes; the organic phase was then separated from the aqueous phase, then washed with water, and then dried under vacuum and filtered.

Example 2 – preparation of 1,2-propanediyl divalerate

Example 1 was repeated, using 292.18 g (3.84 moles) of 1,2- propanediol instead of 400 g of neopentyl glycol, and obtaining at the end of the valeric acid removal an acid value of 5 mgKOH/g.

Example 3 – preparation of 1,3-propanediyl divalerate

Example 1 was repeated, using 292.18 g (3.84 moles) of 1,3-propanediol instead of 400 g of neopentyl glycol, and obtaining at the end of the valeric acid removal an acid value of 5 mgKOH/g.

Example 4 – preparation of 2-methyl-1,3-propanediyl divalerate

Example 1 was repeated, using 346 g (3.84 moles) of 2-methyl-1,3-propanediol instead of 400 g of neopentyl glycol, and obtaining at the end of the valeric acid removal an acid value of 5 mgKOH/g.

Example 5 - characterization of the diesters

The diesters obtained according to examples 1 - 4 were characterized in terms of dynamic viscosity at – 30 °C according to ISO 3219, flash point according to ASTM D7094-04, pour point according to ASTM D5950, and volume resistivity at 25 °C according to ASTM D1169. The results are reported in Table 1 below.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Dynamic viscosity (mPa*s) at - 30 °C	40	24	25	36
Flash point (°C)	154	130	145	145
Pour point (°C)	-93	-96	-66	-96
Volume resistivity (TΩ*cm) at 25 °C	2.0	0.69	0.97	0.89

Example 6 - characterization of the diesters

The diesters obtained according to examples 1 - 4 were characterized in terms of thermal conductivity, thermal diffusivity and specific heat .

The analysis were performed with transient hot wire method, according to ASTM D7896-19. The test equipment was Thermtest THW-L2; thermal conductivity and diffusivity were measured at 40°C whereas the specific heat was calculated as: $C_p \text{ at } 40^\circ\text{C} = \text{Thermal conductivity at } 40^\circ\text{C} / (\text{Thermal diffusivity at } 40^\circ\text{C} * \text{Density at } 40^\circ\text{C})$

The results are reported in Table 2 below.

Table 2

	Ex 1	Ex 2	Ex 3	Ex 4
Thermal conductivity (W/m*K) at 40°C	0.1449	0.1360	0.1449	0.1387
Thermal diffusivity (mm ² /s) at 40°C	0.0675	0.0631	0.0651	0.0638
Specific heat (J/g*K) at 40°C	2.31	2.15	2.23	2.18

Based on the comprehensive characterization of the developed and characterized diesters of the examples above, it is evident that these fluids present highly promising attributes as alternative solutions to PFAS-based fluids. The diesters exhibit remarkable features such as low viscosity at ultra-low temperatures, ensuring efficient flow and circulation even in demanding cooling applications. Additionally, their high flash point enhances safety measures, reducing the risk of potential fire hazards.

Moreover, the diesters demonstrate excellent volume resistivity and permittivity, guaranteeing optimal electrical insulation properties. Furthermore, their exceptional thermal conductivity and heat transfer capacity enable efficient dissipation of heat, contributing to enhanced performance and reliability of electronic systems. Considering these advantageous characteristics, the diesters represent highly favourable substitutes to PFAS fluids in the realm of electronic cooling applications.

In summary, the diesters offer a more sustainable and environmentally friendly option compared to PFAS fluids, particularly in terms of greenhouse gas emissions. Their superior characteristics, coupled with reduced environmental impact, make them highly favourable alternatives for cooling semiconductor components.

CLAIMS

1. Use of a heat-transfer fluid comprising at least one diester of at least one C₂-C₉ aliphatic diol with at least one linear or branched C₂-C₇ aliphatic monocarboxylic acid, in at least one manufacturing step of a semiconductor component.
2. The use according to claim 1, wherein in said heat-transfer fluid said C₂-C₉ aliphatic diol of said diester is selected from the group consisting of: ethylene glycol, 1,2- propanediol, 1,3- propanediol, 1,4-butanediol, 1,3-butanediol, di-ethylene glycol, tri-ethylene glycol, di-propylene glycol, neopentyl glycol, 2-methyl-1,3-propanediol, 1,5-pentanediol, 1,6-hexanediol, 3-metyl-1,5-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol and mixtures thereof.
3. The use according to claim 1 or 2, wherein in said heat-transfer fluid said aliphatic diol of the diester is a C₃-C₆ aliphatic diol.
4. The use according to claim 3, wherein in said heat-transfer fluid said aliphatic diol of said diester is a C₃-C₅ aliphatic diol.
5. The use according to any one of claims from 1 to 4, wherein in said heat-transfer fluid said monocarboxylic acid of said diester is a C₃-C₅ aliphatic monocarboxylic acid.
6. The use according to any one of claims from 1 to 4, wherein in said heat-transfer fluid said monocarboxylic acid of said diester is a C₅-C₇ aliphatic monocarboxylic acid.
7. The use according to any one of claims from 1 to 6, wherein in said heat-transfer fluid said diester is selected from the group consisting of: neopentyl glycol divalerate, 1,2-propanediyl divalerate, 1,3- propanediyl divalerate, 2-methyl-1,3-propanediyl divalerate and mixtures thereof.
8. The use according to any one of claims from 1 to 7, wherein said heat-transfer fluid is used in an indirect cooling system.
9. The use according to claim 8, wherein said indirect liquid cooling system comprises:
 - a liquid cooling loop apt to circulate said heat-transfer fluid;
 - a pump apt to pump said heat-transfer fluid throughout said liquid cooling loop;
 - an heat exchanger apt to cool said heat-transfer fluid; and
 - optionally, a reservoir apt to contain said heat-transfer fluid.

10. The use according to any one of claims from 1 to 9, wherein said semiconductor component is selected from the group consisting of: a microprocessor, a semiconductor wafer, a power control semiconductor, and a semiconductor integrated circuit.
11. The use according to any one of claims from 1 to 10, wherein said at least one manufacturing step of said semiconductor component is selected from the group consisting of: wafer fabrication, polishing, oxidation, photoresist coating, photolithography, etching, deposition, ion implantation, annealing, metal wiring, and testing.
12. A method of manufacturing a semiconductor component, said method including at least one step wherein said semiconductor component exchanges heat with a heat transfer fluid, said heat transfer fluid comprising at least one diester of at least one C₂-C₉ aliphatic diol with at least one linear or branched C₂-C₇ aliphatic monocarboxylic acid.
13. The method according to claim 12, wherein said heat-transfer fluid is an heat-transfer fluid according to any claims from 1 to 7.