(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 028 432 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
25.02.2009 Bulletin 2009/09

(21) Application number: **07113887.9**

(22) Date of filing: **06.08.2007**

(51) Int Cl.:
F28F 13/18 $^{(2006.01)}$
B05D 1/18 $^{(2006.01)}$
B05D 5/08 $^{(2006.01)}$
C08J 7/04 $^{(2006.01)}$
C08J 7/16 $^{(2006.01)}$
C23C 22/00 $^{(2006.01)}$

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

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Remarks:
Claims 11-16 are deemed to be abandoned due to non-payment of the claims fees (Rule 45(3) EPC).

(54) Devices and method for enhanced heat transfer

(57) The present invention relates to devices and method for enhanced heat transfer, in particular to a heat exchanger comprising at least one hydrophilic heat exchanging surface to be thermally contacted with a cooling fluid, wherein said hydrophilic surface has a surface roughness inferior to 1 μm and wherein said hydrophilic surface comprises: at least one discrete area whereon are covalently grafted hydrophobic molecules for controlling onset boiling, or at least one discrete area whereon is coated a hydrophobic polymer for controlling onset boiling. The present invention also relates to a process for constructing a heat exchanger according to the invention.

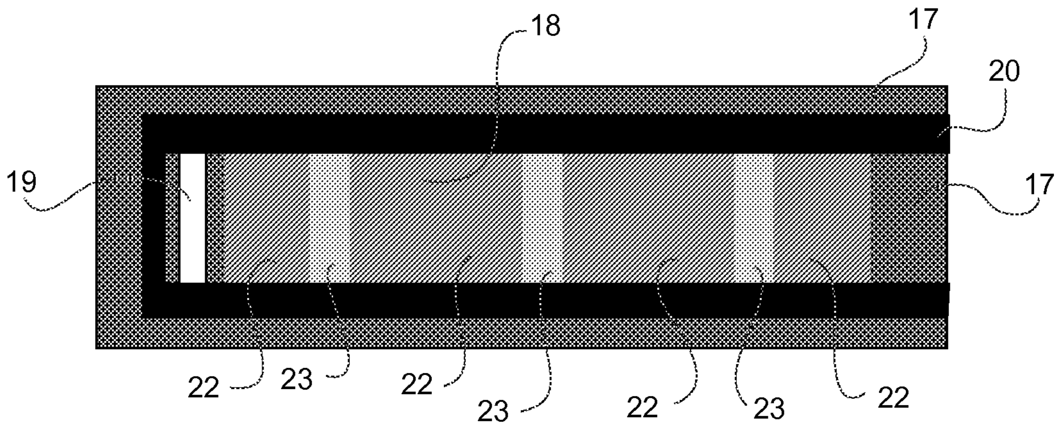

FIG. 2C

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Description

Field of the invention

[0001] This invention relates to devices for efficient heat transfer. More particularly, the present invention relates to a device and method for cooling heat-producing bodies or components using a two-phase cooling heat transfer device comprising surfaces having modified surface wettability to control thermal transfer in multi-phase flows.

Background of the invention

[0002] Controlling heat transfer is a major preoccupation of the industry, and especially of the electronic industry. Particularly in microprocessors, the rise in heat dissipation levels accompanied by a shrinking thermal budget has resulted in the need for new cooling solutions beyond conventional thermal management techniques. In the microelectronics industry, for example, advances in technology have brought about an increase in transistor density and faster electronic chips. As electronic packages increase in speed and capability, the heat flux that must be dissipated to maintain reasonable chip temperatures has also risen. Thermal management is recognized as a major challenge in the design and packaging of state-of-the-art integrated circuits in -single-chip and multichip modules.

Two-phase or "boiling" heat transfer is a method of dissipating high amounts of thermal energy. Tw-o-phase heat transfer involves, generally, the evaporation of a liquid in a hot region and the condensation of the resulting vapor in a cooler region. It has been shown that more heat is removed as the nucleation site density of the surface increases. The phase transition or entrance region lengths in a tube for standard applications is typically 5-10 % of the total and it is usually not important, but for the compactness and miniaturization perspectives of microcooling systems, these lengths may be 20-40% or more of the whole duct length. Therefore, controlling the transition regimes and zones may produce a clear advantage for the phase transition cooling systems.

Furthermore, it is well known that surface roughness significantly affects incipient superheat and nucleate boiling heat transfer.

US patent No 5,814,392 for example discloses a boiling enhancement coating composition comprising a glue, particulate material, and solvent which imparts a surface microstructure. The disadvantage of these coatings is that when applied to semiconductors for example, they can cause adverse effects such as material incompatibility.

[0003] US patent No 4,050,507 discloses a method for customizing nucleate boiling heat transfer from electronic units immersed in a dielectric coolant using a dielectric liquid as refrigerant and a surface structure containing laser drilled holes at determined places. The disadvantage of this technique is that drilling can cause damaging of certain components of electronic equipment, furthermore drilled surfaces provide minimal enhancement.

[0004] US patent No 3,301,314, a method and means for increasing the heat transfer coefficient between a wall and boiling liquid are disclosed wherein cavities are introduced on the surface and suitable treatment for cavities is provided by using low surface energy material for example.

[0005] W00118462 discloses a plasma polymerized coating with hydrophilic groups.

[0006] US20060191671 relates to improving heat exchange by providing a hydrophilic surface by means of grafted and/or coated nanoparticles.

[0007] W02005/124257 discloses increasing heat transfer from a heat generating device to a circulating fluid by artificially adding bubbles at a calculated frequency.

[0008] The aim of the invention is to control the onset of boiling in preferably a two-phase heat transfer system using the control of local wettability of a surface.

Summary of the invention

[0009] The present invention comprises achieving surface wettability manipulation to control thermal transfer in multiphase flows by controlling onset boiling.

[0010] In a first aspect, the present invention provides a heat exchanger or heat exchange device comprising at least one hydrophilic heat exchanging surface to be thermally contacted with a cooling fluid, wherein said hydrophilic surface has a surface roughness inferior to 1 μm and wherein said hydrophilic surface comprises at least one discrete area whereon is covalently grafted hydrophobic molecules for controlling onset boiling, or, at least one discrete area whereon is coated a hydrophobic polymer or a solution of hydrophobic molecule for controlling onset boiling.

[0011] In a second aspect, the present invention provides a process for cooling an object to be cooled comprising thermally contacting an object to be cooled with at least one heat exchanger according to the present invention and cooling said object by operating said device. In a third aspect, the present invention provides a process for controlling the boiling onset of a fluid, comprising thermally connecting said fluid with at least one hydrophilic surface,

wherein said hydrophilic surface has a surface roughness inferior to 1 μm and wherein said hydrophilic surface comprises at least one discrete area whereon are covalently grafted hydrophobic molecules for controlling onset boiling or at least one discrete area which is coated with a hydrophobic polymer.

[0012] In a four aspect, the present invention provides a process for constructing a heat exchanger according to the present invention, comprising the steps of:

a) treating at least one surface having a surface roughness inferior to 1 μm and wherein said hydrophilic surface by wet chemistry using oxidation/hydroxylation/reduction in an acid or alkaline environment, thereby rendering said surface hydrophilic, and

b) coating or covalently grafting at least one discrete area of the activated surface of step

(a) with hydrophobic molecules, thereby obtaining at least one hydrophilic surface having a surface roughness inferior to 1 μm and wherein said hydrophilic surface, and provided with at least one area which is coated or covalently grafted with hydrophobic molecules.

The present process comprises adding controlled chemical heterogeneities to the surface. This is achieved by chemical grafting or coating. Chemical heterogeneities are created and formation of bubbles or microbubbles can be controlled at precise localizations on the surface.

The present invention will now be further described. In the following passages, different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous. The description is only given by way of example and does not limit the invention. The reference numbers relate to the hereto-annexed figures.

Brief description of drawings

[0013]

Figure 1 represents a schematic experimental set-up of a device according to an embodiment of the present invention.

Figure 2A represents the cross-sectional side view of a schematic set-up of a surface according to an embodiment of the present invention. Figure 2 B represents the cross-sectional front view of a schematic set-up of a surface according to an embodiment of the present invention. Figure 3A represents the top view of a schematic set-up of a surface according to an embodiment of the present invention.

Figure 3 represents an assembling scheme showing the set up of a surface of a device according to an embodiment of the present invention.

Figures 4 and 5 represent schemes showing the set up of a surface of a device according to an embodiment of the present invention.

Figure 6 represents snapshot photographs of the surface of a device according to an embodiment of the present invention in use.

Detailed description of the invention

[0014] The control of the boiling onset in a heat transfer system according to the invention comprises modifying the local spatial surface wettability. The present invention is particularly suitable for the thermal control in two-phase heat exchangers.

[0015] The "liquid wettability", or "wettability," of a solid surface is determined by observing the nature of the interaction occurring between the surface and a drop of a given liquid disposed on the surface. A surface having a high wettability for the liquid tends to allow the drop to spread over a relatively wide area of the surface (thereby "wetting" the surface). In the extreme case, the liquid spreads into a film over the surface. On the other hand, where the surface has a low wettability for the liquid, the liquid tends to retain a well-formed, ball-shaped drop. In the extreme case, the liquid forms nearly spherical drops on the surface that easily roll off of the surface at the slightest disturbance.

The term "contact angle" or "wetting contact angle" as used herein refers to a parameter which quantifies the intrinsic affinity between a liquid and a solid (or another non-miscible liquid) in another fluid environment, usually gas and more usually air. The contact angle is the angle formed by the liquid edge at the solid (or three-phase contact line) and the solid surface plane. There are various methods to measure the contact angle but the most usual one is the sessile drop method. The sessile drop method consists in depositing a drop of liquid on a solid surface and the contact angle is measured visually with a goniometer. Practically the contact angle is a function of possible heterogeneities on the solid surface (usually, roughness and chemical heterogeneities). As perfectly homogeneous surfaces are very rare, when one measure the contact angle, there is a hysteresis. The contact angle can take any value, depending on the way the contact line was formed at a precise location, between two extremes: the so-called advancing static contact angle and the so-called receding static contact angle. The advancing static contact angle is the maximum value the contact angle can take without movement of the contact line while the receding static contact angle is the minimum value that it can take.)

[0016] As used in this specification, the term "at least one discrete area" refers to at least one individual, isolated area. In an embodiment, said at least one discrete area is selected such as to be near or at the location of a hot spot in an element to be cooled. The term "hot spot" or "local overheating area" refers to a point where a peak temperature is generated. For example, a hot spot may be a point where an abnormally high temperature is maintained due to excessive heat generation or heat accumulation.

[0017] The present invention thus concerns, a heat transfer or heat exchange device for cooling an object to be cooled comprising at least one hydrophilic heat exchanging surface to be thermally contacted with a cooling fluid, wherein said hydrophilic surface is smooth, i.e., has a surface roughness inferior to 1 μm and wherein said hydrophilic surface comprises at least one discrete area whereon hydrophobic molecules are covalently grafted, or at least one discrete area whereon is coated a hydrophobic polymer for controlling onset boiling.

[0018] As used herein, the term "surface roughness" encompasses mean amplitude, maximum amplitude and RMS roughness, and is a measure of the relative elevations of surface irregularities. According to the present invention the surface is particularly smooth, i.e. has a surface roughness (RMS average) below 1 μm.

[0019] In an embodiment, said hydrophilic surface has a roughness below 1μm, preferably below 0.1 μm.

[0020] Preferably, the at least one discrete area is provided with a hydrophobic coating having a thickness lower than 1 μm, preferably from 1 nm to 700 nm.

[0021] In an embodiment, at least two hydrophilic areas are spaced by a distance in the range of about 0.01 mm to about 10 mm, preferably about 0.05 mm to about 5 mm.

[0022] In an embodiment, the grafted area has a surface ranging from 0.001 mm^2 to about 10 mm^2, preferably 0.005 mm^2 to about 5mm^2.

[0023] The present invention provides a system with a so-called relative hydrophobic pattern in a so-called relative hydrophilic environment. In an embodiment, there must be a difference of contact angle of at least 10° between the relative hydrophobic and hydrophilic areas. This can be achieved with for example an area having a contact angle of at least 110° which will be called "relative hydrophobic"; and an area having a contact angle of at most 100° which will be called "relative hydrophilic" or in another example, with an area having a contact angle of 45° ("relative hydrophobic") and an area having a contact angle of 10° ("relative hydrophilic"). In both cases the system will work, i.e., boiling will appear preferably on the "relative hydrophobic" patterns of the surface.

[0024] Preferably, the difference of contact angle between the hydrophilic surface and the hydrophobic grafted area is at least 10°, preferably at least 20°, preferably at least 30°, preferably at least 40°, more preferably at least 50°, for example at least 60°, at least 80°, at least 90°, at least 120°, at least 150°, or 180°.

[0025] In an embodiment, the present process comprises adding controlled chemical heterogeneities to the surface by chemical grafting.

[0026] In an embodiment, an important factor is the difference in contact angle. This difference can be the result of various type of grafting: a highly hydrophobic molecule grafted with a low density of molecule per unit surface on the hydrophobic zone or a less hydrophobic molecule grafted with a high density of molecule on the hydrophobic zone.

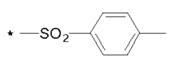
[0027] In an embodiment, said hydrophobic molecules are silane derivative of the general formula

[0028] $X_3Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$, $X_2(R^1)Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$ or $X(R^1)(R^2)Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$,
wherein X is selected from halogen or $C_{1\text{-}6}$ alkoxy, preferably Cl, Br or OMe, OEt; n is an integer selected from 1 to 20; m is an integer selected from 0 to 20; R^1, R^2 are independently $C_{1\text{-}10}$ alkyl; Y is selected from Me, CF_3, CHF_2, CH_2F, $CH{=}CH_2$, CN, CH=O, phenyl, epoxide, halogen, SH, NH_2, OH, N=C=O, N=C=S, CO_2H or derived esters thereof.

[0029] For example, said hydrophobic molecule can be selected from the group comprising ethyltrichlorosilane, n-propyltrichlorosilane, n-butyltrichlorosilane, n-hexyltrichlorosilane, n-octyltrichlorosilane, octenyltrichlorosilane, octylmethyldichlorosilane, n-nonyltrichlorosilane, n-decyltrichlorosilane, dodecyltrichlorosilane, dihexyldichlorosilane, dioctyldichlorosilane, tridecyltrichlorosilane, hexadecyltrichlorosilane, octadecyltrichlorosilane, n-eicosyltrichlorosilane, n-docosyltrichlorosilane, phenylytrichlorosilane, (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1-trichlorosilane, ethyltriethoxysilane, n-propyltrimethoxyslane, n-butyltrimethoxysilane, n-hexyltrimethoxysilane, n-octyltriethoxysilane, n-dodecyltriethoxysilane, n-octadecyltriethoxysilane, n-octadecyltrimethoxysilane, phenyltriethoxysilane, (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1-triethoxysilane, and mixture thereof.

[0030] In an embodiment, said hydrophilic surface can be a hydroxylated surface. In an embodiment said hydrophilic surface can be a hydrogenated surface.

[0031] In an embodiment, said hydrophobic molecules are alkene or alkyne, each optionally substituted by one or more substituent selected from alkyl, haloalkyl, halo, alkenyl, cyano, epoxy, thio, amino, hydroxyl, isocyano, isothiocyano, carboxy, polyalkoxy, alkylarylsulfoxypolyalkoxy, heteroaryloxycarbonylalkylpolyalkoxy. In an embodiment, said optionally substituted alkene is of Formula CH_2=CH-R^3 wherein R^3 is selected from C_xH_{2x+1}, C_xF_{2x+1}, -$(CH_2)_q$-(O-CH_2-$CH_2)_p$-OR^4, wherein R^4 is selected from C_{1-3}alkyl, alkylarylsulfoxide, heteroaryloxycarbonylalkyl,



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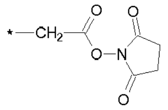

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or mixture thereof,
wherein x is an integer from 3 to 50, wherein q is an integer from 0 to 20, and wherein p is an integer from 3 to 20. Suitable compounds include but are not limited to heptadecafluoro-1-decene and octadecene.

[0032] The term "alkene" refers to a straight or branched alkane chain containing at least one unsaturation in the form of a single carbon to carbon double bond and having 3 to 52 carbon atoms, for example 3 to 40 carbon atoms.

[0033] The term "alkyl" by itself or as part of another substituent, refers to a straight or branched saturated hydrocarbon group joined by single carbon-carbon bonds having 1 to 10 carbon atoms, for example 1 to 8 carbon atoms, for example 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. Thus, for example, C_{1-4}alkyl means an alkyl of one to four carbon atoms. Examples of alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, *tert*-butyl, 2-methylbutyl, pentyl iso-amyl and its isomers, hexyl and its isomers, heptyl and its isomers and octyl and its isomers. Where alkyl groups as defined are divalent, i.e., with two single bonds for attachment to two other groups, they are termed "alkylene" groups. Non-limiting examples of alkylene groups includes methylene, ethylene, methylmethylene, propylene, ethylethylene, and 1,2-dimethylethylene.

[0034] The term "aryl" as used herein by itself or as part of another group refers but is not limited to 5 to 14 carbon-atom homocyclic (i.e., hydrocarbon) monocyclic, bicyclic or tricyclic aromatic rings or ring systems containing 1 to 4 rings which are fused together or linked covalently, typically containing 5 to 8 atoms; at least one of which is aromatic. Where aryl groups as defined are divalent, i.e., with two single bonds for attachment to two other groups, they are termed "arylene" groups.

[0035] The terms "heterocyclyl" as used herein by itself or as part of another group refer to an optionally substituted non-aromatic, fully saturated or partially unsaturated cyclic groups (for example, 3 to 13 member monocyclic, 7 to 17 member bicyclic, or 10 to 20 member tricyclic ring systems, or containing a total of 3 to 10 ring atoms) which have at least one heteroatom in at least one carbon atom-containing ring, optionally substituted with 1, 2 or 3 substituents selected from oxy, alkyl, halo, haloalkyl, carboxy, amino or sulfonyl . Each ring of the heterocyclic group containing a heteroatom may have 1, 2, 3 or 4 heteroatoms selected from nitrogen atoms, oxygen atoms and/or sulfur atoms, where the nitrogen and sulfur heteroatoms may optionally be oxidized and the nitrogen heteroatoms may optionally be quaternized. The heterocyclic group may be attached at any heteroatom or carbon atom of the ring or ring system, where valence allows. Exemplary heterocyclic groups include maleimidyl, succinimidyl, piperidinyl, imidazolinyl, imidazolidinyl, isoxazolinyl, oxazolidinyl, isoxazolidinyl, thiazolidinyl, isothiazolidinyl, piperidyl, succinimidyl, 3H-indolyl, indolinyl, isoindolinyl, chromenyl, isochromanyl, xanthenyl, 2H-pyrrolyl, 1-, 2-, 3-pyrrolinyl.
The term "amino" refers to the group -NH_2.

[0036] The term "halo" or "halogen" as a group or part of a group is generic for fluoro, chloro, bromo or iodo.

[0037] The term "haloalkyl" alone or in combination, refers to an alkyl radical having the meaning as defined above wherein one or more hydrogens are replaced with a halogen as defined above. Non-limiting examples of such haloalkyl radicals include chloromethyl, 1-bromoethyl, fluoromethyl, difluoromethyl, trifluoromethyl, 1,1,1-trifluoroethyl and the like.

[0038] The term "epoxy" as used herein refers to cyclic ether with only three ring atoms.

[0039] The term "thio" as used herein refers to the -SH group.

[0040] The term "isocyano" as used herein refers to the group of formula -N=C=O.

[0041] The term "isothiocyano" as used herein refers to a group of formula -N=C=S.

[0042] The term "polyalkoxy" as used herein refers to a group of formula -(O-$R^7)_t$-OR^8, wherein t is an integer from 1 to 8, and R^7 is alkylene and R^8 is alkyl.

[0043] The term "alkylarylsulfoxypolyalkoxy" as used herein refers to a group of formula

- (O-$R^7)_t$-OSO_2-R^9-R^{10}, wherein t is an integer from 1 to 8, and R^7 is alkylene, wherein R^9 is arylene and R^{10} is alkyl.

[0044] The term "heteroaryloxycarbonylalkylpolyalkoxy", as used herein refers to a group of formula $-(O-R^7)_t-CO-O-R^{11}$, wherein t is an integer from 1 to 8, and R^7 is alkylene and R^{11} is heterocyclyl, preferably maleimidyl or succinimidyl

[0045] As used in the specification and the appended claims, the singular forms "a", "an," and "the" include plural referents unless the context clearly dictates otherwise. By way of example, "an alkene" means one alkene or more than one alkene.

[0046] Asterisks (*) are used herein to indicate the point at which a mono-, bi- or trivalent radical depicted is connected to the structure to which it relates and of which the radical forms part.

[0047] In an embodiment, the present process comprises adding controlled chemical heterogeneities to the surface by coating hydrophobic polymer to at least one discrete area of a smooth hydrophilic surface.

[0048] In an embodiment, the hydrophobic polymer can be selected from polypropylenes, polyethylenes, polytetrafluoroethylenes, polyvinylidene fluorides, polysulfones, polyethersulfones, polyvinylchlorides, fluorinated polymers, polyacrylics, polyamides, polyimides, polyesters, polyolefins, polyethers, polyamines, polyanhydrides, polycarbosilanes, polysilanes, polysilazanes, polysulfides, polyurethanes, polysiloxanes, polystyrenes, vinyl polymers, polyvinyl acetates, vinylidenes polymers, epoxy resins, polyamide imide, polybutylene terephtalate, polyether imides, polyethylene terephtalate, polymethylene oxides, diene elastomers, carbohydrate polymers, polyacetals, polynitriles, polyketones, polyphosphazenes, polypeptides, polysaccharides, polyisocyanides, polyisocyanades, polycarbonates or copolymers of these basic structures.

[0049] In particular, at least one discrete area of a smooth hydrophilic surface is provided with thin hydrophobic coating. For example, the hydrophobic coating can have a thickness of less than 1 μm, preferably less than 100 nm, more preferably less than 50 nm.

[0050] The hydrophobic polymer can be provided in a coating composition comprising suitable additives and solvents or diluent if needed. The hydrophobic polymer or the coating composition may be applied to the surface by any known technique using a mask and including photolithography, dip coating, spin coating, scan coating, spray coating, bar coating, CVD, PVD, curtain coating and plasma spraying.

[0051] The present invention encompasses the use of a heat exchanger according to the invention for thermally controlling a device to be cooled. In particular, the present invention encompasses the use of a heat exchanger according to the invention for cooling electric, microelectric, electronic and microelectronic components.

[0052] The present invention provides a process for cooling an object to be cooled comprising thermally connecting an object to be cooled with at least one heat exchanger according to the invention and cooling said heated object by operating said exchanger. The present invention has many applications such as cooling systems for electronic devices such as chips, laptops, desktop computers, camera elements, laser diodes, and the like.

[0053] In an embodiment, the present invention provides a process for the thermal control of solid surfaces, characterized by the onset of a two-phase flow regime on a given portion of a solid surface, provided with a hydrophilic/hydrophobic pattern in order to localize the onset of the phase transition. In an embodiment, said process uses a patternation able to start phase transition in a given position.

[0054] The present cooling process can be used for the cooling of a dissipating mechanical solid component based on the onset of high convection fluxes only in the close region near hot spots. The process provides for the enhancement of heat fluxes in desired positions of a component.

[0055] The present invention provides the ability of localizing the boiling or the condensation onset, which is highly profitable for small, compact heat exchanger, even in a microscale size.

[0056] The present process and device are particularly suitable for the cooling of an electronic component, based on the controlled onset of boiling only in the region near hot spots.

[0057] In an embodiment, said thermal control fluid is selected from the group comprising liquids including but not limited to water, hydrofluorocarbons (HFC), glycol, ammonia, isopropylene, ethanol and other alcohols.

[0058] In an embodiment, said coated or grafted surface is selected from the group comprising glass, aluminium, steel, copper, iron alloys, and silicon wafers.

[0059] The coated or grafted surfaces can be obtained using method selected from coating, dip-coating, spin-coating, spray-coating, covalent chemical grafting and microcontact printing (μCP).

[0060] The present invention provides for the controlled onset of boiling which can be used to compensate hot and cold spots onto surfaces, in order to decrease the thermomechanical stresses in presence of strong temperature gradients. Preferably, the position of the onset of boiling is decided by an analytical method and by a patternation of the solid surface with a hydrophobic molecule.

[0061] The inventors have found out that the localization of the boiling starting point, i.e. the position where bubbles begin to appear on the solid surface (of any possible shape and flatness) when this surface is heated, is influenced by the local wettability of the heated solid surface where the liquid refrigerant flows and in particular by the presence of wettability patterns. When the solid is homogeneous in chemistry and structure, and its surface is smooth, bubbles tend to nucleate preferably on the hydrophobic patterns, and so the onset of boiling can be controlled by the position of these patterns. According to the present invention, around these hydrophobic patterns the surface is hydrophilic.

[0062] The present invention also encompasses a process for constructing a heat exchanger according to the invention, comprising the steps of:

a) treating at least one surface having a surface roughness inferior to 1 μm and wherein said hydrophilic surface by wet chemistry using oxidation/hydroxylation/reduction in an acid or alkaline environment, thereby rendering said surface hydrophilic, and

b) coating or covalently grafting at least one discrete area of the activated surface of step

(a) with hydrophobic molecules, thereby obtaining at least one hydrophilic surface having a surface roughness inferior to 1 μm and wherein said hydrophilic surface , provided with at least one area which is coated or covalently grafted with hydrophobic molecules.
Preferably, said surface is selected from glass, aluminium, steel, copper, iron alloys, or silicon wafers.
Step (a) can comprise the oxidation/hydroxylation of the surface by any available technique (physical or chemical), preferably the wet-chemistry technique using a solution of an oxidant in acidic or basic media, such as H_2O_2/H_2SO_4, H_2O_2/TFA, H_2O_2/HF, $K_2Cr_2O_7/H_2SO_4$, oxone/H_2SO_4, H_2O_2/NH_4OH, or in organic media, such as an organic peracid, Br_2 in solution. The activation may also be carried out by dipping the solid surface in sequences of solutions of an oxidant in acidic or basic media. Suitable solutions of an oxidant in acidic or basic media, are e.g. H_2O_2/H_2SO_4, H_2O_2/TFA, H_2O_2/HF, $K_2Cr_2O_7/H_2SO_4$, oxone/H_2SO_4, H_2O_2/NH_4OH, or e.g. in organic media, such as an organic peracid, Br_2 in a suitable solution, or a combination of these solutions in specific sequences, such as HF in water followed by H_2O_2 in water iterated for several times (e.g. number of repetitions: 3) or NH_4OH/H_2O_2 in water followed by HCl/H_2O_2 in water (e.g. number of repetitions: 1). Preferably, the surface treatment of step (a) can be performed by treating said surface with: (i) a mixture H_2SO_4/H_2O_2 in water, or (ii) a sulfochromic mixtures, or (iii) a mixture NH_4OH/H_2O_2 in water followed by HCl/H_2O_2 in water, optionally iterated, or (iv) HF in water followed by H_2O_2 in water and optionally iterated. The temperature is preferably comprised between -15°C and +150°C and the duration of the treatment comprised between a few seconds to several hours.

[0063] In an embodiment, the surface grafting of step (b) is performed through covalent coupling with a silane derivative of the general formula $X_3Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$, $X_2(R^1)Si\text{-}(CH_2)_n$ - $(CF_2)_m\text{-}Y$ or $X(R^1)(R^2)Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$, as defined above.

[0064] In another embodiment, the surface grafting of step (b) is performed through covalent coupling with an alkene or an alkyne, each optionally substituted by one or more substituent selected from alkyl, haloalkyl, halo, alkenyl, cyano, epoxy, thio, amino, hydroxyl, isocyano, isothiocyano, carboxy, polyalkoxy, alkylarylsulfoxypolyalkoxy, or heteroaryloxycarbonylalkylpolyalkoxy.

[0065] Preferably, the covalent grafting of step (b) is performed by microcontact -printing.

[0066] In yet another embodiment, the surface coating of step (b) is performed by coated said hydrophilic surface with a hydrophobic polymer selected from polypropylenes, polyethylenes, polytetrafluoroethylenes, polyvinylidene fluorides, polysulfones, polyethersulfones, polyvinylchlorides, fluorinated polymers, polyacrylics, polyamides, polyimides, polyesters, polyolefins, polyethers, polyamines, polyanhydrides, polycarbosilanes, polysilanes, polysilazanes, polysulfides, polyurethanes, polysiloxanes, polystyrenes, vinyl polymers, polyvinyl acetates, vinylidenes polymers, epoxy resins, polyamide imide, polybutylene terephtalate, polyether imides, polyethylene terephtalate, polymethylene oxides, diene elastomers, carbohydrate polymers, polyacetals, polynitriles, polyketones, polyphosphazenes, polypeptides, polysaccharides, polyisocyanides, polyisocyanades, polycarbonates or copolymers of these basic structures.

[0067] The following examples are presented to further illustrate exemplary embodiments of the invention and should not be construed as limiting the invention in any way.

Examples

[0068] Experiments were conducted on globally flat surfaces, smooth down to a nanometer scale. Both glass and silicium surfaces were used.

[0069] Before building the experimental testing rig as represented in Figures 1, 2 and 3, a Maple program was written to calculate:

1. the power needed to have boiling at a fixed flow rate in a reasonable position of the plate;

2. the temperature surface of the heater;

3. the inlet temperature of the fluid.

[0070] The equation governing the heat transfer in the test section was written starting from an energy balance between all the layers of the testing part.

[0071] Because the flow inside a channel is completely enclosed, an energy balance may be applied to determine how the mean temperature T(x) varies with position along the channel and how the total convection heat transfer q_{conv} is related to the difference in temperatures at the channel inlet and outlet. Figures 4 and 5 represent schemes showing the set up of the experimental testing section with the different parameters and constants measured.

[0072] In particular, Figure 4 represents the geometry of the test section, illustrating all the components making the test section itself. The components are described in details with respect to Figures 1 to 3. The test section is made up of a channel closed on the top, and in the Figure 4 it is possible to see the geometry of the element of fluid moving inside the channel. The individuation illustrated in Figure 4 was used to mathematically model the heat transfer inside the test section.

Figure 5 represents a side view of the test section and highlights the positioning and the boundary of the control volume respect to the geometry. The location of the thermal resistances, both convective and conductive that are involved in the global heat transfer process inside the test section is shown.

[0073] Consider the tube flow of Figure 5. Fluid moves at a constant flow rate, and convective and conductive heat transfer occurs at the inner surface of the channel and in the vertical direction of glass and aluminum. Typically, fluid kinetic and potential energy changes, as well as energy transfer by conduction in the axial direction, are negligible. Hence, if no shaft work is done by the fluid as it moves by the tube, the only significant effect will be those associated with thermal energy changes.

[0074] Applying conservation of energy to the differential control volume of Figure 5, we obtain

$$\frac{dT(x)}{dx} * \dot{m}_w * c_{p\_w} * \frac{1}{P} = \frac{T_s - T(x)}{R_{base}(x)} - \frac{T(x) - T_{ext}}{R_{up}(x)}$$

wherein:

- $T(x)$ = temperature of the water film according to the x-coordinate, [K];
- $\dot{m}_w$ = water mass flow rate, [kg/s] ;
- c_{p_w} = specific heat of water, $\left[\frac{kJ}{kg * K}\right]$;
- P = perimeter of the control volume of the flow, [m];
- T_s = surface temperature of the heater (assumed constant and not space-depending), [K];
- T_{ext} = ambient temperature, [K];
- $$R_{base} = R_{plate} + R_{basement} + R_{water}$$
- $$R_{up} = R_{ext} + R_{glass} + R_{water}$$

- $R_{basement} = \frac{sp\_Al}{k_{Al}}$, being:

  sp_Al = thickness of the aluminum plate, [m];

  k_{Al} = conductive heat transfer coefficient of aluminum, $\left[\frac{W}{m*K}\right]$;

  $R_{basement}$= conductive heat transfer resistance of the aluminum basement, $\left[\frac{m^2*K}{W}\right]$.

-

$$R_{plate} = \frac{sp\_plate}{k_{plate}},$$

  being:
  sp_plate = thickness of the glass coated plate, [*m*];

  k_{plate} = conductive heat transfer coefficient of the glass plate, $\left[\frac{W}{m*K}\right]$;

  R_{plate}= which represents the conductive heat transfer resistance of the glass coated plate, $\left[\frac{m^2*K}{W}\right]$.

[0075] •

$$R_{water} = \frac{1}{h_{water(x)}},$$

being:
[0076] $h_{water(x)}$ = convective heat transfer coefficient of the water flowing in the channel,

[0077] $\left[\frac{W}{m^2*K}\right]$;

[0078] R_{water}= convective heat transfer resistance of the fluid flowing on the coated plate, $\left[\frac{m^2*K}{W}\right]$.

[0079] •

$$R_{glass} = \frac{sp\_glass}{k_{glass}},$$

being: *sp_glass* = thickness of the covering glass, [m]; k_{glass} = conductive heat transfer coefficient of the covering glass,

$\left[\frac{W}{m*K}\right]$; R_{glass} = conductive heat transfer resistance of the glass plate used to close the top of the channel, $\left[\frac{m^2*K}{W}\right]$.

[0080] •

$$R_{ext}=\frac{1}{h_{ext}},$$

h_{ext} = convective heat transfer coefficient of the air outside the test section, $\left[\frac{W}{m^2*K}\right]$; R_{ext} = convective heat transfer resistance of the air outside the system, $\left[\frac{m^2*K}{W}\right]$.

[0081] The rate of convection heat transfer to the fluid should equal the rate at which the fluid thermal energy increases. The fixed solid surface temperature situation was considered.

[0082] The experimental results of the boiling onset described hereunder and the position predicted by the program were in good agreement.

Example 1: Experimental apparatus

[0083] Figure 1 represents schematically the experimental set-up built for the experiments. The experimental rig 1 was made of different components: a tank 8 for the water, a helium tank 10, a temperature regulator 9, a gear magnetically driven pump 7, a temperature controller 6 with a thermal sensor, a heater 5 and the testing section. The testing section comprised on the surface of the heater 5 a surface 2 with hydrophobic pattern provided in a channel 3. The water tank 8 was thermally isolated with polystyrene (not shown) on the top and a double wall on the rest of the tank. A helium bubbling tube 11 was inserted into the tank 8 in order to remove possible gas and micro bubbles in the water tank 8. The refilling of water was regular and the water coming out of the channel 3 was simply removed.

[0084] The circuit (tube) 12 providing the water from the reservoir 8 to the gear pump 7 and the circuit (tubing) 13 providing water from the gear pump 7 to the channel 3 was isolated with polystyrene (not shown) to reduce the thermal losses and to keep the temperature of the fluid entering the testing section almost at the same value as the one of the reservoir 8 (water tank). The water temperature was measured at the exit of the channel. All the experiment were performed with an incoming water temperature of 90°C, but the temperature range 4can vary from the ambient temperature to 95°C.

[0085] The heater 5 of the plates was a Chromalox WS-605 providing 500W heat on its surface, this being of approximatively 120 x 60 mm. The heater 5 was regulated by a power controller (Watlow DIN-A-MITE) (not shown), a temperature controller 6 (Watlow EC) and a J-type thermocouple 4. The temperature controller 6 was operably connected to heater 5 through wire 14 and to the thermocouple 4 through wire 15.

[0086] The sensor was used to measure the temperature of the surface of the heater 5 and to compare it with the preset value; if there was a difference between the numbers (for example, if the temperature of the heater 5 was below the preset temperature) the controller 6 gave power to the heater 5 in order to reach the desired condition.

[0087] Figures 2A, 2B, 3C show detailed description of the testing section comprising the patterned surface 18. On the top and side views of Figure 2 the flow was going from left to right.

[0088] The testing section comprised an aluminum plate 17 provided with a cavity lodging the patterned surface 18. The channel for the water was created using a Teflon spacer 20 and a glass plate 21 provided thereon. The testing section was fixed on the heater 5 with a high conductivity paste 16 in order to ensure good contact and uniform heat flux between the two parts. The patterned surface 18 comprises hydrophilic areas 22 and hydrophobic areas 23.

[0089] Figure 3 represents an exploded view of the testing section. The basement of the testing section was made of an aluminum plate 17 having a thickness of 2mm. In the middle of the plate 17, a cavity 27 for holding the patterned surface 18 was provided having a depth of one millimeter and sides of 25mm and 76mm using a numeric controlled cutter machine. The plate 17 further comprised a slit 27 to allow the filling of the channel with water. The plate 17 is further operably connected to a water box 25 comprising an inlet (not shown) for receiving water and an outlet 26 for providing water to the channel through the slit 24 of the plate 17. The box is operably connected through tubing 13 to the pump 7. The coated glass plate 18 was positioned in the cavity and high conductivity paste (not shown) was provided between the two parts.

[0090] The walls 20 delimiting the channel 19 were made of Teflon as its back side (height of the channel: 0.6 mm; width of the channel: 18 mm; length of the channel: almost 100 mm).

[0091] The top of the channel 19 was made of glass plate 21 to ensure the recording by a high speed camera of the bubbles formation and growth and their possible movements.

[0092] The patterned solid surface 18 was made of a glass plate (1 mm x 25 mm x 75 mm) on which an OTS (octadecyltrichlorosilane) monolayer was grafted using the microcontact printing method on defined zones 22. The glass was beforehand activated by use of a piranha solution (H_2SO_4/H_2O_2). Microcontact printing comprised using a polydimethylsiloxane (PDMS) stamp (which was dipped in an OTS solution. The stamp can be made of any other suitable elastomeric material with a slight porosity. The PDMS stamp was then stamped on the activated solid surface. The typical duration of the stamping ranged from 30 seconds to few minutes (it can be shorter in time). In the present example the OTS stamped area had U-shape.

[0093] The patterned site were hydrophobic (θ_{adv}= 107°, $\theta_{rec=}$ 80°) while the rest of the plate was more hydrophilic (θ_{adv}= 95°, θ_{rec}=55°).

[0094] The testing section created was a wafer with different components kept together by two pair of iron bars and screws.

[0095] In the working conditions, the channel was completely filled with water.

Example 2:

[0096] The characteristics of each experiment were completely fixed deciding three variables: the volumetric flow rate of water, the water inlet temperature and the heater surface temperature.

[0097] During the experiments, these three features have been adjusted in order to localize the position of the boiling onset at few centimeters after the entrance of the channel.

[0098] The gear pump allowed different volumetric flow rate. Two different values of flow rate have been selected for the experiment: 20 ml/min and 25 ml/min. In both cases, the position of the boiling onset was almost the same and it coincided with the position of the first hydrophobic pattern.

[0099] The temperature of the heater was fixed at 110°C on the controller (+/- 1°C), and there was a uniform distribution of this temperature also on the basement of the testing section.

[0100] Figure 6 represents snapshots temporal phases of the appearing of the bubbles in the coated region. Patterned glass surface: T_W=90°C; T_S=120°C and V_F=20 mL/mn (left); V_F=25 mL/mn (middle); Patterned silicon surface: V_F=25 mL/mn (left). The boiling shape is progressively appearing on and following preferably the hydrophobic pattern. In the images, the dimensions represent in reality an area of 24.91 mm x 12.46 mm. The flow was going from right to left, and the viewing was focused at the central zone of the channel.

[0101] It can be seen from the picture in Figure 6 that the bubbling zone is expanding with time. The bubbling zone after appearing near one side of the wall is expanding strongly to the centre of the channel, and also slightly upward. For both flow rates, the expanding zone is following the hydrophobic part.

Even if the position of the boiling onset are slightly different (at least 0.15 mm) for the two flow rates considered, the two sequences are similar in the behavior of the expanding zone, where its upfront part follows the upfront limit of the first hydrophobic zone in order to fill completely the hydrophobic zone. The bubbling zone is expanding with the "tongue" like shape, and behind this area the bubbling disappears. The tongue-like shape has, in the example, the largeness of the hydrophobic pattern, i.e., 3 mm. In the hydrophobic zone, because of mass conservation simple arguments, the velocity is higher than behind the "tongue" like zone; nevertheless in the hydrophobic part the liquid is continuing to evaporate while on the part behind (and so slower and further from the entrance) it is not.

Claims

1. Heat exchanger comprising at least one hydrophilic heat exchanging surface to be thermally contacted with a cooling fluid, wherein said hydrophilic surface has a surface roughness inferior to 1 μm and wherein said hydrophilic surface comprises:

   at least one discrete area whereon are covalently grafted hydrophobic molecules for controlling onset boiling, or at least one discrete area whereon is coated a hydrophobic polymer for controlling onset boiling.

2. Heat exchanger according to claim 1, wherein at least two hydrophilic areas are spaced by a distance in the range of about 0.01 mm to about 5 mm.

3. Heat exchanger according to claim 1, wherein the grafted or coated area has a surface ranging from 0.01 mm^2 to about 5 mm^2.

4. Heat exchanger according to any of claims1 to 3, wherein the difference of wetting contact angle between the hydrophilic surface and the hydrophobic grafted or coated area is at least 10°, preferably at least 20°, preferably at least 30°.

5. Heat exchanger according to any of claims 1 to 4, wherein the hydrophobic molecule is a silane derivative of the general formula $X_3Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$, $X_2(R^1)Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$ or $X(R^1)(R^2)Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$, wherein X is selected from halogen or $C_{1\text{-}6}$ alkoxy, preferably Cl, Br or OMe, OEt; n is an integer selected from 1 to 20; m is an integer selected from 0 to 20; R^1, R^2 are independently $C_{1\text{-}10}$ alkyl; Y is selected from Me, CF_3, CHF_2, CH_2F, $CH{=}CH_2$, CN, CH=O, phenyl, epoxide, halogen, SH, NH_2, OH, N=C=O, N=C=S, CO_2H or derived esters thereof.

6. Heat exchanger according to any of claims 1 to 4, wherein the hydrophobic molecule is an alkene or an alkyne, each optionally substituted by one or more substituent selected from alkyl, haloalkyl, halo, alkenyl, cyano, epoxy, thio, amino, hydroxyl, isocyano, isothiocyano, carboxy, polyalkoxy, alkylarylsulfoxypolyalkoxy, or heteroaryloxycarbonylalkylpolyalkoxy.

7. Heat exchanger according to any of claims 1 to 4, wherein the hydrophobic polymer is selected from polypropylenes, polyethylenes, polytetrafluoroethylenes, polyvinylidene fluorides, polysulfones, polyethersulfones, polyvinylchlorides, fluorinated polymers, polyacrylics, polyamides, polyimides, polyesters, polyolefins, polyethers, polyamines, polyanhydrides, polycarbosilanes, polysilanes, polysilazanes, polysulfides, polyurethanes, polysiloxanes, polystyrenes, vinyl polymers, polyvinyl acetates, vinylidenes polymers, epoxy resins, polyamide imide, polybutylene terephtalate, polyether imides, polyethylene terephtalate, polymethylene oxides, diene elastomers, carbohydrate polymers, polyacetals, polynitriles, polyketones, polyphosphazenes, polypeptides, polysaccharides, polyisocyanides, polyisocyanades, polycarbonates or copolymers of these basic structures.

8. Heat exchanger according to any of claim 1 to 7, wherein the hydrophilic surface is a hydroxylated surface or a hydrogenated surface.

9. Process for controlling the boiling onset of a fluid, comprising thermally connecting said fluid with at least one hydrophilic surface, wherein said hydrophilic surface has a surface roughness inferior to 1 μm and wherein said hydrophilic surface comprises:

at least one discrete area which is covalently grafted with hydrophobic molecules,
or at least one discrete area which is coated with a hydrophobic polymer.

10. Process for constructing a heat exchanger according to any of claims 1 to 8, comprising the steps of:

a) treating at least one surface having a surface roughness inferior to 1 μm and
wherein said hydrophilic surface by wet chemistry using oxidation/hydroxylation/reduction in an acid or alkaline environment, thereby rendering said surface hydrophilic, and
b) coating or covalently grafting at least one discrete area of the activated surface of step (a) with hydrophobic molecules, thereby obtaining at least one hydrophilic surface having a surface roughness inferior to 1 μm and wherein said hydrophilic surface, provided with at least one area which is coated or covalently grafted with hydrophobic molecules.

11. Process according to claim 10, wherein the surface grafting of step (b) is performed through covalent coupling with a silane derivative of the general formula $X_3Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$, $X_2(R^1)Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$ or $X(R^1)(R^2)Si\text{-}(CH_2)_n\text{-}(CF_2)_m\text{-}Y$,
wherein X is selected from halogen or $C_{1\text{-}6}$ alkoxy, preferably Cl, Br or OMe, OEt; n is an integer selected from 1 to 20; m is an integer selected from 0 to 20; R^1, R^2 are independently $C_{1\text{-}10}$ alkyl; Y is selected from Me, CF_3, CHF_2, CH_2F, $CH{=}CH_2$, CN, CH=O, phenyl, epoxide, halogen, SH, NH_2, OH, N=C=O, N=C=S, CO_2H or derived esters

thereof.

12. Process according to claim 10, wherein the surface grafting of step (b) is performed through covalent coupling with an alkene or an alkyne, each optionally substituted by one or more substituent selected from alkyl, haloalkyl, halo, alkenyl, cyano, epoxy, thio, amino, hydroxyl, isocyano, isothiocyano, carboxy, polyalkoxy, alkylarylsulfoxypolyalkoxy, or heteroaryloxycarbonylalkylpolyalkoxy.

13. Process according to any of claims 10 to 12, wherein the covalent grafting of step (b) is performed by microcontact -printing.

14. Process according to claim 10, wherein the surface coating of step (b) is performed by coated said hydrophilic surface with a hydrophobic polymer selected from polypropylenes, polyethylenes, polytetrafluoroethylenes, polyvinylidene fluorides, polysulfones, polyethersulfones, polyvinylchlorides, fluorinated polymers, polyacrylics, polyamides, polyimides, polyesters, polyolefins, polyethers, polyamines, polyanhydrides, polycarbosilanes, polysilanes, polysilazanes, polysulfides, polyurethanes, polysiloxanes, polystyrenes, vinyl polymers, polyvinyl acetates, vinylidenes polymers, epoxy resins, polyamide imide, polybutylene terephtalate, polyether imides, polyethylene terephtalate, polymethylene oxides, diene elastomers, carbohydrate polymers, polyacetals, polynitriles, polyketones, polyphosphazenes, polypeptides, polysaccharides, polyisocyanides, polyisocyanades, polycarbonates or copolymers of these basic structures.

15. Process according to any of claims 10 to 14 wherein said surface is selected from the group comprising glass, aluminium, steel, copper, iron alloys, and silicon wafers.

16. Process according to any of claims 10 to 14, wherein the surface treatment of step (a) is performed by treating said surface with:

    (i) a mixture H_2SO_4/H_2O_2 in water, or
    (ii) a sulfochromic mixtures, or
    (iii) a mixture NH_4OH/H_2O_2 in water followed by HCl/H_2O_2 in water, optionally iterated, or
    (iv) HF in water followed by H_2O_2 in water and optionally iterated.

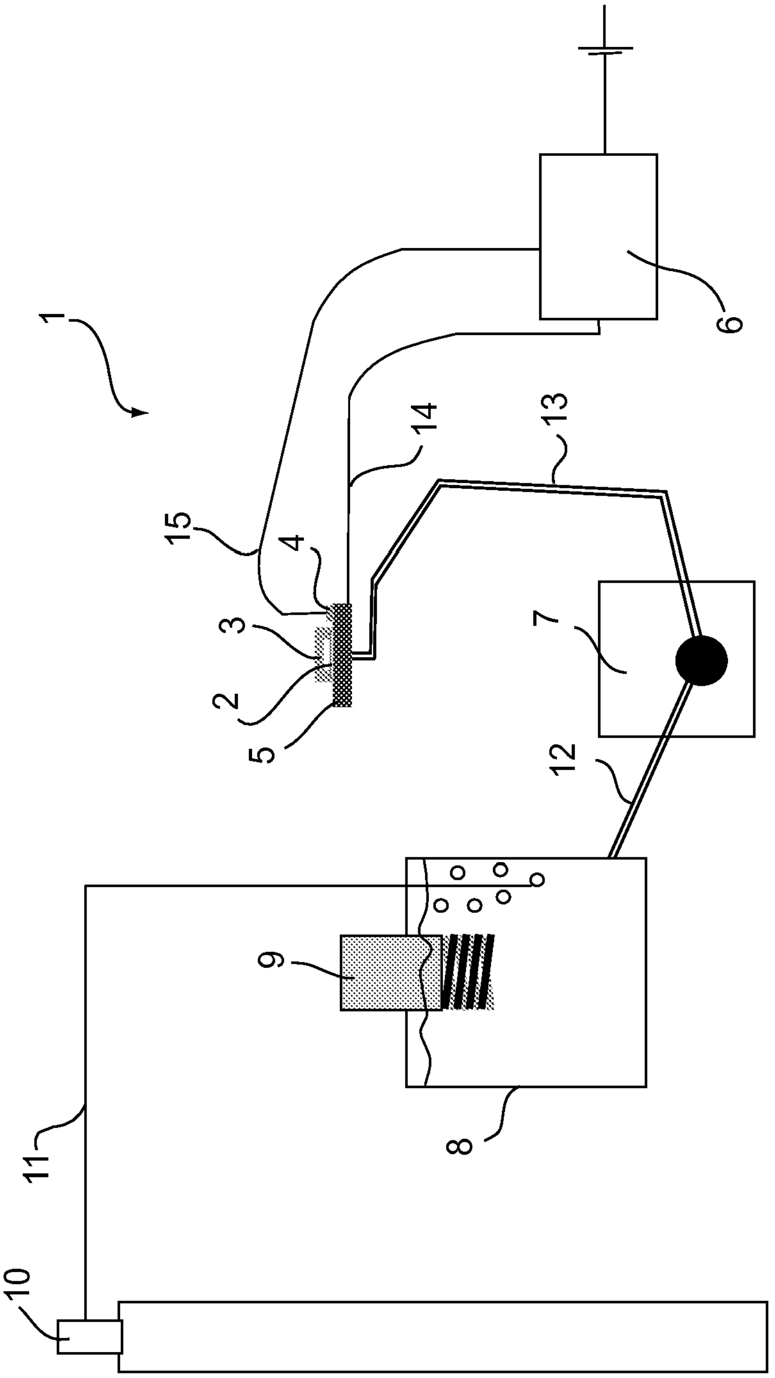

FIG. 1

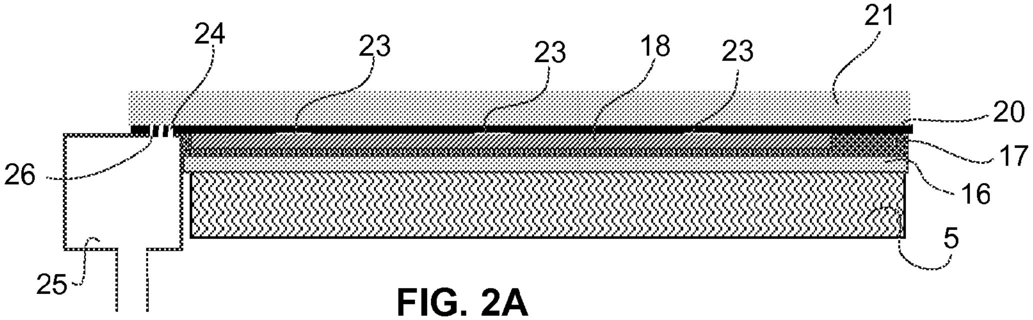

FIG. 2A

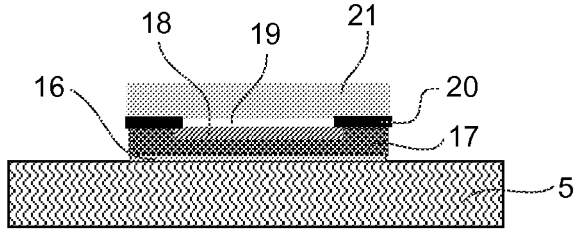

FIG. 2B

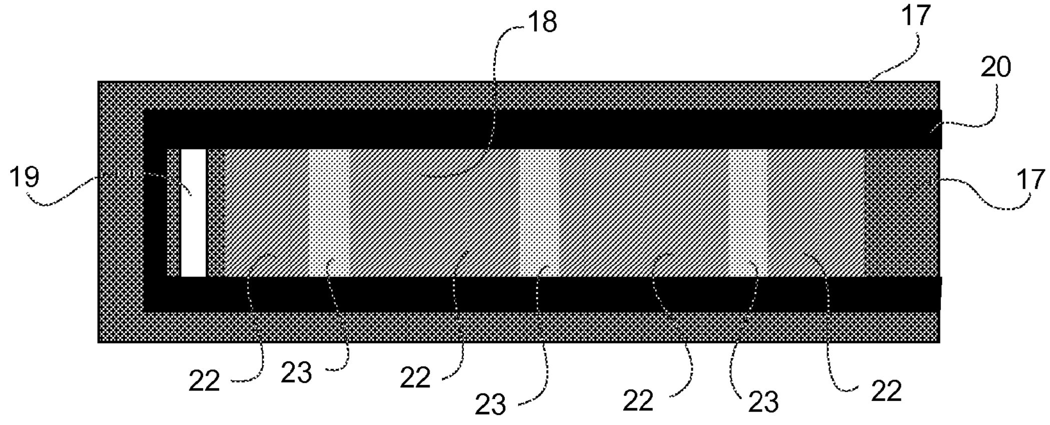

FIG. 2C

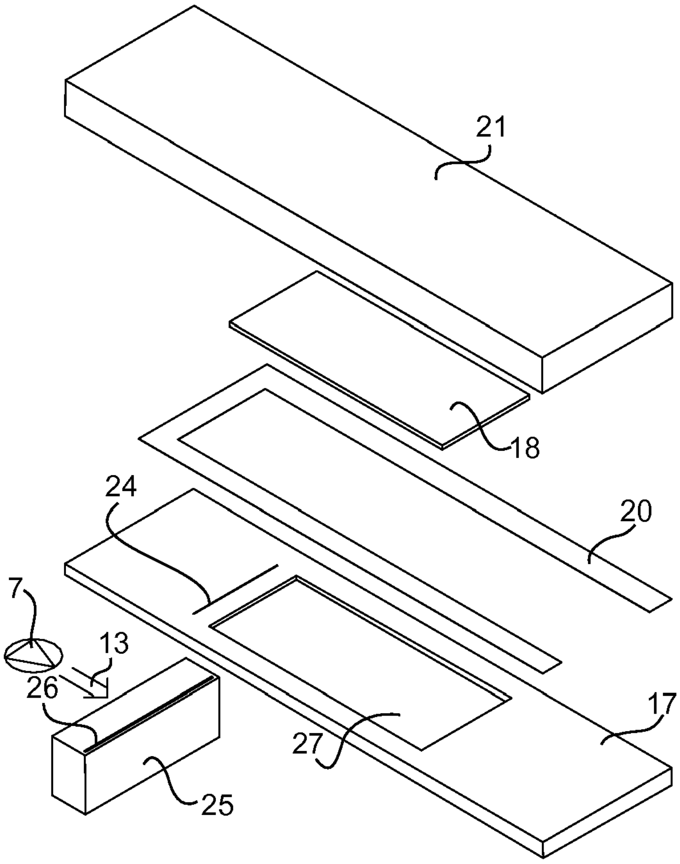

FIG. 3

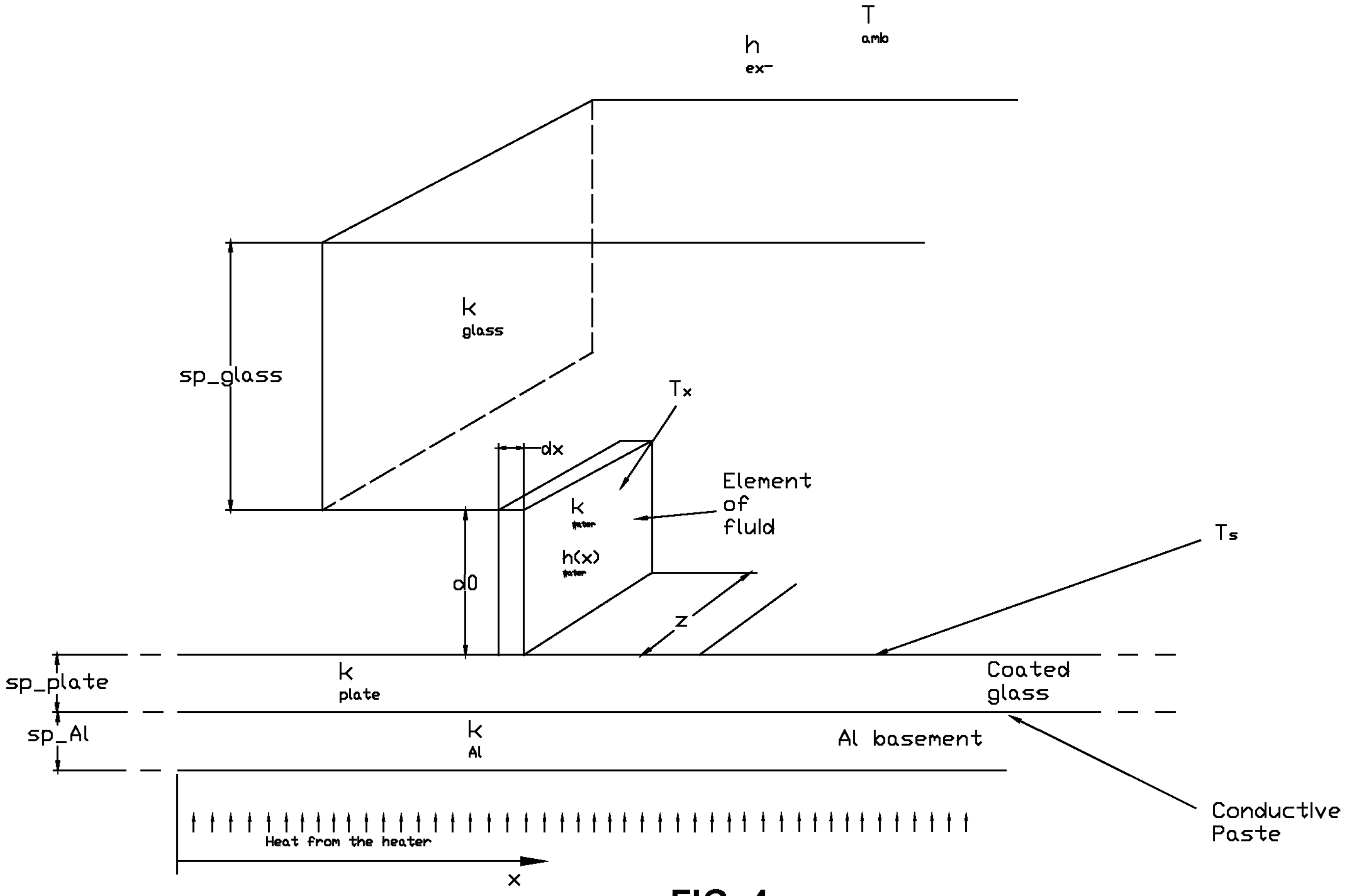
h ex-
T amb
k glass
sp_glass
Tx
dx
Element of fluid
k water
h(x) water
d0
z
Ts
sp_plate
k plate
Coated glass
sp_Al
k Al
Al basement
Conductive Paste
Heat from the heater
x

FIG. 4

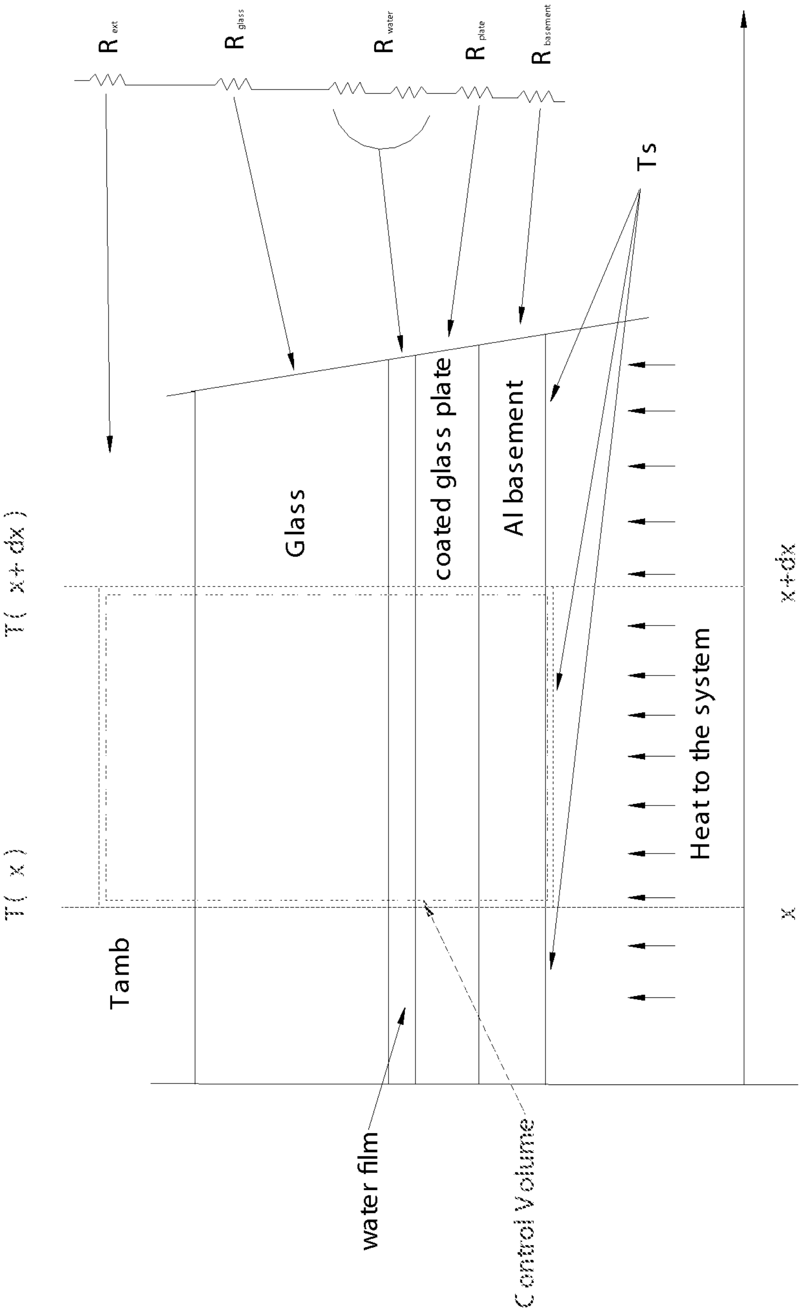
R ext
R glass
R water
R plate
R basement
Ts
Glass
coated glass plate
Al basement
T(x+ dx)
T(x)
Tamb
x+dx
x
Heat to the system
water film
Control Volume

FIG. 5

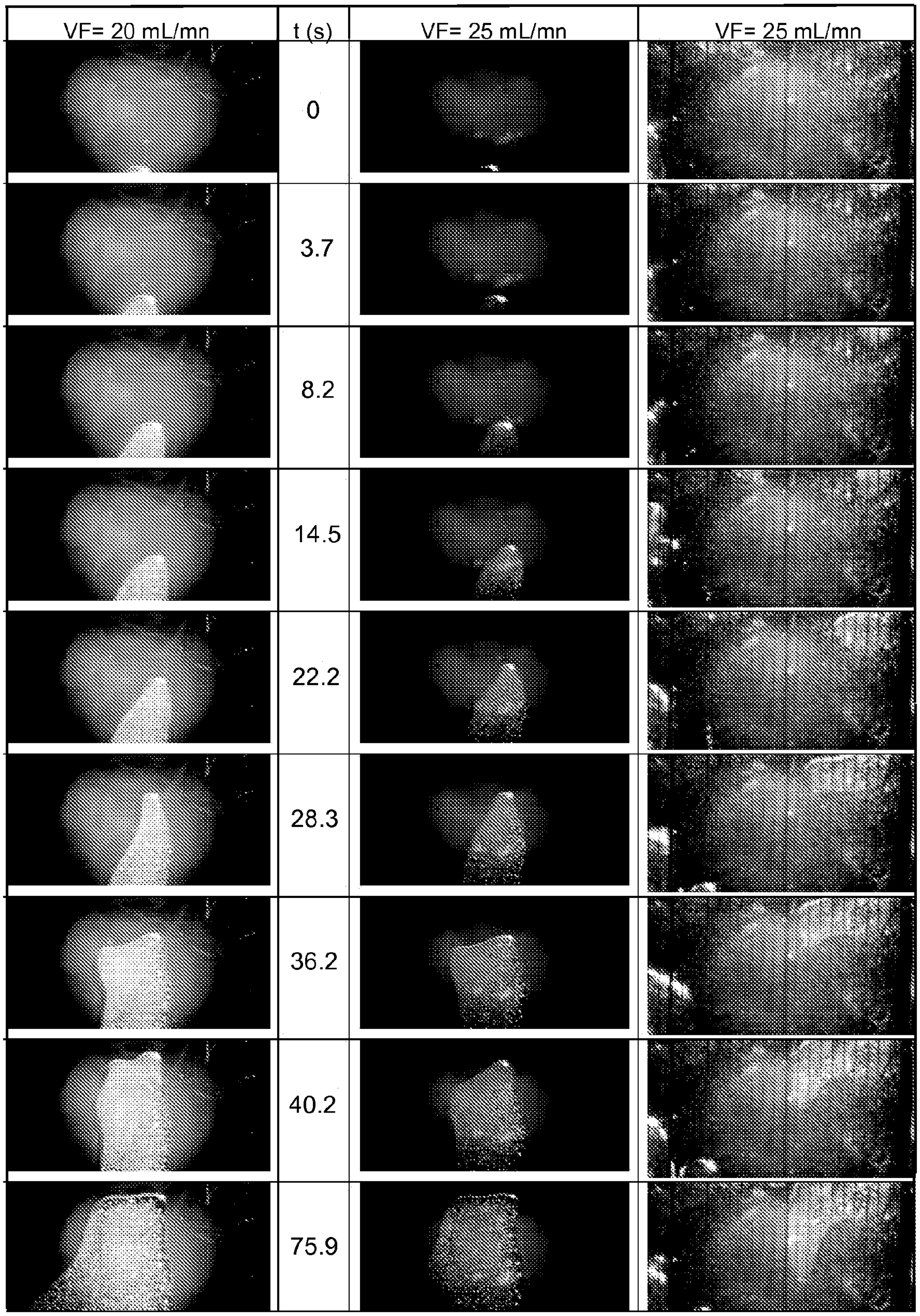

FIG. 6

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Application Number
EP 07 11 3887

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Place of search	Date of completion of the search	Examiner
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4

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T : theory or principle underlying the invention
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D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

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			TECHNICAL FIELDS SEARCHED (IPC)

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