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(54) Title: METHOD FOR CLEANING PHOTOMASKS USING MEGASONIC ENERGY

(57) Abstract: A method for cleaning photomasks is described, in which megasonic energy is introduced into a liquid on the surface of the photomask to be cleaned. In order to promote cleaning and to control cavitation events within the liquid, the liquid contains mainly Dl-water and at least one first component mixed therein, said first component being present at a concentration of between 0.0001% and 1.00% by volume and said first component having a pH of at least 7, a zeta potential of at most -20 mV, a boiling point of at least 60°C and a vapour pressure of less than 5333 Pa (40mm Hg) at 25°C.

METHOD FOR CLEANING PHOTOMASKS USING MEGASONIC ENERGY

Background

The present invention relates to the cleaning of photomasks using acoustic energy, in particular, MegaSonic and the chemistry used thereby.

Advances in lithography and device shrink are driving significant changes in photomask design and fabrication. Imaging strategies to extend optical lithography technology, such as sub-resolution assist features (SRAFs), have exponentially increased the complexity and fragility of the photomask. Not intended to be imaged on the wafer, SRAFs are very small and, according to the latest ITRS roadmap (International Technology Roadmap for Semiconductors (Front End Processes), (2010)), SRAFs will shrink to a size comparable to the defect allowed for that technology node. These features, which have a high aspect ratio, are made of materials that differ from the underlying material layer and, as a result, thermal expansion coefficient mismatch of the materials can cause residual stresses at the interface, making the features extremely fragile and prone to damage during e.g. cleaning processes.

There is a need for physical force cleaning methods that can effectively remove very small particles from an advanced photomask surface. Physical force cleaning transfers momentum to the particle in order to dislodge it from the photomask surface without re-deposition. In principle, to remove a particle without pattern damage the physical force applied must be higher than particle adhesion but lower than feature interface strength. Typically, the lifting force needed to remove soft particles (adhered to the mask surface by mainly van der Waals force) is less than the interface strength, implying that a process window for damage-free cleaning exists. Current state-of-the-art physical force technologies seem to already have difficulties in providing the level of precision and control needed to match the available damage-free cleaning process window for todays photomasks.

However, as the complexity and fragility of photomask features continue to increase, there is an urgent need to more closely control the energy applied to the mask during cleaning. S. Helbig, S. Urban, E. Klein, S. Singh: "Impact of MegaSonic process conditions on PRE and Sub-resolution assist feature
5 damage"; Photomask Technology 2008, SPIE Vol. 7122 (2008) discuss this need with respect to one of the most widely accepted physical force cleaning methods used today, which is MegaSonic cleaning.

MegaSonic cleaning is a wet cleaning technique which relies on the transfer of
10 acoustic energy from a piezoelectric transducer to a liquid cleaning media. This acoustic energy transfer results mainly in two fundamental mechanisms named acoustic streaming and acoustic cavitation.

Acoustic streaming is a time-independent fluid motion caused by the attenuation of
15 sound waves travelling in the liquid. Acoustic streaming reduces the thickness of a hydrodynamic boundary layer on the surface of a photomask to be cleaned. Due to this reduction, smaller sized particles are exposed to larger velocity gradients, which inter alia lead to drag forces and rolling moments which subsequently overcome the adhesion force between particle and surface, as discussed in V.
20 Kapila, P. Deymier, H. Shende, V. Pandit, S. Raghavan, and F. O. Eschbach "Acoustic streaming effects in MegaSonic cleaning of EUV photomasks: A continuum model"; SPIE Vol. 5992, p. 59923X1-59923X10, 2005.

Acoustic cavitation occurs due to the sinusoidal pressure variations that travel
25 through the liquid along with the acoustic wave. During the low pressure component of the acoustic wave, small cavities or bubbles form in the liquid which tend to implode in the high pressure part of the propagating wave. This type of cavitation is also called transient cavitation. Transient cavitation is reported to affect particles on the surface of a substrate, such as a photomask, in different
30 ways. Implosions of cavitating bubbles for example lead to high pressures and temperatures which create shock waves in the liquid. Furthermore, fluid jets can form due to asymmetric implosions of these bubbles.

Some stable cavities (no bubble implosion) can undergo large amplitude pulsations which results in micro-streaming and such micro-streaming can lead to shear stresses along the liquid-solid boundary as discussed in P. A. Deymier, J. O. Vasseur, A. Khelif, and S. Raghavan: "Second-order sound field during
5 MegaSonic cleaning of patterned silicon wafers: Application to ridges and trenches"; J. Appl. Phys., Vol. 90, 8, p. 4211-4218, 2001. This type of cavitation is called stable cavitation in the following.

In typical MegaSonic cleaning processes both transient and stable cavitation act
10 as a secondary source of Shock Waves, Micro-Streaming, and Fluid Jets, which are helpful in particle removal from the mask surface. However, transient cavitation being more aggressive is also responsible for feature damage either due to violent implosions of cavities right next to a feature, or due to high pressure fluid jets. Micro-Streaming as a result of stable cavitation is more favourable for particle
15 removal without damage as it provides controlled and narrow energy distribution.

DE 102 12 657 A1 describes a cleaning method for cleaning a silicon wafer after a chemical-mechanical polishing process using an abrasive material. For the cleaning process the surface to be cleaned is first brought into contact with
20 hydrofluoric acid and subsequently into contact with an aqueous solution containing an oxidant. During the contact with the aqueous solution containing the oxidant, which may inter alia contain TMAH, introduction of ultrasound into the solution is described.

25 It is therefore an object of the invention to provide a cleaning process promoting stable cavitation, in an attempt to achieve high particle removal efficiency (PRE) without pattern damage.

The inventors have found that certain chemical and physical properties of the
30 cleaning liquid largely influence the type of cavitation (stable or transient).

In accordance with a first aspect, a method for cleaning photomasks is provided, in which megasonic energy is introduced into a liquid on the surface of the

photomask to be cleaned, wherein the liquid contains mainly DI-water and at least one first component said first component being present at a concentration of between 0.0001% and 1.00% by volume and said first component having a pH of at least 7, a Zeta Potential of at most -20 mV, a boiling point of at least 60°C and a
5 vapour pressure of less than 5333 Pa (40mm Hg) at 25°C.

The invention will be described herein below in more detail with respect to the drawings; in the drawings:

10 Fig. 1 is a graph showing a pattern damage comparison between NH_4OH + H_2-DI, TMAH + H_2-DI, TMAH + DI and TMAH + H_2O_2 + DI;

Fig. 2 is a graph showing zeta potential comparison of NH_4OH, SC1 and TMAH;

15 Fig. 3 is a graph showing pH comparison of NH_4OH, SC1 and TMAH;

Fig. 4 is a graph showing OMOG CD shift comparison between SC1+ DI, TMAH + DI and TMAH + H_2O_2 + DI;

20 Fig. 5 is a graph showing a particle removal efficiency (PRE) comparison between SC1 + DI, TMAH + DI and TMAH + H_2O_2 + DI.

In the following, it will be explained how to control acoustic cavitation (by favouring generation of stable cavities) during wet cleaning of photomasks by selecting
25 cleaning liquids with properties suited for stable cavitation phenomenon.

Typically MegaSonic cleaning of photomasks is carried out by transferring acoustic energy into cleaning liquids (such as NH_4OH-DI, NH_4OH+H_2O_2-DI or SC1, H_2-DI+NH_4OH, DI-CO_2, etc., whereby DI stands for de-ionized water) using a
30 piezoelectric transducer. The size and shape of the piezoelectric transducer as well as the design of the overall system varies depending on the cleaning tool as well as the photomask being cleaned. The transducer can be implemented in a nozzle configuration where cleaning media is flown through this nozzle and then

dispensed on the photomask. It can also be implemented as a standalone unit (flat, conical, etc.) where the cleaning media is already present on the photomask surface and the transducer irradiates the cleaning media with acoustic energy. In some cases such transducers are also implemented in a bath configuration where the photomask is immersed in a wet bath filled with cleaning chemistry and the transducer is equipped either at the bottom/top or side of the bath. One example of a system for use in cleaning photomasks is the HamaTech MaskTrackPro (MTPro) mask cleaning tool, which was used in the Examples given herein below.

In addition to the physical force applied by MegaSonic, the composition of the liquid is also an important factor in removing particles. A cleaning solution needs to provide sufficient zeta potential as well as pH to prevent particle re-deposition, as is known in the art. Certain chemistries used in the liquid may provide under-etching of inorganic particles and thus help in weakening the adhesion force between the particles and the surface. NH_4OH is a common chemistry used to provide this effect in SC1 solution or Hydrogenated water (H_2-DI).

The inventors have found that cleaning liquids containing the above composition produce cavitation bubbles filled with dissolved gas (gaseous cavities) or vapors of the chemical (vaporous cavities) when it is exposed to acoustic energy in the form of MegaSonic. NH_4OH has a vapor pressure of 74.261 PA (557mmHg) and a boiling point of 27°C. Since the boiling point of NH_4OH is very low, it starts to evaporate into NH_3 gas at room temperature under low acoustic pressure cycle and thus this liquid favors the cavitation bubbles to be filled with NH_3. Similarly in the case of H_2-DI+NH_4OH, the cavitation bubbles are mainly filled with H_2 and NH_3 gas.

The transient cavitation threshold for gaseous cavities is much lower than for vaporous cavities. Therefore the chances of a gaseous cavity to undergo a transient cavitation phenomenon (bubble implosion) are much higher than for vaporous cavities. Since cleaning liquids containing a component such as NH_4OH-DI tend to favor the bubbles being filled with gas and thus the gaseous cavitation phenomenon, they are prone to induce pattern damage during MegaSonic

cleaning. Furthermore, the polytrophic index of NH_3 gas is one of the lowest among gases (only 1.3 as compared to H_2 = 1.38, N_2 = 1.4) which means when a NH_3 gas filled cavity implodes, it produces extremely aggressive temperature and pressure effects.

5

Vaporous cavities on the other hand are more favorable to form vapor filled bubbles and to show a stable cavitation phenomenon (micro-streaming). Also the vapors present in a bubble (cavity) would tend to condense back into the liquid during a high pressure part of the sinusoidal acoustic wave, which will shrink the
10 bubble size. So the continuous expand/shrink cycle of the stable cavities produce controlled pressure variations, which are helpful in particle removal without damage.

Therefore, to promote formation of vapor filled bubbles, the inventors concluded
15 that the NH_4OH component had to be replaced in the cleaning liquid by a component that while favoring formation of vaporous cavities still provides a high pH and zeta potential.

It was found that the formation of vapor filled bubbles could be promoted by using
20 a component having a low vapor pressure and a high boiling point. Thus, a chemical with high pH, high zeta potential, low vapor pressure and high boiling point when used as a stand alone chemical or added to de-gassed DI-water, was considered for high particle removal efficiency without pattern damage on photomasks. Obviously such chemical at the concentration used should not etch
25 the surface of the photomask.

Tetra methyl ammonium hydroxide (TMAH) was found to be a suitable chemistry, which may be used alone, in combination with DI-water and possibly further chemistry. TMAH has a low vapor pressure of 2333 Pa (17.5mm Hg) and a boiling
30 point of 100°C. Because of the high boiling point, there is a very low probability of TMAH gasifying under acoustic pressure at room temperature, which is a typical processing temperature. However, since the vapor pressure of TMAH is just 2333 Pa (17.5mmHg), it can easily form vapors. Therefore, when TMAH is

exposed to acoustic pressure variations it tends to mainly or almost exclusively form vapor filled bubbles (also called vaporous cavities) as opposed to gas filled bubbles (also called gaseous cavities), which are mainly formed with liquids including NH_4OH and/or H_2-DI. The inventors have found that using TMAH in a cleaning process as described above decreases the formation of pattern damage.

Fig 1 shows test results of cleaning tests performed on photomasks having 40nm sub-resolution assist features (SRAFs) having aspect ratios of 1:1 to 1.8:1. Cleaning was performed on separate sections of the photomask. Pattern damage tests and MegaSonic characterizations were performed using the HamaTech MaskTrackPro (MTPro) mask cleaning tool and a test bench designed specifically for this evaluation. In particular, an advanced mechanical feature of the MTPro was utilized, Focused Spot Cleaning (FSC) to allow the different sections to be cleaned using different parameters. The process parameters were automatically monitored and controlled with a standard recipe program on the MTPro tool. Tests were performed at different power levels (given in % of the maximum rated MegaSonic power to be applied via the respective tool) and for different cleaning liquids. Each cleaning liquid contained as a main component degassed DI-water. DI-water used for the tests was de-gassed before it was supplied to the cleaning chemical distribution system. The separate sections were then inspected with respect to pattern damage. Pattern damage induced by different MegaSonic cleaning process conditions was analyzed using a pattern mask inspection tool.

As can be seen in Fig. 1, the cleaning liquid containing H_2-DI-water with NH_4OH leads to the highest levels of pattern damage. Already at 35% of the maximum rated MegaSonic power, pattern damages may be observed. Using the above chemistry for photomasks either leads to only low MegaSonic power being allowed for the cleaning process, or pattern damages, both of which are obviously undesirable. Low MegaSonic power may not provide sufficient cleaning, while Pattern damages lead to a shorter lifetime of the photomasks. Similarly, H_2-DI-water including TMAH was not found to be ideal, as pattern damages were found to first occur at 45% of the maximum rated MegaSonic power and rapidly increasing at higher power levels. Despite the fact that TMAH improves pattern

damages over NH_4OH, when using H_2-DI-Water, the H_2 component was considered to be predominant in the formation of gas filled bubbles at the TMAH level tested, thus leading to undesired pattern damages. TMAH and TMAH+H_2O_2 on the other hand did not show any pattern damages even at high MegaSonic
5 power levels of 85%.

TMAH also has a much higher zeta potential and higher pH than NH_4OH or SC1, as can be seen in Figs. 2 and 3. With respect to the values for the zeta potential shown and also for the values as discussed in this application, they relate to
10 values measured at pH 4 to 20. Therefore, it prevents particle re-deposition and improves particle removal efficiency (PRE) as can bee seen in Fig. 5. Since TMAH-DI solutions give higher pH and higher zeta potential than NH_4OH-DI for even a 10 times more diluted solution, etching effects are significantly reduced, which lowers CD loss (surface integrity) during cleaning, as can be seen in Fig. 4.
15

Even though TMAH was used for the above examples, other chemistries are contemplated to be useful in the cleaning of photomasks, as long as they have a high boiling point and a low vapor pressure, to promote the formation of vapor filled bubbles for stable cavitation. It is contemplated that chemistries having, a
20 boiling point of at least 60°C and a vapour pressure of less than 5333 Pa (40mm Hg) at 25°C already lead to promoting the formation of vapour filled bubbles in the above described cleaning processes. Higher boiling points are considered to further improve the formation as local temperature increases in the cleaning liquid would not lead to the formation of gas bubbles. Thus, boiling points of at least
25 80°C, in particular of at least 100°C are considered to be beneficial. Also, in order to further promote the formation of vapour filled bubbles, an even lower vapour pressure of for example less than 2666 Pa (20mm Hg) at 25°C is considered to be beneficial. In order to reduce particle re-deposition during the cleaning, the chemistry should at the same time have a high ph and a high zeta potential. A pH
30 of at least 7 and a zeta potential of at most -20 mV were considered to be sufficient. However, higher pH values of at least 10, in particular of at least 12 are contemplated to be even better. Similarly, higher zeta potentials of at most -50 mV, in particular of at most -100 mV are again considered to be beneficial.

In the following an exemplary photomask cleaning process using TMAH will be explained. First, ultra-pure de-ionized water (DI-water) is de-gassed completely. Then a very controlled amount of TMAH is added (0.0001 – 1.00Vol%) into the de-
5 gassed water. Now the photomask to be cleaned is simultaneously exposed to the TMAH-DI-water mixture and MegaSonic acoustic energy. There could be various methods by which this can be accomplished. A MegaSonic transducer can be integrated in a nozzle form or a standalone unit. The photomask to be cleaned can either be spinning on a chuck or stationary. The TMAH-DI mixture can either be
10 supplied from the transducer nozzle itself or a separate nozzle. The photomask can also be immersed into a wet bath of the TMAH-DI-water mixture, where MegaSonic energy is applied through transducers integrated around or inside the bath itself.

15 In another process a different formulation of this mixture can also be applied. In this formulation, a very small amount of H_2O_2 (0.01 to 2.00Vol%) can also be added into the TMAH-DI-water solution. The method of application on the photomask surface is same as explained above. The H_2O_2 may positively influence the ph and the zeta potential of the mixture, without negatively
20 influencing the stable cavitation phenomenon.

Even though TMAH was explicitly mentioned in the application, as test were performed using TMAH, other chemistries or formulations which have similar properties as TMAH (i.e. high pH, high zeta potential, low vapor pressure and high
25 boiling point) can also be added to de-gassed DI-water, and exposed to MegaSonic energy as explained in the above paragraphs.

Claims

1. A method for cleaning photomasks is provided, in which megasonic energy is
5 introduced into a liquid on the surface of the photomask to be cleaned, wherein the liquid contains mainly DI-water and at least one first component mixed therein, said first component being present at a concentration of between 0.0001% and 1.00% by volume and said first component having a pH of at least 7, a zeta potential of at most -20 mV, a boiling point of at least
10 60°C and a vapour pressure of less than 5333 Pa (40mm Hg) at 25°C.

2. A method as set forth in claim 1, wherein the at least one component has a pH of at least 10.

15 3. A method as set forth in claim 1 or 2, wherein the at least one component has a zeta potential of at most -50 mV.

4. A method as set forth in any one of the preceding claims, wherein the at least one component has a boiling point of at least 80°C.

20

5. A method as set forth in any one of the preceding claims, wherein the at least one component has a vapour pressure of less than 2666 Pa (20mm Hg) at 25°C.

25 6. A method as set forth in any one of the preceding claims, wherein the DI-water is degassed prior to mixing with the at least one liquid.

7. A method as set forth in any one of the preceding claims, wherein the liquid contains as at least one second component H_2O_2.

30

8. A method as claimed in claim 7, wherein the liquid contains H_2O_2 at a concentration of between 0.01% and 2.00% by volume.

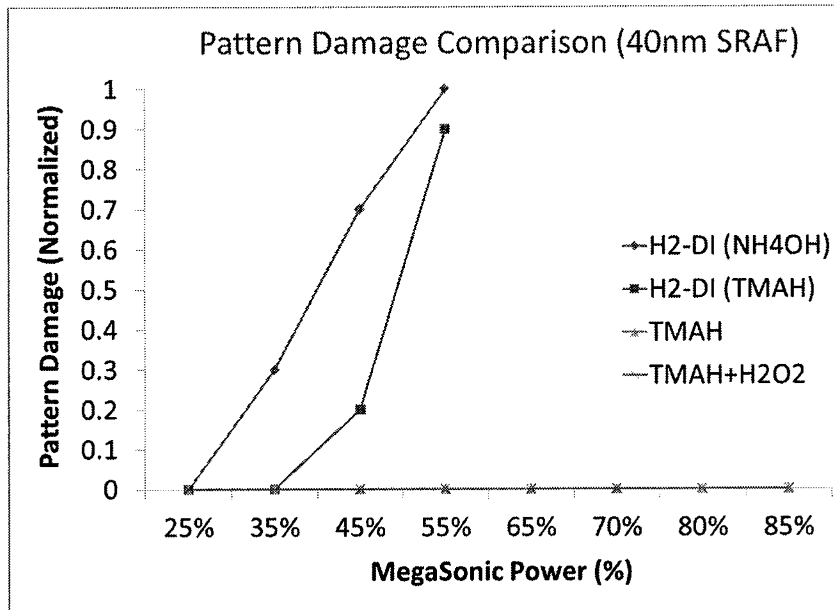

Fig. 1

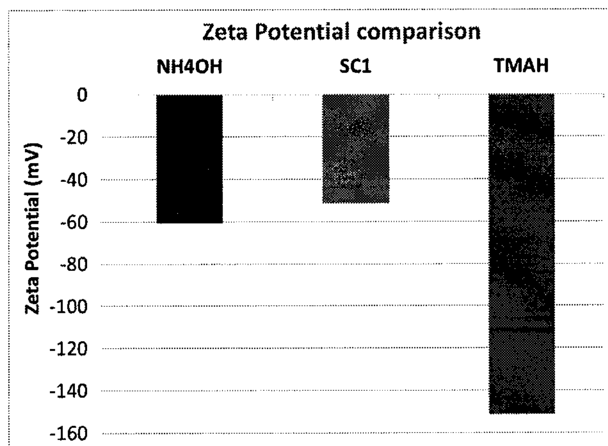

Fig. 2

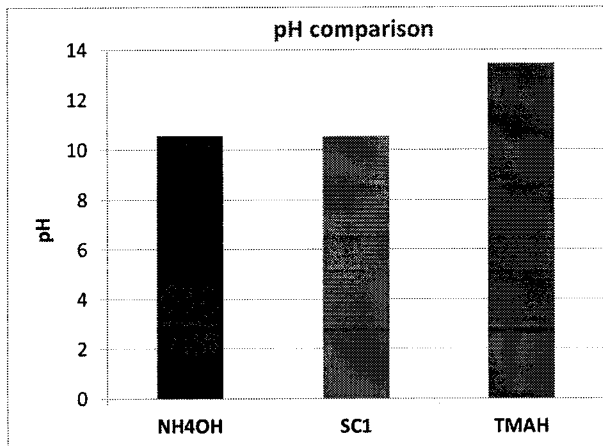

Fig. 3

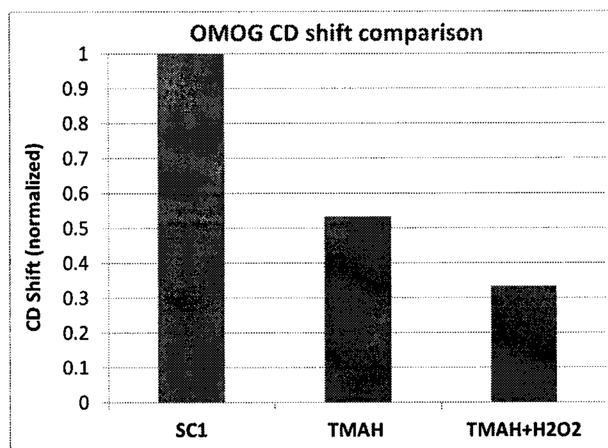

Fig. 4

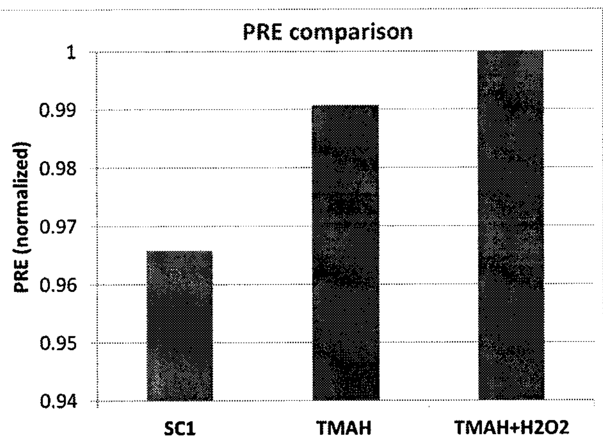

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. G03F1/00 G03F1/82
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
11 July 2013	11/09/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/025001

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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