1. The formation of insoluble precipitates due to strong interaction between the opposite charged entities and formation of a very hydrophobic complex, which can precipitate out of the formulation, or affect the medium and long-term stability of the anionic-cationic surfactant formulations.

2. In-situ generation of fine particles and aggregates (precipitates) may occur if the anionic and cationic surfactants are in concentrations of near or above the solubility product of the anionic/cationic complex, or due to local variations in concentration.

3. The Cleaning solutions may not prevent dirt, or particle re-deposition on the surface due to reduced capacity of increasing the magnitude of the surface zeta potential as compared to pure anionic, or cationic surfactants.

4. Unpredictable system in terms of system stability and surfactant-surface interaction.

Objects of the ~~Invention~~ Embodiments Disclosed Herein

It is an object of the ~~present invention~~embodiments disclosed herein to provide a method for manufacturing integrated circuits for nodes of 50 nm and lower, in particular for nodes of 32 nm and lower and, especially, for nodes of 22 nm and lower, which method no longer exhibits the disadvantages of prior art manufacturing methods.

In particular, the compounds according to the present ~~invention~~ disclosure shall allow for the immersion photolithography of photoresist layers,
the developing of the photoresist layers exposed to actinic radiation through a mask
the chemical rinse of patterned material layers
comprising patterns with a high aspect ratio and line-space dimensions of 50 nm and less, in particular, of 32 nm and less, especially, of 22 nm and less, without causing pattern collapse, an increase of LER and LWR and watermark defects.

The components according to the present ~~invention~~ disclosure should allow for a significant reduction of LER and LWR by smoothing the roughness of the surfaces of the developed photoresist patterns. It should also allow for the efficient prevention and/or the removal of watermark defects on patterned material layers, in particular but not limited to photoresist patterns. Furthermore it should allow for the efficient removal of particles in order to achieve a significant defect reduction on patterned material layers, in particular but not limited to photoresist patterns.

Summary ~~of the Invention~~

~~A first embodiment of the present invention is~~There is provided the use of an aqueous composition comprising at least one non-ionic or zwitterionic surfactant A and at least one hydrophobizer B for treating substrates comprising patterns having line-space dimensions of 50 nm or below, wherein

(a) the surfactant A has an equilibrium surface tension of 10 mN/m to 35 mN/m, determined from a solution of surfactant A in water at the critical micelle concentration, and

(b) the hydrophobizer B is selected so that the contact angle of water to the substrate is increased by contacting the substrate with a solution of the hydrophobizer B in water by 5-95° compared to the contact angle of water to the substrate before such contacting.

In an aspect, there is provided the use of an aqueous composition comprising at least one non-ionic surfactant A and at least one hydrophobizer B for treating substrates comprising patterns having line-space dimensions of 50 nm or below, wherein

(a) the at least one surfactant A has an equilibrium surface tension of 10 mN/m to 35 mN/m, determined from a solution of the at least one surfactant A in water at the critical micelle concentration, and

(b) the hydrophobizer B is selected so that the contact angle of water to the substrate is increased by contacting the substrate with a solution of the hydrophobizer B in water by 5-95° compared to the contact angle of water to the substrate before such contacting.

~~Another embodiment of the present invention is~~There is also provided a process for manufacturing integrated circuit devices, optical devices, micromachines and mechanical precision devices has been found, the said method comprising the steps of

(1) providing a substrate having patterned material layers having line-space dimensions of 50 nm and less and aspect ratios of greater or equal 2;

(2) contacting the substrate at least once with an aqueous solution comprising at least a surfactants A and a hydrophobizer B as defined above,

and

(3) removing the aqueous solution from the contact with the substrate.

In another aspect, there is provided a method for manufacturing integrated circuit devices, optical devices, micromachines and mechanical precision devices, the said method comprising the steps of

(1) providing a substrate having patterned material layers having line-space dimensions of 50 nm and less and aspect ratios of greater or equal 2,

(2) contacting the substrate at least once with an aqueous solution comprising at least one surfactant A and at least one hydrophobizer B as defined in anyone of the preceding claims,

and

(3) removing the aqueous solution from the contact with the substrate.

In view of the prior art, it was surprising and could not be expected by the skilled artisan that the objects of the ~~invention~~ embodiments disclosed herein could be solved by the use or method ~~according to the invention~~as defined above.

The present disclosure~~invention~~ completely avoids, in a surprising way, all the disadvantages of the prior art by using combinations of non-ionic and cationic surfactants. The fundamental difference is that the intrinsic cause for the insolubility of surfactant mixture is eliminated. The present ~~invention~~ disclsoure uses mixtures of non-ionic with cationic compounds that are selected according to the defined criteria. Formulations based on non-ionic compounds with cationic ones have a better long-term stability, better particle removal efficiency, reduced or no intrinsic particle generation ability compared to formulations based on anionic-cationic surfactant mixtures.

The surfactant A and hydrophobizer B may be in relatively high concentrations without the risk of precipitation of at least one of the components.

The use of at least two different additives, a non-ionic surfactant A and a hydrophobizer B according to the ~~invention~~ disclosure is particularly useful for patterned developed photoresist layers

comprising patterns having line-space dimensions of 50 nm or less, particularly of 32 nm or less and, most particularly 22 nm or less.

Furthermore, the use of at least two different additives, a surfactant A and a hydrophobizer B according to the inventionas defined above is particularly useful for aspect ratios greater or equal 2 in the case of photoresist structures, and, in particular, greater or equal 10 in the case of non-photoresist structures, without causing pattern collapse, line edge roughness (LER), line width roughness (LWR) and watermark defects.
It has to be noted that the cleaning solutions comprising the at least two different additives according to the present inventionas defined above are generally useful for avoiding anti pattern collapse of photoresist structures as well as of non-photoresist patterns with high aspect ratios stacks (HARS).

In the photoresist case anti-pattern collapse, LER and LWR reduction and defect removal. (typical aspect ratios are from 2 to 4). For the HARS case we need anti pattern collapse and defect reduction / cleaning (typical aspect ratios are greater or equal 10). However, the fundamental concept to suppress pattern collapse by using at least two different surfactants according to the present inventionas defined above is the same.

Quite to the contrary, the method as defined aboveof the invention allowed for a significant reduction of LER and LWR by smoothing the roughness of the surfaces of the developed photoresist patterns caused, for the efficient prevention and/or the removal of watermark defects not only on photoresist patterns, but also on other patterned material layers, and the efficient removal of particles whereby a significant defect reduction not only on photoresist patterns but also on other patterned material layers could be achieved.

Detailed Description of the Invention

The present invention is directed to a composition particularly suitable for manufacturing patterned materials comprising sub 32 nm sized features like integrated circuit (IC) devices, optical devices, micromachines and mechanical precision devices, in particular IC devices.

Any customary and known substrates used for manufacturing IC devices, optical devices, micromachines and mechanical precision devices can be used in the process of the invention. Preferably, the substrate is a semiconductor substrate, more preferably a silicon wafer including a silicon-gallium wafer, which wafers are customarily used for manufacturing IC devices, in particular IC devices comprising ICs having LSI, VLSI and ULSI.

The composition is particularly suitable for treating substrates having patterned material layers having line-space dimensions of 50 nm and less, in particular, 32 nm and less and, especially, 22 nm and less, i.e. patterned material layers for the sub-22 nm technology nodes. The patterned material layers preferably have ratios above 2, preferably above 10, even more