

## Device and Method for Coating of a Substrate

The invention relates to a device for coating of a surface of a substrate and a corresponding method.

In the coating of wafers in resist spraying systems there is the problem of homogenous application of the coating, especially the resist, to the wafers which have a very large area in the meantime, for example with a diameter of 300 mm. The uniform coating of structured substrates is especially problematical.

Embodiments of the invention disclose a device and a method for coating of substrates in which more uniform coating takes place.

According to a first aspect of the present invention, there is provided a device for spray coating of a surface of a substrate with a resist which has at least one coating component and at least one solvent, with the following features: a chamber which can be pressurized with a pressure, a holding apparatus for holding the substrate on a holding surface and a spray nozzle for coating of the substrate, wherein the device has cooling means for cooling of at least the surface of the substrate which is held on the holding surface of the holding apparatus during the coating such that the resist is not applied in fluid form on the surface of the substrate but that the resist is shock frozen already during application on the surface of the substrate.

According to a second aspect of the present invention, there is provided a method for spray coating of a surface of a substrate with a resist which has at least one coating component and at least one solvent, wherein at least the surface of the substrate is cooled during the coating such that the resist is not applied in fluid form on the surface of the substrate but that the resist is shock frozen already during application on the surface of the substrate.

All combinations of at least two of the features given in the specification, the claims and/or the figures also fall within the scope of the invention. At the given value ranges, values within the indicated limits will also be considered to be disclosed as boundary values and will be claimed in any combination.

Embodiments of the invention describe a system and a method using which spray-coated resist layers as uniform as possible can be deposited on structured surfaces. The homogeneity relates generally to all parameters, therefore layer thickness, chemical composition, etc. Hereinafter the homogeneity relates mainly to the layer thickness. One finding as per embodiments of the invention lies especially in that a coating component, especially a resist, must be diluted with solvent and is therefore relatively

"mobile". The solvent is used for spraying of the viscous liquid coating component. At latest in the vapor deposition of the solvent this can lead to a more or less rough surface. Embodiments of the invention make this finding its own by the phase transitions of the coating material being used in a dedicated manner for producing a surface as uniform as possible in the spray application of the resist coating, especially by pressure control and/or temperature control.

The solvents used are generally different from resist to resist. Generally they are organic solvents. Solvents preferred as per embodiments of the invention are the following:

- PGMEA
- Diethylether
- Isopropanol
- Hexafluoroethane
- Mesitylene
- Ethanol
- Propanol
- Acetone
- Water

The advantages of the invention consist in that a simple, gentle, economical and efficient method is shown for how a uniform and preferably smooth surface can be produced by spray coating.

A phase is defined as an inherently uniform region of largely identical chemical and physical properties which is separated from another phase by a phase boundary.

A component is defined as a unit which can no longer be physically and chemically divided

during thermodynamic examination. Examples of components would be the elements of the periodic chart, molecules such as water, ethane, propane, butene, diethylether or even macromolecules such as proteins. The solvents examined below and the substances dissolved in them, as per embodiments of the invention mainly resists, can therefore be regarded as components.

A phase diagram is defined as a representation of the regions of existence of phases as a function of different, especially thermodynamic parameters, especially as a function of pressure and temperature.

The regions of existence of the phases of a single-component system are shown in a pressure-temperature diagram. Figure 1 shows a symbolic pressure-temperature phase diagram of a single-component system of any solvent as per embodiments of the invention at moderate temperatures and pressures.

The behavior of the systems examined below, therefore the solvents and their dissolved substances, at extremely low and extremely high temperatures, as well as at extremely high pressures, is not of interest for embodiments of the invention. Therefore the pressure-temperature phase diagram is shown mainly around the triple point T. The three phase regions of solid, liquid and gaseous are separated from one another by characteristic pressure-temperature curves. The curve 1 is the so-called sublimation or resublimation curve which separates the phase existence region of the solid phase from the phase existence region of the gaseous phase. Curve 2 is the vaporization or condensation curve which represents the set of all pressure-temperature combinations on which liquid and gaseous phases are in equilibrium with one another. Curve 3 is the melting or solidification curve. Along the curves two phases are always in thermodynamic equilibrium with one another.

The following typical temperature and pressure values for the triple points of some substances are disclosed:

- diethylether (156.93K)
- acetone (178.86K)
- isopropanol (184.96K)
- hexafluoroethane (173.08K, 26.60 kPa)
- water (273.16K, 0.6117 kPa)

The temperature region which is preferred as per embodiments of the invention at least on one holding surface of a holding apparatus for holding the substrate to be coated is therefore between 300K and 0K, preferably between 275K and 0K, more preferably between 250K and 0K, still more preferably between 200K and 0K and most preferably between 150K and 0K. The cooling can take place for example electrically via Peltier element or via cooling means, especially cooling liquid and/or cooling gases. If heating of the holding apparatus should be necessary, this takes place preferably electrically.

The preferred pressure working region of a (resist spraying) chamber of the device as per embodiments of the invention, which chamber can be pressurized, is between  $10^5$  Pa and 1 Pa, more preferably between  $10^4$  Pa and 1 Pa, still more preferably between  $10^3$  Pa and 1 Pa and most preferably between  $10^2$  Pa and 1 Pa.

For a single-component system there is exactly one point in the pressure-temperature phase diagram, therefore a pressure-temperature combination in which all three phases are in thermodynamic equilibrium with one another. This point is called the triple point T.

A two-component system in simplified form is examined below. The two-component

system consists of a solvent and the first component which is present in excess. The second component is a coating component, the substance dissolved in the solvent, as per embodiments of the invention preferably a resist. It is apparent that by introducing a second component the complete and correct representation of a thermodynamic system can take place only in a pressure-temperature-concentration diagram. Based on the fact that we are interested in any case only in the physical and chemical properties of the solvent, the altered pressure-temperature phase diagram after dissolution of the dissolved substance is sufficient for the description of embodiments of the invention (Figure 2).

If a dissolved substance is added to a solvent, the phase equilibrium boundaries of the solvent which is now a two-component system, a binary system, change (Figure 2). The elevation of the boiling point at a certain pressure is called the boiling point elevation. Since this boiling point elevation generally applies to the entire pressure domain along the boiling curve 2, the boiling line of the pure solvent when a dissolved substance is added shifts to the right. Accordingly, along the solidification curve 3 there is a freezing point depression, i.e. by dissolving a substance the freezing point of the solvent shifts to lower temperatures at constant pressure.

The depression of the vapor pressure at a certain temperature is called the vapor pressure depression. The vapor pressure depression and the boiling point elevation or freezing point depression are generally directly proportional to one another. The boiling point elevation, the freezing point depression and the vapor pressure depression depend solely on the concentration and not the type of dissolved substances. The ability of a substance to change the physical and/or chemical properties of a second substance independently of its chemistry, but only by its amount, is called the colligative property.

The pressure-temperature phase diagram which is fixed by the colligative properties of the dissolved substance is used as a foundation for the (resist spraying) method as per embodiments of the invention.

In industry solely resist spraying systems have been operated to date which atomize the solution of solvent and resist in the liquid state and apply it to the substrate at moderate temperatures and pressures. Figure 3 shows the process region B (coating, especially resist-coating application) of current resist spraying systems. Temperatures and/or pressures can be changed or are very probably changed. In any case the two-component system solvent-resist is always in the liquid state. This liquid state causes a correspondingly low viscosity. The low viscosity is caused mainly by the solvent. A not inconsiderable part of the solvent also vaporizes during the actual spraying process.

After the actual resist spraying process in the process region B the substrate is heat-treated either on a heating plate provided for this purpose or directly on the heatable sample holder. This heat treatment 4 is used to accelerate the vaporization of the solvent. Preferably the solvent to be vaporized has higher volatility, therefore a higher vapor pressure, than the resist which is actually of interest and which covers the surface. The resist partially sets by the continuous removal of the solvent and heat. In some types of resists an additional heat treatment step which occurs at higher temperatures can take place.

The major disadvantage in this type of spray application of the resist-coating consists in that before and possibly also during the vaporization of the solvent the resist on its surface forms a rough surface due to the increased mobility of the liquid solvent.

The idea as per embodiments of the invention is based on not applying the resist dissolved in the

solvent in the liquid state to the surface of an especially structured substrate, preferably a wafer, but on freezing the resist during the coating, especially the spray application of the resist-coating, or during the impact of the coating material on the surface of the substrate, especially in the manner of a shock (Figure 4).

The execution as per embodiments of the invention takes place in a special chamber in which there is a sample holder which can accommodate the substrate and which can cool it especially at the same time. Furthermore the spray chamber is optionally designed as a vacuum chamber in which the pressure can be regulated at least within the pressure ranges which are relevant to the phase transitions as per embodiments of the invention, in particular by means of a control apparatus as per embodiments of the invention.

The process flow as per embodiments of the invention is shown in the pressure-temperature phase diagram according to Figure 4. Proceeding from a coating region B' on which the coating material is still liquid, when the coating material is incident on the cooled surface of the sample holder, shock freezing (5) takes place. Due to the shock freezing (5) it is made impossible as per embodiments of the invention for the resist which is dissolved in the solvent to produce a rough surface by thermal movements.

In another step (6) as per embodiments of the invention, the gentle sublimation transition of the solvent contained in the coating material into the gaseous state, which transition takes place at low temperatures, takes place especially without vaporizing the coating component. Preferably under these process parameters the vapor pressure of the solvent is at least 1.001 times as great, preferably twice as great, more preferably at least 10 times as great, still more preferably 100 times as great, most preferably of all at least 1000 times as great as the vapor pressure of the coating component

which has been dissolved in the solvent. By gentle sublimation of the solvent and due to the low temperatures the coating material is concentrated more and more with the coating component since the solvent gradually evaporates. The resist is deposited more and more until starting at a certain point all the solvent is evaporated.

As per embodiments of the invention, a corresponding (resist spraying) chamber consists of an especially coolable (cooling means) sample holder and a vacuum-tight housing of the chamber which can be evacuated. The attainable vacuum is especially smaller than  $10^{-1}$  mbar, preferably smaller than  $10^{-3}$  mbar, more preferably smaller than  $10^{-5}$  mbar, still more preferably smaller than  $10^{-7}$  mbar, most preferably smaller than  $10^{-9}$  mbar.

The sample holder can be especially one of the following types of sample holders:

- vacuum sample holder
- electrostatic sample holder
- magnetic sample holder
- sample holder with mechanical clamping
- sample holder with adhesive surfaces

In one special embodiment which can be combined in particular with the above described ones, the surface of the wafer can be cooled via a cooling nozzle (cooling means) also by cold gases, shortly before and/or during the coating. This would have the advantage that the entire substrate need not be thoroughly cooled, but that the surface of the substrate is briefly cooled very locally before the resist is sprayed on. Preferably vaporized liquid nitrogen or helium is used for this purpose. The entire process is controlled and optimized by the external, especially software-supported control apparatus. All the fundamental capabilities of a coating device (especially a resist

spraying system) which are known to one skilled in the art are not influenced by the use of the process as per embodiments of the invention. The manner in which the spray nozzle which applies the dissolved resist, with which speed, movement can remain unchanged [sic].

In the (resist spraying) chamber there is especially one holding apparatus which can be temperature-regulated at least on the holding surface. The adjustable temperature range of the holding device is preferably between  $-200^{\circ}\text{C}$  and  $400^{\circ}\text{C}$ , preferably between  $-200^{\circ}\text{C}$  and  $200^{\circ}\text{C}$ , more preferably between  $-200^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ .

Other advantages, features and details of the invention will become apparent from the following description of preferred exemplary embodiments and using the drawings.

Figure 1 shows a p-T phase diagram of a single-component system,

Figure 2 shows a p-T phase diagram of a two-component system as claimed in the invention,

Figure 3 shows a p-T phase diagram of a two-component system as claimed in the invention with a method according to the prior art,

Figure 4 shows a p-T phase diagram of a two-component system as claimed in the invention with a method sequence as claimed in the invention and

Figure 5 shows a schematic of one embodiment of the device as claimed in the invention.

Figures 1 to 4 were described above for the general part of the invention.

Figure 5 shows a schematic of a chamber 7 which can be evacuated, with a holding apparatus 8 whose temperature can be regulated and which can be mainly cooled, on whose holding surface 12 is a substrate 9 (especially a wafer). Above the holding apparatus 8 a spray nozzle 11 and an (optional) cold nozzle 10 are attached to a holding device 13. The spray nozzle 11 and the cold

nozzle 10 can preferably be adjusted/controlled independently of one another by a control apparatus which is not shown, and can reach the entire surface 9o of the substrate 9 to be coated.

## Reference number list

- 1      sublimation or resublimation curve
- 2      evaporation or condensation curve
- 3      melting or solidification curve
- 4      heat treatment
- 5      freezing
- 6      sublimation transition
- 7      chamber
- 8      holding apparatus
- 9      substrate
- 9o    surface
- 10    cold nozzle
- 11    spray nozzle
- 12    holding surface
- 13    holding device
- s     solid phase
- l     liquid phase
- g     gaseous phase
- B     coating
- B'    coating

## Claims

1. A device for spray coating of a surface (9o) of a substrate (9) with a resist which has at least one coating component and at least one solvent, with the following features:

- a chamber (7) which can be pressurized with a pressure,
- a holding apparatus (8) for holding the substrate (9) on a holding surface (12) and
- a spray nozzle (11) for coating of the substrate (9),

wherein the device has cooling means for cooling of at least the surface (9o) of the substrate (9) which is held on the holding surface (12) of the holding apparatus (8) during the coating such that the resist is not applied in fluid form on the surface (9o) of the substrate (9) but that the resist is shock frozen already during application on the surface (9o) of the substrate (9).

2. The device as claimed in Claim 1, wherein the cooling means comprise at least one cooling nozzle (10) and/or a holding apparatus (8) which can be cooled at least on the holding surface (12).

3. The device as claimed in Claim 2, wherein the cooling nozzle (10) is or can be located above the holding surface (12).

4. The device as claimed in one of the preceding claims, wherein the device comprises an especially software-supported control apparatus with which the spray nozzle (11) and the cooling means can be triggered, especially separately.

5. The device as claimed in Claim 4, wherein the cooling means are controlled by the control apparatus such that the substrate (9) during coating at least on its surface (9o) has a temperature below the phase transition temperature of the coating material from liquid to solid.

6. The device as claimed in one of Claims 4 or 5, wherein pressurization means which are controlled by the control apparatus are controlled after coating such that especially at a roughly uniform temperature the pressure in the chamber (7) drops over a phase boundary of the solvent from solid to gaseous, while the phase boundary of the coating component from solid to gaseous is not exceeded.

7. The device as claimed in one of the preceding claims, wherein the device has measuring means for measuring the temperature on the substrate surface (9o) and/or on the holding surface (12) and/or for measuring the pressure in the chamber (7).

8. A method for spray coating of a surface (9o) of a substrate (9) with a resist which has at least one coating component and at least one solvent, wherein at least the surface (9o) of the substrate (9) is cooled during the coating such that the resist is not applied in fluid form on the surface (9o) of the substrate (9) but that the resist is shock frozen already during application on the surface (9o) of the substrate (9).

9. The method as claimed in Claim 8, in which during coating the pressure and the temperature on the surface (9o) are controlled by a control apparatus.

10. The method as claimed in Claim 8, wherein the substrate (9) during coating at least on its surface (9o) has a temperature below the phase transition temperature of the coating material from liquid to solid.

11. The method as claimed in one of Claims 9 or 10, wherein after the coating, especially at a roughly uniform temperature on the surface (9o), the control apparatus effects an increase of the pressure over the phase boundary of the solvent from solid to gaseous, while the phase boundary of the coating component from solid to gaseous is not exceeded.