

Aqueous dispersion, a process for the preparation and the use thereof

The invention relates to the preparation of aqueous dispersions containing silica produced by pyrogenic means,
5 a process for the preparation and the use of the dispersions for polishing semi-conductor substrates.

Aqueous dispersions containing silica have a broad field of application. The applications include, for example, the coating of paper, the manufacture of glass fibres and
10 quartz glass, and the chemical-mechanical polishing of semi-conductor substrates (CMP process).

Conventional dispersions are based either on colloidal silica, silica sols, or silica produced by pyrogenic means.

Colloidal silica is produced in the solution of sodium
15 silicate and yields dispersions with a very small particle size and very good dispersion stability. A disadvantage, particularly when polishing semi-conductor substrates, is the amount of impurities introduced by the starting material sodium silicate, and the adhesion of the particles
20 to polished surfaces.

Pyrogenic silica, on the other hand, produced by flame oxidation or flame hydrolysis from silicon tetrachloride, hydrogen and oxygen, exhibits a very high purity and a primary particle size comparable with that of colloidal
25 silica. Said primary particles aggregate and agglomerate, however, producing hard particles. Dispersion of the aggregates and agglomerates proves to be difficult, the dispersions are less stable and are susceptible to sedimentation or gelling.

30 A possibility of increasing the stability of the dispersion is described in US 5 116 535 and US 5 246 624. A particular feature is the BET surface which should be no greater than

75 m²/g, preferably from 30 to 60 m²/g. Here, too, however, as described in US 5 904 159, only a slightly better stability can be expected. Sedimentation occurs after only two months.

5 US 5 904 159 describes an aqueous dispersion containing silica produced by pyrogenic means which has improved stability. This is achieved by a particular form of dispersion process. The use of a high-pressure homogeniser permits the preparation of aqueous silica dispersions with
10 average particle diameters from 30 nm to 100 nm which are claimed to be stable for several months without sedimentation occurring.

A similar form of dispersion process is also described in EP-A-876 841. The average particle size of the claimed
15 metal oxides produced by pyrogenic means is given here as 10 nm to 2 µm and the stability is given in the examples as at least 30 days.

This dispersion process is also claimed in WO 00/17282 A1 for silica, cerium oxide and zirconium oxide, with particle
20 sizes from 30 nm to 500 nm. No indications about the stability of the dispersion are given.

Despite this improved stability of the aqueous dispersions, the reagglomeration behaviour of the dispersed silica particles remains, limiting the stability of the dispersion
25 and leading to scratches when surfaces are polished in the CMP process.

The object of the present invention was, therefore, to provide an aqueous dispersion which contains silica produced by pyrogenic means but which, compared with the
30 prior art, has a markedly reduced reagglomeration behaviour, greater stability and which, during chemical-mechanical polishing, yields high removal rates and leads

to a surface which is very largely free from microscratches.

The technical object is achieved by an aqueous dispersion containing an alkali-doped pyrogenic silica prepared by means of aerosol, characterised in that said silica, in the dispersion, has an average particle diameter of the secondary particles of less than 100 nm and the quotient d_n/d_s of the arithmetic mean of the number distribution d_n and the arithmetic mean of the surface distribution d_s of the primary particles is at least 0.7.

The terms primary and secondary particles originate from the pyrogenic production of the alkali-doped silica. In a pyrogenic process for the production of doped and undoped silica, the so-called primary particles initially have a size which is dependent on the reaction parameters selected and which is approximately from 5 nm to 40 nm. The size of said primary particles may be determined, for example, by TEM pictures. The primary particles are not, however, present in the isolated form but intergrow to aggregates, or join together to form agglomerates which are described hereinafter as secondary particles.

The quotient d_n/d_s in the alkali-doped silicas of at least 0.7 describes a markedly narrower particle size distribution than in an undoped silica produced by pyrogenic means. The quotient d_n/d_s in a silica produced by pyrogenic means with a BET surface of 130 m²/g (Aerosil 130, Degussa AG) is 0.52.

This dispersion has a greater stability than a comparable dispersion prepared according to the prior art but without alkali oxide doping. Greater stability of the doped dispersion means that the time at which the dispersion increases in viscosity, gels or settles occurs later than in dispersions with undoped silica.

It also became apparent that the time for incorporating the alkali-doped silica produced by pyrogenic means is shorter than without doping.

This result is surprising because aqueous dispersions
5 containing silica produced by pyrogenic means may be stabilised anyway, according to the prior art, by the addition of alkali or another basic substance. Potassium-doped silica has a modified aggregate or agglomerate structure compared with undoped silica. The doping
10 substance is homogeneously incorporated, that is, the alkali is situated both inside the particle and on the surface. For this reason, a dispersion which contains alkali-doped silica and alkali differs clearly from one which contains undoped silica and alkali. In the case of
15 alkali-doped silica, this different structure leads to more rapid incorporation, a lower reagglomeration tendency, and hence to greater stability of the aqueous dispersions.

In the case of silica produced by pyrogenic means and doped by means of aerosol, the doping component is fed into the
20 flame, of the kind used in the known way for the production of pyrogenic oxides by flame hydrolysis, in the form of an aerosol, for example, in the form of an aqueous solution of alkali chlorides. This process is described in DE-A-196 50 500. The aerosol is mixed homogeneously prior
25 to the reaction with the gas mixture of flame oxidation or flame hydrolysis, silicon tetrachloride, hydrogen and oxygen. The aerosol-gas mixture is allowed to react in a flame and the resulting doped silica produced by pyrogenic means is separated from the gas stream in the known way.
30 The starting product of the aerosol is a salt solution or suspension containing the component of the doping substance. During the genesis of the pyrogenic oxide, the doping medium is in the fine-particle form in the gas phase, so that homogeneous incorporation of the doping
35 component in the silica produced by pyrogenic means is

possible. Consequently, the aggregate or agglomerate structure of the pyrogenic silica is also influenced.

- The degree of doping may be varied widely in the silica prepared by the above process, from 0.00001 wt.% to 20 wt.%. In the use for the preparation of an aqueous dispersion according to the present invention, the degree of doping is preferably from 10 ppm to 10 wt.%, particularly preferably in the range from 300 ppm to 2 wt.%.
10 The BET surface of the alkali-doped silica in a preferred embodiment of the invention is from 5 to 600 m²/g. A range from 50 to 400 m²/g is particularly preferred, in which the dispersion exhibits good stability and the preparation of the alkali-doped silica is technically simple to carry out.
15 The solids content of the dispersion containing alkali-doped silica depends primarily on the intended use. In order to save on transport costs, a dispersion with the highest possible solids content is desirable, whereas for certain applications, such as, for example, for polishing
20 silicon wafers, dispersions with low solids contents are used. The range from 0.1 wt.% to 70 wt.% is preferred according to the invention, the range from 1 wt.% to 30 wt.% being particularly preferred. In these ranges, the alkali-doped dispersion shows good stability.
25 Due to the fact that the silica is doped with alkali, the pH of the dispersion is higher than in an undoped one, from about 5 to 8 depending on the degree of doping (pH of the four percent dispersion). The dispersion may be used such as it is, for example, for polishing. As in the case of
30 dispersions containing undoped silica, however, the viscosity in this case is markedly increased in a pH range from acid to slightly alkaline. According to a preferred embodiment of the invention, the pH of the dispersion is adjusted to a value from 8 to 12 by adding alkali

hydroxides or amines, potassium hydroxide and ammonia or ammonium hydroxide being particularly preferred. This leads to a marked stabilisation of the dispersion, and condensation reactions of the silica are thereby avoided.

- 5 According to DE-A-196 50 500, all alkali metals are suitable for doping silica produced by flame oxidation or flame hydrolysis. Doping with potassium is, however, particularly preferred. When potassium salts are used as the doping component, the structure alters decisively, that
10 is, the degree of intergrowth and also the morphology (that is, the appearance) of the primary particles. In potassium-doped silica, this change in morphology starts at a potassium content of more than 300 ppm.

- Surprisingly, the pyrogenic oxides doped in this way with potassium exhibit spherical round primary particles with
15 only very little intergrowth in the electron micrograph, which also manifests itself in the fact that no end point is detectable when the structure is determined by the dibutyl phthalate method (DBP method). The potassium is
20 uniformly distributed in the doped pyrogenic oxides. This cannot be seen on the electron micrographs.

Figure 1 shows an electron micrograph of a silica produced by pyrogenic means without doping (Aerosil 130, Degussa).

- Figure 2 shows an electron micrograph of a silica produced
25 by pyrogenic means and doped with 0.44 wt.% potassium, with a specific surface (BET) of 131 g/m².

- The invention also provides a process for the preparation of the dispersion containing alkali-doped silica. Dispersion methods suitable for this purpose are those in
30 which a sufficiently high energy input permits dispersion of even very hard and highly aggregated materials. These include systems operating on the rotor-stator principle, for example, Ultra-Turrax machines or agitated ball mills.

Higher energy input is possible with a planetary
kader/mixer. The effectiveness of this system is
associated, however, with a sufficiently high viscosity of
the treated mixture in order to introduce the requisite
5 high shear energies for breaking down the particles.

When doped oxide particles are ground and dispersed, there
is a risk that the dopant will become detached during
grinding and dispersion. If the dispersion is to be used in
the CMP process as a polishing agent, this leads to uneven
10 polishing results.

It has now been found that aqueous dispersions containing
alkali-doped silica particles which are smaller than 100 nm
and in which the dopant does not become detached may be
obtained with high-pressure homogenisers, hereinafter also
15 called wet-jet-mill.

In these devices, two pre-dispersed streams of suspension
under a pressure of up to 3500 kg/cm² are depressurised by
means of a nozzle. Both dispersion jets strike each other
exactly and the particles grind themselves. In another
20 embodiment, the pre-dispersion is likewise placed under
high pressure, but the collision of the particles takes
place against armour-plated wall regions.

Said devices have been used hitherto only for the
dispersion of undoped oxides such as zinc oxide, silica,
25 aluminium oxide (UK-A-2 063 695, EP-A-876 841,
EP-A-773 270, WO 00/172 282 A1). The grinding and
dispersion of doped oxides with these devices has not been
described hitherto.

The invention also provides the use of the aqueous
30 dispersion of alkali-doped silica for planarising semi-
conductor substrates or layers applied thereto. A
microscratch-free surface may be obtained with the
dispersion of alkali-doped silica with a high rate of

polishing. Moreover, said dispersions are suitable for the preparation of very fine-particle surface coatings in the paper sector, or as a raw material in the cosmetics and glass sector.

Examples

Methods of analysis

The particle size distribution d_n/d_a of the primary particles in the solid was determined by counting the
5 particles from the electron micrographs.

The average secondary particle size in the dispersion was determined with the Zetasizer 3000 Hsa from Malvern.

The surface of the powders used was determined by the method of S. Brunauer, P.H. Emmet and I. Teller, J. Am.
10 Chemical Society, volume 60, page 309 (1938) and is generally known as the BET surface.

The viscosity of the dispersions produced was determined with a rotational rheometer from Physica Model MCR 300 and the CC 27 cup. The viscosity value was determined at a
15 shear rate of 500 1/sec. This shear rate lies in a range in which the viscosity is practically independent of the shear stress.

The sediment formation was assessed by a visual assessment in a 1000 ml wide-mouth polyethylene bottle after a
20 standing time of one week. Any sediment present may readily be detected by carefully tilting the bottle.

The synthesis of the potassium-doped silica particles was carried out in accordance with DE-A-196-50 500.

Preparation of potassium-doped silica (K content 0.44 wt.%,
25 as K_2O)

4.44 kg/h of $SiCl_4$ were evaporated at about 130 °C and transferred to the central tube of the burner of known design in accordance with DE 196 50 500 A1. In addition,
30 4.7 Nm^3/h of hydrogen and 3.7 Nm^3/h of primary air and 1.15 Nm^3/h of oxygen were fed into this tube. This gas

mixture flowed out of the inner burner jet and burned in the burner space of the water-cooled flame tube.

In order to prevent caking, an additional 0.5 Nm³/h of (secondary) hydrogen and 0.3 Nm³/h of nitrogen were fed
5 into the jacket jet surrounding the central jet.

About 10 Nm³/h of air were also drawn in from the surroundings into the flame tube which was under a pressure slightly below atmospheric. (Open burner method.)

The second gas component, which was introduced into the
10 axial tube, consisted of an aerosol generated from a 12.55 percent aqueous potassium chloride solution. Two two-component nozzles yielding an atomisation capacity of 255 g/h of aerosol acted as the aerosol generator. This aqueous salt aerosol was passed through externally heated
15 lines by means of 2 Nm³/h of carrier air and left the inner nozzle at an outlet temperature of about 180 °C. The aerosol was introduced into the flame.

After flame hydrolysis, the reaction gases and the resulting potassium-doped silica were drawn through a
20 cooling system in a known manner by applying a pressure below atmospheric, and in so doing the particle/gas stream was cooled to about 100 °C to 160 °C. The solids were separated from the waste gas stream in a filter or cyclone.

The potassium-doped silica was obtained in the form of a
25 white, fine-particle powder. In a further step, hydrochloric acid residues still adhering were removed at elevated temperature by treatment with air containing water vapour.

The analytical data of the potassium-doped silicas prepared
30 in this way are reproduced in Table 1.

Table 1: Analytical data of the potassium-doped silicas

	No.	BET m^2/g	Potassium content wt.% (as K_2O)	Primary particle
				size distribution d_n/d_2
5	1	131	0.44	0.84
	2	121	0.49	0.81
	3	104	0.12	0.78
	4	113	0.24	0.80
10	5	120	0.69	0.86
	6	117	1.18	0.84

Preparation of dispersions

Method A: 36 kg of deionised water and 104 g of 30% KOH solution were placed in a 60 l refined steel preparation vessel. Using a dispersion and suction mixer from Ystral (at 4500 rpm), 16.5 kg of the silica doped with 0.44 wt.% potassium as prepared above and were drawn in by suction and roughly predispersed. This predispersion was supported by a Z 66 type rotor/stator continuous-flow homogeniser from Ystral with four processing rings, a stator slot width of 1 mm and a speed of 3000 rpm. After the introduction of the powder, dispersion was completed with the Z 66 type rotor/stator continuous-flow homogeniser from Ystral at a speed of 11,500 rpm. During this 15 minute dispersion at 11,500, the pH was adjusted to and kept at pH 10.5 by adding more KOH solution. A further 779 g of KOH solution were used in so doing and a solids concentration of 30 wt.% was obtained by adding 1.5 kg of water.

Instead of the potassium-doped silica, dispersion was also carried out according to method A for Aerosil 130 (BET surface 130 m²/g) from Degussa.

Method B: About half of the dispersions obtained by method
5 A were ground with a wet-jet-mill, Ultimaizer System from Sugino Machine Ltd., HJP-25050 model, at a pressure of 250 MPa and with a diamond jet diameter of 0.3 mm and two mill passes.

In total, three dispersions were prepared for polishing
10 purposes:

Dispersion 1: silica doped with 0.44 wt.% potassium,
dispersed by method B; solids content
30 wt.%, pH 10.5.

Dispersion 2: silica doped with 0.44 wt.% potassium,
15 dispersed by method A; solids content
30 wt.%, pH 10.5.

Dispersion 3: Aerosil 130, Degussa AG, without K-doping;
dispersed by method B; solids content
30 wt.%, pH 10.5.

20 Dispersion 2, prepared by method A, exhibited a markedly higher viscosity and the formation of sediment compared with dispersions 1 and 3 which were prepared by method B.

Further analytical data on these dispersions are given in Table 2.

Table 2: Analytical data of dispersions 1 to 3

5	Disp.	Arithmetic means of secondary particle diameters in the dispersion			Sediment
		Number [nm]	Volume [nm]	Viscosity ⁽¹⁾ [mPas]	
	1	49	71	7.5	no
10	2	77	142	50	yes
	3	100	140	15	no

(1) at 500 1/sec

15 The particle size distribution of the primary particles
does not alter due to dispersion.

Incorporation in dispersion/wettability: Considerable
differences in handling became apparent during the
incorporation of potassium-doped silica and Aerosil 130.
The potassium-doped material could be incorporated within
20 1.5 h using the dispersion and suction mixer from Ystral. A
period of 2.5 h was required to incorporate the amount of
Aerosil 130.

Moreover, it was not possible to predisperse the entire
amount of Aerosil 130 only with the Z 66 type rotor/stator
25 continuous-flow homogeniser from Ystral. From a
concentration of about 20 wt.%, it was no longer possible
to draw in Aerosil 130 by suction due to the high viscosity
caused by partial reagglomeration. This behaviour was
markedly less pronounced with potassium-doped silica
30 dispersions. Only when supported by the wet-jet-mill at 75
Mpa operated with recycling could the viscosity be reduced
again to such an extent that further Aerosil 130 material
could be incorporated.

The different rate of incorporation may possibly be attributable to a different wetting behaviour.

To this end, an amount of 5-10 mg of the appropriate sample was placed carefully on the surface of a test tube filled with twice-distilled water to a height of 6 cm, care being taken to ensure that there was no contact between the sample substance and the glass wall of the vessel. In order to determine the rate of wetting, the time taken for the sample to sink completely was measured. The test was repeated three times in each case.

It was observed that all the samples became thoroughly wetted immediately after being placed on the surface of the water. Complete wetting is considered to be the time taken for the sample to come into contact with water to such an extent that it becomes detached from the surface of the water and sinks to the bottom.

The wetting times of potassium-doped silica vary with the potassium doping. They are substantially shorter than for undoped silica (Aerosil 130) (Table 3).

Table 3: Wetting times of potassium-doped silica ⁽¹⁾

Wt.% K (as K ₂ O)	0.12	0.24	0.44	0.69	1.18	0 ⁽²⁾
Wetting time (s)	31	31	39	39	43	120

(1) Mean of 3 measurements; (2) Aerosil 130

Polishing process

Dispersions used: Apart from dispersions 1 to 3, the following commercially available dispersions were also used for polishing:

Klebosol 30N50 (Rodel), solids content 30 wt.%, stabilised with ammonia, pH 9.5

Klebosol 1501 (Rodel), solids content 30 wt.%, stabilised with KOH, pH 10.9

- 5 Semi-Sperse 25 (Cabot Microelectronics), solids content 25 wt.%, KOH-stabilised, pH 11.0, diluted 1:1 with water

Apparatus: A P200 CMP cluster tool from Peter Wolters CMP Systems, fitted with a PM200 polishing machine and a brush cleaner from Contrade was used for the polishing tests.

- 10 Cleaning tests were carried out with water and with ammonia.

The polishing head was fitted with a DF200 backing film from Rodel, and the polishing cloth used was an IC1000/SubaIV pad, also from Rodel. The set of parameters
15 listed in Table 4 was used for the polishing process.

Table 4: Set of parameters for the polishing process ⁽¹⁾

	Force	1500 N
	Contact point ⁽²⁾	190 mm
5	Back surface pressure, internal ⁽³⁾	0 kPa
	Back surface pressure, external ⁽³⁾	10 kPa
	Oscillation	- 10 mm
	Chuck speed	20 rpm
	Polishing disc speed	33 rpm
10	Dispersion flow rate	180 ml/min
	Polishing time	60 sec

- 1) Temperature: about 25 °C; 2) The distance, in mm, between the centre of the chuck and the centre of the polishing disc (diameter of polishing disc 600 mm); 3) a two-zone chuck was used where, to improve the uniformity adjustment, two regions can be treated separately with back surface pressure;

Wafers: 200 mm Si wafers coated with 1000 nm LPCVD TEOS (670 °C, 750 mTorr).

20 Evaluation of the polishing results

- Rate of removal and non-uniformity: the rates of removal obtained with the dispersions and the non-uniformity were determined by measuring the film thickness with an Axiospeed spectrophotometer from Zeiss. 49-point measurements were performed on the wafer with a 6 mm edge exclusion zone in each case. 25 wafers in each case were polished and evaluated in order to determine the average rate of removal.

- In view of the pronounced gelling behaviour on the polishing disc, it was not possible to achieve a stable polishing process capable of evaluation with dispersion 2.

Only three wafers could be polished, the rate of removal being below that of dispersions 1 and 3.

The results are set out in Table 5.

Table 5: Polishing results, 49-point measurement⁽¹⁾

	Disp. 1	Disp. 3	Klebosol 30N50	Klebosol 1501	SS 25 ⁽²⁾
5 Removal (nm/min)	445	355	287	326	353
Non-uniformity ⁽³⁾ (%)	5.5	6.7	5.7	6.2	5.9
10 Particle number after post-CMP ⁽⁴⁾	181	176	171	178	176

15 (1) Edge exclusion zone 6 mm; (2) Diluted 1:1 with water; (3) Standard deviation 1 sigma; (4) Particle size 0.25 - 1.00 μ m; Brushclean with 2.0% ammonia

Defects: The examinations in respect of defects (scratches and particles) were carried out visually under a Haze lamp and with a Censor ANS 100 surface particle counter
20 respectively.

The determination of the surface particles after post-CMP cleaning gives similar values for all the dispersions examined (Table 5).

25 The potassium-doped silica dispersion prepared by the wet-jet-mill with an average particle size of less than 100 nm. exhibits advantages during polishing in terms of the rate of removal and non-uniformity compared with dispersions based on colloidal silica Klebosol 30N50 and 1501, and compared with the SS25 dispersion based on pyrogenic
30 silica. With regard to the defects brought about on the

surface of the wafers during polishing, the behaviour of the above-mentioned dispersions is almost equally good.



Patent claims

1. Aqueous dispersion containing a silica produced by pyrogenic means and alkali-doped by means of aerosol, characterised in that said silica, in the dispersion, has an average particle diameter of the secondary particles of less than 100 nm and the quotient d_n/d_s of the arithmetic mean of the number distribution d_n and the arithmetic mean of the surface distribution d_s of the primary particles is at least 0.7.
2. Aqueous dispersion according to claim 1, characterised in that the alkali content of the doped silica is from 10 ppm to 10 wt.%.
3. Aqueous dispersion according to claims 1 or 2, characterised in that the BET surface of the alkali-doped silica is from 5 to 600 m²/g.
4. Aqueous dispersion according to claims 1 to 3, characterised in that the solids content is from 0.1 wt.% to 70 wt.%.
5. Aqueous dispersion according to claims 1 to 4, characterised in that the dispersion has a pH from 8 to 12.
6. Aqueous dispersion according to claims 1 to 5, characterised in that the alkali component used is potassium.
7. A process for the preparation of an aqueous dispersion according to claims 1 to 6, characterised in that the alkali-doped silica produced by pyrogenic means is dispersed in aqueous solution by means of a high energy input.



8. A process for the preparation of an aqueous dispersion according to claim 7, characterised in that, in order to disperse an alkali-doped silica in an aqueous solvent, a device is used in which the particles to be dispersed are under a pressure of up to 3500 kg/cm², depressurized by means of a nozzle and collide with one another or against wall regions of the device.
9. The use of the aqueous dispersion according to claims 1 to 6 for planarising semi-conductor substrates or layers applied thereto, for the production of fine-particle surface coatings in the paper sector, and in the cosmetics and glass sector.