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Mechanochemical Sense of the Technology of Chemical Mechanical Polishing of Materials

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Abstract

Interpretation of the mechanochemical aspect from the viewpoint of the manifestation of P. A. Rebinder effect is proposed on the basis of the experimental investigation of the kinetics and mechanism of the processes taking place during chemical mechanical polishing semiconductors, dielectric and metal crystals. The possibility of the tribochemical activation of chemical reactions by the flow of liquid silica sols under the joint action of chemical mechanical factors on the surface is demonstrated. It is established that solid particles promote activation and localization of chemical reactions on the surface of crystals on the atomic scale, and removal of the products of chemical reactions in the nanoscale. As a result, a mirror-smooth surface with subnanosecond relief is formed; containing no micro and nano scratches, pits, etched regions and other microdefects.

Key words: chemical and mechanical polishing, amorphous SiO_2 particles, polishers, single crystals, mechanochemical activation

INTRODUCTION

Chemical mechanical polishing (CMP) plays a decisive part in the technology of the final preparation of the surface of semiconductor and dielectric plates (substrates) and other hardware for subsequent processes, in of epitaxy, oxidation, diffusion, photolithography, coating deposition *etc*. Technologies of CMP materials involving compositions based on amorphous nanometre-sized spherical particles of oxides (SiO_2 sols *etc.*) dispersed in a liquid medium containing etchants are of special interest. The mechanism of material removal from the surface with simultaneous surface relief smoothing is complicated and multifactorial. The specificity is in the fact that chemical and mechanical factors separately do not give positive results on the quality and productivity of the preparation of polished surface. Chemical, electrochemical, hydrodynamic and other processes that take place at the solid to liquid interface in polishers under the conditions of CMP.

The goal of the present work is to reveal and interpret mechanochemical processes that occur during CMP of various crystals by chemically active compositions based on sols of amorphous nanometre-sized SiO_2 particles both at the moment of mechanical action and as a result of this action [1].

RESULTS AND DISCUSSION

The mechanochemical aspect of CMP materials will be considered from two points of view: 1) the possible occurrence of the effect described by P. A. Rebinder [2] and facilitation of crystal deformability as a consequence of adsorption of surface-active substances (SAS), which promotes an decrease in the surface energy and change of mechanical properties; 2) possible participation in CMP of mechanochemical processes resulting in the acceleration of chemical reactions on the surface under the mechanical action [3–5].

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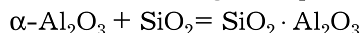
Rebinder effect

A specific feature of Rebinder effect is that SAS have a substantial influence in minimal concentrations in chemically inactive media [2]. Usually, SAS are complicated organic compounds with long hydrocarbon chains: synthetic higher acids and alcohols of the fatty series, mineral oil *etc*. Unlike the corrosive chemically active medium, the medium itself or SAS solutions do not cause the destruction. A SAS-containing medium facilitates the action of mechanical factors due to a decrease in the work necessary for the formation of new surfaces. The mechanical destruction (cutting, drilling, polishing, abrasive polishing) is facilitated as a result of the continuous formation of microcracks with juvenile surface the atoms of which provide chemisorption of liquid SAS in the form of monomolecular layers. The latter cause an especially substantial decrease in the resistance to the plastic flow, microhardness or strength.

This effect is not pronounced for CMP of semiconductor covalent crystals, because of relatively high rates of removal (0.2–1.0 μm/min), which is carried out not in the inert medium but in aggressive chemical medium. As a consequence, at the background of high rates of the dissolution of materials, SAS adsorption is slow; Rebinder effect remains unnoticed and has almost no influence on the integral rate of the removal. Under these conditions, surface layers distorted in preliminary mechanical treatment and not weakened by SAS are rapidly removed. It has been established experimentally that SAS promote a decrease in microhardness under the kinetic micro-indentation with the low load (<1 N) of semiconductor crystals (GaAs *etc*.), that model the abrasive treatment occurring rather slowly, in comparison with CMP. The behaviour of α-Al_2O_3 ionic crystal during mechanical treatment in the presence of SAS differs from the behaviour of covalent crystals. All the compositions applied to accelerate or optimize mechanical treatment of α-Al_2O_3 may be divided into two types: the compositions that do not enter chemical interaction with the material, and the compositions reacting with it [6]. As a rule, the compositions of the first type contain oleic or stearic acid, polyoxide, additives to broaden the possibilities of application (polyethylene glycol, synthanol, potassic soap *etc*.). The second type includes ultrafine powders of SiO_2 and alumino-organic silica, either in the dry form or in suspensions. It is likely that in the first case polishing involves a solid-phase reaction which accelerates at high temperature and pressure:



$$\alpha\text{-}Al_2O_3 + SiO_2 = SiO_2 \cdot Al_2O_3$$

and in the second case a liquid-phase reaction occurs:

$$\alpha\text{-}Al_2O_3 + 2H_2O + 2SiO_2 = Al_2Si_2O_7 + 2H_2O$$

Active liquid media (water, pure ethylene glycol or with organic additives) have different effects on the rate of mechanical polishing sapphire [7]. In some of them, it increases by a factor of several units, in comparison with experiments where diamond pastes in water were used without additives. The polishing rate in the presence of SAS changes inversely proportional to the viscosity of destruction, at the same time, the microhardness decreases, and micro-fragility increases (according to the data obtained by indenting). Water adsorption plays a substantial part, as it decreases the activation energy of the destruction due to the action on bonds in the lattice.

So, Rebinder effect manifests itself in different ways during the mechanical treatment of the sapphire surface: as an increase in the fragility or plasticization. However, there are no literature data on this effect during sapphire CMP. Our experimental results indicate that high removal rates (0.2–0.5 μm/min) achieved during CMP of α-Al_2O_3 (0001) by alkaline compositions of amorphous silica cannot be explained by the adsorption-related decrease in the strength alone. Similarly to the case of CMP of semiconductors, the chemical dissolution in alkali intensified by amorphous colloidal SiO_2 particles prevails in this case.

Effect of mechanochemical processes

Mechanochemical processes are based on the phenomena arising in solids under the action of high pressures, shock loads [1, 5]. As a result, structural and chemical defects are formed on the surface and within the volume of the materials. This is a principal difference of mechanochemical processes from grinding the major result of which is the formation of the

new surface. However, CMP does not involve grinding of the material under treatment, and this treatment is directed at the formation of the perfect crystal surface containing no linear and other defects. In this connection, it is impossible to use mechanical solid-phase activation by shock action for the purpose of smoothing the relief of solids for high nanotechnologies. A correct comparative analysis of the processes involved in CMP with respect to mechanochemical processes is possible only in the case if the solid–liquid system is considered but not solid–gas or solid–solid.

Here, we detect an analogy with tribocorrosion processes that are initiated on the surface of metals and semiconductors under various kinds of mechanical action: tension, compression, bending, torsion, cutting, scratching, generation of internal strain under mechanical pulses, friction, shock action by solid particles (sand-jet treatment), gases, liquids, cavitation bubbles *etc*. Goals of CMP are mainly satisfied by the excitation by the liquid flow with high flow rate under non-laminar conditions. In the latter case, the excitation is increased many times by nanometre-sized particles present in the etchant. The specific feature is that these particles are amorphous and spherical, so a detailed consideration of the elementary acts of their interaction with the surface of different single crystals under dynamic conditions requires more attention.

It is necessary to stress a number of the revealed features of CMP. For instance, solid amorphous oxide particles (SiO_2, $SiO_2 \cdot Al_2O$, γ-Al_2O_3 *etc.*) do not cause the shock action on the surface, plastic deformation (the formation of micro- and nano-scratches, dislocations, surface micro(nano)cracks). Chemical mechanical polishing proceeds in the liquid medium under atmospheric conditions, without the periodic vibrational load applied. CMP processes take place only on the surface, involve sub- or nanometre atomic layers and do not involve deep lying volume of crystals. Due to the intense removal of heat by the liquid-phase component composition on a cooled (as a rule) polisher, the processes take place at the constant integral T_{room} or somewhat higher (up to 50 °C). Exclusion is CMP of crystals poorly soluble in alkaline or acidic etching solutions, for example α-Al_2O_3, α-SiC and so on. However, they also do not cause temperature destructions in materials, though the formation of regions of local heating as one of the types of the excited states of the lattice is possible. Chemical mechanical polishing is not accompanied by the photon and electron emission, unlike processes of mechanical crushing and splitting (triboluminescence, tribo-induced electron emission). The bodies under CMP treatment do not undergo stretching, compression, torsion or scratching, while simultaneous chemical dissolution promotes a decrease in elastic strain or the removal of elastically strained regions from the crystals. These facts strongly distinguish CMP processes from mechanochemical processes activated by the direct mechanical action.

Thus, the mechanical action in direct mechanochemical processes accelerates sharply solid-phase reactions; however, reaction rate decreases either sharply or smoothly after the action is ceased. Similar phenomena are observed during CMP of silicon or other crystals in which the mechanical action of amorphous nanometre-sized spherical particles is localized in oxide surface compounds. With an increase in SiO_2 concentration to 14–15 vol. % in solution of a strong organic base, the rate of removal increases (Fig. 1). Replacement of the colloid composition in the course of CMP by the solution of the same amine in the same concentration causes a sharp decrease in removal rate from 0.4 0–0.6 μm/min to the level corresponding to the action of etching solution

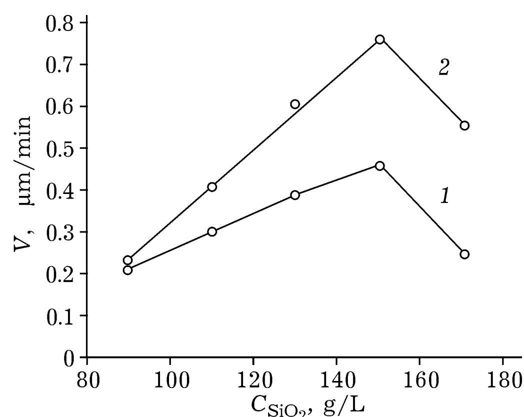


Fig. 1. Dependence of removal rate for Si (111) of KEF-7.5 grade on the concentration of aerosil A-380 in the optimal composition containing ethylene diamine. P, g/cm^2: 199 (*1*), 240 (*2*).

alone (<0.1 μm/min) and the absence of polishing. This confirms the participation of particles in the destruction of oxide compounds and activation of the chemical dissolution of Si. However, unlike for the mechanochemical process, where the activation of solid-phase or heterogeneous reactions proceeds through shock action (for example, by fine abrasive particles in liquid medium during vibrational polishing), during CMP amorphous particles in the liquid-phase medium provide mainly the action in the tangential direction to the surface. Due to the motion of particles, conditions for the continuous formation of the juvenile surface are created in nanometre-scale local regions simultaneously over the whole surface treated. Another example of the participation of solid particles in CMP process and activation of chemical reactions is the dependence of the removal rate for CdS crystal (0001) on the composition and concentrations of components in mixtures of amorphous aerosil and microcrystalline SiO_2 powder Elplaz-K in different polishing devices (Fig. 2). Here, two mechanical factors are involved in this process: solid particles and the polisher. One can see that rather concentrated (10 %) solutions of strong acidic etchants within the whole range of concentrations ratio in the optimal treatment modes do not affect removal rate and do not cause relief smoothing. The mechanical participation of polishers is also minimal, (see Fig. 2, curves *1*, *2*). The process behaviour changes in the presence of solid amorphous particles; an increase in removal rate within the whole range of etchant concentrations is stronger pronounced in a more rigid polisher (see Fig. 2, curves *3*, *4*). Even stronger mechanical action on the material is produced by polydisperse particles taken from the suspension of Elplaz-K powder, with rather broad size scattering (see Fig. 2, curve *5*). This action increases when a tight polisher is used. The ratio of concentrations of two etchants also affects relief smoothing: polishing occurs only when their certain combination is applied.

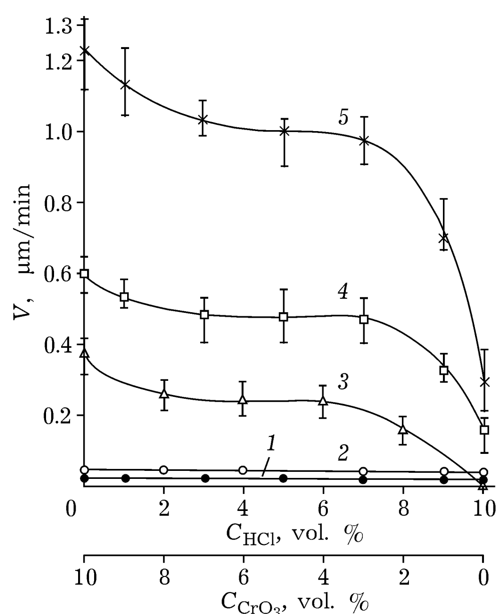


Fig. 2. Dependence of removal rate for CdS (0001) on the composition and concentration of components in etchant without SiO_2 and in different compositions in the presence of SiO_2 on different polishing pads: *1* – 10 vol. % solution of HCl + CrO_3, sintepol; *2* – the same, politeks; *3* – 10 vol. % HCl + CrO_3 in 8 % SiO_2 composition, sintepol; *4* – the same, politeks; *5* – 10 vol. % HCl + CrO_3 in Elplaz-K powder suspension, politeks.

The comparative analysis of the action of particles in mechanochemical reactions and CMP processes reveals both common and distinguishing signs. Thus, the rate of product formation in mechanochemical processes is strongly dependent on the number, mass and hardness of beads in the vibrational vessel: the larger in the number of beads, their mass and hardness (*e. g.* glass and steel beads), the higher is the rate and the yield of products of reactions in ball or planetary mills. The kinetic curves of reaction rate *versus* the mass of beads are similar to $V = f(C_{SiO_2})$ curves for CMP with amorphous SiO_2: at first, a linear region appears, and then saturation is observed. However, in CMP processes microhardness of amorphous nanometre-scale SiO_2 particles is practically unimportant, unlike for mechanochemical processes with shock and pulverizing action. The number of particles, similarly to the case of mechanochemical reactions, is important for obtaining uniformly polished surface: in the case if the lack of amorphous particles in etching solutions, partial or total surface etching is observed, while their excess causes a decrease in removal rate (because of passivation) and the loss of quality (see Fig. 1).

So, solid particles of silica sol do not cause the direct mechanical action on crystals and do not cause typical mechanochemical reactions during CMP (nanocracks and dislocations caused by treatment are absent according to TEM data).

They affect only the products of the chemical dissolution of crystals, located on the surface in the form of thin nanometre-sized hydrated oxide-hydroxide films or complex colloid compounds of different chemical composition. As a result of intensification of nanolocalized topochemical reactions, the rate of material removal increases. These reactions proceed on the local freshly formed regions of nanometre size which may be considered as active centres.

Here, it should be kept in mind that the surface of real crystals bears various defects that are differentiated by their size into point, two-dimensional linear and three-dimensional. Depending on the crystal perfection, defects in full or partially take part in CMP processes having different effects on the rate of material removal and the quality of the treated surface. Defects of all kinds may be active centres on which, for example, the chemical dissolution may proceed with different rates (anisotropically). If the relief is sufficiently smooth (polished), chemical interaction involved in CMP starts at active nanocentres of crystal surface that are formed as a result of the removal of oxide by solid particles. If the relief is developed and subsurface structure is destroyed, as after polishing, the interaction initially affects high ledges of surface roughness, the products of micro-destruction in hollows, and then the boundaries of blocks, microcracks *etc*. As destroyed surface regions are removed, more perfect regions are involved in the process, and a continuous reaction zone between the material, composition and polisher is formed with time. With the density of growth dislocations in silicon about $N_{\perp} \approx 10^7$ cm^{-2}, the area of active centres is almost 70 % of the plate area [8], which means that practically whole surface becomes active, and the size of active dislocation regions becomes equal to almost 3 μm as average. These experimental facts are also manifested with other crystals with $N_{\perp} \approx 10^5$–10^7 cm^{-2} (Ge, GaAs, ZnO, CdS *etc*.). However, at the optimal CMP the dislocation structure in not revealed, which indicates that chemical dissolution reactions are localized on the regions <<1 μm in size. As a rule, chemical mechanical polishing reveals the coarse and modular structure, as well as three-dimensional defects (pores, microblocks, internal cracks, inclusions), that is, macrodefects. However, in each specific case, the process takes place in different manners, namely with a higher or lower involvement of defects.

The kinetics of generation of active centres during CMP with SiO_2 amorphous nanoparticles may be described by kinetic equations of mechanochemical reactions proposed by P. Yu. Butyagin [9], with the following assumptions based on the experiments on CMP: active centres are localized only on the fresh surface; the rate of formation of the centres is proportional to the rate of formation of juvenile surface, that is, the number of centres per unit freshly formed surface is constant for a given solid under the conditions of optimal CMP; all the generated active centres are of equal worth from the point of view of energy. The equation is

$$V_0 = \frac{dN_{A^+}}{dt} = n\frac{dS}{dt} \quad (1)$$

where V_0 is the rate of formation of active centres; N_{A^+} is the number of active centres; t is time; n is concentration of the centres on fresh surface; S_{sp} is specific surface. The rate of the interaction of active centre with the nearest molecules of the liquid medium (for Si these are OH^- ions) is defined as

$$-\frac{dN_{A^+}}{dt} = \alpha K N_{A^+}[C_{OH^-}] \quad (2)$$

where α is the probability of chemical reaction of OH^- ions with the active centre; $[C_{OH^-}]$ is the concentration of OH^- ions; K is the constant equal to $K = \omega/\sqrt{2\pi m k_B T}$ (ω is the collision cross-section equal to 10^{-15} cm^{-2}); m is the mass of attacking ion; T is temperature; k_B is Boltzmann constant.

It is established experimentally that CMP of all crystals proceeds efficiently, independently of their diameter (for Si it is 10–300 mm) for C_{SiO_2} = 8–12 mass %. Therefore, the average value C_{SiO_2} = 10 mass % in 10 % alkaline solution may be accepted as the concentration with which 100 % of active surface centres are formed. So, each SiO_2 particle causes the formation of one centre at a given moment of time, so their number is proportional to the number of particles participating in the interaction.

On the other hand, if the concentration of active centres (n_s) is equal to the concentration of surface atoms: $N_s = n_s$, that is, about 10^{15}

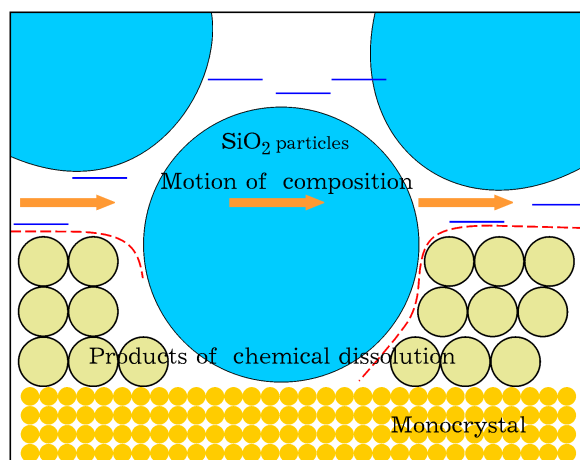


Fig. 3. Schematic diagram of the mechanochemical aspect for CMP of crystal surface: formation of nanometre-sized active centres due to the motion of nanometre-sized amorphous SiO_2 particles; activation of chemical dissolution localized on atoms, and removal of surface compounds by solid particles.

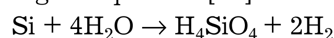
at./cm^2, and the activated centre oscillates with the frequency ν which is equal to the thermal frequency of atomic oscillations (about 10^{12} s^{-1}), the pre-exponential factor in the equation for dissolution rate will be equal to 10^{27} at./(cm^2 · s):

$$V = n_s \nu \exp(-E_A/RT) \quad (3)$$

where E_A is activation energy, R is constant.

The dynamic (momentary) activation of Si surface by a separate SiO_2 particle through the removal of oxide compounds transforms the surface element (Si atom) into the non-equilibrium metastable state with very short lifetime (about 10^{-4}–10^{-7} s). Hydroxide ions which are at that moment in contact with the active surface structural elements have enough time to react with them. Ion chemisorption is maximal when the number of active surface elements is equal to the number of surface atoms. The effect of the set of particles and their motion provide continuous opening of the juvenile surface and the formation of a set of nanolocal short-lived surface centres (Fig. 3). As a consequence, structure-sensitive parameters of silicon and other crystals (solubility, chemical activity *etc.*) increase substantially. This may be also related to the crystals with relatively low rates of chemical dissolution at room temperature, for example ZrO_2 : Y, $LiNbO_3$, their rate of CMP increases to 10–12 μm/h and 1–1.5 μm/min, respectively.

The activity of the surface of a material may be assessed on the basis of its real structure and the presence of surface defects. For example, it defect content decreases as a result of treatment, as during CMP, we may state that the given material was in more active state before treatment. This is confirmed by an increase in photo- and cathode luminescence of CdS crystals after CMP; the intensity of luminescence is directly dependent on the volume and surface concentrations of defects and their type. This is also evidenced by a sharp decrease in the intensity of CdS surface thermally stimulated by exo-electron emission EEE after CMP in comparison with diamond polishing: the removal of dislocations and a decrease in the fraction of free electrons [10]. So, CMP transforms materials from more active state to a less active one by means of a decrease in defect content of the surface. However, the surface itself is chemically very active, first of all with respect to oxidation reactions: all polished crystal surfaces at room temperature have protective oxide films of different stoichiometric compositions and thickness, which is confirmed by ellipsometry, electron diffraction studies and EOS. If the products of chemical action formed on the surface are well soluble in water and are almost completely absent from the surface, the rate of chemical reaction is proportional to the total surface of the material. This situation is realized during mechanochemical dissolution of Si in water according to equation [11]



$$Si + 4H_2O \rightarrow H_4SiO_4 + 2H_2$$

The rate of this reaction at the moment of the mechanical activation is two-three times higher than that on preliminarily activated Si. A similar picture is also observed in CMP by colloid particles; they remove the formed products from Si surface under dynamic conditions. Process rate is proportional not to the whole surface but only to the rate of formation of the juvenile freshly formed surface (kinetic mode). The removal of the formed oxide compounds, possessing lower mechanical strength than that of the crystal, creates conditions for the formation of new protective oxide compounds. This process runs with very high rates decreasing with thickness growth. However, surface atoms, uncovered by the solid particles

TABLE 1

Independence of CMP rate from crystal microhardness

Materials	H_μ, kg-f/mm^2	V_{CMP}*, μm/min	$T_{m.p}$, °C	E_g, eV (300 K)
α-SiC	2350	0.2; до 0.5	2200–2700	2.9
α-Al_2O_3	1940 ∥ to axis *c*	5–7 μm/h; up to 1.0	2030	–
$Y_3Al_5O_{12}$	1550 (100)	0.2–0.3	1950	–
ZrO_2 : Y	1455 (111)	02	2700–2850	–
MgO	1145	02	2800	–
$Gd_3Ga_5O_{12}$	1100	0.2–0.3; 0.5	1750	–
Si	1100	0.3; 0.5; до 1.0	1417	1.1
Ge	900	0.2–0.5; до 1.0	936	0.66
GaP	850–940	0.5–2.0	1467	2.25
GaAs	700–750	0.5–2.0	1238	1.43
α-SiO_2	741	0.2–0.4	1470	–
$SrTiO_3$	600	0.15	2080	–
$LiNbO_3$	450–500	до 1.0	1250	–
GaSb	420	0.1–0.2; 0.6	712	0.80
$CdAs_2$	310–390	0.2–0.3	621	1.11
PbSe	55	0.6–2.5	1076	0.29

* The data were obtained using different equipment.

removing the oxide, again get oxidized with the same high rate. These processes provide the high rates of CMP not only for semiconductors (Si, Ge, GaAs, CdS, CdP_2) but also for other crystals. Total rate of material removal during CMP depends mainly not on mechanical properties of the material but on the rate of chemical reactions proceeding according to the electrochemical mechanism, for metals and semiconductors, and on the rate of ion exchange processes for dielectrics. This is confirmed experimentally by CMP of the crystals with different microhardness by the compositions of amorphous SiO_2 (Table 1).

Thus, CMP and mechanochemical processes in the system solid–liquid have a common property: reaction rate is determined by the rate of formation of active surface centres, on which, in turn, the rate of surface product formation inn chemical reactions depends.

CONCLUSION

It was established as a result of investigations that the adsorption decrease in material strength known as P. A. Rebinder effect was not detected in CMP of crystals by chemically active compositions of nanometre-sized amorphous colloid SiO_2 particles proceeding with high rates.

Both analogies and differences were revealed between CMP and mechanochemical processes in the system solid–liquid. CMP involves the activation of the initially passive crystal surface by amorphous silica particles due to elementary acts localized on a nanometre scale and removing the surface compounds, thus uncovering the juvenile surface and accelerating its oxidation under the conditions of chemically active liquid medium. The rate of surface layer removal and surface quality are strongly affected by the phase state, size and concentration of solid particles, chemical composition and concentration of etchants, conditions of their interaction on materials (technological regimes), properties of polishers, types of defects in crystals, their size, concentration and other factors.

Nanolocalization of the action of amorphous particles in oxide layers and uncovering of the juvenile surface are evidenced by the experimentally established independence of the removal rate and high quality of the surface crystals from their hardness and the formation of the nano-roughened relief R_a = 0.1–0.5 nm in optimal CMP.

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