

Mechanically induced transformations in silicon

Nadežda Številová¹, Vladimír Šepelák¹ and Klára Tkáčová¹

Mechanicky indukované premeny kremíka

V práci sa študujú zmeny veľkosti častíc a štruktúry kremíka pri vibračnom a planetárnom mletí vo vzduchu a v kvapalinách rôznej permitivity (metanol, acetón a benzén). Kinetika redukcie veľkosti častíc a zmien štruktúry závisí od relatívneho zrýchlenia pohybu mlecích telies a od povahy mlecieho prostredia. Najefektívnejšie zjemnenie a ochrana povrchu prášku kremíka voči oxidácii prebieha pri mletí v nepolárnom benzéne. Rýchlosť zmien veľkosti kryštálov a mriežkovej deformácie klesá v nasledovnom poradí mlecích prostredí: vzduch > metanol > acetón ≈ benzén. Zmeny hustoty atómov, určené metódou radiálnej distribučnej analýzy, prebiehajú pri planetárnom mletí v študovaných prostrediach v zhode so vzrastom limitných hodnôt mriežkovej deformácie.

Kľúčové slová: mletie, kremík, veľkosť kryštálov, mriežková deformácia, radiálna distribučná analýza.

Introduction

Silicon, the most important semiconductor material in electronics and electrotechnics, is one of the most frequently studied substances in solid state physics and chemistry. During more than a forty years period of intensive research, an information has been collected about the surface structure, surface states and the morphology of compact and porous silicon.

The basic information about the nature of surface centres was obtained by the ESR spectroscopy made on clean single-crystal cleavage surfaces as well as on vacuum and air crushed powders. Papers (Haneman, 1968; Chung et al., 1966; Caplan et al., 1976; Kolbanov et al., 1982) refer to a strong ESR signal arising at $g = 2.0055$. The signal is often called a „damage signal“ and represents dangling orbitals in Si^{III} which have not been paired in bonding with oxygen or otherwise compensated.

The preparation of silicon-based alloys, composites and ceramics by mechanochemical procedures stimulates the investigation in mechanically induced amorphisation. A partial amorphisation up to 10 percent of volume was first observed by Gaffet and Harmelin (Gaffet, 1990). It has been supposed to be the consequence of a continuous refinement of crystallite size during milling. Bokhonov et al (Bokhonov et al., 1993) subsequently also observed a formation of amorphous phase during milling, which was, however, attributed to amorphous silicon suboxide.

According to pioneering works of Gaffet and Harmelin the crystalline to amorphous phase transition of Si seems to be highly dependent on the milling conditions. Investigations made in the early 1990s confirmed the influence of milling energy and atmosphere on the amorphisation and contributed to the elucidation of the mechanism of crystalline to the amorphous transition at milling (Gaffet, 1990; Gaffet et al., 1989). Recent papers confirmed the original assumptions made by Gaffet and Harmeline: the amorphisation is assumed to be the consequence of a decrease in the crystallite size, i.e. the region of coherent X-ray scattering (Milet et al., 1994; Shen et al., 1989).

Based on the above cited papers as well as on the results of our previous works (Tkáčová et al., 1995; Številová et al., in press) in the present work the changes in particle size and structure disordering proceeding at grinding of silicon in different mills and grinding environments have been studied.

Experimental

Samples containing 99.95 % of Si were obtained as a by product of the monocrystalline ingot production (Tesla Sezam, Rožnov) with the B content of 10^{13} to 10^{12} atoms and the P content of 10^{15}

¹ RNDr. Nadežda Številová, CSc., RNDr. Vladimír Šepelák, CSc. a Prof. RNDr. Klára Tkáčová, DrSc. Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 04353 Košice, Slovakia, Fax number: +421-95-6323402, E-mail address: stevila@Linux1.saske.sk

(Recenzovali: Dr. Ing. Milan Škrobán, CSc. a RNDr. Peter Baláž, DrSc. Revidovaná verzia doručená 29.10.1997)

to 10^{13} atoms in mm^{-3} . After preliminary crushing to the particle size of 0.5 - 0.2 mm, a material charge was ground in a vibration mill (at the amplitude $a = 5.7$ mm and number of revolutions, $n = 20.5 \text{ s}^{-1}$) and a planetary mill (Pulverisette 4, Fritsch, Idar-Oberstein). The ball milling conditions are summarised in Table 1. The steel and tungsten carbide (for Pulverisette) grinding chamber and media were used. The grinding experiments were carried out under dry conditions and in methanol, acetone and benzene at a solid to liquid ratio 1:1 by weight.

A non-activated sample with relatively well preserved crystallinity was prepared by a careful attrition in an agate mortar.

Table 1. Grinding conditions in the vibration and planetary mill.

Parameter	Vibration mill	Planetary mill
relative acceleration	8.1	12.9
powder-to-ball weight ratio	1: 20	1: 22
milling time (h)	0.125 - 4 (8)	0.08 - 4

The particle size distribution of ground silicon powders was measured by the method of laser beam scattering in a Helos and Rodos granulometer (Sympatec GmbH, Claustahl-Zellerfeld). The mean particle diameter was calculated as the first moment of the density of the volume size distribution function.

The X-ray diffraction measurements were carried out using the Dron 2.0 diffractometer equipped with a goniometer GUR 5 (Technabsexport, Moscow) at the stabilised voltage of 24 kV and a current of 20 mA. The vertical divergence of X-ray beam (MoK_α radiation, $\lambda = 0.07107 \text{ nm}$) was restricted using two Soller's diaphragms. The horizontal divergence was 1.5° . The observed s-range was $15 < s < 153 \text{ nm}^{-1}$. The radial distribution function (RDF) was calculated in accordance with Richter (Richter, 1977) using the following relation:

$$4 \pi r^2 \delta(r) = 4 \pi r^2 \delta_U + 2 r \int_{s_{\min}}^{s_{\max}} \pi I(s) |N f^2 - 1| \sin(sr) ds$$

where I is the intensity of the X-ray diffracted by the disordered array of atoms at the angle θ , f is the atomic scattering factor, N is the number of atoms, r is the spherical radius, δ_U and δ are the average and normal atom density, respectively, $s = 4 \pi \sin \theta \lambda^{-1}$ (λ is wavelength).

The crystallite size and microstrains were calculated by the method of harmonic analysis of the XRD line profiles.

Results

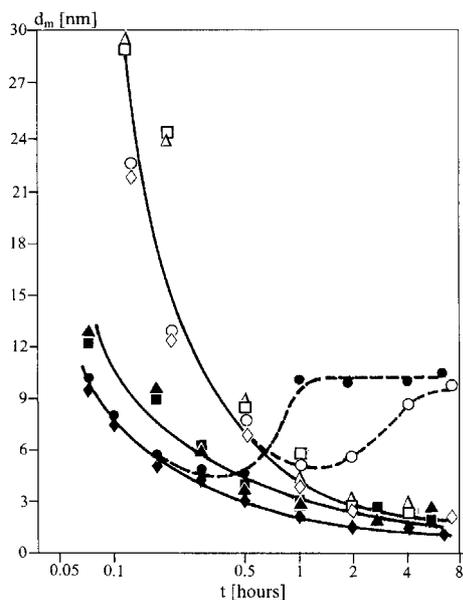


Fig.1 an particle diameter, d_m , vs. grinding time, t , for silicon ground in a vibration (empty points) and planetary (full points) mill in air (o), methanol (Δ), acetone (\bullet) and benzene (\blacktriangledown).

Fig. 1 shows the changes in the mean particle diameter during grinding in the vibration and planetary mill. The particle size reduction in both investigated mills proceeds to critical values of mean particle diameter. While the kinetics of the particle size reduction is influenced mainly by the intensity of stress in compared mills, the differences in critical particle diameter depend on the aggregate state of particles being ground.

The mean particle diameter, d_m , calculated from the particle size distribution depends upon the size of individual particles or stable aggregates formed at grinding. Stable aggregates termed also agglomerates are formed at milling in the atmospheric environment. The critical particle size when agglomeration prevails fragmentation is in both vibration and planetary mill $d_m = 4.6 \mu\text{m}$. Milling in the

investigated liquids

in both mills proceeds to a limiting particle diameter, about 1 μm .

According to studies presented in our previous work (Tkáčová et al., 1995) the particle size distribution of intensively milled silicon is influenced also by the thickness of the oxide surface shell. The above influence is demonstrated by the results of XPS in Table 2.

Table 2. Relative permittivity of liquids, ϵ_r , mean particle diameter, d_m , intensity ratio, $\text{Si}^{\text{OX}}/\text{Si}^{\text{O}}$ and atomic concentration ratio, $\text{O}/\text{Si}^{\text{OX}}$, determined from XPS data referred in Tkáčová et al. (1995).

Environment	ϵ_r [Fm^{-1}]	d_m [μm]	$\text{Si}^{\text{OX}}/\text{Si}^{\text{O}}$	$\text{O}/\text{Si}^{\text{OX}}$
Air	-	10,11	0,3	3,58
Benzene	2,28	1,66	0,22	3,12
Acetone	21,4	2,64	0,37	2,42
Methanol	33,5	2,84	0,45	2,33

In the course of milling of silicon in both vibration and planetary mill, a gradual decrease in the crystallite size and a increase in the relative lattice strain to limiting values was observed. Figs. 2 and 3 confirm the above differences in the efficiency between the planetary and the vibration mill. The presented kinetic curves enable also a sensitive evaluation of the effect of grinding environment on structural changes proceeding in the bulk of particles being ground. The rate of structural changes decreases in the following sequence: air > methanol > acetone \approx benzene.

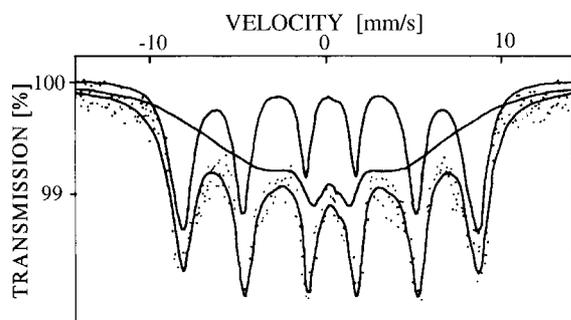


Fig. 2. Crystallite size, λ , (full points) and lattice strain, $\Delta a/a$, (empty points) vs. grinding time, t , for silicon ground in a vibration mill in air (o), methanol (Δ), acetone (-) and benzene (\square).

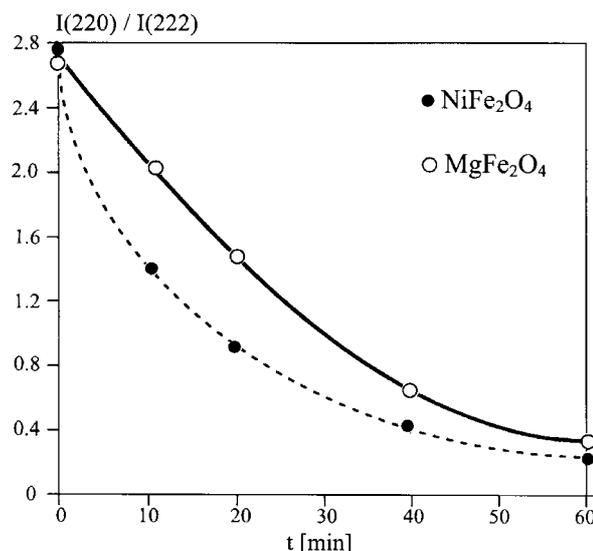


Fig. 3. Crystallite size, λ , (full points) and lattice strain, $\Delta a/a$, (empty points) vs. grinding time, t , for silicon ground in a planetary mill in air (o), methanol (Δ), acetone (-) and benzene (\square).

In an attempt to contribute to deeper understanding of the atomic disordering in mechanically disordered Si, the differences between the RDF of the non-activated sample and selected planetary ground samples have been interpreted up to a radial distance $r = 0.8$ nm.

Silicon has a face-centred cubic lattice ($a = 0.542$ nm) which contains further four tetrahedrally arranged atoms belonging to another face centred cubic lattice which is shifted by $1/4$ of the body diagonal with regard of the first lattice. On the RDF of the non-activated sample the first maximum of the atoms density at around $r_1 = 0.235$ nm corresponds to the four tetrahedrally arranged Si atoms. Further maxima were identified at $r_2 = 0.384$, $r_3 = 0.479$, $r_4 = 0.619$ and $r_5 = 0.705$ nm (Fig. 4). The most remarkable atomic disorder represented by a decrease in atoms density at the radial distance $r_3 = 0.479$ nm has been observed for the dry ground sample. The differences between the non-activated

sample and samples ground in organic liquids are manifested by decrease in atoms density in radial distances larger than r_3 (Fig. 4). The extent of changes in atoms density occurs in accordance with the limiting values of the crystallite size and the lattice strain in the studied environments.

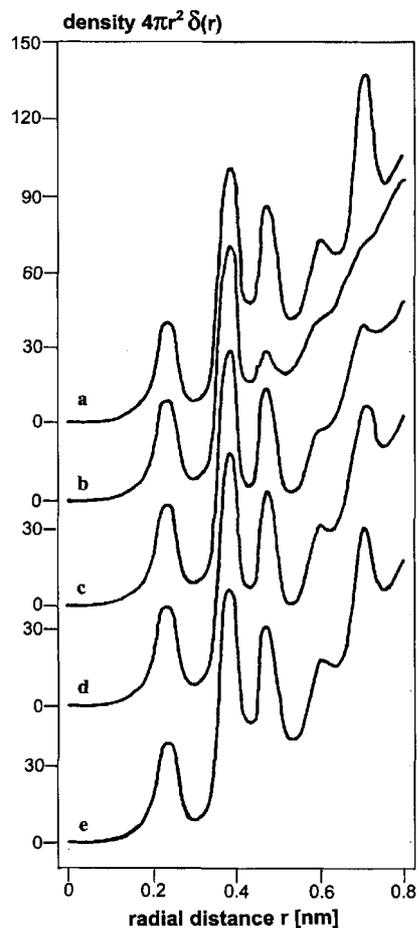


Fig.4. RDF of the non-activated silicon sample (a) and samples ground in a planetary mill for 4 h in air (b), methanol (c), acetone (d) and benzene (e).

Discussion and conclusions

Contemporary tendencies in the design and operation of ultrafine grinding equipments may be characterised by practices which lead to the enhanced milling effect resulting from the increased energy and increased frequency of the mechanical stress. In non-rotary ball mills, this effect can be achieved conveniently by altering the grinding regime but more effectively by increasing the acceleration of the motion of crushing elements, i.e. the cylinder and grinding media. The above mentioned influence can be supposed as the reason of remarkable differences in the kinetics of the particle size reduction and structure disordering at grinding in vibration and planetary mills (see again the relative acceleration data in Table 1).

Grinding and handling of finely dispersed powders in vacuum or organic liquids are belong to methods of surface protection. According to our previous results (Tkáčová et al., 1995) as well as to results in the present work, the most effective particle size reduction and protection of the Si surface against oxidation can be reached by grinding in nonpolar benzene. The liquid environment causes also a suppression of the mechanically induced disordering proceeding in the bulk of ground particles.

The application of sophisticated procedures for the evaluation of X-ray powder diffraction data opened new ways to get more precise information on the real structure of ground silicon. The known data referring about crystallite refinement at grinding were completed by the evaluation of the lattice strain created by microstresses which may be in equilibrium within part of a crystallite, the entire crystallite or even within larger grains consisting of several crystallites. Integral data of amorphisation have been completed by determining changes in the atoms density during the mechanically induced structure disordering.

The structural disordering proceeding on the crystallite and subcrystallite level are influenced in the same way by the nature of the grinding environment: In agreement with published data referring about dry and wet grinding, collected, e. g. in (Tkáčová, 1989), the most effective crystallite size reduction and lattice strain increase proceed in both mills when grinding in atmospheric environment. The rate of structural changes during grinding in liquids decreases with a decreasing relative permittivity of the liquids (see again Table 2). The extent of the changes in the atoms density occurs in accordance with the increase in limiting values of the lattice strain.

Acknowledgement: The authors are grateful to the Slovak Grant Agency for Science (Grant No. 2/4179/97) for the financial support of this work.

References

- Bokhonov, B. B., Konstanchuk, I. G. & Boldyrev, V. V.: *Alloys J and Compounds*, 191, 1993, 239 pp.
 Caplan, P.J., Herbert, J.N., Wagner, B.E. & Pointdexter, E.H.: *Surface Sci.*, 54, 1976, 33 pp.
 Gaffet, E. & M. Harmelin, J.: *Less-Comm. Met.*, 157, 1990, 201 pp.

- Gaffet, E., Merk, N., Martin, G. & Bigot, J.: In: E. Arzt and L. Schultz (Eds.), *Proc. DGM Conf. on New Materials by Mechanical Alloying Techniques*, Deutsche Gesellschaft für Metallkunde, Darmstadt, 1989, p. 95-102.
- Haneman, D.: *Physical Review*, 170, 1968, 705 pp.
- Chung, M.F. & Haneman, D.: *J. Appl. Phys.*, 37, 1966, 1879 pp.
- Koch, C. C., Shen, T. D. & Fahmy, Y.: *Mat. Sci. Forum*, 235-238, 1997, 2728.
- Kolbanev, I. V. & Yu, P.: *Butyagin, Kinet. Katal.*, 23, 1982, 327.
- Millet, P. & Calka, A.: *Mat. Sci. and Eng.*, A181/A182, 1994, 1222.
- Richter, K. G.: In V.N. Kolomiichuk (Ed.), *Proc. Methods of the investigations of catalytic systems, Sib. Otd. Nauk SSSR, Novosibirsk, 1977, pp. 5-40.*
- Shen, T. D., Koch, C. C., McCormick, T. L., Nemanich, R.J., Huang, J.Y. & Huang, J. G.: *J. Mater. Res.*, 10, 1995, 139.
- Številová, N., Suzuki, T., Senna, M., Bálintová, M., Šepelák V. & Tkáčová, K.: *Solid State Ionics*, in press.
- Tkáčová, K., Številová, N., Bastl, Z., Stopka, P. & Bálintová, M.: *J. Mater. Res.*, 10, 1995, 2728.
- Tkáčová, K.: *Mechanical Activation of Minerals*, Elsevier, Amsterdam, Oxford, New York, Tokyo, 1989.