

STRUCTURAL ORGANIZATION OF LAYERS IN OCTAKIS-(TRIMETHYLSILOXY)OCTASILSESQUIOXANE

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UDC 541.49+548.734

Oktakis-(trimethylsiloxy)octasilsesquioxane $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ has been studied by X-ray diffraction (DRON-RM4, $R = 192$ mm, CuK_α radiation) and structural organization of layers in this compound has been analyzed. Irrespective of the type of the support used, the layers obtained by chemical vapor deposition are ideally orientated polycrystalline films in the [001] direction. The type of the planar lattice followed by the molecules was determined from crystal structure analysis in the direction indicated.

Key words: X-ray diffraction, polycrystals, volatile compounds.

Organosilicon compounds of octaorganylsilsesquioxane type are promising materials for vacuum lithography used as photo, electron, and X-ray resists [1]. They can be deposited by thermal vacuum sublimation on various supports and are sensitive to various types of radiation; for electron resists, the best resolution is 50 nm [2].

While oligoorganylsilsesquioxanes are widely used and have been studied extensively, the dependence of their physicochemical properties on crystal structure organization in a layer has not yet been discussed. In our opinion, crystal-chemical investigation of the structural organization of adsorbed layers will provide a clue to mechanisms of surface processes at the molecular level, useful for the development of the physicochemical principles of the production of articles with specified characteristics.

This paper reports the results of our study of layers of octakis-(trimethylsiloxy)octasilsesquioxane, $(\text{Me}_3\text{SiO})_8 \times (\text{SiO}_{1.5})_8$. The molecular formula of this compound is $\text{C}_{24}\text{H}_{72}\text{O}_{20}\text{Si}_{16}$, which is below contracted to AT_8 . Synthesis of this substance is described in [3]. The crystal structure of AT_8 was investigated by single-crystal X-ray diffraction analysis [4]. We have studied oriented polycrystalline samples. Analysis of such samples permits one to go from a three-dimensional crystal structure to its two-dimensional section, i.e., to an isolated crystallographic plane. We used X-ray diffraction analysis data; fine methods such as electron microscopy, EXAFS, etc., can also be employed in future studies.

Experimental. AT_8 layers were obtained by vapor condensation (HBA-1 Carl Zeiss Jena vacuum instrument, vacuum $\sim 10^{-5}$ torr, open type source, temperature $140 \pm 10^\circ\text{C}$) on various supports: Si plates, melted quartz supports, etc. The supports were kept at room temperature. Deposition rate ~ 30 Å/s, final layer thickness 0.5-1 μm .

The samples were transparent colorless thin uniform solid layers (spot diameter ~ 1 cm) on the above-indicated supports. The supports were fixed with plasticine on a quartz cell from the set of a GUR-8 goniometer. The sample plane and the upper surface of the cell were superimposed using a glass plate.

An X-ray diffraction study was performed on a DRON-RM4 diffractometer ($R = 192$ mm, CuK_α radiation, Ni filter,

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scintillation detector with amplitude discrimination) in the range of 2θ angles from 5 to 40° at room temperature. The diffraction pattern (Fig. 1) shows reflections from only one crystallographic plane. This points to the ideal orientation of all crystallites relative to the support.

Discussion of results. Conclusions. The diffractograms were indexed using the data of [4]. The theoretical diffractogram ($a = 11.046$, $b = 11.104$, $c = 13.554$ Å, $\alpha = 77.68$, $\beta = 82.08$, $\gamma = 84.04^\circ$, space group $P\bar{1}$) was compared with the experimental one, and it was concluded that all samples under study have an ideal orientation of crystallites in the [001] direction. It should be emphasized that the preferred direction is characterized by the largest interplanar distance of all those available in the crystal lattice, $d = 13.15$ Å, and these layers are accordingly most densely occupied by atoms. This structural

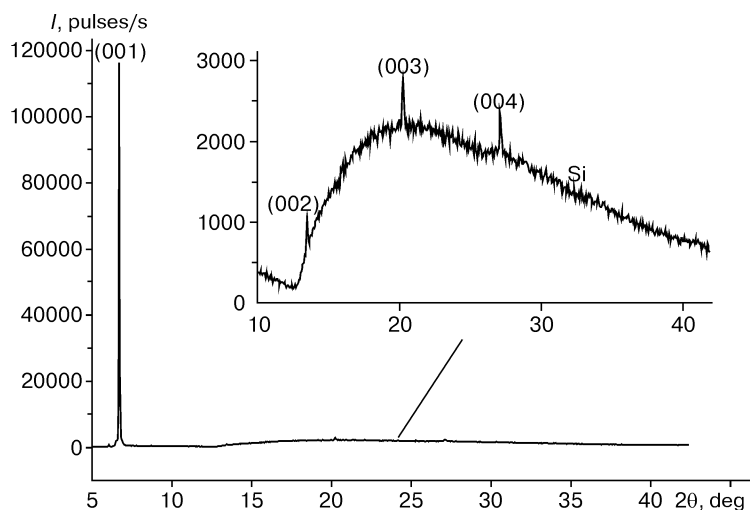


Fig. 1. Diffractogram of the AT_8 sample on the polished surface of the Si support. Insert — section with 2θ 10-40°.

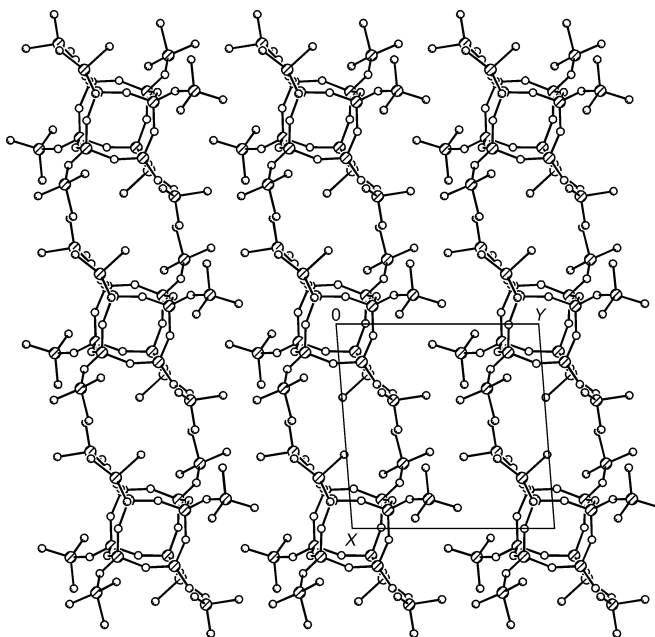


Fig. 2. Organization of preferred layers in the crystal structure of AT_8 in the [001] direction.

TABLE 1. Geometrical Characteristics of Octaorganylsilsesquioxane Layers

Compound	$a \times b$, Å	α , deg	d_{001} , Å
Methyl-T ₈ [6]	8.432×8.432	95.66	8.34
Vinyl-T ₈ [7]	9.189×9.189	95.32	9.72
Ethyl-T ₈ [8]	9.433×9.433	95.92	9.49
AT ₈ [This work]	11.046×11.104	77.68	13.15

peculiarity of layers in other volatile compounds, including octaorganylsilsesquioxanes [CH₃SiO_{1.5}]₈ (methyl-T₈), [C₂H₃SiO_{1.5}]₈ (vinyl-T₈), and [C₂H₅SiO_{1.5}]₈ (ethyl-T₈) was previously indicated in [5].

The crystallite orientation and X-ray diffraction data [4] obtained for AT₈ permit one to analyze the structural organization of the best-developed upper faces. For this, in the crystal structure of AT₈, we isolate a plane the normal to which coincides with the [001] direction. Figure 2 shows a layer of complexes parallel to the (001) family of crystallographic planes. The preferred direction is perpendicular to the plane of the drawing. Film growth occurs by repetition of such layers at intervals equal to the interplanar distance d_{001} .

Layer structure in other octaorganylsilsesquioxanes was investigated in [5]. It was established that irrespective of the type of the support used (polished plates of melted quartz, glass, and single-crystal silicon of varying orientation, β -diketonate and copper phthalocyanine sublayers, etc.), the layers are oriented polycrystalline films. Table 1 presents some characteristics of octaorganylsilsesquioxanes. It can be seen that the geometrical characteristics vary within wide limits, from 8.4 to 11.1 Å.

Syntheses of new volatile compounds and preparation of oriented layers permit one to control the geometrical characteristics of the surface pattern. The creation of layers of compounds with known structural organization will entail the development of procedures for the preparation of complex multilayer objects (atomic layer epitaxy), including those with chemical interactions between molecules. For example, the results of IR and EXAFS studies [9] on adsorbed layers of Cu(II) and Ca(II) dipivaloylmethanates indicate that these compounds selectively and stoichiometrically react with hydroxyl groups on the surface of a specially prepared support.

Thus using vacuum deposition, we have prepared layers of octakis-(trimethylsiloxy)octasilsesquioxane [(CH₃)₃SiO]₈(SiO_{1.5})₈ and studied them by X-ray diffraction. We emphasize that we dealt with oriented polycrystalline films; i.e., there was one preferred direction of crystallites relative to the sample surface.

We are grateful to Dr. R. G. Mirskov for providing us with the substance.

REFERENCES

1. F. A. Kuznetsov (ed.), *Problems in Electronic Materials Science* [in Russian], Nauka, Novosibirsk (1986).
2. V. I. Lavrentiev, "Polyhedral oligosilsesquioxanes. Synthesis, studies of formation, properties, and applications," Chemical Sciences Doctoral Dissertation, Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk (1996).
3. G. V. Kalmychkov, V. I. Rakhlin, B. A. Gostevskii, et al., *Dokl. Akad. Nauk*, **362**, No. 3, 359-361 (1998).
4. N. Auner, B. Ziemer, B. Herrschaft, et al., *Eur. J. Inorg. Chem.*, 1087-1094 (1999).
5. S. A. Gromilov, S. A. Prokhorova, and I. A. Baidina, *Zh. Strukt. Khim.*, **37**, No. 5, 923-928 (1996).
6. K. Larson, *Ark. Kemi*, **16**, 203 (1960).
7. I. A. Baidina, N. V. Podberezskaya, V. I. Alekseev, et al., *Zh. Strukt. Khim.*, **20**, No. 4, 648-652 (1979).
8. N. V. Podberezskaya, S. A. Magarill, I. A. Baidina, et al., *ibid.*, **23**, No. 3, 120-129 (1982).
9. R. Sekine, M. Kawai, K. Asakura, et al., *Surf. Sci.*, **278**, Nos. 1/2, 175-182 (1992).

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