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LETTERS
TO THE EDITOR

1-Hydrocarbylsilatranes as New Precursors for Nanolayers of Polyhydrocarbylsilsesquioxanes

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Network or spherical oligohydrocarbylsilsesquioxanes when applied on the surface of solid materials form nanolayers, which after heating or irradiation are structured into the corresponding insoluble and nonvolatile polyhydrocarbylsilsesquioxanes necessary for preparation of dielectric coatings and resists for electronic, X-ray, and ionic nanolithography for design of modern electronic devices [1, 2]. We have found that 1-hydrocarbylsilatranes (HS) which have already found wide application in medicine and agriculture [3] are promising precursors for preparation of nanodimensional polyhydrocarbylsilsesquioxane coatings.

The investigated HS (**I–VI**) were synthesized by transetherification of hydrocarbyltriethoxysilanes with triethanolamine [4, 5] according to the scheme:

$$RSi(OC_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow RSi(OCH_2CH_2N)_3 + C_2H_5OH,$$

I–VI

R = CH_3 (**I**), C_2H_5 (**II**), $ClCH_2$ (**III**), CH_2=CH (**IV**), CH_2=$CHCH_2$ (**V**), HC≡C (**VI**).

Compounds **I–VI** were purified by sublimation in a vacuum in a device of melt quartz. The content of traces of metals (Na, K, Ca, Fe, Ni, Co, etc.) in **I–VI** did not exceed 10^{-5}–10^{-6} wt % as showed the data of atomic adsorption analysis.

Polyhydrocarbylsilsesquioxane coatings were prepared as follows. The layers of the corresponding HS were applied onto a semiconducting, dielectric, or metal support by spraying in a vacuum. The coatings of thickness 0.2–0.3 μm were exposed to an electron beam. With this, on the irradiated parts of the coating the hidden image of the polyhydrocarbylsilsesquioxane structure is formed.

The earlier mass spectrometry studies of HS [6, 7] have shown that under the action of electron impact they are cleaved with retention of the R–Si–O bonds. Nonexposed parts of the coating containing HS were evaporated by heating the support in vacuum.

The sensitivity of the HS-coatings to electronic irradiation is determined by substituents R and decreased in the order **VI** > **V** > **IV** > **III** > **I** > **II** from 5×10^{-7} to 5×10^{-4} C cm^{-2}. This dependence is caused by the ability of thin films of HS (**IV–VI**) to polymerize under the action of the electron beam with participation of not only the siloxane but also the multiple bonds. The performed studies allow to recommend HS for further investigation as resists for nanolithography.

Polymerization of 1-methylsilatrane. In an evaporator was placed 1.0 g of **I** and deposited onto silicon supports of 60 mm diameter at 140°C and 10^{-5} mm Hg. The duration of deposition was 45 s, thickness of the formed coating 0.2 μm (LEM-2 unit). The support was exposed on a Jeol-T 200 instrument (ELAMS). Optimal dose of irradiation was 10^{-5} C cm^{-2}. The support was heated in a vacuum for 14 min at 120°C, and thereafter the hidden image became apparent (the minimal size of the elements 0.5 μm) consisting of the layer of polymethylsilsesquioxane; nonexposed parts of the layer of **I** were removed by heating the support in a vacuum.

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