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Title	ハロゲン化シランの塩基付加体を経由したオリゴラダーフェニルシルセスキオキサンの合成とフォトリソグラフィーへの応用に関する研究
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Abstract

The organic-inorganic hybrid materials have received considerable interest in the past decades because of their prospects in developing materials with unique optical, thermal and electronic properties. Recently, silsesquioxanes (SQ) have been noticed as organic-inorganic hybrid material in the field of Flat Panel Displays. Especially, SQ's with high regularity structures like a ladder is expected to give superb properties such as high thermal resistance, high transparency, low dielectric constant, and high cracking threshold as compared to SQ with a low regularity structure.

Here, I found new synthesis methods for oligo-ladder PPSQ via silicon-amine adducts using phenyltrichlorosilane (TCP) as monomers by one-pot synthesis at an aqueous-organic boundary (*n*-propylacetate (nPA) /water). Furthermore, I also showed the possiblity of photosensitive material formulation using oligo-ladder PPSQ to be applied to a photo-patternable dielectric layer in TFT (Thin Film Transistor)s.

In Chapter 2, silicon–amine(alkali ligand) adducts which affect the hydrolysis of TCP was described. The liquid boundary reaction which has a slow kinetic rate of homo-condensation is limited by the reaction area at the nPA-water liquid boundary. This leads to a thermodynamically stable ladder structure. The direct synthesis of ladder SQ using silicon-amine adduct at water-nPA liquid boundary has not been reported yet. Several amines such as pyridine, TMEDA(tetramethylethylenediamine), PMDETA(pentamethyldiethylenetriamine) were tested. These amines have a lone electron-pair initiates formation of interaction compounds with TCP via d_{π}-p_{π} overlap. The oligo-ladder PPSQ was fromed in all types of amines (ligand), but best results were obtained by TMEDA.The developed methods are based on simple one-step reaction, which will open possibility for low cost ladder SQ production for industrial use. Moreover, reaction mechanism was studied using simulation techniques for the density of pyridine-complex by MP6 and MALDI-TOF/TOF MS. In the synthesis of ladder structure, most important process was formation of phenyltrisilanole ($PhSi(OH)_3$). The condensation scheme for this ladder structure was proposed as sequential reaction based on $PhSi(OH)_3$. Amine-ligands are effective in controlling the hydrolysis reaction and homo-condensation of silanol.

Chapter 3 described positive-/negative-tone photosensitive oligo-ladder PPSQ based on Novolak resin's photoresist formulations. The pattern resolution was about 3μm in L/S. This value is also acceptable for dielectric layer in the display region. The silanol (-Si-OH) has its acidity higher than phenol in Novolak resin. Then negative-tone system with photo acid generator showed high resolution and high sensitivity for photon energies of 20 mJ/cm^2. The basic reaction in this case is also controlled by the homo-condensation of silanol.

On the other hand, electrical properties exhibit superior characteristics for application in optical and electrical field. Optical transmittance was over 98% at 400nm, this value is enough for optical devices. Dielectric constant was between 3.1 - 3.2. Our SQ showed characteristics similar to low-k materials. Furthermore, TGA analysis showed high thermal stability with a 5% weight loss at temperature 500℃ and ceramics yield of 80% at 800℃.

Consequently, I found out new synthesis scheme for oligo-ladder PPSQ via silicon-amine (mono-, bi-, tri- ligand) adducts. TMEDA (bi-ligand amine compound) was most superior in term of the yield and reaction controllability. The photosensitive SQ was also investigated. It was shown that lithography is highly possible using synthesized oligo-ladder PPSQ. I believe that my research will open new pathway for mass production of ladder SQ and will be applicable to new architecture of display in near future.

Key words: silsesquioxane, ladder structure, amine-ligand, pyridine, TMEDA, PMDETA, photosensitive.