



Cyclic Azasilanes and Cyclic Thiasilanes for Nano-Surface Modification

Gelest's Susan H Tilford, Barry Arkles and Jonathan Goff explain how cyclic azasilanes and cyclic thiasilanes, a new class of silane coupling agents, modify nanoparticles and create nano-scale features.

Cyclic azasilanes and cyclic thiasilanes are a relatively new class of silane coupling agent that are especially well-suited for the surface modification of nanoparticles and the creation of nanoscale features.^{1,2} These surface treatment agents are fundamentally different from traditional silanes and have great potential for use in applications such as microelectronics and optoelectronic devices. They can also be used to modify hard to treat inorganic substrates such as titanium, copper, and aluminum as well as difficult organic substrates such as polyvinyl alcohol and cellulosic resins.

Traditional organosilane surface modification reagents contain one to three hydrolysable groups, typically chloro or alkoxy. Figure 1 depicts the hydrolytic deposition of a trimethoxy silane with organofunctional group R. Exposure to moisture results in hydrolysis of the methoxy groups to generate a silanol compound and liberate methanol. The silanol species condense into oligomers and hydrogen bond with the hydroxyl groups (-OH) on the substrate. A covalent Si-O bond to the substrate is formed during the drying stage, which is usually performed at elevated temperature (50-120°C). Silanes with three hydrolysable groups will tend to form multi-layers on the substrate.

Cyclic azasilanes react rapidly at room temperature via a ring-opening mechanism to generate smooth high-density monolayers. Since there is no hydrolysis step, there is no moisture required and there are no hazardous byproducts. The ring-opening reaction shown in Figure 2 is thermodynamically driven by the difference in the Si-N ($\approx 410 \text{ kJ mol}^{-1}$) and Si-O ($\approx 569 \text{ kJ mol}^{-1}$) bond energies and by the relief of ring strain. The cleavage of the Si-N bond is accompanied by the formation of a covalent Si-O bond to the substrate and the transfer of hydrogen to give a secondary amine. If there are alkoxy groups bound to the Si (Figure 2b), they will remain intact during the ring-opening reaction and will be available for hydrolysis and condensation reactions upon exposure to moisture. The cyclic azasilanes can be applied as 100% active liquids, in anhydrous aprotic solvents such as hydrocarbons or THF, or by vapour phase deposition. Similar ring-opening reactions can be performed with cyclic thiasilanes to form thiol functional surfaces.

Nanoparticles treated with cyclic azasilanes have applications in composites and adhesives. Cyclic thiasilanes have particular benefits in high-performance nano-particle modified UV coatings and adhesives. These compounds can be used to generate functional monolayers that can undergo further reactivity with a wide-range of organic compounds to form self-assembled nanostructures. Possibilities include one-pot tandem coupling reactions² ranging from nano-composite formation to the immobilization of DNA and proteins on the treated substrates.

The high vapour pressures of cyclic azasilanes and cyclic thiasilanes facilitate vapour-phase reactions, typical column head vapour pressures range from 50-70°C at 1-3mm Hg. Unlike traditional silanes that often

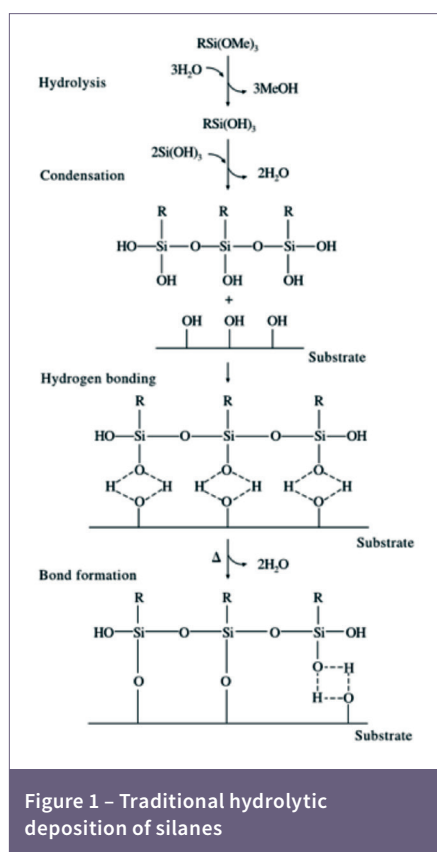


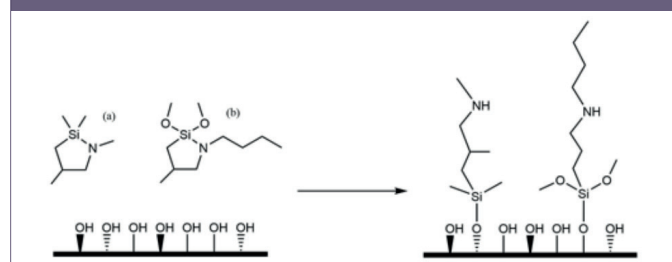
Figure 1 – Traditional hydrolytic deposition of silanes

have to be dispersed with solvent to react with particle surfaces, the high vapour-pressure allows solvent-free reaction by diffusion to the particle surface. Due to their rapid reaction rates, these materials are especially useful for high-speed nanofabrication processes such as molecular layer deposition (MLD) or spin-on deposition. The rate of reaction of a cyclic azasilane with amorphous fumed silica was monitored by diffuse reflectance infrared fourier transform (DRIFT) spectroscopy.² Surface modification was complete in less than 1 minute at 25°C as evidenced by the disappearance of the peak for the terminal hydroxyl groups on the silica (3745 cm^{-1}). Cyclic azasilanes have also been demonstrated to be fast and efficient reagents for atomic layer deposition³ and layer-by-layer deposition.⁴

The formation of monolayers has been confirmed by analysis of cyclic azasilane treated surfaces by ellipsometry and atomic force microscopy. Monolayers ranged from 2-5nm and had an average roughness of 0.3nm. In separate work, porous silicon structures treated with cyclic azasilanes and cyclic thiasilanes retained their open pore structure and photoluminescence.⁵ There was no significant increase in nanoparticle size and no aggregates were observed.

Cyclic azasilanes and cyclic thiasilanes are ideal surface modification reagents for nanoparticles and nano-scale features and have potential for broad application in a wide-range of nanotechnology field.

Figure 2 – New surface modification technique using a cyclic azasilane (a) and a moisture cross-linking cyclic azasilane (b)



CONTACT

Susan H Tilford,
Barry Arkles and
Jonathan Goff
Gelest, Inc
Morrisville, PA, USA
www.gelest.com

REFERENCES

1. B Arkles *et al.* Silanes and Other Coupling Agents 2004;3:179-91.
2. Y Pan *et al.* *Chem Asian J* 2017;12:1198-203.
3. L Ju, N Strandwitz. *J Mater Chem C* 2016;4:4034-9.
4. V Gupta *et al.* *J Vac Sci Technol B* 2014;32:068103/1-9.
5. D Kim *et al.* *J Am Chem Soc* 2016;138:15106-9.