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Optical Bonding Using Silica Nanoparticle Sol–Gel Chemistry

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ABSTRACT

A simple method is described to bond optical components using silica nanoparticle sol–gel chemistry. The silica nanoparticles polymerize into highly branched networks that link the surfaces together. The nanoparticle mediated bonding has several advantages to currently used optical joining technologies. The bonding is a room-temperature process and does not require any clean room facilities. The bonded interface has a high mechanical strength and low scattering. The bonding is resistant to organic solvents on silylation with hydrophobic surface groups. This method achieves 100% successful bonding rates between soda-lime glass slides. The bond-setting time can be tailored to allow time for precision optical alignment.

Optical components are traditionally assembled using epoxy bonding,[1,2] frit bonding,[1] diffusion bonding,[3−5] and optical contacting[1,3,6] technologies. These bonding methods are limited by high bonding temperatures, low reliability, stringent requirements for surface flatness and cleanliness, complicated bonding protocols, low mechanical strength, and poor optical properties of the bonded interface.[3] Some of these drawbacks are overcome by the technique of hydroxide catalysis bonding or silicate bonding that was first proposed by Gwo.[7−9] In this bonding scheme, an alkaline bonding solution, typically sodium or potassium hydroxide or sodium silicate, is placed between the surfaces to be bonded. The OH^- ions in the bonding solution etch the surfaces and form siloxane chains that bond the two surfaces. However the technique of hydroxide catalysis bonding has poor reproducibility and can only been used to bond substrates that satisfy stringent requirements of surface flatness and cleanliness.[7,10]

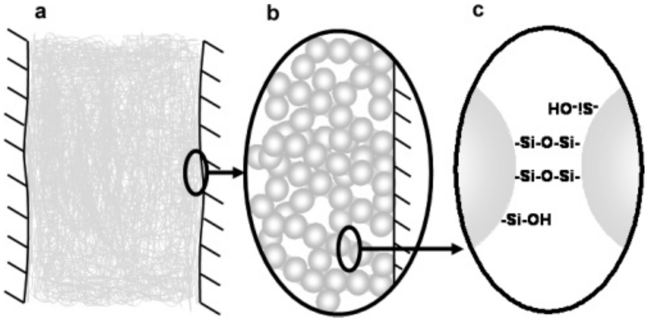

Figure 1. Schematic of the bonded interface at different magnifications. (a) The silica nanoparticles polymerize into a highly branched 3D network and bond glass, silica and quartz surfaces that do not have a perfect bonding-surface figure match. (b) At pH < 10.7, the nanoparticles bind together by siloxane linkages. Silicate ions are deposited at the junction between neighboring nanoparticles, which further strengthens the network. (c) The nanoparticles bind together via the reaction nanoparticle−Si−OH + HO−Si−nanoparticle → nanoparticle−Si−O−Si−nanoparticle + H_2O. Dehydration of the interface drives the reaction forward.

To overcome these limitations, we have extended the technique of hydroxide catalysis bonding using silica nanoparticle sol−gel chemistry.[11−18] The essential idea of this new technique is that the silica nanoparticles fill in microscopic voids and irregularities and then the hydroxide catalysis is used to polymerize the particles into a branched, connected network[11,12] (see Figure 1). As a result, the silica-particle mediated bonding does not require the clean room facilities used in hydroxide catalysis bonding,[7,10] diffusion bonding,[4] and optical contacting.[1,6] Unlike hydroxide catalysis bonding[7,10] and optical contacting,[1] the nanoparticle mediated bonding is very reproducible. By controlling the stoichiometry of the silica nanoparticles and hydroxyl ions, we achieve 100% successful bonding rates between soda-lime glass slides. The time required for bond setting can be tailored to allow precise alignment of the optics by controlling the concentration of the silica nanoparticles and hydroxyl ions. The bonding is a room-temperature process, as opposed to diffusion bonding[4] and glass frit bonding,[1] which are carried out at high temperatures where optical coatings and surface flatness may be compromised and materials can be thermally stressed. The bonded interface has a high mechanical strength. After curing the bond for 300 h, the tensile strength of the interface exceeds 14 MPa. Unlike optical cements, the bonding is resistant to organic solvents on

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silylation with hydrophobic surface groups.[19] Optics bonded with silica nanoparticles and then silylated can be cleaned with organic solvents like acetone and ethanol.

When silica is exposed to water for an extended period of time, its surface gets hydroxylated and presents short protruding siloxane chains ($-Si(OH)_2-O-Si(OH)_2-OH$).[11,13−16] These groups can chemically bond two perfectly flat fused-silica surfaces at room temperature. Because it is difficult to obtain a perfect bonding-surface figure match, the gap between the surfaces was filled with silica nanoparticles suspended in a potassium hydroxide solution that serves as an index matched filler material. The silica nanoparticles polymerize into highly branched 3D networks[11,16,18] that link the surfaces together (Figure 1). The OH^- ions in the bonding solution hydrolyze and etch the silica nanoparticles and the glass surfaces. As a result, the surfaces liberate silicate ions and the pH of the bonding solution gradually decreases via the reaction[11]

$$SiO_2 + OH^- + 2H_2O \rightarrow Si(OH)_5^- \qquad (1)$$

Once the pH of the bonding solution decreases below 10.7, the nanoparticles bind together by siloxane linkages[11] and form a three-dimensional network that bond the surfaces (Figure 1) via the reactions

$$\text{nanoparticle}-Si-OH + HO-Si-\text{nanoparticle} \rightarrow \text{nanoparticle}-Si-O-Si-\text{nanoparticle} + H_2O$$

$$\text{nanoparticle}-Si-OH + HO-Si-\text{surface} \rightarrow \text{nanoparticle}-Si-O-Si-\text{surface} + H_2O$$

Dehydration of the interface drives the reaction forward. The free silicate ions are deposited at the junction between neighboring nanoparticles, which further strengthens the network.[11] Also, the silicate ions dissociate to form $Si(OH)_4$, which polymerize to form siloxane chains.[10,11] As the water evaporates and migrates into the bulk of the material, the network of nanoparticles and siloxane chains rigidly joins the surfaces (Figure 1).[13]

The time required for bond setting can be altered by varying the concentrations of the silica nanoparticles and hydroxyl ions so that surfaces can be precisely aligned before the bond sets (Figure 2). The OH^- ions in the bonding solution etch the silica nanoparticles and the glass surfaces and the pH gradually decreases via eq 1.[11] Because the silica nanoparticles polymerize at pH less than 10.7, increasing the initial pH of the bonding solution increases the bond setting time (Figure 2). Similarly decreasing the nanoparticle concentration also increases the bond setting time (Figure 2).

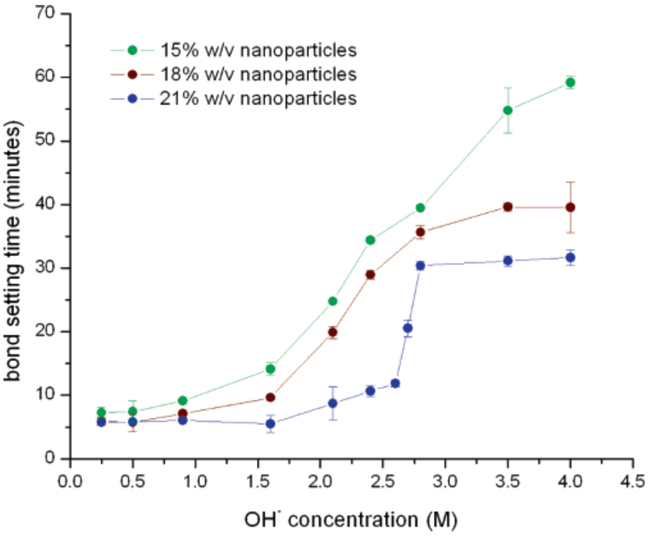

Figure 2. Bond setting time increases with pH of the bonding solution and decreases with nanoparticle concentration. The bond setting times for soda-lime glass microscope slides was measured for three different concentrations of Luddox 5 nm silica nanoparticles by putting 3 μL cm^{-2} of bonding solution between the surfaces. As the bond formed, the glass slides were slightly perturbed at small time intervals until they became difficult to move.

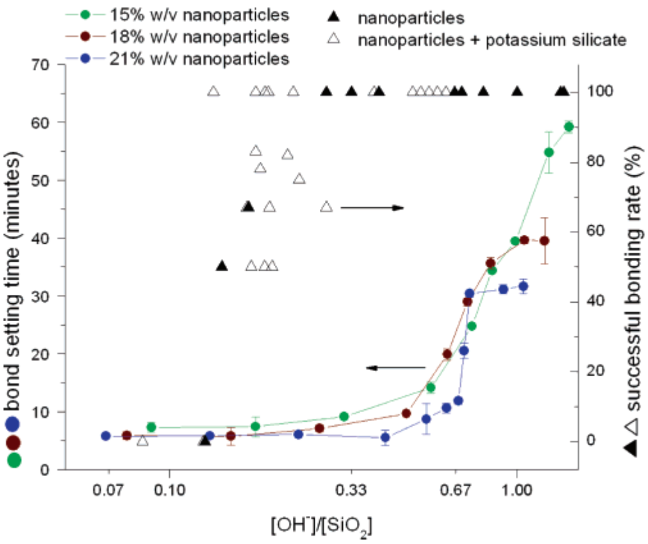

Figure 3. Rate of successful bonding (axis on the right) depends on the OH^-/SiO_2 molar ratio. We bonded between 3 and 10 pairs of glass slides using 38 different bonding conditions with OH^-/SiO_2 ratios ranging from 0.05 to 1.5. Of the 38 bonding conditions, 13 conditions had 5 and/or 7 nm nanoparticles suspended in a solution of potassium hydroxide (filled triangles), while the remaining 25 bonding conditions had mixtures of 5 and/or 7 nm nanoparticles suspended in potassium silicate and potassium hydroxide (open triangles). All of the 16 conditions with OH^-/SiO_2 molar ratios above 0.35 bonded successfully (axis on the right). The bond setting times measured using 15% w/v nanoparticles (green trace), 18% w/v nanoparticles (red trace), and 21% w/v nanoparticles (blue trace) suspended in a solution containing 10% v/v potassium silicate and potassium hydroxide are also plotted (axis on the left).

The nanoparticle bonding is very reproducible unlike optical contacting[1] and hydroxide catalysis bonding.[7] By controlling the stoichiometry of the silica nanoparticles and hydroxyl ions, 100% successful bonding rates between soda-lime glass slides was achieved. When the OH^-/SiO_2 molar ratio is greater than 0.35, the surfaces bond successfully 100% of the time (triangles in Figure 3). Soda-lime glass slides were bonded using 38 different bonding conditions, with OH^-/SiO_2 ratios ranging from 0.05 to 1.5. All of the

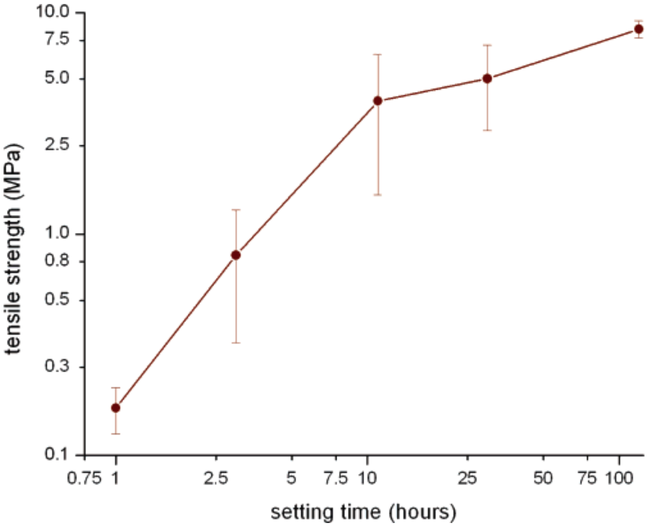

Figure 4. The mechanical strength of the bonded interface increases with time. We measured the tensile strength of the interface between soda-lime glass coverslips bonded using 12% w/v silica nanoparticles in a 10% v/v potassium silicate and 900 mM KOH solution using a force gauge (Shimpo Instruments).

16 conditions with OH^-/SiO_2 molar ratios above 0.35 bonded successfully (Figure 3).

To test the strength of bonding, soda-lime glass coverslips were bonded using 5 nm silica nanoparticles, and the tensile strength of the bonded interface was measured over a period of time (Figure 4). The strength of the bonded interface increased from 0.2 MPa after 1 h to 8.5 MPa after 120 h of bonding (Figure 4). After 300 h, the tensile strength of the interface exceeds 14 MPa.

To quantify defects in the bonding interface, soda-lime glass slides bonded using either silica nanoparticles or potassium hydroxide (1.6 M and 2 M)[7,10] or potassium silicate (SiO_2/K_2O mole ratio 3.3) were compared.[10] Slides joined using only a potassium hydroxide solution did not bond. The surfaces that were joined using 100% potassium silicate contained 0.3−1 mm sized circular defects all over the bonded region. On the average, each bonded slide (25 cm × 75 cm) had 79 such defects (figure in Supporting Information). On the other hand, the slides bonded using the silica nanoparticles contained only eight small defects, mostly along their edges (figure in Supporting Information). These defects were approximately an order of magnitude smaller than the defects seen with the silicate bonding technique.

The smallest number of defects was obtained when the bonding solution contained nanoparticles, potassium hydroxide, and between 5% v/v and 20% v/v potassium silicate. In the absence of potassium silicate, the number of defects in the bonded surface increased to 18 per slide (25 cm × 75 cm). On the other hand, when the potassium silicate concentration was increased to 30% v/v, there were on the average 22 defects per bonded slide.

To test the optical quality of the bonding, the scattering and transmittance of surfaces bonded using 25.5% w/v silica nanoparticles suspended in a solution containing 10% v/v potassium silicate and 1 M potassium hydroxide was measured and compared to the light scattered from surfaces bonded with Norland-63, a commercial optical adhesive. The intensity of light scattered from the nanoparticle bonded surface was roughly identical at all four angles (+45°, +30°, −30°, and −45°). The surfaces scattered 60%, 75%, 73%, and 65% more light at these angles than a bare glass slide. On the other hand, the slides bonded using Norland-63 scattered light more anisotropically. These surfaces scattered 49%, 205%, 148%, and 40% more light than a bare glass slide at +45°, +30°, −30°, and −45°, respectively. The transmittance of the bonded surfaces was measured using a spectrophotometer. Between 400 and 900 nm, the slides bonded with the silica nanoparticles transmitted 99.58% ± 0.24% of the light transmitted by a single bare glass slide cleaned using the same protocols as the nanoparticle bonded slides.

A practical optical bonding technique must also be chemically resistant to organic solvents routinely used to clean optical components. However, nanoparticle bonded glass slides exposed to acetone and ethanol partially debonded within 1 h. We conjectured that capillary action pulls acetone and ethanol into the nanoparticle network that bond the surfaces together. The capillary pressure exerted on the nanometer sized pores in the network can reach hundreds of bars, and the network collapses irreversibly.[11] This effect was previously implicated in the collapse of silica aerogels dried at ambient pressure.[11,19] If the bonding interface were functionalized with hydrophobic molecules,[19,20] the amount of liquid pulled in the nanoparticle network and the capillary pressure across the network pores would be reduced. The nanoparticle network was modified by silylating the bonded glass slides with a 30% solution of hexadimethylsilazane in *n*-heptane for 24 h at 50 °C.[20] The silylated surfaces remained well bonded and defect free after a 12 h exposure to acetone and ethanol.

In conclusion, we describe a simple method to bond glass, silica, and quartz using silica nanoparticle sol−gel chemistry.[11,12] The bonding method is an extension of hydroxide catalysis bonding that was first proposed by Gwo.[7−9] While silica sol−gel chemistry has previously been used to bond ceramic substrates and silicon wafers in microelectromechanical system (MEMS) and microfabrication applications,[21−23] our technique is the first application of silica nanoparticle sol−gel chemistry to optical bonding.

This technique has several advantages compared to optical adhesives, glass frits, diffusion bonding, optical contacting, and traditional hydroxide catalysis bonding technologies. (1) The nanoparticle bonding does not require any clean room facilities unlike optical contacting,[6] diffusion bonding,[4] and hydroxide catalysis bonding,[7,10] which are performed in clean rooms to avoid particulate contamination. (2) The nanoparticle bonding is a room-temperature process unlike frit bonding[1] and diffusion bonding,[4] which are carried out at high temperatures where optical coatings and surface flatness can be compromised and materials can be thermally stressed. (3) The bonded interface has less scattering than optical adhesives. (4) The nanoparticle bonding is very reproducible unlike optical contacting[1] and hydroxide catalysis bonding.[7] By using a OH^-/SiO_2 molar ratio above 0.35, we achieve

100% successful bonding rates between soda-lime glass slides. (5) The time required for bond setting can be tailored by controlling the concentration of the silica nanoparticles and hydroxyl ions to allow a precise optical alignment. (6) The bonded interface has a high mechanical strength. After curing the bond for 300 h, the tensile strength of the interface exceeds 14 MPa. (7) Unlike optical cements, the bonding is resistant to organic solvents on silylation with hydrophobic surface groups. Optics bonded with silica nanoparticles can thus be cleaned with organic solvents like acetone and ethanol. The bond layer formed using the silica nanoparticles is thicker than optical contacting and direct sol−gel bonding and is less suitable for constructing optical systems with low mechanical dissipation such as gravitational wave detectors.[24]

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Supporting Information Available: Protocol for bonding substrates and bright field images of substrates bonded using nanoparticle mediated bonding and silicate bonding. This material is available free of charge via the Internet at http://pubs.acs.org

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