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Room Temperature Silicon Wafer Bonding with Ultra-Thin Polymer Films**

By Gertrud Kräuter,* Andreas Schumacher, Ulrich Gösele, Thomas Jaworek, and Gerhard Wegner

If two smooth and clean surfaces are brought into intimate contact, bonding occurs due to attractive forces between the opposing surfaces. This phenomenon was first investigated by Lord Rayleigh in 1936^[1] and has been rediscovered in recent years, being studied extensively for silicon wafers and oxidized silicon wafers. First reported in 1986,^[2,3] the so-called 'wafer bonding technique' has emerged as an indispensable tool both in microelectronics, for the production of silicon-on-insulator (SOI) wafers, and in micromechanics, for the fabrication of sensors and actuators.^[4] Commercial Si-wafers possess a native oxide layer of 15–20 Å thickness, particularly after the conventional cleaning procedures, e.g. heating the wafers in a mixture of H₂O:H₂O₂:NH₄OH (5:1:1) (RCA 1) at 75 °C for 10 min and, after rinsing the wafers with ultra-pure water, immersing them in a mixture of H₂O:H₂O₂:HCl (6:1:1) (RCA 2) at 75 °C for 10 min. The surface is terminated by hydroxyl groups, rendering it hydrophilic. If two hydrophilic silicon wafers are contacted, hydrogen bonding between the water molecules, which are attached to the opposing surfaces, as well as van der Waals forces cause the wafers to bond. The surface energy or bond strength between two hydrophilic wafers is in the range of 0.1 to 0.2 J/m² at room temperature and the wafers can be separated by inserting a wedge at their rim.^[5] For most applications, higher bond strengths are required. This is achieved by a heat treatment at tempera-

tures above 800 °C and leads to irreversible bonding due to the formation of covalent bonds between the two surfaces. A model proposed by Stengl et al. describes the various stages of the bonding process at different temperatures.^[6]

Hydrophobic silicon surfaces can also be bonded. If the native oxide layer is removed by dipping a Si wafer into an aqueous solution of hydrofluoric acid, the surface becomes mainly H terminated and thus hydrophobic.^[7] The bond energy between two hydrophobic surfaces is about 0.02–0.03 J/m², which is considerably lower than for hydrophilic wafers. The reduced bond strength is mainly due to the absence of hydrogen bonding. The bonding of hydrophobic surfaces is caused by van der Waals forces which are much weaker than hydrogen bonding. As in the case of hydrophilic wafers, the bond strengths can be increased by heat treatment at high temperatures. For applications involving semi-processed devices which already contain temperature-sensitive structures and for the bonding of dissimilar materials with different thermal expansion coefficients it is necessary to develop a bonding process which leads to sufficient bond strengths at moderate temperatures (e.g. below 400 °C) or, even more desirable, at room temperature. Recently we reported that the treatment of hydrophilic silicon wafers with hydrolyzed tetramethoxysilane solution before bonding already yields high bond strengths at temperatures of 300–400 °C.^[8] Here, we describe the room temperature bonding of hydrophobic silicon wafers through an ultra-thin Langmuir–Blodgett film (LB film) of a liquid crystalline polymer, which serves as an intermediate layer between the two wafers.

The idea of using a polymer as an interlayer between two silicon wafers itself is not new. Previously, negative photoresist, polyimide, and epoxy polymers have been spin-coated onto a test wafer and transferred subsequently to silicon wafers using a method similar to an ordinary stamp.^[9] Immediately thereafter, the wafers were bonded. The thickness of the polymer layers varied from 130 nm to 1.1 µm. In a different report the bonding of silicon wafers after applying a 1 µm thick polymethylmethacrylate (PMMA) layer is described.^[10] In each case the bond strength at room temperature is in the range of that observed for hydrophilic wafers. However, it can be increased considerably by a heat treatment at moderate temperatures (below 200 °C). The dramatic increase in bond strength can be explained by the high flexibility of the polymer chains at elevated temperatures, which causes them to become entangled with chains of the opposing wafer. The bonding of polished polymer wafers to silicon has also been reported.^[11–12] The, in many respects, interesting class of films of a thickness considerably below 1 µm is difficult to obtain using conventional spin coating techniques. Thin films prepared by these methods often display an unacceptably high density of pin holes and a non-uniform thickness. Thus, an alternative technique, especially designed for the formation of very thin films, was chosen to study ultra-thin films on silicon substrates.

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The Langmuir-Blodgett technique has proven to be a powerful tool for the deposition of ultra-thin films onto suitable substrates.^[13-15] The exact control of the thickness of LB films down to dimensions as low as 1 nm, and the orientation features of the high quality monolayers deposited, make this technique particularly attractive for employment in the fabrication of microelectronic devices.^[16] Since ultra-thin organic films may allow charge carriers to pass through, their use as an intermediate layer between two wafers has great potential for applications in microelectronics.

It has been demonstrated that rod-like macromolecules with short hydrophobic sidechains (Fig. 1) can be transferred to suitable substrates using the LB technique.^[17-19] The sidechains are thought to provide the shape-persistent backbone with a liquid-like skin. Layered assemblies of such hairy-rod like macromolecules formed during the LB-process have a liquid crystalline texture and show no pin holes when transferred onto a continuous solid sub-

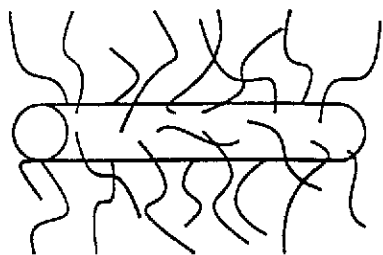
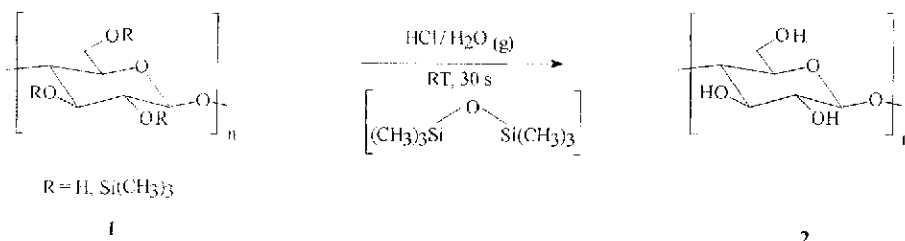


Fig. 1. Schematic diagram of a hairy rod molecule.

strate.^[19-20] They have been described as molecularly-reinforced liquids in which the backbone elements are embedded in a matrix of interdigitating sidechains.^[17-19] Examples of hairy rod-type macromolecules include co(polyglutamates) in their helical form^[21-23] and certain derivatives of cellulose.^[24-25] LB-films of these compounds have been used as hosts for chromophores and ionophores in the fabrication of highly sensitive and selective membranes.^[26] Multilayers of polyglutamates have been successfully employed as waveguides, which underlines the high quality of such films. If photoreactive guest molecules are covalently bound to the sidechains of these polymers, a photo-crosslinkable LB film is obtained.^[27] Such assemblies can be used in the lithographic generation of patterns.

For our experiments we have chosen trimethylsilylcellulose (TMSC) **1**, a compound with short trimethylsilyl groups.^[24-25] This macromolecule can be converted into cellulose **2** by exposing it to gaseous wet hydrogen chloride.^[24] Thus, ultra-thin cellulose films can be regenerated in situ



from **1**. The thickness of one layer of **1** is ca. 9–10 Å, whereas a layer of **2** exhibits a thickness of 4–5 Å.^[28] We have confirmed these values by spectroscopic ellipsometry.

The polypeptides used are derivatives of poly(methyl-co-octadecylglutamate) in which 20%, 30%, 40%, or 70% of the sidechains are methyl, respectively, while the remaining sidechains are octadecyl groups (OM 80 (**3**), OM 70 (**4**), OM 60 (**5**), OM 30 (**6**)). Each of these polypeptides exhibits a thickness of 17–18 Å per layer.^[21-23]

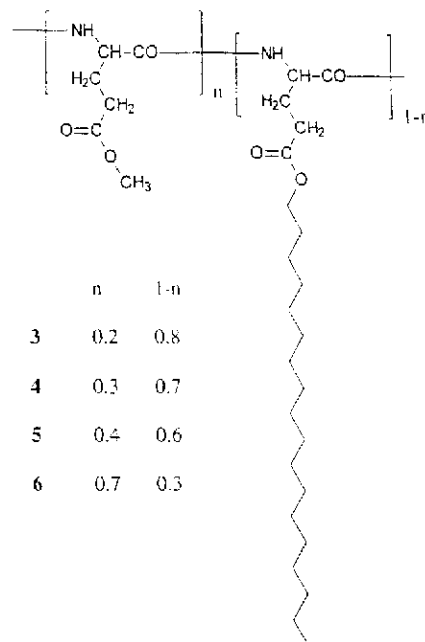


Table 1 gives the number of transferred layers and the observed bond strengths. Bonded Si wafers containing polyglutamates as intermediate layers yield bond strengths in the range of 0.3 to 0.5 J/m² at room temperature. This value is more than ten times the values observed for untreated hydrophobic Si wafers and more than twice the values obtained for wafers with 1 μm thick polymer films (e.g. PMMA). The bond strengths for wafers covered with thin films of TMSC or cellulose are comparable to those observed for untreated hydrophilic wafers (0.1–0.2 J/m²). A heat treatment (50–200 °C) of bonded wafers covered with compounds **1–6** does not lead to an increase in bond strength. This distinguishes LB films of hairy rod-like macromolecules from thick polymer films of PMMA or polyimide spin-coated on Si wafers, which show a considerable increase in bond strength at elevated temperatures.

Table 1. Properties of films deposited.

Compound	Number of layers	Film thickness [Å]	Bond strength [J/m ²]
1	8	76	0.25
2	4	18	0.1
3	8	144	0.35
4	4	74	0.35
5	4	74	0.30
6	4	74	0.48

One could argue that the difference in thickness of the spin-coated polymers on the one hand and the LB films on the other is responsible for the different bonding behavior. At elevated temperatures a polymer film with a thickness in the range of 1 μm becomes fluid and highly flexible. Existing rough areas are leveled out under these conditions and entanglements between the chains of the opposing wafers are formed easily. In the case of the LB films described here, there exist only a few monolayers of polymer in the interphase limiting the number of entanglements which can be formed. Furthermore, the highly ordered structure of the hairy rod-like polymers may inhibit the formation of entanglements even at elevated temperatures. However, at room temperature the high structural order displayed by hairy rod-like molecules proves to be an asset since it ensures a large number of interactions leading to an unusually high bond strength.

The surface micro-roughness of untreated mirror-polished Si wafers is about 1–5 Å. The deposition of the LB films does not lead to an increase in surface roughness. The atomic force microscopy (AFM) micrographs obtained from the ultra-thin films on silicon substrates show a smooth surface free of pin holes, such as in Figure 2, which shows a silicon wafer covered with two monolayers of OM 80 (3).

In conclusion, we have described, to the best of our knowledge, the first application of the Langmuir–Blodgett technology to silicon wafer bonding. The ultra-thin films of hairy rod-like polymers do not increase the surface roughness of mirror-polished silicon wafers and yield high bond strengths at room temperature. Future work will be directed at improving the adhesion of the LB films to various substrates and at studying the transfer of charge carriers through the interface.

Experimental

Four inch diameter p-type Si wafers were dipped in aqueous hydrofluoric acid (2%) for 1 min to render them hydrophobic. Each of the compounds 1 and 3–6 was dissolved in chloroform (5–6 mg in 10 mL of CHCl_3), spread on the water surface of a KSV-5000 LB system and transferred to the hydrophobic Si-wafers at a surface pressure of 20 mN/m. Each polymer was transferred to two Si wafers. The two wafers were subsequently placed into a micro-cleanroom [29], rinsed with ultra-pure water for 2 min to remove dust particles, spin-dried for 7 min (3000 rpm) and bonded. In another experi-

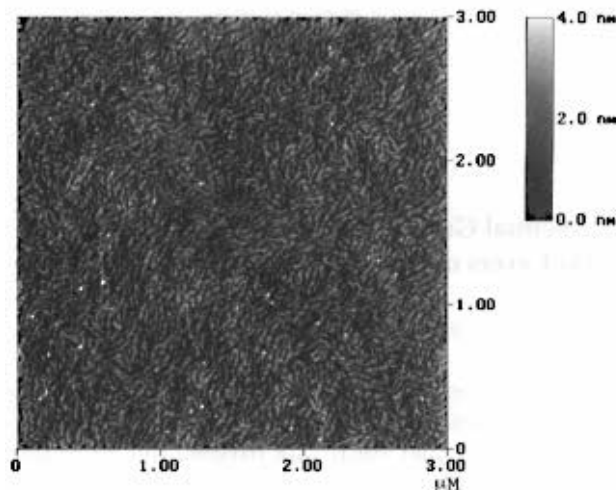


Fig. 2. AFM micrograph of two monolayers of OM 80 on a silicon substrate.

ment a Si-wafer covered with four layers of TMSC was exposed to gaseous wet HCl for 30 s and, after the rinsing and drying procedure described above, bonded to an untreated hydrophilic Si wafer. The bonding was imaged by IR transmission through a bonded wafer pair. The bond energy was determined with the blade insertion method described by Maszara et al.[5].

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Sequential Gas-Phase Formation of Al₂O₃ and SiO₂ Layers on Aerosol-Made TiO₂ Particles**

By George P. Fotou and Toivo T. Kodas*

Sequential formation of Al₂O₃ and SiO₂ layers on titania aerosol particles was achieved via gas-phase and surface reactions of SiCl₄ and AlCl₃ with oxygen. This single-step coating process resulted in dense and coherent alumina layers covered by porous silica layers. Coating pathways for silica and alumina were proposed. The technique may allow manufacture of TiO₂ pigment with improved properties.

Coatings can significantly alter the characteristics and behavior of fine particles. They allow improvement of their dispersion properties, chemical reactivity, photochemical behavior, and thermal stability.^[1] In certain cases, coatings can improve the catalytic, optical, magnetic, and electronic properties of materials.^[2]

We have recently studied the gas-phase formation of coatings of various metal oxides on submicron-sized titania aerosol particles.^[3-5] These studies involved formation of titania particles and subsequent coating with thin layers (5–50 nm) of alumina and silica in a single-step process using gaseous reactants. Mixed SiO₂/Al₂O₃ coatings were also obtained by premixing the coating precursors prior to introduction into the reactor.^[5] In these studies, emphasis was placed on understanding the phenomena governing the gas-phase, in-situ coating of submicron particles. Possible pathways leading to coating layers of different morphologies were identified and include chemical vapor deposition of the coating reactants on a particle's surface as well as gas-phase particle formation, deposition, and sintering.

Multilayer coatings are of particular interest because of their many potential applications. A particle coated with consecutive layers of materials with different physicochemical characteristics may possess a property gradient from its core to the surface. This can be exploited in the synthesis of

optical and electronic materials, and catalysts. For instance, a monolayer of silica deposited onto alumina catalytic supports improves the thermal stability of the latter.^[6] This provides a catalytic particle consisting of an alumina core, a silica monolayer and a top layer of an active component that is more durable than conventional alumina-supported catalysts. Another application is the synthesis of multi-layer-structured catalysts consisting of a glass core covered with a TiO₂ layer on which Pd, Pt, or other metals are dispersed. Catalysts of this type were synthesized in the past by sol-gel techniques and used for hydrogenation of olefins.^[7] Composite particles with a magnetic, electrically conductive, optically transparent or simply inexpensive core can be useful in many other applications.

In the manufacture of titania-based pigments, multilayers of silica and alumina are applied to titania particles by precipitation from solutions of the respective hydroxides.^[1,8] The silica and alumina layers act as radiation barriers and thus shield the titania particles from UV photons when they are exposed to sunlight, which otherwise could initiate photocatalytic reactions. These reactions can potentially degrade the organic binder used in paints which reduces the life of the pigment.^[9] However, these wet-chemistry coating techniques require several process steps, do not provide good control of the coating morphology, and normally result in porous coatings.^[8]

We report here on the in-situ formation of an alumina-silica bilayer on titania aerosol particles in an externally heated tubular reactor. Titania particles were synthesized by reacting TiCl₄ vapor with O₂ at 1300 °C. In all experiments, the TiCl₄ concentration in the reactor was maintained at 8×10^{-4} mol/L and excess O₂ was used (ten times the stoichiometric amount) to assure complete conversion of TiCl₄ to TiO₂. The total residence time of the particles in the reactor was about 5 s. The titania particles produced under these conditions were unagglomerated and polyhedral in shape, with sizes ranging from 0.1 to 0.8 μm. The weight fraction of rutile in the uncoated powders was 87 %.

Coating with alumina and silica was performed using the conditions listed in Table 1. The titania particles made upstream in the reactor entered the first coating zone where they were mixed with AlCl₃ vapor (2×10^{-4} – 1.0×10^{-6} mol/L) generated by heating AlCl₃ in an external sublimation bed as described in the experimental section. Further downstream, the alumina-coated titania particles were mixed with SiCl₄ vapor (5×10^{-6} – 1.6×10^{-5} mol/L) generated by passing N₂ gas through liquid SiCl₄. The residence time of the particles in the two coating zones was 3 s.

Figure 1a shows transmission electron micrographs (TEM) of titania particles coated with silica and alumina at the conditions corresponding to Run 1. These particles were completely covered with alumina and silica as verified by energy dispersive spectroscopy (EDS). The total thickness of the coating ranged from 10 to 50 nm. The layered structure of the coating can be seen in detail in Figure 1b,

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