modified with a custom-designed ultrasonic bath (Advanced Sonic Processing) was programmed to perform layer-by-layer assembly. For each sample, five preparatory bilayers of polyamine–PAA (where polyamine = PAH, BPEI, or LPEI) followed by ten bilayers of polyamine/Ru dye were deposited at pH values of 2.5, 4.8, and 7.0. The preparatory bilayers were formed by dipping first for 20 min in the polyamine solution, followed by 1 min in pH-adjusted Milli-Q water, a 20 min dip in PAA solution, a 1 min dip in another pH-adjusted Milli-Q water bath, a 4 min soak in the ultrasonic bath, and another dip in a pH-adjusted Milli-Q bath before returning to the polyamine solution. Ru dye multilayers were built up much the same way. The Ru dye dip directly replaced the PAA dip in the above cycle but with three pH-adjusted Milli-Q water baths following the substrate's immersion in the negatively charged dye. The pH was kept constant between all the solutions and water baths. All polyelectrolytes were mixed up as 10 mM solutions in Milli-Q water on a repeat unit basis. HCl and NaOH were used to adjust the pH to the appropriate value.

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The Joining of Parallel Plates via Organic Monolayers: Chemical Reactions in a Spatially Confined System**

By *Gertrud Kräuter*,* *Yvonne Bluhm*, *Christoph Batz-Sohn*, and *Ulrich Gösele*

The modification of solid surfaces by the deposition of organic monolayers with tailored architecture has attracted much interest in recent years.[1] Chemical reactions at monolayers are usually carried out by exposing the solid-immobilized molecules to reactive species in the liquid or the gas phase. We have investigated the interaction between two monolayers which are immobilized on two opposing solid substrates. Such reactions proceed in the solid state in a sterically highly constrained system. The surfaces of solids are usually rough on the atomic scale and when placed together at ambient conditions, intimate contact can only take place at a few asperities. Sparked by the tremendous developments in microelectronics, the last decade has seen rapid improvements in the surface quality of electronic materials. Today the microroughness of prime-grade polished materials like silicon is in the angstrom range. If two clean silicon wafers are brought into contact, the surface atoms and molecules of opposing wafer sides approach each other to within the distance of interatomic or intermolecular interactions, so that the two bodies adhere to each other. This phenomenon is referred to as "direct bonding" or "wafer bonding" and is caused by van der Waals forces or hydrogen bonds formed at room temperature between surface molecules located on the opposing wafer sides.[2–4] Covalent bonds between opposing surface species can usually only be formed at high temperature.

Since uniform organic layers do not increase the microroughness of the surface on which they are deposited, in principle it should be possible to use the wafer bonding phenomenon as a tool to study chemical reactions in spatially confined systems. Recently, it has been demonstrated that ultrathin interlayers consisting of four monolayers of either polyglutamates or cellulose derivatives can be prepared through wafer bonding.[5] Due to the absence of reactive groups in these molecules the adhesion to the wafer as well as the cohesion between two monolayers is accomplished through van der Waals forces and additionally through the formation of mechanical entanglements between the flexible side chains. Here, we describe the in-situ formation of covalent bonds between two immobilized organic monolayers located on two opposing substrates. A potential candidate for monolayer deposition and subsequent reaction with an opposing monolayer has to fulfill several requirements: It should be an at least bi-functional organic compound that can be attached to the surface groups of the substrate. The second functionality should be preserved for the interface reaction with the monolayer attached to the opposing wafer. The two functional groups within one molecule should not react with each other nor should the second functional group interact with the surface groups of the silicon wafer as it has to be preserved for the interface reaction. An interface reaction between two solid-immobilized monolayers can only take place if the reactive groups of opposing wafer sides approach each other to a distance required for a chemical reaction to proceed. Covalent bonds are short range interactions, so that the reactive groups have to come within a distance of about 0.1–0.3 nm. This puts steric demands on the deposited monolayer. Finally, the formation of by-products during the

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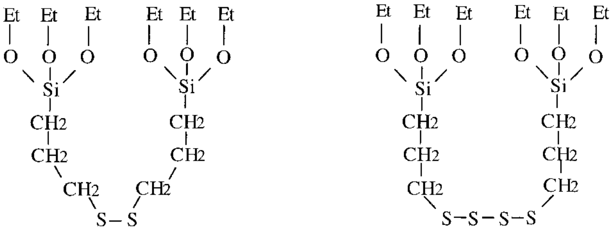
interface reaction between the two monolayers has to be excluded since such by-products cannot be removed from the interface. One promising class of compounds for such experiments are organosilanes. Organosilanes are frequently used as coupling reagents in adhesion technology.[6] The compounds typically possess several functionalities including groups with a potential reactivity towards surface hydroxy groups as well as additional reactive moieties for a coupling reaction. It has been reported that many bi-functional silanes, when deposited onto a substrate, show the tendency to form non-uniform multilayers of varying thickness and structure instead of uniform monolayers.[7] To inhibit the formation of a multilayer, organosilanes containing functional groups which are relatively inert at room temperature were selected for the interface reaction. Promising candidates for the reaction described are organosilanes with di- or polysulfide units. These compounds are commonly used in the rubber industries as adhesion promoters between the hydrophilic silica filler material and the hydrophobic rubber molecules. The compounds attach covalently to silica (and silicon) surfaces while at the same time being able to react with the carbon–carbon double bonds of rubber molecules at elevated temperatures.[8] The two compounds selected for the coupling between two solids are depicted in Figure 1, and denoted by compound **1** and compound **2** in the following. The ethoxy silane groups either react with the silanol groups located on the silicon wafer surface to form covalent Si–O bonds or they may crosslink with neighboring silanol groups formed through the hydrolysis of Si–OEt groups with traces of water. In case of a dense monolayer it is likely that one or two ethoxy groups out of each $Si(OEt)_3$ unit form a covalent bond with the silicon surface while the remaining ethoxy groups crosslink with neighboring groups. The di- or tetrasulfide unit was selected for the interface reaction. Di-and tetrasulfide moieties are known to homolytically cleave when exposed to either UV light or elevated temperatures.[9–11] Tetrasulfides, in particular, are susceptible to decomposition.[10] The scission of the S–S bonds leads to highly reactive radicals which recombine immediately with other radicals present. Since radicals are formed on both opposing wafer sides it is likely that covalent bonds are formed across the interface (Scheme 1). In general, prime-grade polished 4 inch silicon wafers were used as substrates in this study. However, for experiments in which the interface reaction was initiated by UV light, one of the silicon wafers was replaced by a polished 4 inch quartz glass wafer (amorphous SiO_2). Quartz glass exhibits a surface chemistry very similar to that of silicon, but is—unlike silicon—transparent for UV light.

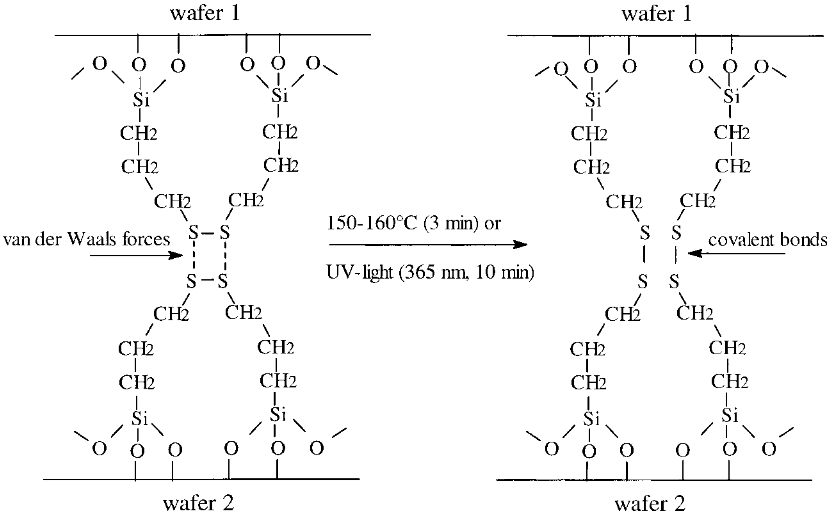
The solid-immobilized tetrasulfide turned out to be reactive at room temperature. To prevent a premature scission of the tetrasulfide unit, the deposition of compound **2** has to be carried out under the exclusion of light.

A wafer treated with compound **1** shows an increase in thickness of about 0.5 nm, compound **2** of about 0.7 nm. These values agree well with the expected thickness of one monolayer of compound **1** or compound **2**, respectively, if the head and tail trialkoxy unit of each molecule bonds to the same silicon wafer. The contact angle with water measured on a silicon wafer surface treated with compound **1** or **2** is 62°, a value which is indicative of a relatively hydrophobic surface. Atomic force micrographs of silicon surfaces treated with **1** or **2** show a smooth surface without pin holes. The microroughness of the silicon surface does not increase upon deposition of compound **1** or **2** (root mean square (rms) roughness = 0.1–0.2 nm before and after the treatment). After the deposition of the monolayers two wafers that have both been treated either with compound **1** or **2** are contacted face to face. Figure 2 shows a photograph of a bonded silicon wafer pair in IR transmission. Both wafers have been treated with compound **1** prior to bonding. At the bonded areas the IR light passes through without any



compound 1 **compound 2**

Fig. 1. Structural formula of the organosilanes **1** and **2** used in the study presented.



Scheme 1. Proposed interface reaction between two solid-immobilized molecules of compound **1**.

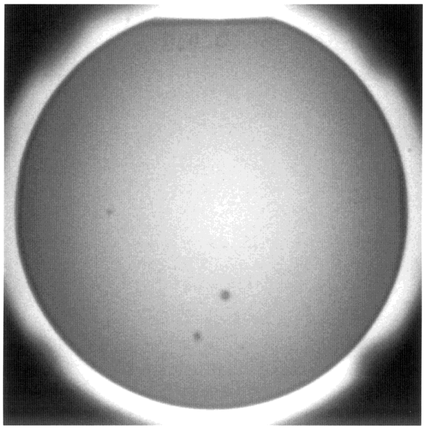


Fig. 2. Photograph of a bonded silicon wafer pair in IR transmission. The silicon wafers have been treated with compound **1** before bonding. The IR light passes the bonding interface without being reflected. The dark spots are caused by particles present on the wafer surface before bonding.

reflection. The dark spots are unbonded areas and are caused by particles in the interface. The bonded interface was additionally investigated by scanning acoustic microscopy, a method with a considerably higher resolution compared to the IR transmission method.[4] Bonded wafer pairs that have been treated with compound **1** before bonding exhibit a fracture surface energy of 50–80 mJ/m^2. This indicates that the interaction between the two surfaces is mainly caused by van der Waals forces. To induce the scission of the S–S bonds the wafer pair is heated to 150–160 °C for 3 min. After cooling the pair to room temperature, the bonding energy was determined once again and was found to increase to 400–500 mJ/m^2. Covalent S–S bonds have been formed across the interface (Scheme 1). Photographs taken in IR transmission before and after the heat treatment reveal no changes in the interface. However, inspection with the more sensitive ultrasound microscopy shows that small gas bubbles have been generated at the interface. The bubbles are presumably caused by the decomposition of some of the organic molecules at 160 °C. It has been reported that S–S bonds cleave readily if they are exposed to UV light.[9] Thus, we wanted to know whether the interface reaction between two solid-immobilized monolayers containing disulfide-linkages would also proceed at room temperature under the influence of UV light. One silicon wafer and one quartz glass wafer were treated with compound **1** and subsequently brought into contact at room temperature. Bonding occurred spontaneously. In this case the bonding process can be monitored with the naked eye through the transparent quartz glass wafer. After the bonding is completed, the wafer pair is introduced into a vacuum–UV-exposure box equipped with four UV lamps (15 W; λ = 365 nm). The fracture surface energy is determined before the exposure with UV light and after 1 min, 5 min, and 10 min of exposure. It increases from 120 mJ/m^2 before the treatment with UV light to 750 mJ/m^2 after an exposure of 10 min. This result confirms that the expected photochemical scission of S–S bonds and their re-formation across the interface does indeed take place. By shadowing parts of the wafer pair with aluminum foil it is now possible to increase the adhesion between the two solids in certain areas while leaving it unchanged in the covered areas. Silicon wafers that have been treated with compound **2** can also be joined by wafer bonding at room temperature. A short heat treatment (3 min) at 80 °C leads to the scission of the tetrasulfide moiety. The decomposition of the solid-immobilized monolayer containing a S_4 unit even takes place at room temperature. If room temperature-bonded silicon wafers which have been treated with the tetrasulfide compound are kept at ambient conditions, the fracture surface energy slowly increases yielding a constant value after 10–14 days. This reinforces the fact that the tetrasulfide is considerably less stable than the disulfide. The facile thermal decomposition of tetrasulfides is well-known.[10] The pronounced instability at room temperature, however, seems to be limited to the solid-immobilized monolayer prior to the interface reaction. This instability may be related to a certain strain induced by cyclization, which takes place upon adsorption of the monolayer onto the substrate. Immediately after the bonding a fracture surface energy of 60–90 mJ/m^2 is measured. After the heat treatment at 80 °C or after a storage time of 10–14 days at room temperature this energy increases to about 400–450 mJ/m^2. To put the increase in adhesion energy reported in this study into perspective, a rough estimate of the maximum attainable fracture surface energy can be made. The number of surface silanol groups is reportedly in the order of 5 per nm^2 in the case of silica.[11] Approximately the same number of surface silanol groups can be expected for silicon and quartz glass wafers. If we assume that each molecule of compound **1** or **2** occupies six surface silanol sites (either by the formation of a covalent bond or by blocking a site for steric reasons) the number of adsorbed molecules can be roughly estimated. It can be expected that each adsorbed di- or tetrasulfide molecule forms a maximum of two new S–S bonds across the interface. The bond energy of a S–S bond in dialkyl disulfides is reportedly about 280–300 kJ/mol.[12] In contrast, the bond energy of the S–S bond in dialkyl tetrasulfides is only in the range of 150 kJ/mol.[13] Taking this into account, the maximum fracture surface energy should be in the range of 850 mJ/m^2 for a wafer pair treated with the disulfide and 450 mJ/m^2 for a pair treated with the tetrasulfide. Based on this simple calculation roughly half of the disulfide molecules form new S–S bonds across the interface if the reaction is initiated thermally. The photochemical reaction yields about 90 % of the attainable fracture surface energy. The dependence on the initiation method is attributed to the fact that at 160 °C decomposition of the organic molecules slowly sets in. The gas bubbles which are formed in the interface cause a decrease in adhesion. In contrast, the photochemical scission of S–S bonds proceeds under mild conditions without the formation of gas bubbles and thus yields a higher fracture surface energy. In agree-

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ment with this interpretation the monolayers containing the thermally less stable tetrasulfide linkages react at moderate temperatures without the generation of gaseous decomposition products yielding again approximately the calculated fracture surface energy.

In conclusion it was shown that solid-phase reactions can be initiated between organic monolayers that are immobilized at smooth solid surfaces. Due to steric constraints, wafer bonding represents a novel environment for the study of chemical reactions.

The well-known ability of di- and polysulfides to react with carbon–carbon double bonds in olefins[14] gives rise to the expectation that other interface reactions can be carried out following the scheme presented here.

Experimental

Prime-grade polished silicon and quartz glass wafers were cleaned using a standard cleaning procedure: 1. $NH_4OH:H_2O_2:H_2O$ (1:1:6; 70 °C; 10 min); 2. Rinse with ultra-pure water (10 min); 3. $HCl:H_2O_2:H_2O$ (1:1:5; 70 °C; 10 min); 4. Rinse with ultra-pure water (10 min).

Monolayers of compound **1** and **2** (both compounds are commercially available) are deposited by exposing the freshly cleaned substrates to a solution of **1** or **2** in toluene ($c = 10^{-3}$ mol/L) for 4 h at room temperature in an inert atmosphere. After the deposition is complete unreacted compound is removed by extensive rinsing with toluene, acetone, *i*-propanol, and methanol. The wafers are spin-dried and contacted face to face under vacuum (4 mbar). The bonding of silicon wafers is monitored by illuminating the back of the wafer pair with IR light while observing the front with an IR-sensitive camera. For the detection of small particles and gas bubbles ultrasound microscopy is performed (Sonoscan-C-SAM 300 DX). The fracture surface energy is determined by inserting a wedge at the rim of the wafer pair (double cantilever method). The crack that opens up relates to the fracture surface energy [15–17]. A Woolham variable angle spectroscopic ellipsometer (WVASE 32) was used to measure the thickness of the monolayers. The surface roughness was determined using a large area atomic force microscope (Digital Instruments Dimension 5000). The contact angles were measured with a Krüss Contact Angle Measuring System G 10.

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Formation of Patterned Microstructures of Conducting Polymers by Soft Lithography, and Applications in Microelectronic Device Fabrication[**]

By *Weng Sing Beh, In Tae Kim, Dong Qin, Younan Xia,*[*] and *George M. Whitesides*

This paper describes the use of one of the soft lithographic methods—micromolding in capillaries (MIMIC)[1]—in the fabrication of patterned microstructures of conducting polymers with feature sizes ranging from ~350 nm to ~50 µm. These electrically conductive microstructures were further used as patterned electrodes to fabricate flexible, all-plastic devices such as field effect transistors (FETs).

"Soft lithography" is the collective name for a group of non-photolithographic methods that are capable of generating patterned structures with feature sizes as small as ~30 nm.[2] Soft lithography offers immediate advantages over photolithography or other conventional lithographic techniques for a wide range of applications in which modification of surfaces, variation in materials, or patterning of non-planar substrates is the major concern. The initial success of soft lithography indicates that it has the potential to become an important addition to the field of micro- and nanofabrication.

Conducting polymers have been extensively explored as alternatives to metals or inorganic semiconductors in the fabrication of microelectronic, optoelectronic, and microelectromechanical devices.[3] Functional components such as diodes,[4] transistors,[5] FETs,[6] light emitting diodes (LEDs),[7] mechanical actuators or transducers,[8] and optical modulators[9] have been successfully fabricated from conjugated organic polymers in prototype forms. Most of these applications require the formation of patterned microstructures of conducting polymers with feature sizes less than 100 µm. A number of methods have been investigated for this purpose; notable examples include photolithography,[10] e-beam writing,[11] surface-templated deposition,[12] screen printing,[13] and ink-jet printing.[14] In most cases, however, conducting polymers have to be modified to work

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