Investigations of both the ferroelectric and electroclinic properties of the new chiral palladium mesogen L_2Pd have been performed. A comparison of the spontaneous polarization and the response time measured in the S_{C^*} phase of L_2Pd and the corresponding values previously reported for other metallomesogens (see above) shows that the spontaneous polarization of L_2Pd has the smallest value while the response time is essentially the same. The most striking features of L_2Pd are the electroclinic properties. Despite the small value of the spontaneous polarization in the S_{C^*} phase, the field-induced tilt in the chiral smectic A phase (S_{A^*}) has a value of about 12° near the S_{A^*}–S_{C^*} phase transition on applying relatively moderate electric field. So far, such large induced tilt angles have been measured only in specially designed electroclinic liquid crystals.[20]

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Silicon Wafer Bonding via Designed Monolayers**

By *Johann Steinkirchner, Torsten Martini, Manfred Reiche, Gerhard Kästner,* and *Ulrich Gösele**

Silicon wafer bonding is a technology which allows two silicon wafers to stick together without any glue.[1] Wafer bonding has emerged as an important technology with a wide range of applications in the areas of microelectronics, micromechanics and power electronics.[2, 3]

The currently used wafer bonding process involves the interaction of hydrophilic surfaces and consists of three steps involving a so-called RCA standard cleaning procedure (described later in more detail) to render the silicon wafer surfaces hydrophilic. The second step is the mating of two wafers together at room temperature. The last step is a high temperature annealing process to achieve an acceptable bonding strength.[4] Annealing at high temperatures results in problems such as broadening of etch-stop dopant profiles or dissociation of compound semiconductors which have low dissociation temperatures.

The ability to form strong bonds at low temperatures (below 450 °C) would allow conventional microelectronic aluminum metallization to be present on silicon wafers during the bonding process or the bonding of dissimilar materials without excessive thermal stress which usually develops during heating due to the difference in thermal expansion coefficients between two bonded materials.

Various low-temperature indirect wafer bonding processes have been reported, using anodic bonding via intermediate layers of sodium-rich glass[5, 6] or bonding via polymer layers[7] which are deposited on the wafer surface with a thickness in the range of several μm. The aim of our investigation was to develop a direct wafer bonding process via designed monolayers. Organosilanes $RSiX_3$ like γ-glycidyloxypropyltrimethoxysilane (GPS), γ-mercaptopropyltrimethoxysilane (MCPS) or γ-aminopropyltrimethoxysilane (APS) have been used for many years as coupling agents to enhance the adhesion between two dissimilar materials and as modifiers to control the physical and chemical properties of surfaces.[8] Their application to the wafer bonding process fails due to the thermal instability of the organofunctional group R which results in decomposition of the interface layer and formation of large unbonded areas (interface gas bubbles) after annealing even at intermediate temperatures of 200–600 °C.

The thermal instability can be avoided by using hydrolyzed tetramethoxysilane (TMOS) which contains no temperature-sensitive group. By treating silicon wafers with a dilute solution of tetramethoxysilane, a silicon oxide layer with a thickness in the range of a few Ångstroms is formed

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which contains an increased number of available bonding sites at its surface as compared to RCA treated silicon wafers with a corresponding increase in the interface fracture energy.

In our experiments we used 4 inch, p-type, (100) oriented, Czochralski grown silicon wafers with a thickness of 500–550 μm and a resistivity of 25–45 Ωcm. The specific values of the interface fracture energy generally depend somewhat on the wafer surface conditions. In order to keep such conditions like smoothness or wafer flatness as constant as possible, all wafers used were supplied from one specific wafer manufacturer.

In order to remove organic and inorganic contaminants and to make the wafer surfaces hydrophilic, the silicon wafers were cleaned by the RCA cleaning procedure which is composed of a SC1 and a SC2 cleaning step. The SC1 step consists of heating the wafers in a mixture of H_2O:H_2O_2:NH_4OH (5:1:1) at 75 °C for 10 minutes. After rinsing with deionized water, the wafers were immersed into a solution of H_2O:H_2O_2:HCl (6:1:1) and heated for 15 min at 75 °C (SC2 step). After a further flushing step with deionized water, one group of wafers was bonded immediately. Another group of wafers was treated with 0.2% by weight of TMOS in aqueous solution at a pH value of 2–3. The pH value was adjusted by acetic acid which was used as a catalyst to enhance the rate of the hydrolysis reaction of tetramethoxysilane to monosilicic acid.[9]

The precleaned silicon wafers were immersed into the solution of hydrolyzed TMOS for about 25 min. After withdrawal from the solution, the molecular modified wafers were dried for about 7 min by spinning in a micro-cleanroom set up[10] and bonded immediately without further flushing with deionized water. Rinsing with water might result in hydrolysis reaction of the covalent bonds between the deposited layer and the native oxide and thus removal of the as-formed layer. The bonding experiments were also performed in the micro-cleanroom set up mentioned above. The bonding process was monitored by an infrared camera. After bonding the wafers at room temperature, an annealing step was performed under atmospheric conditions from 100 °C to 800 °C, typically for 20 hours.

The wafer bonding process at room temperature is initiated by van der Waals and hydrogen bonds.[11] The attraction force between hydroxyl groups and adsorbed water molecules on silicon surfaces results in a close contact between the two wafers, but the bonding strength is still low. In order to enhance the interface fracture energy of a bonded wafer pair, an annealing step at elevated temperatures is performed. As the temperature increases to above 110 °C, siloxane bonds can be formed by a condensation reaction between hydroxyl groups on the hydrophilic silicon wafer surface.

For the characterization of the bonding strength, a crack opening method is used. A thin razor blade is inserted between the two wafers of a bonded pair and the two wafers are bent around the inserted blade. The crack length propagates along the bonding interface until an equilibrium is achieved between the elastic forces, created by the bent parts of the bonded wafer pair, and the bonding force of the pair. The crack length is determined by optical inspection of the image from an infrared TV camera. The interface fracture energy γ (frequently also termed surface or interface energy) is calculated from the measured crack length L by the method proposed by Maszara et al. (Eq. 1).[12]

$$\gamma = \frac{3Ed^3y^2}{32L^4} \tag{1}$$

E is Young's modulus of elasticity, d is the thickness of the wafers, and y the thickness of the razor blade. All things being equal, a shorter crack length indicates a larger γ which in turn indicates stronger intersurface bonding.

In the case of wafer pairs which were annealed at elevated temperatures, the crack opening in air continues even several minutes after insertion of the blade, as can be seen in Figure 1. The surface energy is reduced drastically within 1 minute and for hydrophilic wafers the value after 1 min is about 35% of the original value. For a precise determination of the bonding strength, the crack length has to be measured as a function of time. Additional experiments showed that this decrease in interface fracture energy appears to be related to the humidity in the air.

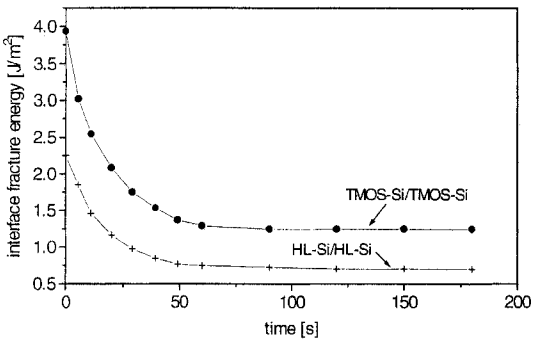

Fig. 1. Interface fracture energy (per generated surface area) of bonded hydrophilic (HL) and TMOS treated Si/Si wafers as a function of time after insertion of a razor blade (relative humidity 32%). The bonded wafers were treated at 400 °C for 20 hours.

The surface energies of untreated and TMOS silylated wafer pairs as a function of annealing temperature can be seen in Figure 2. The interface fracture energy was determined in air 20 seconds after insertion of the razor blade. The solid curves in Figure 2 are simply meant as guides for the eye. The interface fracture energy at room temperature is in the range of 100–140 mJ/m² for hydrophilic wafers and 170–210 mJ/m² for wafers that were dipped into a solution of TMOS.

In the temperature range from room temperature to 150 °C the bonding strength increases substantially and reaches a maximum value at temperatures of about 150 °C. The interface fracture energy increases to values of about 1100–1300 mJ/m² for RCA cleaned wafers and 1900–

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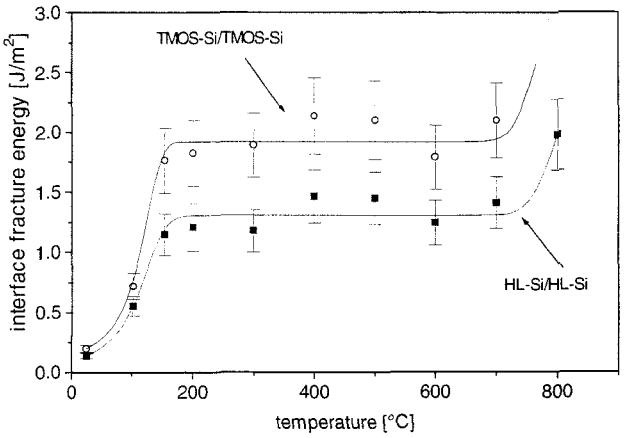

Fig. 2. Interface fracture energy of bonded hydrophilic (HL) and TMOS treated Si/Si wafers as a function of annealing temperature. The annealing time was 20 hours. The interface fracture energy was determined 20 seconds after insertion of the razor blade.

2100 mJ/m² for silylated wafers. In a temperature range of 150 °C to 700 °C γ remains almost constant while at temperatures of 800 °C and higher a further increase of the interface fracture energy occurs. At temperatures of about 800 °C and higher it was impossible to measure γ of a silylated wafer pair by the crack opening method because insertion of a blade caused the bonded wafers to break due to a drastic increase of the bonding strength by formation of strong covalent bonds at the interface.

The interface fracture energy of silicon wafer pairs is significantly enhanced by treating them with a solution of TMOS before the bonding process. This increase appears to be due to the formation of an extremely thin silicon oxide layer which is associated with a larger number of reactive silanol groups than in the case of RCA cleaned wafers. Hydrolyzed TMOS appears to react with hydroxyl groups on the wafer surface by condensation and to form a firmly fixed layer. The siloxane bonds Si–O–Si between OH groups of the native oxide surface layer of the silicon and hydroxyl groups of the hydrolyzed tetramethoxysilane compound make this film particularly robust.

Ellipsometrical measurements were performed for the determination of the thickness of the adsorbed layer. Ellipsometry is a nondestructive technique which shows small changes in the surface conditions (like adsorbed species and surface roughness). Measurements were made by using a variable angle spectroscopic ellipsometer (VASE). VASE data were recorded in the range of 250–800 nm. The angle of incidence was set between 65° and 85°. A Bruggeman effective-medium approximation (EMA) was used to characterize the chemically treated surface. First the thickness of the *native* oxide layer on the RCA cleaned silicon wafer was determined and was about 15.5 Å. Then the silicon wafer was immersed into the solution of TMOS for about 25 minutes. The thickness of the oxide layer increased to a value of 22.0 Å by silylation which corresponds to 2–3 additional layers of SiO_2.

In order to get more information on the wafer surfaces after RCA standard cleaning and subsequent silylation, atomic force microscopy (AFM) measurements using a Nanoscope III AFM were carried out under atmospheric conditions. Areas of 0.5 mm × 0.5 mm were investigated in the tapping mode. The mean roughness R_a of a silicon wafer after RCA standard cleaning procedure was in the range of 0.14 nm and about 0.16 nm after dipping the wafers into a solution of TMOS. No significant change in the surface roughness by silylation could be seen. After bonding and heating to 400 °C for 20 hours the interface region of the bonded wafer pairs was inspected by cross-sectional high-resolution transmission electron microscopy. A typical micrograph (Fig. 3) shows the silicon lattice fringes and an interfacial oxide of about 40 Å. The micrograph looks comparable in terms of oxide thickness to those for bonded RCA cleaned hydrophilic silicon wafers and shows that the silylation treatment has added only a few monolayers of extra SiO_2 material at the bonding interface.

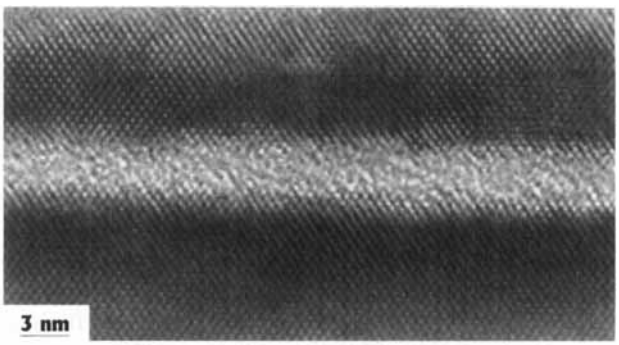

Fig. 3. High-resolution transmission electron micrograph of a cross-section of an interface of two TMOS treated silicon wafers after annealing at 400 °C for 20 hours.

In conclusion, the application of TMOS to hydrophilic silicon wafers is a simple and versatile method to increase the interface fracture energy of a bonded silicon wafer pair. An additional temperature stable surface layer of less than 10 Å thickness is formed which increases the number of available bonding sites on the wafer surface. By this method a high bonding strength can be achieved by annealing at comparatively low temperatures in the range of 200 °C to 400 °C.

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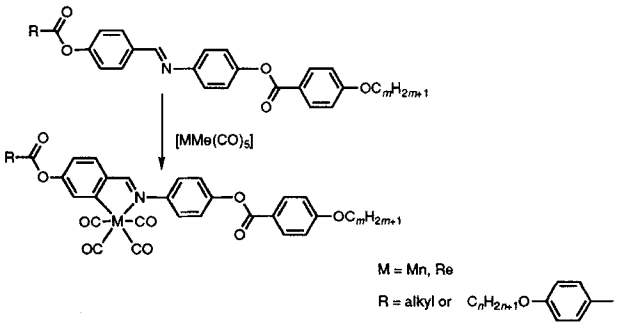


Fig. 1. Mesomorphic octahedral Mn and Re complexes.

Octahedral, Liquid-Crystalline Complexes of 1,4-Diazabutadienes with Rhenium(I)**

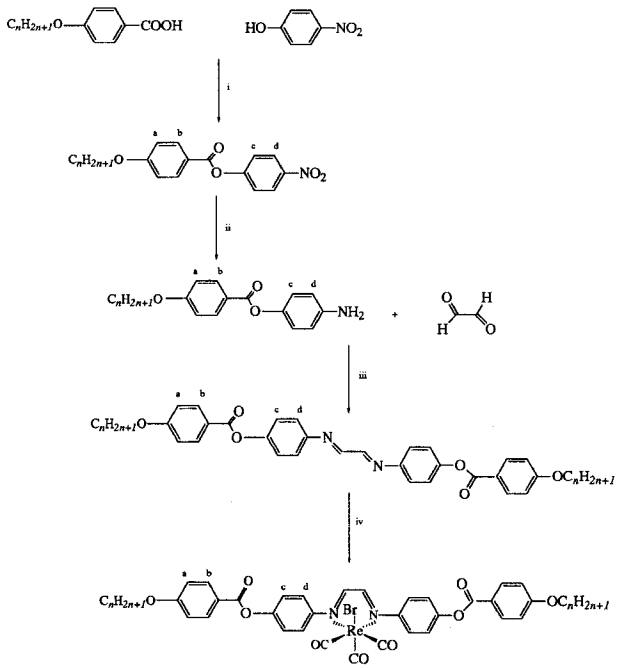
By *Stefania Morrone, Gayle Harrison,* and *Duncan W. Bruce**

The synthesis of mesomorphic transition metal complexes is a research area experiencing continuous expansion.[1–5] The growing interest in these new materials is a consequence of both their peculiar physical properties and, from the point of view of the chemistry involved, the wide range of synthetic possibilities that still have to be explored. Properties such as high birefringence,[6] high linear[7] and nonlinear[8] polarizability, and high linear dichroism[9] have been observed and metal complexes capable of forming lyotropic liquid crystal mesophases[10] have been prepared.

Over the last few years effort has been invested in the synthesis of thermotropic, calamitic liquid-crystalline complexes with high coordination numbers. However, most of these compounds are square pyramidal complexes of V^{IV} or Fe^{III} or ferrocene derivatives.[11, 12] Recently, we have shown that the combination of ligands with high structural anisotropy and relatively bulky organometallic fragments such as $[M(CO)_4]$ (M = Mn, Re) leads to the formation of calamitic liquid-crystalline complexes with octahedral coordination around the metallic center.[13] In particular, the compounds $[ML(CO)_4]$ (L = Schiff base) show mesomorphic properties when three[14] or four[15] rings are included in the ligand structure (Fig. 1).

We wished to extend this work with the aim of generating a general approach to the design and synthesis of metal-containing liquid crystals based on high coordination number centers and therefore devised a methodology for the synthesis of liquid-crystalline complexes obtained by coordination of the $[ReBr(CO)_3]$ fragment to 1,4-diaza-1,3-butadienes. Diazabutadienes have a wide and interesting coordination chemistry which has been subject of several studies[16] but, as far as we know, liquid-crystalline complexes containing this ligand have not previously been reported.

We now wish to report the synthesis of *N,N'-bis*-4-(4-alkoxybenzoyloxyphenyl)-1,4-diaza-1,3-butadienes (L_1–L_3) and their Re(I) complexes. The synthesis of the complexes was carried out following literature methods[17] with the procedure shown in the Scheme and as detailed in the experimental below. Thus, 4-alkoxybenzoyloxy-4'-aniline was obtained from the corresponding nitro derivative (itself from esterification of 4-alkoxybenzoic acid and 4-nitrophenol) on reduction with Sn^{II}. Two equivalents of the aniline were then reacted with aqueous glyoxal[18] in ethanol (ethanol was preferred over methanol as the latter tended to add across the imine bond, whereas we found no evidence of this occurring with the former solvent). The diamagnetic rhenium complexes were then formed by reaction of the ligand with



Scheme 1. Synthesis of the mesomorphic rhenium complexes. n = 8 (L_1); 10 (L_2); 12 (L_3). i) 1,3-Dicyclohexylcarbodiimide, 4-dimethylaminopyridine, CH_2Cl_2. ii) $SnCl_2 \cdot 2H_2O$, EtOH. iii) EtOH. iv) $[ReBr(CO)_5]$, toluene, heptane.

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