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## Photoluminescent Siloxenes in Nanoporous Aluminum Oxide\*\*

By Andreas Heilmann, Peter Jutzi, Andreas Klipp, Uwe Kreibig, Rolf Neuendorf, Thomas Sawitowski, and Günter Schmid\*

Since the discovery of the luminescence of anodically oxidized silicon wafers in 1990<sup>[1]</sup> there has been increasing scientific and technological interest in light-emitting silicon systems. The phenomenon of luminescence is attributed to two different situations:<sup>[2–8]</sup> silicon structures and siloxene-like systems with Si–OH and Si–H moieties. In both cases the luminescence is caused by nanosized building blocks.

Nanoporous aluminum oxide membranes have variously been used to generate nanosized particles of different materials.<sup>[9-11]</sup> Here we report on the formation of photoluminescent siloxenes by spontaneous decomposition of silanes in the channels of aluminum oxide membranes. This method opens novel and simple routes to stable light-emitting systems. The use of nanoporous aluminum oxide membranes allows two decisive factors to be controlled: the size of the photoluminescent system and the chemistry on its surface. In addition, alumina membranes offer a tremendous increase of surface compared to the usual two-dimensional arrays. Assuming an average number of  $10^{10}$  pores/ cm<sup>2</sup> a membrane of 1 cm<sup>2</sup> size with 40 nm pores and 1  $\mu$ m thick has an inner surface of 13 cm<sup>2</sup>.

Nanoporous aluminum oxide membranes are formed by anodization of aluminum in polyprotic acids.<sup>[12-14]</sup> The pore diameter is mainly a function of the applied voltage (about 1.0–1.2 nm per volt) and can be varied between ~5 nm and 250 nm. Using high purity aluminum, the resulting membranes are transparent to light between 350 nm and the near infrared region. The thickness of the membranes depends on the anodization time.

 $Cp*SiH_3$  (Cp\* = pentamethyl cyclopentadienyl) has already been used for CVD processes to generate Si-containing films.<sup>[15,16]</sup> In the case of  $Cp*SiH_3$  spontaneous heating to 800 °C in nitrogen atmosphere leads to the formation of Cp\*H,  $H_2$ , and Si. While organic products and most of the hydrogen leave the pores immediately, the silicon atoms

D-52026 Aachen (Germany)

 <sup>[\*]</sup> Prof. G. Schmid, Dr. A. Heilmann, T. Sawitowski Institut für Anorganische Chemie, Universität Essen Universitätsstrasse 5–7, D-45117 Essen (Germany)
 Prof. P. Jutzi, A. Klipp Fakultät für Chemie, Universität Bielefeld Universitätsstrasse 25, D-33615 Bielefeld (Germany)
 Prof. U. Kreibig, R. Neuendorf

I. Physikalisches Institut, RWTH Aachen

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will spontaneously react with the OH groups of the pore surfaces to give stable Al–O–Si interactions. This is the beginning of siloxene-like structure formation (Fig. 1). The presence of hydrogen causes Si–H bonds to form on the Si surface and Si–OH bond formation is also possible. The degree of coverage of the pore walls by the siloxene structure depends on the amount of silicon that is present during the thermolysis. This amount, in turn, is determined by the yield of silicon in the silane, which is 17 % in Cp\*SiH<sub>3</sub>, and the pore size. The larger the diameter of the pore, the bigger the space to be filled by the silane. Therefore, siloxene areas of different size can be deposited on the pore walls by varying the pore diameters.



Fig. 1. Sketch of a piece of siloxene on the pore wall of nanoporous aluminum oxide.

Assuming that the Si atoms are first deposited as monoatomic layers and that a second layer will be formed only after the monolayer is completed, one can calculate the degree of coverage as a function of the pore diameter.<sup>[17]</sup> Although this rough calculation gives only approximate values, it can be seen that a single thermolysis of Cp\*SiH<sub>3</sub> in a 20 nm pore membrane leads to only ~60 % coverage of the channel surfaces. Continuous siloxene layers are formed only if the thermolysis is repeated. In membranes with pores larger than 35 nm at least one monolayer of siloxene is completed by one thermolysis. To form a siloxene consisting of two siloxene layers 70–80 nm pores are necessary.

In the samples under consideration, a transmission electron microscopy (TEM) image of a piece of filled luminescent alumina, cut along the pores, does not indicate any particle formation. Because of the similar electron diffraction contrast for aluminum oxide and silicon oxide, single or double layers of siloxene could not be observed by TEM. Colloid formation was, however, initiated by re-



peated filling and subsequent thermolysis, but these samples are not considered in this paper.

The infrared spectra of silicon-containing membranes show vibrations typical for siloxenes.<sup>[4]</sup> Figure 2 presents the IR spectrum of the 80 nm pore system. The presence of the v(Si-H) vibrations at 2037 cm<sup>-1</sup> and of v(SiO-H) at 3705 cm<sup>-1</sup> indicates the siloxene-like nature of the species generated on the pore walls. The intense C=O vibration is caused by the formation of CO<sub>2</sub> inside the aluminum oxide.



Fig. 2. FTIR spectrum of a siloxene-containing 20 nm membrane corresponding to an approximate double layer.

The as-prepared aluminum oxide membranes do not show any photoluminescence, but after rapid annealing in  $N_2$  atmosphere to temperatures between 600 °C and 800 °C, photoluminescence was found. Figure 3 gives the photoluminescence spectra of an unfilled aluminum oxide membrane with a pore size of 80 nm. The membrane was heated up to 800 °C and to 900 °C. After the sample was heated up to 800 °C, two photoluminescence peaks were observed, the main peak at 2.20 eV (564 nm) and a second peak at 2.28 eV (544 nm). Both peaks disappeared after annealing to 900 °C. Owing to the different excitation energy, the spectral position of the measured photoluminescence



Fig. 3. Photoluminescence spectra (excitation at  $2.54 \,\mathrm{eV}$ ) of an unfilled membrane with 80 nm pore diameter after heating up to 800 °C (upper trace) and 900 °C (lower trace).



does not correspond to the photoluminescence found on aluminum oxide with oxalic acid films.<sup>[18]</sup>For siloxene-filled membranes with different pore sizes, two photoluminescence peaks at 2.46 eV (504 nm) and 2.31 eV (537 nm) were found (Fig. 4). For the membrane with 20 nm pores, the peak at 2.46 eV dominates. In contrast, the 80 nm membrane shows a photoluminescence maximum at 2.31 eV. The 40 nm membrane with two sharp photoluminescence peaks at 2.31 eV and 2.47 eV demonstrates the intermediate state between the smaller and larger pores.





Considering literature data we assume that the photoluminescence peaks at 2.46 eV and 2.31 eV can both be attributed to the siloxene structure on the pore walls. The photoluminescence spectra of the siloxene-filled membrane in some respects correspond to the spectra of "siloxene crystals".<sup>[19,20]</sup> The exact value of the luminescence peak of siloxenes depends on the sample preparation as well as on the excitation energy. If the siloxene crystals were excited with an energy of 3.25 eV, the photoluminescence peak was found at 2.6 eV for the as-grown sample and at 2.1 eV for the vacuum-annealed sample.<sup>[20]</sup> Using an excitation energy of 2.54 eV, the photoluminescence maxima were observed at 2.22 eV for as-deposited samples, but at 2.30 eV for aged samples and even at 1.6 eV for thermally treated samples.<sup>[21]</sup> The dramatic shift in the thermally treated sample is explained by the formation of porous silicon.<sup>[21]</sup>

Different silicon polymer backbone structures (chains, ladders, siloxenes) were also used to explain the spectral position of the luminescence.<sup>[22]</sup> The observed luminescence at about 2.4 eV using an excitation energy of 3.8 eV was related to a siloxene structure. Furthermore, photoluminescence in the spectral region of interest was also found for Si/SiO<sub>2</sub> superlattices at 2.26 eV<sup>[23]</sup> or for amorphous SiO<sub>x</sub> nanostructures at 2.2 eV.<sup>[23]</sup>

By using these data, we assume that the different intensities of the photoluminescence peaks at 2.46 eV and 2.31 eV for various pore sizes correlate with the degree of siloxene coverage. For small pores, there is incomplete siloxene coverage. With increasing pore size, the siloxene structure will be progressively completed. To date, we have no information about the thickness of the siloxene layer on the pore wall. Further work is in progress to explain the relationship between the spectral position and the intensity of photoluminescence and siloxene formation in more detail, also as a function of the pore size and the siloxene filling procedure.

In conclusion, we have shown that simple thermolysis of organosilanes in nanoporous aluminum oxide membranes results in photoluminescent siloxene structures. Two photoluminescence peaks of the siloxene structure, at 2.46 eV and 2.31 eV, were found. The spectral position of the most intense peak depends on stepwise development of siloxene structures at the pore walls, which is mainly influenced by the pore size.

#### Experimental

Membranes and organosilanes were synthesized as described in the literature [11-16,24]. The unfilled membranes were heated immediately to temperatures between 600 °C and 900 °C. For the filling experiments, the membranes were used after thermal treatment up to 900 °C. Silane filling was achieved by evacuation of the membrane in the presence of the liquid silane. The filled samples were heated to 800 °C in an atmosphere of nitrogen containing a small amount of oxygen to burn traces of carbon from the organic moieties. The samples were cooled to ambient temperatures under nitrogen. Then the samples can be stored in air. There was no change in luminescence after months. The successful filling of the pores by vacuum induction can be shown by dropping small amounts of silane onto the membrane surface followed immediately by heating to 800 °C. After this process the photoluminescence intensity is only very low compared to the vacuumfilled samples. TEM images of the samples were recorded on a Philips FEG 200 Super Twin after embedding the membrane in Spurrs resin and sectioning with an ultramicrotome (Leica Ultracut UCT). FTIR spectra were recorded with a BioRad FTS 175 spectrometer. The background was recorded with an unfilled membrane. For the photoluminescence measurements, the samples were excited by an Ar<sup>+</sup> ion laser (Coherent Innova 70) with an excitation energy of 2.54 eV (488 nm). The photoluminescence spectra were obtained using a multichannel spectrometer MCS 400 (Zeiss).

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### Rough Surfaces by Design: Gold Colloids Tethered to Gold Surfaces as Substrates for CaCO<sub>3</sub> Crystallization\*\*

### By Jörg Küther, Ram Seshadri, Gabriele Nelles, Hans-Jürgen Butt, Wolfgang Knoll, and Wolfgang Tremel\*

The covalent tethering of gold colloids to modified surfaces such as self-assembled monolayers (SAMs)<sup>[1]</sup> immobilizes the colloids and facilitates the observation of interesting physical properties, including Coulomb stairs and other nonlinear phenomena<sup>[2–4]</sup> in electron transport as well as granular bulk conductance.<sup>[5]</sup> Assemblies of metal colloids on modified SAM surfaces are also of interest from an electrochemical viewpoint.<sup>[6]</sup> There is additionally the interest in novel ordered architectures.<sup>[4,7]</sup> The extremely thiophilic nature of gold provides a simple recipe for such

 [\*] Prof. W. Tremel, J. Küther, Dr. R. Seshadri Institut für Anorganische Chemie und Analytische Chemie Johannes-Gutenberg Universität Becherweg 24, D-55099 Mainz (Germany)
 Dr. G. Nelles, Prof. H.-J. Butt Institut für Physikalische Chemie Johannes-Gutenberg Universität Welderweg 11, D-55099 Mainz (Germany)
 Prof. W. Knoll Max-Planck-Institut für Polymerforschung Ackermannweg 10, D-55128 Mainz (Germany) covalent tethering: SAMs of long chain dithiols on Au serve as sticky surfaces for the attachment of gold colloids. Indeed, as Henderson et al.<sup>[6]</sup> have shown, gold colloids will also attach to isocyanides. Through masked UV exposure, Vossmeyer et al.<sup>[8]</sup> were able to expose amino surfaces on an SAM on silicon and then attach gold colloids to the exposed amino groups, resulting in patterned surfaces.

An important issue in the attachment of gold colloids to gold surfaces through the use of  $\alpha, \omega$ -dithiols is to establish the necessity of the thiol. Gold colloids can stick directly to gold surfaces without the mediation of thiols, the driving force being the eventual lowering of surface area. This might happen even when the colloids are stable to aggregation, as, although colloids are mutually repelled by electrostatic forces, this repulsion is absent in the interaction between a colloid and a neutral, conducting wall.<sup>[9]</sup>

Another interesting aspect of tethering gold colloids to SAMs is the possibility of constructing dithiol–colloid sandwich multilayers. Such architectures are of considerable interest as models for granular metals.<sup>[5,10]</sup> Depending on the control that is possible, one could imagine various applications such architectures could be put to, for example, as mirrors for soft X-rays.

A third interesting aspect is the use of gold colloids to modify the surface characteristics of flat gold surfaces, including the roughness, hydrophilicity, etc. This is the main focus of this study.

In this communication, we examine all three of these aspects; by employing surface plasmon spectroscopy (SPS) we establish that gold colloids in the 8–10 nm size range attach much more rapidly to "sticky" gold surfaces than to pristine gold (and not at all to gold surfaces made inert using alkylthiol SAMs). The possibility of constructing ordered multilayers is suggested from UV-vis absorption spectroscopy. Finally, we characterize a gold colloid coated SAM surface by atomic force microscopy (AFM) and use the resulting surface as a substrate for the growth of CaCO<sub>3</sub> crystals at 45 °C from solution, comparing the results with crystallization on unmodified surfaces. The broad outline is thus to produce well-characterized surfaces of controlled roughness for use as substrates in model biomineralization studies.

Gold-coated glass substrates for the recording of SP spectra were fixed to Teflon cells on the coated side and optically coupled to a prism on the other. SP spectra were recorded with cells filled with water as the working medium. Exposure of the gold surface to dithiol (or alkylthiol) in ethanol or to the colloids in toluene was carried out in situ. The spectra, which are plots of reflectivity at a fixed wavelength against scattering angle, are extremely sensitive to the dielectric properties of the media in the immediate vicinity of the gold surface. Shifts in the spectra thus indicate the accretion of materials on the gold surface.

Figure 1 shows how the SP spectra of  $\approx 50$  nm, clean and modified gold films on glass surfaces are affected on exposure to gold colloids. Trace 1 corresponds to clean gold.

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