nanowires were solid inside. A high-resolution transmission electron microscopy (HRTEM) image (Fig. 4) indicates that the nanowires form from the stacking of (001) sheets (see the inset) along the radial directions, which are not rolled as in the case of carbon nanotubes. It can be clearly seen that the growth direction (fiber direction) is along [120]. The photoluminescence (PL) spectrum (as shown in Fig. 5) of the GaN nanowires excited by 290 nm wavelength radiation reveals the blue-shift of bandgap emission compared with the 365 nm work is needed to clarify the underlying mechanism for the existence of defects or surface states. However, further refinement effect since a considerable fraction of the nanowires have diameters less than the Bohr exciton radius for GaN, 11 nm.[17] Another strong and broad peak, centered at 470 nm and with a number of small structures, might be ascribed to the existence of defects or surface states. However, further work is needed to clarify the underlying mechanism for the PL spectrum of the GaN nanowires.

This work demonstrates the feasibility of fabricating straight and smooth GaN nanowires using a nanoparticle catalyst and directed flow of carrier gas. The method is efficient and template-independent. Our preliminary experiments reveal that it will be straightforward to extend our method to fabricate nanowires of other nitrides and oxides.

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Novel Method for Solution Growth of Thin Silica Films from Tetraethoxysilane**

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Thin films of silicon dioxide find numerous applications in electronic and photonic technology. Several techniques have been developed to grow these layers, including sputter deposition, chemical vapor deposition, and thermal oxidation. An alternative technique that is inexpensive, and does not require vacuum or high temperature, uses the sol-gel process.[1] This method relies on a wet chemical reaction leading to the formation of a strong and broad band centered at 342 nm. The blue-shift of the bandgap emission compared with the 365 nm band of bulk GaN[14] might be ascribed to the quantum confinement effect since a considerable fraction of the nanowires have diameters less than the Bohr exciton radius for GaN, 11 nm.[17] Another strong and broad peak, centered at 470 nm and with a number of small structures, might be ascribed to the existence of defects or surface states. However, further work is needed to clarify the underlying mechanism for the PL spectrum of the GaN nanowires.

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formation of a gel that can, upon drying in a spin-coating process and subsequent sintering, transform into a relatively compact oxide. While the sol-gel technique is technically simple, it has an important disadvantage: it is not suitable for deposition on non-planar surfaces as it requires a spin-coating step of a precursor solution. In this communication we describe a different wet chemical method, based on the same precursors as in the sol-gel process but under conditions that lead to the controlled growth of silica in solution. Nanometer control over the layer thickness is possible. The technique does not require spin-coating and can thus be used to coat surface features with large aspect ratio. We also demonstrate that the grown layers can be doped by chemical incorporation with optically active groups, making this method ideally suited to coating photonic structures with optically active probe ions or molecules.

In the sol-gel process, tetraethoxysiline (TEOS) undergoes a hydrolysis and condensation reaction in which small colloidal particles are formed that are not stable and form a gel. In the present method we use a similar reaction, but now under base (ammonia) catalyzed conditions. In a mixture of TEOS, water, ethanol, and ammonia, stable and monodisperse spherical colloidal particles are formed in the bulk of the solution. While this reaction has been thoroughly studied in the past few years with the aim of controlling the growth of colloids, it has not been explored for the formation of thin films. Early on in the reaction small sub-particles are formed that are not yet colloidal stable. These sub-particles aggregate until a size is reached for which electric double layer interaction prevents further aggregation. Exactly when this happens depends on the surface potential and ionic strength, which are sensitive, complicated functions of the amount of water and ammonia and the concentration of dissociated silanol groups. After this nucleation-aggregation stage, surface-reaction-limited growth takes over and the irregularly shaped particles become smooth, spherical, and more monodisperse by a condensation reaction of reactive monomers and small oligomers. The final size of the particles depends on the number of particles that results after the aggregation process and is hard to control with great accuracy experimentally. Nanometer control is possible, though, if a seed suspension is used with well-characterized size and concentration. If the conditions are well chosen all monomers end up on the seeds and sensitive control of the resulting size is possible.

To investigate the thin film growth technique, a thermally oxidized (535 nm) silicon wafer was used as a model substrate. Experiments were also performed on silicon samples with a native oxide layer (∼2 nm) and no differences were found. Three 5 mm × 10 mm samples were simultaneously immersed in a solution containing 7.891 g ethanol, 0.805 g water, 0.693 g ammonia solution (29.1 wt.-%), and 0.376 g TEOS (a). After adding 0.375 g TEOS (b), and after adding another 0.375 g TEOS (c). The insets show typical SEM images of the colloids grown in solution.

Fig. 1. Thickness of the grown silica layer (vertical arrows) and histograms (bin size 5 nm) of the distribution of the radii of the colloids grown in an ethanol solution containing 7.891 g water, 0.805 g ammonia solution (29.1 wt.-%), and 0.376 g TEOS (a), after adding 0.375 g TEOS (b), and after adding another 0.375 g TEOS (c). The insets show typical SEM images of the colloids grown in solution.

was repeated once more. In Figure 1 the insets show typical scanning electron microscopy (SEM) images of the colloids that formed in the bulk and that were collected from the solution after each reaction step was finished. The SEM images were used to determine the colloid radius distribution. The SiO₂ layer thickness increase for the three samples was determined using ellipsometry. The results are indicated in Figure 1.

After the first growth step (Fig. 1a), the grown silica layer thickness was determined to be 65 nm and the mean colloid radius was found to be 122 nm. After the second growth step (Fig. 1b) the layer thickness and the mean radius increased to 95 nm and 156 nm, respectively; after the third step (Fig. 1c) they increased to 114 nm and 175 nm. In the second and third growth steps (where only TEOS was added) the increase in layer thickness was found to be the same as the increase in the mean radius of the colloids within ±4 nm. From this it can be concluded that the silica layer grows with the same surface-reaction-limited growth mechanism as the colloids do, because only in a surface-reaction-limited growth is the absolute increase in radius independent of the particle size. It can also be seen from Figures 1b and 1c that under these conditions after adding additional TEOS no new nucleation reaction took place because no new (small) particles were formed. This implies it is possible to obtain nanometer control over the layer thickness by immersing a substrate in a solution con-
ammonia concentrations of 1.0 M and 2.0 M, respectively. In the 1 M ammonia case the smallest layer thickness (70 nm) was found for a water concentration of 2.3 M. For higher water concentration (4–14 M) the layer thickness is roughly constant at ~100 nm. The colloid radius also shows an initial increase with water concentration and then a saturation for water concentrations above 6 M. For the 2.0 M ammonia solution, the silica layer thickness was ~120 nm for the lowest water concentration of 4.6 M and then shows a steady decrease with increasing water concentration. A similar trend is observed for the colloid radius as a function of water concentration.\textsuperscript{[4]} For both ammonia concentrations, the layer thickness and the colloid radius follow the same trend. The layer thickness is not a sensitive function of the water concentration, although, for one given set of concentrations, there is a variation of about 10% in the layer thickness, as can be seen from the apparent scatter of the data around the smooth lines.

Variation of the initial reaction conditions can thus afford some control over the silica layer thickness, but high accuracy is only possible with seeded growth.

The silicon to oxygen ratio in the grown films determined from Rutherford backscattering spectroscopy (RBS) measurements is 1.2. The density of the film, calculated using the film surface coverage obtained by RBS and the layer thickness determined by ellipsometry, is found to be 2.0 g/cm\textsuperscript{3}. This is lower than the value of 2.2 g/cm\textsuperscript{3} typical for thermally grown SiO\textsubscript{2}.\textsuperscript{[9]} This suggests that the films have a porous structure. Indeed, the refractive index of the films is found to lie in the range from 1.42 to 1.44 at 1000 nm, significantly lower than that of the thermal oxide ($n = 1.45$ at 1000 nm) and characteristic for a porous structure that is not fully condensed, similar to that found for the colloids grown in this way.\textsuperscript{[10,11]}

From the fits of ellipsometry data that are obtained with a spot size of a few millimeters we can conclude that the films have uniformity on a sub-wavelength length scale. Local roughness on a nanometer length scale can be estimated from SEM measurements and, within the resolution of the SEM (3–4 nm), the sample surface is found to be uniform as well.

Next, we will show how this novel method can be used to grow thin silica films on a predefined surface structure. Figure 3a shows a SEM image of an array of silicon pillars with diameters of 1.5 μm and heights of 2.2 μm, placed 6.5 μm apart. The “hat” on the top of the silicon pillars is a leftover from the silica mask used during the etching process. The etched structure was immersed in an ethanol solution containing 6.0 M water, 1.0 M ammonia, and 0.15 M TEOS. Figure 3b shows the same array of pillars after the reaction. As can be seen, the pillar diameter has clearly increased. The film thickness was determined to be 45 ± 10 nm. The layer thickness appears to be quite uniform over the full height of the pillars.

Finally, we show that the grown silica layer can be doped with a fluorescent dye. Eosin-5-isothiocyanate (eosin-ITC) was first coupled to (3-aminopropyl)-triethoxysilane (APS) and then added to the TEOS solution.\textsuperscript{[17,18]} Figure 3c shows an image obtained by fluorescence confocal microscopy of a cross section of an array of silicon pillars coated with a silica layer. From this image it can be seen that the full surface structure is covered with a fluorescent layer. The higher intensity on the tops of the pillars and on the substrate is because the pillars are not transparent in the visible. Therefore the sides are only partially imaged due to the high numerical aperture of the lens used in the confocal microscope, whereas the silica top is transparent. We have also performed preliminary experiments on doping these oxide films with erbium by ion implantation. Clear photoluminescence at 1.5 μm is observed with high quantum efficiency, indicating that these oxide layers are an excellent host for erbium as well.\textsuperscript{[12]}

In conclusion, we have developed a novel and simple method for solution growth of thin silica films using tetraethoxysilane (TEOS). The films are grown on macroscopic surfaces from TEOS in a mixture of ethanol, water, and ammonia. The silica growth is found to take place through a surface-reaction-limited process. The grown layer thickness is not a very
Two types of silicon samples (5 mm × 10 mm, single crystal (100)) one covered by a 535 nm SiO₂ film, which was grown by wet thermal oxidation, and one covered with a native oxide layer of ~2 nm, as well as silicon pillars fabricated using deep anisotropic etching of a Si(100) wafer with a SE₃/O₂ plasma [12] were used as substrates for silica deposition. Prior to deposition, the substrates were cleaned in a 2 M KOH ethanol solution for 15 min and rinsed with pure ethanol. The substrates were then placed in a closed bottle containing ethanol, water, and ammonia. As an example, the quantities used for the layer growth on the silicon pillars were 7.925 g ethanol, 0.805 g water, 0.697 g ammonia solution, and 0.376 g TEOS. For incorporation of a fluorescent dye in the silica layer [7,8], 12.52 mg eosin-ITC was first reacted with 41.8 mg APS in a solution containing 7.641 g ethanol, 0.809 g water, and 0.699 g ammonia. Finally, 0.380 g TEOS was added to the solution. All reactions took place at room temperature and under continuous stirring. In the growth experiments on the silicon wafers the water and ammonia concentrations were varied (Fig. 2). Concentrations were calculated assuming additivity of the individual volumes. The reaction time varied between 25 min and 12 h. After removing the samples from the solution the planar samples were wiped with lens paper and rinsed with ethanol to remove colloidal particles. Early and preliminary results of the method described in this paper were obtained by one of us in the deposition of thin layers of silica on phosphor particles and plant materials [14,15].

Rutherford backscattering spectroscopy (RBS) using 2 MeV He⁺ at a scattering angle of 165° was used to determine the relative silicon and oxygen composition and total surface density of silica of the grown layer. A variable-angle spectroscopic ellipsometer was used to determine the thickness and the refractive index of the films in the spectral range between 300 nm and 1700 nm. Scanning electron microscopy (SEM, Philips XL30FEG) with an acceleration voltage of 10 kV was used to determine the radius of the silica colloids that simultaneously grew in the solution. For this aim the solution containing the silica colloids was dried on a silicon substrate. SEM was also used to determine the thickness of the silica layer that grew on the silicon pillars. Fluorescence confocal microscopy (Leica TCS NT, 100 x lens with N.A. 1.4) at excitation wavelengths of 476 nm and 488 nm was used to image the eosin-ITC-coated silicon rods.

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