One-dimensional nanostructures such as nanowires, nanobelts, and nanotubes have attracted much attention as a result of their unique properties, which can be applied in the fabrication of biomedical sensors, optoelectronic devices, field-effect transistors, and field-emission devices, for example. In particular, one-dimensional nanostructures of metal oxides such as ZnO, SnO₂, α-Fe₂O₃, WO₃, and Ta₂O₅, so-called functional materials, have been widely studied. The synthesis of these functional metal oxide nanostructures are investigated widely through physical and chemical reactions, including vapor–liquid–solid (VLS), solution–liquid–solid (SLS), vapor–solid (VS), and other template-based approaches.

Ta₂O₅ is a fascinating functional material that has been used in applications such as dynamic random access memory (DRAM) devices, antireflection coating layers, gas sensors, photocatalysts, and capacitors owing to its high dielectric constant, high refractive index, chemical stability, and high-temperature piezoelectric properties. However, the synthesis of Ta₂O₅ nanostructures (e.g., nanowires or nanotubes) has had little success as a result of its high melting point. On the other hand, silica (SiO₂) nanowires are well developed for electronic and optoelectronic applications. Various methods of synthesizing SiO₂ nanowires include pulsed laser ablation, directed growth from a silica substrate or silica nanoparticles in a reductive atmosphere, direct growth from a Si substrate with catalyst, carbon-assisted and carbothermal reduction of silicon dioxide or metal oxides, and the sol–gel method. All of these approaches are direct, simple, and high-yielding, which are important factors for commercial applications.

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Herein, we present a technique for the fabrication of SiO₂/Ta₂O₅ core–shell nanotubes, Ta₂O₅ nanotubes, and Ta₂O₅ nanowires by using SiO₂ nanowires as template. The structures were prepared by annealing SiO₂ nanowires in an atmosphere of Ta at 950 °C at a pressure of 1×10⁻⁶ Torr. The diameter of the SiO₂ core in the SiO₂/Ta₂O₅ core–shell structure was readily controlled, and the silica template could be removed from the core–shell structures by using dilute HF solution to leave Ta₂O₅ nanotubes. Furthermore, Ta₂O₅ nanowires could be synthesized by increasing the reduction (annealing) time so that all of the SiO₂ in the core–shell structure was reduced by Ta vapors. The subsequent characterization of the core–shell structures as well as the Ta₂O₅ nanotubes and nanowires was carried out by cathodoluminescence (CL) and field-emission measurements.

The scanning electron microscopy (SEM) image of SiO₂ nanowires, prepared by annealing a 2-nm-thick layer of Au on a Si wafer under N₂ atmosphere at 1150 °C for 2 h, is shown in Figure 1a. The diameter of these SiO₂ nanowires is almost uniform, and the length is up to several hundred micrometers. The corresponding transmission electron microscopy (TEM) image indicates that most of the SiO₂ nanowires have a smooth morphology, with a diameter of 100–150 nm (Figure 1b). The diffraction pattern (upper inset in Figure 1b) displays a highly diffusive ring, indicating that the silica nanowires are amorphous. The atomic concentration of Si and O for these synthesized nanowires is about 34% and 66%, respectively, and a ratio of 1.2 Si/O was inferred from quantitative TEM/EDS (energy-dispersive spectrometry) measurements (lower inset in Figure 1b). After annealing the nanowires at 950 °C for 12 h and subjecting them to a reductive Ta atmosphere, the morphology of the resultant SiO₂/Ta₂O₅ structures was similar (Figure 1c). The corresponding magnified SEM image (upper inset in Figure 1c) clearly shows the wirelike features. The phase and structure of these nanowires was characterized by X-ray diffraction (XRD; Figure 1d) and revealed the Ta₂O₅ phase to have an orthorhombic structure (C2mm space group) and lattice constants of a = 0.618, b = 0.366, and c = 0.388 nm, respectively (ICSD-43498). Note that the TaSi₂ phase found in the XRD spectrum originates from a silicide reaction between the Si substrate and Ta vapors during the reduction procedure.

TEM analysis was essential to examine the detailed microstructures of these nanowires (Figure 1e). The different contrast between the inside and the outside of these nanowires provides significant evidence of a core–shell structure. The lower inset in Figure 1e shows the diffraction pattern and plane indices recorded from a SiO₂/Ta₂O₅ core–shell structure. The pattern is consistent with the results of XRD studies, indicating the polycrystalline characteristic of the SiO₂/Ta₂O₅ core–shell structure (see the Supporting Information). Diffusive white contrast was also observed confirming that SiO₂
nanowires were surrounded by a Ta$_2$O$_5$ shell. Note that SiO$_2$ or Si is incorporated inside the Ta$_2$O$_5$ shell during the reduction process, but the main phase remains that of Ta$_2$O$_5$ as determined by both the XRD and diffraction patterns (Figure 1d and e, respectively). TEM/EDS measurements of the shell of a SiO$_2$/Ta$_2$O$_5$ structure revealed that it consists of 20 % Ta, 71 % O, and 9 % Si. Upon examining in detail many SiO$_2$/Ta$_2$O$_5$ core–shell structures, the maximum concentration of Si in these Ta$_2$O$_5$ shells was found to be no more than 15 %.

The morphology of the core–shell structure was tunable, depending on the original shape of the SiO$_2$ nanowire. If the SiO$_2$ nanowire had a spiral morphology, the SiO$_2$/Ta$_2$O$_5$ core–shell structure formed after the reduction process also revealed a spiral morphology. An example of the spiral morphology of a SiO$_2$/Ta$_2$O$_5$ core–shell structure is highlighted in Figure 2a (see also the Supporting Information), while the corresponding TEM image is shown in Figure 2b. The phase was confirmed to be that of Ta$_2$O$_5$ by the diffraction pattern (see inset in Figure 2b). The thickness of the Ta$_2$O$_5$ layer outside the SiO$_2$ nanowires could be tuned by controlling the annealing (reduction) time (see Supporting Information). The thickness of the Ta$_2$O$_5$ shell increased as the reduction time was increased at a constant temperature of 950°C or simply if the temperature was increased.

How do the Ta atoms reduce the SiO$_2$ to form the SiO$_2$/Ta$_2$O$_5$ core–shell structure? Figure 2c shows the heat of formation ($-\Delta H_f$ [kcal atom$^{-1}$]) per oxygen atom for various transition-metal oxides and SiO$_2$.\footnote{Note that the heats of formation for transition-metal oxides such as HfO$_2$, TiO$_2$, and Ta$_2$O$_5$ are lower than that of SiO$_2$, which results in the reduction of SiO$_2$ at high annealing temperatures. On the other hand, the reduction of SiO$_2$ is prohibited if the heat of formation of transition-metal oxides such as MnO$_2$ is higher than that of SiO$_2$. Figure 2d shows plots of the thickness of the Ta$_2$O$_5$ shell of the SiO$_2$/Ta$_2$O$_5$ core–shell structure as a function of the reduction time at 950°C. The relationship between the thickness of the Ta$_2$O$_5$ shell and the reduction time is nonlinear, revealing that the reduction mechanism is under diffusion control, that is, $X^2 = DT$ ($X$, $D$, and $t$ denote the oxide thickness, parabolic reduction rate constant, and reduction time, respectively).\footnote{The reduction rate constant, $D$, was evaluated as about $2 \times 10^{-16}$ cm$^2$/s by plotting the thickness of the oxide shell as a function of the square root of the reduction time (see inset in Figure 2d). The thermal kinetic motion of Ta ions during the reduction process involves their diffusion through SiO$_2$ and reduction of the Ta$_2$O$_5$ layer. The diffusion-limited mechanism indicates that the diffusion through the Ta$_2$O$_5$ layer is rather slow, resulting in easier control over the reduction process. The measured rate constant represents the rate constant of diffusion. Also, the Si signal detected in EDS studies in various Ta$_2$O$_5$ shells indicates that the Si atoms from SiO$_2$ reduced by Ta vapors are involved in the Ta$_2$O$_5$ sublattice or excluded from the grain boundary.}

After dipping the core–shell structures in a diluted solution of HF to remove the SiO$_2$ inside the SiO$_2$/Ta$_2$O$_5$ core–shell structure, the morphology was unchanged. The inner SiO$_2$ nanowires could be removed to leave Ta$_2$O$_5$ nanotubes intact (see Figure 3a and Supporting Information). The residual TaSi$_2$ formed by the reduction procedure could be completely etched by HF solution. The XRD results for the nanotubes showed no peaks for TaSi$_2$ and indicate that the amorphous SiO$_2$ region was eliminated (see Supporting Information).\footnote{Ta$_2$O$_5$ nanowires could also be prepared by increasing the reduction time of the silica nanowires. For example, after annealing SiO$_2$ nanowires with a diameter of less than 60 nm in a reductive Ta atmosphere at 950°C for 32 h, then Ta$_2$O$_5$ nanowires with lengths of over several hundred micrometers were formed instead of the SiO$_2$/Ta$_2$O$_5$ core–shell structure (Figure 3b). The TEM image of a Ta$_2$O$_5$ nanowire with a diameter of 100 nm is shown in Figure 3c and indicates the polycrystalline feature of the structure. From the quantitative EDS measurements, it can be seen that the concentration of Si is about 3–14 %. Although
the concentration of Si inside the Ta$_2$O$_5$ nanowires is fairly high, the main phase remains that of Ta$_2$O$_5$, as confirmed by the diffraction pattern shown in the lower inset in Figure 3c. The morphology of the Ta$_2$O$_5$ nanowires could be modified according to the original morphology of the SiO$_2$ nanowire template (lower right inset of Figure 3b shows the spiral morphology of Ta$_2$O$_5$ nanowires). The magnified SEM image of the spiral morphology of the Ta$_2$O$_5$ nanowires as well as a magnification of this spiral structure are clearly seen in Figure 3d. The polycrystalline feature is suggested to arise as a result of two possible factors: 1) the segregation of Si during the reduction process through the grain boundary of Ta$_2$O$_5$ nanowires and 2) anisotropic reduction along the SiO$_2$ nanowires. Moreover, dislocations can be found inside the grain of Ta$_2$O$_5$ which may be caused by the location of Si atoms in the substitutional or interstitial sites in the sublattice of Ta$_2$O$_5$ (see Supporting Information).

Figure 4a shows the SEM image of a Ta$_2$O$_5$ nanotube after dipping it into a dilute solution of HF for 5 h. The CL spectra record from two areas of the sample labeled as A and B are shown in the insets of Figure 4a. Two peaks from the area labeled as A were detected, whereas no peak was found from the area B. The CL image under excitation at 15 kV was also measured (Figure 4b). Figure 4c shows the CL spectrum from the Ta$_2$O$_5$ nanotube sample (area A) after Gaussian fitting and reveals two clear peaks at 563 nm (2.2 eV) and 301 nm (4.1 eV), as well as a broad peak in the range of 2–5 eV. The band gap of Ta$_2$O$_5$ is about 4.1–4.2 eV, which results in some radiative recombination emission caused by oxygen deficiency.$^{[20]}$ The peak at 563 nm (2.2 eV) is attributed to the oxygen vacancies inside the Ta$_2$O$_5$ shell. The broad band at 2–5 eV may be derived from a combination of two peaks at 460 and 355 nm which originate from the residual SiO$_2$ inside the Ta$_2$O$_5$ nanotube or from the initial Si substrate. The peak at 301 nm (4.1 eV, violet region) in the CL spectrum originates from the d-band transition between the e$_g$ and t$_{2g}$ states, induced by
ligand-field splitting (see Supporting Information). A similar phenomenon is found in other materials, such as α-Fe$_2$O$_3$ nanoparticles. The violet peak derived from the oxygen deficiency transition inside the Ta$_2$O$_5$ is also the factor for the CL peak at 301 nm. Violet light is of interest in fundamental research and for applications in full-color displays. Here, by controlling the thickness of the SiO$_2$ core of the SiO$_2$/Ta$_2$O$_5$ core–shell structure, which in turn defines the CL wavelength, the nanotubes may be used in optical transportation phenomena, such as light propagation.

The current density as a function of the applied electric field for the Ta$_2$O$_5$ nanotube sample at a fixed distance of 100 μm between the anode and the surface of the nanotube is shown in Figure 4d. Two parameters, the turn-on field and the threshold field, are defined as the applied voltage (E) needed to produce a current density of 0.01 and 10 mA cm$^{-2}$, respectively, for which respective values of 8 and 13 V μm$^{-1}$ were determined. The inset in Figure 4d shows a plot of ln(i/ $E^2$) versus 1/E. The linear relationship is consistent with the so-called Fowler–Nordheim plot ( Figure 4d) and indicates that the field-emission behavior obeys the F–N rule, that is, electrons tunnel through the potential barrier from the conduction band to the vacuum state. Although these values are somewhat higher than for other oxide materials, such as ZnO, SnO$_2$, and W$_18$O$_49$, the core–shell structures here still show great promise in display applications owing to their straightforward and high-yielding production and the ease with which they can be integrated in silicon-based industries.

In summary, SiO$_2$/Ta$_2$O$_5$ core–shell structures were synthesized by annealing SiO$_2$ nanowires under a reductive atmosphere of Ta at 950°C. The morphology of the nanowires was tunable depending on the morphology of the original SiO$_2$ nanowires, and the diameter of the SiO$_2$ nanowire inside the SiO$_2$/Ta$_2$O$_5$ core–shell structure could also be modified. Furthermore, Ta$_2$O$_5$ nanotubes could be prepared by removal of the template from the core–shell structures and Ta$_2$O$_5$ nanowires could be prepared directly by increasing the reduction time. The electrical and optical properties reported herein indicate that the SiO$_2$/Ta$_2$O$_5$ core–shell structures, Ta$_2$O$_5$ nanotubes, and Ta$_2$O$_5$ nanowires may have many interesting applications in nanotechnology.

**Experimental Section**

Single-crystal Si(001) wafers (resistivity: 1–30 Ω cm) were cleaned using standard cleaning procedures and then dipped in diluted HF solution (1:50 HF/H$_2$O) for 30 s before being loaded into the deposition system (P > 5 × 10$^{-6}$ Torr). A 2-nm-thick layer of Au was deposited on the Si substrate at a pressure of 5 × 10$^{-7}$ Torr with a deposition rate of 0.01 nm s$^{-1}$. Subsequently, as-deposited samples were annealed in a horizontal furnace at 1150°C for 2 h under an atmosphere of N$_2$ to grow the SiO$_2$ nanowires. The high-density SiO$_2$ nanowire samples were transferred into a Ta-filament heating chamber for annealing (P > 1 × 10$^{-6}$ Torr) at 950°C for 12–32 h to produce SiO$_2$/Ta$_2$O$_5$ core–shell nanowire structures. Ta atoms were constantly vaporized from the supplementary source in this chamber (see Supporting Information). Ta$_2$O$_5$ nanotubes could be formed by dipping the core–shell structures into dilute HF solution (1:50 HF/H$_2$O) to remove the inner SiO$_2$ nanowires.

Grazing incidence X-ray diffractometry (GIXRD) with a fixed incident angle at 0.5° was carried out to identify the phases of the nanostructures. The surface morphology was examined by a field-emission scanning electron microscope (JSM-6500F) operated at 15 kV. To prepare the TEM specimen, all samples were sonicated in ethanol and then dispersed on a copper grid supported by a holey carbon film. A field-emission transmission electron microscope (JEM-3000F) operated at 300 kV, with a point-to-point resolution of 0.17 nm and equipped with an energy-dispersion spectrometer, an electron energy loss spectrometer, as well as a high-angle annular dark field detector, was used to characterize the microstructures and chemical compositions. Electron field-emission behavior was measured in a vacuum of 1 × 10$^{-7}$ Torr by using a spherical stainless-steel probe (1-mm diameter) as the anode. The lowest emission current was recorded on the level of nA. The measurement distance between the anode and the emitting surface was fixed at 100 μm. The CL spectrum was measured in the scanning electron microscope with an electron probe microanalyzer (Shimadzu EPMA-1500). CL spectra were accumulated in single-shot mode within a short time of 1 s. In general, the CL excitation was performed with a beam current of about 100 nA in television scanning mode of 2.9 × 10$^{-5}$ cm$^2$.

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[17] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+ 49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informations-dienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number ICSD-43498.


