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Titanium-assisted growth of silica nanowires: from surface-matched to free-standing morphologies

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Abstract

We report on an oxide-assisted growth technique for silica nanowires which allows tuning the growth from surface-matched nanowires to free-standing morphologies based on growth control by Ti in the role of a catalyst and surfactant. Using an adjustable Ti concentration, we grew silica nanowires with lengths ranging from 100 nm up to several millimetres whose defect chemistry was analysed by electron microscopy tools, monochromatic cathodoluminescence imaging and time resolved photoluminescence spectroscopy. The knowledge of the luminescence properties and the related defect occurrence along with their spatial distribution is pivotal for advancing silica nanowire growth in order to realize successful device designs based on self-assembled Si/SiO\(_x\) nanostructures. We demonstrate a core–shell structure of the grown nanowires with a highly luminescent 150 nm thick shell and outstandingly fast decaying dynamics (\(\approx 1\) ns) for glass-like materials. The conjunction of the observed efficient and stable luminescences with their attributed decaying behaviours suggests applications for silica nanowires such as active and passive optical interconnectors and white light phosphors. The identification of a time domain difference for the spectral regime from 2.3 to 3.3 eV, within the confined spatial dimensions of a single nanowire, is very promising for future, e.g. data transmission applications, employing silica nanowires which exhibit achievable compatibility with commonly applied silicon-based electronics. A qualitative growth model based on silica particle diffusion and Ti-assisted seed formation is developed for the various types of segregated silica nanowires which extends commonly assumed oxide-assisted growth mechanisms.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional SiO\(_x\) nanostructures have gained considerable recent interest due to their high yield growth [1], their achievable compatibility with Si-based electronics, their mechanical stiffness [2, 3], their optical waveguide properties [4] and their various defect luminescence centres which emit light over the full visible range [1, 5]. Commonly applied growth methods for Si and SiO\(_x\) nanowires (NWs) are based on vapour–liquid–solid (VLS) [1, 6, 7], vapour–solid–solid (VSS) and oxide-assisted growth mechanisms [9–11] which are capable of producing a large variety of nanostructured morphologies. The physical properties of the resulting nanostructures strongly depend on size, shape and defect incorporation, constituting the need for a growth technique which enables tunable control of these vital parameters. While size and shape can be straightforwardly analyzed by routine microscopy tools, the analysis of the defect incorporation in nanostructures is comparatively challenging. Therefore, a deep understanding of the steady state optical properties of SiO\(_x\),
NWs and the corresponding decay dynamics, which are both strongly altered by the defect incorporation, is pivotal for advancing SiO₂ NW growth methods and fundamental luminescence studies. Only the conjunction of these still pending advances will finally realize successful device designs based on nanostructured and self-assembled Si/SiO₂ morphologies.

In contrast to the outlined growth requirements, it appears that the understanding of the influence of growth conditions and, for example, catalyst selection on size, shape and defect incorporation control has not been systematically studied for SiO₂ NWs. For the case of Si NWs size, shape and positioning control was achieved up to a level where the nanowires grew well aligned in selected areas [8, 12, 13] which suggests potential applications as electrical interconnectors [14, 15] between conventional circuits based on self-assembled NW growth. In contrast to that, SiO₂ NWs could function, for example, as an optical interconnector which requires size, shape, positioning and defect incorporation control with a so far not reached feasibility. Therefore, due to the required transparency or luminescence for passive or active optical applications, the analysis of defects by evaluating the optical properties of SiO₂ NWs plays an outstanding role. The defect sensitive optical properties of bulk SiO₂ and the related decay dynamics have been studied [16–20] but similar detailed investigations for the case of SiO₂ NWs have not been reported which constitutes the strong motivation for the present work.

In this paper we report a facile and scalable growth technique for SiO₂ NWs which is based on growth kinetics control and seed formation by Ti in the role of a catalyst and surfactant. Employment of an adjustable concentration of Ti allows continuous tuning of the growth results from free-standing and comparatively long (2 mm) SiO₂ NWs (type 1) to the formation of round NW type 2 seeding defects which were investigated by photoluminescence (PL) and cathodoluminescence (CL) spectroscopy. Using the high spatial resolution capabilities of the CL technique, we demonstrate a core–shell structure in the defect distribution of the type 2 SiO₂ NWs. Furthermore, we show that the defect luminescence decay of the type 2 NWs exhibits a comparatively slow monoexponential decay component [18] (τ₁ ≈ 0.2 μs), originating from the NWs’ cores, and also a significantly faster component (τ₂ ≈ 1 ns) with a stretched exponential decay character [5] that arises from the about 150 nm thick NWs’ shells. This time domain difference of over two orders of magnitude for the spectral regime from 2.3 to 3.3 eV, within the confined spatial dimensions of a single NW, is very promising for future, e.g. data transmission applications. Finally, qualitative growth models for the two grown NW types are described based on a deductive combination of the microscopic and spectroscopic results with special consideration given to the observed defect luminescences.

2. Results and discussion

Figure 1 presents an exemplary selection of SEM images which show the full variety of grown SiO₂ NWs. Image A and its inset I show the perpendicularly aligned type 1 NWs, while image D illustrates the opposite case of free-standing NWs of type 2. During the growth process the present Ti concentration rises from image A to D due to a decreasing distance from the Si substrate to the mesoscopic Ti powder source (d = 10–0.1 cm). Therefore, image B and C and their respective insets show intermediate growth stages between the NWs of type 1 and 2, which represent the growth results for medium Ti concentrations.

The diameter of the surface-matched grown type 1 NWs is 200 ± 50 nm with lengths of up to 1 μm. Conversely, the free-standing type 2 NWs are larger with diameters of about 500 ± 200 nm and average lengths of 2 mm. With the applied growth method homogeneous type 1 and 2 NW segregation can be achieved on surface areas as large as 5 mm × 5 mm. The surface-matched growth of the NWs on the Si-[100]-surface in image A of figure 1 (d = 10 cm) follows the perpendicularly aligned edges on such Si substrate occurring terraces [21], as illustrated in figure 2. These terraces are a common structural feature on commercially available Si substrates and can be measured by, for example, STM analyses. Supersaturation of Si, stemming from the Si substrate (figure 2), leads to the NW formation via an oxide-assisted growth mechanism [9] which originates from oxygen introduced during the growth process. No NW formation is observed without the presence of Ti. This result strongly suggests that Ti acts as a solute which lowers the melting point of the present eutectic Ti–Si–O alloy [22] and supports the structuring process as a surfactant at 1100 °C by altering the surface kinetics. Furthermore, the type 1 NW’s diameter is continuously extended by a radial growth component, as shown in figure 2 which is perpendicularly orientated in relation to the Si substrate terrace edge and hence individual NW elongations.

Reduction of the distance to the Ti source to d = 8 cm yields the growth of NWs with a length of several tenths of a micrometre as depicted in image B of figure 1. These longer NWs, as also shown in insets I and II of image B, seem to be formed by a self-assembling growth process gathering the required Si–O species from the type I NWs which leads to the observed uneven NW surface and the occurring non-surface-matched growth. Further reduction of the distance to the Ti source to d = 3 cm leads to longer surface-matched type I NWs but also to the formation of round NW type 2 seeding centres with a diameter of approximately 10 μm, as shown in image C and its inset I. These seeding centres for the NW type 2 growth are the origin of the morphology of the free-standing NWs of type 2 and NW bunches in image D which were grown at a distance to the Ti source of d = 0.1 cm. The inset of image D in figure 1 illustrates the grainy seed layer at the base of the type 2 NWs which contains major amounts of Si and Ti with trace amounts of oxygen as measured by energy dispersive x-ray spectroscopy (EDS). No trace impurities of Ti can be detected by EDS analysis in the SiO₂ → SiO₂ NWs of type 2 as it is also the case for the type 1 NWs. This suggests the qualitative growth model illustrated in figure 2 for the type 2 SiO₂ NWs which is based on vertical Si/Si–O particle diffusion from the Si substrate through the deposited Ti–Si–O seed layer. The variations of the Ti concentration over the seed
layer due to particle formation as measurable by SEM/EDS correlate with variations of the diffusion rate of Si through the Ti–Si–O layer [22] which possibly acts as a nucleation centre for the type 2 NWs. Si diffusing through the seed layer forms approximately $1.0 \pm 0.5 \mu m$ sized SiO$_x$ particles, as shown in the inset of image D (figure 1). These particles combine throughout the growth process, as shown in figure 2, and form the ‘curly’ appearing type 2 SiO$_2$ NWs which yield the observed NW diameter fluctuation. Lee et al observed the formation of Si/SiO$_x$ NWs based on similar nucleation and growth mechanisms [10]. However, the structural analysis by XRD and Raman measurements has demonstrated a purely amorphous structure for the type 2 SiO$_2$ NWs in which no Si crystallites were found due to the deliberate application of oxygen during the growth process. Furthermore, the variation of the distance of the Si substrate to the Ti source leads to a regulated competition between the formation of Si–O- and Ti–O-species which additionally governs the formation of the two different types of observed SiO$_2$ NWs. Similar experiments with other catalysts (Au, TiO$_2$) were not successful, even though effectively applied for Si NW growth [23]. Only the utilization of the mesoscopic Ti powder led to the presented type 1 and 2 NW formation at $1100^\circ C$ on the same Si substrate.

2.1. Cathodoluminescence signal of the nanostructures

The different morphologies of the type 1 and 2 NWs are also reflected by their different optical properties. Figure 3 shows the recorded CL spectra of the seed layer of the type 2 NWs, of multiple type 2 NWs and a single NW of type 1 and 2.

Figure 1. (A) Type 1 nanowires ($d = 10 \text{ cm}$, distance to the Ti source), (B) surface-matched type 1 nanowires and self-organized growth ($d = 8 \text{ cm}$), (C) surface-matched growth along with type 2 nanowire seeding centres ($d = 3 \text{ cm}$), (D) type 2 nanowires ($d = 0.1 \text{ cm}$). The coordinate system indicates the Si- [100]-surface orientation.

Figure 2. Si–O and Ti–O particles form the Ti–Si–O alloy which facilitates the illustrated nanowire (NW) growth of type 1 and 2. The type 1 NWs are aligned along terrace edges on Si substrates and their diameter is continuously extended via a radial growth component. Type 2 NW growth occurs at higher Ti concentrations and is seeded by Ti fluctuations in the grainy Ti–Si–O alloy seed layer. The high yield growth of the type 2 NWs based on Si–O particle diffusion from the Si substrate causes the depicted rough Si substrate surface. Si–O particles from the gas phase smooth the surfaces of the NWs.

Within the recorded series of CL spectra we observe five main optical transitions at 1.89, 2.46, 2.66, 2.88 and 3.15 eV which all result from the type 1 and 2 NWs. The Si substrate does not show any detectable luminescence in the displayed wavelength range. The optical transition at 1.89 eV has been observed in amorphous bulk SiO$_2$ samples by CL [24], PL [25] and x-ray [19] spectroscopy and is generally attributed to non-bridging oxygen hole centres and related surface defects. This defect structure seems to be most prominent in the seed layer of the type 2 NWs, as shown in the inset of image D from figure 1,
Figure 3. Cathodoluminescence spectra of the type 1 and 2 SiO$_2$ NWs and the corresponding seed layer measured at 300 K. The spectra were vertically shifted for clarity.

significantly weaker in intensity on the grown SiO$_2$ type 2 NW bunches and even diminishing in intensity on selected single type 2 NWs as demonstrated in figure 3. The most prominent CL feature of the grown type 2 NWs is observed at 2.46 eV close to a band at 2.66 eV which can exclusively be found in the corresponding seed layer (figure 3). Therefore, the growth process in the seed layer creates the 2.66 eV transition-attributed intrinsic defect centres which are suggested to be E’ centres [26], SiO$_2$ triplet $\rightarrow$ singlet transitions [27] and/or self-trapped excitons (STEs) [28]. However, the SiO$_2$ type 2 NWs seem to favour the formation of defect centres that produce a prominent 2.46 eV band. The precise origin of this defect luminescence is still a matter of active debate; however, for example, an extrinsic defect centre has been suggested for an emission band at 2.5 eV [17, 24, 29]. In contrast to the type 2 NWs, the CL spectrum of a single type 1 NW does not show well distinguished spectral features but a rather broad emission band from 1.7 to 3.4 eV which might originate from the built-in strain present in these nanostructures. More distinct spectral features of the type 1 NW are observed at 2.88 and 3.15 eV with STEs [30] and O$_2^-$ molecular ions [31] as most relevant candidates for their origin.

Further information on the presence of various defects as well as their spatial distribution, can be gained by monochromatic CL imaging. Figure 4 presents monochromatic (2.46 and 2.66 eV) CL images of the SiO$_2$ type 2 (image A) and type 1 NWs (image B) which show a core–shell structure for the type 2 NWs, and a more homogeneous intensity distribution for the surface-matched grown type 1 NWs.

The strongest defect luminescence of the type 2 NWs at 2.46 eV originates from their sidewalls and the thickness of this defect-rich region can be estimated to 150 $\pm$ 20 nm, as shown in the inset of figure 4. The observation of a core–shell structure in the type 2 SiO$_2$ NWs allows the extension of the described growth model which is illustrated in figure 2. The Si supply involved in the growth process does not exclusively take place via a diffusion of Si through the seed layer and immediate incorporation into the NW via SiO$_2$ particles as suggested based on figure 1 (image D, inset I). The existence of supplemental Si–O and/or Si–Ti species from the gas phase seems to continuously extend and smooth the NWs’ diameters throughout the growth process which is the origin of the observed core–shell structure and explains the diameter fluctuation for the type 2 NWs as depicted in figure 2.

2.2. Photoluminescence contrast in the time domain

The combined results of PL and time resolved PL (TRPL) measurements on the type 2 SiO$_2$ NWs are summarized in figure 5 yielding detailed defect and growth related information in perfect accordance with the CL observations from figure 4 which revealed the core–shell structure and the ‘curly’ NW morphology. Unfortunately, insufficient PL signal was detected from the type 1 NWs for a similar detailed analysis.

The observed PL signal from the type 2 SiO$_2$ NWs is centred at 2.60 eV and does not exhibit any clearly resolved spectral features. The opposing continuous evolution of the measured lifetimes $\tau_1$ (monoexponential) and $\tau_2$ (stretched exponential, see inset of figure 5) as a function of emission energy suggests two different defect centres with overlapping PL signal as possible luminescence decay origins. While the lifetime $\tau_2$ and associated stretching factor $\beta$ are constant within the errors as a function of the energy, it can be
seen in figure 5 that the lifetime $\tau_1$ rises with the emission energy. STEs as possible luminescence origins [32] can be excluded due to the applied laser excitation energy of 4.66 eV which, in contrast to the CL measurements from figure 3, is well below the bandgap of SiO$_2$. Glinka et al [32, 33] observed a PL feature at 2.37 eV with similar spectral width in mesoporous silica and SiO$_2$ particles and attribute its origin to non-bridging oxygen hole centres and hydrogen related surface species. In bulk silica glasses, sintered from nanometre-sized silica particles, Uchino et al [5] observed a PL band at 2.43 eV with, in comparison to figure 5, even spectral width and luminescence stability but an exclusively stretched decaying behaviour. However, for the case of the type 2 SiO$_2$ NWs the PL decay dynamics cannot sufficiently be described by a stretched exponential decay [5, 34]; a monoeXponential contribution is apparent in the decay, as shown in the inset of figure 5. Such unusual monoeXponential decay behaviours for glasses were reported by Stathis et al [18] and Skuja et al [27] to be centred in SiO$_2$ at 2.7 and 2.65 eV, with decay times up to the ms-range and triplet $\rightarrow$ singlet transitions in Si related defect centres as the origin. However, the reported lifetimes [18, 27] stand in contrast to the observed monoeXponential decay for the NWs of type 2 which exhibit time constants of $\tau_1 \approx 0.2 \mu s$. This observation can tentatively be attributed to an increased defect concentration in the type 2 SiO$_2$ NWs in comparison to bulk samples, e.g. due to an enhanced surface to volume ratio. The comparison of the highly spatially resolved monochromatic CL image in figure 4 with the corresponding decay behaviour in the inset of figure 5 reveals a similar interval for the intensity dynamics of the luminescences. In the cross section scan over the core–shell structure of the NW (inset of figure 4) a luminescence contrast of about 1.5 orders of magnitude is observed which matches the contrast between the two PL components in the transient recorded at 2.60 eV, as shown in the inset of figure 5. Therefore, it can tentatively be concluded that the slower stretched exponential decay component $\tau_2$ arises from the NWs’ defect-rich and hence strongly luminescent surfaces. Additionally, the stretched exponential decay component $\tau_2$ is correlated with a stretching factor of $\beta \approx 0.48$ indicating a broad distribution of actual contributing lifetimes which possibly arises from thickness variation (approximately $\pm 50$ nm) in the defect-rich NW surface layer. Therefore, the core of the type 2 SiO$_2$ NWs which consists of SiO$_2$ particles, as observed by CL imaging, could be a prime candidate for the measured monoexponential decay with the lifetime $\tau_1$. Compared to the bulk SiO$_2$ case a drastically smaller monoexponential decay lifetime $\tau_1$ is observed which can conclusively be explained by the adjacent defect-rich interface to the NWs’ surface layer. Hence, the energy dependency of $\tau_1$ could arise from the various occurring and the NW establishing SiO$_2$ particle sizes ($1.0 \pm 0.5 \mu m$) which comprise different strain states of the material and in turn alter the transition energy and decaying behaviour. Within this framework the type 2 NWs can be understood as a luminescent chain of SiO$_2$ particles with slow decaying behaviour, whose outer edge is coated by a rather defect-rich SiO$_2$ layer with over two orders of magnitude faster decay dynamics, as indicated by consolidation of TRPL and monochromatic CL imaging.

3. Conclusions

We present Ti catalysed scalable growth of two types of SiO$_2$ NWs on a Si substrate. SEM and CL imaging results suggest the presented qualitative growths models for the NWs which are additionally supported by the applied spectroscopic techniques (CL, PL, TRPL, EDS). A core–shell structure for the spatial distribution of the 2.46 eV defect luminescence of the type 2 SiO$_2$ NWs was observed by monochromatic CL imaging which supported the observed NW morphology and growth mechanism. Consequently, the combination of TRPL and CL measurements allowed the identification of a defect-rich and strongly luminescent surface layer of the type 2 SiO$_2$ NWs with a stretched exponential decaying behaviour ($\tau_2 \approx 1$ ns) and a thickness of 150 $\pm$ 20 nm. The observed increase of the luminescence lifetime $\tau_1 \approx 75$–250 ns of the cores of the type 2 NWs with increasing emission energy substantiated the incorporation of SiO$_2$ particles with varying diameters (1.0 $\pm$ 0.5 $\mu m$) and supported the suggested oxide-assisted growth model [9]. Additionally, the observation of the surface-matched grown SiO$_2$ type 1 NWs, along with the measured intense and stable defect luminescences from both NW types, can potentially enable a number of exciting technological applications, for example Si-based white light phosphors [5]. The contrast in the decay times of the luminescence of over two orders of magnitude over the spectral interval from 2.3 to 3.3 eV, emitted from the confined spatial dimensions of a core–shell structured single NW, is useful for applications where such a time domain selection is of importance. The fast optical response of the shell of the type 2 SiO$_2$ NWs makes it a possibly promising candidate for the transmission of highly modulated signals whereas the core of the type 2 SiO$_2$ NWs with its slower optical response suggests its simultaneous and independent usage as a channel for light guiding purposes. The simplicity of the Ti catalysed SiO$_2$ NW growth, the wide range of realizable structures from surface-matched grown NWs to
free-standing NWs with an average length of 2 mm, the strong and stable luminescence in the visible regime and the related contrast in the luminescence decay dynamics make SiO$_2$ NW an outstanding candidate for future active and passive optoelectronic interconnecting applications.

4. Experimental details

The growth of the SiO$_2$ NWs was conducted in a home-built CVD reactor on Si-[100]-substrates. The growth temperature was ramped from room temperature to 1100°C within 30 min and was then held constant for 3 h. The cooling down of the CVD reactor was realized within a time frame of 6 h. After loading the CVD reactor it was evacuated to 1 mbar and was then held constant for 3 h. The cooling down of the CVD reactor was realized within a time frame of 6 h. After loading the CVD reactor it was evacuated to 1 mbar and was then held constant for 3 h. The cooling down of the CVD reactor was realized within a time frame of 6 h. After

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