Catalyzed oxidation for nanowire growth

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Abstract

A simple, low-cost and scalable route to substrate-supported nanowire growth is reported based on catalyzed oxidation. The process shares common features with popular catalyzed nanowire growth techniques such as vapor–liquid–solid (VLS), vapor–solid–solid (VSS), or vapor–quasi-solid (VQS) that use catalyst nanoparticles to direct the deposition of reactants from the vapor phase. Catalyzed oxidation for nanowire growth (CONG) utilizes catalyzed anion (e.g. O$_2$) reduction from the vapor phase and metal (e.g. Fe) oxidation from the substrate to produce oxide nanowires (e.g. Fe$_3$O$_4$). The approach represents a new class of nanowire growth methodology that may be applied to a broad range of systems. CONG does not require expensive chemical vapor deposition or physical vapor deposition equipment and can be implemented at intermediate temperatures (400–600 °C) in a standard laboratory furnace. This work also demonstrates a passive approach to catalyst deposition that allows the process to be implemented simply with no lithography or physical vapor deposition steps. This effort validates the general approach by synthesizing MnO, Fe$_3$O$_4$, WO$_3$, MgO, TiO$_2$, ZnO, ReO$_3$, and NiO nanowires via CONG. The process produces single crystalline nanowires that can be grown to high aspect ratio and as high-density nanowire forests. Applications of the as-grown Fe$_3$O$_4$ and ReO$_3$ nanowires for lithium ion battery systems are demonstrated to display high areal energy density and power.

Keywords: oxide nanowire growth, catalyzed oxidation, interface reaction, diffusion, lithium ion battery

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(Some figures may appear in colour only in the online journal)

1. Introduction

Oxide nanowires possess great promise in applications ranging from energy harvesting and storage to drug delivery and therapy [1, 2]. These structures may be synthesized through a variety of techniques including solution growth, evaporation–condensation, direct oxidation, templating, lithography, controlled etching, plasma-induced growth, electrochemical growth, or catalyzed physical vapor deposition (PVD) and chemical vapor deposition (CVD) [3]. Nanowire forms of most technologically relevant materials exist as demonstrations within the literature [4]. The low-cost and abundant nature of their precursors make oxide nanowires particularly attractive for applications such as energy harvesting and storage, where large quantities will be required to make societal impact. While a large number of nanowire synthesis processes exist, only a few purport low cost and scalability. Example processes that achieve both, such as certain oxidation, electrochemical, or wet chemical processes, are not generally applicable to a broad range of chemistries. Additionally, some of these processes are not well suited to synthesizing substrate-supported nanowires that are electrically contacted. One of the simplest processes for nanowire growth uses direct oxidation of metals and alloys [5, 6]. While the mechanism is still debated, rapid cations diffusion out of grain boundaries can promote nanowire growth in systems such as Cu and Fe. The major drawback to
this approach is that the thickness of underlying oxide layer greatly exceeds the length of the nanowires since both growth processes are governed by diffusional kinetics. The growth of nanowires by direct thermal oxidation is also difficult to pattern and control.

This work develops a simple scalable approach to substrate-supported nanowire synthesis based on catalyzed oxidation for nanowire growth (CONG). The process is broadly applicable in systems that oxidize under conditions where the reduced and oxidized forms are both solid at the processing temperature. CONG benefits from its ability to grow oxide nanowires on metal substrates at relatively low temperatures in standard furnaces. Like direct oxidation, CONG relies on the fact that cation diffusion outpaces anion diffusion in most oxides. However, when oxidation occurs under conditions of interface reaction rate limited kinetics, oxygen-reducing catalysts can localize the reaction and drive nanowire growth [7, 8] while suppressing rapid growth of the underlying oxide scale. This allows the nanowires to maintain good physical and electrical contact to the underlying substrate and enables improved control of the overall structure. For example, the process could be coupled with lithography to pattern the nanowire growth, which is difficult to realize by the conventional thermal oxidation approach [9]. The schematic representation of the CONG growth mechanism where a metal catalyzes the oxygen reduction reaction, rapid cation diffusion occurs through the oxide scale and along the nanowire, is presented in figure 1. Rapid oxygen exchange at the catalyst nanoparticle localizes the reaction in a manner that promotes nanowire growth. This concept shares kinetic underpinnings with the vapor–liquid–solid, vapor–solid–solid, and vapor–quasi-solid nanowire growth processes that have been applied to reduced elements and oxides. However, the large driving force for oxidation allows the process to be active at relatively low temperatures, and eliminates the need for expensive CVD precursors or costly PVD equipment.

2. Experimental details

2.1. Preparation of nanowire

Pure metal substrates (Zn 99.999%, Fe 99.95%, W 99.995%, Mg 99.99%, Ti 99.95%, Mn 99.995%, Re 99.95%, Ni 99.99%) were pre-oxidized at ambient conditions on a hot plate with surface temperature at 250 °C for 30 min. The intent of this step was to form a thin continuous oxide on the surfaces of the metals. No nanowires formed during this processing step. The pre-oxidized metals were placed in an alumina crucible covered by Cu foil (MTI Company, >99.99%), and loaded in quartz tube furnace (MTI Company). One Fe and Ti sample processed with Bi was placed above Bi in an enclosed alumina crucible. A rough vacuum (∼2 Pa) was obtained before backfilling with high-purity Ar gas. Ar gas flowed (∼12 sccm) through toluene prior to entering the furnace. Samples were heated at 10 °C min⁻¹ to a hold temperature between 400 and 600 °C (400 °C for Zn, 500 °C for Mg, 550 °C for Mn, and 600 °C for W, Re, Ti, Ni, and Cr). The lower temperatures used for Mg and Zn reflects their low melting temperatures. The Ti and Mg samples were annealed for 3 h and all other samples were annealed for 5 h. An oxygen sensor (MBRAUN, MB OX-SE-1) indicated a concentration of ∼100 ppm at the outlet of the furnace.
2.2. Patterned nanowire growth

Cu thin films ∼3 nm were deposited on polished Fe substrates pre-oxidized on a hot plate at 250 °C for 30 min. The samples were oxidized in Ar-4%H₂ at 600 °C for 5 h.

2.3. Characterization

The as-synthesized nanowires were characterized by scanning electron microscopy (JEOL-6060LV SEM), and transmission electron microscopy (JEOL-2010LaB₆, JOEL-2010F TEM). Element analysis was performed using energy dispersive spectroscopy (EDS) in the TEM.

3. Results and discussion

Interface reaction rate limited kinetics occurs in cases of thin oxide layers and low oxygen partial pressure. When the reaction is interface reaction rate limited by the oxygen reduction reaction, catalysts may be used to accelerate the reaction locally leading to nanowire growth below the catalyst. Thin oxide scales develop during a pre-oxidation step on a hot plate in air at ∼250 °C. Oxidation proceeds in a tube furnace through which Ar gas flows during growth. To further reduce the oxygen partial pressure (∼100 ppm), the gas flows through toluene prior to entering the furnace. A passive approach to catalyst deposition applied here dramatically simplifies the processing scheme. The substrate on which the nanowires grow sits adjacent to pure Cu metal foil in the furnace. Oxidation of Cu produces a volatile oxide (ideally CuO at 100 ppm O₂) that transports through the gas phase and reduces to form stable metallic nanoparticles when it contacts a less noble metal (see figure S1 available at stacks.iop.org/Nano/25/145603/mmedia). Cu efficiently catalyzes oxygen reduction and will catalyze nanowire growth when present on an oxide of a less noble metal under conditions of interface reaction rate limited kinetics [10]. Nanowires are grown by CONG in the current work in the temperature range of 400–600 °C. The partial pressure of CuO in this range is estimated to be ∼10⁻⁷–10⁻⁵ Pa. The vapor pressure of Cu at 600 °C is ∼10⁻⁹ Pa. This passive approach to catalyst deposition is quite effective in producing high densities of nanowires under appropriate conditions. To further prove the flexibility and efficacy of CONG, a similar process was also applied to promote deposition of Bi catalyst nanoparticles, whose oxide formation energy is lower than that of copper oxide, but higher than that of other metal oxides (e.g. Fe, Ti et al). Here we use the Ellingham diagram (see figure S1 available at stacks.iop.org/Nano/25/145603/mmedia) as a simple guide for catalyst selection. The catalyst should be more noble than the base metal forming the oxide nanowire, as it should accelerate oxygen reduction, but also donate the reduced anions towards oxidation of the base metal.

Figure 2 demonstrates nanowire growth on Fe, Mg, Mn, W, Zn, Ti, and Re pre-oxidized metal substrates between 400 and 600 °C. Cu nanoparticles cap the nanowires in all systems observed except ZnO (see figure 3). Lower temperatures were used for Zn and Mg due to their relatively low melting points. Based on the high-resolution TEM (see figure 4) and electron diffraction (see figure S2 available at stacks.iop.org/Nano/25/145603/mmedia) the nanowires are identified as Fe₂O₃, MgO, MnO, WO₃, ZnO, TiO₂, and ReO₃. Figure S2 (available at stacks.iop.org/Nano/25/145603/mmedia) indicates the growth direction in each selected area electron diffraction (SAED) pattern. The lattice spacing observed in indexed SAED (figure S2 available at stacks.iop.org/Nano/25/145603/mmedia), and high-resolution transmission electron microscopy (HRTEM, see figure 4) are consistent and both sets of data are used to define the preferred growth direction. Cubic Fe₂O₃ grows along the [110] direction, i.e. the preferred growth direction. Cubic MgO grows along the [100]. Cubic MnO has a preferred growth direction of [211]. Cubic WO₃ grows in the [010] direction. Hexagonal ZnO has preferred growth direction along the [1120]. Tetragonal TiO₂ grows along the [001]. Hexagonal ReO₃ prefers growth along the [1120]. EDS mapping and electron diffraction confirm the presence of Cu metal at the tips of the nanowires (see figures S5 and S3 available at stacks.iop.org/Nano/25/145603/mmedia). Fe₂O₃ and TiO₂ (see figure S4 available at stacks.iop.org/Nano/25/145603/mmedia) nanowires were also grown with Bi catalysts to highlight the generality of the approach.

The thermodynamics of mixing, oxidation, and wetting [11, 12] will influence the process along with the relative cation diffusivities along the nanowire. For example, Cu–Fe, Cu–W, and Cu–Re have reasonably large positive heats of mixing [13] that prevent the Cu from alloying significantly, Cu–Mn, Cu–Zn, Cu–Mg and Cu–Ti can form concentrated alloys and intermetallic compounds. However, when the difference in oxidation enthalpy is large, such as Cu–Zn and Cu–Ti, limited metallic mixing is expected. Small MnO nanowires protrude beyond the Cu catalyst particle near the tip (see figure S5 available at stacks.iop.org/Nano/25/145603/mmedia) and others show tapering near the end of the nanowire just below the catalyst particle. This likely results as the Mn in solution with Cu de-alloys and oxidizes as the temperature decreases, which decreases the entropy of mixing but increases the entropy of formation for the oxide. The length of TiO₂ nanowires is limited to ∼0.6 µm for samples annealed for ∼3 h at 600 °C. Small Cu nanoparticles (∼5 nm) appear along the length of the TiO₂ nanowire and the Cu nanoparticles at the tip are relatively small (see figure S6 available at stacks.iop.org/Nano/25/145603/mmedia) and others show tapering near the end of the nanowire just below the catalyst particle. This likely results as the Mn in solution with Cu de-alloys and oxidizes as the temperature decreases, which decreases the entropy of mixing but increases the entropy of formation for the oxide. The length of TiO₂ nanowires is limited to ∼0.6 µm for samples annealed for ∼3 h at 600 °C. Small Cu nanoparticles (∼5 nm) appear along the length of the TiO₂ nanowire and the Cu nanoparticles at the tip are relatively small (see figure S6 available at stacks.iop.org/Nano/25/145603/mmedia) and others show tapering near the end of the nanowire just below the catalyst particle. This likely results as the Mn in solution with Cu de-alloys and oxidizes as the temperature decreases, which decreases the entropy of mixing but increases the entropy of formation for the oxide. The length of TiO₂ nanowires is limited to ∼0.6 µm for samples annealed for ∼3 h at 600 °C. Small Cu nanoparticles (∼5 nm) appear along the length of the TiO₂ nanowire and the Cu nanoparticles at the tip are relatively small (see figure S6 available at stacks.iop.org/Nano/25/145603/mmedia) and others show tapering near the end of the nanowire just below the catalyst particle. This likely results as the Mn in solution with Cu de-alloys and oxidizes as the temperature decreases, which decreases the entropy of mixing but increases the entropy of formation for the oxide. The length of TiO₂ nanowires is limited to ∼0.6 µm for samples annealed for ∼3 h at 600 °C. Small Cu nanoparticles (∼5 nm) appear along the length of the TiO₂ nanowire and the Cu nanoparticles at the tip are relatively small (see figure S6 available at stacks.iop.org/Nano/25/145603/mmedia) and others show tapering near the end of the nanowire just below the catalyst particle. This likely results as the Mn in solution with Cu de-alloys and oxidizes as the temperature decreases, which decreases the entropy of mixing but increases the entropy of formation for the oxide. The length of TiO₂ nanowires is limited to ∼0.6 µm for samples annealed for ∼3 h at 600 °C. Small Cu nanoparticles (∼5 nm) appear along the length of the TiO₂ nanowire and the Cu nanoparticles at the tip are relatively small (see figure S6 available at stacks.iop.org/Nano/25/145603/mmedia) and others show tapering near the end of the nanowire just below the catalyst particle. This likely results as
Figure 2. SEM micrographs of oxide nanowires grown from various metal substrates. (a)-(g) demonstrate Cu catalyzed growth while (h) shows Bi catalyzed growth.

45603/mmedia), but their low density and the magnetism of the Ni substrate made them difficult to characterize by TEM. ReO$_3$ nanowires were grown here specifically because nanowires of this chemistry have seldom been reported in the literature [15]. The demonstration supports the hypothesis that the CONG process may be applied broadly to systems where the metal and oxide are solid at temperatures at which the thermal oxidation rate is appreciable and cation diffusion exceeds anion diffusion. Systems where anion and cation diffusion are comparable during oxidation, such as Al and Cr may not be amenable to the process. In fact, CONG did not produce nanowires on Cr at 600°C. Fe$_3$O$_4$, WO$_3$, and TiO$_2$ nanowires were encased by ordered (~0.36 nm spacing) [16, 17] carbon layers on their surface (see figures 4 and S9 available at stacks.iop.org/Nano/25/145603/mmedia). Cu catalyzes the growth of carbon nanotubes in the presence of a carbon precursor, such as toluene [18]. Toluene decomposition can be performed over the catalyst surface resulting in carbon atoms via dehydrogenation [19]. The migration and rearrangement of the surface carbon atoms can results in the formation of the carbon nanotubes. The crystallinity of the reduced carbon should generally increase with increasing temperature [20]. In the present study, the samples are heated at relative low temperatures ~600°C. So, it is reasonable to expect that the carbon nanotubes are not well-crystallized. However, the planar spacing observed in HRTEM is consistent with carbon nanotubes. This carbon nanotube wrapping can be removed via reactive ion etching (see figure S10 available at stacks.iop.org/Nano/25/145603/mmedia). However, they could be useful in applications such as oxide nanowire electrodes (e.g. in lithium ion battery) where charge transport is an important consideration. In fact, a number of studies have sought specifically to wrap nanostructures in graphene or carbon nanotubes [21, 22]. The nanotube wrapping did not occur in the MnO, MgO, ReO$_3$ and ZnO systems. Alloying impurities in the Cu could affect carbon catalysis. Also, the stability of graphitic carbon on the specific oxides could affect its formation. Further effort is needed in future work to thoroughly clarify the formation mechanism of carbon nanotube on specific metal oxide nanowires. Regardless, the result indicates that the carbon coating is not necessary to promote oxide nanowire growth. This is reinforced by the fact that Fe$_3$O$_4$ nanowires could be grown in forming gas (Ar-4%H$_2$) without the presence of toluene. To demonstrate that the catalyst is indeed responsible for the growth, a Cu film was patterned onto a pre-oxidized iron substrate, which does not contain pre-existing nanowires.
Nanowires were grown at 600 °C in forming gas without extra Cu metal present in the furnace or toluene. Figure 6 clearly demonstrates that dense nanowire growth occurs in the region where the ~3 nm thick Cu film was sputtered. The results in figure 6 also highlight the potential of the process to be utilized to lithographically pattern oxide nanowire growth via the CONG process. The results clearly differentiate the process from growth of nanowires through conventional thermal oxidation approach [6]. Figure 7 compares nanowires growth from Fe using the two different processes CONG and thermal oxidation. The phase, morphology, aspect ratio, and thickness of the underlying oxide layer all differ significantly.

The commonly utilized approaches for catalyzed nanowire growth from the vapor phase include vapor–liquid–solid (VLS) [23], vapor–solid–solid (VSS) [24], vapor–quasisolid–solid (VQS) [25]. The associated growth mechanism requires the catalyst alloys (transition-metal or noble-metal) to effectively dissolve species from the vapor phase, and localize precipitation from the supersaturated particle onto the growing nanowire. The reactants arrive primarily through the vapor phase and the catalyst particles preferentially absorb the reactants through an accelerated interfacial reaction, relative to the substrate. These processes source all of the reactants from the gas phase and the nanowire growth is driven by the change in free energy associated with precipitating solute from a supersaturated solution. The CONG process sources anions from the vapor phase and cations from the substrate, the metal nanoparticle catalyzes the oxygen reduction reaction, and the overall driving force is the oxide formation energy. Cu is known to function as catalyst for the oxygen reduction reaction [26] and while it is not efficient enough for applications such as fuel cells it is effective enough to inexpensively catalyze oxide nanowire growth for CONG. The rate of oxygen reduction on the bulk oxide covering the substrate will be considerably lower than at the catalyst. It should be noted that all nanowire growth occurs in the hot zone of the furnace and there is no material source for growth by an evaporation–condensation type mechanism or a catalyzed CVD or PVD type mechanism.

Heating metal foils or plates in a furnace in air or oxygen environment (as low as several percent oxygen level) has been widely reported for producing metal oxide nanowires [5, 5].
This thermal oxidation (TO) method has been proposed to be stress driven \[28\] induced by a preferential crystallographic direction growth \[29\], mediated through internal diffusion along screw dislocations, twins, grain boundaries, or nanowire surfaces which continuously provide cations from the substrate. No general consensus exists for the mechanism. Alternatively, in this work, the oxygen level is 3–5 orders of magnitude lower than in conventional TO and the presence of the catalyst nanoparticle is crucial to the nanowire growth (see figure 6). As shown in figure 7, the growth morphology and phase evolution also significantly differ from those grown by the traditional TO. Therefore, a distinct catalyzed oxidation procedure is proposed below to explain the growth mechanism for the nanowires in this work.

In the general view of metal oxidation \[30, 31\], an oxide scale forms through which metal cations and anions diffuse. In many systems, cation diffusion exceeds anion diffusion during oxidation, mostly along planar and line defects, and combines with oxygen reduced on the scale surface. The process typically produces an unbalance diffusion (i.e. Kirkendall effect) couple of the metal and oxygen \[32, 33\]. When the supply of anions is high and the oxide scale is relatively thick, as is typical during oxidation under ambient conditions, the process is diffusion controlled. However, when the partial pressure of oxygen is sufficiently low, the process will be interface reaction rate controlled by the oxygen reduction reaction. In this work, we suppressed the oxygen partial pressure by the use of a sacrificial carbon vapor (toluene) or forming gas. The rate of the oxygen reduction reaction was accelerated locally using metal catalysts that enhance the oxygen reduction reaction rate (Cu or Bi) relative to the surrounding oxide scale. These catalysts were introduced either passively, through evaporation and condensation or actively through PVD. Since the Gibbs free energy of formation for the catalyst oxide (CuO, Cu$_2$O, and Bi$_2$O$_3$) is less negative than those of the oxide nanowires the catalyst donates its oxygen to nanowire growth. Therefore, the Me atoms (Me = Fe, W, Zn, Mn, Ti, Re, etc) can be directly oxidized by the oxygen with the catalyst functioning as an intermediary. Since the catalyst accelerates the oxygen reduction reaction rate relative to the surrounding oxide, the nanowire preferentially grows below the catalyst. The pre-oxidized layer is important for allowing the oxygen gas to kinetically distinguish the catalyst from the surrounding material. It also inhibits the co-oxidation and incorporation of the catalyst into the initially formed oxide. In principle, catalyst selection is flexible, as long as its oxide formation energy is less negative than that of the oxide nanowire. For example, the Bi oxides and Cu oxides are more noble than Fe oxides or Ti oxides and thus serve as efficient catalysts for nanowire growth. Some nanowires are observed to be diffusion bonded together, suggesting that sufficient cation
surface diffusion occurs along the nanowire, which is also typical of TO nanowire growth [34].

The main benefit of the CONG process is its ability to grow high-density nanowire forests inexpensively. Such qualities make the process ideal for applications such as photocatalysis, batteries, or electrochemical capacitors, where low-cost substrate-supported nanostructures are required [35]. We specifically demonstrate Fe\(_3\)O\(_4\) and ReO\(_3\) nanowires grown here as electrodes for lithium ion systems that display high areal energy density and power (see figure S11 available at stacks.iop.org/Nano/25/145603/mmedia). For example, the areal energy density and power of the Fe\(_3\)O\(_4\) nanowires exceed that of iron oxide based anodes reported in the literature [36]. We anticipate that this catalyzed oxidation process may be extended to the growth of nanowires in non-oxide systems, such as nitrides, sulfides, or fluorides, that could be of particular interest for energy storage and conversion.

4. Conclusions

CONG has been demonstrated to produce oxide nanowires from a number of metallic precursors. This effort did not seek to optimize time, temperature, or pO\(_2\) schedules during processing and such optimization will undoubtedly lead to improvements in nanowire length, quality, and density. The remarkable ability to produce substrate-supported nanowires with little process optimization highlights the flexibility of the CONG approach. CONG should likely be applicable to growing a broader range of oxide nanowires from their metallic precursors. In theory it should also find application in growing non-oxide (e.g. sulfide or fluoride) ionic crystal nanowires through direct oxidation.

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