Magnesium oxide nanowires synthesized by pulsed liquid-injection metal organic chemical vapor deposition

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Vertically aligned MgO nanowires were epitaxially grown at 600 °C on Au-coated MgO (001) substrates by metal organic chemical vapor deposition using Mg(tmhd)2 precursor. Discrete Au particles were embedded in the wires and distributed along the central axis. Scanning and transmission electron microscopy show that the orientation, diameter, and length of the wires strongly depend on the processing conditions such as oxygen partial pressure and reactive species flow rate as well as the starting Au thickness. Diameters down to 15–20 nm were obtained. The growth can be switched from vertical to horizontal wires by decreasing the period at which reactants are supplied. © 2009 American Institute of Physics. [DOI: 10.1063/1.3064134]

In order to address beyond Moore’s nanoelectronics, radically new approaches and devices are needed. Nanowires are one of the building blocks that could be used in future electronic devices. In this perspective, IV/IV as well as III/V semiconductor nanowires are extensively studied, and one-dimensional (1D) growth has been extended to oxides, selenides, and tellurides. Integrating functional oxides in the form of nanowires could open up the route to new functionalities. Magnesium oxide MgO has been recently the subject of attention. Besides a wide-band gap insulating material, MgO is also used as a buffer layer for the growth of ferroelectric or magnetic oxides, or as a tunneling barrier in magnetic tunnel memories. The synthesis of MgO nanowires has been achieved mainly by chemical vapor deposition (CVD) and by pulsed laser deposition (PLD). CVD allows a flexible change in composition compared to physical vapor deposition techniques, and it is compatible with future device fabrication technologies. One major difficulty in the CVD of complex oxides is the control of the composition; the metal organic precursors are indeed highly thermally unstable and cannot sustain a prolonged heating. A liquid-injection delivery scheme was proposed in order to solve such issues. It allows for the growth of oxides at nanometer scale and has been used for the epitaxial growth of a variety of complex functional oxides such as ferroelectrics, magnetic oxides, or multiferroics. The sequential use of several injectors offers a large flexibility for film doping or for superlattice growth. The extension of the method to the growth of oxide nanowires would be extremely promising; indeed composition of nanowires could be, for example, graded or modulated at nanometer scale using several injectors. So far, MgO nanowires have been synthesized by CVD mainly through the thermal evaporation of MgB2 (Refs. 8 and 10) or Mg3N2 (Refs. 9 and 13) powders and the condensation of MgO from the vapors (transported by a carrier gas) on a substrate placed in the furnace, next to the evaporation zone. This method requires a quite high processing temperature of 700–900 °C for MgB2 and 900–925 °C for Mg3N2. Even higher temperatures (1200 °C) are required when a mixture of MgO and carbon powder is used. Here we demonstrate the growth of epitaxial vertical MgO nanowires on MgO substrates by metal organic CVD (MOCVD), using a β-dikionate molecule as a precursor (evaporation temperature of 220 °C) and a growth temperature of 600 °C. Gold was used as a catalyst. We discuss the growth mode and the dimensions of the wires as a function of processing conditions.

The β-dikionate Mg(tmhd)2 (tmhd=2,2,6,6-tetramethyl-3,5-heptanedionate, with formula C11H19O2) was dissolved in 1,2-dimethoxyethane solvent at 0.02 mol/l. The synthesis was carried out on MgO (001) substrates at 600 °C. Argon was used as a carrier gas and O2 as an oxidizing agent. The total pressure was 10 Torr. The oxygen partial pressure was of 2.4 Torr. Before the synthesis, a thin gold layer, typically of 2 nm thickness, was sputtered onto the substrates. Prior to deposition, the coated substrates were heated at 600 °C for 10 min under 10 Torr under the deposition atmosphere (mixture of oxygen and argon). In order to vary the reactive species flow rate impinging the substrate, the injection period was changed in the range of 0.1–5 s. After the synthesis, the samples were cooled under 1 bar O2. The morphology and the dimensions of the nanowires were studied by field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM), averaging data from several images. The crystallinity of the wires was studied by x-ray diffraction and electron diffraction.

Figure 1 shows SEM images of nanowires grown on ~2 nm gold-coated MgO (001) and, for comparison, on Si (001) substrates. On MgO, the wires are vertically aligned with the [001] direction perpendicular to the substrate plane, while on Si (001), various orientations are observed, as shown by x-ray diffraction (Si wafers were prepared by HF—last in order to remove the SiO2). On Si, TEM shows, however, that the growth direction within the wire is [001] as well. The simultaneous deposition on bare substrates leads to the formation of continuous MgO films. The gold acts clearly as a catalyst. In the following, we focus on the growth on MgO.

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The formation of MgO cubic structure is confirmed by electron diffraction and high-resolution TEM images, as shown in Fig. 2. An interplane $d_{002}$ spacing of 0.21 nm is measured, in good agreement with the expected value ($d_{	ext{MgO}}=0.421$ nm). The growth direction along the [001] direction is also confirmed. The wires exhibit a square-rod shape, with gradually narrowing size from bottom to top. The bottom “diameter” is typically 15–20 nm, while the top diameter is 4–5 nm. The length is 700 nm for 85 min deposition using an injection period of 3 s. A round-shaped gold nanoparticle is found at the tip of the wires, indicating the role of gold as catalyst and pointing out to a vapor-liquid-solid (VLS) growth mechanism.20 In most of the wires, discrete gold nanoparticles with ovoidal shape are observed inside the wires, distributed along the central axis and with a decreasing diameter from bottom to top, as shown in Fig. 2(b). Few reports also mention the possibility to embed Au nanoparticles in oxide nanowires, such as SiO$_2$ or Ga$_2$O$_3$.21,22 It was proposed that the Au-in-Ga$_2$O$_3$ peapods spontaneously crystallize under phase separation induced by the formation of twin boundaries in Ga$_2$O$_3$.22 In our case, no extended defects are observed inside the wires. As seen in Fig. 2(c), facets of {001}-type are observed on the sides. The clean {001} MgO surface has the lowest surface energy.23,24 Density functional theory simulations of the growth of (MgO)$_n$ islands on MgO {001} terraces have shown that the most stable islands expose nonpolar steps rather than polar ones.24 These energetic considerations are in favor of an epitaxial growth along the [001] axis and of {001} facets, as obtained. The tapered shape of the wires was also reported by other groups, for CVD as well as PVD growth.8,11 In the VLS mechanism proposed for the growth of Si nanowires,20 the liquid Au–Si droplet acts as an energetically favorable site for the adsorption of the gas phase species. Si vapor atoms enter the droplet and supersaturate it, leading to a condensation of Si at the interface between solid Si and the liquid alloy. In our case, the gaseous reactive species arriving on the droplets are bulky Mg$_2$(thmd)$_2$ molecules. They decompose at the surface of the droplets and release Mg or Mg–O gaseous species to enter the droplets. These chemical reactions involved in the thermal decomposition of thmd precursors are more complex than those occurring for solid precursors such as MgB$_2$. The CVD process involves the diffusion out of the droplet’s surface of C- and H-containing species, which are gaseous byproducts of the chemical reactions taking place at the surface. The diffusion of Mg atoms (or Mg–O dimers) at the catalyst droplet’s surface is certainly impeded by the large amount of in- and outdiffusing species at this surface. At the same time, heterogeneous reactions involving the Mg$_2$(thmd)$_2$ precursor will also take place on the MgO substrate surface and at the sidewalls of the growing wires. Thus it is probable that the growth from the side of the wires is considerably favored. Moreover, the supersaturation of the liquid droplets may not be uniform as C, H, and O species are probably also incorporated. This may explain the presence of gold inside the wires, and this is consistent with the facets and tapered shape of the wires. The phase diagram of the Au–Mg system shows that a Au-rich eutectic (Au: Mg = 67.5:32.5) appears at 872 °C, while Mg-rich eutectic (Au: Mg = 7:93) is formed at 576 °C, which is similar to the growing temperature of the wires. Thus contribution from a solid/vapor mechanism cannot be precluded.25 In order to possibly eliminate the gold particles from the wires—for applications where pure wires are required—other less bulky precursors should be tested, such as Mg(acac)$_2$ or, more interestingly, Mg(Cp)$_2$.

Catalyst starting thickness is one of the parameters determining the growth and dimensions of the wires. As observed after heating of a coated substrate, the continuous gold layer transforms into islands. The size of the islands increases with increasing gold thickness. A gold layer with thickness of 2–3 nm leads to vertically aligned nanowires with a bottom diameter of ~15–20 nm (top diameter of 4–5 nm). A thicker catalyst of ~4 nm hampers the vertical growth, as can be seen on Fig. 3, and produces wires with a faceted sides.
much larger difference between bottom and top dimensions and with a larger bottom diameter (~35–40 nm).

It has been reported that ambient pressure plays an important role in the PLD growth of MgO nanowires and that increasing the ambient pressure led to an enhancement of the wire growth even under Ar atmosphere, while the O$_2$ partial pressure impacted the oxide crystallinity rather than the wire morphology. In CVD, when the gas phase is generated by the thermal evaporation of powders such as MgB$_2$ or Mg$_3$N$_2$, only trace of oxygen is used during deposition. In our case, the situation is quite different. Although oxygen is present in the precursor Mg(tmhd)$_2$ (four atoms of O for one atom of Mg), a rather high oxygen partial pressure is needed in order to avoid carbon contamination; the cracking of the solvent produces indeed a lot of C and H species, and oxygen is required to burn out these species. Contrary to the PLD growth, the oxygen partial pressure (at constant total working pressure of 10 Torr) is found to strongly affect the wire morphology. Increasing the oxygen flow rate hampers the vertical epitaxial growth and leads to the growth of randomly distributed wires.

Finally, a clear switch from vertical to horizontal growth is observed when changing the time period at which the gas reactants are injected to the reaction zone. For injection periods of 2 s or larger, the nanowires grow vertically with a bottom diameter of 15–20 nm, while for smaller periods (0.1–1 s), they grow along the substrate surface and the tapered shape is enhanced, as shown by the top views in Fig. 4.

For a small injection period, which means a high injection rate (a period of 0.1 s corresponds to ten precursor droplets injected per second), the diffusion along the vertical direction is thus impeded. The driving force in the VLS mechanism is the supersaturation in the liquid catalyst droplet. The increase in precursor supply may lower the adsorption of reactants at the droplet’s surface, and thus leads to a lowering of the supersaturation.

In summary, vertical epitaxial MgO nanowires with Au particles embedded along the radial axis were synthesized by MOCVD. Metal-dielectric 1D nanostructures are of interest for optoelectronics or optics applications such as ultrafast optical switching devices. Moreover, we showed that oxide nanowires can be grown using precursors, which are conventionally used for the MOCVD of complex functional oxides. This opens up the route to the design by CVD of new heterostructures such as superlattices or core-shell nanowires combining various oxides.