

A Generic Approach for Embedded Catalyst-Supported Vertically Aligned Nanowire Growth

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ABSTRACT

We demonstrate a general approach for growing vertically aligned, single-crystalline nanowires of any material on arbitrary substrates by using plasma-sputtered Au/Pd thin films as a catalyst through the vapor–liquid–solid process. The high-energy sputtered Au/Pd atoms form a reactive interface with the substrate forming nanoclusters which get embedded in the substrate, thus providing mechanical stability for vertically aligned nanowire growth. We demonstrate that our approach for vertically aligned nanowire growth is generic and can be extended to various complex substrates such as conducting indium tin oxide.

One-dimensional nanostructures such as nanowires and nanotubes are being researched extensively owing to their novel properties resulting from their unique geometry, which enables them to function as active device elements and passive interconnects simultaneously.^{1,2} Semiconducting nanowires have been configured into nanoscale electronic/optical devices including field-effect transistors (FETs), light-emitting diodes, lasers, sensors, and photodetectors.^{1,3} Along with recent explosive interest in exploring new functionalities in nanowires, there have been sustained efforts to configure them into hierarchically ordered devices by rational synthesis with well-defined sizes,⁴ controlled growth orientation,⁵ and large-scale alignment.⁶ Two main strategies for alignment of nanowires are in-plane (horizontal)^{6,7} and vertical alignment with wires standing up on substrates.^{8,9} Specifically, vertically aligned architectures can truly utilize their potential owing to their sublithographic dimensions critical for high-density device assembly.^{8,9} Large-area vertically aligned arrays of nanowires on arbitrary substrates will make fabrication of electronic/photonic devices, such as transistors, light- and field-emission displays, or photovoltaics,^{3,8–10} more versatile and also provide direct charge-transport pathways to connecting top/bottom electrodes. Achievement of single-crystalline vertically aligned nanowires is typically obtained

by epitaxial growth on lattice-matched crystalline substrates,^{11–14} which is expensive and limits the potential of integrating diverse materials with different crystal structures and functionalities on a common platform. More significantly, vertical alignment of nanowires on amorphous substrates is severely limited since amorphous substrates do not “guide” nanowire directions due to lack of crystallographic relationship with the nanowires, therefore rendering conventional epitaxial growth schemes ineffective. Therefore, it is desirable to develop techniques that allow single-crystalline vertically aligned growth of nanowires on arbitrary substrate for high-performance devices. Here, we demonstrate that annealed plasma-sputtered Au/Pd thin-film catalyst can be a general technique to produce vertically aligned single-crystalline nanowires on arbitrary substrates over large areas through the vapor–liquid–solid (VLS) growth mechanism,¹⁵ which presents new opportunities for assembling large-scale nanowire-based devices.

We use II–VI nanowires as a model system to demonstrate vertically aligned growth on various substrates by exploiting the VLS mechanism. We synthesized ZnS and CdS nanowires by using two different catalyst deposition techniques, plasma-sputtered Au/Pd thin film and Au colloidal deposition. A Au/Pd (molar ratio 4:6) thin film was plasma-sputtered for 30 s on a thermally grown oxide-covered Si substrate, Si₃N₄/Si substrate, and indium tin oxide coated quartz substrate by using a commercial dc plasma sputter (CRESSINGTON 108) in an Ar atmosphere (75 Torr) at 30

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mA ion current. This process results in typical Au/Pd film thickness of 10–15 nm. In the case of Au colloidal deposition, the substrates were first coated with positively charged 0.1% poly-L-lysine solution (Ted Pella) to incorporate negatively charged Au nanocolloids.¹⁷ Following the rinse out of the poly-L-lysine solution with deionized water, drops of Au nanocolloids (Ted Pella, ~80 nm in diameter) solution were deposited on the substrates.

The catalyst-deposited substrates were then placed at the downstream side of a horizontal tube furnace, and (Zn/Cd(S₂CNEt₂)₂) single molecular precursors were positioned at the upstream side.¹⁶ The furnace temperature was slowly raised to 890 °C (ZnS nanowire growth) and 710 °C (CdS nanowire growth) (substrate temperature ~770 and 590 °C, respectively) and the quartz tube was pumped down to a base pressure of 10⁻² Torr with pure Ar (99.99% purity) introduced into the tube at a flow rate of 100 SCCM (SCCM denotes standard cubic centimeter per minute at STP). After the furnace was stabilized at the process pressure of 300 Torr typically after 20 min, the substrates were annealed for extra 10 min, and subsequently, the precursors were slowly pushed into the high-temperature zone of the furnace and nanowire growth was performed for 5 min. The above experimental conditions were identical for growths with both sputtered Au/Pd films and Au colloidal deposition.

We first focus on ZnS nanowires grown on SiO₂/Si (SiO₂ thickness ~200 nm) substrates with the main difference of depositing the metal catalyst. Much to our surprise, the as-grown ZnS nanowires on the growth substrate catalyzed by sputtered-Au/Pd thin film were predominantly vertically aligned with respect to the substrate as seen in scanning electron microscopy (SEM, FEI NOVA) images (panels a and b of Figure 1); the majority of nanowires (length 10–15 μ m; diameter 50–80 nm) stand upright with intimate contact only at the nanowire/substrate interface. In the top-view image (Figure 1b), only the tips of the nanowires are seen with metal-catalyst particles attached at the end. This is a surprising observation since the nanowires are grown on an amorphous substrate bearing no crystallographic compatibility, and previous studies of nanowires grown via gold colloids or thermally evaporated thin-film deposition of catalyst produce random orientation of nanowires.^{17,18} Even though the nanowires are very long (10–15 μ m), they are still capable of standing up and not falling over on the substrate, therefore suggesting significant mechanical interaction at the nanowire–substrate interface.

In order to make direct comparison of the effect of catalysts deposition method on vertical alignment, we also grew ZnS nanowires from gold colloids dispersed on SiO₂/Si substrates under the same growth conditions as Au/Pd sputtered films. The resulting nanowires (panels c and d of Figure 1) did not grow vertically aligned with respect to the substrate, and rather resembled an interconnected meshlike structure. Vertically aligned growth routinely achieved with sputtered Au/Pd thin films was never obtained in any control experiments with Au colloids under various growth parameters. Au colloid catalyzed vertical nanowire growth has been previously reported, however, only enabled by epitaxial

crystallographic relationship between the nanowires and substrates.^{12–14} To make a more quantitative comparison of the degree of vertical alignment between sputter-deposition of catalysts with Au colloid based nanowire growth, we also measured the angular distribution of individual nanowires with respect to the growth substrate normal axis, by characterizing a large number of cross-sectional SEM images of as-grown substrates (e.g., panels a and c of Figure 1). The distribution plots (insets in panels a and c of Figure 1), obtained by sampling over 300 nanowires for each case, clearly show the higher degree of vertical alignment obtained for sputter deposition of catalysts (75% of the measured nanowires within a range of $\pm 10^\circ$ to the surface normal) in comparison to Au colloids (<10% of the nanowires within a range of $\pm 10^\circ$ to the surface normal).

In order to demonstrate the critical role of sputtered thin film of Au/Pd as catalysts for nanowire growth, we selectively deposited the catalyst using a stainless steel hard mask with circular features of 80 μ m diameters. High-density vertically aligned nanowires (length >15 μ m) were observed only on the catalyst-deposited regions (Figure 1e) and no nanowires were found elsewhere. When viewed from the top (Figure 1e inset), mostly the nanowire tips with metal catalyst are observed, strong evidence for vertically aligned nanowire growth via the VLS mechanism. A side view SEM image of the patterned growth areas shows that vertical alignment of nanowires is obtained even at the edge of the patterned areas suggesting that the large density of the nanowires and steric effects cannot be the main factors for obtaining vertical alignment (Supporting Information, Figure S1). Such combined capability of large-area, vertically aligned and patterned growth on amorphous substrates is very promising toward realization of large-area electronic/photonic devices.

Nanowires with small lengths were found to typically grow completely vertically aligned to the substrate in comparison to longer nanowires (Figure 1f, growth time 40 s, nanowire length 160 nm). The structure of ZnS nanowires was determined to be single-crystalline face-centered cubic (sphalerite) along [111] growth direction by X-ray diffraction and high-resolution transmission electron microscopy (HR-TEM) studies, while the particles at the tip of the nanowires were composed of Au/Pd elements, further confirming the Au/Pd-assisted VLS growth (Supporting Information, Figure S2).

To gain better insight on the underlying mechanism of vertical nanowire growth on amorphous substrates, we first investigated the effect of the sputtering process in depositing Au/Pd catalysts as this is the main difference between our method and other techniques for catalyst deposition. The structure of annealed Au/Pd thin films on SiO₂ substrate was studied systematically using SEM, focused ion beam (FIB, FEI NOVA) and transmission electron microscopy (TEM, JEOL-JEM3000F), and energy dispersive spectrometry (EDS, INCA) techniques. The top view SEM image (Figure 2a inset) of sputtered Au/Pd film after annealing (890 °C, 10 min) mimicking ZnS nanowire growth conditions shows formation of nanoclusters with diameters in a range of

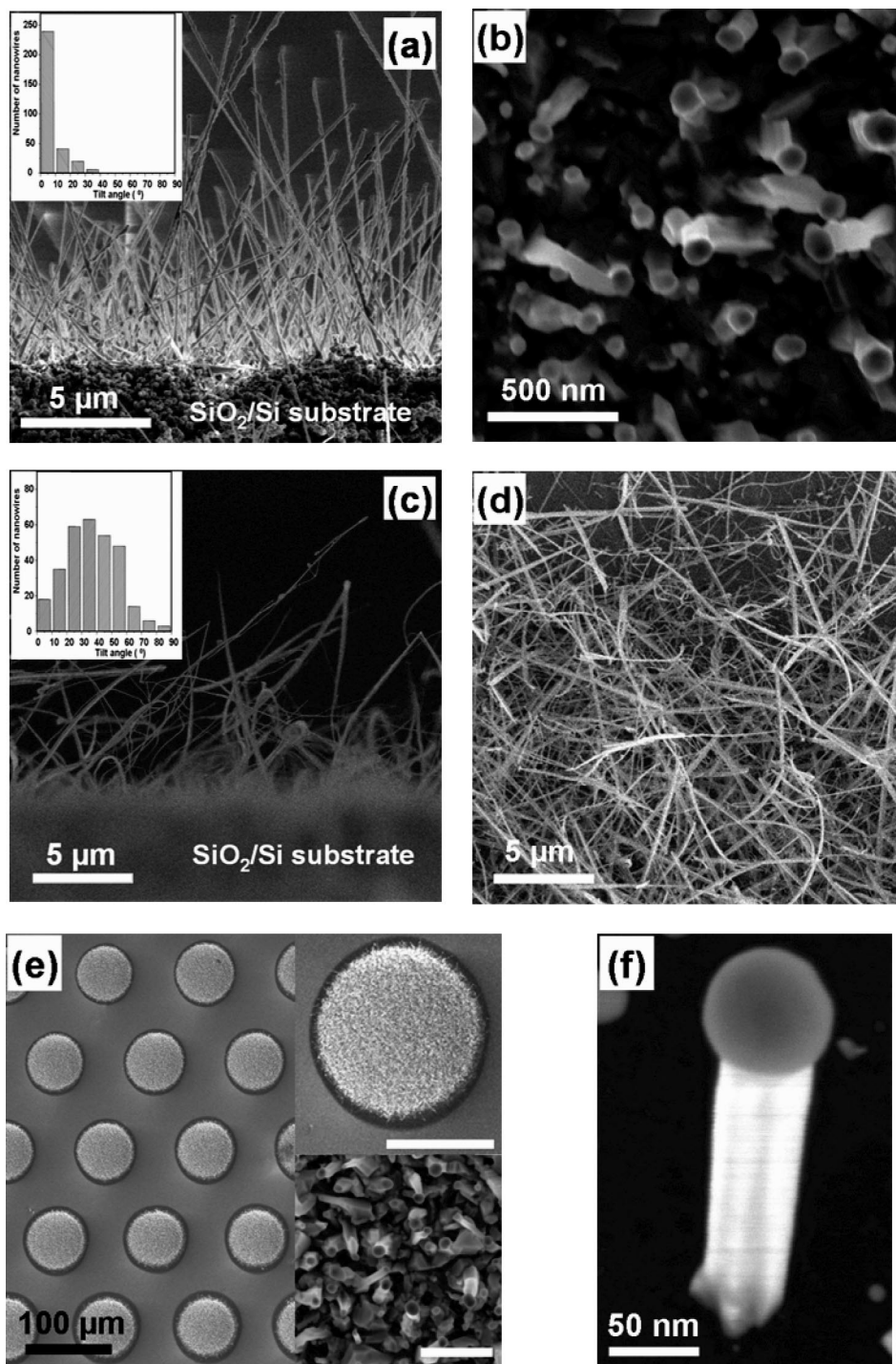


Figure 1. (a) Side view SEM image of as-grown ZnS nanowires on SiO₂/Si substrate catalyzed by sputtered Au/Pd thin film. The inset shows the angular distribution of the individual nanowires with respect to the surface normal. (b) Top view SEM image of the ZnS nanowires from the same sample in (a) showing the nanowire tips. (c) Side view SEM image of Au colloid catalyzed ZnS nanowires grown on SiO₂/Si substrate. The inset shows the angular distribution of the individual nanowires with respect to the surface normal. (d) Top view SEM image of the Au colloid catalyzed ZnS nanowires showing an interconnected mesh of nanowires, in sharp contrast to (b). (e) SEM image of ZnS nanowires selectively grown on a large area of SiO₂/Si substrate patterned with Au/Pd thin film. Top inset: Magnified SEM image of the patterned growth region (scale bar, 40 μm). Bottom inset: Magnified SEM image of top inset (scale bar, 500 nm) showing nanowire tips. (f) SEM image of a short length ZnS nanowire grown for 40 s.

30–100 nm. The nanoclusters were observed to grow in size with longer annealing time due to Oswald ripening.

We also investigated the interfacial structure of sputtered Au/Pd catalysts on SiO₂/Si substrates by combining FIB-TEM cross-sectional structural analysis. For this purpose,

the TEM specimen of the annealed Au/Pd nanoclusters on SiO₂ substrate was prepared by a FIB lift-out technique. First, e-beam (5 keV, 98 pA) induced Pt capping layer was deposited to protect the target area and Ga ion beam (30 keV, 50 pA) induced Pt capping layer was subsequently

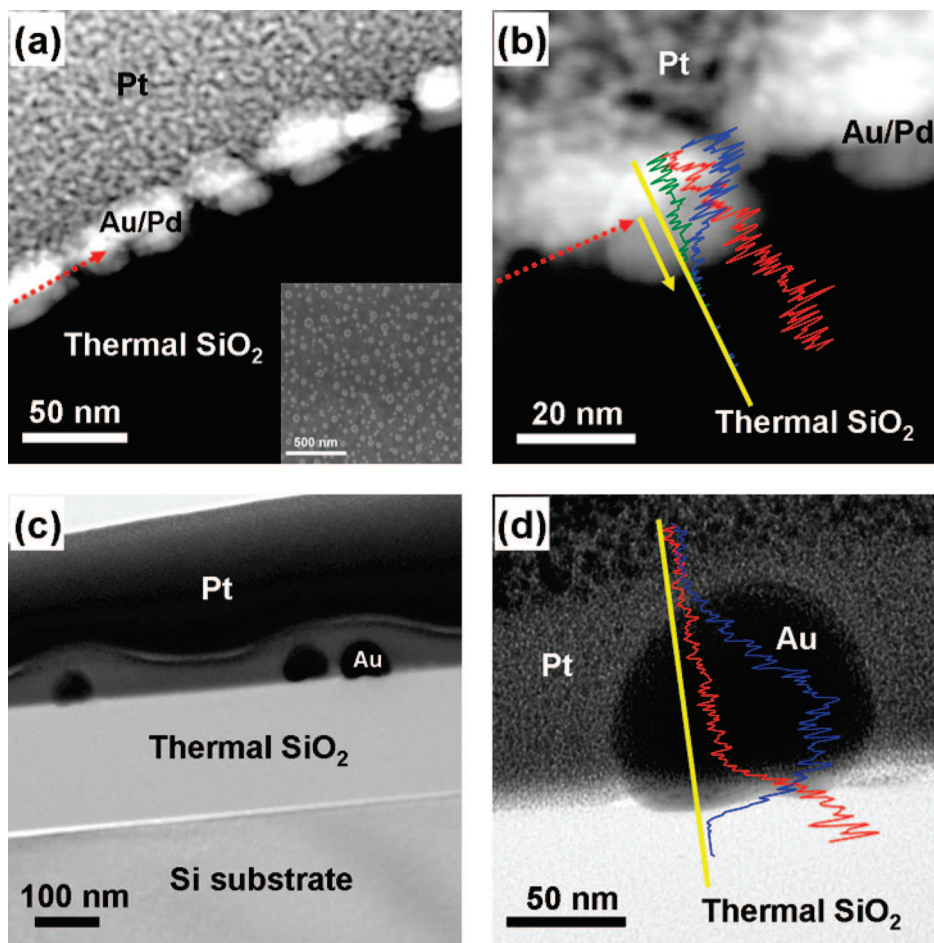


Figure 2. (a) Cross-sectional ADF-STEM image of annealed Au/Pd on SiO₂/Si with protective Pt capping layer on the top, prepared by FIB lift-out technique (red dotted line indicates SiO₂/Si substrate surface). Inset is top view SEM image of annealed Au/Pd thin film revealing formation of nanoclusters. (b) Magnified ADF-STEM image of panel a with the corresponding EDS line scan profile along the yellow line (blue = Au, green = Pd, red = Si). (c) TEM bright field image of annealed Au colloids on SiO₂/Si with Pt capping layer. (d) STEM bright field image of annealed Au colloid with corresponding EDS line scan profile along the yellow line (blue = Au, red = Si).

deposited. After capping layer deposition, Ga ion milling was performed until the target area became electron-transparent (~ 70 nm thick) suitable for TEM imaging and the prepared specimen was put onto a Cu TEM grid with a micromanipulator inside the FIB. Notably, the cross-sectional annular dark-field-scanning TEM (ADF-STEM) image of the annealed-Au/Pd nanoclusters on SiO₂ substrate (Figure 2a) clearly shows that the nanoclusters get embedded with almost half of their volume into the SiO₂ layer to a depth of 15–20 nm, forming ellipsoidal structures. The ADF-STEM image with superimposing EDS line-scan profile (Figure 2b) reveals that Au/Pd nanoclusters were interdiffused with thermal SiO₂ ~ 15 nm depth (yellow arrow) while Si is evenly distributed over the entire Au/Pd nanoclusters. The formation of the embedded reactive interfacial layer can be explained by the physical sputtering effect which produces Au/Pd atoms with high kinetic energies ($\sim 10^4$ m/s velocity), which can react with the substrate surface forming an interfacial layer. Our results are in agreement with previous studies showing high reactivity of sputtered Au/Pd with SiO₂ to form Au and Pd silicide inside SiO₂ amorphous matrix studied by X-ray photoelectron spectroscopy.¹⁹ The formation of embedded

Au and Pd silicide most likely enhances the structural stability influencing the nanowire growth orientation toward high vertical alignment. We believe that there should be no noticeable difference between pure Au and Pd in terms of degree of penetration into SiO₂ amorphous layer, since these two elements are known to possess very similar physical properties; Pd and Au are completely miscible forming solid solutions, and there exists only $\sim 4\%$ lattice mismatch with similar work functions (Au 5.3 eV; Pd 5.6 eV) and nearly identical electronegativities.¹⁹ This hypothesis is indeed supported by the EDS line-scan profile which shows that the relative atomic ratio of Au/Pd in the penetrated region (Figure 2b) remains nearly constant throughout the scanned region, suggesting similar penetration behavior for both these elements.

To further verify if the partially embedded nanoclusters into SiO₂ is specific to the sputtering technique and not existent with other methods of catalyst deposition such as Au-colloid deposition, we performed similar cross-sectional TEM experiments on annealed Au colloids deposited on SiO₂/Si substrates (panels c and d of Figure 2). A Au colloid of ~ 80 nm diameter can be seen possessing a very thin

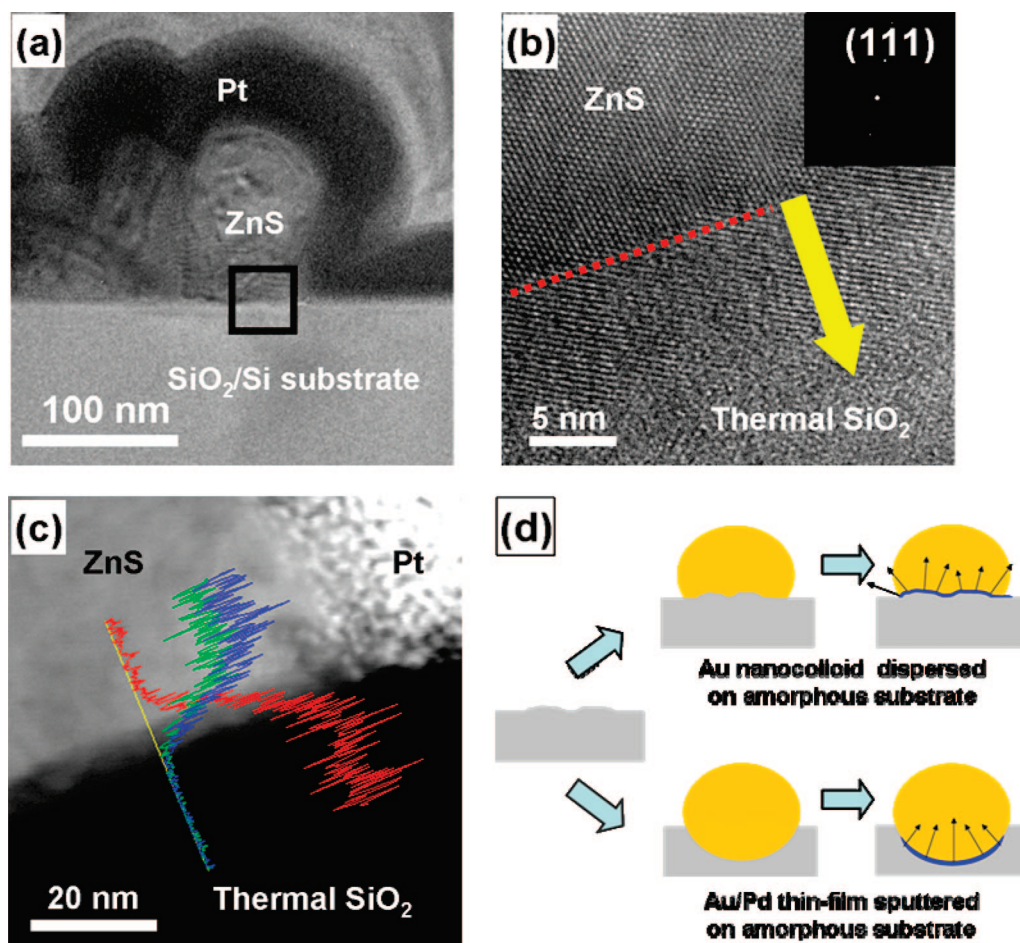


Figure 3. (a) Cross-sectional bright field TEM image of a ZnS nanowire vertically grown on a SiO₂/Si substrate. (b) HRTEM image of the ZnS/SiO₂ interface (from the black box region in (a)) showing interdiffusion of ZnS into SiO₂. Dotted red line indicates nanowire/SiO₂ interface. Inset: Selected area diffraction pattern shows ZnS (111) planes at the interface. (c) ADF-STEM image of the ZnS/SiO₂ interface and its corresponding EDS line-scan profile (blue = Zn, green = S, red = Si). (d) Schematic illustrating initial stage of nanowire growth on rough amorphous substrates. Top: growth catalyzed by Au colloids. Bottom: nanowire growth catalyzed by sputtered thin film.

interfacial layer (<3 nm) into amorphous SiO₂, in sharp contrast to the ellipsoidal Au/Pd nanoclusters deeply embedded into SiO₂ (panels a and b of Figure 2). STEM-EDS line scan analysis performed across the Au/SiO₂ interface (Figure 2d) reveals that Au and Si elements are segregated, suggesting the absence of the reactive interface between the metal/SiO₂ layer, unlike Au/Pd sputtered films.

Having verified that Au/Pd sputtering technique produces an embedded interfacial reactive layer with amorphous SiO₂, the next step is to investigate how this interfacial layer can lead to vertically aligned nanowire growth. To answer this question, detailed structural and chemical composition analyses were performed at the interface of the as-grown ZnS nanowires/SiO₂ substrate. Figure 3a is a low-magnification bright field cross-sectional TEM image of a vertically grown ZnS nanowire on a SiO₂/Si substrate prepared by a FIB lift-out technique. In the HRTEM image of the nanowire/SiO₂ interface (Figure 3b), the (111) single-crystalline structure of the ZnS nanowire was observed to extend into the amorphous SiO₂ layer ~20 nm in depth, as marked by the arrow. This observation is remarkable given the high thermal stability of amorphous SiO₂ (melting point, 1600 °C) and much lower nanowire growth temperature (~770 °C). The

chemical composition of the nanowire/substrate interface characterized by the EDS line-profile reveals Zn and S interdiffused with amorphous SiO₂ approximately 20 nm across the interface (Figure 3c), consistent with the length scale of interdiffused Au/Pd into SiO₂ (Figure 2b). This indicates that the observed interdiffusion of ZnS into SiO₂ initiates at a very early stage of VLS process, facilitated by the interdiffusion of Au/Pd melt with SiO₂ during the catalyst deposition and subsequent annealing.

Root structure at the nanowire–substrate interface has been previously reported for GaAs nanowires on GaAs and for GaP nanowires on Si substrates,^{11,20,21} however in these systems, a crystallographic compatible relationship exists between the nanowires and substrate. Our study presents a unique and previously unexplored feature regarding vertically aligned nanowire growth on amorphous substrates that cannot govern nanowire orientation crystallographically. The schematic in Figure 3d explains the high tendency of vertically aligned nanowire growth on substrates catalyzed via sputtered thin film, in comparison to colloidal catalyst deposition. In typical VLS growth mechanism, the interfacial state of metal/substrate generally affects the nanowire growth direction, which determines the initial nucleation of the nanowire.^{22,23}

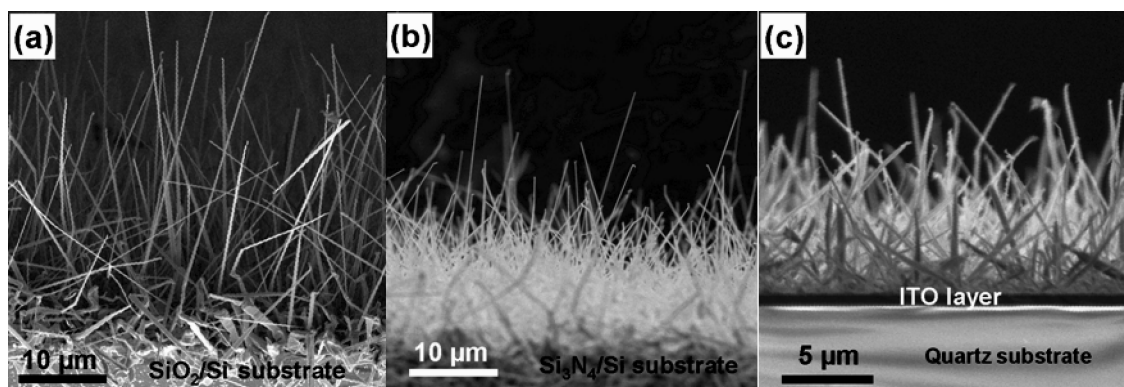


Figure 4. SEM side view images of sputtered Au/Pd thin film catalyzed CdS nanowires on (a) SiO₂/Si, (b) Si₃N₄/Si, and (c) ITO/quartz substrates.

Nanowires tend to grow in random orientations on amorphous substrates where nanowire growth direction is not guided by the substrate crystallography. Conceivably, this is because even a small degree of surface roughness can greatly affect the metal/substrate interface by providing random heterogeneous sites for nanowire nucleation. Such heterogeneities are not compensated by the relatively small area of metal-catalyst/substrate interface, and consequently no particular orientation is preferred for nucleation. Meanwhile, for the case of sputtered thin films, the surface roughness is more than compensated by the embedded metal nanoclusters into the substrate providing larger interfacial area for heterogeneous nucleation. In this case, nanowire nucleation proceeds normal to the metal/substrate interface and is bounded by the confined metal catalyst, therefore limiting the freedom in growth direction as well as providing high mechanical stability (Figure 3d) due to continuous atomic bonding into the substrate.

The above schematic implies that vertically aligned nanowires of any material can be obtained on any substrate via sputtered-catalyst approach. To demonstrate the generality of our technique, we grew CdS nanowires on SiO₂/Si, Si₃N₄/Si (Si₃N₄ thickness ~ 100 nm), and indium tin oxide (ITO) coated (thickness ~ 1 μ m) quartz substrates (Figure 4).¹⁶ Significantly, the sputtered Au/Pd thin film catalyzed CdS nanowires grew vertically aligned on all the substrates suggesting that this technique is indeed general and versatile although detailed interfacial analysis would be important for further studies. Nevertheless, growth of vertically aligned nanowires will be technologically important in integrating crystallographically incompatible nanowires on an arbitrary common platform. In particular, vertically aligned nanowires grown on complex ITO substrate will be critical to assemble nanowire-based photovoltaic cells where efficient carrier transport is realized directly through nanowires between top/bottom electrodes.

The results and analysis in this letter imply that the interface of the catalyst/substrate plays an important role in determining the initial stage of nanowire orientation through heterogeneous nucleation/growth process. Even in epitaxially oriented nanowires, upon nucleation and little growth, the catalyst is lifted from the substrate and subsequent growth occurs at the catalyst-nanowire interface and not at the

substrate, which is similar to our vertically aligned nanowires. Therefore, one of the reasons for not being able to achieve complete vertical alignment in our experiments in comparison to epitaxially oriented nanowires could be the relatively high base pressure of our growth system (300 torr) which is known to affect the general morphology of growing nanowires via catalyst/nanowire reaction. Kodambaka et al. showed via in situ TEM techniques that variations in oxygen content and vacuum pressure drastically change the degree of vertical alignment of epitaxially growing Si nanowires on crystalline Si substrates.²⁴ This in addition to other factors such as structural variations, kinks and stacking faults in growing nanowires under highly nonequilibrium growth conditions at high pressures in comparison to ultrahigh-vacuum systems where epitaxial growth of nanowires is typically performed at mTorr level vacuum base pressures could also be responsible to limit the degree of vertical alignment. Nevertheless, our experiments clearly demonstrate that vertical alignment of nanowires can be achieved using our technique and is a significant advance toward achieving general alignment of nanowires on arbitrary substrates.

In conclusion, we have demonstrated a versatile technique to grow single-crystalline, vertically aligned nanowires on arbitrary substrates using sputtered thin-film catalyst deposition. High Resolution TEM data at the interface clearly shows that embedding the catalyst in the substrate is the key to achieve vertical alignment by providing mechanical stability to the nanowires at the interface. Further control over vertical-alignment can be obtained by growth at ultrahigh vacuum conditions while control over nanowire density can be achieved down to single-nanowire level by patterning catalyst nanoislands with sputtering by using nanoimprint or nanosphere lithography.^{25–28} We believe such a general approach to grow vertically aligned nanowires will become an important step toward assembling highly integrated electronic,^{8,9,29} photonic³ and photovoltaic¹⁰ devices on any conventional or unconventional substrates and can also enable novel three-dimensional architectures.^{30,31}

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Supporting Information Available: Figures showing side view SEM image of nanowire growth and X-ray diffraction pattern of ZnS nanowires. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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