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Vapor-Liquid-Solid Etch of Semiconductor Surface Channels by Running Gold Nanodroplets

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Abstract

We show that Au nanoparticles spontaneously move across the (001) surface of InP, InAs, and GaP when heated in the presence of water vapor. As they move, the particles etch crystallographically aligned grooves into the surface. We show that this process is a negative analog of the vapor-liquid-solid (VLS) growth of semiconductor nanowires: semiconductor dissolves into the catalyst, and reacts with water vapor at the catalyst surface to create volatile oxides, depleting the dissolved cations and anions and so sustaining the dissolution process. This VLS etching process provides a new tool for directed assembly of structures with sub-lithographic dimensions, as small as a few nanometers in diameter. Au particles above 100 nm in size do not exhibit this process but remain stationary, with oxide accumulating around the particles.

Keywords

surface-directed; VLS; nanochannel; surface etch; directed assembly; scalable; semiconductor

The self-assembly of semiconductor nanostructures has always held a great fascination, as it opens up new possibilities for nanoscale technologies and at the same time offers novel growth phenomena of fundamental interest. In this regard, the traditional metal-catalyzed Vapor-Liquid-Solid (VLS) growth of semiconductor nanocrystals has resulted in formation of a wide variety of free-standing semiconducting nanowires (NWs) and novel device architectures and concepts.^{1–11} In recent years, observation of crawling metal droplets led to the development of surface-directed VLS growth of nanowires,^{12, 13} including lateral heteroepitaxial growth of ZnO,¹⁴ GaN,¹⁵ Mg₂SiO₄,¹⁶ ZnSe¹⁷ nanowires on various substrates, and homoepitaxial growth of GaAs,¹⁸ Ge,¹⁹ and Si²⁰ nanowires. This type of

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ASSOCIATED CONTENT

Supporting Information. Examples of trenches formed within a Au pattern on InP, SEM images of formed nanochannels on GaP and InAs and corresponding XEDS elemental analysis, phase diagram of Au-In, and SEM images of millimeter long nanochannels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

*Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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surface-guided growth is inherently capable of precise control over orientation of the overgrown nanocrystals and is particularly promising for integration into more complex device structures.

Here we demonstrate a process in which a nanoscale Au alloy droplet moves along a semiconductor surface leaving behind a long straight trench. The trenches so formed are crystallographically aligned, and appear smooth and free of residue. The process does not occur in vacuum or dry nitrogen, but occurs on semiconductors such as InP, GaP, or InAs when water vapor is introduced. This process is expected to have diverse potential applications, including cutting apart regions of a thin film, serving as template for subsequent growth, and integration of electro-optical microdevices with nanofluidic platforms.

Many mechanisms can cause metal droplets to run across a semiconductor surface.^{21–24} Our experiments indicate that here we are observing etching by a reverse VLS process,²⁵ a reverse analog of the lateral nanowire growth described above: the Au dissolves the semiconductor, and catalyzes a reaction with the water vapor, converting the semiconductor to volatile oxides which escape into the vapor. Just as in VLS growth, this allows the continuous linear growth of a quasi-one-dimensional nanostructure, with the diameter determined simply by the size of the catalyst particle.

We begin by patterning an InP (001) surface with regions of very thin Au film, which breaks up into small particles upon heating. The sample is then heated in a horizontal tube furnace with a ramp rate of 33 °C/min under an ultra-dry nitrogen carrier gas and a flow rate of 0.5 standard liters per minute (SLPM). To introduce water vapor in the system, the carrier gas is bubbled through water at room temperature. Alternatively, hydration water of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was used as a water source by heating its 98% powder when placed upstream relative to the gas flow direction under the specified heating condition above. For a 7 nm thick Au pattern on InP, if the carrier gas and water vapor are introduced while the temperature is below 300 °C (Figure 1a), InP shows etched pits that are formed within the Au coated areas as shown in Figure 1b (supporting information, Figure S1). These faceted pits can merge and form larger oriented trenches in the $\langle 110 \rangle$ direction. Similar lattice void formation at interfaces of Au/GaAs or Au/InP has been observed in the absence of oxygen or water and attributed to the loss of volatile reaction products such as Arsenic or Au_2P_3 .^{26, 27}

If instead the carrier gas and water vapor are introduced in the temperature range of 300 °C to 520 °C (Figure 1c), long oriented nanochannels form on the InP (Figure 1d). The leading ends of the resulting nanochannels contain Au droplets, as marked with arrows in the figure. This observation indicates that the channel is formed by Au droplets at the periphery of the Au pattern which become mobile on the surface and form the channels by a metal-catalyzed etch process.

In an effort to further understand this behavior, we terminated the reaction at lower temperatures. The minimum temperature required to observe nanochannels on InP is found to be roughly 440 °C (Figure 1e-f), below which no obvious surface reaction is observed (Figure 1g-h), even in the presence of water vapor. However, atomic force microscopy

(AFM) size measurements (inset) show a two-fold increase in the height of the Au droplets at 410 °C indicating infusion of In and perhaps P into Au, which is known to occur at temperatures as low as 320 °C.²⁸

Figure 2a shows the cross-section of a nanochannel along its length (inset shows plan view) illustrating the position and shape of the Au droplet at its leading edge and the lattice void left behind by the droplet motion. Examining the interface of Au/InP in Figure 2b using scanning transmission electron microscopy in a high-angle annular dark field mode (STEM-HAADF) shows the sharp interface is made from a (111) plane of single crystal InP interfaced with Au. TEM analysis also shows the interface is free of any new crystal phases, amorphous or intermediary layers. A cross-section along the channel width (Figure 2c) shows a crystalline V-shaped groove, reflecting the slow etch rate of the (111) planes relative to the (100) at the bottom of the channel. During the reaction (at elevated temperatures), the liquid AuIn alloy would presumably have a flat interface with InP (111) at the etch front and a round shape at the L-V interface much like what is observed in VLS growth of nanowires.

As the temperature drops below the miscibility range of Au/In, some of the excess In, which remains quite mobile, diffuses away and leaves Au. In this process, the metal alloy shrinks and its free surface becomes distorted as seen in the cross-section of Figure 2a. Elemental maps acquired via X-ray energy dispersive spectroscopy (XEDS) show that the Au particle (Figure 2d-e) still contains a few % In. Oxygen is also detected in the Au particle (figure 2f), most likely indicative of residual oxidized In and P species. This oxidation is believed to occur by reaction with water at the droplet surface, as no gas phase decomposition of water is expected at the applied temperature.

As illustrated in Figure 3, we propose that, at the initial low temperatures, the Au droplet swells due to incorporation of In and P from the underlying substrate while sinking into the InP (Fig. 3a-b) forming nanoscale pits with four (111) facets. We note that two of these facets are nominally In-terminated while the others are P-terminated. Previously, it has been shown that the In-terminated {111} facets interfaced with Au have an etch rate three times faster than those which are P-terminated.²⁹ However, this difference in etch rate does not seem to play a role in anisotropic growth of Au-catalyzed nanochannels; ultimately the Au droplet only wets one of these facets and thus continues its reaction irrespective of the etch rates of the other facet (Figure 3c-d). Examining the orientation of the four side facets of a nanochannel indicate that nanochannels elongate from the P-terminated facets; therefore, a nanochannel has two possible growth directions, along [110] or $\overline{[110]}$.

During the reaction, dissolved In and P saturate the Au droplet. In the presence of water, apparently indium oxide and phosphorus oxide form at the droplet surface and then evaporate. The under-saturated droplet can then further dissolve the surrounding InP resulting in continuous etching of the substrate at the L-S interface. We observe a similar process for surface-directed VLS etching of other semiconductors such as InAs and GaP at 540 °C and 800 °C, respectively. In those cases, we also observed free-standing nanowires of their metal oxides at the location of the original Au patterns on the substrate (Figure S2). Drilling of vertical holes by a reverse-VLS process via Au-catalyzed etching has been

observed previously for Si in the presence of an etchant gas of Cl_2 . This process involved Au-Si alloying followed by reaction of Si with the halogen gas resulting in the escape of SiCl_4 at about 450 °C and formation of pores in silicon.²⁵

We also observe the surface-directed VLS etch process for Au droplets as small as a few nanometers, resulting in very narrow nanochannels on the surface. Examples are shown in Figure 4 (a-d) where nanochannels more than 40 μm in length and as thin as 2 nm are formed from 3 nm thick Au patterns. As seen in Figures 4(a-c), the initial site of the nanochannels can be defined by the metal catalyst, with the substrate determining the $\langle 110 \rangle$ channel orientation.

At 520 °C, In has a solubility of about 8 at.% - 9 at.% in Au,³⁰ which according to the In-Au phase diagram corresponds to a AuIn droplet that could be in solid or liquid form (Figure S3), raising the possibility of a vapor-solid-solid (VSS) etch process as well. We believe the process here must be VLS, for two reasons. First, we observe that long nanochannels are typically formed within 15 minutes of reaction time. This suggests a VLS process, as the VSS process is generally much slower. Second, the minimum temperature for channel formation (roughly 440 °C) is in good agreement with the minimum temperature for forming a Au-rich liquid (450 °C) (see phase diagram, Fig. S3). High-angle-annular bright-field STEM of the cross-section of long nanochannels (and insets) in Figure 4d show the nanochannels typically have 2 or 3 sides depending on the size of the bottom (100) plane. This figure also shows, in some cases, an amorphous layer forms at the vicinity of nanochannels as shown in the lattice resolved image of Figure 4e. SIMS profiling at the location of long nanochannels shows that the amorphous layer is an oxidized layer containing considerably more phosphorus oxide than the indium oxide (Figure 4f). This could indicate a higher rate of loss of the oxidized indium species from the amorphized layer of InP. Since the substrate must be crystalline to allow formation of these highly oriented nanochannels, we believe this oxidation is a secondary effect and occurs after channels are formed in InP. By controlling the period that water vapor is introduced, it is expected to avoid oxidation of the formed nanochannels.

By increasing the Au film thickness or use of larger size colloidal Au nanoparticles, it is possible to increase the channel width; however, thick nanochannels systematically grow more slowly and are shorter than thin ones. An example is shown in Figure 4g (also Fig.S4) where nanochannels are formed from an about 7 nm thick Au film. As seen, for these larger-diameter nanochannels the facets are more readily identified in the micrographs. As the Au droplet size increases above 100 nm or larger, the surface-directed etch process completely stops. This is further demonstrated in Figure 5a, where Au nanoparticles with an average size of about 100 nm dispersed on InP undergo the nanochannel etch condition shown in Figure 1c.

For larger particles of this size distribution, a non-faceted pit with an average diameter of about 400 nm forms underneath the Au particles indicating loss of the underlying InP. The etched cavity as well as the top surface of the Au particle were coated with an electron-deposited carbon layer (appears in dark gray) to protect the structure during ion milling and polishing. This area can be seen as the dark gray region in the STEM-HAADF cross-

sectional image of Figure 5b. According to XEDS maps in Figure 5c (gray scale maps for each element are shown in Fig.S5), there are two regions (colored in cyan) that contain oxidized InP, namely, the internal surface of the cavity and a thin shell surrounding the Au particle. (The green area shows the deposited protective carbon, which was introduced during the cross-section preparation.) The formation of an oxide layer at the InP interface with particles larger than 100 nm in size (Figure 5c-d) indicates that the oxide forms more rapidly than it can escape, resulting in accumulation at the Au/InP interface (Figure 2). The oxide layer formed at the interface can block a VLS mechanism by preventing direct contact between metal and semiconductor. The oxide formation step in this case seems analogous to chemical or photochemical oxidation step of metal-assisted wet etch of semiconductors such as Si or InP using noble metal catalysts of Pt and Au.^{31, 32} Typically, in such processes the semiconductor at the vicinity of the metal catalyst is etched through iteration of oxidation and oxide dissolution steps.³¹

In addition to particle size, the temperature at which water is introduced to the system is crucial to form direct contact between Au and InP in order to promote the VLS-based surface channel etch. If water is introduced prior to the heating and kept on continuously through the heating phase (condition of Figure 1a), the Au motion never occurs, even for well-separated Au nanoparticles smaller than 100 nm. Under this condition, it is likely that a process analogous to that proposed for larger particles takes place, namely, formation of an oxide layer at the Au/InP interface. Given the fact that the Au and InP alloying reactions starts at temperatures as low as 320°C,²⁸ occurrence of oxide formation at the interface of the InP/Au droplet is highly probable during early introduction of water to the process. The oxide at the interface stops the necessary Au/InP interface for nanochannel formation.

For applications as hollow channels, as for nanofluidics, it is important to be able to properly seal nanochannels from their top side. Here we demonstrate some early results on the ability to form nanochannels on designated areas of InP that are pre-coated with a protective top layer. A simple flow process is illustrated in Figure 6a, where, first, a pattern of Au catalyst is deposited (i) to define the starting point of the nanochannels. Then a channel cover layer is placed on the growth path of nanochannels (ii). Our results show that a cover layer consisting of electron-beam deposited carbon (≈ 1000 nm thick) placed on the path of nanochannels does not impede their growth (iii). Figure 6b shows passage of nanochannels underneath the carbon layer, indicating that the water vapor diffusion could take place through the cover layer provided that it does not react or trap the water molecules. Interestingly, the nanochannels that undergo the cover layer slow down in growth and grow shorter than the uncovered ones during the 15 minutes duration of the experiment. This approach also allows adjusting the channel length by fully quenching the etch process via either blocking the permeability of water through the cover layer or poisoning the metal catalyst at a specific position.

Flow of this process is schematically shown in Figure 6c, where a channel blocking layer is placed at the projected termination site of the nanochannels. An example is shown in Figure 6d, in which 500 nm-thick FIB-deposited Pt pads deposited prior to the growth of nanochannels block growth of a select group of nanochannels due to its alloying reaction with Au. Overall, our work suggests that the surface-directed VLS etch process could be

used as a new bottom-up nanofabrication approach for the large scale integration of nanoscale devices and means for nanoscale material delivery and processing.

In summary, we presented a new type of metal-assisted semiconductor etch process which operates based on a VLS process. Some of the key characteristics of the formed nanochannels were illustrated including structure and etch and based on the observed V-L and L-S interfaces an etch mechanism was proposed. It was shown that a Au catalyst below a certain size alloys with the underlying semiconductor and in the presence of water locally catalyzes oxidation of the semiconductor. The oxidized elements depart the alloyed catalyst droplet forming a nanochannel behind. Au catalysts with very small sizes were shown to travel to remarkable distances forming directed nanochannels on the surface. The etch process was shown to be site specific allowing control over the direction of the nanochannels. Control over the dimensions of nanochannels as well as site specific coating or blockage of nanochannels were illustrated underlining the potentials of this process for scalable surface nanoengineering. The reported surface phenomenon is expected to find use in development of advanced materials as well as multifunctional heterogeneous nanosystems including electro-optical and nanofluidics.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Change in surface structure of InP (001) coated with 7 nm thick Au patterns upon increasing the water content of the carrier gas. (a) Water vapor is introduced between 25 °C and 300 °C and (b) its representative SEM image shows thick trenches are formed within the Au pattern. (c) Water vapor is introduced between 300 °C and 520 °C and (d) its representative SEM image shows nanochannels are formed at the edge of the Au pattern. The leading ends of the resulting nanochannels contain Au droplets, as marked with arrows. (e-h) Minimum temperature that nanochannels are formed on InP; below this temperature (g-h) Au droplets

alloy with InP without appearance of nanochannels. Inset shows the AFM line profile of the Au droplets before (dark line) and after heat treatment at 410 °C (red line).

Figure 2.

(a) STEM-HAADF image of a cross-section of a nanochannel along its length formed on InP (100). The preferred growth direction of nanochannels is $\langle 110 \rangle$. The upper half of the image is the FIB-deposited protective carbon layer. The bright region at the left end of the nanochannel is a Au catalyst droplet. The L-S interface is where the Au droplet dissolves InP. Inset is a SEM image showing the plan view of the nanochannel. (b) STEM-HAADF image of Au catalyst at its nearly flat interface with InP (111). (c) STEM-HAADF image of the cross-section of a nanochannel along its width shows the InP (111) planes and its V-shaped profile. (d-f) Elemental maps of Au, In and O collected from the image shown in part (a).

Figure 3.

Different stages of the proposed VLS etch mechanism illustrated in side and top views. a) Au droplet starts alloying and sinks into InP, where it forms its side (111) and bottom (100) faces (b). c-d) At high temperature, semiconductor dissolves into the catalyst, is oxidized, and escapes into the vapor, forming a faceted channel on the crystal surface.

Figure 4.

(a) Arrays of 3 nm thick Au lines deposited orthogonally to the $\langle 110 \rangle$ direction of InP result in arrays of nanochannels on both sides of the Au pattern. The highlighted box is magnified in (b) indicating the surface density, directionality and remarkable length of the nanochannels. Morphology of nanochannels at one end of the Au pattern is shown in part (c). As seen, the bulk of the Au pattern completely reacts with InP and it is only at the edge of the pattern that nanochannels are formed. (d) Representative STEM-HAADF image of the cross-section of long nanochannels. Inset shows a close view of channel cross-sections, which appear in V-shape and trapezoid. The highlighted box in red shows part of the 50 nm thick amorphous layer formed on InP surface. This interface is shown in the bright-field STEM image of part (e). (f) SIMS profile of the amorphous layer collected from an area covered with very long nanochannels reveals the high concentration of oxidized phosphorous in this layer. (g) Increasing the Au pattern thickness from 3 nm to 7 nm results in formation of thicker nanochannels with well-developed facets.

Figure 5.

(a) Plan view of Au nanoparticles with an average size of 100 nm deposited on InP (100), after reaction with water vapor. Irregular pits form underneath the larger size particles, while the smaller ones undergo the VLS etch and form channels. (b) A representative STEM-HAADF cross-sectional image of a Au particle/InP. The dark area underneath the particle is the etched crystal that is filled with FIB-deposited carbon. The XEDS elemental map of this region in part (c) shows the presence of an InP oxide layer (cyan) surrounding the carbon-filled area (blue). Red indicates the unaffected InP substrate. Data shows that the Au particle (yellow) is also coated with a thin shell of oxidized InP. (d) The faceted Au particle coated with an about 20 nm oxide layer.

Figure 6.

(a) Steps for forming covered nanochannels. (b) The Au catalyst droplets can lead nanochannels underneath a 1 μm -thick FIB-deposited carbon layer; however, their length becomes shorter (red arrows) compared to the unexposed ones (blue arrows). (c) Steps for blocking the growth of nanochannels. (d) 500 nm thick Pt layers terminate the growth of nanochannels (red arrows); however, the nanochannels between the Pt layers continue their growth (blue arrows).