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A unique solid-solid transformation of silver nanoparticles on reactive ion-etching-processed silicon

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Abstract

Processes that combine nanoparticle suspensions with micromechanical or microelectronics platforms can reveal new phenomena unique to nanoscale objects. We report that silver nanoparticles react with silicon wafers that have been patterned by reactive ion etching (RIE) in SF_6/O_2 plasma. This reaction results in the localized deposition of silver on the patterns. Through the modification of the reaction conditions, the reaction mechanism was explored. Redeposition of the sputtered RIE products is suggested as the key to this transformation. The new silver deposition process was utilized to localize the growth of gold nanoparticles and silicon nanowires on the vertical sidewalls of patterns in silicon, demonstrating a simple route to the fabrication of overhanging nanoscale objects.

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

1. Introduction

The electrical, electrochemical and chemical properties of metal/semiconductor interfaces are of interest to fundamental and applied science [1]. The interface between group IV semiconductors and metals, particularly in the presence of fluoride-containing electrolytes, has been extensively studied [1-16]. Galvanic displacement is observed at this interface leading to metal ion reduction and metal deposition coupled with semiconductor oxidation and dissolution [9]. These processes, on the one hand, are undesirable consequences of the presence of metal ion impurities in microelectronics fabrication facilities. On the other hand, these processes provide routes to metal plating and metal nanostructure fabrication [8]. A particularly versatile metal-semiconductor combination is that of silver and silicon. Immersion of silicon substrates in baths containing Ag(I) salts and fluoride derivatives can result in the plating of films, the deposition of nanoparticles of various shapes [5, 6, 17], the formation of high-aspect ratio channels in silicon [10] and the formation of silicon nanowire arrays [11–13, 18, 19].

In all of the above processes, the silver source is soluble Ag⁺ and silicon is oxidized and removed by reacting with the fluoride provided by the solution. Here, we report on the reactivity of crystalline silver nanoparticles towards silicon wafers that have been patterned by reactive ion etching (RIE). This reaction is unique to the nanoscale form of the silver source, is not observed with silver ions and does not require fluoride in the solution. As with other transformations unique to nanoparticles, the outcome of the reaction depends on the size of the nanoparticles and on the surfactants passivating the nanoparticle surface [20-22]. This solid-solid transformation results in the recrystallization of the nanoparticles into new nanoparticle shapes. However, there is little or no chemical transformation driving the process. In this paper, we study the mechanism of the reaction between silver nanoparticles and patterned silicon wafers and demonstrate the utility of this process for the selective growth of silver nanoparticles, gold nanoparticles and silicon nanowires on the vertical sidewalls of a patterned substrate. The unexpected interaction between the etched substrate and the nanoparticles draws attention to new phenomena that may be recognized as researchers combine techniques for the top-down fabrication of microelectronic structures with techniques for the bottom-up fabrication of nanostructures, and combine micro- and nanoscale objects in ever more sophisticated and complex devices [23–26].

2. Experimental procedures

2.1. Materials

1,5-pentanediol (Acros, 98%), silver nitrate (Alfa-Aesar, 99.995% metal base), copper(II) chloride (Sigma-Aldrich, 97%), polyvinylpyrrolidone (Sigma-Aldrich, $M_w = 55$ K), 4-mercapto-1-butanol (Sigma-Aldrich, 95%), sodium borohydride (Fisher Scientific) and ethanol (Pharmaco-AAPER, 200 proof, anhydrous) were used as received. P-type (100) boron-doped silicon wafers, 20–30 Ω cm resistivity, were used as substrates (Silicon Inc.). Polymethylmethacrylate e-beam resist (950PMMA A4) and developer (MIBK/IPA 1:3 developer) were purchased from MicroChem Corp. S1813 photoresist and CD-30 developer were purchased from Shipley. Deionized (DI) water was obtained from a Thermo Scientific EASYpure[®] RoDi ultrapure water purification system.

2.2. Pattern formation by e-beam lithography (EBL)

Polymethylmethacrylate (PMMA) resist was spin-coated on silicon substrates at 4000 rpm for 45 s and subsequently baked at 180°C for 1 min. E-beam writing was performed with a Raith e_LiNE system, an electron beam lithography tool, using an accelerating voltage of 15 keV and an exposure dose of 145 μ C cm⁻² with a 10 μ m aperture. In patterning dose matrices, exposure dose was varied in the range of 70-301 μ C cm⁻². After the patterns were developed in a MIBK/IPA developer solution, the patterns were transferred to the underlying silicon substrates by dry etching. The dry etch was carried out in a reactive ion etching system (Trion Tech.) for 10 s with 100 W power and a pressure of 50 mTorr in a flow of SF₆/O₂ (50:10 sccm). Unless noted otherwise, the PMMA resist was retained during subsequent steps. The EBL patterns were square arrays of circular pores 0-250 nm in diameter, lines 100 μ m long and 150 nm wide, and rings 2.15 μ m wide. Additionally, a clean silicon wafer was processed by RIE as a control.

2.3. Pattern formation by photolithography

100 μ m squares, 50 μ m cross bars and 10 μ m wide line trenches were patterned onto silicon by conventional photolithography and dry etching. Shipley1813 photoresist was spin-coated on silicon substrates at 3000 rpm for 40 s, followed by soft bake of the coated substrate at 90 °C for 1 min. The exposure was carried out for 6 s using a Cr mask (EVG 620 mask aligner). Patterns were developed in the CD-30 developer for 60 s. The patterns were transferred to the silicon substrates in a reactive ion etching system (Trion Tech.) using the same conditions as with the EBL patterns. After the RIE process, the photoresist layer was removed with toluene. Additional control experiments were performed without removing the photoresist from the patterned wafers.

2.4. Preparation of Ag solutions

Solutions of silver ions and suspensions of silver nanospheres (AgNSs) and silver nanoparticles (AgNCs) were freshly prepared. The suspensions contained borate-coated AgNSs 20 ± 10 nm in diameter (1 or 0.025 mM by metal) or polyvinylpyrrolidone-coated AgNCs $70 \pm 5-100 \pm 10$ nm in edge length (1 or 0.5 mM by metal). Silver ion solutions were prepared as 1 mM AgNO₃ in DI water or ethanol.

AgNCs were synthesized in pentanediol by the polyol reduction process [27]. The AgNCs were cleaned with four centrifugation-resuspension cycles (5 min, 13 000 rpm) in ethanol (EtOH) to remove pentanediol, excess polyvinylpyrrolidone (PVP) and residual silver ions. The AgNCs were resuspended in EtOH or DI water for the experiments.

AgNSs were synthesized by reduction with sodium borohydride [28]. The AgNS suspensions were used as made or after dilution with DI water.

For ligand exchange, 10 μ l of 10 mM 4-mercapto-1butanol (MBuOH) solution were added to 1 ml of the nanoparticle suspensions (0.025 mM AgNSs or 0.5 mM AgNCs). The solutions were then cleaned by centrifugation–resuspension cycles to remove excess MBuOH molecules.

2.5. Oxygen plasma treatment

The O_2 plasma treatment of the substrates was carried out in a reactive ion etching system (Trion Tech.) using 150 mTorr O_2 atmosphere at a power of 50 W for 30, 45, 60, 150 and 300 s.

2.6. Formation of silver deposits on patterned silicon substrates

Silicon substrates were submerged in the silver solutions for 30 min and 15 h at room temperature. At the end of the reaction period, the substrates were thoroughly rinsed with ethanol and DI water.

2.7. Galvanic exchange

Gold nanoparticles were grown by galvanic exchange at an elevated temperature (100 °C) [29]. Silicon substrates were placed in a vial containing 10 ml of boiling DI water. While stirring, 5 ml of 0.1 mM HAuCl₄ were added dropwise to the vial. After 10 min, the substrates were retrieved, thoroughly rinsed with DI water and dried.

2.8. Silicon nanowire (SiNW) growth

Growth of SiNWs was conducted in a CVD reactor (Atomate Corp.). Silicon substrates bearing gold nanoparticles were placed in the center of the reactor. The chamber was evacuated with a roughing pump and back-filled with Ar (0.5 Torr, 100 sccm). The substrate temperature was raised to 480 °C at a rate of 10 °C min⁻¹. SiH₄ was introduced into the chamber at a flow rate of 20 sccm and pressure of 2 Torr for 2 min, resulting in gold-catalyzed nanowire growth.



Figure 1. SEM images of silver deposits on EBL-patterned substrates that were dipped in EtOH suspensions of AgNCs for 15 h. (a) Deposits in a dose matrix. Exposure dose: 70–301 μ C cm⁻². Scale bar: 1 μ m. (b) Deposits in a section of a wide ring pattern. Scale bar: 500 nm. (c) Deposits along a crossing of two narrow lines. Scale bar: 1 μ m. (d) A deposit with dendritic shape and faceted ends on a defect site. Scale bar: 2 μ m.

3. Results and discussion

3.1. Conditions affecting the solid–solid transformation of silver nanoparticles

Silver nanoparticles in EtOH or DI water suspensions react at room temperature with lithographically patterned silicon substrates to generate deposits of silver ranging in size from several nanometers to several microns. We will first present the results from the reaction between PVP-coated AgNCs in EtOH and e-beam-patterned, dry-etched substrates (covered with the patterned PMMA layer). As a model reaction, this reaction was studied to the largest extent.

Figure 1 shows the morphology of the reaction products obtained in (a) small pores, (b) a portion of a wide ring-shaped trench, (c) thin, long trenches and (d) an isolated, micron-size defect in the PMMA film. The morphology of the deposit can be globular, faceted or dendritic, and has no resemblance to the original cubic shape of the silver nanoparticles in solution. Furthermore, deposits smaller in size than the original AgNCs and others much larger in size were found on the silicon substrates. The images clearly demonstrate that the deposition of silver is localized to the patterned areas that were exposed to the electron beam and the reactive ion beam. No silver particles were found on planar areas covered with PMMA. Moreover, regardless of the aspect ratio of the patterns the product forms at substantially higher densities along the edges

and the vertical walls of the patterns than along its horizontal surfaces. This is clearly observed in the micron-size patterns in figures 1(b) and (d), where the larger and denser silver deposits line the vertical walls of the trench and the perimeter of the defect. The same trend holds for the sub-micron patterns in figures 1(a) and (c), yet due to the large size of the deposits compared to the patterns, the edges are not always discerned.

The pattern shown in figure 1(a) is a 'dose matrix' consisting of a 5×5 array of small pores, ranging from 0 to 250 nm in diameter. The diagonal dashed lines separate groups of pores by size (i.e. by e-beam dose). The pore diameter increases as the dose of the e-beam increases from 70 μ C cm⁻² (bottom left pore) to 301 μ C cm⁻² (top right pore). The distribution of reaction products seen in this matrix demonstrates that the size and morphology of the silver deposits has a complex dependence on the lithography parameters. While there is a wide variation in the size and shape of the deposits in the pores, the average size of the deposits increases with pore size up to ~ 200 nm in diameter, and then decreases. We attribute this non-monotonic trend to the competing dependences of the amount of silver deposited on both pore size and pore aspect ratio: large diameter pores and high-aspect ratio pores yield large silver deposits. The effect of aspect ratio on the silver deposits is demonstrated in the comparison between a wide trench (figure 1(b)) and narrow line patterns (figure 1(c)). Larger silver deposits are found in the high-aspect ratio line pattern.



Figure 2. SEM images of silicon substrates that were dipped in EtOH suspensions of AgNCs for 24 h at various patterning stages. (a) After electron beam exposure (array of uniform circles patterned at 145 μ C cm⁻²). (b) After developing the PMMA resist. (c) After RIE. (d) Silicon wafer dipped in an EtOH suspension after SF₆/O₂ RIE with no resist (not patterned). All scale bars: 2 μ m.

Figure 1(c) provides an additional clue to the mechanism of formation of silver deposits. The line pattern created by the EBL writer on the PMMA film and transferred to the silicon by RIE is 150 nm wide. While the substrate was immersed in EtOH the PMMA layer shrank and shifted with respect to the underlying substrate to expose a $\sim 1-3 \mu$ m wide band of silicon. We observe that the planar silicon layers surface exposed by a shift of the PMMA is free of silver, while the vertical walls of the line pattern in both the PMMA and the silicon layers are decorated with silver nanoparticles. The nanoparticles attached to the upper section of the sidewall (PMMA layer) are larger than those in the lower section (silicon layer).

The silver deposit shown in figure 1(d) is typical to those seen in defect sites. The center of the structure displays a dendritic morphology, suggesting a high reaction rate at the initial stage of formation, and the peripheral grains are large, faceted single crystals that were formed at a slower rate. The size of the silver structures formed in the defect sites is, on average, larger than the structures formed in the EBL patterns, possibly due to the lack of competing nucleation sites in close proximity.

The conditions for the formation of silver nanostructures along the lithographic patterns were investigated by varying the substrate (figures 2, 3(b) and (e)) and the silver source (figure 3). The formation of the silver deposits was investigated by submerging the silicon substrate in the AgNC suspension following every step in the sequence of the

nanofabrication of arrays of uniform pores. The substrate was tested after spin-coating, after exposure to the electron beam (figure 2(a)), after soaking in the developer (figure 2(b)), after the exposure to the ion beam (figure 2(c)) and after removal of the resist in acetone. No silver deposits were found in substrates prior to the SF₆/O₂ RIE treatment and all silicon substrates contained silver deposits if they have been previously treated by SF₆/O₂ RIE. Furthermore, experiments to form silver deposits on a RIE-treated silicon wafer that contained no lithographic patterns tested negatively (figure 2(d)), with only unperturbed AgNCs occasionally adhering to the surface. These tests indicate that the RIE process makes the silicon reactive towards silver nanoparticles and that the EBL step has an indirect role in facilitating the solid-solid silver transformation. To exclude the possibility that sensitized PMMA polymer chains interacted with the AgNCs to form the deposits, the transformation was demonstrated to occur also (i) when PMMA was replaced by Shipley 1813 photoresist and e-beam lithography was replaced by photolithography (figure 3(e)) and (ii) after the removal of the resist with an organic solvent.

Experiments were repeated with different sources of silver, namely Ag(I) ions from solvated AgNO₃ (figures 3(a) and (d)), PVP-coated AgNCs (figures 3(b) and (e)) and borate-coated AgNSs (figures 3(c) and (f)). The AgNCs and AgNSs formed silver deposits on the edges of EBL and photolithography patterns. Silver deposits did not form when AgNO₃ solutions were used. The nanoparticle suspensions



Figure 3. Deposits in EBL-patterned dose matrices (exposure dose: $70-214 \ \mu C \ cm^{-2}$) using different sources of silver: (a) 1 mM AgNO₃ in EtOH, (b) 1 mM AgNCs in EtOH and (c) 1 mM AgNSs in water. Deposits in photolithography-patterned step edges using different sources of silver: (d) 1 mM AgNO₃ in water, (e) 0.5 mM AgNCs in water and (f) 0.025 mM AgNSs in water. Substrates (d)–(f) were cleaned with O₂ plasma for 45 s prior to the reaction with silver. All scale bars: 1 μ m.

may contain trace amounts of silver ions, but substantially less than 1 mM (the concentration of Ag^+ in the AgNO₃ solutions). These experiments establish that silver deposits do not form through the reduction of silver ions from solution. When supplied with a high concentration of AgNSs (1 mM), the solid-solid transformation resulted in two new silver deposit morphologies: nanoflowers, similar to the dendritic morphologies seen with AgNCs but lacking faceted regions, and nanofilaments with high-aspect ratios. These morphologies suggest that the reaction rate is higher for the AgNSs compared to the AgNCs. The stronger driving force for the reaction with AgNSs may originate from their smaller size, their lattice defects (e.g. twin planes) or the weak surface passivation by the borate groups. With lower concentrations of AgNSs (25 μ M) and larger patterns, dense and faceted silver nanoparticles were obtained with AgNSs, predominantly in platelet shape (figure 3(f)).

3.2. Mechanism of the solid–solid transformation of silver nanoparticles

The aggregate evidence presented in section 3.1 suggests that the formation of silver deposits on patterned silicon substrates is a reaction that is unique to metallic nanoparticles. The reaction observed here does not result in galvanic exchange. Silver does not change its oxidation state when transforming from reactant to product. The rate of reduction of silver ions on silicon is insignificant under the reaction conditions, because of the absence of an etchant for the semiconductor (e.g. HF). The reaction is induced by SF_6/O_2 RIE and is localized to the vertical sidewalls of lithographic patterns. The reaction proceeds with nanoparticles of different shapes, sizes and surfactants, in water and EtOH as solvents, and is independent of the type of resist used for patterning.

The proposed reaction mechanism involves the interaction of silver nanoparticles with residual products of the RIE process. In RIE processes, plasma components remove material from the substrate via a combination of physical and chemical etching. RIE of Si using fluorine-based plasmas results in a surface layer of SiF_x and amorphized silicon [30–32]. Reaction of silver with dangling bonds in this surface layer [5] is excluded as the main mechanism for silver deposition, because deposits were found on the edge of the resist and were not found on the planar wafer. Based on the localization of the silver deposits to the vertical walls, the reaction is proposed to involve sputtered RIE etch products. These products originate from molecular fragments that are ejected from the substrate when it is impinged by energetic ions from the plasma [33-35]. Molecular fragments that are ejected from the bottom of the patterns either dissipate into the plasma or collide with the walls of the pattern and redeposit there [36]. With SF_6/O_2 etching plasmas, the products found on the sidewall have the composition SiO_xF_y [37–39]. The redeposition of the sputtered fragments is critical for the sidewall passivation that leads to the anisotropic etch and vertical features [37, 40, 41]. As a consequence of the shape evolution of the pattern and the etch undercut, redeposition of RIE products is more prevalent in high-aspect ratio features, on the sidewalls compared to the horizontal surfaces, and on the upper sections of the vertical walls. The distribution of silver deposits in the patterns perfectly matches the anticipated distribution of redeposited RIE products. The redeposition of the sputtered products and the subsequent formation of silver nanoparticles, including the effect of the solvent on the resist layer, are illustrated in scheme 1. The RIE sputtered products that initiate the transformation of the silver particles are expected to consist mainly of non-volatile polymeric fluorosilicone and fluoroxysilicone



Scheme 1. (a) The redeposition of RIE products in a trench. (b) Formation of silver deposits and the shrinkage of PMMA. Color key: blue—silicon substrate; yellow—resist; green—reactive ion etching products (SiO_xF_y) ; pink—silver nanocube suspension; red—silver.

radicals. It is possible that they also incorporate carbon and hydrogen from RIE products of the resist. The sputtered products store chemical energy that is sufficiently large to detach atoms (or clusters) from the AgNCs and AgNSs. Silver can be regarded as catalyzing the decomposition of the fluoroxysilicone radicals. The rate of the reaction slows as the reaction progresses, as the more energetic chemical species are consumed. As SiO_xF_y is removed from the silicon surface, the metal fragments bond to it and form silver deposits bearing a completely new shape. The solid–solid reactions occurring at the interface between the etched silicon and the ligand-capped silver nanoparticle are not known at this point.

New chemical transformations exclusive to the nanoscale are continually discovered as the interest in nanomaterialbased technology grows. However, the unique and sizedependent properties of nanostructures make it particularly difficult to predict their chemical, mechanical and electronic interactions with micro- and macroscale objects. This element of serendipity provides technological opportunities and challenges. In the following sections, we show that the unique silver transformation studied in this paper can be (1) suppressed and (2) utilized to promote the selective growth of gold nanoparticles and silicon nanowires from the sidewalls of lithographically patterned trenches. These silicon nanowire-based nanobeams and nanobridges are of particular interest for the miniaturization of electronic and acoustic devices [42–45].

3.3. Controlling silver nanoparticle deposition on sidewalls

The insights gained through the study of the conditions affecting the solid–solid transformation of the silver nanoparticles can be used to eliminate the reaction or to engineer the reaction to proceed more uniformly. For example, we will seek to eliminate the transformation when we are interested in preserving the cubic shape of nanoparticles deposited on the substrate for their plasmonic properties, which are shape-dependent [25]. Alternatively, we will seek to generate deposits uniform in size on patterned vertical walls when we are interested in assembling overhanging nanostructures [42, 43, 45–48].

The solid-solid transformation can be suppressed by removing the redeposited RIE products prior to immersing the substrate in the nanoparticle suspension. RIE products can be selectively removed using an oxygen plasma treatment. Moreover, by tuning the duration of the O_2 plasma treatment it is possible to regulate the amount and distribution of silver deposits formed on the substrate. Figure 4 shows the distribution of deposits at the edge of a wide trench as a function of O₂ plasma treatment duration. In this example, after the RIE process and the dissolution of the resist in acetone, an oxygen plasma treatment was carried out for 0-150 s followed by soaking in the AgNC EtOH suspension for 30 min. The substrate that experienced no oxygen plasma (figure 4(a)) is dotted with silver deposits both on the vertical wall and on the floor of the trench. The substrate that was treated for 150 s by O₂ plasma did not promote any transformations in the AgNCs (figure 4(d)). With intermediate durations, the nucleation of silver deposits was restricted to the vertical sidewalls of the patterns, with fewer nucleation sites and larger deposits the longer the oxygen plasma treatment. Clearly the O₂ plasma treatment is capable of converting the redeposited RIE radicals to volatile or inactive forms. Because of shadow effects, the plasma etch is most effective on horizontal surfaces and least effective on vertical/overhanging surfaces.

The transformation can also be chemically controlled by adjusting the affinity of the ligands to the surface of the nanoparticles. The AgNCs and AgNSs were coated with 4-mercapto-1-butanol by a ligand exchange process. The thiol molecule is known to effectively passivate the surfaces of silver nanocrystals, particularly the {001} planes which terminate our AgNCs. In figure 5 we compare the results of submerging O₂ plasma-treated, photolithographically patterned silicon wafers for 2 h in ethanoic suspensions of



Figure 4. Influence of oxygen plasma on the distribution of silver deposits on the patterned silicon surface. Duration of O_2 plasma treatment: (a) 0 s, (b) 30 s, (c) 60 s and (d) 150 s. Duration of growth: 30 min. All scale bars: 2 μ m.



Figure 5. Deposits in photolithography-patterned step edges grown in DI water with (a) 0.5 mM PVP-capped AgNCs, (b) 0.5 mM MBuOH-capped AgNCs, (c) 0.025 mM borate-capped AgNSs and (d) 0.025 mM MBuOH-capped AgNSs. The substrates were treated with O₂ plasma for 45 s prior to the reaction with silver. Duration of growth: 15 h. All scale bars: 500 nm.



Figure 6. SEM images of ((a), (b)) gold nanoparticles formed via galvanic exchange and ((c), (d)) silicon nanowires grown via gold-catalyzed CVD. The nanostructures are localized to the edges of the lithographic patterns. 0.025 mM MBuOH-capped AgNSs were used as precursors in (a) and (c) and 0.5 mM PVP-capped AgNCs were used for (b) and (d). The substrates were treated with O₂ plasma for 60 s prior to the reaction with silver. Duration of growth: 15 h. Scale bar: (a) 2 μ m, (b) 4 μ m, (c) 16 μ m and (d) 8 μ m.

AgNCs and AgNSs before and after ligand exchange. The process with PVP-coated AgNCs and borate-coated AgNSs resulted in large deposits on the sidewall (figures 5(a) and (c)). MBuOH-coated AgNCs yielded no deposits on the patterned substrate (figure 5(b)), while MBuOH-coated AgNSs resulted in small deposits (figure 5(d)). This comparison illustrates that surface modifications affect both the ability of the nanoparticle to participate in the solid-solid transformation and the shape of the silver deposits on the silicon surface. The thiol-capped nanoparticles show lower efficiency and more uniformity in generating deposits when compared to their PVP-capped and borate-capped counterparts. Thus, it is plausible that the solid-solid transformation is initiated by contact between the redeposited RIE products and a bare area on the silver nanoparticle surface. The ligands may also affect the outcome of the reaction by adsorbing on the growing deposit, although their concentration in the reaction mixture is typically not high.

3.4. Sidewall localization of silicon nanowires

The controlled deposition of nanoscale silver on the sidewalls of silicon structures (e.g. mesas) can be utilized to seed the deposition and the growth of other types of nanostructures and materials in the same locations. We turn our attention to the seeding of gold nanoparticles and the growth of silicon

nanowires. Silver is exchanged galvanically with more noble metals under mild conditions. In figures 6(a) and (b) the products of galvanic exchange with chloroauric acid are shown. Simultaneous Au plating and Ag dissolution lead to the formation of perforated nanoshells of gold on the sites where silver deposits previously resided. Despite gold not plating on bare silicon surfaces, the Au products of the galvanic exchange with silver adhered well to the edges of the patterns. No residual silver was detected by energy dispersive spectroscopy (EDS) performed in the SEM. The seeded Au nanoparticles were employed to catalyze the CVD growth of silicon nanowires. The Au catalyst mediates the one-dimensional growth of the silicon crystal (suppressing three-dimensional growth) and also determines the site of attachment of the nanowire to the substrate. Gold is a suitable catalyst for the growth of a variety of inorganic nanowires by the VLS mechanism, namely of those materials with which Au forms a eutectic. Silver may also act as a catalyst for nanowire growth without the need for galvanic exchange. As can be appreciated from figures 6(c) and (d)the Au nanoparticles were highly effective in growing silicon nanowires so that the edges of the patterns became covered with a dense forest of ultra-thin nanowires. Additionally, there are thicker nanowires that are straight, more spaced out and project off the pattern edge. The latter would be useful as nanocantilevers or as horizontal conductors bridging over a trench. Further optimization of the lithographic pattern and the nanowire growth conditions is needed to achieve reproducible growth for device fabrication.

4. Conclusion

Mixing reactive ion-etched silicon substrates with silver nanoparticles results in a dramatic change in the nanoparticle shape and metal deposition, mediated by redeposited RIE products that accumulate primarily along the sidewalls of the patterns. The transformation is unique to metal nanoparticles, and can be modulated by controlling the particle type, the surfactants and the distribution of reactive sites on the silicon wafer. Faceted, globular, dendritic and fiber-like deposits of silver were obtained. The metal deposits can facilitate the growth of other nanostructures on the vertical walls of patterns. This process could be the basis for the simple fabrication of acoustic and electronic devices. The combination of bottom-up and top-down approaches for nanofabrication will certainly result in the discovery of atypical transformations that do not occur under other circumstances.

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