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Templated cluster assembly for production of metallic nanowires in passivated silicon V-grooves

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Abstract

Wires with meso-scale and nano-scale widths have been fabricated using a novel templated cluster assembly technique. Soft-landed Sb clusters are assembled into wires at the apexes of V-grooves (widths 2–7 μm) formed in Si substrates using anisotropic KOH etching. Two methods for forming nano-wires using templated cluster assembly have been demonstrated. Depending on the chosen method of wire formation, the Si V-grooved substrates are either thermally passivated with SiO_2, or passivated with SiO_2 and then coated with evaporated Ti/Au. On passivated substrates, the metallic wires are formed directly by aggregation of the Sb clusters. On metallised substrates, Ar-plasma etching was used to remove the Ti/Au film around the Sb cluster wires to produce nano-scale width (~100 nm) Ti/Au wires. Following a selective wet chemical etch, Energy Dispersive X-ray analysis confirmed the complete removal of the Sb cluster assembled mask from the substrate, and the presence of Au wires within the passivated V-grooves.
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1. Introduction

Atomic clusters show great potential as building blocks for nano-scale electronic and photonic devices [1–5]. In many of the proposed applications it will be necessary to produce cluster chains or wires to form devices and interconnects. An attractive feature of this method is that the width of wires can in principle be controlled by the size of its constituent clusters. Various groups have shown that cluster diffusion can be arrested by defects or surface steps to generate cluster-chain structures resembling wires [6–9]. However, the fact that these experiments have been performed on substrate materials which are incompatible with standard microelectronics processes, and that they rely on surface defects with random locations, means that scaling them up for mass-production is

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improbable. Si would be one of the most desirable choices in order to address substrate compatibility problems and Si [10] and SiO_2 passivated Si [11] substrates have already been used in conjunction with optical photoresist templates to form uncontacted wire-like chains of clusters. The cluster assembly in [10,11] still relies on diffusion of clusters to promote wire growth at the template edges and therefore cluster aggregation at surface defects away from the intended templates is a likely feature of both processes.

Two methods for forming nano-wires on V-grooved Si substrates through momentum driven assembly of clusters are reported here. In both methods assembly of the cluster wires occurs because the momentum of the deposited clusters causes them to move to the apex of the V-groove, where they assemble into a wire. Since diffusion is not an important factor, the assembly process is insensitive to surface defects.

In the first method, Sb cluster-assembled wires are formed on passivated V-grooves and conduction occurs through a cluster chain. In the second method, clusters assembled on metallised V-grooves are used as etch masks and planar nano-wires are created from the underlying metallic layer using dry, anisotropic etching. Standard optical lithography is used to form the V-groove and ensures accurate control over the position of the wire. Sb cluster wires of width ~100 nm have been produced on SiO_2 passivated V-grooves, whilst Au/Ti wires with widths of ~100 nm have been produced using dry etching around Sb cluster wire masks.

2. Fabrication of passivated metallised V-grooved substrates

Prior to cluster deposition, passivated and metallised V-grooved Si ⟨100⟩ substrates were prepared using standard optical lithography. The Si wafers were cleaned and thermally oxidised in a dry furnace at 1050 °C for 1 h to produce an oxide layer of thickness 120 nm. A Suss MA6 aligner was used to expose AZ1500 photoresist with 2–5 μm wide slots which were developed and transferred into the underlying oxide layer using buffered-HF etching. The resist was removed from the substrates and they were placed in 40% wt KOH solution heated to 65 °C in a temperature controlled, ultrasonic bath. 5% IPA was added just before the substrates were introduced and served as a surfactant for the etching process. Complete V-grooving occurred in 5–10 min (depending on the slot width). After the V-grooves were fully etched, the substrates were stripped of oxide (using HF) and cleaned in piranha solution (1:4 by vol. H_2O_2:H_2SO_4). Passivation of the entire substrate surface with SiO_2 (thickness 120 nm) was once again achieved using dry oxidation with the same process parameters as those used for initial oxidation. Finally, for samples on which the cluster-assembled wires are to be used as an etch mask, Ti (7 nm adhesion layer) and Au (25 nm top layer) were evaporated onto the passivated, V-grooved substrates. The layer structure of passivated and passivates/metallised V-grooved samples are shown in Fig. 1.

3. Cluster deposition

The Sb clusters used for templated-assembly within the passivated/metallised V-grooves are produced in, and deposited from, an inert gas aggregation source [12] as shown in Fig. 2. The metallic vapour necessary for cluster production is produced from a crucible containing Sb which is heated in a source chamber using a tungsten

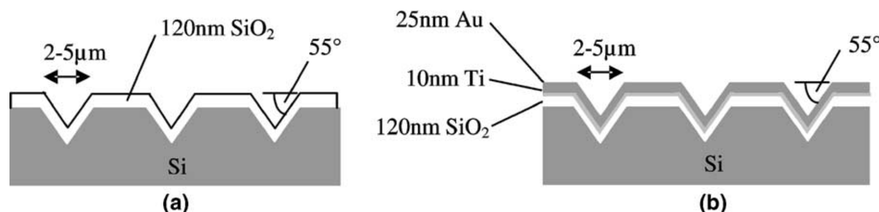

Fig. 1. Cross-sectional diagram of a V-groove templated (a) passivated Si substrate, (b) metallised substrate, prior to cluster deposition.

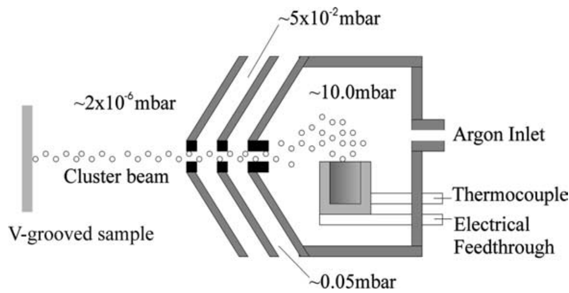

Fig. 2. Schematic diagram of the inert gas aggregation source for metallic cluster production [12].

filament. The crucible temperature is monitored and controlled via a thermocouple mounted in the base of the crucible. Ar is fed through a flow controller and then directly into the source chamber where it assists in the condensation/aggregation process required for cluster growth. Once the crucible temperature is raised sufficiently to achieve a vapour pressure of 0.1–1.0 mbar, clusters are grown from the supersaturated metallic vapour. A source exit nozzle generates an argon/cluster output beam which is directed through nozzles in two differential pumping stages and finally into a high vacuum chamber (base pressure $\sim 10^{-6}$ mbar). The high vacuum chamber houses a sample arm/shutter mechanism and a deposition rate monitor. The sample arm is designed to carry multiple non-contacted V-grooved substrates, or one contacted sample.

The source Ar inlet flow-rate is used to control the average momentum of the clusters. When operating the source with Ar flow-rates above 100 sccm, clusters landing on 4 μm wide SiO_2 V-grooves bounce or slide until they reach the apexes where they accumulate to form wires, whilst almost all clusters landing on the plateaus (between the V-grooves) have sufficient momentum to be reflected from them. For the purposes of nano-wire fabrication, the Ar flow-rate is selected to ensure that clusters landing anywhere within the 'mouth' of the V-groove were driven to its apex. The deposition rate for a given gas flow rate is adjusted via the temperature of the source and is monitored with a quartz crystal film thickness monitor (FTM) mounted behind the sample and in line with the cluster beam. A measured deposition rate of 0.3 Å/s, with Ar flow-rate of 150 sccm, produces wires with nano-scale widths on 3 μm wide V-grooves in approximately 120 s. For Sb, the crucible temperature is typically between 550 and 580 °C in order to achieve this deposition rate. An electronic shutter attached to the sample arm is opened in order to begin deposition onto the sample at room temperature. Following the deposition, samples are removed from the vacuum system and the cluster films are inspected.

4. FE-SEM/energy dispersive X-ray analysis of nano-wires

Fig. 3 shows field-emission scanning electron microscope (FE-SEM) images of Sb clusters deposited with Ar source inlet flow rate of 150 sccm on SiO_2 (a) and metallised/passivated Si V-grooves (b). In both Figs. 3(a) and (b) cluster assembly has taken place at the apex of the V-groove and cluster free regions exist on the walls of the groove above the apex.

The cluster-beam spot is more intense in the centre than at the edges, and was ~ 2 mm in diameter. At the centre of the cluster-beam spot, clusters accumulate and back-up on each other at the apexes of the V-groove and the larger density of clusters means that the width of the wires formed there is larger than those formed at the edge of the beam spot. Across the entire area of the beam spot, cluster coverage on the plateaus between the V-grooves is well below the percolation threshold required for conduction [3].

Oxidation effects have been seen in previous Bi cluster deposition experiments [13] and preliminary conductivity measurements taken from contacted Sb mesowires suggest that rapid oxidation of the constituent clusters occurs when they are deposited in high-vacuum conditions. As a result, an investigation was carried out in which Sb cluster assembled wires were used as a mask for anisotropic etching of metallic films beneath them (the process diagram is shown in Fig. 4). In this way it was hoped that it would be possible to produce non-oxidising Au wires with widths comparable to those of the Sb cluster wires

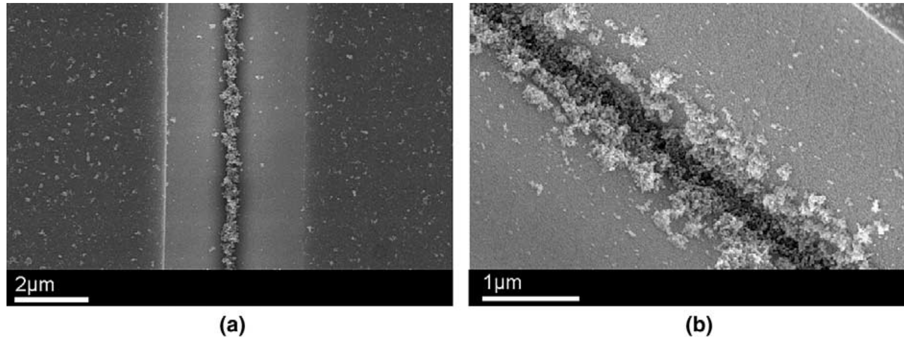

Fig. 3. Sb clusters assembled at the apex of (a) a SiO_2 passivated V-groove, (b) a Ti/Au coated V-groove.

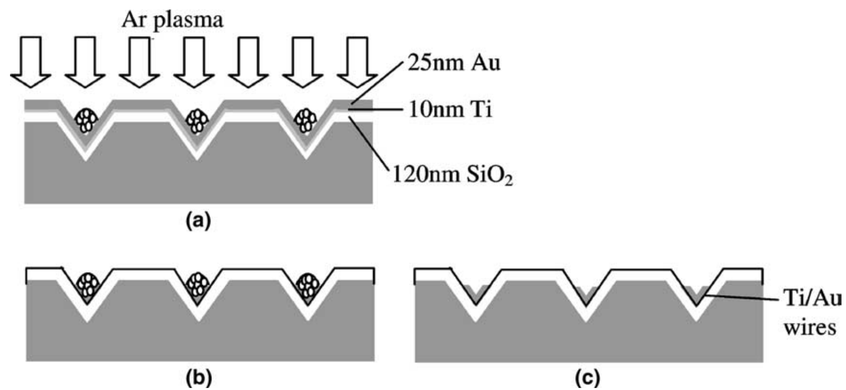

Fig. 4. Cross-sectional diagrams of substrate with cluster-assembled wires on $Si/SiO_2/Ti/Au$ layers (a) pre-RIE, (b) post Ar plasma etch and (c) post wet selective Sb etch.

themselves. FE-SEM images of an anisotropically Ar plasma-etched Ti/Au wire are shown in Fig. 5. The Ar-plasma etch parameters for the wire in Fig. 5 were Ar flow-rate: 70 sccm, process pressure: 0.05 mbar, DC bias: −460 V and RF power: 200 W. The etch process took 270 s. Following the plasma-etch, a wet selective etch was used to remove the Sb mask. (This selective etch consisted

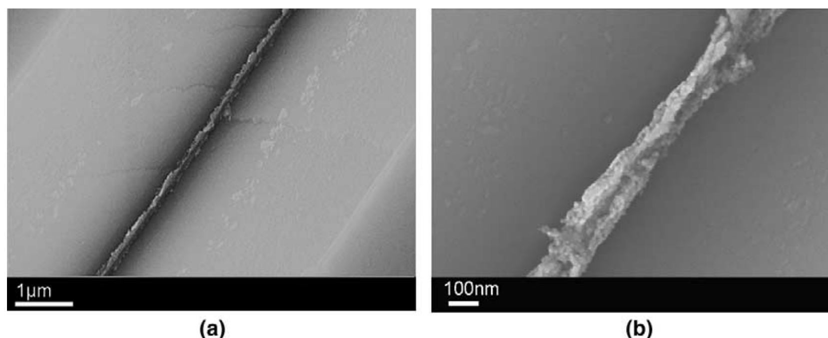

Fig. 5. FE-SEM images of Au nano-wires created beneath Sb cluster assembled nano-wires. The Au/Ti wire and passivated V-groove is shown in (a), (b) shows (at higher magnification) the morphology of the wire.

of 100 ml deionised water, 25 g citric acid and 10 g ammonium molybdate. The immersion time was 360 s at room temperature.)

The maximum and minimum widths of the wire were ~300 and ~100 nm, respectively, over a length exceeding 100 μm. The wire demonstrates the same selective formation properties as the Sb cluster assembled wires: following the dry etch process no parasitic conduction paths existed on the planar substrate areas or on the V-groove walls. The 120 nm thick SiO_2 passivation layer was etched back 10–20 nm by the Ar plasma process – this figure could be reduced further by timing the process more precisely. Redeposition of Sb cluster material occurs on the V-groove sidewalls during the plasma etch but is not significant enough to cause masking of the metallic film there.

Energy dispersive X-ray (EDX) analysis was performed on the Sb cluster masked samples following the Ar-plasma process and after the selective etch process. EDX scans covering the entire substrate confirmed the presence of Sb and Au prior to the selective etch, whilst peaks corresponding to Au but not Sb were recorded afterwards. It was therefore concluded that the remaining wires were Au.

5. Conclusion

In this paper the momentum-driven assembly of Sb atomic clusters (deposited from an inert gas aggregation source) on passivated, V-grooved Si substrates has been described. The V-grooves are formed using optical lithography and established Si processing techniques. Large arrays of V-grooves can be fabricated and clusters deposited onto them to produce hundreds of nano-wires in a 'parallel-write' process. Using momentum-driven cluster assembly on SiO_2 passivated Si substrates, continuous cluster wires with widths down to ~100 nm (1/40th of the optically defined V-groove width) have been produced.

Ti/Au nano-wires with minimum widths of less than 100 nm have also been produced using Sb cluster-assembly on Ti/Au coated V-grooved Si substrates. Here the Sb cluster wires are used as a mask and Ar-plasma etching transfers the dimensions of these wires into the underlying Ti/Au film. This latter method offers the ability to fabricate nano-wires from materials which cannot be deposited from an inert gas aggregation source.

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References

[1] W. Chen, H. Ahmed, K. Nakazoto, Appl. Phys. Lett. 66 (1995) 3383.
[2] D.L. Klein, P.L. McEuen, J.E. Bowen Katari, R.E. Roth, A. Paul Alivisatos, Appl. Phys. Lett. 68 (1996) 2574.
[3] J. Schmelzer Jr., S.A. Brown, A. Wurl, M. Hyslop, R.J. Blaikie, Phys. Rev. Lett. 88 (2002) 226802.
[4] A. Bezryadin, C. Dekker, G. Schmid, Appl. Phys. Lett. 71 (1997) 1273.
[5] C. Thelander, M.H. Magnusson, K. Deppert, L. Samuelson, P. Rugaard Poulsen, J. Nygard, J. Borggreen, J. Appl. Phys. Lett. 79 (2001) 2106.
[6] B. Kaiser, B. Stegemann, H. Kaukel, K. Rademann, Surf. Sci. Lett. 496 (2002) L18.
[7] A.R. Howells, L. Hung, G.S. Chottiner, D.A. Scherson, Solid State Ionics 150 (2002) 53.
[8] G.M. Francis, L. Kuipers, J.R.A. Cleaver, R.E. Palmer, J. Appl. Phys. 79 (1996) 2942.
[9] C. Brechignac, P. Cahuzac, F. Carlier, C. Colliex, J. Leroux, A. Masson, B. Yoon, U. Landman, Phys. Rev. Lett. 88 (2002) 196103.
[10] J. Liu, J.C. Barnard, K. Seeger, R.E. Palmer, Appl. Phys. Lett. 73 (1998) 2030.
[11] A.J. Parker, P.A. Childs, R.E. Palmer, M. Brust, Appl. Phys. Lett. 74 (1999) 2833.
[12] W.A. deHeer, Rev. Mod. Phys. 65 (1993) 611.
[13] M. Schulze, S. Gourley, S.A. Brown, A.D.F. Dunbar, J.G. Partridge, R.J. Blaikie, Eur. Phys. J. D 24 (2003) 291.