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Self-formed platform for *in situ* measurement of electrical transport of individual copper nanowires

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ABSTRACT

Exploring electrical transport in a single individual nanowire provides unique opportunities to fundamental research and practical applications in nanowire-based electronics as well as energy applications. However, measuring such electrical transport in an individual nanowire generally involves nanowire release process followed by electrode patterning steps, which are difficult and tedious tasks. We demonstrate a simple *in situ* method for rapid measurement of the electrical transport in a single individual copper nanowire that is grown by template-assisted electrodeposition method. By depositing a thin metal layer on top of the nanowire template, a single individual nanowire circuit can be easily formed *in situ* by self-limiting the growth of other entire nanowires that are not connected, thereby creating a single individual nanowire contact. The measurement results are shown to be reliable, with average electrical resistivity value of 3.55 μΩ·cm, which is in a good agreement with theoretical value. We also show that this method is superior to oxidation due to the *in situ* measurement environment. This self-formed platform not only shows a convenient method for transport property measurement, but it also suggests a possible utilization to future single nanowire-based applications.

1. Introduction

The explosive growth of semiconductor industries during the past few decades has always been driven by the demand for better performance in terms of larger capacity and faster switching speed. To this end, the density and the speed of integrated circuits have rapidly risen along with decreasing feature size. The shrinkage of the feature size inevitably accommodates parasitic resistance/capacitance/inductance [1], emphasizing the role of interconnects as never before. Such interconnects are now becoming a technology bottleneck as interconnects provoke significant problems such as RC delay and parasitic power consumption, which arise with decrease of the interconnect size. To date, copper has been the representative material for interconnects, and still has the critical potential in the future semiconductor industries due to its excellent electrical properties [2]. Although newly found materials such as carbon nanotubes or graphenes are being largely exploited due to its superb electrical transport properties, replacing copper as interconnects is still remote.

It is evident that the electrical transport measurement is the key study of quantifying copper nanowires as interconnects or other applications that are related to electronics. To date, many researchers have investigated copper nanowires for its fundamental properties as well as practical applications either by experiment or simulation, and central to such research is the electrical transport in a single individual nanowire. Although synthesizing arrays of copper nanowire can be easily done by various methods such as vapor-solid method [3], chemical vapor deposition method [4], template-assisted electrodeposition [5], hydrothermal method [6], etc., measuring electrical transport in a single individual nanowire requires sophisticated effort. Many studies rely on the drop-casting of randomly dispersed nanowires on a substrate followed by lithographic patterning of the electrodes, which involves intricate and tedious efforts [5–8]. Also, this method is highly vulnerable to oxidation, which critically alters the electrical properties, as it is inevitable for the nanowires to be exposed to the ambient [5,8]. Table 1 summarizes the electrical transport properties of individual copper nanowires collected from various literatures [5–14]. It is shown that the measured electrical resistivity values are highly dispersed, differing in several orders. To this end, several efforts have been carried out in order to develop an *in situ* method for measuring electrical transport properties of individual nanowires that does not require any process for isolating the nanowires from the host template or substrate. For instance, Fusil *et al.* have utilized atomic force microscope tip to expose only a single nanowire out of the entire nanowire array, followed by deposition of metal electrode that only contacts one single nanowire [15]. Wu *et al.* have proposed a unique method that eventually creates contact between a single nanowire and an electrode by electrodeposition [16]. These methods show strong endurance to oxidation due to the

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Table 1
A survey of electrical transport properties of individual copper nanowires from various literatures.

Synthesis method	Cross-section size[a] (nm)	Length (μm)	Resistance at 300 K (Ω)	Resistivity at 300 K (μΩ·cm)	Reference
Template-assisted electrodeposition	$d = 60$	2.4	145	17.1	[5]
	$d = 50$		642	52.5	
Hydrothermal	$d = 64$	1.5	1000	214.5	[6]
Chemical vapor deposition	$d = 80$			44.1	[7]
Template-assisted electrodeposition	$d = 65$	3		56.3×10^{12}	[8]
Template-assisted electrodeposition	$d = 50$	6	3.3	0.11	[9]
	$d = 200$		0.45	0.24	
E-beam lithography	$h \times w = 90 \times 50$	2.04		6.4	[10]
Photolithography	$h \times w = 100 \times 100$	100	170	1.7	[11]
	$h \times w = 200 \times 200$		44	1.8	
Electrodeposition	$h \times w = 43 \times 230$	200		4.62	[12]
	$h \times w = 110 \times 230$			3.17	
	$h \times w = 277 \times 230$			2.64	
Photolithography	$h \times w = 200 \times 300$	10	6.5	3.9	[13]
Photolithography	$h \times w = 240 \times 70$	2	6	4.6	[14]
	$h \times w = 240 \times 500$	15	4.8	3.7	
	$h \times w = 240 \times 1000$	25	3.6	3.4	

[a] d = diameter; h = height; w = width.

in situ measurement, but still, it is not simple enough and does not guarantee single nanowire measurements.

More than a decade ago, Wegrowe et al. have developed a facile method that could easily form an individual nanowire contact during template-assisted electrodeposition [17]. By forming a thin metal film on top of the template that does not cover the entire pores but leaves open, a nanowire that is grown outside of the template could be in contact with the top thin film, thereby forming a single individual nanowire contact. Despite the easiness and versatility of this technique, the technique itself did not receive much of attention, but only a several following studies that focus on magnetoresistivity or thermoelectricity in a single nanowire were conducted. These studies intended to form an individual nanowire via such method, but did not confirm whether it was actually an individual nanowire connection or not [18–23].

Here, we investigate a systematic study on such method that realizes an *in situ* platform for reliable measurement of electrical resistance of individual copper nanowires that are grown by template-assisted electrodeposition method. The method involves a thin metal layer that is deposited on top of the nanowire template, and this metal layer plays a key role in self-forming the single individual nanowire contact while subsequently stops further growth of non-contacted nanowires, which prevents from simultaneous contacting of multiple nanowires. We demonstrate that this measurement method is reliable, repeatable, and highly resistant to oxidation. Moreover, we envision this method as a powerful tool for realizing large-scale single-nanowire electronics.

2. Experimental

2.1. Template-assisted electrodeposition.

The porous template for the synthesis of nanowires was chosen as a commercial anodic aluminum oxide (AAO) membrane, Anodisc®. On one side (bottom side) of the AAO, 300 nm-thin copper was sputtered along with 30 nm titanium adhesion layer for use as a seed layer in electrodeposition. On the other side (top side), 10 nm-thin titanium followed by 100 nm-thin copper was sputtered which does not block the entire pore but leaves open.

Electrolyte for synthesizing copper nanowires was 0.5 M $CuSO_4 \cdot 5H_2O$ (Samchun Pure Chemical). The electrodeposition area was controlled by varying the exposed area of the mask layer (nail polish). Electrodeposition was carried out with conventional potentiostat (VersaSTAT3, Princeton Applied Research) with two electrodes setup. The counter electrode (platinum mesh electrode) was always placed 5 mm apart from the working electrode (seed layer). Overpotential was given as -2 V vs. counter electrode. Electrodeposition continued until the surface of the nanowire template was fully covered with overgrown copper as determined from the current-time (chronoamperometric) curve. The morphology of the overgrowth was observed by scanning electron microscope (JSM-6510, JEOL).

2.2. Electrical transport measurement.

For the electrical transport measurement, gold/palladium alloy with thickness of about 200 nm was sputtered on top of the overgrown copper, followed by deposition of silver paste to create a robust measurement circuit that runs through the fully grown nanowires. Electrical resistance measurement was conducted inside Faraday cage using the same potentiostat that was utilized in electrodeposition. Current-voltage (I-V) curve was obtained by scanning from -100 mV to 100 mV, which does not induce any electrical breakdown of the nanowires, and the electrical resistance was determined by the slope at 0 V. All experiments were carried out at room temperature (20 °C).

3. Results and discussion

3.1. Fabrication and growth behavior.

Fig. 1 compares the growth behavior of the nanowires synthesized by ordinary template-assisted electrodeposition and template-assisted electrodeposition with top metal layer. For ordinary template-assisted electrodeposition (Fig. 1(a)), as the electrodeposition proceeds the reduced ions eventually fills up the pores and forms into nanowires. Due to the non-uniform growth rate among each pores, the length of the nanowires are observed to be all different [24]. The nanowire with the fastest growth rate (i.e. longest nanowire) reaches the pore end foremost and overgrows into a hemispherical cap. This is a general process in ordinary template-assisted electrodeposition that is described elsewhere [24].

However, when a thin metal layer is deposited on top of the porous template that does not block the whole pore but only sits on the top of the pore walls, the overgrowth behavior is totally different from the ordinary process (Fig. 1(b)). As the longest nanowire reaches the pore end, it eventually gets in contact with the top metal layer. Then, electrodeposition starts to take place on the top metal layer, which subsequently closes all the open pores instantaneously. Therefore, the nanowires that are not in contact with the top layer eventually stops to grow because of the blocked pore,