Porous Silicon and Electrochemical Deposition

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Contents

Abstract

Porous silicon is a promising template for the preparation of metal nanostructures by electrochemical deposition. Because porous silicon is a semiconductive porous electrode, electrochemical deposition of metals occurs not only at the bottom of pores but also on the pore wall and pore openings. Thus, the control of electrochemical deposition within porous silicon has been a challenging issue. Electrochemical deposition on porous silicon is influenced by illumination conditions. Metal deposition on porous silicon is possible by displacement deposition. Many studies have reported on electrochemical deposition of metal for practical applications. In this chapter, electrodeposition under polarization is firstly reviewed. Secondly, displacement deposition on porous silicon is explained. Finally, the microscopic structure formation by electrodeposition on porous silicon is summarized.
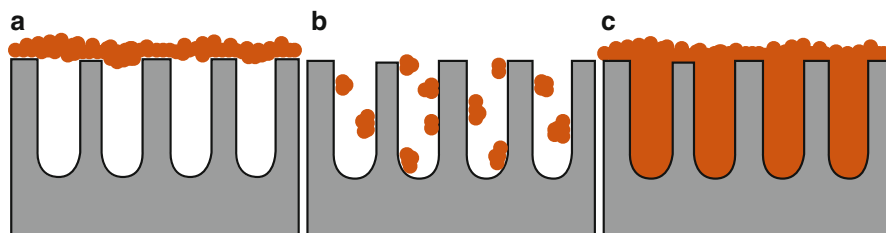
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Fig. 1 Schematic illustrations of typical morphologies obtained in electrodeposition on porous silicon. Illustrations of (**a**), (**b**), and (**c**), respectively, show pores capped with a metal film, pores modified with discrete metal islands, and pores completely filled with metal

Introduction

Metal deposition on porous silicon has been studied since the early period of porous silicon research. The major target started from the improvement of the luminescent properties (Canham 1997), the formation of an effective heterojunction between semiconductor and metal for applying the junction to various types of electronic devices at the time. Afterwards, the target spreads to versatile fields such as optical diagnostics/plasmonics, fabrication of metal–silicon hybrid materials for catalyst, microstructure formation of a metal–silicon hybrid material, and low-dimensional structure formation. These applications utilize the characteristic structure of porous silicon: (a) fine porous structure with high aspect ratio; (b) easily oxidizable nature; and (c) neither conductive nor nonconductive, but semiconductive material. Basic understanding on the deposition behavior on a porous silicon surface is indispensable for meeting a variety of requirements depending upon the application (Hyde and Compton 2003; Oskam et al. 1998; Zhang 2001).

Since application of a wet process for copper wiring was demonstrated by the IBM group in 1997 (Andrecacos et al. 1998), applicability of the electrochemical deposition to fine structure formation has been widely recognized. Electrochemical deposition enables to prepare various types of porous silicon modified with metal as illustrated in Fig. 1. We confine the topic in this section to the wet processes here. The processes consist of electrodeposition and displacement or electroless deposition.

Electrodeposition

Silicon is a semiconductor and it causes specific characteristics which are not expected in the deposition on a conductive substrate. Metal deposition or reduction reaction requires the supply of electrons at the conductive band or the hole injection to the valence band.

$$Me^{n+} + ne^- \rightarrow Me \quad or \quad Me^{n+} \rightarrow Me + nh^+ \qquad (1)$$
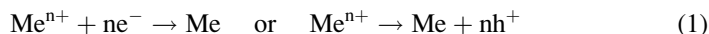
where Me stands for metal. The hole-injection process is only possible when the redox potential or the Fermi level of metal/metal-ion system stays below the energy level of the valence band. It happens in some noble metal systems. Otherwise electrons at the conduction band are required for the progress of metal deposition reaction. n-type silicon meets this requirement, whereas p-type silicon lacks this condition. Illumination helps the progress of deposition on p-type porous silicon. Deposition becomes possible even on p-type silicon when breakdown occurs under very high polarization. Heavily doped silicon or degenerate silicon, n^+ or p^+ silicon, behaves like conductor, where illumination is not the requirement even it is p-type silicon. It must be noted that cathodic reaction proceeds on a semiconductor surface following its kinetics at the beginning of deposition, but the surface covered with deposited metal behaves as a metal electrode. The two kinetics are usually very different from each other.

Displacement Deposition

Silicon is a less-noble material. The redox potential (2) is difficult to measure directly in aqueous solution since silicon is easy to be oxidized and cannot stay as silicon itself. The value estimated from thermodynamic data (Bard et al. 1985) is as follows:

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^- \qquad E_o = -0.85 \text{ V versus SHE} \qquad (2)$$

Porous silicon readily undergoes oxidation in aqueous solution. Electrons formed by the oxidation reduce metal ions thermodynamically, if the equilibrium potential stays positive compared with the potential of reaction (2).

When porous silicon is immersed in an aqueous solution containing noble metal ions such as silver and copper, the metal is deposited on porous silicon. Oxidation of the porous silicon surface is confirmed by IR spectroscopy (Hilliard et al. 1994) and XPS spectroscopy (Jeske et al. 1995). In contrast, displacement reaction does not take place in deposition of less-noble metals such as nickel and iron (Tsuboi et al. 1998; Ronkel et al. 1996). Deposition behavior does not show a significant difference between n-type and p-type silicon substrates (Tsuboi et al. 1999). The potential is determined by a mixed potential of the cathodic and anodic reactions. The rate of reaction (2) slows down in progression since the reaction leaves insulative SiO_2 resulting in the decrease of active silicon surface. It leads to the decrease in metal deposition rate. In some cases, holes participate in place of electrons. The deposition and oxidation do not necessarily take place at the same site. Produced charge carriers can migrate in silicon or metal, and they can be consumed at the different sites from the electron source

(Harraz et al. 2002). The deposition ceases after the silicon surface exposing to electrolyte is completely oxidized.

There are competitive reactions to metal deposition. The most influential reaction is hydrogen evolution reaction. The reaction competes with metal deposition reaction. As a result, noble metal is deposited, but less-noble metal is difficult to be deposited. The potential of hydrogen evolution reaction shifts toward negative with increasing solution pH. One can deposit less-noble metals in solution of high pH (Takano et al. 2000; Harraz et al. 2003). Solution containing fluorides is also used for the displacement solution. Presence of fluorides reduces it to a binary system eliminating the oxides (Harraz et al. 2003). The oxidized silicon dissolves or silicon directly dissolves away into the solution.

Micro- and Nanostructure Formation

Metal deposition creates a hybrid material of metal and semiconductor and the new material is expected to develop a new function, where microstructuring is crucial. A variety of techniques have been utilized for producing the 2D and 3D structures. They are controlled physically, mechanically, optically, and electrochemically. Some examples of the 2D or position-selective local deposition are summarized in Table 1. The optical control is only possible on p-type silicon and deposition of less-noble metal. Illumination creates charge carriers and the illuminated spot undergoes deposition. Otherwise, excess free electrons and displacement deposition hinder the selective deposition.

The advantage or uniqueness arises from the micro- and nanostructures. It is often preferred that deposition copies precisely the porous silicon structure. The hybrid structure or the structure after removing the porous silicon substrate can be utilized in a wide variety of applications. Metal deposition in these structures and the successive silicon dissolution have been utilized to form the 3D structures. Many interesting results have been obtained (Table 2).

Conclusions

Electrochemical deposition enables wide applications of porous silicon in many fields such as optics, sensing, microfabrication, and catalysis. Fine tuning in morphology of deposits, which is crucial for applications, has been desired. As reviewed in this chapter, control of metal electrodeposition has greatly improved in the recent decades. However, there still exist many open questions, such as nucleation and growth and mass transfer for 3D structure formation. They are doubtlessly important and seem to be future issues.

Table 1 2D structure formation of deposits on porous silicon

Type	Deposit	Technique	Remarks	References
Optical	Ni, Cu	DP, 532 nm laser irradiation	Smallest diam. 5 μm with P ion implantation	Kordas et al. (2001), Scheck et al. (2004)
	Ni, Cu	ED, Ar$^+$ laser, scanning	Metal patterning without mask or resist. Suppression of DP is necessary for Cu. 20 μm	Sasano et al. (2003; 2004)
	Au	Laser heating with its interference pattern, alloying	Laser heating after uniform Au deposition. Etch pattern formation: pit, ring, line	Koynov et al. (2006)
Physical	Au, Cu	ED, Si^{2+} ion implantation	High deposition rate at the defected sites. Patterning	Schmuki and Erickson (2000)
	Ag, Cu	DP, porous Al$_2$O$_3$ or polystyrene colloidal crystal as mask	Natural lithography, 50–100 nm size, starting from flat Si	Ono et al. (2007)
	Ag	DP, inkjet printing	Direct patterning on porous silicon. SERS applications	Chiolerio et al. (2012)
Mechanical	Pd	ED, AFM-scratching through the SiO$_2$ layer	Defects, sub-100 nm width	Santinacci et al. (2003)
	Au, Ag Co	DP, nano-indentation	Defects, 30–50 nm resolution	Kubo et al. (2005)
Electrochemical	Cu	ED, electrochemical machining with ultrashort voltage pulses	Roughened surface accept the nucleation, 500 nm size. Starting from flat Si	Trimmer et al. (2005)
	Cu	ED, electrochemical scanning capillary microscope	Pure electrochemical, 200 nm size, using a flat Si	Staemmler et al. (2004)

DP displacement deposition, *ED* electrodeposition

Table 2 3D structure formation and deposition control on porous silicon

Porous silicon	Deposit	Technique	Remarks	References
Mesoporous (fine: 3–5 nm in diameter)	Pt	DP	n-Si, micro and meso, catalyst for fuel cells	Brito-Neto et al. (2006), Hayase et al. (2004)
	Pt	DP	p-Si, catalytic activity of Pt nanoparticles on CO oxidation, methanol as solvent for the deposition bath	Polisski et al. (2008)
	Au	DP	p-Si, micro and meso, plasmon resonance studies, ethanol as solvent for the deposition bath	Polisski et al. (2011)
	Pt	ED, DP	p-Si, chemical modifications of the pore wall, effect of the affinity of pore wall with water	Fukami et al. (2012)
Mesoporous (normal: 5–50 nm in diameter)	Ag, Au	DP	p-Si, dendrite growth, Si nanowire formation	Peng and Zhu (2004)
	Cu	DP	p-Si, n-Si. Deposition behavior at the pore opening	Bandarenka et al. (2012; 2013)
	Fe	ED	p-Si. Chronoamperometry	Renaux et al. (2000)
	Fe	ED	n-Si. Characterization by XPS	Ronkel et al. (1996)
	Ni-Fe/Au	ED	p-Si, n-Si. 40 nm and 290 nm in diameter	Aravamudhan et al. (2007)
	Co-Fe	ED	XANES investigation. Coverage of the top surface by Fe, but penetration of Co in pores	Kashkarov et al. (2009)
	Ni, Co, NiCo, Fe	ED	n-Si, shape varied between spheres, ellipsoids, and wires, and their magnetic properties	Rumpf et al. (2010), Granitzer et al. (2010)

(continued)

Table 2 (continued)

Porous silicon	Deposit	Technique	Remarks	References
Macroporous	Ni	DP, pore widening of with oxidation and dissolution in HF	p-Si, complete replication of pores. Freestanding arrays of high-aspect-ratio Ni pillars	Zhang et al. (2006)
	Ni	ED, single solution for porosification and deposition	n-Si, microneedles with 10 μm diam	Sato et al. (2005)
	Cu, Ni	ED, dark for Cu, illumination for Ni	p-Si, n-Si, Cu micro-rods, Ni micro-tubes	Kobayashi et al. (2006), Fang et al. (2007)
	Cu	ED	p-Si, application of Cu deposited Si nanowires to Li-ion batteries	Foell et al. (2010)
	Au	ED	n-Si, medium-sized pores (~100 nm in diameter), surface plasmon resonance study	Muñoz-Noval et al. (2013)
Others	Au	DP, metal-catalyzed CVD	p-Si (111), Si nanowire arrays, vapor–liquid–solid growth	Yasseri et al. (2006)
	Cu, Ni-B	Electroless deposition	p-Si, mesopores formed by metal-assisted etching, adhesive metal films	Yae et al. (2011)
	Cu	ED	n-Si, macropores formed by metal-assisted etching	Lee et al. (2009)

DP displacement deposition, *ED* electrodeposition

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