Theoretical studies of displacement deposition of nickel into porous silicon with ultrahigh aspect ratio

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Abstract

A model is developed to address the uniformity of displacement deposition of nickel inside porous silicon with an ultrahigh aspect ratio as high as 200. The nickel distribution is treated as a current distribution issue as in electrodeposition. It is shown that the deposition distribution along the pore depth exhibits a strong dependence on a polarization parameter ξ. High values of ξ correspond to mass transport limitations and lead to non-uniform distributions, whereas small ξ values, representing interfacial reaction control, produce uniform distributions. Non-uniform deposition primarily occurs at an initial stage in which the reaction is dominated by mass transfer. As the deposition process continues, the deposition rate drops to a low value, and the deposition uniformity shifts from Ni^{2+} mass transport limitations to its interfacial reaction control, leading to uniform Ni^{2+} concentration and deposition rate distributions. It is predicted that the non-uniformity at the initial stage could be remedied by increasing the bulk concentration of the nickel ions and decreasing the plating bath pH. In addition, the uniformity of the deposition distribution can be significantly improved by introducing inhibiting additive coumarin to the plating solution.
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Keywords: Displacement deposition; Porous silicon; Current distribution; Nickel plating; Deposition uniformity

1. Introduction

Metal deposition into porous silicon (PS) is of great significance for the improvement of electroluminescence of the PS by forming a good electrical contact [1–12,15–17]. It also finds use in fabrication of highly sensitive surface-enhanced Raman scattering substrates [13,14]. Recently, this technique was explored as a means to create a substrate impedance architecture for microwave isolation in mixed-signal integrated circuits [18]. Such architecture can be fabricated by etching a porous region of pore size 1–2 μm and depth ∼200 μm on a Si substrate, followed by depositing metal into the pores. The deposited metal must be uniformly distributed inside the pores.

Displacement deposition is the most promising process for such deep pores based on its unlimited throwing power under uniform concentration distribution of depositing species [19]. However, for pores with an aspect ratio up to 200, uniform deposition from the pore top to bottom is not readily obtained because of the restricted mass transport and consequent non-uniform concentration distribution of the depositing species [20].

A number of experimental studies have been carried out to investigate deposition of metal into the PS. Hamm et al. made extensive investigation in this field [1–3,5,10–12]. Herino reviewed a wide variety of processes used for this deposition [19]. The review indicates that pore filling is not readily achieved and most of the investigated deposition processes lead to a pronounced deposit gradient profile. Usually, the deposited PS reported in literature has a porous layer thickness of 0.5–15 μm with maximum deposition depth being 1.3 μm. Most of the studies were directed toward the influence of bath chemistry on the effectiveness of the plating and deposition mechanism. Apparently, the current technologies cannot meet the challenge of plating the PS with depth of 200 μm and an aspect ratio of ∼200.

Although theoretical and experimental studies of deposition distribution for similar geometries, such as through-holes [20–28] and trenches or vias [20,29–47], are abundant, the nature

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of the deposition process for the geometry in the present study is vastly different from those in literature. In through-hole plating, concerns on mass transport deficiency are unwarranted since the inside of the holes is accessible to agitation because of their relatively large dimensions; the non-uniformity caused by reactant depletion is readily avoided by adequate agitation [20,21]. In the case of copper plating for on-chip interconnection, superconformal bottom-up filling was accomplished by use of multiple additives. The role of the organic additives was described by a diffusion–adsorption leveling theory for a leveler-dominated system [32,34–36], or by accelerator or catalyst models for systems with accelerators and suppressors [39–42,44–47]. In either of the models, metal deposition is activation controlled.

For the nickel displacement deposition process studied in this paper, as will be seen, mass transport rate is a very important factor governing the deposition distribution because of ineffectiveness of external agitation in penetrating into the pores of such ultrahigh aspect ratio. In addition, the surface kinetics also influence the plating uniformity as the system mixed potential varies considerably with deposition time.

This paper theoretically addresses the issue of the deposition uniformity assuming that a displacement process is used for nickel deposition into the PS. The nickel distribution is treated as a current distribution issue as in electrodeposition. We derive a model, which takes into account the variation of the interfacial kinetics with time and the consumption of depositing species along their diffusion path, to acquire an in-depth understanding of the dependence of the uniformity of nickel deposition into the PS on the interfacial reaction and diffusion kinetics, and identify approaches to improve the uniformity based on the plating bath chemistry. Moreover, a modified version of models developed by Dukovic and Tobias [48] and Madore et al. [49] is used to explore the applicability of inhibiting additive coumarin to the uniformity issue in the present study.

2. Theory

2.1. Model development

It is assumed that nickel is the metal of choice to deposit the PS. When a piece of porous Si substrate is immersed into a solution containing nickel ions and fluoride but no reducing regent, following electrochemical reactions occur simultaneously at the silicon/solution interface:

- Anodic dissolution:

$$Si + 6F^- = SiF_6{}^{2-} + 4e \qquad (1)$$

- Cathodic reduction:

$$Ni^{2+} + 2e = Ni \qquad (2)$$

$$2H^+ + 2e = H_2 \qquad (3)$$

The uniformity of deposited nickel inside the pores depends on the distribution of the deposition rate of nickel along the pore depth. For the displacement deposition reaction of nickel on
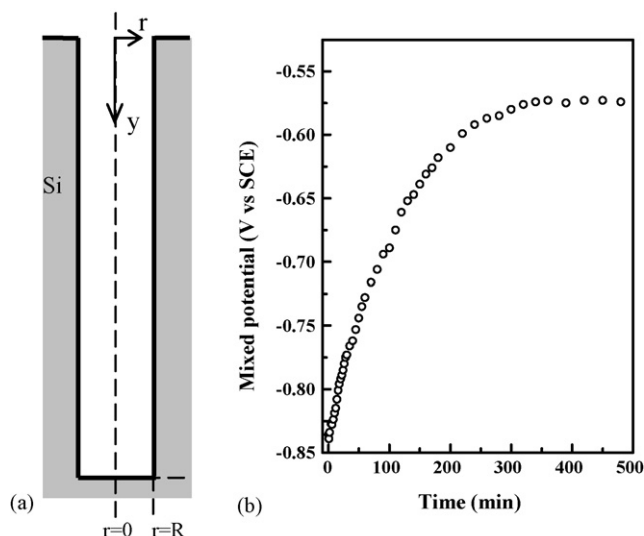

Fig. 1. (a) Schematic diagram of the pore geometry. (b) Variation of the system mixed potential E_{MP} with deposition time, measured in a solution of 1 M NiSO$_4$ + 2.5 M NH$_4$F + 0.2 g/L sodium dodecyl sulfate at pH 8 and 60 °C.

the silicon substrate, although there is no current flow through the electrolyte, electrochemical reactions with the donation and acceptance of electrons shown in Eqs. (1)–(3) still occur at the silicon/electrolyte interface. Therefore, the deposition distribution of nickel inside the pores can be treated as a problem of current distribution as in electrochemical systems, with deposition rate being represented by nickel ion diffusion rate or cathodic reduction rate. In electrochemical systems, the current distribution is determined by ohmic potential drop in solution, mass transport, and/or electrode kinetics. However, for the present case of nickel displacement deposition on Si, there is no current flowing through the solution. Electric field effects or potential distribution in the electrolyte corresponding to the current flow is not present. The deposition distribution is then determined by mass transport inside the pores and surface kinetics of nickel depositing reaction. A solution to the diffusion equation can be applied to the inside of the pores. The deposition rate is obtainable from the concentration gradient Ni^{2+} reduction rate. The surface kinetics provides boundary conditions for the diffusion equation.

The cross-section geometry of the pore is shown in Fig. 1(a). Two dimensional coordinate system (r,y) is employed for the mathematical modeling. It is assumed that the plating solution outside the pores is well agitated and mass transport inside the pores occurs only by diffusion because the pores are much deeper than they are wide. Since the pore wall is continually covered by the deposited nickel, its surface area and therefore the system mixed potential vary with time. Thus, the deposition process is operating under non-steady state conditions.

Based on above assumptions, the following non-steady state diffusion equation is solved for Ni^{2+} concentration distribution inside the pores:

$$\frac{\partial c^*}{\partial t^*} + \frac{D_{Ni^{2+}}t^0}{L_p^2}\frac{\partial^2 c^*}{\partial y^{*2}} + \frac{D_{Ni^{2+}}t^0}{R_p^2}\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial c^*}{\partial r^*}\right) = 0 \qquad (4)$$