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Double-layer capacitors composed of interconnected silver particles and with a high-frequency response

Dmitri A. Brevnov*, Tim S. Olson

Department of Chemical and Nuclear Engineering, Center for Micro-Engineered Materials, The University of New Mexico,
209 Farris Engineering Building, Albuquerque, NM 87131, USA

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Abstract

Porous and multi-layer network of interconnected silver particles is deposited by galvanic displacement on a technologically relevant substrate, silicon with an aluminum/copper film. The mean particle diameter is approximately 200 nm and the particle density in a single layer is 10^9 particles per cm^2. Cyclic voltammetry and electrochemical impedance spectroscopy reveal that capacitance normalized to the electrode geometric area reaches a value of $1.7 \pm 0.2\ mF/cm^2$, which is about two orders of magnitude higher than that observed on a smooth silver/electrolyte interface. The specific surface area of silver particles, which are assumed to be spherical, is $2.7\ m^2/g$. The electrolyte accessible surface area is slightly larger ($3.5\ m^2/g$) due to the surface roughness of silver particles. The frequency response of the porous network of silver particles is analyzed using the transmission line model. The "knee" frequency is determined to be around 200 Hz. The described capacitor could find applications for special electronic circuits where a high-frequency response is needed.

Keywords: Galvanic displacement; Porous electrode; Double-layer capacitor

1. Introduction

Double-layer capacitors are devices that store electrical energy by sustaining an electrical charge in a thin double layer at the interface between an ionically conducting electrolyte and an electronically conducting electrode [1–7]. In contrast to batteries, the mechanism of energy storing involves no Faradaic reactions. Potential applications for double-layer capacitors include memory protection in electronic circuitry, portable electronic, and communication devices. Double-layer capacitors can be built as either a self-standing device or a part of integrated electronic system. Mesoporous carbon [8–11], carbon nanotubes [12–15] and other carbonaceous materials [3–5] have been extensively investigated for use in double-layer capacitors because of their very high specific surface areas. Limitations of double-layer capacitors based upon carbonaceous materials are two-fold. First, capacitance of these materials typically degrades at frequencies higher than 10 Hz. The second limitation arises from problematic incorporation of these capacitors into technologically relevant materials such as silicon.

In this paper, we describe a novel method for fabrication of a porous and metallic structure, which sustains a high double-layer capacitance up to 200 Hz. This method is based upon the electroless deposition of silver particles by galvanic displacement on a 99.5% aluminum film containing 0.5% copper [16]. Electrically interconnected particles of silver form a porous and electrolyte accessible three-dimensional network. Due to a high ratio between electrolyte accessible and geometric surface areas, this structure is shown to have a double-layer capacitance significantly higher than those usually observed for the smooth silver/electrolyte interface. In addition, silver particles are deposited on a technologically relevant substrate, silicon with an aluminum/copper film. Therefore, the utilization of this substrate to fabricate double-layer capacitors is attractive from a point of view of incorporating electroless deposition into an existing fabrication line.

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* Corresponding author. Tel.: +1 505 277 2563; fax: +1 505 277 5433.
E-mail address: dbrevnov@unm.edu (D.A. Brevnov).

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2. Experimental

Silicon wafers with a 600 nm thick layer of SiO_2 overlaid with a 3 μm thick layer of 99.5 wt.% Al and 0.5 wt.% Cu were used in all experiments. The layer of Al/Cu alloy was deposited by physical vapor deposition at Sandia National Laboratories (Albuquerque, NM). The layer of Al/Cu was anodized at 50 V dc for 20 min in 3 wt.% $H_2C_2O_4$ acid and at 0 °C. The electrical contact was made to the top metallic layer outside the electrochemical cell. The steady state current density, established after 5 min of anodization, was approximately 1.4 mA/cm^2. Preliminary experiments revealed that the entire 3 μm thick metallic layer was anodized in approximately 80–85 min. Thus, anodization for 20 min consumed about 0.75 μm of the metallic layer. Following anodization, the porous and barrier layers of aluminum oxide were etched in a mixture of 0.4 M H_3PO_4 and 0.2 M H_2CrO_4 acids at 60 °C and for approximately 1 h. Chromic acid is known to be an inhibitor for corrosion of aluminum and was used to decelerate the dissolution of the remaining metallic layer. Electroless deposition of silver (1.5 mM $AgNO_3$) was performed in a mixture of 0.4 M H_3PO_4 and 0.2 M H_2CrO_4 acids, at 60 °C with no stirring and for approximately 48 h. Anodization of Al/Cu films was carried out with a Pt mesh counter electrode. All electrochemical measurements were carried out using a three-electrode cell with the Pt mesh counter electrode and a reference electrode (either a Pt wire or a Ag/AgCl electrode). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with an IM6-e impedance measurement unit (Zahner), in the same mixture of 0.4 M H_3PO_4 and 0.2 M H_2CrO_4 acids, at 22 °C. EIS data were acquired at open circuit potential (OCP) over a frequency range between 0.1 Hz and 100 kHz and with a potential amplitude of 5 mV. The CV and EIS data were normalized to the geometric electrode area (1.4 cm^2). During the course of electroless deposition, the depletion of silver and accumulation of copper in the deposition solution were monitored with an inductively coupled plasma (ICP) atomic absorption Perkin-Elmer spectrophotometer. The surface morphology of deposited silver particles was evaluated by a Hitachi (S-5200) scanning electron microscope operated at 2–3 kV.

3. Results and discussion

Electroless deposition by galvanic displacement proceeds via two concurrent electrochemical reactions: the reduction of metal ions and oxidation of the substrate surface [17]. If a substrate has a layer of surface oxide, electroless deposition follows and/or coincides with chemical etching of the oxide layer. Galvanic displacement has been reported for deposition of Au on Si [17–19], Ag on Si [20], Au, Pd, Pt on Ge [21], Cu on Si [22], Cu on Al [23], Ag on Cu [24,25], Ni on Zn [26], Ni on Si [27], Zn on Al [28]. In contrast to the widely employed zincate activation of aluminum [28], little is known about the displacement electroless deposition of silver on aluminum films containing copper in acidic media. Therefore, it is important to address the issue of the substrate pretreatment for the electroless deposition of silver on aluminum/copper films.

Three main observations were made during the course of this study. First, under the conditions of the present work no electroless deposition of silver was observed with the pure aluminum substrate (99.997% aluminum foil, Alfa Aesar), which was processed in the same way as films containing 99.5 wt.% Al and 0.5 wt.% Cu. Second, electroless deposition of silver did not take place on either of these two substrates if anodization and etching steps were omitted. Third, to our knowledge, we were the first to report that Al/Cu films are made amenable for electroless deposition of silver by anodization followed by complete chemical etching of porous aluminum oxide and partial chemical etching of barrier aluminum oxide [16]. Upon completion of chemical etching, the thickness of barrier aluminum oxide is approximately 1.5 nm [16]. A combination of anodization and chemical etching results in the copper enrichment in and underneath the thin layer of barrier aluminum oxide [29]. This enrichment enables the charge transfer between silver cations and the metallic substrate. In contrast to pure aluminum substrates, the reduction of silver cations on anodized and etched Al/Cu substrates becomes possible. Thus, silver particles are deposited by galvanic displacement.

In addition to explaining the surface activation procedure, it is valuable to establish what species are oxidized during the electroless deposition. After approximately 48 h of electroless deposition, the depletion of silver in the electrochemical cell corresponded to the deposition of 4.0 mg (37 μmol) of silver. In contrast, only 0.45 mg (7 μmol) of copper was determined to accumulate in the deposition solution. If copper were the only reducing species, the molar ratio between amounts of depleted silver and accumulated copper would be 2–1. The high molar ratio of approximately 5 suggests that both copper and aluminum are oxidized during the electroless deposition. One can expect that aluminum is oxidized because aluminum alloys containing copper are known to have lower corrosion resistance and are more susceptible for an attack by an oxidizing agent (silver cations in our case) than pure aluminum [30].

Additional evidence that aluminum along with copper is oxidized during the electroless deposition of silver comes from examining the steady state mixed potential, E_{mp}, established during the electroless deposition of silver. Based upon the mixed potential theory [31], E_{mp} is located between the formal potentials of the reduced and oxidized species. Under our experimental conditions, E_{mp} (−0.7/−0.5 V versus Ag/AgCl) was more negative than the formal potential of Cu^{2+}/Cu. Such a negative value can be rationalized if the partial reaction of oxidation involves a species with a sufficiently negative formal potential (in our case aluminum).

Our previous publication on the electroless deposition of silver performed for 3 h provides some additional insights on