

Nucleation and growth kinetics of electrodeposited Ni films on Si(100) surfaces



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ARTICLE INFO

Article history:

Received 5 December 2016

Received in revised form 25 January 2017

Accepted 3 February 2017

Available online 4 February 2017

Keywords:

Nickel

Silicon

Light induced plating (LIP)

Growth kinetics

Electrodeposition

ABSTRACT

Nucleation and growth of nickel on n- and p-type Si(100) is investigated, using a plating bath composed of nickel sulphamate and boric acid. For n-type Si, the impact of applied potential and current density on nuclei density and deposit defectivity due to hydrogen gas bubble adsorption are studied. Cathodic current transients for p-type Si show a monotonous decay as a function of time, due to light 'shadowing' of the growing nuclei. A simple model is used to explain the observations. Additionally, the impact of the Si surface chemistry on the Ni deposition process is studied. On hydrogen-terminated Si, the nuclei have a hemispherical shape, while on anodically oxidized surfaces spherical nuclei are obtained.

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1. Introduction

The wet-chemical deposition of nickel (Ni) directly on silicon (Si) has received considerable attention for solar cell metallization [1–7]. Typically, Ni is first deposited by Light Induced Plating (LIP), followed by a copper (Cu) layer and then tin (Sn) or silver (Ag), serving as contacting layer, electrical conductor and solderable layer, respectively. After metallization, an anneal step follows, for which the temperature is chosen such, that a low-resistivity Ni silicide is formed by in-diffusion of Ni into the solar cell [2,5,7,8]. The thickness of the Ni layer, as well as its continuity, should be sufficient to provide a barrier function for Cu diffusion [1,7]. Such an all-wet metallization scheme has the advantage that it is self-aligned, i.e. metallization occurs only in regions where Si is exposed to solution.

For the metallization of planar substrates one can use a simple plating bath composed of only a Ni source, e.g. nickel sulphamate ($\text{Ni}(\text{SO}_3\text{NH}_2)_2$), nickel chloride (NiCl_2), or nickel sulphate (NiSO_4). Work done by Moffat and co-workers has been focusing on superconformal filling of both nano and micro structures by Ni, for which additives are essential to achieve defect-free filling [9,10]. For the stabilization of semiconductor photoelectrodes, the

deposition of continuous metal layers is critical [11]. Recently, various reports have been published in which it is shown that an ultrathin Ni layer deposited on macroscopic Si or on a solar cell prevents corrosion of the photoanode and thereby enables prolonged water splitting in alkaline solution [12]. In addition to the aforementioned applications for which *continuous* metal layers are required, the deposition of (noble) metal nuclei can be used to etch and porosify Si in fluoride media containing a strong oxidizing agent, such as hydrogen peroxide [13–15].

In this work, a detailed study of the electrodeposition of Ni on n- and p-type Si wafer pieces is performed with the goal of characterizing the Ni nucleation and growth kinetics as well as investigating the effect of the doping type on various cathodic and anodic processes. For n-type Si, the impact of applied cathodic potential and current density on the resulting nuclei density and deposit defectivity is shown. For deposition on p-type Si, a simple model is used which can explain the current transients during metal growth. In addition to metal deposition, anodic oxidation and passivation of both Ni and Si as well as Ni stripping are investigated. Furthermore, it is shown that by anodically oxidizing Si before depositing Ni, the nuclei shape can be changed from hemispherical to spherical.

2. Experimental

Experiments were performed using stationary and rotating disk electrodes, for which the electrode surface was facing upwards and

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downwards, respectively. For the stationary measurements, samples were mounted in a Kel-F holder, exposing only the front side to the solution (electrode area = 1.26 cm²). A rotating disk electrode (RDE, electrode area = 1.79 or 0.95 cm²) was used for controlling hydrodynamics (Autolab, RDE-2). The electrochemical measurements were performed with a potentiostat (Autolab, PGSTAT-30) using a silver/silver chloride (Ag/AgCl) reference electrode (Metrohm, # 6.0726.100) and a platinum (Pt) counter electrode (Radiometer, # M241Pt).

The solution used for depositing Ni contained 0.62 M nickel sulphamate (solution prepared from a concentrate solution of 65%, Dow) and 0.62 M boric acid (B(OH)₃; Merck, P.A. grade) (pH = 3.9). Freshly prepared solutions (volume 300 mL) were used and experiments were performed at room temperature. For bubbling the solution with nitrogen or oxygen, a glass tube with a porous frit was used. The bubbling intensity was adjusted such that a 'blanket' of foam covered the entire beaker (diameter 11 cm). To avoid gas trapping under the RDE sample holder, the bubbling was interrupted when a sample was inserted. To ensure a steady-state concentration of dissolved gas, the electrodes were allowed to stabilize for at least 3 min at open-circuit potential (OCP).

Illumination of Si electrodes was done by a green LED panel (40 W, 21 × 27 cm², λ_{max} = 520 nm). Unless explicitly stated otherwise, the maximum LED drive current (I_{LED}) of 2.00 A was used. The light path length through the solution was about 3 cm. UV-vis absorption spectra of the electrolyte were measured using quartz cuvettes (Hellma Analytics, # 110-QS, SUPRASIL, 10.00 mm light path length).

Samples used for the experiments consisted of macroscopic pieces of n- and p-type Si(100) (resistivity 9–15 and 16–24 Ω·cm, respectively), as well as PVD-Pt thin films (stack of Pt/Ti/oxide with thicknesses 50/30/300 nm, R_s = 3.2 Ω/□) deposited on a Si wafer. All substrates were diced into square samples having dimensions of 2 × 2 cm². In case of Si, samples were cleaned by piranha (5 min) and native oxide was removed by HF (1%, 1 min). Electrical contacts were provided by applying gallium/indium eutectic on the scratched back side. PVD-Pt samples were cleaned by rinsing with acetone, isopropyl alcohol, and water. Electrical contact was made with copper tape on the sample front side. Limited experiments were done using nitride-masked p-Si(100) samples containing an array of 35 × 35 circular mask openings (diameter 100 μm, active total surface area = 0.096 cm²). After Ni deposition, samples were copiously rinsed with water and blown dry in a stream of nitrogen.

3. Results and Discussion

3.1. Ni deposition on n-type Si

Although the focus of the present work is on the nucleation and growth kinetics of Ni on Si, the general electrochemistry features are first explored on PVD-Pt substrates. Fig. 1(a) shows voltammograms for two different Pt electrodes in a nitrogen-bubbled solution, which were both started at open-circuit potential and then scanned either in cathodic or anodic direction first. In both cases, a Ni reduction peak is observed:



It has to be noted that the underlying processes and nucleation behaviour are more complex than this Reaction suggests and depend on the substrate [16,17]. After the Ni feature, the onset of water reduction is observed at about -0.85 V:

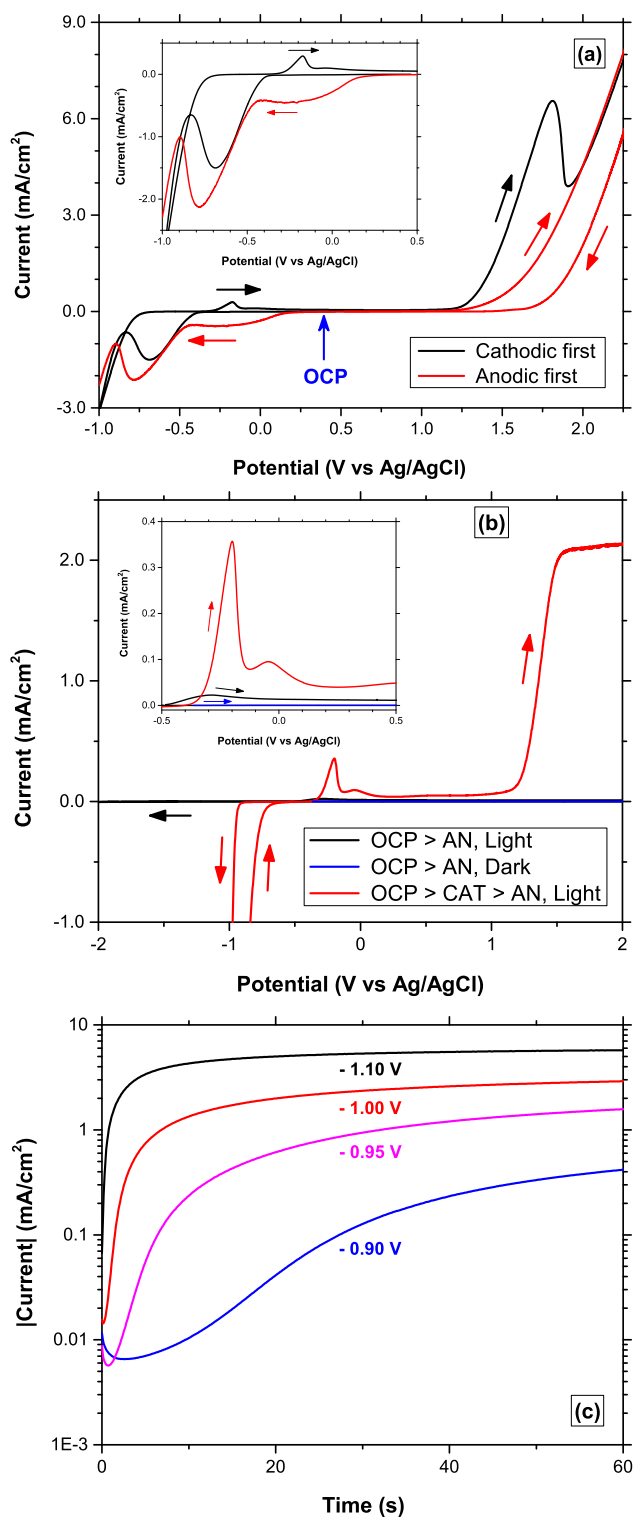
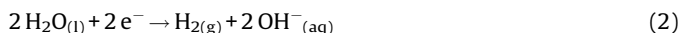


Fig. 1. (a) Voltammograms for Pt in a nitrogen-bubbled solution, started at OCP and scanned in cathodic direction first (black curve) or anodic direction first (red curve). Potential range: -1.0 to +3.0 V, scan rate 10 mV/s. (b) Voltammograms for n-type Si, measured in the dark and under illumination. All measurements were started at OCP and scanned in anodic ('AN') or cathodic ('CAT') direction first. Anodic vertex potential +4.0 V. Cathodic vertex potential -1.2 V and -2.0 V for Ni-modified and anodically oxidized Si electrodes, respectively. Scan rate 10 mV/s. (c) Current transients after a potential step from OCP to a cathodic potential. Note: The absolute value of the cathodic current is plotted on a logarithmic scale. Nitrogen-bubbled, ω = 100 rpm. Electrodes were illuminated continuously.

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