



Autonomous Oscillations and Pattern Formation with Zero External Resistance during Silicon Electrodeposition



Maximilian Patzauer, Richard Hueck, Anton Tosolini, Konrad Schönleber, Katharina Krischer*

Nonequilibrium Chemical Physics, Department of Physics, Technical University of Munich, 85747 Garching, Germany

ARTICLE INFO

Article history:

Received 7 February 2017
 Received in revised form 31 May 2017
 Accepted 1 June 2017
 Available online 8 June 2017

Keywords:

Silicon electrochemistry
 Electrochemical oscillations
 Reaction diffusion system
 Chimera states
 Nonlinear dynamics

ABSTRACT

We report the existence of small autonomous amplitude oscillations without the presence of an external series resistor during electrodeposition of both p- and highly illuminated n-type Si electrodes in a 60 mM NH_4F electrolyte at pH 1. This finding enabled us to study possible emergence of patterns without the presence of the global coupling induced by an external resistance. While with p-type electrodes we could not find a spatial bifurcation upon varying the parameters, stable domain-type patterns with distinct dynamics formed spontaneously when lowering the illumination intensity. Their emergence could be linked to the lateral coupling through valence band holes. Experiments where only part of the electrode was illuminated gave further insight into the role of the hole dynamics for the formation of spatio-temporal dissipative structures.

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1. Introduction

Oscillations during Si electrodeposition have attracted an unbroken interest since their discovery more than half a century ago [1]. They occur in wide parameter ranges and were studied with a multitude of methods, most of the studies focusing on elucidating the oscillation mechanism (for an overview see chapter 5 in [2]). Yet, the origin of the oscillations could still not be explained satisfactorily. The main approaches are discussed in [3–8]. A more recent publication from our group points to the existence of different types of oscillations, most likely involving different feedback loops [9]. We have also started to investigate the formation of spatio-temporal patterns in the oxide layer thickness with an emphasis on elucidating the universal properties of the self-organisation phenomena [10–12].

Among the observed patterns were so-called chimera states [11,12], a dynamical state that received an enormous attention during the last decade in the nonlinear dynamic community [13]. Chimera states form in oscillatory systems, or ensembles of identical, coupled oscillators, and denote states which are composed of parts which oscillate in synchrony and parts that exhibit incoherent oscillations with different mean frequencies. The formation of such a state is highly counter intuitive, exhibiting

the opposite behaviour of what we experience in everyday life, namely the synchronisation of oscillators with different frequencies [14]. Yet, chimera states might be linked to phenomena such as unihemispheric sleep, blackouts in power grids, or bump-states observed in neural systems [13], which calls for detailed theoretical and experimental studies in laboratory settings. As for the latter, truly self-organised chimera states were first observed in the Si electrodeposition system. Here, 'truly self-organised' indicates that they formed spontaneously with neither a computer fed back spatial coupling nor special preparation of initial condition as in most other experimental realisations [15–19], and it remains one of the few experimental systems in which their emergence and properties can be studied. The Si electrodeposition chimera states were found for n-type Si electrodes under moderate illumination intensities, and the spatial coupling through the illumination is believed to be responsible for their emergence. With a generic model assuming a nonlinear global coupling the observed states could be reproduced [11,20], however, a link between the physical and electrochemical quantities and the model parameters has still to be established.

An understanding of what triggers the emergence of chimera states during Si electrodeposition requires more insight in the spatial coupling. In the experiments conducted so far in our group, there were mostly two sources of spatial coupling present, a global coupling induced by an external ohmic series resistance and a coupling through valence band holes imposed by the reduced illumination intensity [12].

* Corresponding author.

E-mail address: krischer@tum.de (K. Krischer).

In this paper, we present experiments that focus on further insights into the impact of the spatial coupling through valence band holes on pattern formation. Therefore, no external resistance is used throughout. We first show that self-sustained current oscillations with a very small amplitude also exist without an external ohmic series resistance for both p-type and highly illuminated n-type electrodes. Then, we demonstrate that reducing the illumination of n-type Si leads to a spatial symmetry breaking, and even to the coexistence of coherently and incoherently oscillating parts of the electrode surface, reminiscent of chimera states.

2. Experimental

2.1. Sample preparation

The experiments were conducted with single crystalline Si (111) wafers with a resistivity of 5–25 Ωcm (p-doped) or 1–10 Ωcm (n-doped). To ensure an ohmic back contact a 200 nm Al layer was thermally evaporated and annealed at 400 °C for 30 min (p-doped) or at 250 °C for 15 min (n-doped) under 100 mbar nitrogen atmosphere. The Si wafers were treated with an oxygen plasma at 200 W for 5 min under 1.4 mbar oxygen atmosphere, mounted on a custom made polytetrafluoroethylene (PTFE) holder, contacted with silver paste on the back, and sealed using silicone rubber (Srintex 901, Ralicks GmbH, Rees-Haldern, Germany), leaving an opening of 15–25 mm². Before the experiment the mounted working electrode was cleaned from organic contamination and dust by first gently wiping it with a tissue drenched in acetone (Merck, p.a.) and subsequently immersing it in acetone (Merck, p. a.) (10 min), ethanol (Merck, p.a.) (5 min), methanol (Merck, p.a.) (5 min) and ultra pure water (18.2 M Ωcm) (5 min).

2.2. Electrolyte

An aqueous solution, prepared with ultra pure water (18.2 M Ωcm), containing 60 mM NH₄F (Merck, p.a.) and 142 mM H₂SO₄ (Merck, Suprapur) with a total volume of 500 ml was used as electrolyte for all experiments, if not mentioned otherwise. Literature values [21] for the dissociation constants of HF and H₂SO₄ were used to calculate the pH value to be 1.

2.3. Electrochemical Set-up

The experiment was performed in a custom-made three electrode electrochemical cell with a circular shaped platinum wire (99.99%, Chempur), $\varnothing \approx 5$ cm, as counter electrode and a commercial Hg|Hg₂SO₄ reference electrode. The counter electrode was placed symmetrically in front of the working electrode and the reference electrode several centimetres behind the working electrode. Before the experiments the electrolyte was purged with argon for 30 min and constantly stirred with a magnetic stirrer at 10 Hz. The glass bubblers used for purging the electrolyte were removed before the measurements to prevent an undefined change in the fluoride concentration due to the glass dissolving in the electrolyte. An argon overpressure was kept with an additional gas inlet and the stirring was maintained throughout the experiment. The potential was controlled using a FHI-2740 potentiostat (electronic laboratory of the Fritz-Haber-Institut, Berlin, Germany) and the current and voltage were digitized using a data acquisition board (PCI-6221, National Instruments). All PTFE and platinum parts were cleaned regularly in Piranha solution. The glassware was cleaned by sequentially immersing it in nitric acid and in an 1 M aqueous potassium hydroxide solution. All parts were stored in covered ultra pure water baths.

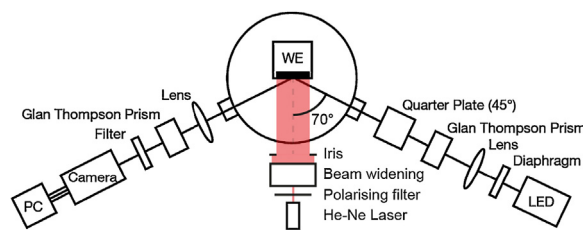


Fig. 1. Illustration of the optical set-up used for the in-situ measurements of the Si electrode surface.

2.4. Ellipsometric Imaging Set-up

The ellipsometric silicon oxide detection was realised using a LED (Linos, HiLED, $\lambda = 470$ nm). The light was polarised using a Glan-Thompson prism and a zero order $\lambda/4$ -plate ($\lambda = 488$ nm) and then directed at the sample with an incident angle close to the Brewster angle ($\alpha = 70^\circ$) to ensure maximal contrast. Upon reflection the polarisation changes depending on the optical path through the oxide. The reflected polarised light then passed through a second Glan-Thompson prism for contrast enhancement and subsequently imaged on a charge-coupled device with 640x480 pixels (JAI CV-A50). The signal was then digitised using a frame grabber card (PCI-1405, National Instruments). The optical components were mounted and aligned using a microbench system (LINOS). A schematic of the optical set-up can be seen in Fig. 1.

2.5. Illumination Set-up

The illumination of the n-doped samples was realised using a linearly polarised He-Ne laser (HNL150L-EC, Thorlabs). The illumination intensity was adjusted using an adjustable polarisation filter. To ensure a spatially homogeneous illumination the beam was optically expanded to a diameter of 1.5 cm and subsequently passed through an iris diaphragm so that only the central part of the beam was incident on the sample. To test for the homogeneity of the illumination, experiments were repeated using an extra mirror in the optical path of the He-Ne laser, resulting in a mirroring of possible spatial asymmetries in the illumination intensity.

3. Results

3.1. Sustained current oscillations

Fig. 2a shows a cyclic voltammogram (CV) of p-doped Si in our fluoride containing base electrolyte (pH 1) taken at 2 mV/s. At this slow scan rate the current-voltage curve is quasi-stationary. The electropolishing region of Si is found at voltages below the pronounced current maximum at 2 V vs. SHE. Above this peak an oxide layer forms at the Si|electrolyte interface which is first wet and gradually turns into a rather compact, dry form that is fully developed above approximately 3 V vs. SHE [2]. When the dry oxide has formed, the oxidation current is limited by the etching rate of the oxide layer, becoming practically independent of the potential up to about 7 V vs. SHE where morphological changes in the oxide layer allow for a modest increase in oxidation current with potential. These features are well known to exist in a wide pH and fluoride concentration range [2]. In Fig. 2b, CVs obtained with a highly illuminated n-type electrode in this base electrolyte as well as with a p-type electrode in a 50 mM NH₄F electrolyte (pH2.3) are shown for comparison. Besides a shift of the n-doped CV by +350 mV, corresponding to the difference in open circuit potential, the

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