



Photoelectrochemical reduction of nitrate on p-Si coated with metallic Re thin films

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ABSTRACT

In this study we examined the rhenium electrodeposition process onto p-Si(100) from acidic media. The study was carried out by means of cyclic voltammetry and the potential-steps method from which the corresponding nucleation and growth mechanism were determined. Both methods were performed under illumination using a solar simulator for electron photogeneration. A 3D progressive nucleation, diffusion-controlled growth of rhenium films was found. Likewise, a morphologic analysis was completed for the deposits obtained at different potential values by means of atomic force microscopy. An energetic characterization through capacitance measurements (Mott–Schottky plots and parallel capacitance) of the p-Si/NO₃⁻ and p-Si/Re/NO₃⁻ interfaces was done.

The photoelectrochemical reduction of nitrate ions, PERN, on the different p-Si/Re electrode systems synthesized was studied. An overpotential decrease of 0.3 V and a photocurrent increase for the PERN on p-Si(100)/Re electrode systems compared with p-Si(100) and metallic Re was found. Finally, the kinetic parameters of the cathodic reactions in the p-Si and p-Si/Re acidic media were estimated using intensity modulated photocurrent spectroscopy. A brief analysis from this technique was done. According to these results, the p-Si/Re electrode system could be a potential photoelectrocatalyst for the PERN.

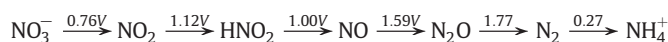
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1. Introduction

Nitrate ions are found naturally in vegetables. Their presence is a result of the nitrogen cycle in which plants assimilate inorganic nitrogen, in the form of nitrates, for use in vegetable–protein synthesis. Nitrates are also found in drinkable water, principally due to a natural presence or as a consequence of contamination from agricultural practices (fertilizers and manure). Nitrates are also employed as additives in cured flesh, due to their bacteriostatic properties (prevents botulism) and their capacity to fix red color. Therefore, there are three principal sources of nitrate ingestion in our diet: vegetables, water and cured meat. Vegetables constitute the most important source of nitrates in the diet, contributing 80% of daily ingestion. The public and the government concern regarding nitrate presence in food has two aspects: first, nitrite toxicity, which derives from nitrate reduction. This species is capable of oxidizing the hemoglobin in globules red, transforming it into methemoglobin [1]. Methemoglobin has difficulty transporting oxygen to the cells. The second concern is that nitrates and nitrites can form *N*-nitrosoamines and *N*-nitrosoamides (precursors to cancer causing agents) [2].

Water can be considered the most valued resource on earth, therefore, it is necessary to propose methodologies that allow for the reduction of nitrate levels from water sources: drinkable water, residual water, ionic exchange resins, reverse osmosis, etc. In this context, the direct reduction of nitrate on metallic electrodes has been investigated. This research focused on the thermodynamic, kinetic, and mechanistic aspects of nitrate reduction on this type of electrode. The most commonly used electrode has been Pt [3,4], due to its evident electrocatalytic effect. This is attributed to the vacancy that offers a *d* band, which converts in a metal with a strong adsorb capacity in front of chemical species such as reactants and intermediates.

From the thermodynamic point of view, if we analyze the standard equilibrium potentials we have [5]



And it is possible to go from NO₃⁻ $\xrightarrow{0.96\text{V}}$ NO, and from NO₃⁻ $\xrightarrow{1.25\text{V}}$ N₂. From this, it can be concluded that independent of the reduction product, this must be attained in the interval of water discharge potentials. However, in practice, the nitrate reduction requires large overpotentials. This means that the problem in this reaction is principally due to kinetic aspects. Due to this, the most commonly used materials in this reaction have been Pt, Pd, Rh, and Ru [3,4,6] due to

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their well-known electrocatalyst character. Also, nitrate reduction has been studied on naked semiconductor materials as well as those modified with metals deposited on its surface. In fact, studies have been done on nitrate and nitrite reduction to ammonia on ZnS [7], Ru/TiO₂ [6,8], Ag/TiO₂ [9,10], and Cu/TiO₂ [11]. In this context, the p-Si surface modification by means of Re was studied and tested using the hydrogen evolution reaction (HER) [12]. The data indicated that the modified substrates present promissory results due to an overpotential decrease of 0.25 V and a current increase of one order of magnitude. This behavior could be associated with a photoelectrocatalytic effect of this electrode system (p-Si/Re) in the HER. Therefore, the goal of this current study was to investigate the photoelectrochemical reduction of nitrate ions (PERN) on the electrode system formed by p-Si, as a semiconductor, and metallic rhenium films deposited by means of an electrodeposition technique on this substrate.

2. Experimental details

Electrodeposition was performed on monocrystalline p-Si (100) with a resistivity between 0.01–0.3 Ω cm ($N_A \cong 5 \times 10^{17} \text{ cm}^{-3}$), B-doped and polished/etched surfaces (Int. Wafer Service, CA, USA). The silicon wafer was cut into rectangles (1.0 × 2.5 cm²) that were degreased in boiling acetone for 10 min. Next they were cleaned ultrasonically for 10 min in acetone, then ethanol and finally in water. The electrodes were treated for 10 min with a 1:1 H₂SO₄:H₂O₂ mixture heated to 80 °C, in order to remove any trace of heavy metals and organic species. Afterwards, the oxide film was removed by etching with a 4% HF solution for 2 min and thoroughly rinsed with ultra pure water. The ohmic contact was made with InGa eutectic on the etched face of the samples and the electrodes were mounted onto a Teflon holder. The silicon area exposed to the solution was 1.0 cm². Before the electrochemical experiments, the electrode surface was again etched for 2 min in 4% HF solution. For each measurement, a new p-Si(100) electrode was used, due to the well known fact that some metals can diffuse toward the inside of silicon [13,14].

For the voltammetric studies on rhenium electrodeposition and the photoelectrochemical reduction of nitrates ions, a platinum wire was used as a counterelectrode and a mercury/mercury sulfate electrode (Hg/Hg₂SO₄, K₂SO₄ (saturated), 0.640 V vs. normal hydrogen electrode) was used as a reference electrode. All the potentials reported in this study refer to this reference electrode.

The electrolytic solutions were prepared using distilled and deionized water with a resistivity of 18 MΩ cm. Analytical grade reagents from Fluka (NH₄ReO₄) and Merck (NaNO₃, H₂SO₄) were used.

Two electrochemical cells were used in all experiments. A pulse step potential technique was employed on cell (1) for the rhenium electrodeposition. The chronoamperograms were recorded in NH₄ReO₄/H₂SO₄ solutions. In cell (2) the photoelectrocatalytic activity of the p-Si(100)/Re electrodic system in the PERN was tested. The electrodeposition baths were aqueous solutions constituted of 50 mM NH₄ReO₄ in 0.1 M H₂SO₄ in Cell (1). For the PERN process an aqueous solution of 0.1 M NaNO₃ at pH = 2 in Cell (2) was used.

The following procedures have been employed. The p-Si(100) treated electrode was mounted in a teflon holder and transferred to Cell (1). In a first stage was realized a voltammetric analysis and later a new p-Si substrate for the rhenium electrodeposition process was used (chronoamperometric study). These last experiments were stopped after a constant total cathodic charge passed between 0.02 C cm⁻²–4.5 C cm⁻². Considering that in these conditions the faradaic efficiency for rhenium electrodeposition corresponds to approximately 16% [15,16], these charges are equivalent to 1.2–281 monolayers. If we consider that each monolayer is constituted only of metallic rhenium, the thickness of the films can be estimated between 0.3 nm–77 nm approximately. However, it must be considered that the rhenium films obtained are not continuous (atomic force microscopy images, AFM);

therefore this is only estimation. After this procedure, the electrode was washed and transferred to Cell (2) in order to record the cyclic voltammogram corresponding to a p-Si(100)/Re electrodic system for the PERN (photoelectrocatalytic activity test).

For the electrochemical impedance spectroscopy (EIS) measurements (Mott–Schottky plots) a new p-Si sample, and a p-Si/Re electrode system in Cell (1) with 0.1 M NaNO₃ at pH = 2 solution was employed. The experiments were recorded at potentials values from –0.8 V to –0.3 V, at an AC frequency of 25 kHz and AC amplitude of 10 mV.

Cyclic voltammetry experiments (NH₄ReO₄/H₂SO₄ solutions and PERN) were carried out at room temperature and at a scan rate of 0.010 V s⁻¹. All the measurements were carried out under illumination conditions, unless the opposite was indicated, using a Solar Simulator system. A Xenon-UV Lamp of 150 W (Newport Oriel Instruments 6254) mounted in a lamp holder (Oriel 67005) was connected to the cell through a water filter (Oriel 61945) and a 1 m length optical fiber (Oriel 77578) was used. A power supply of 40–300 W (Newport Oriel Instruments 69907) was used to generate the arc in the lamp. The illumination power was quantified inside of the cell by means of an energy radiant meter (Oriel 70260). The samples illuminated with the Xe-UV lamp reached a light intensity of 0.1 suns (1 sun = 1 kW m⁻²). A pure argon stream was passed through the solution for 30 min before measurements, and over the solution when the experiments were under way.

The electrochemical measurements (cyclic voltammetry and chronopotentiometry) were done using Princeton Applied Research (PAR) model 273A equipment. The EIS measurements (Mott–Schottky plots) were made using a Zahner model IM6e equipment. All samples used for ex situ AFM were prepared in the electrochemical Cell (1). The AFM images were obtained with a Digital Instrument Nanoscope IIIa series employed in tapping mode at a scan rate of 0.02 μm/s. The tips used were 1–10 Ω cm Phosphorus (n) doped Si, with resonance frequency between 200–400 kHz, model Olympus AC240TS from Asylum Research.

The Intensity Modulated Photocurrent Spectroscopy (IMPS) experimental setup consisted of the Cell (2) illuminated by a 5 mW red (635 nm) Lasiris laser, provided by Stocker Yale as the light source. The laser was modulated by a Model 2030 Global Specialities Instruments Function Generator. A 10X beam expander provided by Edmund Optics was used to uniformly illuminate the cell window. The illuminated area over the sample at the cell was 50 mm². A circular neutral density filter with variable optical density was used to adjust the light intensity reaching the sample. This intensity mean value was measured with a 70260 Oriel radiant power meter with a 70288 silicon probe, while a 53375 silicon photodiode provided by Edmund Optics was used to detect the instantaneous value of this signal. The intensity mean value was kept at ~300 μW/cm⁻², which was the minimum value [17] that allowed a good signal to noise ratio.

A two channel lock-in amplifier Model 5210 from Signal Recovery was used to measure the complex (modulus and phase) AC current from the photodiode. In order to calibrate the lock-in before each measurement, a PDA 750 Photodiode Preamplifier from Terahertz Technology Inc. was used. An analog to digital converter and a PC acquired the signal from the preamplifier to assure a good sinusoidal shape. This shape was adjusted with the DC offset of the function generator, whose amplitude was kept at its minimum value. This adjustment was carried out at 1 kHz where the preamplifier had a constant response. This preamplifier was not used when measuring signal at varying frequency. The photodiode was checked to have an almost flat response from DC to 30 kHz, with no delay time, by comparing its response against a very fast 1 GHz avalanche photodiode.

A second two channel lock-in amplifier Model 5210 from EG&G PAR measured the photocurrent from the electrochemical cell. This signal was obtained from the current intensity monitor output of the potentiostat (PAR model 273A). This instrument was configured to

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