Electrochemistry Communications 76 (2017) 75–78

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Conduction through a SiO_2 layer studied by electrochemical impedance analysis

Jae Gyeong Lee [a,1], Jin-Young Lee [b,1], Jeongse Yun [a], Yongjae Lee [a], Sunmi Lee [c], Samuel Jaeho Shin [a], Je Hyun Bae [a], Taek Dong Chung [a,b,*]

[a] Department of Chemistry, Seoul National University, Seoul 00826, Republic of Korea
[b] Advanced Institutes of Convergence Technology, Suwon-si, Gyeonggi-do 16229, Republic of Korea
[c] Graduate School of Convergence Science and Technology, Seoul National University, Suwon-si, Gyeonggi-do 16229, Republic of Korea

ARTICLE INFO

Article history:
Received 10 December 2016
Received in revised form 24 January 2017
Accepted 3 February 2017
Available online 4 February 2017

Keywords:
Electrochemistry
Silicon dioxide
Dielectric layer
Impedance
Charge transfer resistance

ABSTRACT

This study addresses the effect of protons migrating from an aqueous solution on conduction through a dielectric SiO_2 layer thermally synthesized on a highly n-doped silicon electrode (n^+-Si). We investigate the conduction process, which involves an electrogenerated radical (hydrogen atom) in an n^+-Si/SiO_2/aqueous system, using electrochemical impedance analysis. With a sufficiently negative potential such as −2 V (vs. Ag/AgCl), the charge transfer resistance decreases as a function of time and no SiO_2 layer breakdown is observed. A much thicker SiO_2 layer exhibits similar behavior, which ensures negligible tunneling or leakage. Based on a Randles equivalent circuit involving a variable resistance, the impedance responses enable us to see what occurs in the SiO_2 layer in this system. The results strongly imply that the faradaic reduction of protons occurs at the interface between n^+-Si and SiO_2.

1. Introduction

Dielectric materials such as SiO_2 have been widely used as gate insulators in the semiconductor industry. Thermally grown SiO_2 film, which is a typical dielectric layer, is undoubtedly an intrinsic insulator. However, when it is exposed to protic media, e.g., an aqueous solution, considerable currents can flow if a moderately negative bias is applied at room temperature [1]. The cathodic current depends sensitively on pH, so the SiO_2 layer no longer acts as an insulator. Linear sweep voltammetry and cyclic voltammetry can provide information about how the system responds to various conditions, but another experimental approach is required to understand the mechanism of charge transfer in the thermally grown SiO_2 film. A deeper understanding of the reason for this conduction in a conventional dielectric layer and what actually occurs within it is important for the semiconductor industry and related applications.

AC impedance analysis is a strong candidate for this purpose. In 1964, A. Slobodskoy examined the charge carrier distribution in a metal-insulator-semiconductor system using AC impedance analysis [2]. Since then, AC impedance analysis has been used to study the heterogeneous systems involved in conduction processes [3–6].

Electrochemical impedance spectroscopy (EIS) has proven to be useful for investigating metal oxides [7], which have emerged as useful electrode materials [8]. This method has elucidated the reason for the dissolution of passive layers at specific electrochemical potentials [9]. The passive phosphate film on aluminum [10] and the corrosion inhibitor on nickel [11] have been characterized as a function of corrosion resistance. There have also been a few reports on the conduction due to electrogenerated [1,12] or photoinduced [13] radicals from metal oxides.

In this study, we investigate the conduction due to electrogenerated radicals in thermally grown SiO_2 on highly n-doped silicon (n^+-Si) using EIS.

2. Material and methods

2.1. Preparation of thermal oxidized SiO_2 and low-pressure chemical vapor deposition (LPCVD) Si_3N_4

N-type (n^+-Si), arsenic-doped, ⟨100⟩ -oriented Si wafers with a resistivity as low as 0.005 Ω cm were obtained from STC (Japan). After cleaning with a mixture of H_2SO_4 and H_2O_2, the native oxide was stripped by HF dipping, and a 20-nm-thick thermal SiO_2 layer was produced at 850 °C in a furnace with dry O_2 blowing. Next, the 20-nm-thick thermal oxide layer was stripped again by HF dipping. After repetitive cleaning, 6- and 200-nm-thick thermal SiO_2 layers were formed at 850 °C and 1000 °C, respectively, in a furnace with dry O_2 blowing.

* Corresponding author at: Seoul National University, Seoul 00826, Republic of Korea.
E-mail address: tdchung@snu.ac.kr (T.D. Chung).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.elecom.2017.02.003
1388-2481/

LPCVD Si_3N_4 was produced from dichlorosilane and ammonia in the LPCVD reactor at 828 °C.

2.2. Chemicals and electrochemical experiments

For every experiment, diced n^+-Si/SiO_2 pieces were degreased by sonication in acetone and isopropanol and rinsed with methanol or deionized water. The back side of the wafer was scratched with a diamond knife to remove the air-formed SiO_2 film and smeared with a Ga–In eutectic for electrical contact. With a metal support attached, the ohmic nature of the contact was verified using electrical measurements. The prepared electrodes were pressed against the O-ring of an electrochemical cell, leaving 0.28 cm^2 exposed to an aqueous solution of 0.1 M potassium phosphate (Daejung Chemicals & Metals Co., Ltd) in deionized water. A pH electrode (ROSS 8102, Orion) was used to check the pH of the aqueous solution. The electrochemical experiments were performed at room temperature in a three-electrode electrochemical cell connected to a potentiostat (Reference 600, Gamry Instruments). Ag/AgCl (in a 3 M NaCl internal filling solution, BAS Inc.) and a Pt wire (0.5 mm in diameter) were used as the reference and counter electrodes, respectively.

3. Results & discussion

When a DC electric field is applied across a SiO_2 film, protons migrate through the film at room temperature to polarize the n^+-Si/SiO_2 interface [14]. In the electrochemical system formed by the n^+-Si/SiO_2 electrode in protic media, e.g., an aqueous solution, protons can be taken into the SiO_2 film, driven by the electric field gradient. The suggested theory for this phenomenon is that the protons in SiO_2 films are responsible for electrical conduction in this conventional dielectric layer. Linear sweep voltammograms (LSV) of the n^+-Si/SiO_2 electrode (Fig. 1a, c) show that little current flows at potentials less negative than −1.2 V, which is the onset potential, regardless of the oxide film thickness.

The thermally grown SiO_2 film used in this study is very dense and an excellent insulator, as shown in a previous study [1]. Tunneling and electron leakage through the SiO_2 film owing to defects are negligible. No faradaic reaction is expected at −0.4 V, as confirmed by the Nyquist plot, which shows a nearly perfect vertical line indicating a pure capacitor. When −1.2 V is applied to the n^+-Si/SiO_2 electrode, a hint of a semicircle appears in the Nyquist plot, which reflects the beginning of the faradaic reaction. Because the only reducible species in the oxide layer are protons, we can reasonably predict that protons are electrochemically reduced, which may produce a hydrogen molecule and/or hydrogen atom (H atom) [1].

As protons from the aqueous medium migrate toward the electron-conducting domain, n^+-Si, the probability of faradaic reduction of protons increases near the interface between n^+-Si and SiO_2, where various chemical defects have been reported that can effectively catalyze proton reduction. It is known that the protons that migrate through the SiO_2 layer can be reduced to H atoms in similar solid-state systems, e.g., metal/oxide/semiconductor devices [15]. In this work, the aqueous electrolyte serves as the proton source, and the faradaic reduction of protons is predicted to occur in a similar way at the interface between n^+-Si and SiO_2, where various chemical defects are abundant.

At more negative potentials, e.g., −2.0 V (vs. Ag/AgCl), the faradaic current increases because of the high overpotential, and the resistance component is expected to decrease correspondingly. EIS provides quantitative information that enables us to examine what truly occurs in the system. If the resistance varies with the faradaic reaction, the dielectric membrane resistance and charge transfer resistance should be responsible for this variance. The dielectric membrane resistance is

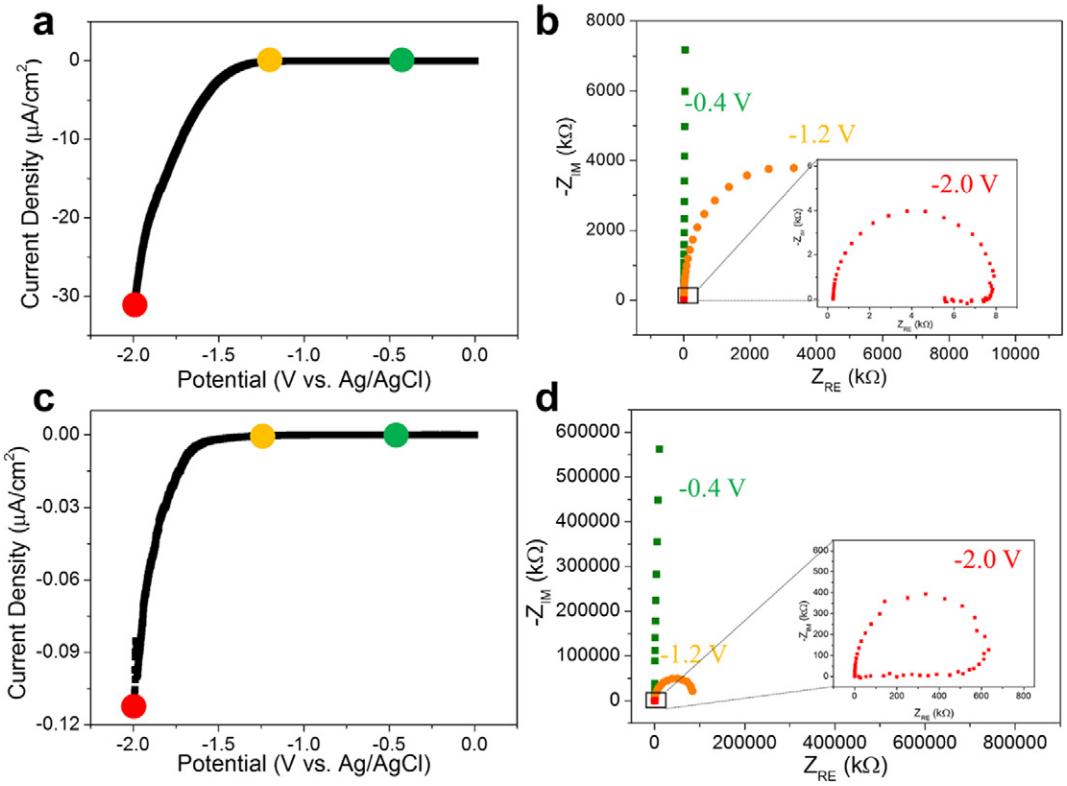

Fig. 1. (a) Linear sweep voltammogram of an n^+-Si/SiO_2 (6 nm) electrode in a N_2-purged solution of 0.1 M potassium phosphate at pH 3. (b) Nyquist plots obtained by AC-impedance analysis at −0.4 V (vs. Ag/AgCl, green), −1.2 V (vs. Ag/AgCl, orange), and −2.0 V (vs. Ag/AgCl, red). (c) Linear sweep voltammogram of a n^+-Si/SiO_2 (200 nm) electrode in a N_2-purged solution of 0.1 M potassium phosphate at pH 3. (d) Nyquist plots obtained by AC-impedance analysis at −0.4 V (vs. Ag/AgCl, green), −1.2 V (vs. Ag/AgCl, orange), and −2.0 V (vs. Ag/AgCl, red). The root mean square AC amplitude was 10 mV.