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Hydrogen Incorporation during Aluminium Anodisation on Silicon Wafer Surfaces

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ABSTRACT

Hydrogen can act to reduce recombination at silicon surfaces for solar cell devices and consequently the ability of dielectric layers to provide a source of hydrogen for this purpose is of interest. However, due to the ubiquitous nature of hydrogen and its mobility, direct measurements of hydrogen incorporation in dielectric layers are challenging. In this paper, we report the use of secondary ion mass spectrometry measurements to show that deuterium from an electrolyte can be incorporated in an anodic aluminium oxide (AAO) layer and be introduced into an underlying amorphous silicon layer during anodisation of aluminium on silicon wafers. After annealing at 400 °C, the concentration of deuterium in the AAO was reduced by a factor of two, as the deuterium was re-distributed to the interface between the amorphous silicon and AAO and to the amorphous silicon. The assumption that hydrogen, from an aqueous electrolyte, could be similarly incorporated in AAO, is supported by the observation that the hydrogen content in the underlying amorphous silicon was increased by a factor of ∼ 3 after anodisation. Evidence for hydrogen being introduced into crystalline silicon after aluminium anodisation was provided by electrochemical capacitance voltage measurements indicating boron electrical deactivation in the underlying crystalline silicon. If introduced hydrogen can electrically deactivate dopant atoms at the surface, then it is reasonable to assume that it could also deactivate recombination-active states at the crystalline silicon interface therefore enabling higher minority carrier lifetimes in the silicon wafer.

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1. Introduction

Previous studies have shown that when nano-porous anodic aluminium oxide (AAO) layers are formed by anodising an aluminium layer over an intervening silicon dioxide or silicon nitride dielectric layer on a silicon wafer surface, the effective minority carrier lifetime of the wafer can be increased [1–3]. This increase may, at least in part, be due to the positive electrostatic charge that becomes stored in the dielectric stack structure during anodisation[1]. This stored charge can effectively increase the electron concentration at the silicon interface and create an inversion layer in p-type silicon or accumulation layer in n-type silicon. By reducing the concentration of one carrier type at the surface, the recombination can be decreased. However, it has also been shown that hydrogen can be introduced into substrates during electrochemical [4–7] and annealing processes [8–11]. This hydrogen may contribute to the deactivation of recombination-active states that exist at the interface [12] or in the bulk of the silicon wafer [13,14].

Anodisation is an electrochemical process whereby a metal is anodically oxidised in an electrolyte. When electrolytes are used in which the anodic oxide has partial solubility, an impervious barrier layer oxide forms at the metal interface and a porous outer layer exists in contact with the electrolyte [15]. It is generally accepted that the anodic oxide grows at both the metal-oxide interface and at the electrolyte interface. In the case of anodisation of aluminium, Al^{3+} ions drift to the surface due to the high electric field and react with water forming Al_2O_3 and H^+. Simultaneously, O^{2-} and OH^- from the electrolyte drift to the metal surface where they react with aluminium also forming Al_2O_3 [16]. Hydrogen could therefore foreseeably become incorporated in the anodic films by way of trapped OH^-, H^+ or from water of hydration. However, it is difficult to directly measure hydrogen that may be incorporated in a dielectric-coated silicon wafer as it is the lightest element and hence can be mobile during methods designed to detect its presence [9,17]. Furthermore, the amount of hydrogen within the silicon is typically below the detection limit of many analytical techniques.

Despite these measurement challenges, hydrogen has been previously detected in AAO layers [6,7,18,19] with the hydrogen content of films depending on electrolyte and anodisation voltage. Rabbo et al. [7] employed secondary ion mass spectroscopy (SIMS)

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to measure H^+ and OH- profiles in the AAO layers and observed that the intensity of the detected H^+ increased with increasing pH of electrolyte, most likely due to the increased hydration of the films at the higher pH. However, they noted that the bombarding ion beam in the SIMS measurements may have caused a re-distribution of hydrogen within the film and so only trends between different electrolytes were considered. Lanford et al. [6] addressed this issue of hydrogen mobility by using a ^{15}N resonant nuclear reaction technique to profile hydrogen content in AAO films formed in tartaric, glycol-boric and phosphoric acids. Using this technique they were able to detect hydrogen at a concentration corresponding to one hydrogen atom for every 50 Al_2O_3 units. The detection limit of the ^{15}N nuclear resonance method was 1×10^{20} atom cm^{-3}, however it was difficult to calibrate the depth axis of the profiles due to the non-uniform porous surface layer of hydrous aluminium oxide.

Another way to approach the detection of incorporated hydrogen is to anodise in a deuterated electrolyte and then attempt to detect incorporated deuterium. This method was used to study hydrogen incorporation into silicon during anodic porous silicon formation [20,21]. Using quantitative SIMS it was shown that deuterium was incorporated in the porous silicon, where its concentration approached 10^{19} cm^{-3} at the pore tips and decreased rapidly toward the bulk silicon [20]. Deuterium has also been used to estimate hydrogen incorporation in a silicon wafer structure from a silicon nitride layer deposited using deuterated pre-cursor gases [22,23]. Sheoran et al. showed that deuterium from deuterated silicon nitride could pass through a n-type 575 μm thick Czochralski (Cz) silicon wafer after heating at 750 °C for few seconds and be detected in a highly-defective amorphous silicon layer on the other surface of the wafer using SIMS [23]. It was concluded that the deuterium was liberated from the silicon nitride layer during the annealing, and due to the few defects in the silicon wafers, quickly diffused through the entire wafer to become trapped in the amorphous silicon layer.

This paper investigates the possibility that the hydrogen is incorporated either within the formed AAO layer or alternatively introduced into the underlying silicon wafer during anodisation of aluminium layers on silicon wafers and thus contributes to the increased effective lifetimes that have been measured in wafers passivated with AAO layers [1–3]. Anodisation of aluminium was performed in deuterated sulphuric acid with SIMS and electrochemical capacitance voltage (ECV) measurements being employed to detect and, where possible, quantify any incorporated deuterium in the formed AAO layer and the underlying silicon. Evidence of deuterium, above a level expected by natural abundance, in the formed AAO layer and underlying silicon would suggest that the hydrogen from the electrolyte could also become incorporated in both the formed oxide and the silicon device during anodisation.

2. Experimental

A first set of 4 cm × 4 cm test structures was fabricated using one-side polished 0.42-0.57 Ω cm p-type FZ silicon wafers (purchased from Wacker-Chemitronic GMBH, West Germany) of thickness 524 μm. A 200 nm thick layer of amorphous silicon, doped with boron to a concentration of 10^{18} cm^{-3}, was deposited on the polished surface using e-beam evaporation at 200 °C. The high boron doping was employed to enable detection of the interface between the amorphous silicon layer and the more lightly-doped silicon wafer.

A second set of 4 cm × 4 cm test structures was fabricated using the same one-side polished wafers and a 15-20 nm thick SiO_2 layer was thermally-grown on both silicon surfaces in a tube furnace at 980 °C for 20 mins. This structure was selected because it was similar to that used in the experiments described in [1].

An aluminum layer of thickness ∼ 600 nm was thermally-evaporated from aluminum wire of 5 N purity onto the amorphous silicon or SiO_2 layers on the polished surfaces of the wafers. The aluminum layer was anodised by clipping the wafer to the anode of a power supply as described in [1]. Both test structures were anodised at an external voltage of 25 V in 0.5 M sulphuric acid diluted from 98% (w/w) H_2SO_4 (electronic grade, J.T Baker) using 99.9% deuterium oxide (obtained from Cambridge Isotope Laboratories, Inc). Test structures with amorphous silicon were also identically anodised in a non-deuterated electrolyte comprising 0.5 M sulphuric acid diluted from 98% (w/w) H_2SO_4 (electronic grade, J.T Baker) using deionised water of resistivity 18 MΩ cm.

Anodisation was terminated when the current decreased to a value of 0.01A and the test structures were rinsed for 5 min in running deionised water. During anodisation, the non-polished surface remained protected by the resist, the latter being able to be removed using a nitrogen gun after anodisation due to the acid electrolyte reducing its adhesion to the silicon surface.

In all experiments, the formed AAO layers adhered well to the silicon wafer and so it was assumed that no silicon anodisation occurred as earlier studies have shown that, if silicon is allowed to anodise by not ceasing the process once the current has reduced to a small value (0.01 A in this work), then adhesion of the formed dielectric layer on the silicon wafer is compromised. The anodised test structures were cut into two equal-sized fragments by laser cleaving from the non-polished side. Half of the test structures were annealed with the polished surface facing up in an industrial belt furnace where they experienced a peak set temperature at 400 °C for less than 1 min.

Scanning electron microscope (SEM) images of the anodised surface were recorded using an S900 instrument and compared to images previously recorded for similar test structures anodised in 0.5 M H_2SO_4 acid diluted in deionised water. Secondary ion mass spectroscopy (SIMS) profiles were recorded using a Cameca ims4f instrument with oxygen (O_2^+) sputtering ions at voltage of 15 kV with positive secondary ions. Silicon and aluminium were detected using their doubly-charged ions (Al^{2+} and Si^{2+}) because the intensities of their single-charged ions were too high for the electron multiplier detector. There are two ions with a mass of 2, H_2^+ and D^+. Although it is possible to separate these two ions using a high mass resolution power, this would have reduced the transmission and hence the intensity of the D^+ signals. Consequently, the D^+ signal represented the sum of the two possible signals. The hydrogen and boron concentrations in the amorphous silicon were calculated based on an implanted reference sample from CiS Forschungsinstitut für Mikrosensorik und Photovoltaik (Germany).

For the second set of test structures with the thin SiO_2 formed on the wafer surfaces, the AAO and thin SiO_2 layers were removed by immersing the test structures in 49% HF before SIMS profiles and electrochemical capacitance voltage (ECV) profiles were recorded. SIMS profiles for the second set of test structures were recorded using the Cameca ims4f instrument with cesium (Cs^+) sputtering ions at voltage of 10 kV with negative secondary ions.

Electrochemical capacitance voltage measurements were performed from a circular measuring area with a diameter of 3.57 mm and starting at a depth of 0.005 μm to 0.06 μm with a voltage step of 0.02 V. During the ECV measurements, the silicon surface was in contact with an NH_4NF_2 electrolyte with a wetting area of 10 mm^2 delimited by a sealing ring [24]. By applying an external voltage, the silicon was etched and the capacitance of the depletion region was measured at each etching step, enabling the carrier concentration to be extracted from $\frac{d^1/C^2}{dv}$ where C and V represent the measured capacitance and voltage [25]. It can be difficult to perform ECV measurements in heavily-doped semiconductors because the depletion region can be too shallow. Consequently, polished wafers

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