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Atmospheric pressure plasma etching of silicon dioxide using diffuse coplanar surface barrier discharge generated in pure hydrogen

Richard Krumpolec [a,*], Jan Čech [a], Jana Jurmanová [a], Pavol Ďurina [b], Mirko Černák [a]

[a] R&D Centre for Low-Cost Plasma and Nanotechnology Surface Modifications (CEPLANT), Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 267/2, 611 37 Brno, Czech Republic

[b] Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovakia

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ABSTRACT

We report on the method of dry etching of silicon dioxide (SiO_2) layers by cold plasma treatment at atmospheric pressure in pure hydrogen using Diffuse Coplanar Surface Barrier Discharge (DCSBD). The SiO_2 etching rate was estimated at ~1 nm/min. The studied plasma process was found to be the composition of plasma induced reduction and etching. The changes in surface morphology of etched samples were observed by scanning electron microscopy. X-ray photoelectron spectroscopy analysis was applied to identify the surface chemical changes due to the reduction processes. Two regimes of plasma treatment were examined. While the dynamic treatment, where the treated surface was moved relative to the plasma source, led to a homogeneous process, the treatment in static conditions resulted in a stripe-type pattern on the surface of the samples reflecting the electrode structure of the plasma source. The results provide a basis for a new and simple way to prepare clean, native oxide free silicon surfaces in dry plasma process at atmospheric pressure.

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1. Introduction

Silicon is an important part of modern micro- and nanoelectronics. The ability to form a chemically stable protective layer of silicon dioxide (SiO_2) at the surface of silicon is one of the main reasons that make silicon the most widely used semiconductor material. Due to its dominant role in silicon device technologies [1,2] the SiO_2/Si interface has been intensively studied in the last five decades. Chemically prepared surfaces of crystalline silicon (c-Si), handled in ambient air, are typically covered by native surface oxide layers and hydrocarbon contamination layers. Removal of such layers from silicon surfaces is required prior to many submicron integrated circuit processing steps.

Besides wet etching by HF solutions, several plasma based methods using fluorocarbons [3–6] have been developed for plasma etching of glass or SiO_2 layer from the top layer of silicon wafers. Such wet or plasma based methods, however, use strong acid or base liquid solutions or sometimes dangerous gases. The need exists for a simple and environmentally acceptable method for SiO_2 etching at atmospheric pressure for novel thin films applications.

It has been reported that hydrogen plasma is capable of etching a number of different semiconductors, metals and their oxides, including SiO_2/Si structures [7–9]. Several papers have been published regarding the hydrogen plasma treatment of silicon dioxide surfaces by applying RF or ECR plasma systems [10,11] and atmospheric plasma jets [12].

The plasma cleaning of SiO_2/Si surfaces at atmospheric pressure using Diffuse Coplanar Surface Barrier Discharge (DCSBD) has been reported previously [13,14], taking the advantages of DCSBD plasma source. The DCSBD generates highly non-equilibrium plasma with high power density of the order of 100 W/cm^3 that is visually diffuse and forms a sub-millimetre thin plasma layer on top of the flat or curved dielectrics [15,16]. Oxidation and reduction properties of DCSBD plasma can be tuned by the working gas used. For example, while an oxidising atmosphere can be generated by DCSBD e.g. in ambient air or pure oxygen [13], it was found [9] that a native surface CuO/CuO_2 layer can be reduced to metallic copper within several seconds using DCSBD plasma in atmospheric-pressure hydrogen.

In this work we studied the reduction and etching of the native or thermal oxide layers using DCSBD discharge generated in pure hydrogen atmosphere. The plasma treatment was done at room temperature at atmospheric pressure conditions.

2. Experimental details

2.1. SiO_2 films preparation

Four types of silicon dioxide (SiO_2) films were prepared in this work to study the effect of DCSBD plasma treatment in pure hydrogen. Native-oxide and thermal-oxide films grown on the surface of standard

* Corresponding author.
E-mail address: krumpolec@mail.muni.cz (R. Krumpolec).

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Table 1
The silicon dioxide films and their thicknesses used in the experiments of SiO_2 treatment by H_2 DCSBD plasma.

Sample	Annealing time (ramp + dwell time)	SiO_2 thickness (nm)
Si-0	−/Bare Si wafer	1.9
Si-1	95 min (10 °C/min)	14
Si-2	95 min (10 °C/min) + 2 h at 950 °C	55
Si-3	95 min (10 °C/min) + 5 h at 950 °C	105

single side polished wafers of p-type Si(100) boron doped substrates (On-Semiconductor, Czech Republic) with resistivity of 0.010–0.020 Ωcm were used. The thickness and the preparation conditions of the SiO_2 films are summarized in Table 1. The first type of SiO_2 film, labelled Si-0, was native oxide film of thickness about 1.9 nm grown at standard conditions in ambient air. The other types of SiO_2 films, labelled Si-1, Si-2 and Si-3, were silicon dioxide films prepared by the thermal oxidation method. These thermal-oxide SiO_2 films were prepared by annealing of cleaned silicon wafers in dry O_2 atmosphere in a conventional horizontal atmospheric pressure furnace. The annealing procedure consists of 95 min period of programmed temperature rise to 950 °C (with the ramp of 10 °C/min) and variable dwell-time at the temperature of 950 °C. Sample Si-1 was annealed only during the first period with no dwell-time at 950 °C. The thickness of SiO_2 films was measured using standard ellipsometry measurements. 10 mm × 10 mm samples were used for plasma processing and they were cut out of the Si wafers after SiO_2 film preparation.

2.2. Plasma treatment of SiO_2 films

The plasma treatment of SiO_2 films was performed in a reactor consisting of the treatment chamber placed on top of the DCSBD plasma source (see Fig. 1). Small reactor chamber of inner volume about 50 cm^3 was carefully sealed from the ambient environment. The gas pressure of inlet hydrogen was about 1.0–1.2 bar. The gas outlet was realized as a free flow to the ambient air combined with the controlled combustion of hydrogen. This gas flow regime was sufficient to set up and maintain the atmospheric pressure conditions inside reactor chamber without the need for vacuum pump to be used. The basic properties of DCSBD in hydrogen was discussed in [9], where similar setup was used to reduce CuO/CuO_2 layers on metallic Cu specimens.

In hydrogen the DCSBD forms a visually diffuse highly non-equilibrium plasma in thin sub-millimetre layer on the top of the dielectric plate (alumina ceramics). The DCSBD surface power density for plasma treatment was chosen in the range from 1.8 to 3 $W \cdot cm^{-2}$. That corresponds to the DCSBD total input power of 300 W at 15 kHz or 500 W at 30 kHz of high voltage frequency, respectively. The samples were treated either in a static or in dynamic mode. In the static regime, the sample was at the same position above the DCSBD electrode during the experiment, while the dynamic treatment was carried out by moving the sample above the DCSBD plasma layer in a direction perpendicular to the strip electrodes at moving speed of 6 $cm \cdot s^{-1}$. The dynamic treatment was used to provide homogeneous treatment, while the static treatment was used to investigate the effect of the non-uniformity of the DCSBD-

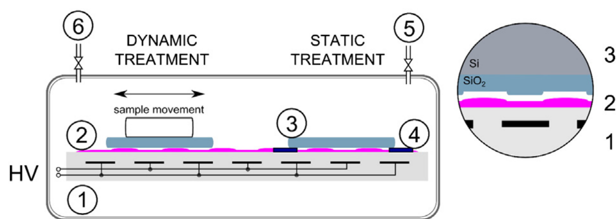

Fig. 1. Schematics of the experiment. (1) – Al_2O_3 plate with embedded DCSBD electrode system; (2)– DCSBD plasma layer; (3) – Si wafer with SiO_2 layer; (4) – fixed spacer; (5) – gas inlet and (6) – gas outlet with controlled combustion of hydrogen effluent.

plasma due to the electrode structure on the plasma reduction of SiO_2 in pure hydrogen. Both static and dynamic treatments were investigated at two distances of samples from the DCSBD electrode surface − 0.15 mm or 0.30 mm.

The experiment was carried out as follows: The silicon dioxide samples were attached to the sample holder/placed in the fixed spacers and the reactor chamber was closed. Prior to treatment pure nitrogen flow (Messer, 99.998% purity) was used to purge the chamber thoroughly. Then pure hydrogen flow (Messer, 99.998% purity) was established at a specified flow rate (ranging from 0.1 to 1.0 $l \cdot min^{-1}$) and the chamber was purged for 2 min without plasma ignition. Then the DCSBD discharge was ignited for specified time and after the plasma treatment the chamber was again purged with pure nitrogen for 2 min prior to chamber opening.

2.3. Diagnostics

A scanning electron microscope (SEM) MIRA3 (TESCAN, Czech Republic) was used to observe the surface morphology of silicon dioxide surface before/after plasma treatment. An SEM VEGA II SBH (TESCAN, Czech Republic) was used to observe the etching rate of SiO_2 films. MIRA3 is a FEG SEM (Field Emission Gun Scanning Microscope) with high brightness Schottky emitter and In-Beam SE (Secondary Electron) Detector with resolution of 1 nm at 30 kV. VEGA II is a SEM with tungsten thermal emission gun and resolution of 3 nm. Therefore, high-resolution imaging of the surface of plasma-treated films and the determination of etching rate using the imaging of cross sectional area of fractured samples was possible. All dimensions of stripes produced due to non-uniform etching were measured by means of SEM MIRA3, because the reflectivity of the surface was too high for a confocal microscope. Surface images of the uncoated samples were made using the accelerating voltage 10 kV, edge samples were observed at accelerating voltage 30 kV.

Chemical changes in the surface composition after the plasma treatments were studied using a high resolution XPS (X-ray Photoelectron Spectroscopy) performed with the XPS spectrometer ESCALAB 250 Xi (Thermo Fisher Scientific Inc., UK). The system is equipped with 500 mm Rowland circle monochromator with microfocused Al Kα X-Ray source. The survey spectra were acquired with pass energy of 50 eV and resolution of 1 eV. High-resolution scans were acquired with pass energy of 20 eV and resolution of 0.1 eV. The photoelectron spectra were referenced to the peak of aliphatic C—C bonds at 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software. The transfer time between opening the plasma reactor, manipulation and inserting of the samples into XPS load-lock chamber was approximately 10 min.

3. Results and discussion

The effect of H_2 plasma treatment on silicon dioxide layers of different thicknesses was studied at various experimental conditions. The hydrogen gas flow varied in the range 0.135–1.0 $l \cdot min^{-1}$. Two distances of SiO_2 surface from Al_2O_3 dielectric barrier of DCSBD electrode system (surface-to-surface distance) were compared. The treatment time was varied from 5 min up to 30 min. The etching effect of hydrogen plasma was confirmed even for the shortest treatment time.

3.1. The effect of plasma treatment on the surface morphology of SiO_2 films

Visually homogeneous plasma generated by DCSBD consists, in fact, of the diffuse plasma generated on the electrode system surface over the metal electrodes together with a brighter filamentary streamer plasma on the surface over the gap between electrodes. The apparent homogeneity occurs because the discharge consists of numerous H-shaped elementary discharges developing with a high density and running on the electrode system surface along the embedded strip electrodes. The

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