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Plasma cleaning and activation of silicon surface in Dielectric Coplanar Surface Barrier Discharge

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ABSTRACT

Surface of crystalline silicon (c-Si) wafers was treated in dielectric barrier discharge and the cleaning effect, wettability and adhesion of gold nanoparticles were investigated. Treatment of c-Si was realised in air plasma at atmospheric pressure in Diffuse Coplanar Surface Barrier Discharge (DCSBD). Plasma cleaning and gold nanoparticle adhesion were investigated by means of Laser Desorption Ionisation Time of Flight Mass Spectrometry (LDI TOF MS) and X-ray photoelectron spectroscopy (XPS). Wettability and surface morphology were studied by contact angle measurement and atomic force microscopy, respectively. By laser desorption in positive ion mode, C_n^+ and Na^+, K^+, etc. ions were detected on the industrially cleaned surface of silicon wafers. After plasma treatment the substantial decrease of such ions was observed. Plasma treatment of the surface increased also its hydrophilicity and adsorption of gold nanoparticles on the Si surface significantly increased after 5 s cleaning in plasma. Intensity of gold clusters Au_n^+ absorbed on the plasma treated Si surface was in order of magnitude higher than intensity of clusters absorbed on the untreated surface.

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1. Introduction

The purity of silicon is substantial for a good quality of silicon wafers in electronics, computer technology, solar panel constructions, etc. Silicon is produced by several methods, e.g. by the carbothermal reduction process [1] while Si monocrystals are then made by zonal melting mostly in graphite ovens [2,3]. Purity of Si-wafers in bulk or on the surface is very important and before their use for various purposes cleaning of the surface should be done. Wet procedures using chemicals should be avoided and plasma cleaning of surfaces is preferred [4].

Contamination of silicon by carbon is a serious problem. The removal of carbon contamination on silicon wafer surfaces by dry clean method using micro-wave induced oxygen plasma was studied [5]. For example, the organic contamination can create problems in silicon wafer production. Therefore, it is necessary to remove the organic contaminants from silicon before wafer fabrication process. The methods used in wafer cleaning technology are mostly wet chemical cleaning techniques and they are based for example on Radio Corporation of America (RCA) cleaning [6]. From various dry cleaning methods [7] we can mention: thermal cleaning, gas phase cleaning, photochemical enhanced cleaning, plasma cleaning, etc. Among dry cleaning methods, plasma cleaning [8–10] is one of the most important dry cleaning techniques used to remove organic contamination from the silicon wafer surfaces.

Plasma treatment surface modification technology is a kind of environmentally friendly procedure representing a simple, short time and fast modification procedure without any pollution. Plasma modification takes place on the upper surface of the wafers however the bulk properties of materials remain unchanged [11,12]. In plasma processes chemical functional groups can be generated by film deposition or surface modification on various materials like glasses, polymers, ceramics, metalloids and also conductive surfaces like metals [13–15].

Although many plasma techniques are actually used for modification of various surfaces, atmospheric pressure plasma processes appear to be more economical as compared with vacuum processes. Dielectric barrier discharges (DBDs) conflate the advantage of non-equilibrium plasma properties and easy and low-cost operation at atmospheric-pressure. Due to their properties DBDs are commonly used for plasma cleaning and activation of various materials [16–18], ozone production [19], biological and medicine application [20] etc. Nevertheless, commonly used volume DBDs plasma is not uniform; consisting from filamentary microdischarges oriented perpendicular to the treated surface, producing the pin holes on the surface and causing the surface treatment non-uniformity or even damaging the substrate. Cernak et al.

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have developed so called Diffuse Coplanar Surface Barrier Discharge (DCSBD) [21] enabling to generate visually uniform plasma large area thin film of plasma and its high plasma power density allows a fast and efficient in-line plasma treatment of various materials such as wood, nonwoven textiles, glass etc. [22–25].

Silicon surfaces exposed to an ambient atmosphere are immediately contaminated by organic molecules that are bond covalently via SiC bonds on the silicon surface [17]. By means of time-of-flight quadrupole mass spectrometry laser ablation of SiC on the surface, the mechanism of formation of $Si_nC_m^+$ ions was studied [26]. Density functional calculations were carried out for singly charged mixed silicon–carbon anions $Si_nC_m^+$ and for neutral Si_nC_m clusters with up to eight atoms to study the structure and bonding in mixed silicon–carbon clusters and their anions [27].

We have recently shown in several papers that LDI-TOF MS is a suitable and effective method to generate and study clusters formed by laser ablation from various solid materials like nano-diamonds [28], $AgSbS_2$ [29], As-sulfides [30] and to analyse the nano-layers of various solid materials e.g. As–Se [31] and As–S–Se [32] glasses or phosphorus nitride [33]. It was found that this technique like FT-IR, SIMS-MS and TD-MS is also able to perform species desorption and ionisation from the surface and thus to detect surface contaminants and characterise eventually the efficiency of various surface cleaning technologies.

The aim of this work was to study the cleaning effect of DCSBD plasma on silicon. Plasma cleaning and activation of Si surface were investigated by means of the TOF MS. Surface free energy and wettability were studied by contact angle measurement, chemical composition and surface morphology were also studied by XPS and AFM, respectively. Improvement of adhesion of gold nanoparticles on the Si surface after plasma treatment was also investigated.

2. Experimental

2.1. Plasma treatment

The plasma treatment of silicon wafers has been carried out by DCSBD. DCSBD consists of two systems of parallel strip-like electrodes embedded in 96% alumina where the ceramic layer between the plasma and electrodes was 0.4 mm. Applying sinusoidal high-frequency high voltage (14 kHz, 10 kV peak to peak) between both electrode systems, the large thin layer of visually diffuse cold plasma with high non isothermicity is created. The schema of plasma electrode is shown in Fig. 1. The thickness of uniform DCSBD plasma layer is ~0.33 mm and the power density can vary from 50 to 300 W/cm^2.

Si samples were fixed to a holder that moves samples over the plasma (Fig. 1 B). The distance between the sample and the ceramics plate was 0.3 mm, thus sample surfaces were exposed to the active plasma. Treatment was realised in ambient air plasma at atmospheric pressure at various time (5, 15, 30 and 50 s) at constant power density of 100 W/cm^2.

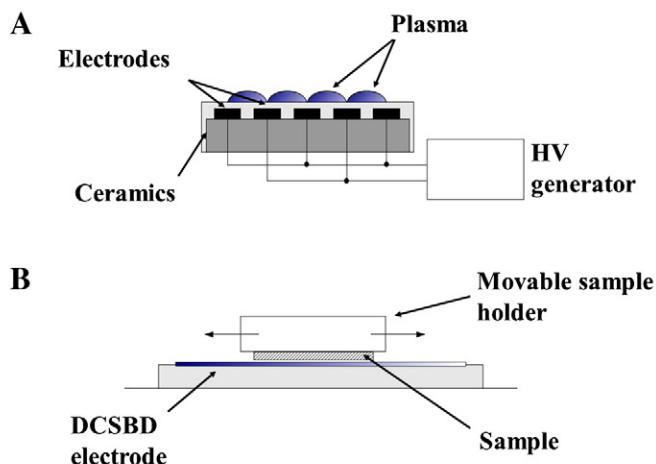

Fig. 1. A. Cross-section of electrode DCSBD system. **B** Laboratory DCSBD reactor with movable sample holder.

The silicon wafers used in this study were polished crystalline silicon wafers (111) orientation, p-type with thickness of 450 μm, doped with boron purchased from ON Semiconductor (Rožnov pod Radhoštěm, Czech Republic).

2.2. Surface characterization

AXIMA CFR TOF mass spectrometer (Kratos Analytical, Manchester, UK) equipped with a nitrogen laser (337 nm) from Laser Science Inc. (Franklin, MA, USA) was used to acquire mass spectra of silicon wafers surface. Instrumentation was purchased from Shimadzu Company (Prague, Czech Republic). The repetition mode of experiments was performed at a frequency of 10 Hz and a pulse time width of 3 ns. The laser fluency was 60 mJ per pulse. The laser power was scaled in arbitrary units from 0 to 180 a.u. (20 mW) while the irradiated spot size was approximately 150 μm in diameter. Mass spectrometric analyses were carried out at a pressure of 10^{-4} Pa in the TOF analyser. Positive or negative ion spectra were recorded in linear and reflectron modes. However, it was found that ionisation in negative ion mode was quite low and therefore only results in positive ion mode were given. Mass spectrometric analysis was performed collecting mass spectra from at least 50 shots and the obtained data were accumulated. External mass calibration was done in both ionisation modes using red phosphorous clusters [34]. The red phosphorus was obtained from Riedel de Haën (Hannover, Germany).

Identification of the ions observed in mass spectra was done using a comparison with theoretical isotopic envelopes. Theoretical isotopic envelopes were calculated using Launchpad software (Kompact Version 2.3.4, 2003) from Kratos Analytical Ltd. (Manchester, UK).

Si wafers were fixed to a metal target and the target was then introduced into the mass spectrometer and the mass spectra were measured after the pressure had dropped below 10^{-4} Pa.

Contact angle measurements were obtained using Surface Energy Evaluation System from Advex Instruments s.r.o. Total surface free energy γ^{tot} (SFE) was calculated by acid – base model. According with this theory, SFE is the sum of its apolar and polar components according to Eq. (1)

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (1)$$

where LW denotes the total (apolar) dispersive Lifshitz - Van der Walls interaction and AB denotes the acid – base or electron-acceptor/electron-donor interaction [35]. The surface energy can be calculated according to Young–Dupré Eq. (2) expressed by terms as electron donor γ^+ and electron acceptor γ^- parameters:

$$(1 + \cos \Theta_i)\gamma_i = 2\left(\left[\gamma_i^{LW}\gamma_j^{LW}\right]^{1/2}\left[\gamma_i^{+}\gamma_j^{-}\right]^{1/2}\left[\gamma_i^{-}\gamma_j^{+}\right]^{1/2}\right) \quad (2)$$

where *i* refers to liquid and *j* refers to solid material. The values can be determined from contact angle measurement with three liquids of which two of them must have polar component. The testing liquids used for contact angle measurement were water, glycerol and diiodomethane.

The XPS measurements were done on the ESCALAB 250Xi (ThermoFisher Scientific). System is equipped with 500 mm Rowland circle monochromator with microfocused Al Kα X-ray source. An X-ray beam with 200 W power (650 microns spot size) was used. 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 0.05 eV. The measurements were done under an ultrahigh vacuum of 10-10 mbar, at room temperature. All spectra

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