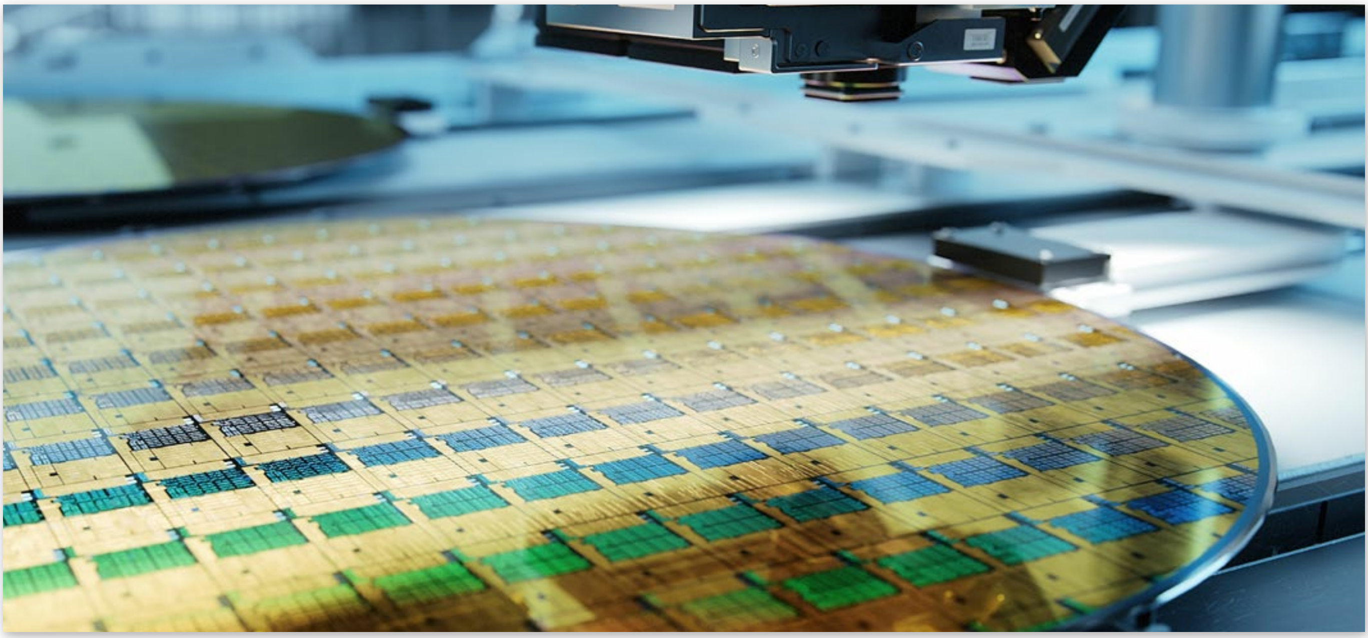


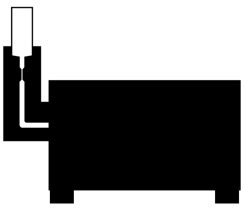
Application Note

Determination of the surface potential and isoelectric point of wafers with a zeta potential analyzer

– In cooperation with Anja Caspari and Dr. Astrid Drechsler, Leibniz-Institut für Polymerforschung Dresden e.V. –

The purity of solid surfaces plays a critical role during the manufacturing process of many products, such as wafers. Particle contaminations on wafer surfaces lead to a drastic decrease in device yield[1]. It is well established that the functionalities of wafer surfaces have an important influence on particle adsorption kinetics, like electrostatic attraction or repulsion. Adsorption kinetics are influenced by the zeta potentials of particles and substrates[1]. Therefore, it is of significance to understand the nature of the charged surface well. However, surface charges cannot be measured directly in dry state, since the derivation of surface charges from spectroscopic methods often lacks sensitivity. A powerful technique to evaluate charged surface functionalities is the measurement of the zeta potential, that is, the electric potential of solid surfaces in contact with an electrolyte solution. With this information it is possible to better understand the dissociation state of functional groups on the surface, and conclude the electrostatic interactions that will occur with other materials, such as particle contaminations. The new ZPA 20 zeta potential analyzer from DataPhysics Instruments (Fig. 1) measures the zeta potential of fibres, powders, and plate-shaped surfaces by means of an oscillating streaming potential or streaming current method. In this application note, we study the functionalities of different wafer surfaces with the ZPA 20. This is of interest not only for semiconductor manufacturing; silicon wafers are also frequently used as standard test surfaces e.g., in scientific research.

Measurement device
Zeta potential analyzer



Measurement method
Streaming current

Measured quantities
Zeta potential
Isoelectric point

Environmental conditions
Room temperature

Samples
SiO_2-Wafer
APS-coated SiO_2-Wafer

Industries
Wafer production
Semiconductor manufacturing

Technique and Method

Solid surfaces in contact with an aqueous solution are in most cases charged – either by dissociation of functional groups or by adsorption of ions and molecules from the solution. Even primarily uncharged surfaces in simple salt solutions usually carry a negative charge due to the adsorption of OH^--ions. If the solution moves with respect to the solid (or vice versa), a shear plane is formed between ions and molecules strongly adsorbed to the surface and the mobile ions in the surrounding solution (Fig. 2). The electrical potential at this shear plane, the so-called zeta potential, is a very sensitive measure for the charge situation on the solid surface. From pH- and concentration-dependent zeta potential measurements, conclusions can be drawn regarding the nature of the functional surface groups and adsorption processes[2].

The ZPA 20 zeta potential analyzer from DataPhysics Instruments uses the streaming potential (Eq. 1) or streaming current (Eq. 2) method to determine the zeta potential. An oscillating flow of an electrolyte solution, through a thin slit between two flat surfaces or the capillary system formed by a dense fibre or powder package, shears off the mobile ion layer and creates an alternating potential and current in the measuring cell. From the ratio of the streaming potential U_{str} or current I_{str} and the pressure difference Δp (Fig. 3), the zeta potential ζ is calculated[3][4]:

$$\zeta = \frac{\eta\kappa}{\epsilon_0\epsilon_r} \cdot \frac{\partial U_{str}}{\partial \Delta p} \qquad \text{(Eq. 1)}$$

$$\zeta = \frac{\eta}{\epsilon_0\epsilon_r} \cdot \frac{L}{HW} \cdot \frac{\partial I_{str}}{\partial \Delta p} \qquad \text{(Eq. 2)}$$

Fig. 1: The ZPA 20 zeta potential analyzer from DataPhysics Instruments

η is the viscosity of the solution, ε_r is the relative permittivity of the solution, ε_0 is the absolute permittivity of vacuum, κ is the electrical conductivity of the solution, L, H and W are the dimensions of the streaming channel between plate-shaped samples.

Data analysis using the streaming current requires knowledge of the dimensions of the streaming channel and can be used for plate-shaped surfaces. The streaming potential allows calculating the zeta potential based on the viscosity and the conductivity of the solution and can be used for measurements of fibres[5], powders[6], and also plate-shaped surfaces[7].

Experiment

In this application note, the zeta potential ζ and the isoelectric point of recently cleaned and activated oxidised silicon wafers (SiO_2-wafers) as well as silicon wafers coated with a thin aminopropylsilane layer (SiO_2-APS-wafers) were determined using the ZPA 20 from DataPhysics Instruments (Fig. 1) and the streaming current method.

To ensure the cleanliness of the measuring device and the MC-ZPA/S measuring cell for plate-shaped materials, the equipment was thoroughly cleaned with ultra-pure water (≤ 0.055 µS/cm) before the wafer samples were put into the measuring cell.

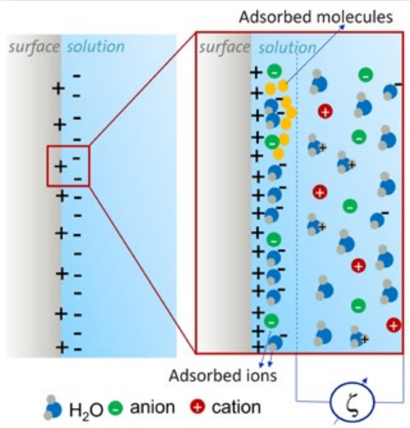


Fig. 2: Charge formation at solid surfaces in aqueous solution

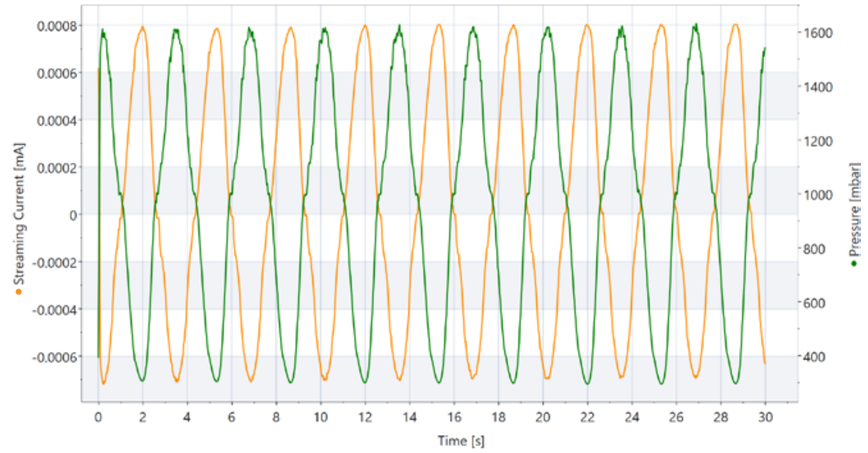


Fig. 3: Oscillating pressure (green) and resulting streaming current (orange) vs. time

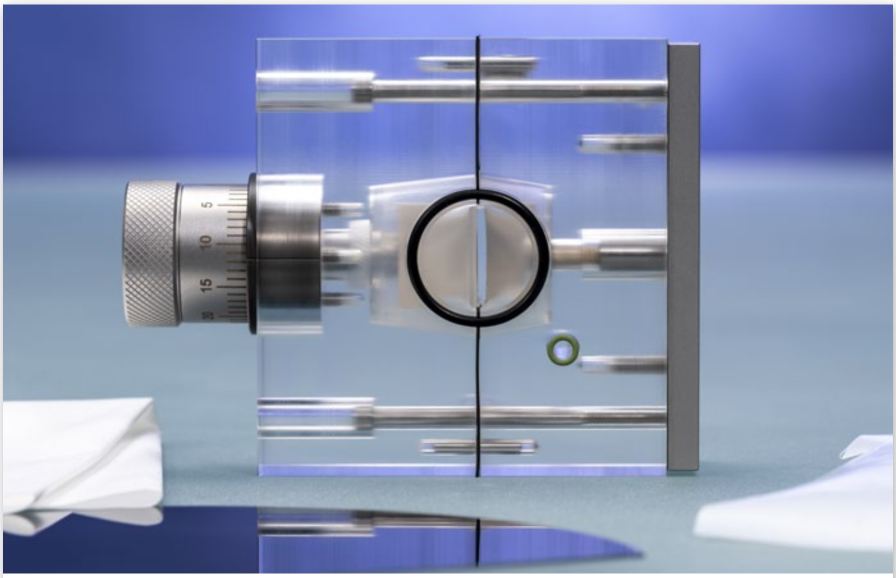


Fig. 4: The MC-ZPA/S measuring cell enables measurements of the zeta potential of plate-shaped solids, such as wafers or plastic sheets.

The wafer samples with a size of 10 mm x 20 mm each were attached to the stamps of the MC-ZPA/S measuring cell by adhesive tape (Fig. 4) and arranged to face each other and form a gap of about 100 µm in height.

After fixing the cell to the ZPA 20, the device's storage vessel was filled with KCl solution (1 mmol/L, pH ≅ 6). By using the 'bubble purging'-function of the ZPA 20, possible air bubbles in the measuring cell and in the device's streaming channel were be removed before starting the measurement. From the streaming current vs. pressure ramps obtained in several oscillations (Fig. 3), the zeta potential was calculated for the given pH values. For each of the solution's pH values, a measurement time of only few seconds is sufficient to generate results with excellent statistical quality, underlining the benefits of the new method, based on a bidirectional and oscillating solution flow. Thanks to the automatic titration function of the LDU 25 liquid dosing unit from DataPhysics Instruments (Fig. 5), the zeta potential can be determined automatically in a pH range from 2 to 10. Titrations were done once from the neutral to the acidic range and once from the neutral to the alkaline range. As titrants, HCl (0.1 mol/L) and KOH (0.1 mol/L) solutions were used.

After the measurement, the device and the measuring cell were thoroughly cleaned using ultra-pure water, which is especially easy since no pipes are used in the ZPA 20, reducing the surface area and complexity of the parts.

Results and Discussion

Fig. 6 shows the zeta potential of the wafer surfaces as function of the solution's pH. The curves show the typical decrease of the zeta potential from positive values at a low pH to negative values at an increasing pH. This is partly an effect of the dissociation of functional groups, but also of the pH-dependent adsorption of H_3O^+- and OH^--ions.

An important parameter for the verification of dissociable functional groups is the so-called isoelectric point, i. e. the pH value at which the zeta potential is zero. An isoelectric point below pH 4 and a plateau in the alkaline range indicate acidic surface groups, an isoelectric point above pH 5 and a plateau at low pH values are characteristic for alkaline groups. Isoelectric points around pH 3 and 4 are obtained for primarily uncharged or amphoteric surfaces.

For the activated oxidised silicon wafer, the isoelectric point is at the pH value of 2.5, showing the presence of acidic hydroxyl groups. The isoelectric point of the silicon surface coated with APS is at a pH value of around 7, which is characteristic for alkaline groups. This proves that the thin alkaline coating was deposited successfully. In contrary to the activated silicon surface, the coated surface is charged positively at pH values < 7. From these results one can conclude that APS-coated silicon wafers have a positive surface potential at a neutral pH value and thus would be less prone

Fig. 5: The LDU 25 liquid dosing unit allows operators to change the concentration inside the solution automatically.

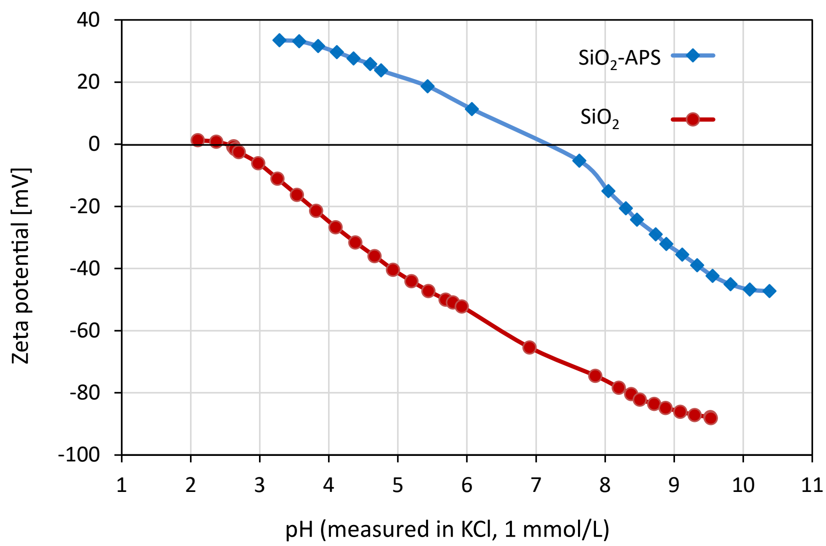


Fig. 6: Zeta potential of the two wafer surface samples as function of the solution's pH value

to attract positively charged particular impurities.

A look at the measurement diagram in Fig. 3 shows that the bidirectional pressure ramps formed an even, sinusoidal curve, giving the operator a clear indication that the sample was prepared well and homogeneously. In addition, the sinusoidal character of the pressure ramps and also the streaming current show that the APS-coating is highly stable and does not peel off during the measurement. In view of the often-challenging preparation of a homogeneous sample layer for zeta potential measurements, the bidirectional approach easily reveals any issues that stay unnoticed with unidirectional measurement techniques.

Summary

The ZPA 20 zeta potential analyzer equipped with the plate measuring cell from DataPhysics Instruments can measure the pH-dependent zeta potential of flat solid surfaces and helps to identify acidic and alkaline surface functionalities. Furthermore, surface modifications or thin coatings can be detected. This was demonstrated by comparing the zeta potential of an oxidised silicon wafer with an APS-coated silicon wafer. The article furthermore showcases the beneficial effects of the bidirectional measurement principle regarding sample preparation verification and measurement speed compared to established methods.

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