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Surface photovoltage in silicon. Novel applications for chemical and biological sensing

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The Surface Photovoltage technique has been recently employed for chemical and biological sensing. Selected chemical and biological species deposited on the crystalline silicon surface introduced surface barrier changes that were detected using the non-contact Surface Photovoltage mode. The magnitude of the surface barrier modifications provided a unique signature of the sensed species. The simplicity and sensitivity of this technique offer an exciting opportunity for a new type of low-cost sensing devices.

Key words: *Surface Photovoltage technique; chemical and biological sensing; crystalline silicon; surface barrier*

1. Introduction

The Surface Photovoltage (SPV) technique monitors semiconductor surface barrier changes introduced by illumination. Since the steady-state semiconductor surface barrier and its illumination induced modifications are related to the surface and bulk properties of the measured material, the technique offers the possibility for simple determination of some fundamental properties of the semiconductor material [1, 2]. SPV measurements can be tailored according to specific needs, for example: sub-bandgap illumination is used to study surface states [3, 4], low intensity above-bandgap illumination is employed to determine minority carrier lifetime [5], light modulation frequency is varied in order to differentiate between the slow surface states and bulk recombination processes [6], and non-contact measurements are selected when the measurement of undisturbed surface properties is desired [6, 7].

The SPV technique has found particularly important applications in the monitoring of silicon wafer properties [7, 8]. Commercial SPV-based monitoring tools were incorporated into silicon integrated circuit (IC) manufacturing processes, facilitating detection in real-time of faulty silicon wafers. These tools were designed specifically for the monitoring of silicon wafers by limiting the measurement parameters (e.g.,

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excitation wavelength, photon flux density) to values appropriate for measuring the silicon electronic properties, while at the same time employing additional features to enhance the measurement capabilities (e.g., multiple probes for detecting the SPV signal, additional illumination, heating stage, corona discharge source).

These applications have led to a better understanding of the Surface Photovoltage phenomena in high quality silicon material and have demonstrated potential applications of the SPV technique beyond silicon IC devices, particularly in the area of nanoscale structures and molecular sensing [9–11]. The last application reflects the growing interest in low-cost sensors for chemical and biological monitoring. The use of the silicon surface as a binding platform for a variety of chemical and biological compounds [12, 13] could lead to SPV sensors that offer the advantages of low manufacturing cost, a device design allowing easy integration with an electronic control platform, sensitivity, the ability to detect multiple species, speed, and reusability. Silicon surface barrier measurements have been previously proposed for sensing small quantities of selected gases [14–16]. Recent reports [17] expanded the technique further to aqueous solutions of a variety of inorganic chemicals, selected organic compounds, and biological DNA species. This paper reviews recent advances in novel SPV applications.

2. Experiment

The SPV technique employed in this work is based on previously described [6] silicon surface charge measurements. The SPV signal Ψ_{SPV} is obtained by illuminating the front side of the silicon wafer with a monochromatic photon flux (λ = 800 nm), while the backside of the wafer is not illuminated (Fig. 1). Photons are absorbed mostly within the region adjacent to the surface and generate excess carriers, decreasing the silicon surface barrier. The potential difference created by the changing surface barrier at the illuminated front side with reference to the unchanged dark back side barrier is the measured SPV signal. At high photon flux, the front surface barrier is reduced to nearly zero, and the SPV signal corresponds to the equilibrium silicon surface barrier.

Since the equilibrium surface barrier height is related to the density and energy spectrum of the surface charges, standard space-charge expressions [1, 2] can be used to calculate the average surface charge density. Intrinsic silicon surface charges are due to bonds terminating at the surface, although the density of broken surface bonds can be reduced by surface reconstruction. In most cases, however, the majority of the silicon surface charges are due to either intentional or unintentional reactions between the silicon surface atoms and the environment. Chemisorbed and physisorbed chemical species change the surface charge density and modify the surface barrier [12, 13, 18]. While monitoring the effect of the surface species, it is important that the measurement does not perturb the surface. Therefore, the present SPV measurements were conducted in a “contactless” mode, without the need for additional silicon processing, and used commercially available SPV measuring equipment [19].

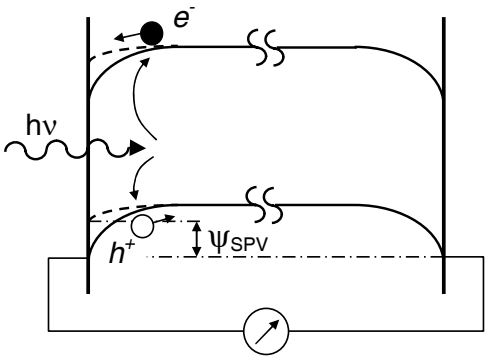

Fig. 1. SPV principle. Illumination with photons with energies higher than the silicon bandgap ($h\nu > E_g$) causes a decrease of the front (illuminated) surface barrier. Under high illumination intensity the surface barrier disappears and the SPV signal corresponds directly to the surface charges

SPV measurements require that the surface be free of defects pinning the Fermi level**;** therefore, only high quality 150 mm diameter silicon wafers were used. They were n-type and p-type, with resistivities between 1 Ω·cm and 25 Ω·cm. Since surface atomic arrangement depends on the surface orientation, only wafers with exact (001) and (111) orientations (±0.5°) or wafers misoriented by 4° from the (111) plane towards [011] were used. The initial uniform surface termination was achieved by annealing the wafers in hydrogen ambient as previously described [9]. Previous reports demonstrated that such a heat treatment can provide a well-organized surface with uniform hydrogen coverage [9, 10].

In order to investigate the effect of chemical species on the silicon surface barrier**,** freshly prepared wafers still maintaining the original H_2 termination were dipped into aqueous solutions of selected inorganic bases and acids. The sensitivity of the technique was tested by varying the chemical concentration and time during which the silicon wafer was exposed to chemicals. The acid pH varied from 1 to 6, and base pH varied from 8 to 13. Corresponding tests were also conducted for constant pH, but with varying chemical species. SPV measurements of the silicon surface barrier were conducted within less than 2 minutes after sample removal from the chemical bath and air drying in order to minimize the reaction between the treated silicon surface and air [9]. Only dry Si surfaces were measured. Occasionally, the surface was blown off with nitrogen after chemical exposure, but before measurements, in order to accelerate the drying of the silicon surface.

In addition, silicon wafers were exposed to a few selected organic compounds belonging to the same family. Wafers were dipped into hot alkanes (pentane, hexane, and octane) for 15 min, and then immediately measured. Either pure alkanes or their solutions in an inert hydrocarbon (xylene) were used. The silicon surface in contact with hot alkanes underwent thermally induced hydrosilylation, providing at least partial, stable monolayer termination [20].

The use of SPV detection was also investigated in a genomic experiment using a single strand, 12-mer DNA probe terminated with an acrylate linker group anchored to a silicon surface functionalised with 3-mercaptopropyl-trimethoxysilane (for a detailed description of sample preparation, see Ref. [11]). The silicon surface barrier

height was then measured and correlated with the presence of the DNA group on the silicon surface. The SPV signal was measured for the single strand DNA probe and also for samples exposed to the completely matched and one-pair mismatched DNA molecules.

3. Results and discussion

The surface band bending, and therefore the measured SPV signal, corresponds to electrical charges residing either on the silicon surface or in its vicinity. Many chemical and biological species are capable of modifying the surface barrier by electrical charge transfer while forming chemical bonds with the silicon surface (chemisorption) or by electrostatic interactions with the silicon surface states (physisorption). In the case of chemisorbed species, the binding energy is usually larger than 0.1 eV. Various processes contributing to physisorption (van der Waals interactions, dipole formation, image forces, etc.) are characterized by binding energies below 0.1 eV [21]. For a given species, the magnitude of the surface photovoltage varies monotonically with the concentration, allowing limited quantification of the concentration. At a fixed concentration, the magnitude of the surface barrier modification is often specific for the molecules reacting with the silicon surface, which offers an opportunity for limited qualitative analysis.

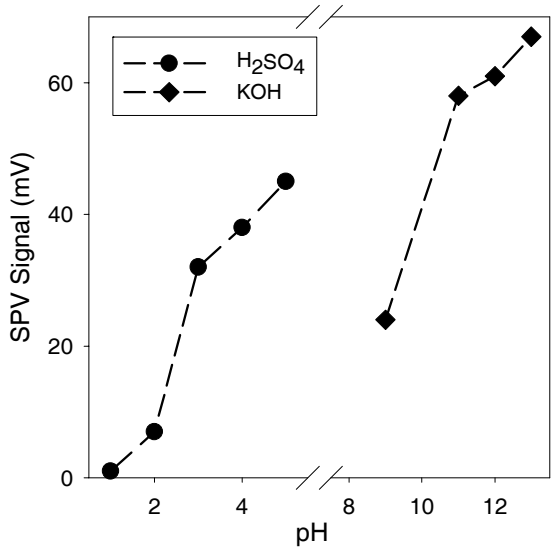

Fig. 2. Correlation between the SPV signal and ionic concentration for selected inorganic base and acid

Exposure of the silicon surface to inorganic bases or acids results primarily in chemisorption of OH^- and H^+ ions, modifying the silicon surface barrier [10, 12, 13].

This process is limited by the number of available ions. The number of ions undergoing reaction with silicon is determined by the base or acid concentration. Figure 2 shows the correlation between the SPV signal and the ionic concentration. The modification of the silicon surface barrier is also related to the type of chemical species. The application of solutions with the same pH, but containing different acids or bases produces different SPV values (Fig. 3). This difference could be related to different counter ions present in the solution (Na and K^+ in the case of bases, and SO_4^- and Cl^- in the case of acids). These counter ions might affect the reaction on the silicon surface or may partially screen the silicon surface charges.

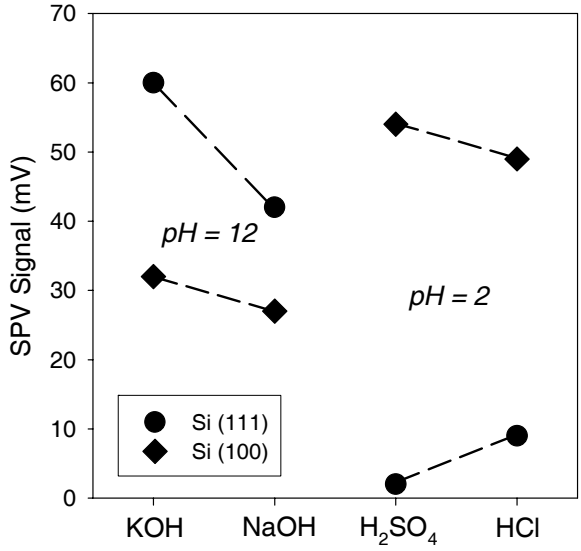

Fig. 3. The SPV signal for different chemical species with the same pH (shown separately for selected acids and bases). SPV detection limit was under 0.2 mV

The surface barrier modification usually occurred within the first 10–20 seconds of chemical exposure, reaching for most chemicals steady state after this period (Fig. 4). Long-term change of the Si surface barrier when exposed to KOH is possibly due to a slow etching of the Si surface. The modifications of the silicon surface charges were completely reversible, as shown in Fig. 5. In this case, Si samples were dipped into the acid, dried, then measured, dipped into base, dried, measured again, and the cycle was repeated. Thus, the binding energies of OH^- and H^+ ions cannot be large. Similar observations were previously reported for the ions deposited on silicon surfaces from a gaseous ambient [9]. The ability to respond to small changes in the ionic concentration in a relatively short time, different SPV signals for the same concentration of ions from different chemical species, and signal reversibility makes SPV a potentially valuable technique for low cost chemical sensors.

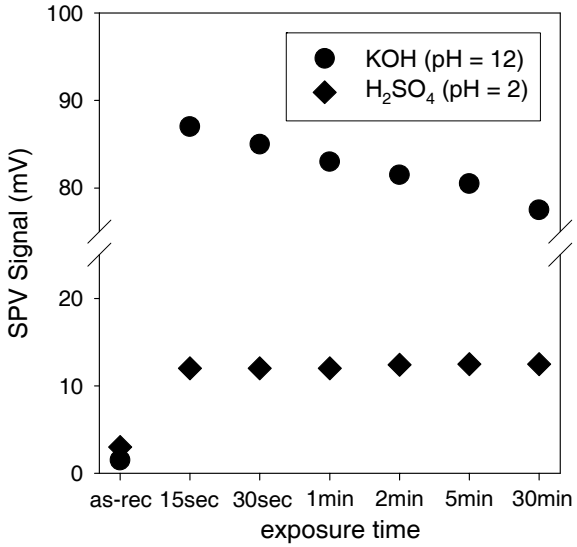

Fig. 4. SPV signal as a function of exposure time for selected acids and bases

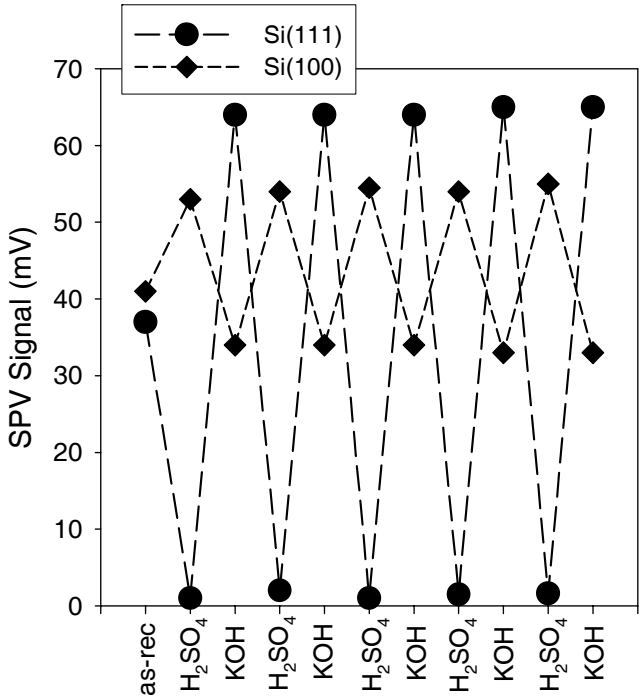

Fig. 5. Change of the SPV signal after sequential acid and base treatments

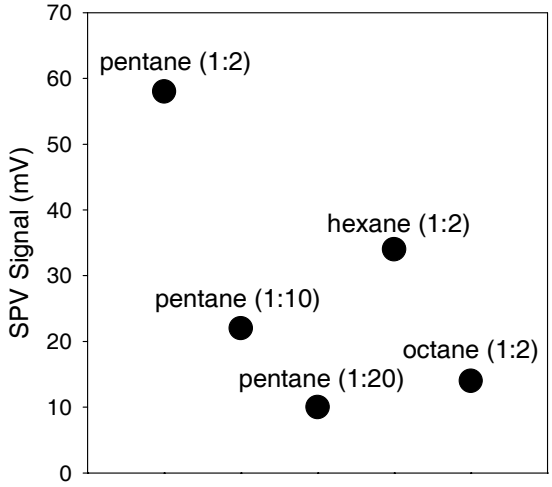

Fig. 6. Changes of the SPV signal induced by exposure to selected alkanes mixed with xylene. Numbers in brackets describe the alkane/xylene ratio. Without any organic species, the SPV signal was 21 mV

Figure 6 shows the response of the silicon surface barrier to the presence of organic species. The goal of this experiment was to investigate the sensitivity of the SPV measurement to an increasing length of the alkane chain. The attachment of alkane molecules can cause partial rearrangement of silicon surface atoms, therefore changing the silicon surface barrier [23, 24]. The degree of this rearrangement is expected to depend on the structure of molecules. The SPV measurement showed correlation between the molecular weight and the extent of silicon surface barrier change. The variation of the SPV signal with changing alkane concentration reflects decreasing surface coverage when the ratio of alkane-to-solvent was decreased.

The measurement of a genomic sample was the first attempt to employ SPV in the area of biological sensing [11]. Assuming DNA density of 3×10^5 12-mer nucleotides per μm^2 from the footprint of a densely packed monolayer [11], we can estimate from the SPV measurement (Fig. 7) that the attachment of a single-strand oligonucleotide to the silicon surface changes the potential barrier by approximately 31.5 meV. This value is in good agreement with an independent experimental result [25] of 30 meV surface potential change when 3×10^5 DNA strands per μm^2 are present.

The hybridisation of the DNA target strands with complementary DNA probe strands reduced the surface barrier by 3 meV. Assuming the same effective charge for the probe and target DNA strands, this change corresponds to a 10% efficiency of hybridization, which is a commonly accepted number. In the control sample, the application of the one-pair mismatched DNA target caused no change in the SPV signal (Fig. 7e), showing that no significant binding between the mismatched target and the probe DNA strands took place.

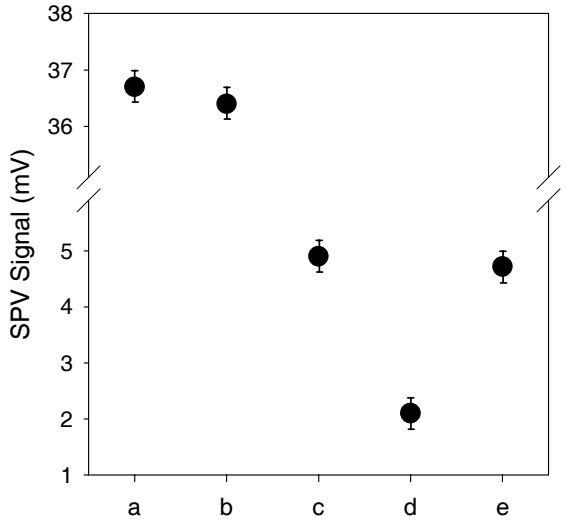

Fig. 7. Genomic experiment – SPV signal corresponding to:
a) silicon substrate terminated with –OH groups,
b) silicon surface functionalised with 3-mercaptopropyl-trimethoxysilane,
c) silicon surface with single strand 12-mer probe DNA attached,
d) sample c) exposed to complementary target DNA, e) sample
c) exposed to non-complementary target DNA (one-pair mismatch)

In conclusion, recent experiments have demonstrated the potential of the Surface Photovoltage technique for chemical and biological sensing. Further work is needed to extend this characterization technique to new chemical and biological applications and to develop a better understanding of the mechanisms behind the observed semiconductor surface barrier changes. Early results, however, indicate that SPV might offer a combination of versatility, low cost, sensitivity, specificity, and sensing speed complementing other chemical and biological characterization techniques.

Acknowledgement

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