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Letter

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Might Silicon Surface Be Used for Electronic Tongue Application?

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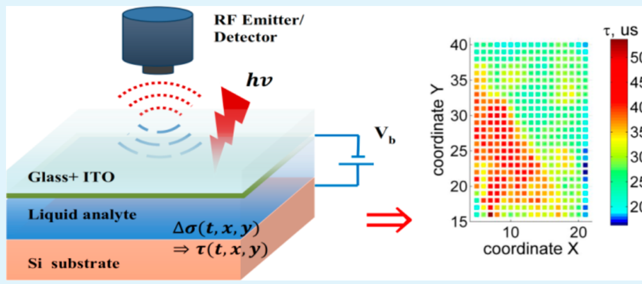
Supporting Information

ABSTRACT: An electronic tongue concept based on 2D mapping of photogenerated charge carrier lifetimes in silicon put in contact with different liquids is reported. Such method based on intrinsic sensitivity of the silicon surface states to the surrounding studied liquids allows creation of their characteristic electronic fingerprints. To increase recognition reliability, a set of characteristic fingerprints for a given liquid/silicon interface is proposed to be recorded at different bias voltages. The applicative potential of our sensing concept was demonstrated for different spirits and water samples.



KEYWORDS: *electronic tongue, silicon, surface electronic states, lifetime of charge carriers, recognition of substances*

The electronic tongue is defined in literature as an analytical instrument comprising an array of nonspecific, low-selective chemical sensors with high stability and cross-sensitivity to different species in solution, and an appropriate method of pattern recognition and/or multivariate calibration for data processing.[1] This kind of powerful analytic systems is designed to be widely used in food industry, medical diagnostics and pharmaceutics, for environment monitoring, detection of endotoxins and pesticides, as well as for many other crucial purposes.[2,3] The idea behind using low-selective sensors is based on analogy to biological organization of taste systems in mammals. In the region of tongue, there are several millions of nonspecific receptors responding to different substances. The taste buds possess several dozens of receptors on the tongue of mammals. The taste signals from the receptors are transmitted to the brain and processed by network of neurons creating the cerebral image of the sensed substance. An electronic taste-sensing system imitates natural processes taking place when molecules interact with the taste buds on the human tongue. The taste buds are represented by a sensor array exposed to these molecules and producing specific signals resulted from this interaction. These signals, similar to physiological action potentials, are recorded by computer, which corresponds to the neural network at the physiological level. The obtained set of the signal data can further be represented as an integral image, saved in a database, which is similar to human memory processing, as well as evaluated by comparison with already existing sensor response matrices characterizing previously recorded taste patterns.

The most developed types of electronic tongue are based on electric potential measurements, optical sensors, impedance spectroscopy, and voltammetry. Potentiometric sensors are the most widespread type of transducers used in electronic taste-sensing systems. The number of sensors in an array may range from 4 to 40.[4] Selectivity and detection limits of a sensor array depend on composition and properties of the involved sensing materials[5] which can be, for example, lipid-based membranes,[6] chalcogenide and oxide glasses for potentiometry,[1] noble metals for amperometric signal detection,[7] plasticized organic polymers for optical sensors,[4] etc. Mathematical procedures applied to the signal processing, such as pattern recognition and multivariate calibration with an artificial neural network, principle component analysis, and self-organizing map techniques, are widely used to analyze very complex multichannel response of the sensor array.

In this letter, we present a recently patented concept of an electronic tongue,[8] which is distinct to the above-described analytical systems employing mainly sensing arrays formed by discrete electronic devices. The approach described herein is based on lifetime measurements of the minority charge carriers photogenerated in silicon substrates put in contact with tested liquids. This is a novel combinatorial electronic solid-state sensing screen for which each pixel corresponds to an illuminated zone of the silicon surface characterized by liquid-induced modulation of charge recombination velocity.

Microwave-induced photoconductive decay method is one of the most efficient contactless ways of measuring minority carrier lifetime in semiconductors.[9] This technique involves the optical excitation and the signal detection by a microwave system as it is described in details in the Supporting Information file and schematically shown in Figure S1 in the Supporting Information. Changing the illuminated zone of the studied sample allows creation of its 2D map in terms of the lifetime values, τ_{meas}, which depends on parameters of silicon substrate and its surface quality as it is illustrated inFigure S1d

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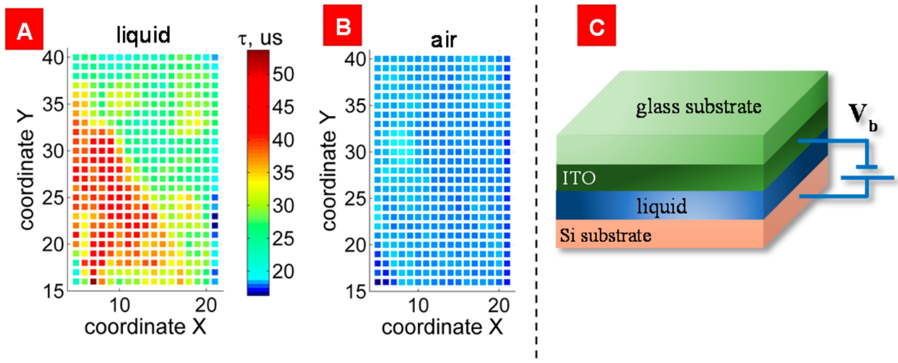

Figure 1. 2D lifetime maps of a silicon wafer put in contact with (A) ethanol and (B) air; (C) sandwich structure used to polarize silicon/liquid interface.

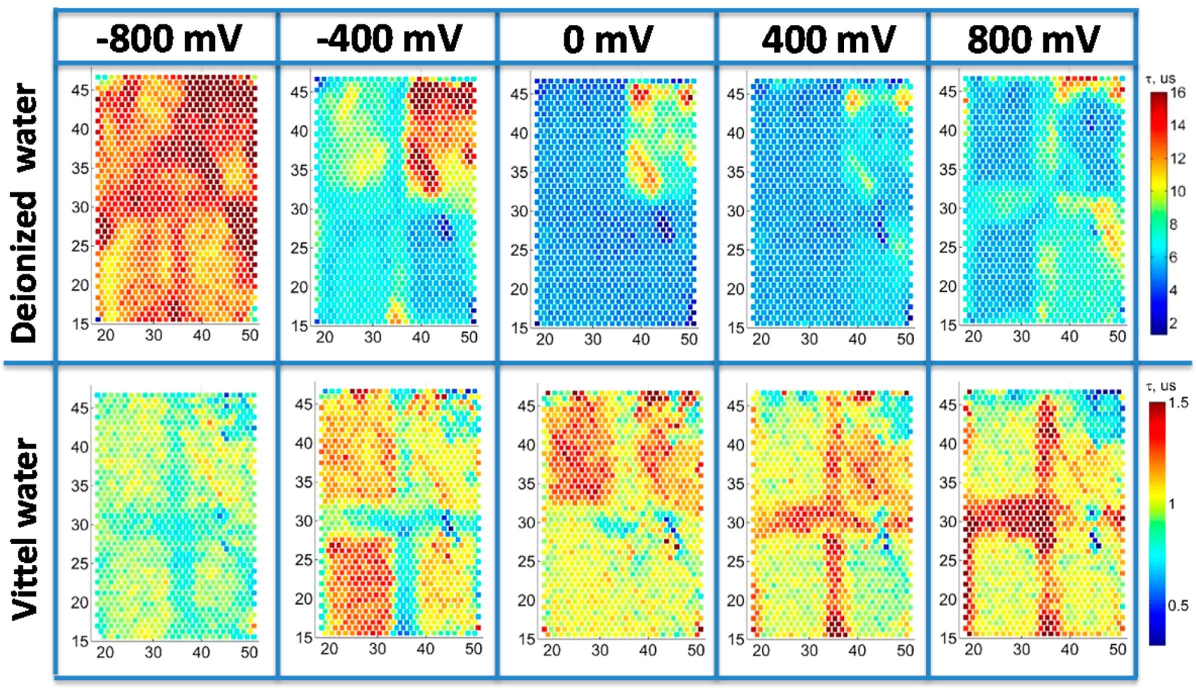

Figure 2. Electronic fingerprints of deionized and Vittel water samples obtained at various polarization potentials on a p-type silicon wafer patterned with thin film SiN_X rectangles.

in the Supporting Information for the case of a naturally aged monocrystalline silicon wafer. There are two main parallel electronic processes taking place during and immediately after the photoexciting IR pulse until the initial electronic equilibrium is reached: (i) bulk recombination and (ii) carrier diffusion toward the sample surface with subsequent surface recombination. The measured lifetime τ_{meas} is a characteristic of the both recombination processes as it is described with the following equation

$$\frac{1}{\tau_{meas}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{diff} + \tau_{surf}}$$

where τ_{bulk} is the bulk recombination time reflecting quality of the used crystalline silicon wafer, τ_{diff} is the characteristic time necessary for carrier diffusion to one of the surfaces of the silicon wafer from the place where the carriers were photogenerated (it depends on the wafer thickness and on the diffusion constant of minority carriers), and τ_{surf} is the characteristic time determined by surface recombination velocity depending on the surface electronic states of bare, naturally aged, or specially treated silicon wafers.

If a silicon sample is put in an intimate contact with a chemical substance, a new measured lifetime τ_{meas} map will directly reflect changing of the τ_{surf} values influenced by the substance molecules (in comparison with those ensured by air) since the values of τ_{bulk} and τ_{diff} remain constant. Thus, any substance is able to create a unique electronic fingerprint due to interface change, which can be visualized in terms of the measured 2D lifetime maps. Because the surface recombination velocity can vary by several orders of magnitude (from 0.25 to 5 $\times$ 10^4 cm/s),[10] τ_{surf} appears as an extremely efficient physical parameter ensuring high sensitivity of the silicon surface to play a role of an electronic screen integrally reflecting the complex physicochemical interaction between the silicon surface and a studied chemical substance. Panels A and B in Figure 1 show examples of such fingerprints obtained on an aged silicon substrate being in contact with ethanol and air, respectively. As one can see, the range of the lifetime values corresponding to the ethanol/silicon interface is in average about 5 times higher

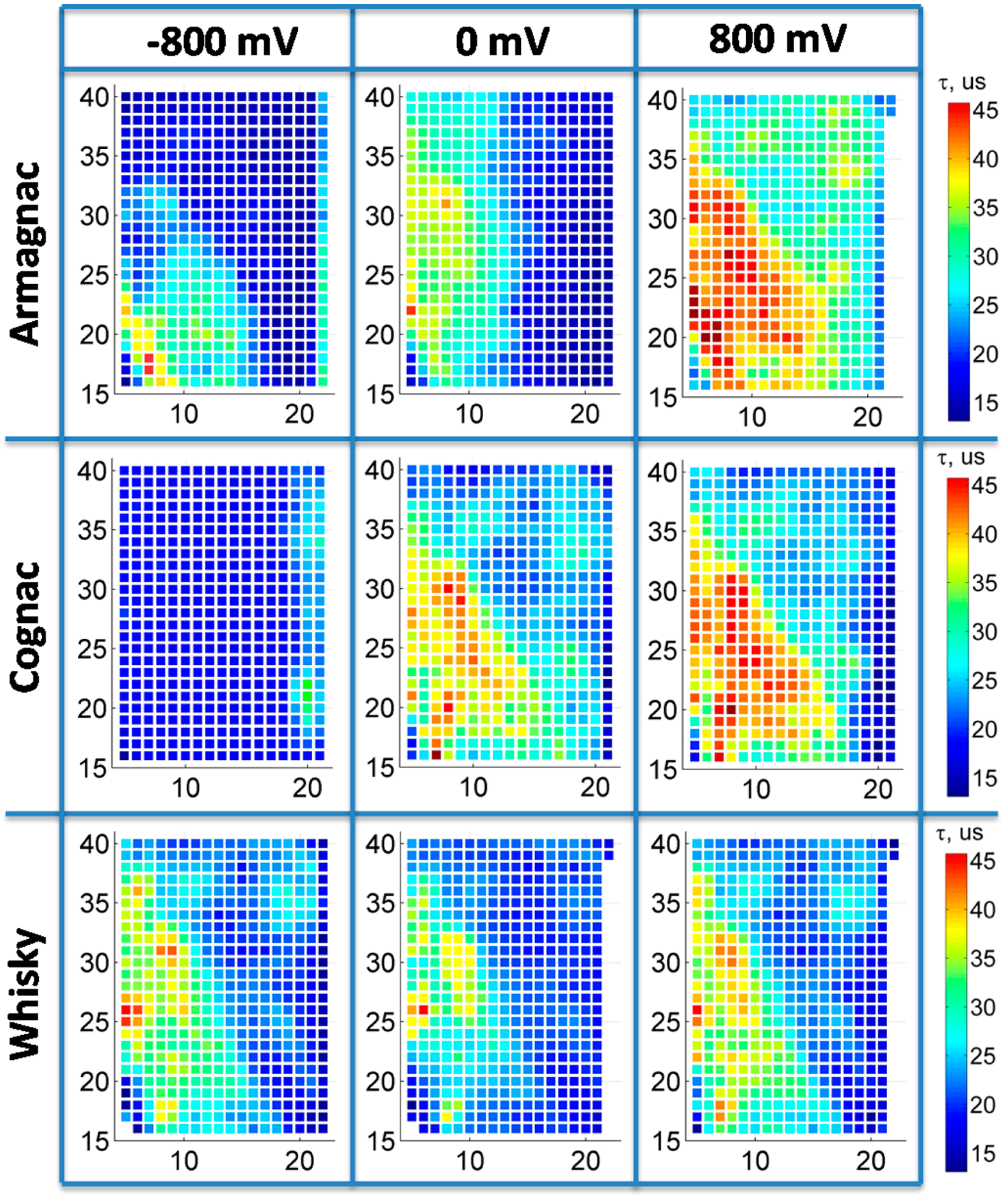

Figure 3. Electronic fingerprints of armagnac, cognac, and whisky obtained at various polarization potentials on a naturally aged p-type silicon wafer.

than the range of the τ_{meas} values obtained for the air/silicon interface, because the ethanol molecules interacting with the silicon surface lead to significant electronic passivation of the surface electronic states. This results in two completely different and easily distinguishable electronic fingerprints of the ethanol and air on the silicon surface.

To increase recognition reliability, one can additionally record a set of characteristic fingerprints for a given liquid/silicon interface by polarizing it with the sandwich structure schematically shown in Figure 1c. Indeed, continuous tuning of the difference of electric potentials V_b applied to the interface will ensure different bending magnitudes of the electronic bands in the near-surface region of the silicon substrate, refilling of interface electronic states and thus to significant voltage-induced modulation of the lifetime fingerprints formed by the studied liquid sample onto the silicon surface. Figure 2 shows an example of the electronic fingerprint series formed by deionized and Vittel water samples onto the surface of p-type silicon wafer patterned with four thin films SiN_X rectangles of different thickness (10, 20, 40, and 60 nm).[11] As one can see, the voltage-induced evolution of the water fingerprints depends on both amplitude and sign of the applied bias voltage defining, respectively, magnitude and mode (accumulation or inversion) of the surface band bending. There are specific V_b values for each regime at which the difference between the corresponding fingerprints (reflecting different chemical composition of the compared water samples) is the most pronounced. In such a way, tuning the voltage applied to a studied liquid/silicon interface allows finding the best contrast of the recorded images for their more reliable recognition. As for the reproducibility of the recorded fingerprints, it has been found to be quite satisfactory. Indeed, because any natural thermodynamic fluctuations taking place at the interface and leading to a certain difference between the fingerprints recorded several times for the same liquid was significantly less pronounced than difference between the fingerprints of different water samples. In addition, patterning of silicon surface with thin solid-state nanostructured films (such as SiN_X, for example) allow to increase reproducibility of the recorded fingerprints as well as to enhance general lifetime of the used substrates.

To demonstrate the applicative potential of our sensing concept for the taste-recognition purpose, we used three alcohol samples, cognac, Armagnac, and whisky with a similar global chemical composition (40% aqueous solutions of ethanol) and different taste agents. The most representative images of the electronic fingerprints created by the spirit samples on the naturally aged surface of p-type silicon substrates at 0 and ±800 mV of the voltage bias V_b are shown in Figure 3. Here, positive sign of voltage corresponds to accumulation band bending of the p-type silicon wafer. As one can see, the most important difference between the 2D lifetime maps formed by the studied samples corresponds to $V_b = -800$ mV. Thus, one could use this V_b value for rapid qualitative recognition of the tested spirits. However, to ensure a high discrimination capability level of the proposed sensing system, clustering of the data obtained for each spirit has to be achieved by means of a pattern recognition method.

In our work, 2D principal component analysis (PCA) method, commonly employed in various combinatorial platforms for discrimination purposes, was applied (see corresponding detailed description in the Supporting Information). This multivariate analysis approach projects a n-dimensional set of data into a new 2D or 3D set of coordinates called principal components. For this, 9 lifetime fingerprints of each spirit corresponding to 9 different values of voltage biases V_b were first recorded. Then, each fingerprint was reduced to 20 arbitrary chosen pixels and their normalized voltage-dependent lifetime values were considered as input data set for the given spirit sample (see Figure S2a in the Supporting Information). Uniting all the experimental data obtained for the three alcohol substances, a final input matrix with 9 × 60 elements was obtained (see Figure S2b in the Supporting Information). Thus, each pixel of the recorded fingerprints can be geometrically represented by a point in a 9D space (see Figure S2c in the Supporting Information). Projection of this space in a 2D subspace can be done by means of the well-known PCA algorithm. As a result, Figure 4 shows a 2D PCA plot

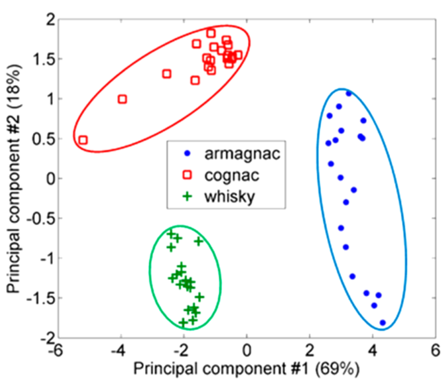

Figure 4. 2D PCA plot corresponding to the electronic fingerprints of the tested spirits formed on a naturally aged silicon wafer.

containing points for each of the tested spirits. The first two principal components account for about 87% of the variance in the measurements that is sufficient for informative description of the data provided by the silicon-based electronic tongue. In particular, since distance between the points reflects their similarity, clear clustering of the data illustrates a significant degree of discrimination capability of our analytical system to recognize among the studied alcohols.

In conclusion, silicon surface can be applied for electronic tongue purposes. Surface recombination velocity determining lifetime of photogenerated charge carriers is an extremely efficient physical parameter ensuring high sensitivity of silicon surface to play a role of an electronic screen reflecting the complex physic-chemical interaction between the silicon surface and a studied chemical substance. This kind of electronic tongues is an inexpensive and environmentally friendly combinatorial electronic sensing platform that is able to create characteristic electronic fingerprints of liquids, detect and recognize them with usual naturally aged or specifically treated silicon substrates. These are considered the first steps toward the use of this sensing approach for taste recognition application of different liquid food samples.

■ ASSOCIATED CONTENT

Supporting Information

Supporting Information file contains detailed descriptions of: (i) experimental setup used to create lifetime fingerprints of liquids put in contact with silicon substrates as well as (ii) procedure used to compose input data matrix for PCA algorithm. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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