Sensors and Actuators B 142 (2009) 418–424

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A micromachined gold–palladium Kelvin probe for hydrogen sensing

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ARTICLE INFO

Article history:
Received 23 December 2008
Received in revised form 11 March 2009
Accepted 16 March 2009
Available online 10 April 2009

Keywords:
Kelvin probe
Palladium
Hydrogen sensor

ABSTRACT

In this paper we discuss the fundamental principles of the Kelvin probe apparatus; in particular, first, we find an analytical relation for the sensitivity of vibrating capacitors, so that the advantages of integration can be quantitatively estimated; second, we describe an equivalent electric circuit for vibrating capacitors, thus allowing to simulate a complete Kelvin probe with a standard electronic circuit simulator; third, we illustrate the most important issues of the electronic interface.

A fundamental part of the research and technological work reported by this paper deals with the fabrication process of micromachined gold–palladium vibrating capacitors fully integrated on silicon, for hydrogen sensing applications. The relevant technological fabrication steps are explained. Preliminary experimental results of the first capacitor prototypes testing are reported as static *C*–*V* (capacitance–voltage) curves and as measurement in air of the gold–palladium work–function difference.

1. Introduction

The surface of materials or even the interface between different materials plays a fundamental role in most solid-state electronic devices. As an example, it is known that in a Schottky barrier between a metal and a semiconductor, a tenth of a monolayer of metal is sufficient to determine about 40% of the built-in barrier between bulk materials, as evidenced by photoemission spectroscopy experiments. Moreover, the practical importance of surface phenomena has become even more evident in the last two decades with the advent of chemical and biological sensors. For instance, the adsorption–desorption processes at the surfaces of chemically interactive materials induce variations in material properties (conductivity, permittivity, refractive index, etc.) which can be measured and related to volatile compounds concentration [1]. Catalysis is also an extremely important surface dependent phenomenon. A thorough discussion of the complex surface concept is out of the scope of this work; we will simply restrict the theme to one of the most important surface parameters, namely the Work–Function (WF). By considering the photoelectric effect, Einstein first understood that the WF is the work to be done in order to extract an electron from the Fermi level and bring it outside the metal without kinetic energy, in a free state. Progresses in molecular engineering and material science for optoelectronic and electronic devices have pushed further the research efforts towards the possibility of choosing and tailoring organic molecules organization having peculiar and tunable properties suitable for sensing applications.

When two materials with different WFs are brought into contact, electrons belonging to the material having a lower WF (higher Fermi energy level) will flow towards the material with higher WF (lower Fermi energy level); the voltage developed at the junction is called contact potential difference [2]. After the pioneering work of Lord Kelvin [3], Zisman showed that a vibrating capacitor could be advantageously used for the estimation of the work–function difference between two metal surfaces, resulting in the so called Kelvin probe (KP) [4]. In practice, if the exposed surfaces of the two plates of a vibrating capacitor have a WF equal to $q\Phi_A$ and $q\Phi_B$, the measurement determines the differential quantity $q\Delta\Phi_{AB}$, so that it is possible to measure $q\Phi_A$ once $q\Phi_B$ is known ($q\Phi_B$ is frequently the WF of a thin film of pure gold, whose value can be accurately measured by photoemission spectroscopy). A revisitation of the KP technique will be presented in Section 2.

KPs are very convenient for work–function measurement: first, the vibrating capacitor approach is intrinsically non-contact and

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doi:10.1016/j.snb.2009.03.076

non-destructive; moreover the KP method can be used for a wider range of materials, temperatures and pressures with respect to other methods [5]. For these reasons in particular KPs have been employed for characterizing the surfaces of semiconductors or metals or polymers, in bulk or thin film form, or even for biological samples. The (not exhaustive) list of applications include: gas detection; monitoring of rotational velocity, torque, misalignment or imbalance of a shaft; corrosion detection; degree of surface contamination; oil condition detection in oiling systems. As important examples, high-resolution surface topography can use a scanning KP (parasitic capacitances limit the spatial resolution); KP may be utilized for the determination of the WF changes induced by strains (at surface level and below) of a given material. Finally, applications in liquids will certainly become more and more relevant in the future considering the growing importance of biotechnologies [6,7].

The use of KP technique to study adsorption phenomena in chemically sensitive materials have been demonstrated with inorganic materials, such as metal-oxide semiconductors [8], and organic materials such as porphyrins [9] and polyacrylic acid [10].

In this paper we, first, discuss the fundamentals of KP design, with reference to:

(a) the sensitivity of vibrating capacitors;
(b) the advantages of integration;
(c) simulation of KP systems;
(d) the design of the electronic interface.

In particular, we will show that the sensitivity of vibrating capacitors can be significantly increased by down-scaling, thus demonstrating the advantages of miniaturized micromachined vibrating capacitors. Though micromachined work–function chemical sensors, based on suspended gate Field Effect Transistors, have already been proposed [11], here we describe a novel micromachined vibrating capacitor with a palladium plate for hydrogen sensing; the sensor takes advantage of the process of H_2 molecules dissociation and absorption by a palladium layer, which has been widely used in previous H_2 sensors [12], included palladium gate FET [13].

Even if attempts to fabricate micromachined KPs have already been performed the better technological control of the processes in terms of more accurate simulation tools allows a more reliable vibrating capacitor able to operate even at frequencies as high as a few MHz.

In particular, the novelty addressed by our proposed devices deals with the voltage actuation in charge of electrostatically moving the vibrating plate; the actuation is designed as two separated bias pads in order to achieve a more symmetric and uniform overall displacement (see Fig. 7).

The micromachined KP capacitor would encourage, in future developments, the incorporation, on the same chip, of a lock-in amplifier which can permit a better signal to noise (S/N) ratio to be achieved. As a consequence this technique could lead to a decrease in the minimum detectable signal. This implication is especially important for gas sensing applications; despite the micromachined KPs already devised since more than 10 years, the impact on the gas sensors field was not significant. This is due to the low sensitivity and not sufficiently low detectable signal allowed by the reported KP devices that are not suitable to work in the gas concentration range of interest (e.g. 100 ppm). In the case of Pd gate MOSFET or even MISFET the application of a modulation technique such as lock-in would be more problematic due to the intrinsic difficulty of modulating at reasonable high frequency a volatile compound flow, in order to have a consequent transconductance modulation in the frequency range where the lock-in strategy could be applied.

As preliminary experimental results, we show the static C–V (capacitance–voltage) curve for the vibrating capacitor and preliminary measurements of the work–function of palladium with the proposed micromachined vibrating capacitor.

2. Sensitivity of a vibrating capacitor

The sensitivity calculus of the KP technique quantitatively demonstrates the advantages of the miniaturization.

In KPs a voltage V_X is applied across a single capacitor whose plates are constituted, respectively, by the reference material, B, and by the sample material, A, whose WF is unknown. The charge Q stored in the capacitor is (1):

$$Q(t) = C[V_X(t) - \Delta\Phi_{AB}] \tag{1}$$

where $\Delta\Phi_{AB}$ is the contact potential difference (corresponding to the WF difference $q\Delta\Phi_{AB}$) and C is the capacitance. In general, if the capacitance is time-dependent, $C(t)$, the current through the capacitor may be expressed as the sum of the Kelvin current $i_K(t)$ and of a disturbing current $i_d(t)$, as follows (2):

$$\begin{aligned} i_c(t) &= \frac{dQ(t)}{dt} = \frac{d\{C(t)[V_X(t) - \Delta\Phi_{AB}]\}}{dt} = i_K(t) + i_d(t) \\ i_K(t) &= \frac{dC(t)}{dt}[V_X(t) - \Delta\Phi_{AB}] \\ i_d(t) &= C(t)\frac{dV_X(t)}{dt} \end{aligned} \tag{2}$$

In practical applications, V_X can be considered as constant; in this condition the capacitor current is (3):

$$i_C(t) = i_K(t) = \frac{dC(t)}{dt}[V_X(t) - \Delta\Phi_{AB}] \tag{3}$$

The voltage V_X may then be changed (slowly, in order to not create a large disturbing current) until the Kelvin current is zeroed, which gives $V_X = \Delta\Phi_{AB}$; in this way the contact potential difference may be measured.

In practice, a time-dependent capacitance may be obtained in different ways: for a parallel plates capacitor ($C = A\varepsilon/d$) the dielectric time constant, ε, the area of the capacitor, A, or the distance between the two plates, d, may be varied. Although all these methods have been explored, the most popular one consists in using a time-dependent distance d (vibrating capacitor) [4]. For simplicity, let us assume the distance between the two plates $d(t)$ be expressed by (4):

$$d(t) = d_0 + d_1 \sin(\omega_0 t) = d_0[1 + \alpha \sin(\omega_0 t)] \tag{4}$$

where α (i.e. d_1/d_0) is the relative distance variation. The hypothesis on the sinusoidal evolution of the distance between the two plates will allow to find a compact relation for the sensitivity of the vibrating capacitor; however, clearly, the main conclusions on the advantages of the integration have a general validity (for a given temperature dependence of the distance between the two metal plates). By considering the above mentioned hypothesis, the Kelvin current may then be expressed as follows (5):

$$i_K(t) = \frac{dC(t)}{dt}[V_X - \Delta\Phi_{AB}] = \left[-\frac{\varepsilon A d_1 \omega_0 \cos(\omega_0 t)}{(d_0 + d_1 \sin(\omega_0 t)^2)}\right](V_X - \Delta\Phi_{AB}) \tag{5}$$

In order to determine the sensitivity of a vibrating capacitor, it is useful to consider the peak value of the Kelvin current. The derivative of the Kelvin current with respect to time is (6):

$$\frac{d[i_K(t)]}{dt} = \varepsilon A \omega_0 (V_X - \Delta\Phi_{AB}) \frac{d}{dt}\left[\frac{-d_1 \cos(\omega_0 t)}{(d_0 + d_1 \sin(\omega_0 t)^2)}\right] \tag{6}$$