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Gas sensor applications of porous Si layers

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Abstract

The porous silicone (PSi) is a relatively new and promising semiconductor material with special physical and chemical properties which somewhat differ from the properties of single crystal Si. Some of these properties are valuable in the field of gas sensor technology, but a lot of questions arise in connection with its application. Do we really need porous semiconductor material for proper gas sensing function? How can electrical properties of the PSi layer be measured if the electrical contacting is problematic? Is it possible to activate the PSi with catalytic noble metal layers or particles? What about the Fermi-level pinning in the PSi layer? The main target of this article is to seek answers to questions listed above and to give a short, but still comprehensive review of the application of the PSi layers on the field of the gas sensor technology, with special care on electrical output signal giving sensors.

Keywords: Porous silicon; Gas sensor; Interface states; Fermi-level pinning

1. Introduction

Anodic oxidisation and etching of the c-silicon surface results in a porous Si (PSi) layer. In the PSi some part of monocrystalline silicon is etched away by electrolytic process in HF content solution. The rest of the silicon layer is still crystalline, but contains a lot of pores, therefore, many strange physical phenomena can be observed in connection with this material.

The technology and different applications of the porous silicone (PSi) have been discussed in detail in the literature [1,2]. Some recent review articles and tutorials help to understand importance of this peculiar material among nanosensors [3]. The fabrication methods and many physical properties are discussed in [4] and [5].

However, in spite of several successful experiments there are some problems on the field of gas sensor applications, especially in the case of electrical readout: the PSi layer contains huge number of volume traps and interface states, resulting in Fermi-level pinning in the layer and at the PSi–Si interface. This may block the electrical response (gas sensitivity) of the PSi–Si structure. The scientific literature mirrors these problems. The expression “porous silicon gas sensor” results in 208 items on internet search engine (Scopus), while the word “resistance” occurs only 8 times among them. The discussion of the resistor type PSi chemical sensors is completely missing from a recent review [3].

2. Semiconductor gas sensor materials

There is a strong connection between the surface and the bulk in the semiconductors. That is why these materials are used as gas sensors too, in addition to many other applications. Practical form of appearances of the semiconductor gas sensors are different: thin film with comparable thickness of space charge layer to the total layer thickness (simple, or with doped surface [6,7]), thick film with comparable thickness of space charge layer to the grain size [7], nanocrystals, where the particle size is smaller than the space charge layer, thus the total volume of the nanoparticle is controlled by the adsorption at the grain boundary [8], macroscopic Schottky barrier [9,10], MOS with Pd gate [11,12], or with some other gas sensitive material on the gate (see Fig. 1). In spite of these structural differences, the experimental values of surface and interface potentials are in the same range. For example, the maximum values of the H_2 adsorption induced potential changes are about 0.5–0.6 V on the Pd surface [12] and Pd–SnO_2 interface [13,14]. Thus the measurement or calculation of the surface and interface potentials enables a comparison between the effects of the adsorption on many different semiconductor gas sensor structures, and reflects the similarity of operation: charge

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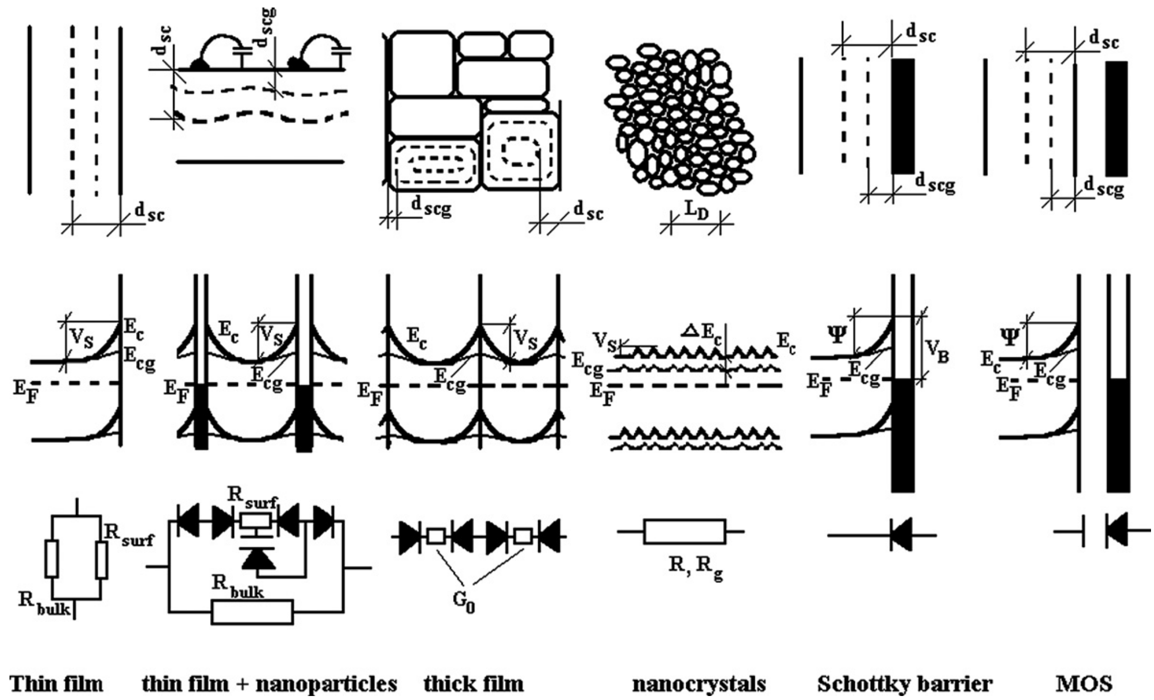

Fig. 1. Practical forms of the semiconductor gas sensor structures (geometry, energy band model, circuit model).

carrier concentrations (currents) are controlled by the adsorption dependent surface potentials, potential barriers.

Work function measurements have revealed the strong correlation between the adsorption induced contact potential change and the chemical potential change calculated by the logarithmic ratio of resistances. The potential barrier controlled charge transport model can explain the background of this strong correlation.

The surface index shows the correlation between the height of the metal-semiconductor Schottky barrier (Ψ) and the value of the work function of different metals (Φ), surface additives [15–17] deposited on the semiconductor surface:

$$s = \frac{\partial \Psi}{\partial \Phi_m}. \quad (1)$$

For elementary semiconductors, such as Si, Ge (with covalent bonding) s is usually near to zero. Large number of surface traps at the midgap results in a quasi-isolated surface (Fermi-level pinning). In that case the potential barrier and the space charge in the depletion layer are independent of surface adsorption: the counterpart of the adsorbed charge (ions) appears in the traps, and not in the space charge layers in the particles or in the crystalline semiconductor. Due to this effect there is no resistance response, but the ion–trap pair forms a dipole layer resulting in CPD response. This means that the barrier height is almost independent of the work function of the surface additives. For this reason, these materials are not appropriate for resistor type gas sensor applications.

Using proper passivation, for example, the growth of a good quality SiO_2 layer over Si (tunnel MOS or MOS structures), the surface (interface) index can be near to one.

For compound semiconductors (with ionic bonding) s is near to one, the barrier height follows the change in the work function. As the work function is very sensitive to the surface adsorption process, the compound semiconductors with catalytically active metal particles on their surfaces give a high resistance response (potential barrier controlled charge transport model).

The porous silicon cannot be inserted easily into the classification discussed above. PSi itself is somewhat similar to the “nanocrystals”, but usually it is formed over a heavily doped silicon surface, thus a macroscopic potential barrier (“Schottky barrier”) exists at the PSi–Si interface in the crystalline substrate, while the potential distribution in the PSi layer is not well known, in spite of many attempts to reveal it by I–V characteristics, vibrating capacitor and surface photovoltage measurements [17–25]. Moreover, due to the large trap density, there is a possibility of Fermi-level pinning either in the PSi layer or at the PSi–Si interface [17].

Activation is very important in the technology of semiconductor gas sensors. Catalytically active surface additives or noble metal particles agglomerated from ultra-thin metal layers improve the sensitivity, selectivity and the response time [26]. The PSi can also be doped by activators. Physical [27], electroless chemical [28–31], or cathodic metal deposition [31] has been used for PSi doping.

3. Application of porous silicon in gas sensor technology

Beside the tin-dioxide the porous silicon is one of the most often mentioned materials in connection with gas sensor technology.

The first group of application fields is passive application, when the PSi acts as heat isolator or sacrificial layer in the