

Chapter 27

New Adsorption Active Nanoclusters for Ecological Monitoring

V.G. Litovchenko, T.I. Gorbanyuk, and V.S. Solntsev

Abstract Gas sensitive metal-insulator-semiconductor (MIS)-structures based on nanoporous silicon (PS) with clusters of transition metals (Pd, Cu, W) and their oxides embedded into the pores have been investigated by means of current–voltage (I-V) and capacitance–voltage (C-V) characteristics. It has been shown that the most sensitive structures to hydrogen sulfide are MIS-structures with top electrodes from W and Cu oxide composite. Our experiments have also demonstrated that thermal annealing of layered semiconductor structures based on nanoporous silicon and copper ultra-thin films (nanoclustered) leads to the formation of nanosize p-n junction (Cu₂O-CuO). The use of the porous semiconductor matrix with the embedded nanosize p-n junctions enable to create highly sensitive sensors for toxic gas molecules in the ambient surrounding.

Keywords Gas sensor • Porous silicon • Metal clusters • Quantum-size effect

27.1 Introduction

In a number of latest publications, the enhanced catalytic properties of the metallic nanoclusters influencing adsorption, rather stable molecules (like H₂, CO, H₂S, organic molecules etc.) have been analyzed. The phenomena have been described even for metals, being non-catalytic in the bulk modification (like Cu, W, Al, Ag, Au) [1–10]. One of the reasons for that anomalous phenomenon, demonstrated by a computer simulation, is a deep reconstruction of the interatomic chemical bonds on the surface and near the boundaries of nanoclusters, which leads to the

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appearance of “strong” and “open” bonds, (at least, partly). There are two reasons for using nanostructures for sensors: (a) the increase in the value of the characteristic surface, (b) the quantum-size effect of electron orbitals (clouds) rehybridization concerning transition metals, where valence electrons (partly) include (beside s, p) some d-orbitals sharply oriented and become more active in chemical reactions (including decomposition catalysis). It is necessary to have unfilled d-orbitals that are typical for W but this is not in the case for Cu, Ag, Ti. For these cases it is necessary to stimulate the empty charge of d-orbitals (upper valence orbits). The calculations from the first principles for nanoclusters of Si (of $d \leq 2$ nm), Au with the extended valence-chemical bonds $sp^{3-n}d$ have been demonstrated [11–14].

In our previous publications [8, 10, 15, 16] we have demonstrated the intensive decomposition of the adsorbed H_2 , H_2O by the porous Si surface, decorated by nanoclusters of Pd, Cu, W, Al. Decomposition of such ecologically dangerous molecules as H_2S , NH_3 , CO at adsorption in the mentioned structures, clearly demonstrates some response effect on the porous Si surface even at room temperature. However, for decomposition and hence for realization of the effect of sensitivity to H_2S on the traditional SnO_2 resistive sensor, it is necessary to heat the structures at about 300–500°C. More enhanced catalytic effects we have observed on oxide WO_3 , CuO_x nanostructures created by incorporation of oxide nanoparticles into the porous silicon matrix [2–4, 6, 7]. Based on these results, we will analyse other perspective metal-oxide nanoparticles to obtain highly active Me-catalytic structures.

27.2 Mechanism of Catalytic Activation

We will consider the electron hollows, responsible for chemical bonds and will take into account the electron exchange mechanism which has the following properties:

1. electrons at the cathode should not be strongly bonded;
2. anode vacancies are not fully occupied, and such orbitals have to be as many as possible. Thus, the number of unoccupied “anode” states will be the maximum possible.
3. distances between atoms in a chemical condensed state $\mathbf{d} = r_{a1} + r_{a2}$ will also be as minimal as possible ($r_{a1} + r_{a2}$ – valance radius of atoms).
4. the active force (\mathbf{F}_{ab}) and the energy of bond (ϵ_M) for creation of interatomic bonds can be estimated as follows:

$$\mathbf{F}_{ab} = A(x_a - x_b)/d, \quad \epsilon_M = F_{ab} \times d. \quad (27.1)$$

Thus, the use of donor atoms near the acceptor gives the redistribution of electrons due to the high values of F_{ab} , and hence it promotes the release of some orbitals which is very important for catalysis, especially, in the d- orbitals. In such a way, new catalytically active materials can be created. For example, Cu ($3d^{10}4s^1$)

Table 27.1 New adsorption active nanostructures for ecological monitoring

Period # in periodic table	Electron configuration	r_k , Å cation radius	$X(M)-X(O)$, electronegativity difference	$r_k + r_a(O)$, Å	$\frac{X(M)-X(O)}{(r_k+r_a)}$
2	O ₂ 2s ² 2p ⁴	0.74			
4	Ti 3d ¹⁰ 4s ²	1.46	2.23	2.22	
	Cu 3d ¹⁰ 4s ¹	1.28	1.76	2.02	0.87
	Zn 3d ¹⁰ 4s ²	1.37	2.02	2.11	
	Fe 3d ⁶ 4s ²	1.26	1.81	2.0	
	Co 3d ⁷ 4s ²	1.25	1.77	1.99	
	Ni 3d ⁸ 4s ²	1.24	1.73	1.98	0.87
5	Pd 4d ¹⁰ 5s ⁰	1.37	2.02	2.11	0.96
	Ag 4d ¹⁰ 5s ¹	1.44	1.74	2.13	
6	Au 5d ¹⁰ 6s ¹	1.44	1.69	2.18	
	W 5d ⁴ 6s ²	1.41	2.14	2.15	0.99
	Pt 5d ⁹ 6s ¹	1.39	1.89	2.13	0.89

with fully occupied d-orbitals, under creation of bonds with oxygen O(2s²2p⁴), will give Cu(3d⁹4s¹) × O(2s²2p⁵) composition.

Table 27.1 shows that the perspective catalysts are metal oxides with partially filled d-orbitals CuO, ZnO, AgO, PdO. The analysis of the Tables makes it possible to predict which of the transition metal oxides will have the enhanced adsorption and the catalytic activity in respect of the molecule of H₂S.

A possible mechanism for the formation of unfilled d-orbitals is the following: the more is the difference in electronegativity between metal and oxygen ($X(M)-X(O)$), the higher is the polarity of bonds in the metal-oxide molecule and the higher is the probability of electron transfer and formation of the electron free d-states. If we divide the difference of electronegativity ($X(M)-X(O)$) by the length of the metal-oxygen bond ($r_k + r_a$), we will obtain effective electrostatic field, which also characterizes the probability of electron transitions between d- and s-orbitals. As it follows from the analysis of the data in Table 27.1, the most catalytically active metal oxide is tungsten oxide, which is confirmed by our experimental data.

Another important fact is the appearance of nanocluster p-n junctions on the surface that are available to the adsorption.

In the Cu case, the p-n junctions under high temperature oxidation of Cu were first discovered by Lashkarev [17].

In our case, the formation of p-n junction (CuO-Cu₂O) are created at much lower temperature, as it is demonstrated below.

27.3 Experimental Techniques

The MIS structures based on PS with catalytic active top electrodes have been prepared by anodically etching boron doped (p-type) (100) oriented single crystal silicon wafers with resistivity of 10 Ω × cm. The electrolyte was a mixtures of

HF acid (49%) and ethanol (98%) in the ratio: HF:C₂H₅OH 2:3/3:2/4:1. The range of current densities was 5–50 mA/cm² for 15 min. The catalytic active metal layer was deposited by magnetron technique onto the porous silicon substrate kept at room temperature. Sputtering was done in purified Ar gas (99.9999%). The target power was kept at 15 W resulting in a deposition rate of approximately 0.2 nm/s. To obtain nano-sized p-n junctions, ultra-thin films of transition metals (thickness 10–25 nm) were deposited on the surface by magnetron sputtering in Ar plasma. Then these structures were annealed in the oxygen–nitrogen atmosphere at the temperature 150–550°C. The purpose of temperature treatment was to fill the pores of metal oxides clusters. Investigation of mechanisms of conduction and adsorption sensitivity of such structures was made by means of the I-V and C-V characteristics. The current shifts of the current versus voltage (I-V) curve of MIS gas sensitive structure during hydrogen/hydrogen sulphide exposure was measured at a constant voltage (~ -3 V) as the response signal. In the case of the structures with top electrodes from W/Cu composite the voltage shifts in the MIS C-V curves were measured as a function of time, as the gas ambient was varied.

27.4 Experimental Results and Discussion

The aim of our research is to study the mechanisms of sensitivity and catalytic activity of the MIS structures with different catalytically active electrodes. The model of nanosize p-n junction has also been discussed and checked by I-V and C-V techniques. It has been found that the surface of p-n junction based on nanoclusters of metal-oxide (Cu₂O-CuO) embedded into porous Si plays the important role in increasing of the gas sensitivity, as a set of our experiments have demonstrated.

It is well known that sensor structures with Pd electrodes are sensitive to hydrogen. In our experiments three types of catalytically active structures have been investigated: (1) MIS-structures based on nanoporous silicon with catalytic active Pd electrode (see Fig. 27.1); (2) MIS-structures based on nanoporous silicon with embedded Cu clusters in pores (see Fig. 27.2); (3) Schottky-like structures based on nanoporous silicon with embedded Cu clusters in porous and catalytic active Pd electrode (see Fig. 27.3).

Figure 27.1 shows the current-voltage characteristics of the MIS-structure with the top Pd electrode (Pd-PS). As we can see from Fig. 27.1, the Schottky barrier is not formed. In this case, the difference between the values of the current in the forward branch of the I-V characteristics (ΔI) at the level of -3 V is 0,155 nA, which represents $\sim 16\%$ ($\Delta I/I_{\max}^{N_2}$) in respect of the current in nitrogen ($\Delta I/I_{\max}^{N_2}$) at this voltage level.

As shown in Fig. 27.2a (for structure Cu-PS), the addition of 25 ppm H₂S to nitrogen atmosphere leads to the decrease in the forward current. In this case, the

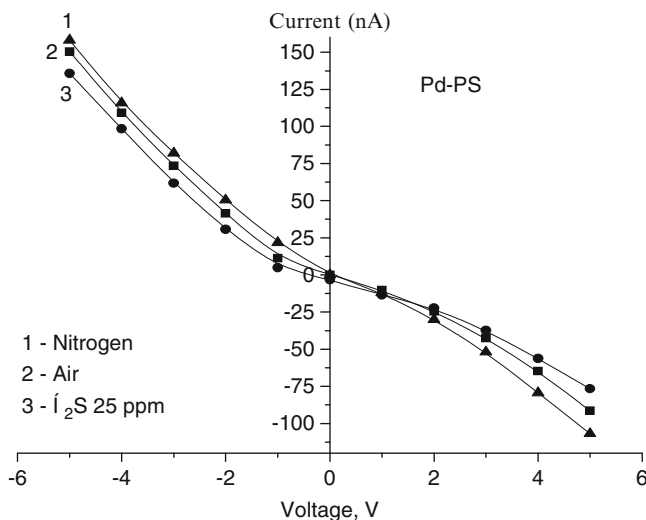


Fig. 27.1 I-V characteristics of Pd-PS structure

difference between the values of the current in the forward branch of the I-V characteristics at the level of -3 V is $\Delta I = 229$ nA, which represents $\sim 13\%$ in respect of the current in nitrogen ($\Delta I/I_{\max}^{N_2}$) at this voltage level. Figure 27.2b shows the typical responses of MIS-structures based on nanoporous silicon with embedded Cu clusters in pores when exposed to 25 ppm H_2S in nitrogen. As it can be seen, $\sim 60\%$ of the response signal reproducibility is observed after five cycles. We expect that the incomplete recovery of the initial signal level may be related to the transformation of copper clusters in the CuS phase according to the following processes:

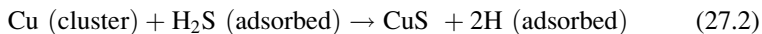


Figure 27.3a shows the variation of the direct current of at -3 V in the range of 10–75 ppm of hydrogen sulfide. It has been found that the difference ΔI is 43 nA for 20 ppm of H_2S , which represents $\sim 54\%$ ($\Delta I/I_{\max}^{N_2}$). The inset in Fig. 27.3 demonstrates the calculated Schottky barrier height depending on the concentration of H_2S . Kinetic characteristics of the forward current change at -3 V level are shown in Fig. 27.3b. As it can be seen from Fig. 27.3b, during the gas inlet of the observed delay in the kinetic curve. This indicates a complicated adsorption processes in such kind of system. Perhaps H_2S dissociation takes place on the surface of palladium, then the hydrogen atoms of H flow on copper clusters in the pores (spillover effect). Thus, the data presented on Figs. 27.1, 27.2, and 27.3, show that the most catalytically active is the Schottky-like structure based on

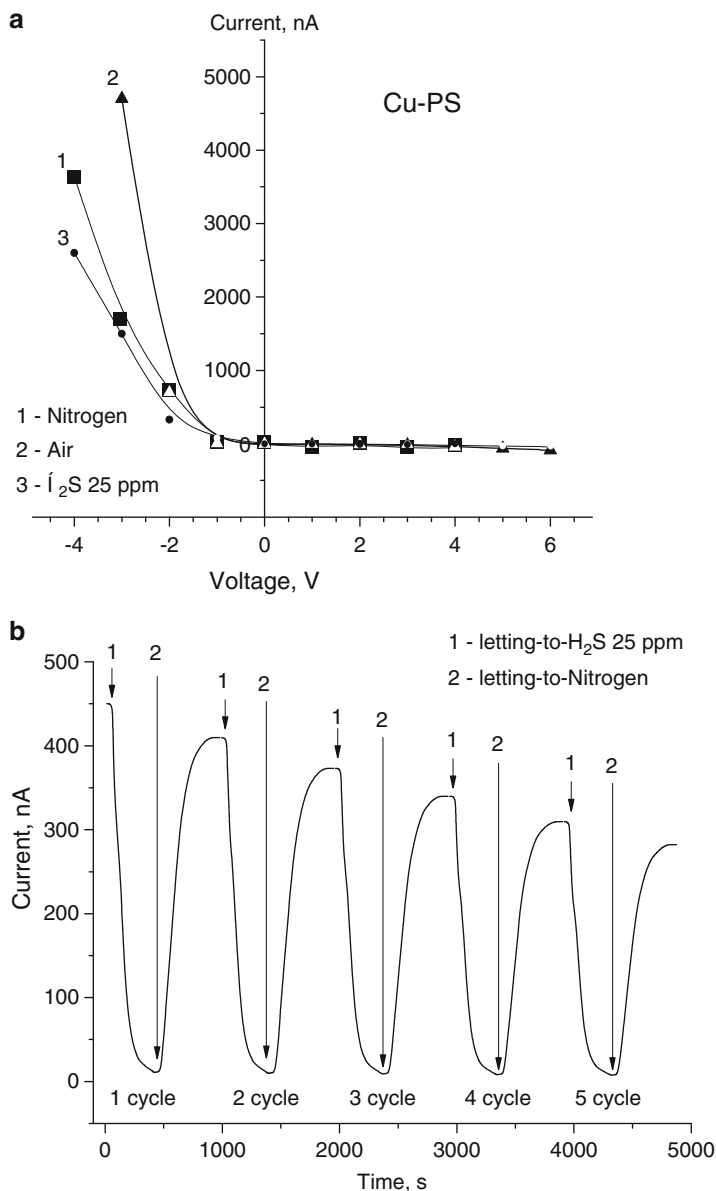


Fig. 27.2 I-V characteristics of Cu-PS structure (a) and kinetics (b)

nanoporous silicon with embedded clusters of copper and the top electrodes of palladium.

For comparison, the structures with top electrodes from W/Pd composite have also been investigated (see Fig. 27.4). In this case, we have registered a change in the capacitance of the structure at a fixed bias voltage. As it can be seen, the

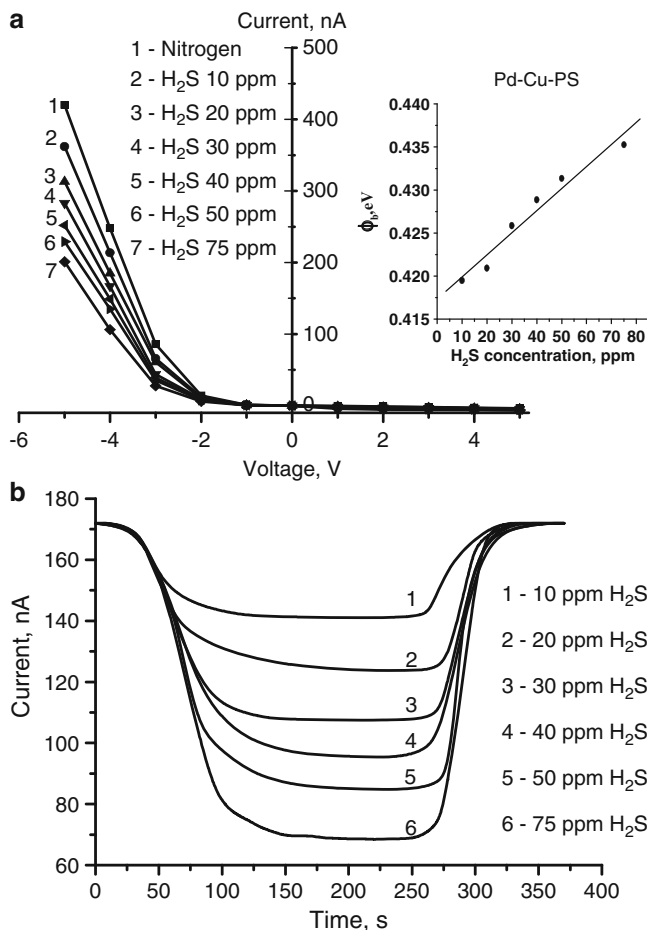


Fig. 27.3 I-V characteristics of Pd-Cu-PS structure (a) and kinetics (b)

structure with a catalytically active electrode of the composite Pd/W is more sensitive to hydrogen sulfide, as compared with the Pd-PS structure.

To improve the sensitivity and selectivity of MIS-structures to hydrogen-containing molecules, the structure based on porous silicon with pores filled by copper oxide has been fabricated and investigated. It has been found that nanosized semiconductor p-n junctions, based on clusters of Cu₂O-CuO, are formed during heat treatments at 400°C in the oxygen-nitrogen atmosphere. Figure 27.5 shows the IV-characteristics of such structures formed at 400°C. In the case of pores filled with clusters of copper oxides, a diode effect occurs, which leads to a sharp increase in the sensitivity of such structures to hydrogen.

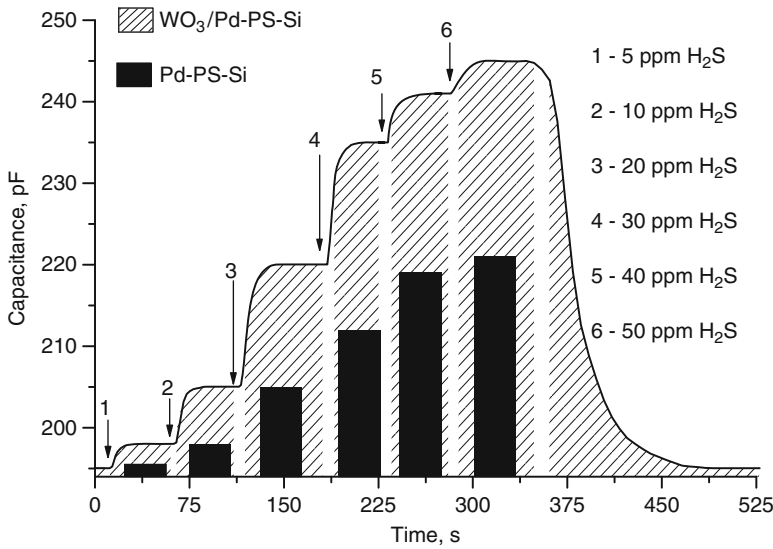


Fig. 27.4 C-V characteristic of Pd-PS structure

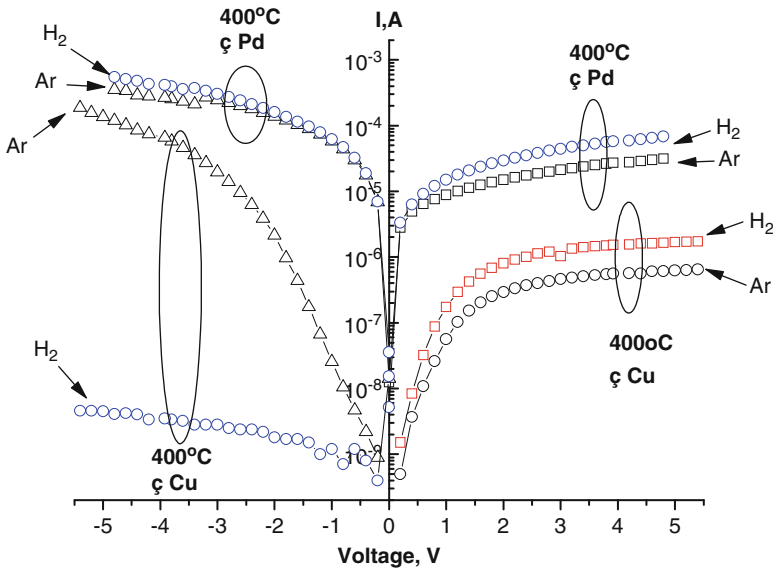


Fig. 27.5 Hydrogen adsorption on I-V characteristics based on silicon matrix with $CuO-Cu_2O$ and Pd clusters

27.5 Conclusion

1. Thermal processing of semiconductor sensor structures based on nanoporous Si with ultra-thin (nanoclusters) metal films on the surface lead to formation of nanosize p–n junctions based on catalytically active metal oxide clusters embedded in a matrix of porous silicon.
2. Adsorption of molecular hydrogen sulphide (hydrogen) on the surface annealed nanocomposite PS/Cu leads to the additional changing in the sign of a potential barrier in case of diode structures Cu₂O/CuO.

This effect causes a sharp increase in the sensitivity of the data structures to hydrogen-containing molecules in comparison with composites based on porous silicon with clusters of Pd.

3. The most active centers for decomposition of ecologically dangerous H₂S molecules on the metal-oxide demonstrate nanoparticles with the maximum difference in electronegativity (WO₃, CuO_x). The analysis of other perspective catalytic pairs for transition metal-oxides has been demonstrated in Table 27.1.

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