

Si and GaAs Nanostructures as Chemical Sensors

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Si and GaAs nanostructures are perspective as chemical sensors. The porSi films with a broad size distribution ranging between 4 and 12 nm, are extensively studied during last decade as gas sensors [1]. The structures ($\square 60 \mu$ thick) were prepared by anodisation of boron-doped p-type substrates in HF containing solutions. The internal surface of pores was passivated due to nearly complete covering by hydrogen (Si-H_x groups). This technology provides a porosity $P \square 60\%$ and specific surface area up to $600 \text{ m}^2 \text{ g}^{-1}$. At low distance between pores, charged surface traps, particularly P_b centers, block the conduction pathways by coulomb repulsion and cause a high resistivity of porSi. In an approximation of a regular cylindrical pores arrangement, the minimum density of ionized donor surface centers for coulomb blockade is defined by

$$N_{S_{\min}}^+ = d_p \left[\left(d_A / d_p \right)^2 - 1 \right] / 2 \times N_A, \quad (1)$$

where d_p is the pore diameter; d_A denotes the distance between the pores axes; N_A is the bulk acceptor concentration. At $P=60\%$, the pores diameter $d_p = 5 \text{ nm}$ and the bulk acceptor concentration $N_A = 1 \cdot 10^{18} \text{ cm}^{-3}$, the minimum surface centers density in pores, as required for coulomb blockade, amounts $N_S^{\min} = 0,78 \cdot 10^{11} \text{ cm}^{-2}$.

In real porSi films, there remain some paths for the p -current. In NO₂ (acceptor like) vapors, the record threshold concentration to be detected was 15 ppb [2]. However, in wet NH₃ (donor like) vapors the current non-monotonously depends on the ammonia partial pressure with a minimum at $\square 5 \text{ Pa}$ [1]. Therefore the minimum explicitly measured NH₃ molecules concentration is 300 ppm. The sensitivity to wet NH₃ vapors amounts up to 30 $\mu\text{A/kPa}$.

The Si nanowires (SiNWs) with diameters of 50–250 nm, formed with metal-assisted etching of intrinsic Si(111) wafers in HF containing solutions, were extensively studied as chemical sensors [3]. P -type conduction of SiNWs was consistently increased in acidic gases (CO₂, SO₂, Cl₂, NO₂, and HCl), acid vapors (H₃PO₄, HCl, H₂SO₄, and HF), or weakly acidic organic solutions (alcohol or acetone), whereas p -type conduction of SiNWs was consistently decreased after purging the acid vapor by dry neutral gas of O₂, Ar, or N₂. In NH₃ vapors (basic atmosphere), the conductivity non-monotonously depends on the ammonia partial pressure, having a minimum at $\square 70 \text{ Pa}$. Therefore the minimum explicitly measured NH₃ molecules concentration is $\square 2000 \text{ ppm}$.

The minimum surface centers density on SiNW, as required for coulomb blockade, is given by

$$N_{s\min}^+ = 0,25dN_A, \quad (2)$$

where d is the SiNW diameter. At $d = 150 \text{ nm}$; $N_A = 1 \cdot 10^{18} \text{ cm}^{-3}$, we obtain $N_{s\min}^+ = 3,8 \cdot 10^{12} \text{ cm}^{-2}$, which is much higher than in porSi.

Thus, the porSi sensors have a very high gas sensitivity, however SiNWs are much lower in dimensions. And the processes, which cause the gas sensitivity of the porSi- and SiNWs structures, are similar to ones in $p-n$ junctions [4]. The reverse current of the Si- and GaAs $p-n$ junctions can be of $10^{-10} - 10^{-11} \text{ A}$. This enables low threshold concentrations of vapors to be detected. The minimum surface centers density in the $p-n$ junction, as required for the midgap Fermi level locking, is given by

$$N_{s\min}^+ = \sqrt{\varepsilon_s E_g / q^2 N_A}, \quad (3)$$

where ε_s is the dielectric constant of the semiconductor; E_g denotes the band gap; q is the elemental charge. At $\varepsilon_s = \varepsilon_0 \varepsilon = 1,04 \cdot 10^{-12} \text{ F/cm}$; $E_g = 1,12 \text{ eV}$; $N_A = 1 \cdot 10^{18} \text{ cm}^{-3}$ we obtain $N_{s\min}^+ = 1,9 \cdot 10^{12} \text{ cm}^{-2}$, which is between the corresponding values for porSi and SiNWs. The threshold NH_3 concentration for Si- and GaAs $p-n$ sensors is of $\square 10 \text{ ppm}$ and 1 ppm , respectively, which is better than for porSi and SiNWs.

The main unsolved problem for all three chemical sensor types is the parameters instability, caused, particularly, by the surface oxidation. And the main direction for the enhancement of their sensitivity and stability is an appropriate surface doping.

1. Boarino L., Borini S., Amato G. Electrical properties of mesoporous silicon: from a surface effect to coulomb blockade and more // J. Electrochem. Soc. – 2009. – V. 156, No. 12. – P. K223–K226.
2. Pancheri L., Oton C. J., Gaburro Z. et al. Very sensitive porous silicon NO_2 sensor // Sensors and actuators B. – 2003. – V. 89. – P. 237–239.
3. Yuan G. D., Zhou Y. B., Guo C. S. et al. Tunable electrical properties of silicon nanowires via surface-ambient chemistry // ACSNANO. – 2010. – V. 4, No. 6. – P. 3045–3052.
4. Ptashchenko O. O., Ptashchenko F. O., Yemets O. V. Effect of ammonia vapors on the surface current in silicon $p-n$ junctions. // Photoelectronics. – 2006. – No. 16. – P. 89 – 93.