POROUS SILICON NANOWIRE ARRAYS FOR REVERSIBLE OPTICAL GAS SENSING

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SUMMARY

Porous silicon nanowire arrays are shown to be used for optical detection of molecular oxygen (O_2). The samples were produced by metal assisted chemical etching of heavily boron-doped wafers of crystalline silicon. It was found that the photoluminescence signal from porous silicon nanowires quenched in O_2 ambience but restored again in N_2 atmosphere, which repeated in several cycles. Electron paramagnetic resonance data demonstrated that number of silicon dangling bonds (Pb-center) increased after O_2 adsorption, but then dropped in vacuum. The experimental results are explained by a microscopic model taking into account the reversible charging/recharging of surface defects (Pb-centers) due to the oxygen adsorption/desorption. The obtained results indicate that porous silicon nanowires are prospective for applications as reversible optical gas sensor.

1. INTRODUCTION

The necessity of the sensitive and selective detection of molecules in the gas phase for environmental monitoring has always existed. Now it concerns not only toxic, but also other gas molecules, because due to the increasing of urbanization and environmental deterioration there is a need to control the atmosphere composition not only in industry and medicine, but also in everyday life. Nanoforms of various materials are considered to be very prospective for sensor creation, because of their high surface-to-volume ratio, and also that one or more of the physical dimensions are less than or comparable to the charge screening length. Therefore, these materials often exhibit superior sensitivity in chemical surface processes[1].

It is known cheap and efficient method of the formation of SiNW layers based on the metal-assisted chemical etching (MACE) of c-Si[2]. MACE-prepared SiNWs consists of an almost non-intersecting nanowires with diameters from several to hundreds nm. The morphology of the as-synthesized SiNWs is highly dependent on the doping level of original silicon wafers and on the concentrations of etching solutions[3]. Also such SiNWs show unique physical properties such as room temperature photoluminescent (PL)[2,3].

In this paper the possibility of using of PL porous SiNW layers (por-SiNWs) as room-temperature reversible optical gas sensor have been demonstrated for the first time.

2. EXPERIMENTAL RESULTS AND DISCUSSIONS

The samples of por-SiNWs were produced on (100)-oriented 4-inch crystalline silicon (c-Si) wafers by the MACE method (Metal Assisted Chemical Etching). For experimental details please see Ref.4.

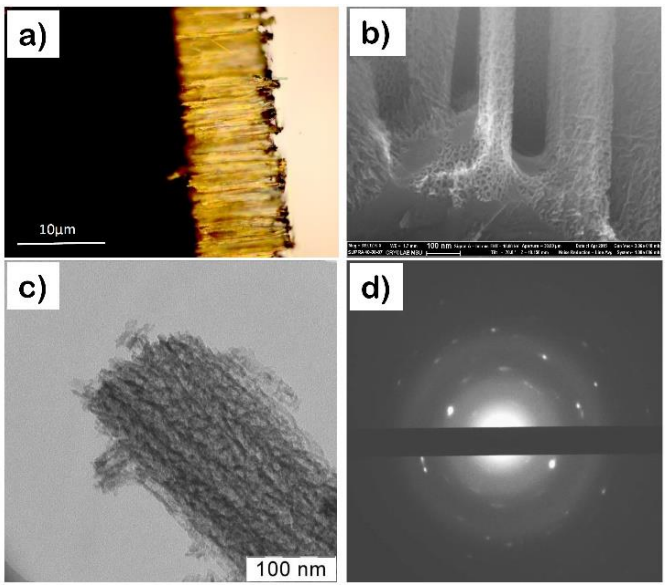

Figure 1: (a) Cross section view of por-SiNW array in optic microscope; (b) SEM of a porous structure of por-SiNWs; (c) TEM image of a single por-SiNW; and (d) the electron diffraction pattern from the single por-SiNW.

The SiNW arrays exhibit a broad PL spectrum in the spectral range 600–1100 nm (1.13–2.06 eV) with a peak at ~785 nm (1.58 eV). Figure 2a shows the PL spectra from por-SiNWs in N_2/O_2 atmosphere. A significant, by a factor of 2.2, quenching of the PL intensity in O_2 atmosphere are observed. Note, that subsequent nitrogen purge resulted in full recovery of por-SiNW's PL signal. Moreover, the PL sensitivity and recovery properties don't change in multiple adsorption-desorption cycles (see inset in figure 2).

EPR spectra of the samples points to the presence of paramagnetic silicon dangling bonds at the Si/SiO_2 interface, i.e. P_b^0-centers[5] with *g*-factor 2.0056 ± 0.0005. So, the increasing of EPR signal intensity in oxygen atmosphere indicate that the number of paramagnetic P_b^0-center are increased. After O_2 desorption, the signal intensity dropped (see figure 2b).

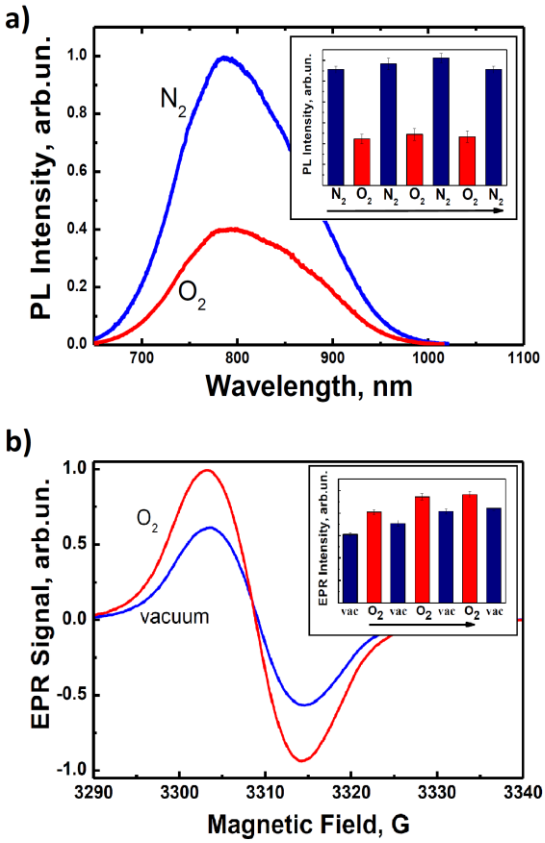

Figure 2: (a) PL spectra of por-SiNWs in nitrogen (blue line) and in oxygen (red line) atmosphere. The inset demonstrates reversible changes in the PL intensity in multiple (3 times) consecutive experiments ; (b) The variation of I/I_0 as a function of oxygen pressure, (b) EPR spectra of por-SiNWs in (blue line) vacuum 10^{-4} mbar and (red line) oxygen atmosphere. The inset demonstrates changes in the EPR intensity in multiple consecutive experiments.

The concentration of P_b^0-centers, N_{pb}, was calculated from the EPR spectra, and have a linear dependence from the intensity of the spectra. For initial samples $N_{pb} \approx 9 \cdot 10^{15}$ g^{-1}. O_2 adsorption was accompanied by an increase in the concentration of paramagnetic defects to $1.2 \cdot 10^{16}$ g^{-1}. Desorption of O_2 leads to a drop in the P_b^0 concentration up to $1 \cdot 10^{16}$. Then a similar N_{pb} dependence was observed in several cycles of oxygen adsorption – desorption (see inset in fig. 2). The incomplete recovery of the EPR signal intensity during the desorption of oxygen can associated with a slight oxidation of the SiNW's surface, which is always accompanied by an increase in the number of paramagnetic silicon dangling bonds.

Based on the obtained data, the following mechanism of O_2 molecule interaction with surface of por-SiNWs was proposed. Generally, a strong capture of free holes by silicon dangling bonds, i.e. P_b-centers, takes place in silicon nanocrystals and P_b-centers are transformed into non-paramagnetic state: $P_b^0 + h^+ = P_b^+$. The Coulomb interaction between adsorbed O_2 molecules and P_b-centers leads to the appearance of donor-acceptor pairs as $P_b^{+\delta}$–$O_2^{-\delta}$ were δ is the part of the transferred charge, 0<δ<1. The formation of such pairs simultaneously causes an increase in the free hole concentration because of the "passivation" of P_b-centers as follows:

$$O_2^- + P_b^0 \rightarrow \left(O_2^{-\delta} - P_b^{+\delta}\right) + h^+. \quad (1)$$

Note that presented physisorption process has not lead to additional dramatically oxidation of the por-SiNW's surface, so the full recovery of the PL signal and partial recovery of EPR signal were observed in multiple adsorption-desorption cycles. The quenching of por-SiNW's PL during the adsorption of O_2 molecules occurs because the $P_b^{+\delta}$ also plays role of the centers of non-radiative recombination of excitons, while the free charge generation results of the non-radiative Auger recombination of excitons. The PL quenching in the both short and long wavelength regions lead to a narrowing of the spectrum and it can be explained by the growth of the electric fields of adsorption complexes (in shortwave region) and small exciton binding energy (in longwave region).

3. CONCLUSIONS

Porous silicon nanowire arrays were shown to be sensitive to molecular oxygen. The influence of O_2 molecules adsorption on PL properties of SiNWs is explained by reversible charging/recharging of surface defects (Pb-centers) due to the oxygen adsorption/desorption. The obtained results show that por-SiNWs are highly prospective nanomaterial for room temperature gas sensing and, moreover, such layers can be used for optical sensors.

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