The gas sensing properties of rutile nano-ribbons obtained by phase transformation of titania nanotubes

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Titania nanotubes were prepared by chemical processing, following the method indicated by Kasuga et al. (1). The aqueous suspension was dispersed on a micro-electronic structure, on top of a pair of comb-shaped, Pt electrodes separated by 10 µm. An integrated heater allowed an accurate temperature control during the electrical measurements. The TEM and XRD characterizations revealed that the crystalline titanate nanotubes transformed upon annealing into rutile nano-ribbons (7-10 nm wide, hundreds of nm long) with a preferential orientation of the (111) rutile atomic planes and a long range crystalline order in the [-111] direction.

The sensing properties of the rutile ribbons were investigated with respect to the O_2 concentration in the gas phase, using N_2 as background gas, in the 600-770 K temperature range. The rutile nano-ribbons have shown remarkable sensing properties such as: large response magnitude (conductance in pure N_2 35 times larger than in pure O_2 , as shown in Figure 1), fast response time (less than 4 s to reach 95% of the equilibrium conductance for a given O_2 concentration), total recovery of the initial conductance upon O_2 desorption, reproducibility and good sensitivity for a wide O_2 concentration range (10^{-2} % - 100%). The sensitivity response was fitted to a power low of conductance (σ) vs. O_2 partial pressure (Figure 2):

$$\sigma = C * (pO_2/p_0)^{-1/N}$$

A typical n-type conductivity was found for the rutile ribbons over the whole O_2 concentration range. The value of N was found to be 3 within the 600-770 K temperature range.

For comparison, the sensing properties of a porous assembly of micrometer-sized grains (from the rutile commercial powder used as a precursor for the nanotube preparation) were investigated, as well as the properties of sputtered films consisting of densely packed nanometric TiO_2 grains. The coefficient of sensitivity changes to N=6 in the case of the micrometer grains, and to N=12 in the case of the sputtered films. Such large values of N correspond to a correspondingly large decrease in sensitivity.

We propose that different sensing mechanisms are at work in these three TiO_2 morphologies, as follows. In the case of micrometer-sized rutile grains, subsurface conductivity changes prevail, based on the annihilation and recovery of doubly ionized oxygen vacancies. This is the same mechanism that has been described for bulk TiO_2 (2). The sputtered films show a smaller sensitivity (N=12). This is essentially due to the film morphology. The sputtered films are dense and only the top subsurface reacts to changes in oxygen concentration. A constant bulk conductance must be added to the variable subsurface conductance. This results in a lower apparent value of N, which actually decreases when the pressure increases. A saturation of the conductance at high oxygen pressure is indeed observed. For nanocrystalline rutile ribbons, a very high concentration of surface defects has been observed by TEM. One can infer, then, that the conductance is controlled by chemically active surface states. The large sensitivity factor (N=3) has been observed in nano-grain structures obtained by screen printing and firing (3). The N=3 factor could possibly be related to the oxidation of Ti^{3+} shallow donors. Under normal use as integrated sensors, the rutile nano-ribbons exhibit a reproducible response and are remarkably stable.

REFERENCES

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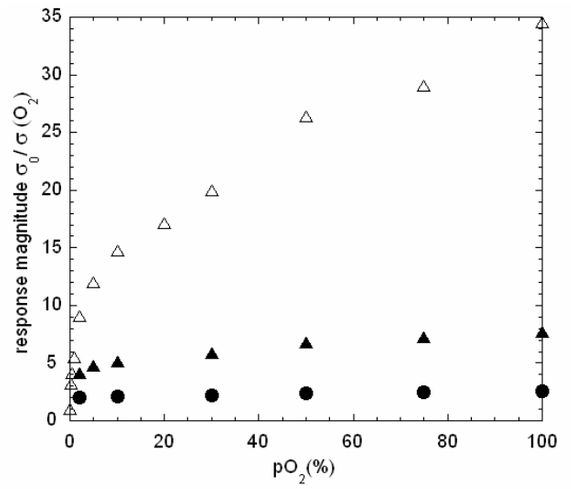

Figure 1: Response magnitude vs. O_2 conentration in gas phase, for: Δ - rutile nano-ribbons, ▲ - rutile micron-sized grains, ● - sputtered TiO_2 film.

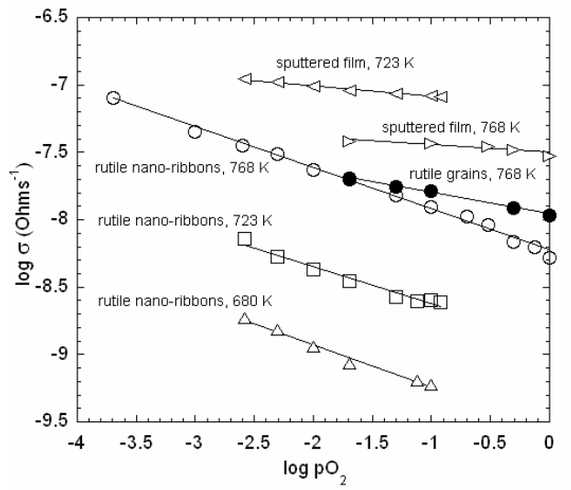

Figure 2: The log-log plot of conductance vs. pO_2 for: a) rutile micron-sized grains, b) rutile nano-ribbons, c) sputtered TiO_2 film.