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Factors affecting the electrical conductivity of TiO_2-based gas sensors

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Abstract:

Polycrystalline TiO_2 submicron-grains with only rutile phase were synthesized via cost-effective thermal oxidation method under high temperature annealing. The gas sensors on these submicron-grains show excellent gas sensing properties in terms of their sensitivity, stability and reaction times. In addition to excellent sensing characteristics the sensors also show strong dependence of n/p type conductivity inversion various measurement conditions such as gas concentration, operating temperature and applied voltage. Further, the effect of surface modification by Ag, Ni, Pt and Au thin film on structural, morphological and gas sensor characteristics is studied in detail. The current study offer novel sensing phenomena that can be exploited to tailor the selectivity of the sensors.

Key words: TiO_2, thermal oxidation, conductivity inversion, surface modification, operating conditions.

Introduction

Metal Oxide (MOX) Semiconductors have attracted the attention of many scientists and engineers in the past few decades to be used as chemical sensors owing to their unique characteristics and simple operation, cost-effective fabrication and wide applicability. The demand for these chemical sensors has been growing continuously due to the emergence of new possible applications in a variety of industries. Due to the availability of modern high-tech equipment and the recent developments, the field of gas sensors can particularly benefit in the field of monitoring processes at high and harsh environments [1].

Among other MOX materials, titanium dioxide (TiO2) is a potential candidate for gas sensing applications due its excellent chemical stability, nontoxicity and innocuousness nature, low-cost and rich earth abundance. Despite these advantages, TiO_2, however, suffer from poor selectivity and high operating temperature issues [2]. In addition, it is demonstrated that TiO_2 when operated under elevated conditions shows anomalous electrical conductivity behavior. In addition, TiO_2 exhibit unintentional conductivity (either n-type or p-type) in their as-grown state and lack of control over this key property has been a great impediment to electronic applications. For instance, the common unintentional n-type conductivity in TiO_2 films has been widely attributed to oxygen vacancies. A solid basis for this hypothesis has been lacking, however. In the other case, it has now been established that the oxygen vacancies that were most often blamed for the observed n-type conductivity do not act as shallow donors. Instead, first-principles electronic structure calculations have suggested that the conductivity is due to unintentional incorporation of impurities, with hydrogen being a very likely candidate [3,4].

Depending on the circumstances, many factors can be considered to influence the charge carrier density ($[e^-]\sim10^{16}–10^{18}$ cm^{-3}) and the mobility value ($\mu\sim10^2–10^3$ cm^2/Vs), including grain boundaries, ionized impurities and electron-phonon interactions [5]. In the current paper, we found that the factors, such gas concentration, operating temperature and applied voltage, can significantly alter the sensor signal if not controlled well.

Experimental

To begin with, high purity Ti-discs (99.9% purity) having diameter of Ø=15 mm and thickness of 1 mm, were washed and polished using standard metallurgical process to remove oil. Then the discs were coated with 30 nm films of Ti, Ni, and Ag using RF magnetron sputtering technique. Finally, nanostructured TiO_2 films were obtained via thermal oxidation under static air condition in a tube furnace OTF-1200X tubular furnace at 1000 °C for 1 hour. Subsequently, the interdigitated electrodes with a spacing of 10 µm were fabricated by photolithography method. The schematic diagram of overall preparation steps is shown in Fig. 1. The sensors were further characterized with XRD, SEM, TEM and gas sensors tests as mentioned in previous reports elsewhere [6,7].

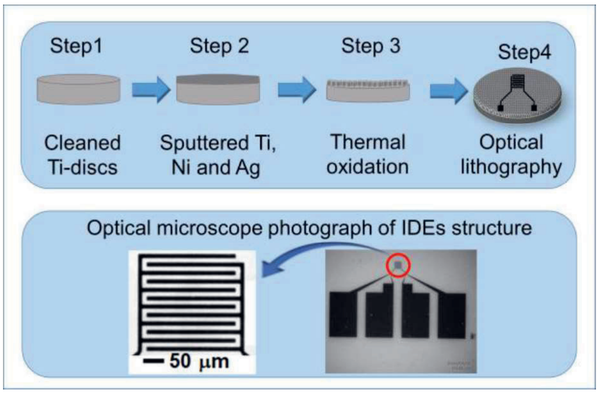

Fig. 1. The schematics of sensor fabrication process.

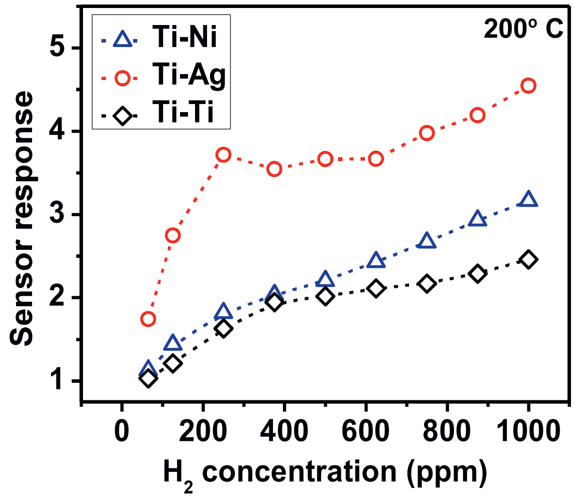

Fig. 2. The sensor response relationship with increased H_2 concentration at operating temperature 200 °C.

Results

The sensors prepared in this work show excellent sensitivity towards H_2 with its selective monitoring thus making it a potential candidate for industrial applications such as fuel-cell. From the calibration of the curves obtained in Fig. 2 which shows the sensor response relationship with increased H_2 concentration at operating temperature 200 °C, it is found that the change in electrical resistance ΔR (sensor response) is expressed by a power law relation between gas concentration and sensor response ($\Delta R \sim kC^a$).

In addition, we found strong co-relation of gas concentration, operating temperature and applied not only with the sensor response but also with electrical conductivity of pure and modified TiO_2. Based on these facts, we will further explore the sensing and electronic transport mechanism to fully understand aforementioned factors.

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