

KIRKENDALL ASSISTED FORMATION OF SnO₂-AG NANOCOMPOSITE FOR PLASMONIC-BASED GAS SENSOR

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Nano-composite layers of SnO₂-Ag are produced after deposition of Sn_{1-x}Ag_x alloy on a fused silica (FS) followed by thermal oxidation. Silver nano-particles are formed inside the SnO₂ layer during segregation into Kirkendall voids. A plasmonic-based optical sensing effect is demonstrated for acetone and alcohol in the temperature range of 200–400 °C. Red- and blue-shifts in the position of the plasmon-resonance peak are monitored for different conditions of SnO₂+Ag layer formation and gas exposure. A dynamical response of the SnO₂/Ag sensor to methane/air cycles is measured, and the sensitivity of the sensor as a function of the operation temperature and illumination is investigated. The concept of plasmonic-based SnO₂ sensors is discussed having in mind two main phenomena: First, the ability of metallic nanoparticles to hold plasmonic resonances which depends on the dielectric properties of surrounding SnO₂ layer and second, the possibility of space-limited heating of nanoparticles and the neighbouring region with light, and in this way to control the chemisorption of oxygen on the sensor's surface.

Key words: SnO₂ nanoparticles; Ag segregation; Kirkendall voids; Gas sensor.

MOTIVATION AND BASIC IDEA

1. Tin dioxide (SnO₂) is used in many applications e.g. opto-electronic devices, gas sensors and photovoltaic cells [1–3];
2. The sensing properties of SnO₂ is improved by doping with nanoparticles of noble metals which change the chemisorption on the surface of a sensor;
3. There is a necessity to develop surface plasmon resonance (SPR)-based fiber-optic sensors [4,5];
4. The mechanisms of plasmon-assisted sensing in the SnO₂-Ag nano-composite is not well known.

The basic idea behind the way of forming a SnO₂-Ag nano-composite for SPR-based gas sensors is to use Kirkendall voids as reservoirs for segregated noble atoms during oxidation.

EXPERIMENTAL

SnO₂/Ag nano-composite layers were produced by magnetron sputtering of 30 nm Sn_{1-x}Ag_x alloy on a fused silica (FS) followed by thermal oxidation in an O₂ ambiance at 450–800 °C for 10–30 min. Silver nano-islands and particles were then segregated inside the SnO₂ layer by means of the Kirkendall process [6] followed by segregation. A plasmonic-based optical sensing effect is demonstrated for selective detection of acetone and alcohol in the temperature range of 200–400 °C. Red- and blue-shifts in the position of the plasmon-resonance peak in optical transmission spectra due to the silver nanoparticles are monitored for different conditions of SnO₂+Ag layer formation and gas exposure. A dynamical response of the SnO₂/Ag sensor to methane (CH₄)/air cycles is measured, and the

sensitivity of the sensor as a function of the operation temperature and illumination is determined. Methods and instruments used in the investigation: RBS (2 MeV He⁺); PVTEM and TED (200 kV Philips CM20); optical spectra (Perkin Elmer Lambda 1050); RTA system JetFirst-100 with light illumination.

RESULTS AND DISCUSSION

The structure and morphology of the SnAg alloy layers after magnetron deposition and thermal oxidation are presented in Fig. 1. The as-deposited layer consists of tightly packed grains of planar size of 100–150 nm (fig. 1, a). It can be determined from the selected area electron diffraction (SAED) pattern (fig. 1, b) that the grains are mixtures of tetragonal β -Sn and orthorhombic Ag₃Sn phases. The thermal treatment in the O₂ ambient at 650 °C for 30 min results in oxidation of tin and segregation of Ag into dots and islands (Fig. 1, c, d). The oxidation of tin is supported by the presence of a SAED pattern in Fig. 1 d which contains diffraction rings, most of which belong to tetragonal SnO₂ (Cassiterite), and to the face-centered cubic structure of silver. However, several additional weak diffraction maxima, corresponding, e.g., to $d_{hkl} \sim 0.36, 0.29, 0.25, 0.156$ nm etc., might be associated with orthorhombic SnO₂ and, probably, with the hexagonal (*4H*) phase of Ag. No evidence of silver oxidation is found in the layers after thermal treatment at temperatures between 400 and 800 °C which is not surprising in view of thermodynamic data and calculations of Gibbs free energy values in the Ag/SnO₂ system as a function of temperature in the temperature range of 200–1000 °C.

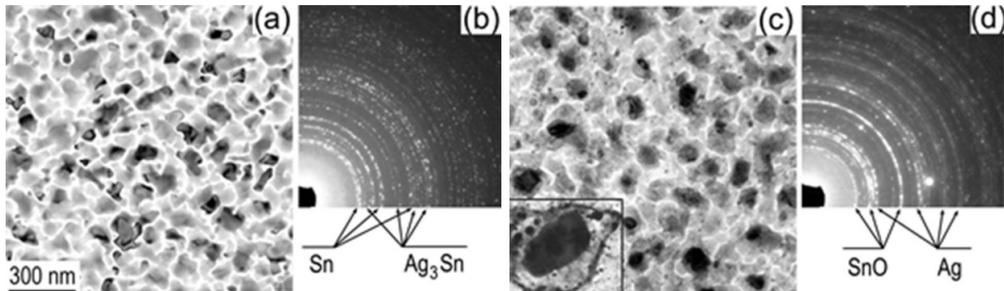


Figure 1. – BFTEM images (*a, c*) and SAED patterns (*b, d*) obtained from a SnAg alloy layer after magnetron deposition (*a, b*) and thermal oxidation at 650 °C for 30 min (*c, d*)

A bimodal size distribution of silver nano-precipitates is observed in the Sn_{1-x}Ag_x alloy layers after thermal oxidation. A high density of smaller Ag precipitates (mean size of 3–8 nm) and lower density of larger Ag islands (~ 50–500 nm) are characteristically observed in the bright field TEM image (Fig. 1, *c*). It is found that the larger Ag islands increase in size with the alloy composition *x* of the initial (as deposited) Sn_{1-x}Ag_x layers. The size of smaller Ag nano-particles is not noticeably affected by alloy composition.

We have recently found that thermal oxidation of Sn dots results in the formation of Kirkendall-related nano-voids [6]. In the present work, a 30 nm layer of pure Sn was deposited on a Si/SiO₂ substrate to confirm the presence of Kirkendall voids in a continuous Sn layer after thermal oxidation. The TEM investigations of the layers in under- and over-focused regimes of image formation in a two-beam diffraction condition with a deviation parameter $s > 0$ (not shown here) demonstrated formation of Kirkendall voids in the Sn_{1-x}Ag_x alloy layers after TO. The density and size of the small Ag precipitates are very similar to

these Kirkendal voids, hence we conclude that this void producing mechanism is responsible for the formation of the small Ag dots. The nature of the larger Ag precipitates is quite different. We believe that the large Ag islands are formed from initially large Ag_3Sn grains as a result of segregation to the center of a grain during oxidation of Sn. This mechanism is inferred from the observation that most of the big Ag islands are surrounded by regions of SnO_2 , fencing the islands as nimbuses (see left-bottom insert of Fig. 1, *c*) illustrating one of the largest island in the $\text{Sn}_{0.65}\text{Ag}_{0.35}$ alloy layer). Hence, it is not surprising that more Ag in the initial AgSn alloy layers leads to more Ag_3Sn grains and, as a consequence, to higher density of large Ag islands after their oxidation. However, it is supposed that similar to the smaller Ag precipitates, the large islands are produced with the assistance of the Kirkendall-effect: Diffusion and accumulation of Ag atoms in the center of Ag_3Sn grains during their oxidation requires out-diffusion of Sn (and in-diffusion of vacancies) to provide enough space for Ag precipitation.

A plasmonic-based optical sensing effect is demonstrated for selective detection of acetone and alcohol. The position of the SPR peak in the transmission spectra depends on the SnO_2+Ag layer quality and gas exposure. After oxidation of the $\text{Sn}_{0.35}\text{Ag}_{0.65}$ alloy layer at 650°C for 30 min the optical transmission spectra contain wide and shallow dip in the wavelength range of 590–620 nm. An additional thermal treatment in the presence of an alcohol or acetone vapor flow (about 1000 ppm) was carried out at 200–400 °C for 10 min, and then the samples were cooled to RT for optical measurements. It is found from the optical measurements that the gas-assisted treatment significantly changes the transmission spectra in the visible wavelength range resulting in a violet shift of the dip and an increase of its amplitude: The dip shifts to 540 nm after the acetone treatment at 270°C , and to 450 nm after the alcohol treatment at 300°C . A gas assisted treatment at higher ($> 400^\circ\text{C}$) or lower ($< 250^\circ\text{C}$) temperature results in only small changes of the transmission spectra as compared to the as-oxidized sample. Finally, the spectral form returns back to the as-oxidized case after an additional thermal treatment in an oxidizing atmosphere at 300–400 °C (not shown here). A comparison of the transmission spectra and TEM images allows the conclusion that the size and density of the Ag islands have an impact on the SPR gas sensitivity as the decrease of the average size of the Ag island results in a shift of the SPR dip towards ultraviolet and a decrease of its amplitude.

In general, the spectrum has a minimum transmitted power at the the SPR wavelength, which depends on the refractive index of the sensing medium and the size/density of the Ag islands. Thermal treatments of the layers in different gases results in adsorption/desorption of oxygen atoms followed by a change of the concentration of electrons in the SnO_2 layers [2]. As a result, a modification of the dielectric properties takes place. Thus, the position of the dip in the spectrum of the transmitted power is the SPR wavelength corresponding to that particular value of the dielectric constant of the sensing medium. If the dielectric properties are changed, then a shift of the SPR wavelength takes place.

A dynamical response of SnO_2+Ag sensor to methane (CH_4)/air cycles is measured and sensitivity of the sensor as a function of temperature and light illumination is determined (Fig.2). The sensing layer of SnO_2 with incorporated Ag dots and islands was used, and the resistivity response to 2000 ppm of methane (CH_4) / air cycles at an operation temperature of 240°C was measured. As compared to a SnO_2 layer without Ag islands, the sensing layer of SnO_2/Ag exhibit shorter response/recovery time, better stability and lower opera-

tion temperature. The latter is well seen from the Fig. 2, *b*, which compares the sensitivity of tin dioxide thin film sensors as a function of the sensor operation temperature for a target gas of 1000 ppm CH₄. Two main effects might be concluded from this behavior. Firstly, the incorporation of Ag islands into a SnO₂ sensing layer reduces the operation temperature of the sensor to about 300 °C, and secondly, illumination with light in a halogen-lamp RTA system further decreases the operation temperature down to 240 °C. We believe that the effect of illumination might be related to plasmonic-related heating in the nano-chemical reactions. Illumination of a metal nanoparticle at the plasmonic resonance conditions leads to enhanced light absorption, which makes it an effective nano-source of heat. Note here that in addition to the nano-thermal action, metal nanoparticles can probably intensify photo-induced chemical reactions due to the enhanced optical fields close to the metal structures due to so the called near-field effect.

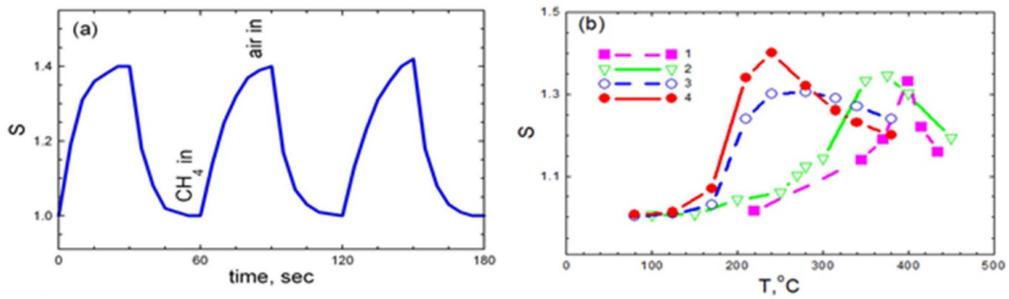


Figure 2. – (a) Dynamical response of SnO₂/Ag sensor at 240 °C. (b) Sensitivity as a function of *T*. 1 and 2 – sensor SnO₂; 3 and 4 – sensor SnO₂/Ag with (4) and without (3) lamp illumination

CONCLUSION

In conclusion, thermal oxidation of the Sn_{1-x}Ag_x alloy layers results in the formation of a Ag/SnO₂ nano-composite with a thin SnO₂ layer located on the surface which incorporates and covers both small Ag dots and large Ag islands, all of which are formed due to Kirkendall-assisted segregation. The size and shape of the large Ag islands (100–300 nm) depend on the initial composition of the SnAg layers. A plasmonic-based optical sensing effect is demonstrated. A change of position and amplitude of the plasmon-resonance peak in an optical transmission spectrum due to the silver nanoparticles are monitored for different conditions of SnO₂+Ag layer formation and gas exposure. A dynamical response of the SnO₂+Ag sensor to methane (CH₄) / air cycles is measured and the sensitivity of the sensor as a function of the operation temperature, illumination and methane concentration is determined. The concept of plasmonic-based SnO₂ sensors is discussed.

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TOWARDS THE UNDERSTANDING OF THE MECHANISM OF DC PROTONIC CONDUCTION IN GRAPHENE OXIDE

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It is found the dependence of the graphene oxide dc electrical conduction vs. temperature at fixed air humidity levels (under the laboratory conditions) to be nonmonotonic with a pronounced maximum. The increasing of the conduction while the temperature drops corresponds to the protonic concentration increase due to water molecules adsorption as the result of condensation (chilled mirror effect). At this condensation process, the dew point temperature can be determined as the temperature of the fastest adsorption rate of water molecules (and the protonic conduction fastest increase vs. temperature). At some temperatures, either at 0 °C under atmospheric pressure, when the adsorbed water turns into ice, or at the dew point at $T < 0$ °C, at further temperature drop the protonic conductivity suddenly starts to exponentially decrease via the Arrhenius-type dependence with the activation energy of ≈ 0.7 eV.

Key words: graphene oxide; dc current; proton electrical conduction; water adsorption; dew point; activation energy; humidity sensor

INTRODUCTION

Graphene is a two-dimensional monolayer of sp^2 -bonded carbon atoms exhibiting exceptional electrical properties [1, 2] and a great potential for ultrasensitive detection. Sensors based on graphene prepared via the micromechanical cleavage of graphite [3, 4] or via the reduction of graphene oxide (GO) [5–11] have raised significant interest. These sensors show very high sensitivity to gases, including NO₂, NH₃ and others. Sensors with single-molecule sensitivity have also been reported as well [12]. The mechanism of these ultrasensitive gas sensors is similar to that of carbon nanotube-based gas sensors [12–16].