Preparation and Characterization of SnO₂ Films for Sensing Applications

P Stefanov¹, G Atanasova¹, E Manolov², Z Raicheva², V Lazarova²

¹ Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia,
² Institute of Solid State Physics, Bulgarian Academy of Sciences, 72, Tzarigradsko chaussee blvd., 1784 Sofia, Bulgaria.

E-mail: stefanov@svr.igic.bas.bg

Abstract. SnO₂ thin films for gas sensing applications were deposited by RF sputtering in a mixture of oxygen and argon. The morphology, structure and composition of the SnO₂ films were analysed by XRD, SEM and XPS. SnO₂ thin films showed a crystalline structure with a submicron particle size of 200 nm. The electronic structure of the film surface was elucidated by analysis of the photoelectron core level and valence band spectra of Sn.

1. Introduction
Tin dioxide based sensors are of both scientific and commercial interest due to their high stability and high sensitivity to a broad range of gases at relatively low operating temperatures [1, 2]. Detailed knowledge of the physical properties of SnO₂, which are relevant to gas interaction, is necessary for understanding and improving the properties of SnO₂ gas sensors. Since the gases interact with the uppermost atomic layers only, a characterization of the tin oxide surface is necessary. In this paper we present the results of our studies on the morphological and structural properties, and the chemical composition of tin oxide films prepared by RF sputtering. The films were deposited on quartz in view to possible applications for detection of NH₃ in the atmosphere. For that purpose, resonator structures were created by deposition of sorption SnO₂ layers on quartz crystals. Detailed characterization of the SnO₂ films was achieved by means of XRD, SEM and XPS.

2. Experimental
2.1 Thin Film Preparation
The sensors were prepared from 15 MHz AT-cut polished quartz crystal disks, 8 mm in diameter, on both sides of which gold or silver electrodes of 4 mm in diameter were fabricated on both sides. Before coating, it is critical to ensure that the crystals are free from impurities and contaminations. The crystals with Au electrodes were cleaned with isopropyl alcohol. Thin (~100nm) SnO₂ layers were deposited by RF sputtering at 13.56 MHz from a sintered SnO₂ target in an (Ar+O₂) mixture containing 10%O₂. The sputtering was carried out at a total pressure (PAr+PO₂) of 3.10⁻² mbar and the deposition rate was about 5.55 nm/min (~100nm/18min).

2.2. Film Characterization
XRD analyses were performed by a Bruker “D8 Advance” diffractometer equipped with a CuKα X-ray source (40 kV, 40 mA). The surface morphology of the films was examined by scanning electron microscopy (SEM) using a JEM-200CX electron microscope. The film composition and electronic structure were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed in a VG ESCALAB II system using AlKα radiation with an energy of 1486.6 eV. The binding energies (BE) were determined with an accuracy of ±0.1 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference. The changes in
composition and chemical surrounding in the depth of the films were determined on the basis of the areas and binding energies of Sn3d, O1s and Si2p photoelectron peaks (after linear subtraction of the background) and Scofield’s photoionization cross-sections. The depth profiles were obtained by ion etching of the films with 3 keV Ar⁺ ions and a current density of 16 μA/cm².

3. Results and Discussion

3.1. Structural characteristics of the SnO₂ films.

The crystallinity of the tin oxide thin films was analysed by X-ray diffraction. Figure 1 shows the XRD spectrum of the tin oxide film. Broad peaks characteristic of a rutile phase of SnO₂ are observed, indicating formation of a rutile lattice structure within the film.

![Figure 1. XRD spectrum of SnO₂ films deposited on a gold-coated quartz crystal.](image)

Fig.2 shows a SEM micrograph of a SnO₂ film deposited on a gold-coated quartz crystal. There is not any sensible contrast in the image and the surface looks completely uniform. However, by close inspection of the micrograph, a dense film with a submicron particle size of 200 nm can be observed.

![Figure 2. SEM image of the surface the SnO₂ film deposited on a gold-coated quartz crystal.](image)
3.2 Chemical composition of the films

Figure 3. Sn3d and O1s core level spectra taken on the surface and after 5 min Ar+ sputtering of the SnO2 film

XPS was used to determine the chemical state of the surface of SnO2 films and their depth. Fig.3. shows the XP spectra of the Sn3d and O1s regions recorded under as-deposited and sputtering conditions. The binding energy of the Sn 3d5/2 peak at 486.6 eV indicates the presence of SnO or SnO2 since their bindings energies are similar [3-5]. The O1s spectrum shows a main peak at 530.6 eV with a slight shoulder at ~532.0 eV. The peak at 530.6 eV is assigned to lattice oxygen, while the small shoulder at 532.1 eV may be attributed to oxygen in adsorbed hydroxyl groups. After 5 min ion sputtering, the Sn3d peaks retain their positions and energy separation, but the FWHM of the peaks increases by 0.4 eV. This is likely due to partial reduction of Sn⁴⁺ since oxygen may be removed from the surface layers during the Ar⁺ sputtering.

In order to elucidate the oxidation state of Sn in the oxide film we recorded the valence band spectra shown in Fig.4. SnO2 is an n-type, wide-band gap semiconductor [6]. The origin of the n-type behavior is the native non-stoichiometry caused by oxygen vacancies. SnO2 has a direct band gap of about 3.6 eV [6]. The valence band spectrum obtained before the ion sputtering shows features which are in accordance with the density of states (DOS) curve calculated for bulk SnO2 [7]. Mainly Sn5s, Sn5d and O2p states contribute to the valence band of SnO2 while the conduction band contains mainly 5s states. After 5 min ion sputtering, the valence band spectrum changes by the appearance of a band gap state with a maximum at about 2.6 eV referenced to the Fermi level. This feature is in accordance with the calculated density of states for SnO [8]. Thus, the reduction of the surface results mainly in the occupation of the empty Sn5s states in Sn(IV). It is suggested that the Sn5s surface states are pushed down into the valence band by the much higher defect density on the sputtered surface [9].

Figure 4. Valence band spectra of a SnO2 film:
(a) as-deposited, (b) after 5 min ion sputtering,
(c) after 20 min ion sputtering.
The XPS depth profile in Fig. 5. provided an insight into the film homogeneity. The carbon C1s signal (not presented) was detected only in the outermost layers and associated with adventitious contamination. The O and Sn atomic concentrations were almost constant from the surface to the substrate/film interface, indicating homogeneous composition. Differently from the surface, the O/Sn intensity ratio is lower (~1.1) in the inner layers. This phenomenon could be ascribed to O preferential sputtering, that might have partially reduced tin dioxide [10].

Fig. 5. XPS depth profile of SnO$_2$ film.

4. Conclusions

Structural, morphological and compositional characterization of the SnO$_2$ films for sensing applications was performed by XRD, SEM and XPS. Examination by XRD and SEM showed that tin dioxide films with submicron grain sizes had been deposited. The core-level and valence-band photoelectron spectra evidenced the formation of SnO$_2$ layers. Significant change in the valence band was observed after Ar$^+$ ion bombardment due to partial reduction leading to appearance of occupied electronic states in the band gap. The gas sensing properties and selectivity of the films will be further investigated.

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