Peculiarities of surface doping with Cu in SnO_2 thin film gas sensors

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Abstract

It is demonstrated that a small amount of Cu impurity (less than 1 at.%) significantly modifies the properties of tin oxide thin films used for the gas sensors. Different amount of Cu (between 0.5 and 7 at.%) was sputtered on the top of the films. The structure, surface chemical composition, optical and electrical properties are studied for these films. It is shown that the surface doping with the sputtered Cu leads to nearly constant doping level in all the volume of the polycrystalline tin oxide thin film. It is shown experimentally that the selectivity of the resistance response to CO, H_2 and Cl_2 gases is improved for the tin oxide sensors by the small amount of the sputtered Cu. A correlation is revealed between the Cu effect and the electronic surface states that were detected by the XPS and the optical analysis. © 1997 Elsevier Science S.A.

Keywords: Film; Gas sensors; Tin oxide

1. Introduction

Metal oxide gas sensors are the most commercialised type of gas sensors [1,2]. Nevertheless these sensors still are studied intensively. The studies tend mainly to define the mechanism of the resistance response to gas in metal oxides [3–5]. The research and development of theoretical models are expected to solve the problems related with practical applications. First, models proved recover the basic limits of the solid-state gas sensors [6,7]. These limits are determined by the fundamental features of the gas sensing mechanism. It is proved by fundamental studies that universal metal oxide gas sensors could not be developed for any conditions of applications. On the other hand, thorough investigations of the sensing mechanism frequently reveal new possibilities to modify the metal oxide sensors. Consequently the parameters of the sensors could be improved for an application in certain circumstances in basically known surrounding of gases [8–11].

Doping is one of the most effective methods for an improvement of sensitivity and selectivity of metal oxide gas sensors [8–11]. Various metallic dopants were tried for these purposes. Usually the doping method is based on the selection of the most effective catalyst that modifies some specific chemical reaction on the surface of the solid state gas sensor. Recently [12,13] the variation of the doping level has been suggested as an additional method for the modification of the metal oxide gas sensors produced by chemical deposition. The main advantage of this method is that the resistance response could be altered by choice of an appropriate concentration of only one acceptor or donor [12]. It was supposed in the work [12] that the effect is controlled by the variation of the Fermi energy level with the impurity concentration in the bulk of the semiconducting film. However this previous analysis was based on the results obtained for the tin oxide films deposited from chemical solution of appropriate components [12]. In this work we tried to distinguish the features of the Cu effect related with the phenomena on the surface from that in the bulk for the films grown by d.c. magnetron sputtering. We used impurity metal sputtering for surface modification as suggested in Ref. [10].

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Copper and platinum were selected for the surface doping. We studied structure, chemical composition, optical transmission, electrical conductivity and resistance response to exposure to gases in tin oxide thin film gas sensors in this work.

2. Experimental

Tin oxide thin film gas sensors were prepared by d.c. magnetron sputtering from metallic tin target in the atmosphere of O_2:Ar = 6:4. The temperature of the substrate was equal to approximately 300°C and stabile during the growth. The details of the technology are described elsewhere [12]. Silicon substrate with insulating SiO_2 layer was used for the sensors. Micro-heater and thermometer were formed on the substrates before the deposition of the sensitive films. Structure, chemical composition and optical properties of the sensitive films were investigated in specially prepared samples consisting only of the tin oxide thin films deposited on special substrates. The same sensor technology was used for the growth of these films.

Tin oxide gas sensors were doped with Cu by a d.c. sputtering method. An ultrathin Cu over-layer was deposited on the top of the sensitive SnO_2 film. The amount of Cu sputtered was varied by a choice of sputtering time t_{evap}. No special thermal annealing was performed after the Cu sputtering. The amount of Cu detected by the surface analysis methods correlates with the Cu doping level by t_{evap} for the doped sensors in this work because the t_{evap} is an 'easy obtain' parameter for each sensor tested. The surface of some sensors was additionally activated by Pt. It is known [4,9,13,14] that the Pt catalyst diminishes the working temperatures that are optimum for detection of various gases. The characteristics of the sensors with only Pt activation are not included in this paper because those are reported elsewhere [14,15].

The structure of the films was studied by transmission electron microscopy (TEM). Microscopic view of the cross-section of the films was obtained in our study. The films were grown on the same substrate as in the case of the sensors. The cross-sectional samples were prepared by gluing two samples together face to face followed by mechanical shining and Ar ion milling at low beam current.

The spectra of optical transmission and reflection were measured by the double-beam spectrometer SPECORD UV-VIS. The spectra were obtained in the wavelength interval from 0.2–0.8 μm at room temperature (approximately 17°C) in clean air. The films were grown on fused quartz substrates for UV-VIS measurements. Effect of substrate was compensated experimentally.

Surface chemical composition was analysed in a VG ESCALAB Mak II spectrometer at $P \leq 5 \times 10^{-8}$ Pa. Low energy Ar^+ ion etching was used for obtaining the variation of the chemical composition with thickness of the films. A standard Mg Kα X-ray source (hv = 1253.6 eV) was used for XPS. The details of the experimental method are described elsewhere [14,15]. The profiles were also measured by the SIMS method. Dynamic SIMS experiments were carried out by using a VG Isotech MicroSIMS spectrometer with a magnetic sector analyser. The instrument was operated in low mass resolution mode M/DM = 300 and the duoplasmotron (O_2^+) source tuned for low ion energy $E_i = 2.0$ keV. Both optical and electronic gates of the secondary ion optics were activated to avoid undesired influence of crater walls.

The d.c. electrical resistance was measured in the sensors in clean an/or contaminated air. The results were obtained at temperatures from 50–350°C. We used the reducing gases CO and H_2 and the oxidising gas Cl_2 for measurements of the resistance response to gas. Room humidity of the clean air was approximately 40–50%.

3. Results and discussion

Polycrystalline structure was detected by TEM for the tin oxide thin films investigated in our work. Typical microscopic view of the cross-section of the films is illustrated in Fig. 1. The photograph is obtained for the film that is surface doped with Cu and Pt. It is clearly seen in Fig. 1 that the grains are arranged like regular columns growing straight up from the substrate. The size of the grains is approximately 50–80 Å. The thickness of the films is about 1000–1500 Å. A black layer is seen on the top of the 'columns' in Fig. 1. This layer could be traced only in the films that are surface doped
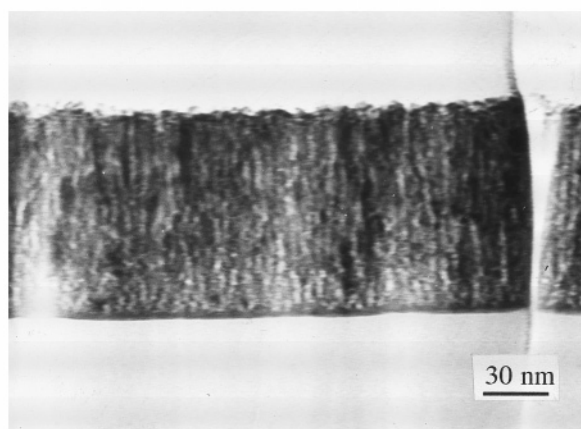

Fig. 1. Cross-sectional TEM micrograph of the tin oxide thin film doped with sputtered Cu (t_{evap} = 20 s) and Pt (t_{evap} = 4 s).
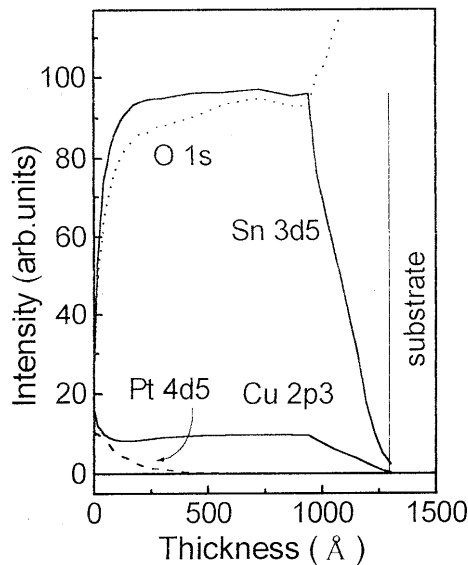
Fig. 2. Typical XPS profile of the SnO_2 film covered with the two overlayers: Pt ($t_{evap} = 4$ s) and Cu ($t_{evap} = 20$ s).

with Pt. In contrast to the Pt doping we do not find any traces of copper in the microphotographs. The same results were obtained even in the films where the amount of Cu is greater than the amount of Pt.

The amount of Cu and Pt was determined from the XPS analysis of surface composition in the special samples. The amount of Cu varied from 0.5–7 at.% in the films doped with different amount of Cu. The amount of Pt was approximately 6 at.% in the samples.

Typical profile of chemical composition of the films is illustrated in Fig. 2. The intensities of the lines of the components Sn 3d5, O 1s, Pt 4d5 and Cu 2p3 are plotted as dependencies on the thickness of the films. It is essentially to note that there was no special annealing during or after the doping process. The most remarkable result of the XPS analysis is that copper was detected in the volume of the films. The intensity of the line Cu 2p3 is constant through all the thickness of the films. In contrast to it the Pt 4d5 line totally vanishes in the depth approximately 300 Å from the surface. The XPS profile explains why the Pt layer is seen in the TEM pictures whereas no Cu layer could be traced.

The same result was obtained by another experimental technique of depth profiling (SIMS). A typical SIMS depth profile is presented for the Cu/SnO_2 sample in Fig. 3. Evidently, the signal of Cu^{63} remains almost constant until the substrate is reached.

The microphotographs and the surface analysis results clearly indicate that the Pt sputtered forms a layer on the top of the tin oxide films. It seems reasonable to suppose that the surfaces of the grains are clear of Pt in the bulk of the films. In this case the Pt sputtered could be expected controlling only chemical reaction on the

surface of the films. Since the Pt sputtered does not modify the surfaces of the grains inside the film, the electrical properties should be independent on the Pt doping directly.

In contrast, the sputtered Cu modifies the surfaces of the grains in the bulk of the films. The tin oxide thin films investigated are of polycrystalline structure as shown by transmission electron microscopy. We think that the nearly constant distribution of Cu could be originated by migration of Cu atoms in material with spacious defects. Moreover it could be expected that the sputtered Cu could modify the electrical activity of the grain boundaries as well as the electrical properties inside the grains. We cannot distinguish between these two effects in this report.

The electrical properties effectively depend on the variation of a small amount of Cu. Typical temperature dependencies of the sheet resistance are illustrated in Fig. 4. The dependencies were measured for the Cu doped sensors in clean air. The Cu effect could be traced by the comparison of the temperature dependencies in the sensors with different Cu amounts, as shown in Fig. 4. The most remarkable feature seen in Fig. 4 is the curving at temperatures 180–270°C. The curving is typical for the sensors with amount of the Cu sputtered characterised by $t_{evap} = 4$ and 12 s. The feature disappears when a higher amount of Cu is sputtered on the films.

The resistance response to gases depends totally on the amount of Cu for the films with the surface doping. Typical results are illustrated in Fig. 5. The Cu doping differently modifies the resistance response at different working temperatures. A small amount of Cu (e.g. 0.5 at.% that was obtained at $t_{evap} = 4$ s) suppresses the
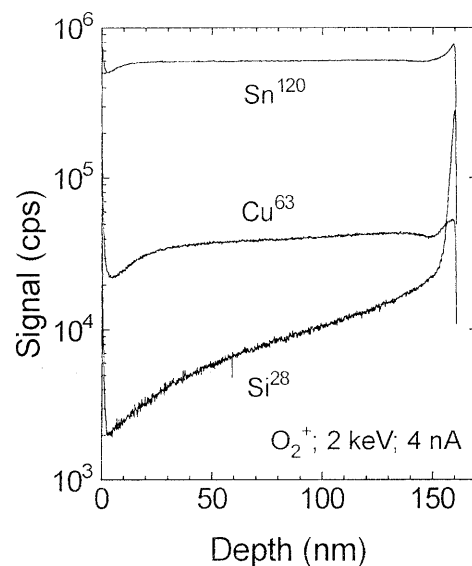

Fig. 3. Typical profile of chemical composition obtained by SIMS method in the SnO_2 films doped with Cu sputtered ($t_{evap} = 20$ s).
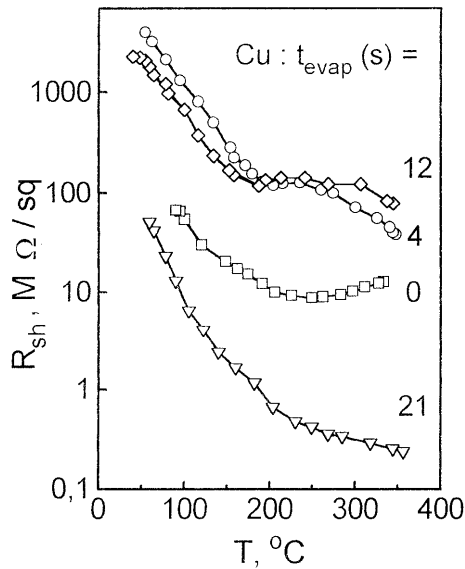
Fig. 4. Temperature dependencies of the sheet resistance of SnO$_2$ based gas sensors differently doped with the Cu. Cu concentration is characterised by the t_{evap}.

resistance response to H$_2$ gas at temperatures less than 150°C. In contrast, the response to CO gas is still large at these temperatures. However the response to CO is fully suppressed by the same amount of Cu at higher temperatures ($T > 180$°C). The sensors are practically insensitive to reducing gases when doped with a Cu amount of more than 3 at.%. Only the response to the oxidising gas Cl$_2$ is detected in highly Cu doped sensors (Fig. 5).
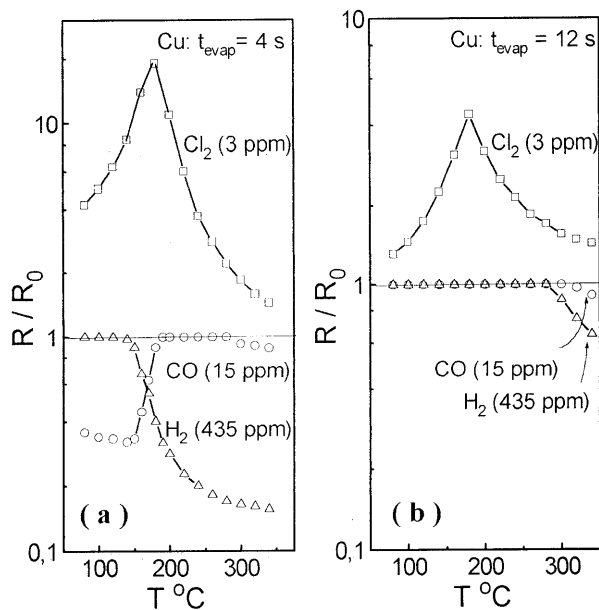

Fig. 5. Normalised resistance respone to gases of SnO$_2$ sensors that are all surface-doped similarly with Pt sputtered ($t_{evap} = 4$ s) but differently with Cu sputtered (a) $t_{evap} = 4$ s and (b) $t_{evap} = 12$ s.

The Cu effect described in this report is consistent with the results reported in Ref. [11]. This similarity between the conclusions of the two works proves that the Cu effect is independent on the technology of the production of the tin oxide sensors. On the other hand the formation of fine particles of CuO could be supposed in the chemically prepared samples [11,12]. This leads to assumption of the p–n junctions in the SnO$_2$– CuO elements [11]. We can suppose only that ultrathin Cu layer is grown on the top of the tin oxide film in our present work. Moreover, as it follows from Ref. [11], in our case the Cu effect is obtained for the amount of Cu (0.5 at.%) that is too small for covering the whole SnO$_2$ surface with CuO particles. Therefore, the change of the Fermi level of SnO$_2$ with the amount of Cu seems the most likely cause of the Cu effect described in our report.

We think that the Cu doping effect obtained by us is related with surface oxygen in the tin oxide thin films. It is known that the electrical resistance is controlled by chemisorption of oxygen in the metal oxide films in oxygen rich atmosphere [1–15]. Two oxygen species dominate on the surface of the metal oxide sensors. The species O$_2^-$ are mainly detected on the surface at temperatures less than approximately 180°C [16]. The dominating species O$_2^-$ are replaced by the O$^-$ species when temperature increases above 200°C [16]. Different oxygen species create the surface electron states with electron states with different activation energy in the grain boundaries of polycrystalline metal oxide films (e.g. [12,13]). The variation of both the density and the occupation of these states lead to the variation of the electron transport phenomena in these films. We suppose that Cu does not affect the process of the replacement of the dominating oxygen species because this process could take place mainly on the top of the Pt layer. However the occupation of the energy states created by the oxygen species on the surface of tin oxide grains could be dependent on the Cu doping level. Therefore we studied optical spectra in the range of wavelength where optical absorption is controlled by impurity states.

Typical results of optical measurements are illustrated in Fig. 6. The spectra are obtained for the films doped with different amount of the Cu sputtered. It could be seen in Fig. 6 that the spectra are practically independent on the Cu doping when the optical absorption is high (hv > 4.5 eV). Two main features of the Cu effect could be pointed out. The first is that the transmission increases at energies near 3.6 eV in slightly doped films Cu(5)/SnO$_2$ when compared with the pure one (in Fig. 6, SnO$_2$ is the pure film and Cu(5)/SnO$_2$ is the film doped with the Cu doped films. The changes depend on the amount of Cu as it could be concluded from comparison of the spectra in Fig. 6.
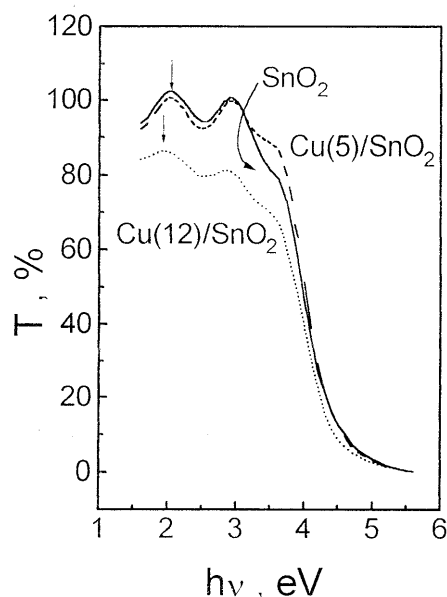
Fig. 6. The spectra of optical transmission of the SnO_2 gas sensors: SnO_2 is the initial sensor; Cu(5)/Sn)2 and Cu(12)/SnO2 are the Cu doped sensors with $t_{evap} = 5$ and 12 s, respectively.

The anomalous increase of the transmission at 3.6 eV (Fig. 6, $t_{sp} \approx 5$ s) could possibly be related with the shift of the maximums generated by additional absorption of the impurities. We suppose that some shallow electronic states lead to the absorption near the fundamental absorption edge. These states are fully occupied in the films doped with Cu. The assumption is supported by the fact that the anomalous increase disappears in the films annealed in clean air (Fig. 6). On the other hand occupied electronic states were also detected by XPS analysis. The extra peak was detected in the XPS valence band spectrum in the Cu doped films [15]. The peak was related to the occupied electronic states just under the Fermi level. So we think that the low level of the Cu doping leads to more effective localisation of free electrons at the surface defects.

An increase of the Cu amount should lead to the increase of the density of the defects because the decrease of the optical transmission is clearly obtained in the spectrum in the interval of energies from 1.5–3.5 eV (see Fig. 6). The decrease could be related with two types of the defects. The first is the point defects induced by Cu. Additional optical absorption could be originated by the optical transitions from the occupied 3d band to the 4s–4p band of the Cu point defects. The second type concerns the charge transport involved transitions between neighbouring atoms Cu and O as in [17]. Assuming that the extra optical absorption is induced by the Cu–O chemical bonds, the most possible state of copper could be identified from the optical spectrum. It was proved in Ref. [17] that the optical absorption is originated by copper monoxide CuO in

the interval of photon energies higher than 1.5 eV. The optical absorption increases drastically at energies exceeding 3.5 eV only if the oxide Cu_2O is involved. From the analysis of the optical spectra we concluded that CuO is formed in the tin oxide films investigated.

4. Conclusions

In this report the influence of doping with copper was studied for tin oxide thin films grown by d.c. magnetron sputtering. The d.c. magnetron sputtering was also utilised for doping of tin oxide based gas sensors. Different amount of Cu was deposited on the top of the gas sensitive tin oxide thin films. Structure, chemical composition, optical transmission and electrical resistance were investigated for these films. Some of the films were additionally activated with Pt that was sputtered on the films similarly as Cu was.

The surface doping with Cu sputtered leads to the nearly constant distribution of the Cu through all the thickness of the films tested. In contrast the doping with Pt sputtered modifies only the very surface of the sensitive films. We demonstrated experimentally that the selectivity of the resistance response is improved for the tin oxide sensors by small amount of the Cu sputtered. Since the Pt activation only decreases the optimum temperature of the resistance response to the gases tested, we think that the influence of the Cu sputtered could not be explained only by catalytic effect similar to that of Pt. The Cu effect is related to electron surface states that were detected in XPS valence band and the optical spectra. Therefore, it is assumed that the Cu sputtered affects the electrical activity of the grain boundaries in the gas sensors based on polycrystalline tin oxide thin films. The Cu effect is independent on the technology used for production of tin oxide gas sensors.

Acknowledgements

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Biographies

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