

# HIGH TEMPERATURE OXIDIZED SnO<sub>2</sub> FILMS PREPARED BY REACTIVE SPUTTERING

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Undoped and Sb-doped tin oxide films were prepared by d.c. reactive ion sputtering in an argon atmosphere with oxygen partial pressures ranging from 0 to 50%. The films were annealed in oxygen in the temperature range 360 – 893°C. The effect of thermal annealing on the changes in electrical and structural properties is described.

**Key words:** thin films, undoped and Sb-doped tin dioxide, resistivity, structure, heat treatment, oxygen environment.

## 1. INTRODUCTION

In recent years there has been renewed research interest in transparent and electrically conducting thin films because of their industrial applications. Numerous materials, prepared by a variety of techniques, have been reported but in practice only two materials, tin oxide doped with antimony and indium oxide doped with tin, are<sup>1-5</sup> widely used. The electrical and optical properties of these films are reviewed mainly in relation to their possible applications.

A vast body of literature exists on the preparation and properties of undoped and doped tin oxide films.

Most commonly the films have been prepared chemically<sup>6-28</sup>; in other researches vacuum evaporation of SnO<sup>7,29</sup> or SnO<sub>2</sub><sup>29-31</sup> and reactive evaporation of tin<sup>32</sup> and thermal oxidation of evaporated tin films<sup>33-35</sup> were used. Finally, SnO<sub>2</sub> films have been successfully prepared by d.c. or r.f. reactive sputtering either of metallic targets, tin or its alloys with dopants<sup>35-40</sup> or of pure or mixed oxide targets<sup>26,41-47</sup> respectively. The effect of annealing on the properties of SnO<sub>2</sub> films prepared by chemical methods was studied<sup>6-9,14,17,22-26</sup> by evaporation techniques; <sup>7,25,29-34</sup> by sputtering<sup>25,35,37,38,41,43,45,46</sup>. Phenomena which occurred during annealing are very complicated and not yet completely understood. The changes in film properties depended on the conditions of preparation (the kind and the temperature of substrate<sup>9,22</sup>, and the quality of dopants<sup>2,8,14,23,35,38,39,45</sup> and the other factors suitable to the deposition method) and on the conditions of annealing especially the range of temperature, time period and gaseous atmosphere (air<sup>6,7,14,17,22,23,25,32,35,37,38,41,45,46</sup>, oxygen<sup>8,17,26,29,30,33,34</sup> argon<sup>17,23</sup>, nitrogen<sup>17,23,28,43</sup>, vacuum<sup>17,23,24,29,31,37,38</sup>, hydrogen<sup>22,23</sup>). Mainly, research workers are interested in resistivity, transmittance, phase composition and the structure of the SnO<sub>2</sub> films and their changes after annealing.

Phenomena during annealing have been much more often for chemical deposited than for sputtered films. It seems that the effect of annealing in oxidizing atmosphere especially at high temperature (of about 710°C<sup>35</sup> up to 1000°C<sup>37</sup>) of sputtered films has been similar to that in chemical deposited films<sup>17</sup>. The results of annealing at the temperatures of 400°C and below have been scattered and difficult to compare because of using various substrates (glass<sup>38,44-46</sup>; ceramics<sup>43</sup>; fused quartz<sup>35</sup>; Al, Ta, V, KCl or SnO<sub>2</sub> single crystals or sintered pellets<sup>37</sup>) and selected experiments (data on either changes of resistivity<sup>41,43-46</sup> or variations in structure<sup>37</sup>).

Our present investigations have concerned the changes in the structure and electrical properties of SnO<sub>x</sub> films on annealing in an oxygen atmosphere. The correlation of these properties was possible due to various measurements being carried out on the same specimen. The undoped and Sb-doped films of different phase composition from β-Sn to SnO<sub>2</sub> (cassiterite) have been investigated. A wide range of temperature of annealing from 360 to 893°C was employed, which make it possible to do comparisons with data on CVD films annealed at high temperatures, and on sputtered films usually annealed at low temperatures.

## 2. EXPERIMENTAL DETAILS

Tin oxide SnO<sub>x</sub> thin films were prepared by reactive sputtering of tin or Sn-10 wt% Sb alloy in an O<sub>2</sub>-Ar atmosphere. The oxygen content K in the gaseous mixture was defined as the ratio of the oxygen partial pressure to the total pressure and was changed from 0 to 50%. K value was kept within the accuracy about ±2%. The preparation conditions have been described in earlier works<sup>38,39</sup>. The films were deposited on fused quartz at the temperature of 150°C. The film thickness was 200 – 300 nm. For each composition and K value three resistors and the sample for X-ray measurements were prepared on one quartz substrate. Al films were used as electrodes of resistors, which were etched every time before annealing. The SnO<sub>x</sub> films, deposited at various K values, were annealed in oxygen atmosphere at four temperatures 360°C, 510°C, 675°C, 893°C. The samples were inserted in the constant temperature zone of the furnace with oxygen flow rate of about 32 l.h<sup>-1</sup>. The annealing was carried out for about 4 hours at each temperature and after each annealing the films were brought to room temperature for measurements. After each annealing the resistance and the temperature coefficient of resistance (TCR) were measured, and the X-ray diffraction studies (Cu K<sub>α</sub>, λ = 1.54178Å) were carried out. The same films were subjected to further annealing.

The X-ray diffraction patterns of the films were compared with ASTM data<sup>48</sup>. The thickness of SnO<sub>x</sub> films were measured after deposition and after annealing by an optical interference method.

## 3. RESULTS

The resistivities of the sputtered films depended on the oxygen content and on the target composition and varied from 10<sup>-4</sup> to 10<sup>-3</sup> Ω.m for 90% Sn – 10% Sb target and from 10<sup>-4</sup> to 10<sup>-1</sup> Ω.m for 100% Sn target. The SnO<sub>x</sub> films showed optical transmission above 80% for undoped and Sb-doped layers. The films thickness decreased by about 10% after four stages of annealing for each film.

### 3.1 The effect of annealing on resistivity and TCR.

Figure 1 shows the variations of the average resistivity after each stage of annealing for films deposited at various conditions. These values were calculated from the

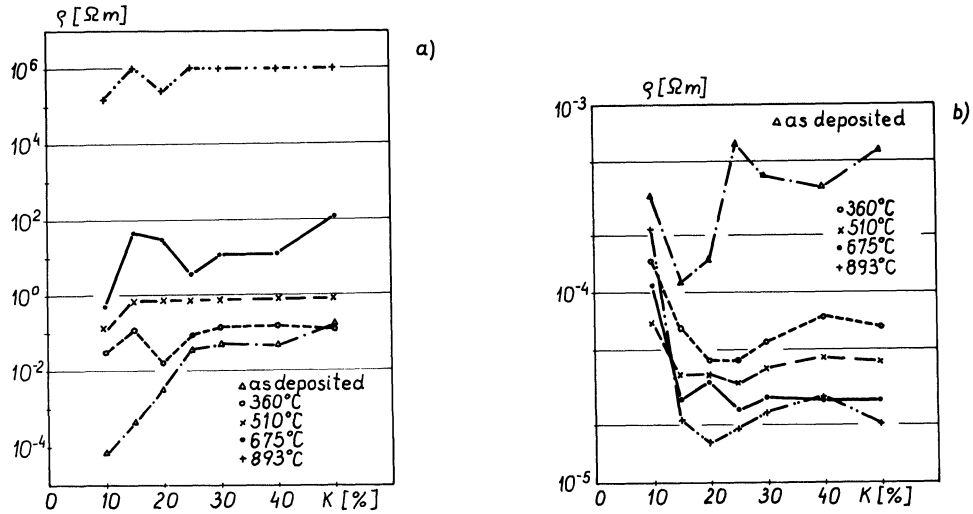


FIGURE 1 Resistivity as a function of oxygen content  $K$  during sputtering before and after each step of annealing: (a) undoped; (b) Sb-doped films.

measurements of three resistors for each  $K$  value. In the case of undoped films the sharp increase in the resistivity was observed. The changes in the range of one to two orders of magnitude were obtained for each stage of annealing up to 675°C. However, after the last stage of annealing the films became non-conducting. The limit of the electrometer measurements was of about  $10^6 \Omega\cdot m$ .

Contrarywise the Sb-doped films showed the decrease of resistivity after annealings in all cases except the layers sputtered at  $K = 10\%$ . The changes in resistivity were one and a half order of magnitude and the  $\rho$  achieved a value of about  $2 \times 10^{-5} \Omega\cdot m$  for the films sputtered at  $K = 15-50\%$ . The values of the temperature coefficient of resistivity (TCR) were estimated for the linear and reversible resistance changes which were measured in the temperature range from 20°C to 120°C.

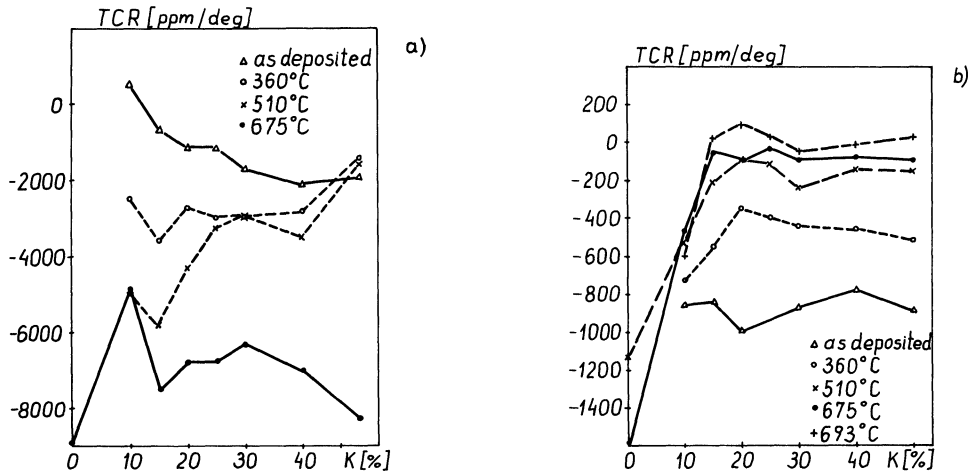


FIGURE 2 TCR value as a function of oxygen content  $K$  during sputtering before and after each step of annealing: (a) undoped; (b) Sb-doped films.

In figure 2 the effect of annealings on TCR value is presented. In the undoped films the value of TCR varied from + 100ppm/deg to - 2000ppm/deg for  $K = 10\%$  and  $50\%$  respectively. During annealing at the temperatures  $360^\circ\text{C}$  and  $510^\circ\text{C}$  the TCR changed more for the films sputtered at lower  $K$  values and achieved the value of about  $-6000$  ppm/deg for  $K = 15\%$ ; whereas for  $K = 50\%$  the TCR changed insignificantly in comparison with as-deposited films.

The third stage of annealing caused the further decrease of TCR values which coincided with the  $\rho$  changes.

In the case of Sb-doped films the TCR values increased after each annealing stage. The TCR of as-deposited Sb-doped films is almost independent on sputtering conditions and is about  $-1000$  ppm/deg. After the last stage of annealing the TCR achieved the value near zero for films sputtered at  $K \geq 15\%$ .

### 3.2 The effects of annealing on film structure.

X-ray diffraction analysis showed that the structure and phase composition of the films deposited on fused quartz were similar to that on Corning 7059 glass<sup>38</sup>. All films sputtered in argon-oxygen atmosphere in the  $K$  range from  $10\%$  to  $50\%$  were polycrystalline. The obtained "d" values have matched those accepted for tetragonal  $\text{SnO}_2^{48}$ .

No other compounds have been found. However, the relative diffraction intensity for each lattice plane did not agree with the ASTM data. Both the undoped and Sb-doped films showed only three peaks namely (110), (200) and (211). For both films the intensities of (110) peaks increased sharply with the increase of  $K$  value. However the intensities of (200) peaks increased only slightly for samples sputtered under small and medium oxygen concentration. The intensity of (211) peak also increased with increased of  $K$  value, especially for Sb-doped films prepared at  $K$  above  $30\%$ . So at a lower oxygen concentration the higher amorphous background is observed.

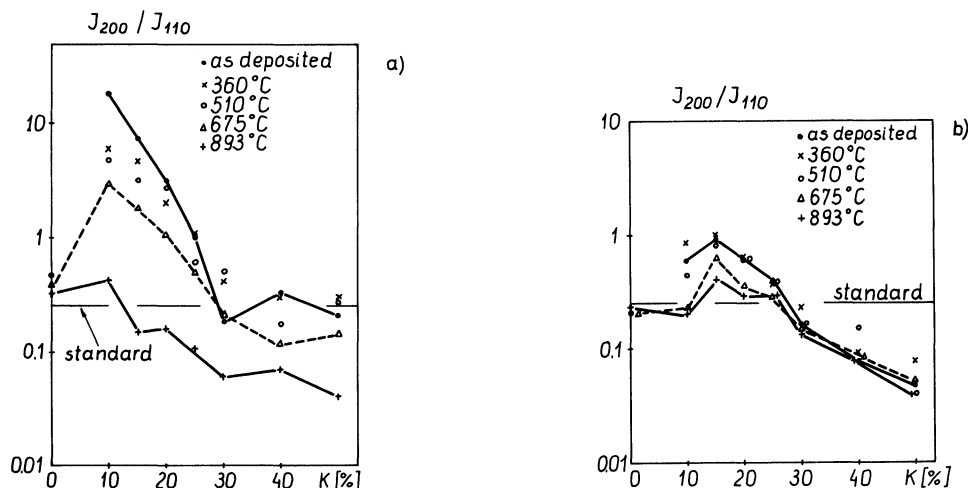


FIGURE 3  $J_{200}/J_{110}$  ration as a function of oxygen content  $K$  during sputtering before and after each step of annealing: (a) undoped; (b) Sb-doped films.

In Figure 3 the ratio of the intensity for the (200) plane to the intensity for the (110) plane is presented for both kinds of films. For comparison, the standard  $I_{200}/I_{110}$  value is shown. The deviation from standard value can be explained in terms of preferential orientation of the planes. The  $\text{SnO}_x$  films have often been textured and generally the strong textures in the directions [200]<sup>9,11-13,15,19,22,27</sup> and [110]<sup>11-13,18,27</sup> or [101]<sup>12,13,17,18,27</sup> have been observed. While our undoped films sputtered at 'K from 10 to 25%' showed the strong [200] texture, the films deposited at 'K above 30%' did not show preferred orientation. A similar situation was observed also in the case of the Sb-doped films, but at 'K above 30%' the [110] texture appeared.

For undoped films the intensity of (110) peaks continuously increased with the increase of annealing temperature much more for films deposited at a low K value. During annealings up to 675°C the intensity increased by about 2 to 3 times in relation to starting values, but at the temperature of 893°C this ratio was equal to 4 or 50 for films sputtered at K = 50% and K = 10% respectively. However, the intensity of (200) peaks increased (about double) and then decreased starting from the third step of annealing. The intensity of (211) reflections increased systematically after each annealing. In the case of Sb-doped films the intensity changes of all reflections were much more smaller than in undoped films, and after all stages of annealing the initial texture was preserved. For undoped films (K below 30%), in spite of a decrease of  $I_{200}/I_{110}$  ratio during annealing up to 675°C the [200] texture was kept (see Figure 3). The [110] texture appeared after annealing in a temperature of 675°C for undoped films sputtered at 'K above 30%'. The variation of preferred orientation of crystallites was the result of the fourth stage of annealing.

Generally, the [110] texture was observed for undoped samples obtained at 'K above 15%'. For comparison, the oxidation process of pure and Sb-doped tin films sputtered in argon atmosphere was investigated. In pure tin film six peaks from  $\beta$ -Sn phase and in Sb-doped tin films six peaks from  $\beta$ -Sn and two from Sb phase were found. After the first stage of annealing (360°C) both films were composed of two phases  $\beta$ -Sn and  $\alpha$ -SnO. In the case of Sb-doped film the additional peak was observed with  $d = 3.05 \text{ \AA}$ , which could be ascribed to  $\text{Sb}_2\text{O}_4$  phase. After annealing at 510°C both films contained only  $\text{SnO}_2$  phase with a good crystallinity. The SnO phase was not observed. For Sb-doped film two additional peaks were identified with  $d = 3.047 \text{ \AA}$  and  $d = 2.159 \text{ \AA}$  which could be correlated with the  $\text{Sb}_2\text{O}_4$  phase, as after the first annealing. The observed reflections from  $\text{SnO}_2$  were in good agreement with the ASTM data. However the intensity of reflection from (200) planes in undoped films was twice as great as in standards. Further annealing stages caused the sharp increase of the intensity of (101) peak, which can be

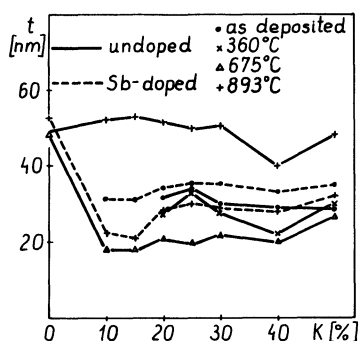


FIGURE 4 Average grain size  $t$  as a function of oxygen content  $K$  during sputtering before and after annealing for both kinds of films.

explained in terms of a preferential orientation of the planes. This peak was not observed so well in the films sputtered in an oxygen - argon atmosphere after deposition as after annealings.

The (111) peak was also found as the result of annealing at the temperature of 893°C. However, in Sb-doped films the intensity level of all diffraction peaks increased uniformly and slightly after annealings.

Considering the diffraction broadening of the peaks the mean size  $t$  of the microcrystallites of  $\text{SnO}_2$  phase was estimated using Scherrer's formula and is presented in Figure 4. As-deposited films both Sb-doped and undoped have had microcrystallite size of about 30 nm almost independent of oxygen doping level during sputtering. After each step of annealing the slight decrease of grain size was observed for the Sb-doped films. For the undoped films the heat treatment up to 675°C caused a decrease in grain size to about 20 nm and after the fourth stage of annealing at a temperature of 893°C a rapid increase was observed. The mean grain size achieved the value of 50 nm. The  $\text{SnO}_2$  films which grew on thermal oxidized tin or Sb-doped tin films have reached a grain size in the same order of magnitude. In the range of about 50 nm the correction procedure was performed to determine the pure diffraction broadening of the  $\text{SnO}_2$  peaks<sup>6,49</sup>. The corrected value of crystallite size was approximately 80 nm. Similarly as in  $\text{SnO}_x$  films deposited on Corning 7059 glass substrates and annealed in air<sup>38</sup>, the (200) line became not only more intense but sometimes appeared to split.

In as-deposited undoped and Sb-doped  $\text{SnO}_x$  films were found lines at the angle of 18.65 - 19.05° and of 18.93 - 19.06° respectively which were ascribed to (200) line from  $\text{SnO}_2$  phase. After annealing at 360°C the two lines appeared in diffraction patterns, first at the angle of 18.48 - 19.80° for undoped  $\text{SnO}_2$  films and at 18.91 - 19.06° for Sb-doped  $\text{SnO}_2$  films, and second, at the angle 19.17 - 19.22° and at 19.17 - 19.23° respectively for undoped and Sb-doped films.

At the higher annealing temperatures both lines slightly shifted to a higher diffraction angle especially for undoped films. We postulated that the additional (second) line can be indexed as (200) and attributed to the  $\text{SnO}_{2-x}$  material crystallized under the influence of annealing.

The intensity ratio of the second peak  $I''$  to the first peak  $I'$  depended on deposition and annealing conditions as shown in Figure 5. In the undoped films the third stage of annealing caused disappearance of the second peak with the temperature rise earlier in the films sputtered at a higher K value.

After annealing at 893°C the additional peaks were absent in all samples. In Sb-doped  $\text{SnO}_x$  films the intensity of the  $I''$  additional (200) peak changed similarly but a ratio of  $I''/I'$  did not achieve so high a value as in the undoped films.

The additional (200) line disappeared just after the second stage of annealing for the films sputtered at  $K = 50\%$  and for the others K values after the further steps of

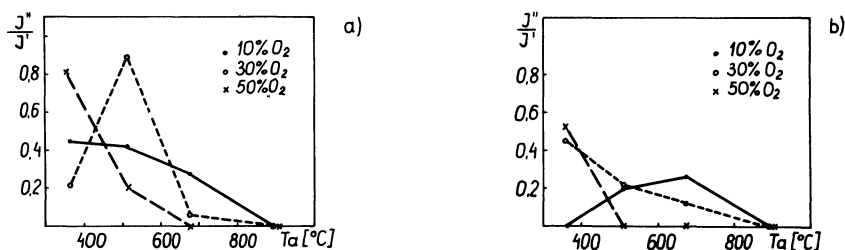


FIGURE 5 Splitting effect of (200) line for various annealing temperatures  $T_a$ : (a) undoped; (b) Sb-doped films.

annealing. The lattice constants "a" and "c" were calculated from all observed peaks positions for each investigated specimen. Their average values before and after each annealing are presented in Figures 6 and 7. The accuracy of "a" calculation from measurements was about  $\pm 0.005 \text{ \AA}$ . For the as-deposited undoped films the "a" values increased with the increase of oxygen content during sputtering and were significantly higher than those of stoichiometric  $\text{SnO}_2$  in the films deposited at K above 15%. For small oxygen-doped films these values were below the standard value. From the results of the first stage of annealing ( $360^\circ\text{C}$ ) a slight increase of "a" values was observed especially for medium oxygen-doped films, but for high oxygen-doped films these values did not change. Beginning from the second cycle of annealing ( $510^\circ\text{C}$ ) the "a" values decreased. After the last annealing step these values were slightly less than those of  $\text{SnO}_2$  standard for all samples, independently of K value.

The lattice constant "c" for some samples, especially low oxygen-doped as-deposited, and after the first step of annealing was not determined with sufficient

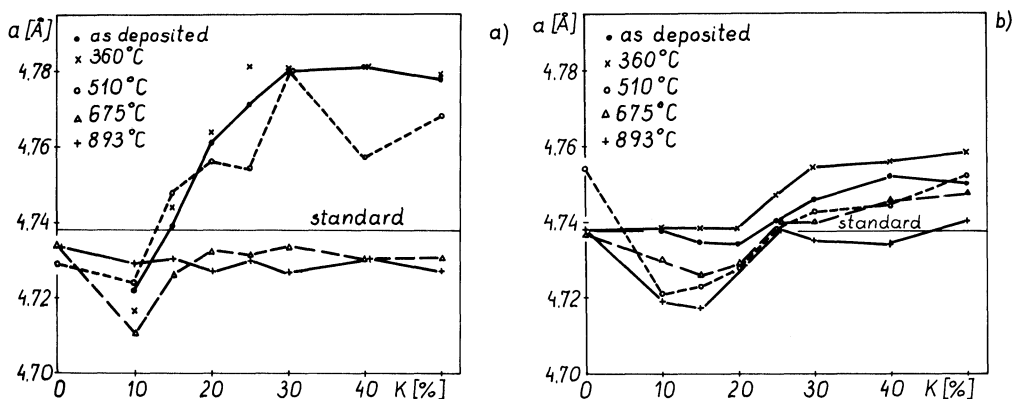


FIGURE 6 Lattice constant "a" as a function of oxygen content K during sputtering before and after each step of annealing: (a) undoped; (b) Sb-doped.

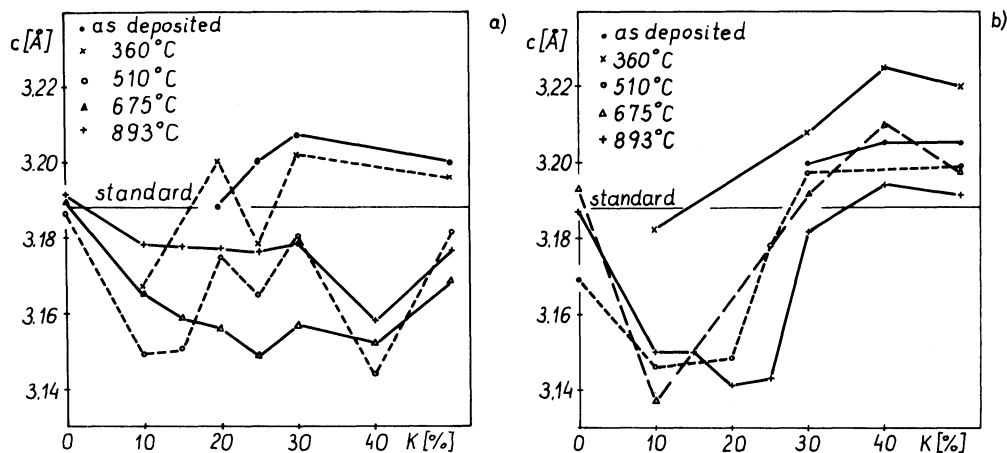


FIGURE 7 Lattice constant "c" as a function of oxygen content K during sputtering before and after each step of annealing: (a) undoped; (b) Sb-doped.

accuracy because of the difficulties with the exact determination of the (211) reflection position. In these samples the (211) peaks had very low intensity and were very broad. The uncertainty of "c" value determination was not less than  $\pm 0.015$  Å.

The "c" value was determined for  $K \geq 20\%$  and was slightly higher than for stoichiometric  $\text{SnO}_2$  in the as-deposited undoped films.

The annealing in oxygen at the temperature of  $360^\circ\text{C}$  caused a small decrease in "c" value.

The second and third annealing stages caused further decreases in lattice constant "c" up to minimal value and the fourth stage caused an increase of this value. Similarly as in the "a" value after the last annealing stage the value of "c" was slightly less than that of  $\text{SnO}_2$  standard for almost all samples. For the Sb-doped  $\text{SnO}_x$  films before annealing the lattice constant "a" was near the standard value but for films sputtered at 'K below 25%' was lower and at 'K above 25%' was greater than the standard value. For all annealing stages the  $a = f(K)$  characteristics were similar.

After annealing at the highest temperature the "a" value achieved the standard value in the films sputtered at 'K above 25%' but at 'K below 25%' it was much smaller.

The dependence of "c" value on K and the annealing temperature have been the same as in the case of the lattice constant "a". The  $\text{SnO}_2$  phase which was obtained by thermal oxidation of Sn and Sb-doped Sn films have had the "a" and "c" lattice constants correlated to standard values just after the second stage of annealing for undoped and after the third stage of annealing for Sb-doped films.

#### 4. DISCUSSION AND CONCLUSIONS

The annealing effect on the properties of the films showed different trends in both undoped and Sb-doped specimens. For the undoped films the resistivity permanently increased with the increase of the annealing temperature. Up to  $675^\circ\text{C}$  the increase was one to two orders of magnitude. A similar increase in resistivity after annealing in oxidizing atmosphere in the temperature range of  $450^\circ\text{C}$  to  $710^\circ\text{C}$  was observed by authors<sup>14,26,35</sup>, which was explained in terms of improvements of crystallinity, and removing oxygen vacancies and reduction of chlorine concentration. As the result of the last stage of annealing ( $893^\circ\text{C}$ ) almost all our films became non-conductive. Such a high value of resistivity, in the order  $10^8$  Ω.cm and above was mentioned for stoichiometric  $\text{SnO}_2$  films by Aitchinson<sup>50</sup>. While in CVD prepared films described by authors<sup>8,17</sup> annealed at the temperature of about  $1000^\circ\text{C}$  the changes of resistivity were not so high. After annealing the undoped films identified as  $\text{SnO}_2$  (cassiterite) showed the changes in the intensity of all diffraction lines. The increase of intensity after annealing at the temperature of  $360^\circ\text{C}$  indicated that the crystallinity improved. But after the next two stages of annealing the changes of lines intensity were not uniform, which can be explained by crystallization of  $\text{SnO}_2$  from amorphous phase and variation in preferred orientation of crystallites. Continuous decrease of  $I_{200}/I_{110}$  ratio (see Figure 3a) during heat treatment was observed mainly for the films sputtered at  $K < 30\%$   $\text{O}_2$  with a high amount of amorphous phase and strong [200] texture after deposition. At the same time the average grain size decreased slightly, which may be explained by an increase in the number of small grains which grew from the amorphous phase (similarly as<sup>17</sup>). After the annealing at the highest temperature a total change of texture and significant increase of grain size up to 80 nm occurred, as well as the disappearance of the additional peak; which can be attributed to full oxidation and reordering of the film material. Also the lattice constants "a" and "c" achieved the values comparable with standard after this annealing. A such alike value of grain size was obtained also for our  $\text{SnO}_2$  films prepared by oxidation of Sn films. The increase in grain size during annealing was mentioned by other workers, for example: up to



40 nm<sup>35</sup> and 150 nm<sup>37</sup> in sputtered films and up to 100 nm<sup>29</sup> and 200 nm<sup>31</sup> in evaporated films. In our Sb-doped films the resistivity decreased by about one and half orders of magnitude during all stages of annealing (see Figure 1b) and reached the value of  $(1.5 - 2.5) \times 10^{-5} \Omega \cdot m$  almost independent on K in the range of 15-50% O<sub>2</sub>. Simultaneously the TCR values increased and achieved values near zero. This behaviour of film properties is in good agreement with the nature of doped semiconductor and was mentioned by authors<sup>6,7,14</sup>.

The films structure insignificantly changed during annealing up to 893°C. These films have had weak textures compared with undoped films, which were preserved during annealing. Reported by many authors<sup>1-5</sup> and confirmed by our investigations the high thermal resistance of Sb-doped SnO<sub>x</sub> films during exposure to oxidizing environment is extremely advantageous from the point of view of their applications.

In spite of carrying out of experiments on only a small number of specimens, we hope that the observed trends are valid because of the satisfactory reproducibility of technological processes<sup>39</sup> and of good correlation with our earlier results<sup>38</sup>.

## ACKNOWLEDGMENTS

The authors wish to thank Dr. M. Szreter, the Chairman of the Semiconductor Laboratory at the Technical University of Wroclaw and Dr. A. Buczkowski for their support in carrying out the experiments.

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