Improved Transparent Gas Sensor Properties of Cu-Doped SnO$_2$ Films using O$_2$ Plasma Treatment

N Somjaijaroen$^1$, R Sakdanuphab$^2$ and A Sakulkalavek$^1$

$^1$Department of Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
$^2$College of Advanced Manufacturing Innovation, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand

E-mail: aparporn.sa@kmitl.ac.th

Abstract. Cu-doped SnO$_2$ films were deposited on glass slide substrate using an RF magnetron sputtering method. The effects of O$_2$ partial pressures in the deposition process and post O$_2$ plasma treatment were assessed for optical and sensing properties. O$_2$ partial pressures from 2% to 10% were assessed. Post-plasma treatment used a 15 mL/min O$_2$ flow, 450 $^\circ$C annealing temperature and 30 min treatment time. Optical transmission spectra showed that the films deposited at higher O$_2$ partial pressures had higher transparency and increased band gaps from 3.08 to 3.78 eV. After O$_2$ plasma treatment, the films showed better than optical transmission. However, when the O$_2$ partial pressure increased to 10%, the optical transmission declined slightly because the film had higher surface roughness, smaller crystals and fewer oxygens in the parent rutile tetragonal cells, enhanced the sensor response at room temperature.

1. Introduction

Metal oxide semiconductors have been used in gas sensors. One of the most important of the metal oxides is the oxygen adsorption–desorption process on the material surface which can change the electrical resistivity. Therefore, the electrical resistivity changes in air and an ambient gas. Based on this phenomenon, the metal oxides are playing an important role in detecting toxic pollutants, such as H$_2$S, CO, NO and NO$_2$ [1].

Among the metal oxide semiconductors, SnO$_2$ is an important material because of its properties. It is an n-type oxide and a wide band gap (3.6 eV) semiconductor. SnO$_2$ has the key properties, such as high electrical conductivity and optical transparency in the visible spectrum with strong mechanical and chemical stability [2,3].

SnO$_2$ has been applied in gas sensors for detecting toxic gases. Such gas sensors should have high sensitivity, stability, fast response times, quick recovery times and good selectivity which are strongly affected by many properties, for example, crystallite size, porosity and surface area [4]. Several researches have improved the sensing properties of SnO$_2$ by Cu doping, which creates oxygen vacancies and decreases crystallite size of SnO$_2$ [5-7].

There are several methods to modify the oxygen content of metal oxide films, such as annealing under O$_2$ and oxygen plasma treatment [8,9]. Oxygen plasma treatment is an efficient technique for surface modification, that controls the oxygen functional groups on the film surface [10]. We studied the effect of O$_2$ plasma treatment on optical and sensing properties of Cu-doped SnO$_2$ films. These Cu-
doped SnO\textsubscript{2} films were deposited on glass slide substrates using radio-frequency magnetron sputtering under O\textsubscript{2} partial pressures from 2\% to 10\%. Then, the films were treated by O\textsubscript{2} plasma treatment.

2. Experiment
The Cu-doped SnO\textsubscript{2} films were deposited on the glass slide substrate using radio frequency (RF) magnetron sputtering. The substrate was cleaned by an ultrasonic cleaner in acetone solution for 30 min and set up vertically at 60 mm from target. A vacuum chamber was used to achieve a base pressure of 6×10\textsuperscript{-4} Pa. Before deposition, the target was pre-sputtered for 15 min in an Ar atmosphere to remove surface contamination. The RF power was fixed at 100 W and the working pressure was controlled at 5×10\textsuperscript{-1} Pa for 120 min. The films were deposited with O\textsubscript{2} partial pressures of 2\%, 5\% and 10\% in an Ar atmosphere. After deposition, the films were used for plasma treatment using a plasma-enhanced chemical vapor deposition (PE-CVD) system. The O\textsubscript{2} plasma treatment was applied using 50W RF power at 450 °C for 30 min.

The crystal structure of the films was studied using X-ray diffraction (XRD, PANalytical Empyrean). The surface morphology of the films was observed by atomic force microscopy (Park System, XE-100). The optical transmittance was measured by a UV-Vis spectrophotometer (PerkinElmer, LAMBDA 365). Finally, gas-sensing properties were measured using a multimeter (KEITHLEY 2400 Digital Source Meter).

3. Results and discussion
Figure 1 shows the XRD patterns of as-deposited and post plasma treatment Cu-doped SnO\textsubscript{2} films. The as-deposited films are still visibly amorphous. The films under the different O\textsubscript{2} partial pressures show the same tetragonal cassiterite SnO\textsubscript{2} phase characteristics after O\textsubscript{2} plasma treatment. Note that with 10\% O\textsubscript{2}, the crystal quality improved with stronger peaks corresponding to the preferred (110), (101) and (211) orientations of SnO\textsubscript{2} and the peaks positions shifted slightly to higher 2θ values. This is the result of doping of the smaller Cu atoms (0.071nm) in SnO\textsubscript{2}. The crystallite lattice reduced from 8.0 nm to 4.9 nm, as the O\textsubscript{2} partial pressure increased from 2\% to 10\% using the Scherrer’s formula. Because the oxygen atoms impact on the energy of nucleation and coalescence in the growth process. The kinetic energy was too low to increase the crystallite size [11].

![Figure 1](image_url)

Figure 1. X-ray diffraction pattern of Cu-doped SnO\textsubscript{2} films vs oxygen partial pressure before and after post O\textsubscript{2} plasma treatment
Figures 2 and 3 show the AFM images of the as-deposited Cu-doped SnO$_2$ films and post O$_2$ plasma treatment films at various oxygen partial pressures. The increase of oxygen partial pressure affected the surface morphology, i.e. roughness. The root-mean-square (RMS) roughness significantly decreased from 2.39 nm to 1.65 nm as the oxygen partial pressure increased from 2% to 10%. for the as-deposited films. The surface roughness decreased with the crystallite size.

After O$_2$ plasma treatment process, the surface morphology of the film changes significantly with decreased surface roughness and increased crystallinity. Hence, the grain boundaries can be distinguished clearly - see figure 3. In addition, the O$_2$ plasma treatment was more effective on the film deposited at high oxygen partial pressure (10%) which increased the film surface roughness. Because the plasma energy interacted with the film surface to lower the surface energy and increased surface roughness as the film originally had the lowest thickness of the surface region (see Figure 2(c) vs Figure 3(c)) and high stress, so it impacted the surface more easily [12,13].
Figure 3. AFM image in 2D and 3D of the Cu-doped SnO$_2$ films vs oxygen partial pressure after post O$_2$ plasma treatment: (a) 2%, (b) 5% and (c) 10%.

Figure 4 presents the optical transmittance of all Cu-doped SnO$_2$ films under each oxygen partial pressure before and after oxygen plasma treatment. The oxygen partial pressure affects transmission in visible region and the optical band gap. After increasing the oxygen partial pressure from 2% to 10%, the average transmission increased from about 50% to 80%. The optical band gap also increased with increase in oxygen partial pressure. After O$_2$ plasma treatment, optical transmission significantly increased and the band gap also increased. This increase is stronger for the film deposited at low oxygen partial pressure. The optical band gap ($E_g$) of the Cu-doped SnO$_2$ films could be estimated from the absorption coefficients ($\alpha$) which is estimated from:

$$\alpha = \frac{1}{d} \ln\left(\frac{T}{T_{	ext{ref}}}ight)$$

(1)

where the $T$ is the transmittance and $d$ is the film thickness. Then $E_g$ could be deduced from [13]:

$$(ahv)^\frac{1}{n} = A(hv - E_g)$$

(2)

where $hv$ is the incident photon energy, $A$ is a constant and the exponent $n$ depends on the type of transition, $n = \frac{1}{2}$ for direct transitions and 2 for indirect ones.

The overall trend of the direct bandgaps is shown in figure 5. The gap is between 3.09 and 3.86 eV. However, the film deposited at 10% oxygen partial pressure in figure 4(b) showed a slightly decreased transmission without band gap change - with increasing surface roughness, the absorption is increased and the transmittance decreased. Thus, the film deposited at high oxygen partial pressure has good stability under the plasma treatment.
Figure 4. Optical transmittance of Cu-doped SnO$_2$ deposited vs oxygen partial pressure: (a) as-deposited films and (b) post O$_2$ plasma treatment films

Figure 5. Direct band gaps of Cu-doped SnO$_2$ films vs oxygen partial pressure before and after O$_2$ plasma treatment

In most semiconductor materials, the Urbach energy indicates the existence of crystallite defects, such as vacancies, surface dangling bonds, imperfections and interstitial holes [14]. The localized states in the band gap which defines the lowering of band gap localized can be used to evaluate the defect concentration in lattice. The Urbach energy, $E_u$, is calculated from

$$\alpha = \alpha_0 \exp\left(\frac{hv}{E_u}\right)$$

(3)

$$\ln \alpha = \ln \alpha_0 + \left(\frac{hv}{E_u}\right)$$

(4)

where $\alpha$ is a absorption coefficient, $hv$ is the incident photon energy and $E_u$ is the band tail width (Urbach energy) [15].
The Urbach energy of Cu-doped SnO$_2$ films is presented in figure 6. $E_u$ decreased to 333.7 meV with increasing oxygen concentration. Reduction of the Urbach energy after deposition under increased oxygen could be attributed to the reduction of the deficient oxygen and lower defects. In the same way, the oxygen plasma treatment could decrease several defects and improve the crystallinity of the films. However, with the higher oxygen concentration at higher oxygen partial pressure of 10%, $E_u$ rose to ~431 meV after oxygen plasma treatment. This is attributed to the presence of localized defect states in the band gap of the film. One of the reasons for the high Urbach energy of the n-type semiconductor is vacancies caused by a large number of oxygen vacancies in the Cu-doped SnO$_2$ films [16,17].

For films applied for the gas sensor application, we need to measure the film electrical resistance. The change of the resistance (or conductance) of the surface layer is mainly caused by the adsorption or desorption of gas molecules on the material surface. The sensor response can be represented by

$$S = \frac{R_a - R_g}{R_a} \times 100\%$$

(5)

where $R_g$ is the resistance in the gas and $R_a$ in air [18].

Figure 7 shows the sensor response to acetone vapour in room temperature (~25°C). Figure 7(a) displays the sensor response of the Cu-doped SnO$_2$ films before plasma treatment. The blue solid line is the 2% as-deposited and shows only the 2% response - the 5% and 10 % films showed very large changes – too large to be effective sensors. After, the plasma treatment, the changing signals for all oxygen partial pressures are shown in figure 7(b). The films showed higher response and shorter recovery time than as-deposited. The sensor response curves indicated that these films have good repeatability and stability. Furthermore, the Cu-doped SnO$_2$ after 10% oxygen showed a high response (significant resistivity change) making them effective as gas sensors. The improvement in sensing properties compared to previous work is attributed to lack of oxygen in defects which increased electron density in the conduction band. Thus, these electrons were captured by the absorption of oxygen from the air and became oxygen ions. This leads to increase in the resistance of surface layer. Simultaneously, the electrons reduced the high resistance in the ambient gas because desorption releases capture electrons back into the conduction band [5,6,19]. Therefore, this oxygen vacancy was one of the several defects leading to improvement in the sensor response and correlated with the increase of the Urbach energy.
Figure 6. Urbach energy of the Cu-doped SnO$_2$ films vs oxygen partial pressure before and after O$_2$ plasma treatment

Figure 7. Sensor responses of Cu-doped SnO$_2$ film for acetone (300 ppt) at room temperature; (a) as-deposited films and (b) post O$_2$ plasma treatment films

4. Conclusions
The Cu-doped SnO$_2$ films showed improved crystallinity after post O$_2$ plasma treatment at 450 ºC and when increase in O$_2$ partial pressure from 2% to 10% led to a decrease the crystallite size from 8.0 nm to 4.9 nm and corresponded to a decrease in surface roughness. The O$_2$ plasma treatment improved the film optical transmission and reduced the deficient oxygen (and consequently lower defects) of the Cu-doped SnO$_2$ films, which would explain the effects of the lower oxygen partial pressure in films (2% and 5%). On the contrary, the high oxygen partial pressure of 10% was treated by O$_2$ plasma treatment so that optical transmission of the films at 10% declined slightly. The O$_2$ plasma treatment caused a higher surface roughness and more oxygen vacancy defects, corresponding to the increase of the Urbach energy. Overall, our results guide the development of improved sensing properties of Cu-doped SnO$_2$ films.
Acknowledgements
We thank the Faculty of the Science, King Mongkut's Institute of Technology Ladkrabang for financial support. John Morris, KRIS, King Mongkut's Institute of Technology Ladkrabang edited this paper and made it more concise and readable.

References
[1] Das S and Jayaraman V 2014 Prog. Mater. Sci. 66 112–255
[2] Alhuthali A, El-Nahass M M, Atta A A, El-Raheem M A, Elsabawy K M and Hassanien A M 2015 J. Lumin. 158 165–171
[3] Aragón F H, Aquino J C R, Gomes N C S, Ardisson J D, da Silva S W, Pacheco-Salazar D G and Coaquira J A H 2017 J. Eur. Ceram. Soc. 37 3375–80
[4] Niranjan R S, Patil K R, Sainkar S R and Mulla I S 2003 Mater. Chem. Phys. 80 250–256
[5] Jin W X, Ma S Y, Tie Z Z, Wei J J, Luo J, Jiang X H, Wang T T, Li W Q, Cheng L and Mao Y Z 2015 Sens. Actuators, B 213 171–180
[6] Brown S, Pandey A, Sainkar S R and Mulla I S 2003 Mater. Chem. Phys. 80 250–256
[7] Niranjan R S, Patil K R, Sainkar S R and Mulla I S 2003 Mater. Chem. Phys. 80 250–256
[8] Khan A F, Mehmoood M, Rana A M and Bhatti M T 2009 Appl. Surf. Sci. 255 8562–65
[9] Joshi S M, Book G W and Gerhardt R A 2012 Thin Solid Films 520 2723–30
[10] Huang H, Lee Y C, Chow C L, Tan O K, Tse M S, Guo J and White T 2009 Sens. Actuators, B 138 201–206
[11] Liu H, Zhou P, Zhang L, Liang Z, Zhao H and Wang Z 2016 Mater. Lett. 164 509–512
[12] Afzal N, Devajaran M and Ibrahim K 2015 J. Alloys Compd. 640 260–266
[13] Zhu H, Wang H, Wan W, Yu S and Feng X W 2014 Thin Solid Films 566 32–37
[14] Xu B, Ren X G, Gu G R, Lan L L and Wu B J 2016 Superlattices Microstruct. 89 34–42
[15] Hassanien A S and Akh A A 2015 J. Alloys Compd. 648 280–290
[16] Lin S S, Tsai Y S and Bai K R 2016 Appl. Surf. Sci. 380 203–209
[17] Biswajit C and Amarjyoti C 2014 Physica E 56 364–371
[18] Prajapati C S and Bhat N 2018 RSC Adv. 8 6590–99
[19] Yuan Y, Wang Y, Wang M, Liu J, Pei C, Liu B, Zhao H, Liu S and Yang H 2017 Sci. Rep. 7 1231