Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

Quantitative Analysis of SnO_2 Film Materials and Doping Research Based on Density Functional Theory

Ling Yi, Xiaojuan Li*, Xing Kang, Bing Ma, Tao Wang, Yanjun Wang, Honglei Guo, Lianyi Jia
Beijing Smart Core Microelectronics Technology Co., Ltd, Changping, Beijing, 102200, China
*Corresponding Author.

Abstract:

In this paper, the structure of tin dioxide material is analyzed by MS software, XPS and AFM. The XPS analysis results of SnO_2 film structure show that:O/Sn composition ratio of tin oxide film is affected by the ratio of argon to oxygen, treating temperature and sputtering time, Annealing treatment and supplementation of O_2 can increase the content of adsorbed oxygen on the surface. Analysis of the structure of the film by AFM shows annealing can make tin oxide film crystal bloom and improve surface defects. The doping of Pd in SnO_2 components can increase the conductivity to explain, and it also provides a reference for the experiment.

Keywords*:* SnO_2, XPS, AFM, Doping, DFT.

I. INTRODUCTION

SnO_2 material has the advantages of stable chemical properties, low price, and good safety. It is a good oxide semiconductor thin film material. Based on these excellent properties, SnO_2 is widely used in liquid crystal displays, solar cells, transparent electrodes, gas sensors and other fields [1-3].

The research on surface doping, surface treatment and surface coating catalytic layer as the main surface modification technology is an effective means to improve the detection ability of gas sensors. Doping can not only improve the conductivity of the component, but also improve the stability and selectivity. It is generally achieved by adding elemental metals, metal oxides and rare earth oxides. The precious metal Pd is a commonly used doping element. Some researchers have found that after doping, Pd exists on the surface of the particles in the state of PdO, which increases the surface depth and accelerates the adsorption of gas on the surface of the element. It is also for H_2, CH_4 and C_4H_{10} in these three flammable gases has higher selectivity. The doped precious metal acts as a catalytic active center, in this way, the chemisorption activation energy of the measured gas will be reduced, the sensitivity of elements will be effectively improved and the response time will be reduced which can reduce the activation energy of the chemical adsorption of the measured gas, effectively improve the sensitivity of the element and shorten the response time. Different catalysts can lead to different adsorption samples and thus have

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

selectivity [4-6].

With the development of MEMS technology, the gas sensor can be made on a tiny chip, and the size of the sensor can be greatly reduced. It can increase integration, reduce power consumption and improve response speed [7-9]. These characteristics make the new generation of MEMS metal oxide semiconductor gas sensors become the most favorable competitor in the consumer market, therefore, the quantitative analysis and doping research of gas-sensitive materials are particularly important.

The stoichiometric ratios of SnO_2 films deposited under different sputtering conditions are different, so the gas-sensing properties of SnO_2 materials are different. SnO_2 films deposited under different sputtering conditions through XPS, and at the same time uses AFM for different annealing the film structure before and after was analyzed, and the SnO_2 doped Pd was simulated and analyzed based on density functional theory in this paper, which can provide a reference for the preparation of excellent SnO_2 gas-sensitive materials. Simulation calculation of SnO_2 bulk structure

II. SIMULATION CALCULATION OF SNO_2 BULK STRUCTURE

The first-principles calculation method analyzes various physical properties of materials through the atomic structure of the material to analyze the energy band structure of the material, the density of state and the electron cloud distribution and other information. The ideal SnO_2 crystal belongs to the tetragonal crystal system, it has a rhodolite-type structure and belongs to the PMM_2 space group [10-12]. The symmetry is C_2V-1. The SnO_2 bulk structure is shown in Fig.1, Sn and O atoms are shown in the right figure. Sn_4+ ions are located at the apex and body center of the unit cell structure, and O_2- ions are located at some specific positions in the unit cell. The coordinates of the particle in the unit cell are:

$$Sn_4+: 000,\ \frac{1}{2}\frac{1}{2}\frac{1}{2} \tag{1}$$

$$O_2\text{-}:uu0,\ (1-u)(1-u)0,\ (\frac{1}{2}\pm u)(\frac{1}{2}\mp u)\frac{1}{2} \tag{2}$$

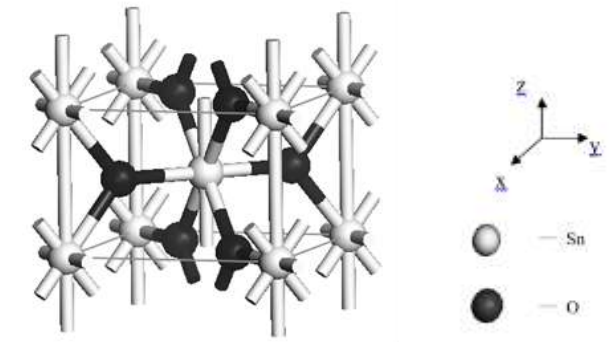

Fig.1 SnO_2 crystal structure diagram

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

III. QUANTITATIVE ANALYSIS OF SNO_2 FILM COMPOSITION

SnO_2 is a metal semiconductor material with a wide band gap. It is an N-type semiconductor and contains oxygen vacancies or tin interstitial ions. Generally speaking, SnO_2 films prepared by sputtering have a stoichiometric mismatch. For SnO_2 gas for sensitive films, the ratio of Sn to O is a key factor affecting the gas-sensing performance. The XPS technology was used to analyze the chemical composition of the film surface in detail in this paper. Fig.2 shows XPS analysis chart of the SnO_2 film Films prepared under different conditions and Table 1 shows Chemical composition of SnO_2 surface. The analysis shows that the Sn on the film surface is completely present in the 4 valence state. Annealing treatment and supplementation of O_2 will not affect the valence state of Sn, but it affects the surface of the film. The content of O, these two methods both increase the content of adsorbed oxygen on the surface, thus improving the gas sensitivity of tin oxide.

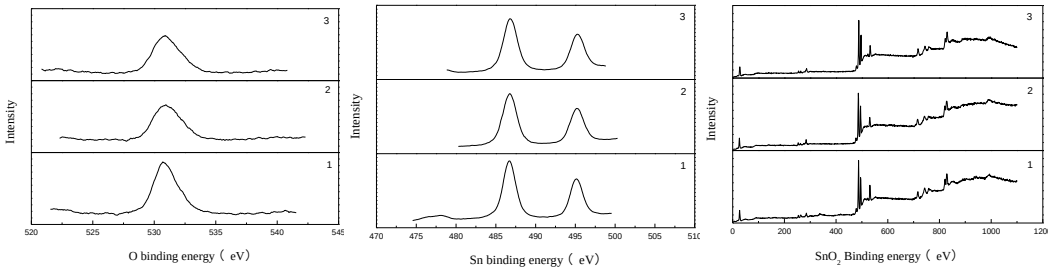

Fig.2 XPS analysis chart of the SnO_2 film
Note: 1——After pure Ar sputtering, it is treated at 500° C for 2h
2——Pure Ar sputtering without any treatment
3——The ratio of argon to oxygen is 4 with Pure Ar sputtering

TABLE I. Chemical composition of SnO_2 surface

Sample number	Spectral peak area		Surface adsorption O	O/Sn
	$Sn_3d_{5/2}$	O_1s		
1	149628.8	40148.74	7874.287	1.3628
2	146200	30487.36	7333.056	1.0592
3	150615.6	30813.01	7935.974	1.0391

Ⅳ. ANNEALING OF SNO_2 FILM

Film samples that have not been annealed are usually amorphous and have many defects, such as tin interstitial atoms and oxygen vacancies. In order to analyze the film structure comprehensively, and also to find the best working temperature of SnO_2 as a gas-sensitive material for different gases, it is usually

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

necessary to perform a certain annealing treatment on the sample. The annealing treatment can provide enough energy to make the atoms migrate. Increased, along with the disappearance and generation of a large number of interstitial atoms and vacancy atoms, crystal grains gradually aggregate and grow, and the crystalline properties of the film are gradually improved. Fig.3 and Fig.4 show the surface morphology of SnO_2 measured by AFM of untreated and treated SnO_2 film. It can be seen that after the annealing treatment, the protrusions begin to diffuse and gradually connect together, and the surface grains of the SnO_2 film show a tendency to grow.

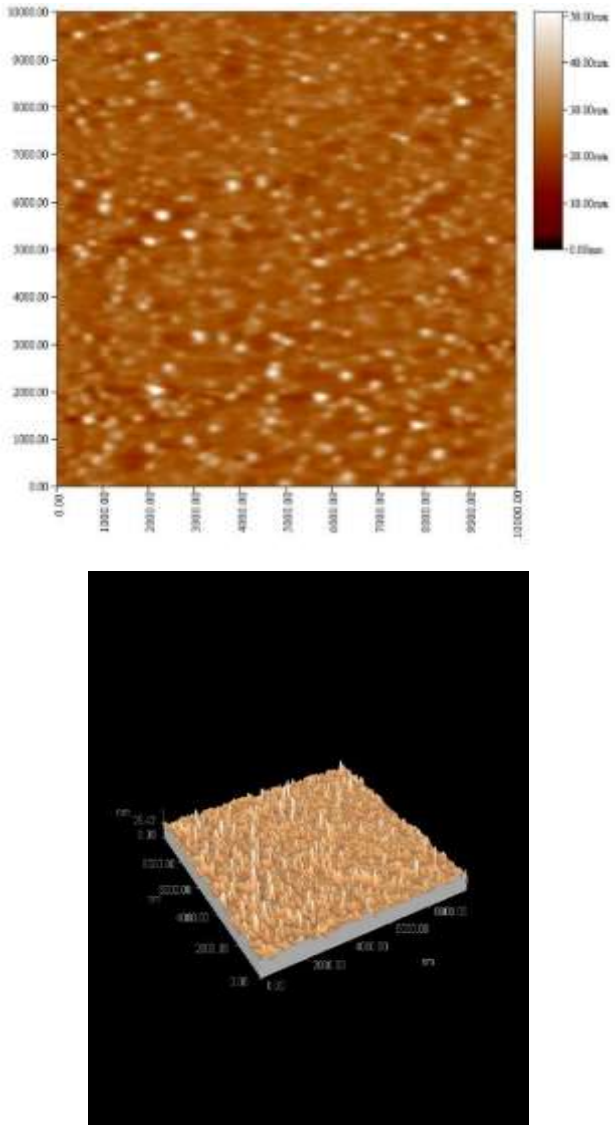

Fig.3 Surface morphology of SnO_2 thin film prepared at room temperature

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

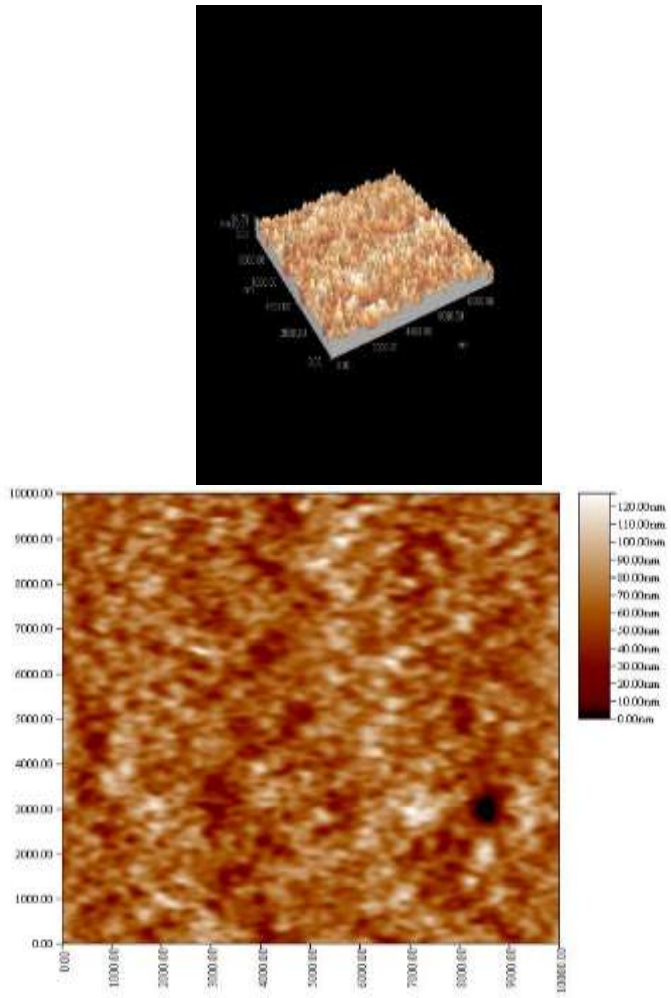

Fig.4 Surface morphology of SnO_2 film annealed at 500° C

Ⅴ. CALCULATION RESULTS AND ANALYSIS

5.1 Electronic structure

Doping modification of SnO_2 materials is the main research hotspot at present [13-15]. In this paper, the noble metal Pd doped with SnO_2 with different concentrations was simulated and analyzed by MS software.

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

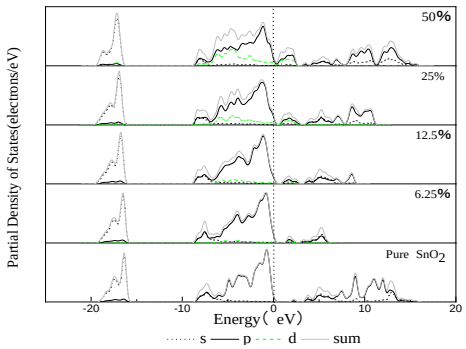

Fig.5 Partial density of states of Pd-doped SnO_2

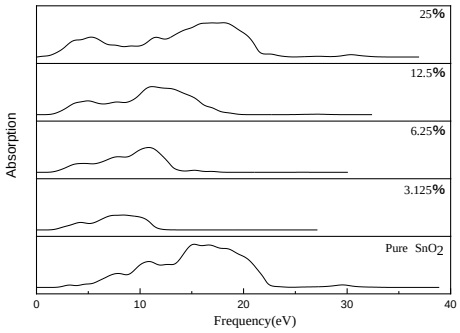

Fig.6 Optical absorption spectra of SnO_2 doped with different Pd concentrations

The valence electrons of each atom are: O 2s2 2p4, Sn 5s2 5p2, Pd 4d10, Fig.5 is the partial wave state density diagram of SnO_2 doped with different concentrations of Pd. With the increasing of Pd doping concentration in SnO_2, the band gap decreases gradually.This is mainly due to the free carriers generated by high concentration doping that change the band gap of the SnO_2 material from the following two aspects: On the one hand, the high-concentration carriers move the Fermi level into the conduction band to produce the so-called Bursteln-Moss movement, which causes the optical absorption edge to move in the direction of high energy and widens the band gap; on the other hand, the interaction between charges produces many-body effects or the overlap between impurity and defect bands narrows the band gap. The latter has a greater effect than the former, and the overall effect is that the band gap becomes smaller as the carrier concentration increases. After doping, the d orbital electrons of Pd enter the valence band and conduction band, and as the doping concentration increases, its contribution gradually increases. At the same time, an impurity state appears at the band gap, s, p, d orbital electrons all appear, this energy band gradually widens with the increase of doping concentration, and the electronic state density also gradually increases, so that when the electron transitions from valence band to conduction band, it can transition to impurity state through valence band and then to conduction band, which is easier than that of undoped state, so the conductivity of SnO_2 will increase after doping. Just like the electronic structure after deoxygenation, the conduction band width of SnO_2 gradually increases after Pd doping. It can be seen from the optical absorption spectrum diagrams of SnO_2 doped with different Pd concentrations in Fig.6. As

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

the concentration increases, the optical absorption band range of SnO_2 gradually increases, and the position of the absorption peak also blue-shifts.

Ⅵ. CONCLUSION

XPS is used to analyze the composition of tin oxide film under different sputtering conditions, AFM is used to analyze SnO_2 film structure before and after annealing and the CASTEP module of the Material studio software was used to analyze the electronic band structure of Pd doping SnO_2 in this paper, the result shows:

1) O/Sn composition ratio of SnO_2 film is affected by the ratio of argon to oxygen, treating temperature and sputtering time, Annealing treatment and supplementation of O_2 can increase the content of surface adsorbing oxygen, thereby improving the gas sensitivity of tin oxide;

2) As the annealing temperature increases, along with the disappearance and generation of a large number of interstitial atoms and vacant atoms, the crystal grains gradually aggregate and grow, and the crystalline properties of the film are gradually improved;

3) The single point energy of the unit cell system gradually decreases and the stability increases, and the volume of the SnO_2 unit cell is slightly reduced;

4) The bottom of the conduction band gradually moves to the lower energy direction, the energy level range of the conduction band increases with the increase of the concentration, the band gap width decreases, and the optical absorption band blue shifts.

REFERENCES

[1] CHOI M S, LEE Y J, KWON J D, et al. Effects of hydrogen plasma treatment on SnO_2: Fsubstrates for amorphous Si thin film solar cells.Curr.Appl.Phys.,2013,13(8):1589-1593.
[2] GUILL N C, MONTE RO J, HERRERO J M. Transparent and conductive electrodes combining AZO and ATO thin films for enhanced light scattering and electrical performance. Appl. Surf. Sci., 2013, 264:448-452.
[3] Wang Y, Zhao Z, Sun Y, et al. 2017. Fabrication and gas sensing properties of Au-loaded SnO_2 composite nanoparticles for highly sensitive hydrogen detection. Sensors and Actuators B:Chemical,240:664-673.
[4] Sun P, Zhao W, Cao Y, et al. Porous SnO_2 hierarchical nanosheets: hydrothermal preparation, growth mechanism, and gas sensing properties. Crystengcomm, 2011, 13(11): 3718-3724.
[5] Thomas B, Skariah B. Spray deposited Mg-doped SnO_2 thin film LPG sensor: XPS and EDX analysis in relation to deposition temperature and doping. Journal of Alloys & Compounds, 2015, 625:231-240.
[6] LIU Y M, ZHAO L Z, LIU X H. SnO_2 transparent conductive film in doping research Progress. Electron. Process Technol., 2015, 36(6):315-318.
[7] Chen M, Peng S, Wang N, et al. 2019. AWide-Range and High-Reaolution Detection Circuit for MEMS Gas Sensor. IEEE Sensors Journal, 19(8):3130-3137.

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2022 Page No. 721-728
Article History: Received: 06 April 2022, Revised: 28 April 2022, Accepted: 04 May 2022, Publication: 15 May 2022

[8] Rao LLR, Singha MK, Subramaniam KM et al. 2017. Molybdenum microheaters for MEMS based gas sensor applications: Fabrication, electro-thermo-mechanical and response characterization. IEEE Sensors Journal,17:22-29.

[9] Chang CH, Chou TC, Chen WC, et al. 2020. Study of a WO_3 thin film based hydrogen gas sensor decorated with platinum nanoparticles. Sensors and Actuators B: Chemical, 317:128-145.

[10] BAKHT K, MAHMOOD T, AHMED M, et al. Pressure Induced Electronic and Optical Properties of Rutile SnO_2 by First Principle Calculations. Superlattices and Microstructures, 2016, 90(2):236-241.

[11] GUO D L, HU C G. First-principles Study on the Electronic Structure and Optical Properties for SnO_2 with Oxygen Vacancy. Applied Surface Science, 2012, 258(18):6987-6992.

[12] Jiang L, Lu Y, Zhang C W, et al. Influence of oxygen vacancy on electronic and magnetic roperties in Cr doped SnO_2 super lattice. J. Phys. Soc. Jpn., 2011, 80:124709.

[13] Wang Z, Feng X Y, Wang P J. Study on magnetics and optical properties of transition metal doped SnO_2 superlattice. Journal of Founct. Mater., 2014, 45:03070.

[14] Jiang L, Wang P J, Zhang C W, et al. Electronic structure and optical properties of Cr doped SnO_2 superlattice. Acta Phys. Sin., 2011, 60(2):093101.

[15] Shao T T, Zhang F C, Cui H G. Density functional theory study on the electronic structure and optical properties of Sb-doped SnO_2. Laser & Optoelectronics Progress, 2015, 52, 081601.