Study on Simulation and Experiment of Y-Mo Co-Doped AgSnO₂ Contact Materials

Jinqin Wang 1,*, Yongqiang Chang 1, Yancai Zhu 1, Guangzhi Zhang 2 and Guanglin Huang 3

State Key Laboratory of Reliability and Intelligence of Electrical Equipment, Hebei University of Technology, Tianjin 300130, China; 201921401083@stu.hebut.edu.cn (Y.C.); zhuyancai@hebut.edu.cn (YZ)
2 Shanghai Liangxin Electrical Co., Ltd., Shanghai 200120, China; zhangguangzhi@sh-liangxin.com
3 Wenzhou Juxing Technology Co., Ltd., Wenzhou 325062, China; csuhgl@hotmail.com.cn
* Correspondence: jqwang@hebut.edu.cn; Tel.: +86-022-60204354

Abstract: Due to the shortcomings of AgSnO₂ as a contact material, models of SnO₂, Y-SnO₂, and Y-Mo-SnO₂ were built to calculate their electrical and mechanical properties based on the first principles of density functional theory. The Y-Mo co-doped SnO₂ was the most stable of all the models according to the enthalpy change and the impurity formation energy. By analyzing the energy band structure and the density of states, it was shown that the doped models are still direct bandgap semiconductor materials. The valence band moved up and the conduction band moved down after doping, reducing the band gap and enhancing conductivity. With the reduced energy for carrier transition, the electrical performance of Y-Mo co-doped SnO₂ was improved best. The mechanical properties of SnO₂ were completely improved by Y-Mo co-doping according to calculation results. The doped SnO₂ materials were prepared by the sol-gel method, and the doped AgSnO₂ materials were prepared by the powder metallurgy method. X-ray diffraction, hardness, conductivity and wettability experiments were undertaken, with experimental results showing that AgSnO₂ can be improved comprehensively by Y-Mo co-doping, verifying the conclusions of the simulation. Overall, the present study provides an effective method for the preparation of high-performance contact materials.

Keywords: first principles; doping; AgSnO₂ contact material; conductivity; mechanical properties; wettability

1. Introduction

Among the most frequently used electrical contact materials, AgCdO is widely utilized in various situations requiring good welding resistance, arc erosion resistance and small contact resistance. However, due to the toxicity of Cd, use of AgCdO has been restricted [1]. Compared with AgCdO, AgSnO₂ not only has superior electrical contact performance, but also its products are not harmful, so it is considered one of the best materials to replace AgCdO. AgSnO₂ is a composite material of Ag and SnO₂, with Ag as the main component and SnO₂ as the auxiliary material, which enhances the viscosity of the silver liquid and prevents the splash of Ag droplets. As a wide band gap semiconductor material, SnO₂ has poor conductivity, which has an impact on the performance of AgSnO₂. Therefore, AgSnO₂ as a contact material has great shortcomings: due to the influence of the arc, a large number of SnO₂ particles are forced to gather on the contact surface to form an insulating layer, which increases contact resistance [2]. It has been found that the formation of the insulating layer is the result of SnO₂ particles being inadequately wetted by the silver matrix [3]. Furthermore, SnO₂ has a high hardness, so it is difficult to further process it. As the reinforcing phase, the performance defects of SnO₂ greatly restrict the promotion and use of AgSnO₂. Therefore, improving the performance of SnO₂ has become an urgent problem to be solved.
Researchers have tried to use different preparation methods to overcome the shortcomings of AgSnO₂, including the mechanical alloying method, the chemical co-precipitation method, the reactive atomization method, the pre-oxidized alloy method and the reactive synthesis method. These methods can improve the performance of the contacts by changing the distribution of SnO₂ particles in the silver matrix [5]. In addition to developing the preparation methods, there has also been focus on adding other elements to improve the performance of AgSnO₂ contact materials. When selecting doping elements, the doping element should have thermal stability and chemical stability. Use of appropriate doping elements can enhance wettability between the silver matrix and SnO₂ particles, preventing the SnO₂ particles from gathering on the contact surface under the influence of the arc [6].

In current doping research, it has been found that the rare earth elements have strong chemical activity and can react with other impurities in the contact material to form rare earth oxides. These rare earth oxides accumulate on the surface of the contact due to the action of the arc, stabilizing arcing time and improving arc erosion resistance [7]. By building a Y-doped SnO₂ model with different concentrations, Zhangying found that the electrical properties of contact material were different with different doping concentrations, and the contact properties were the best with a concentration of 16.67% [8]. In recent years, it has been discovered that doping with high-valence metal elements such as Sb, Mo or Nb can greatly increase the carrier concentration of SnO₂ and improve conductivity [9,10]. TiO₂ film doped with Mo has good microstructure and surface properties, which greatly improve its optical and electrical properties [11].

According to the current research, based on the first principles method of density functional theory, the SnO₂, Y-doped SnO₂, Mo-doped SnO₂ and Y-Mo co-doped SnO₂ models were constructed, and their impurity formation energy, energy band structure, density of state and elastic constants were calculated for theoretical analysis of the influence of doping elements on the electrical and mechanical properties of SnO₂ materials. Then, the AgSnO₂ materials were prepared, verifying the theoretical analysis through a series of experiments. Above all, this study provides a reference for the research and development of contact materials.

2. Calculation Method and Samples Preparation

2.1. Models and Calculation Method

SnO₂ has a tetragonal rutile structure; a SnO₂ unit cell consists of two Sn atoms and four O atoms. In this study, the doping concentration ratio was 16.67%. The SnO₂ cell model was built as shown in Figure 1a. The doping models were obtained by atom substitution. A 1 × 1 × 3 SnO₂ supercell model was built, and one Sn atom was replaced by a Mo atom or a Y atom, as shown in Figure 1b,c. Then, a 1 × 2 × 3 SnO₂ supercell model was built, and two Sn atoms were replaced by a Y atom and a Mo atom, respectively, as shown in Figure 1d.

![Figure 1. Cont.](image-url)
The electrical and mechanical properties of models were calculated by the CASTEP module of Materials Studio software (MS2017, Dassault, France). The plane wave super-soft pseudopotential method based on density functional theory was used to describe the interaction between valence electrons and ions. The exchange correlation between electrons was dealt with by the Perdew–Burke–Ernzerhof (PBE) functional under generalized gradient approximation (GGA) [12,13]. In the calculation process, in order to ensure the correctness of property calculations, the models were firstly optimized to the total energy minimum and the most stable structure. Calculation parameters were set as follows: the cut-off energy was 380 eV, convergence accuracy was $1.0 \times 10^{-6}$ eV/atom, stress deviation was set as 0.02 GPa, interatomic force was set as 0.03 eV/Å, and the k spatial grid point of the Brillouin region was set as $3 \times 2 \times 1$. Then, energy band structure, density of state, and elastic constant were calculated for further analyses. The electronic configuration of the ions is as follows: Sn $5s^25p^6$, O $2s^22p^4$, Y $5s^24d^1$, Mo $5s^14p^64d^5$.

2.2. Samples Preparation

The doping concentration was 16.67%, and the doped SnO$_2$ was prepared by the sol-gel method. The reagents used to prepare the doped SnO$_2$ were SnCl$_4$·5H$_2$O, YCl$_3$·6H$_2$O and MoCl$_5$. The atomic ratio and mass ratio of the reagents required for the experiment are shown in Table 1.

**Table 1. Atomic ratio and mass ratio.**

| Reagent | SnCl$_4$·5H$_2$O/YCl$_3$·6H$_2$O | SnCl$_4$·5H$_2$O/MoCl$_5$ | SnCl$_4$·5H$_2$O/YCl$_3$·6H$_2$O/MoCl$_5$ |
|---------|---------------------------------|--------------------------|-------------------------------------------|
| Atomic ratio | 83.3:16.7 | 83.3:16.7 | 83.3:8.3:8.3 |
| Mass ratio | 1:0.173 | 1:0.156 | 1:0.0873:0.0776 |

The solvent solution was obtained by mixing anhydrous ethanol and distilled water at a volume ratio of 1:1. Then the chlorides of each doping substance were dissolved in the solvent uniformly. The solution was stirred by the S21-2 thermostatic magnetic stirrer to fully mix the solute in the solvent (70 °C, 0.5 h). Subsequently, 10% ammonia was added to the solution and stirred continuously to obtain a colloid. After standing and aging for 24 h, the colloid was washed several times until it was free of chloride ions. The colloid was then dried in a vacuum drying oven (120 °C, 1 h) and burned in a high-temperature resistance box (500 °C, 1.5 h). Finally, the pure SnO$_2$ and the doped SnO$_2$ powders were obtained after grinding and sieving. The doped AgSnO$_2$ contact materials were prepared by power metallurgy. The Ag powder and prepared SnO$_2$ powder were weighed at a ratio of 88:12. After drying (120 °C, 0.5 h), the powder was mixed with a QXQM-2 high-energy ball mill (mixing time 2 h, forward rotation speed 500 r/min). Then, the powder was pressed (25 T, 10 min), sintered (500 °C, 2 h), re-pressed (35 T, 10 min), and re-sintered (700 °C, 2 h). Finally, the AgSnO$_2$ contact samples were obtained (diameter of 20 mm and thickness...
of 3.5 mm), and their surfaces were polished to mirror surfaces with a metallographic polishing machine.

3. Simulation Analysis

3.1. Cell Structure

The structure parameters of the optimized models are shown in Table 2. It can be seen that the lattice constants, the cell volume and the bond length of doped SnO\textsubscript{2} increased compared with that of SnO\textsubscript{2}.

| Model        | a (Å)   | b (Å)   | c (Å)   | Volume (Å\textsuperscript{3}) | Sn-O (Å) | Y-O (Å) | Mo-O (Å) |
|--------------|---------|---------|---------|-------------------------------|----------|----------|----------|
| SnO\textsubscript{2} | 4.737   | 4.737   | 3.186   | 71.508                        | 2.054    |          |          |
| Y-SnO\textsubscript{2} | 4.983   | 4.983   | 3.379   | 83.901                        | 2.135    | 2.341    |          |
| Mo-SnO\textsubscript{2} | 4.864   | 4.864   | 3.306   | 78.215                        | 2.144    | 1.991    |          |
| Y-Mo SnO\textsubscript{2} | 4.928   | 4.908   | 3.327   | 80.468                        | 2.137    | 2.336    | 1.971    |

3.2. Cell Stability

The enthalpy change and impurity formation energy of the models are shown in Table 3.

|                     | SnO\textsubscript{2} | Y-SnO\textsubscript{2} | Mo-SnO\textsubscript{2} | Y-Mo-SnO\textsubscript{2} |
|---------------------|----------------------|------------------------|------------------------|--------------------------|
| Enthalpy change (eV)| −0.012               | −7.601                 | −1.705                 | −9.656                   |
| Formation energy (eV)| -                    | −2.881                 | −9.622                 | 14.072                   |

The stability of the material can be reflected by the enthalpy change. If the enthalpy change is negative, the model is stable. The greater the absolute value of the enthalpy change is, the more stable the model is. The formula of the enthalpy change is:

\[ \Delta H = H_{End} - H_{Ini} \]  

where \( H_{End} \) is the product energy, and \( H_{Ini} \) is the reactant energy. It can be seen that the enthalpy change of all models are negative; therefore, they are stable. The absolute value of the enthalpy change of the doped models was greater than that of the SnO\textsubscript{2} model, indicating that the stability of the doped model improved. The Y-Mo co-doped SnO\textsubscript{2} demonstrated the strongest stability.

The impurity formation energy is used to judge whether the elements can be doped into the structure, and it is very important for the preparation of the samples. The formula for the impurity formation energy of a single doping model is [14]:

\[ E_f(X) = E_{SnO_2X} - E_{SnO_2} - nE_X + mE_{Sn} \]  

The formula for the impurity formation energy of the co-doping model is as follows:

\[ E_f(Y, Mo) = E_{Sn(1-x)Y_xO_2(2-y)Mo_y} - E_{SnO_2} - nE_Y + mE_{Sn} - pE_{Mo} \]  

where \( E_{SnO_2X} \) is the total energy of the X (Y, Mo)-SnO\textsubscript{2} optimized, \( E_{SnO_2} \) is the total energy of the SnO\textsubscript{2}, \( E_{Sn(1-x)Y_xO_2(2-y)Mo_y} \) is the total energy of the co-doping system, \( E_X \) is the X (Y, Mo, Sn, O) atom chemical potential, and \( n, p, \) and \( m \) represent the number of Y and Mo atoms and the number of Sn atoms replaced. When the impurity formation energy of the
model is negative, the model is easy to form. Furthermore, the greater its absolute value is, the easier the model is to form [15]. According to the data in Table 3, the impurity formation energies of Y-SnO$_2$, Mo-SnO$_2$ and Y-Mo co-doped SnO$_2$ were all negative, indicating that these three models had good stability. Notably, the Y-Mo co-doped SnO$_2$ had the largest impurity formation energy and was therefore the easiest to form.

3.3. Band Structure

The band structures of models are shown in Figure 2a–d, and 0 eV is selected as the Fermi level.

Figure 2. Band structure: (a) SnO$_2$; (b) Y-doped SnO$_2$; (c) Mo-doped SnO$_2$; (d) Y-Mo co-doped SnO$_2$.

Figure 2a shows the band structure of SnO$_2$. It can be seen that the top of the valence band and the bottom of the conduction band are located at point G in the Brillouin zone, indicating that SnO$_2$ is a direct band gap semiconductor material. In this study, the band gap of SnO$_2$ was calculated to be 1.059 eV, which is less than the experimental value of 3.6 eV [16]. Ding Chao calculated the band gap of the SnO$_2$ model to be 1.039 eV [17]. Therefore, the calculated band gap value of SnO$_2$ is generally lower than the experimental value. This is the result of the underestimation of the band gap calculated value by the density functional theory. However, the error does not affect the analysis of the band gap before and after doping under the same condition [18].

Figure 2b,c shows the doping models’ energy band. It can be seen that they were still direct band gap semiconductor materials. After doping, the conduction band and the
valence band became denser, and they both moved to the Fermi level, decreasing the band gap. The narrowed band gap can reduce the energy required for electrons to be excited from the valence band to the conduction band and increase the carrier concentration, enhancing the material conductivity. Figure 2b shows the energy band structure of Y-doped SnO\(_2\). When Y-doped, the impurity level was introduced in the bottom of the forbidden band, which makes it easy for the valence electrons to transition. With the electron transitions, there are many unpaired holes in the valence band, increasing the carrier concentration. Additionally, its band gap narrowed to 0.585 eV, improving the conductivity. The Fermi energy level passes through the top of the valence band, indicating the Y-doped SnO\(_2\) is a p-type doped semiconductor. When Mo-doped, more than two electrons are unpaired. With the impurity level introduced in the top of forbidden band, it is easy for the unpaired electrons to transition, and the carrier concentration is enhanced. It can be seen from Figure 2c that the Fermi level entered the conduction band; therefore, the Mo-doped SnO\(_2\) is an n-type semiconductor material, and its band gap is reduced to 0.721 eV. The Y-Mo co-doped SnO\(_2\) also is an n-type semiconductor material. The number of energy levels increased significantly at the conduction band and valence band; additionally, the band gap is narrowed to 0.506 eV, so its conductivity is further improved.

3.4. Density of States

The total and partial density of states of models are shown in Figure 3a–d.

![Figure 3](image-url)  
**Figure 3.** Density of states: (a) SnO\(_2\); (b) Y-doped SnO\(_2\); (c) Mo-doped SnO\(_2\); (d) Y-Mo co-doped SnO\(_2\).

Figure 3a is the density of states diagram of undoped SnO\(_2\); it can be seen that the peak appeared at the deep level (~19.5—15.6 eV), which is mainly due to the energy provided
by the O-2s state. This is far away from the Fermi energy level and therefore has little effect on conductivity. The valence band near the Fermi level (−8.4–0.3 eV) had a peak, which was mainly provided by the O-2p state in addition to a small amount from the Sn-5s state and Sn-5p state. Figure 3b depicts the density of states of Y-doped SnO\(_2\). The peak near the Fermi level (−4.9–0.2 eV) was provided by the O-2p state, Sn-5p state, Sn-5s state and Y-4d state, indicating that there was a hybridization among Y, Sn and O atoms. The conduction band (2.1–25.7 eV) was mainly provided by the Y-4d, Sn-5s and Sn-5p states. Figure 3c shows the density of states of Mo-doped SnO\(_2\). The Mo-4p state and Mo-5s state had a great impact on the conduction band (6.9–20.6 eV), making the energy band in the conduction band denser. The energy band near the Fermi level (−9.2–8.3 eV) was greatly affected by the Mo-4d state. The Sn-5p state and Sn-5s state hybridized with the Mo states, causing the conduction band to move down and pass through the Fermi level. It can be seen from Figure 3d that after Y-Mo co-doping, a peak appeared in the conduction band (5.7–6.3 eV). Meanwhile, the Y-4d, Mo-4d and Sn-5p states also had peaks at the same position, indicating that the three types of atoms had a strong hybridization. Therefore, compared with Mo-doping and Y-doping, Y-Mo co-doping introduced more energy levels, reducing the energy required for electronic transition and improving the conductivity further.

3.5. Mulliken Population Analysis

The Mulliken charge population and bond population of models are shown in Table 4; the data in the table are average values.

| Model       | Atom Charge | | Bond Population |
|-------------|-------------|----------|-----------------|
|             | Sn  | O  | Y  | Mo  | Sn-O | Y-O  | Mo-O |
| SnO\(_2\)  | 1.90| −0.95|     |     | 0.53 |       |      |
| Y-SnO\(_2\)| 1.84| −0.86| 1.14|     | 0.33 | 0.39  |      |
| Mo-SnO\(_2\)| 1.75| −0.84|     | 1.32| 0.30 |       | 0.44 |
| Y-Mo-SnO\(_2\)| 1.81| −0.85| 1.09| 1.32| 0.32| 0.40  | 0.49 |

The Mulliken population analysis can be used to analyze the charge transfer, bond formation and bond strength of each atom. The Sn atom and O atom populations of SnO\(_2\) were 1.90 and −0.95, respectively. The Sn atom loses electrons and carries a positive charge, and O atom gains electrons and carries a negative charge. After doping, the Sn atom populations decreased and the O atom populations increased, indicating that the doping atoms provided more electrons. Comparing the Y atom populations and the Mo atom populations, it can be seen that Y is inclined to lose electrons; therefore, the Y atom population is smaller than the Mo atom population when Y-Mo co-doping. With all atom populations, it can be seen that the Y-Mo co-doped SnO\(_2\) provided more electrons, intensifying the electron transfer. The bond population can reflect the nature and strength of the bond. The larger the bond population is, the stronger the bond force between atoms is. The Y-O bonds and the Mo-O bonds of Y-Mo co-doped SnO\(_2\) were slightly improved compared with that of Y-doped SnO\(_2\) and Mo-doped SnO\(_2\), indicating that the bond covalency is improved and the bond becomes more stable.

3.6. Mechanical Properties

SnO\(_2\) has a high hardness, making it difficult to further process AgSnO\(_2\) material. Elastic constant is an important physical quantity to analyze when examining the mechanical properties of materials. In this study, the elastic constant of models was calculated by the CASTEP module according to the stress–strain relationship; mechanical properties
such as Young’s modulus, bulk modulus and shear modulus were calculated by the elastic constant. The elastic constant results are shown in Table 5.

Table 5. Elastic coefficients of each system.

| Model          | C_{11} | C_{12} | C_{13} | C_{22} | C_{33} | C_{44} | C_{55} | C_{66} |
|----------------|--------|--------|--------|--------|--------|--------|--------|--------|
| SnO_2          | 193.7  | 121.5  | 102.3  | 177.7  | 317.6  | 75.6   | 86.7   | 177.2  |
| Y-SnO_2        | 322.8  | 1.3    | 138.4  | 287.9  | 323.6  | 53.9   | 74.7   | 26.3   |
| Mo-SnO_2       | 313.5  | -10.9  | 103.8  | 337.7  | 357.8  | 82.9   | 80.5   | 37.1   |
| Y-Mo SnO_2     | 178.9  | 103.7  | 125.5  | 330.4  | 195.7  | 76.6   | 156.3  | 72.9   |

The elastic constant can be used to judge the stability of the mechanical structure. SnO_2 has a tetragonal rutile structure and belongs to the tetragonal crystal system. Therefore, its criterion of mechanical stability is [19]:

\[ C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0, \quad (C_{11} - C_{12}) > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0, \quad 2(C_{11} - C_{12}) + C_{33} + 4C_{13} > 0 \]  

(4)

According to the data in Table 5, the calculation results show that all the doping models met the criterion of mechanical stability. There are two calculation models for bulk modulus and shear modulus, named the Voigt model and Reuss model, respectively. The two calculation models are as follows [20]:

\[ G_V = \frac{2C_{11} + C_{33} - C_{12} - 2C_{13} + 2C_{44} + C_{66}}{2(2C_{13} + C_{11})} \]  

(5)

\[ G_R = 15\left(\frac{188V}{(C_{11} + C_{12})C_{33} + 6C_{13} - 2C_{12} - 4C_{13} + 6C_{44} + 3C_{66}}\right)^{-1} \]  

(6)

In the above formulas, the subscripts R and V represent the Voigt model and Reuss approximation algorithm. Hill believes that the shear modulus and bulk modulus calculated by these two algorithms are the maximum and minimum values of crystal elastic modulus, respectively, and the arithmetic average value of the two results is closer to the actual elastic modulus of the crystal. The calculation formulas are as follows [21]:

\[ B_H = \frac{B_V + B_R}{2} \]  

(7)

\[ G_H = \frac{G_V + G_R}{2} \]  

The calculation formula of Young’s modulus \((E)\) under the Hill model is as follows:

\[ E = \frac{9B_HG_H}{3B_H + G_H} \]  

(8)

The calculation formula of the universal elastic anisotropy index \((A^U)\) is as follows [22]:

\[ A^U = 5\frac{G_V + B_V}{G_R + B_R} - 6 \]  

(9)

Table 6 shows the bulk modulus \((B)\), shear modulus \((G)\), Young’s modulus \((E)\) and universal elastic anisotropy index \((A^U)\) of models calculated by Equations (4)–(9).
Table 6. Bulk modulus, shear modulus, Young’s modulus, microhardness and universal elastic anisotropy index.

| Model         | B_H (GPa) | G_H (GPa) | E (GPa) | G_H/B_H | A^U |
|---------------|-----------|-----------|---------|---------|-----|
| SnO_2         | 142.0     | 81.1      | 204.5   | 0.57    | 1.82|
| Y-SnO_2       | 153.2     | 66.2      | 173.6   | 0.43    | 2.01|
| Mo-SnO_2      | 152.8     | 83.8      | 212.5   | 0.54    | 1.42|
| Y-Mo-SnO_2    | 150.7     | 74.9      | 192.8   | 0.49    | 1.67|

The bulk modulus can describe the material’s ability to resist volume change, and the shear modulus can characterize the ability to resist shear strain. It can be seen that the Mo-doped SnO_2 had the greatest bulk modulus and the greatest shear modulus. Young’s modulus is defined as the ratio of linear stress to linear strain, and the smaller the value is, the better the material toughness. The Mo-doped SnO_2 had the largest Young’s modulus, and the Y-doped SnO_2 had the smallest Young’s modulus, indicating that Y-doped SnO_2 had the best toughness. The universal elastic anisotropy index is an important indicator for whether a material is prone to cracks. It can be seen that the universal elastic anisotropy index of Y-doped SnO_2 was greater than that of SnO_2; therefore, Y-doping did not improve the crack condition of SnO_2. According to the Pugh criterion [23], when G_H/B_H < 0.57, the material is tough, and when G_H/B_H > 0.57, the material is brittle. When the material is tough, the material has good ductility for further processing. It can be seen that the doping models were all tough, improving the ductility of SnO_2. However, the value of G_H/B_H of the Mo-doped SnO_2 was similar to that of SnO_2. Furthermore, Mo-doped SnO_2 had the largest Young’s modulus, so it did not improve the mechanical properties of SnO_2. According to all mechanical properties, the Y-Mo co-doped SnO_2 was best of all models.

4. Experiment

4.1. X-ray Diffraction Experiment

The Bruker D8 DISCOVER X-ray diffractometer was used for phase analysis of the prepared SnO_2 powder. The scanning range was set to 10–90°, and the scanning speed was 6°/min. Figure 4 shows the X-ray diffraction patterns of prepared SnO_2 powder. It can be seen from the figure that the diffraction peak position of doped SnO_2 powder corresponded to the diffraction peak positions of SnO_2, indicating that doping elements did not change the crystal structure of SnO_2 when doped into SnO_2 by the sol-gel method. After doping, the intensity of the diffraction peak decreased, indicating that doping can reduce the crystalline degree, the hardness of SnO_2 and improve its toughness and ductility.

4.2. Hardness and Conductivity

A SigmaScope SMP10 metal conductivity tester was used to measure the conductivity of the AgSnO_2 contact samples. A digital microhardness tester was used to measure their hardness. The Vickers hardness of the sample was obtained by pressing diamond into the sample and calculating the length of the two diagonal lines of the surface diamond indentation. The conductivity and hardness of each sample is shown in Table 7.

Table 7. Conductivity and hardness.

| Sample         | Conductivity (IACS%) | Hardness (HV) |
|----------------|---------------------|---------------|
| AgSnO_2        | 40.67               | 127.73        |
| Y-AgSnO_2      | 46.98               | 118.92        |
| Mo-AgSnO_2     | 51.43               | 107.40        |
| Y-Mo-AgSnO_2   | 56.29               | 106.32        |
It can be seen from the data in the table that the conductivity of the doped AgSnO₂ contacts was higher than that of the undoped AgSnO₂ contact, indicating that doping can effectively improve conductivity of the AgSnO₂ contact material. Additionally, the Y-Mo co-doped AgSnO₂ had the largest conductivity, which is consistent with simulation results. The hardness of Y-Mo co-doped was the lowest, increasing the ductility of AgSnO₂.

4.3. Wettability Experiment

The prepared SnO₂ powder was pressed into a substrate with a diameter of 20 mm and a thickness of 2 mm, and then it was sintered into shapes. In order to reduce the influence of gravity on the experimental results, the weight of the silver was selected as 0.3 g. The silver was placed on the substrate, then it was heated to 1050 °C and held for 0.5 h to make the silver melt into droplets and spread on the substrate. After the sample was cooled, the contact angle measuring instrument was used to measure the wetting angle. Figure 5 is the measurement picture of the wetting angle between the prepared SnO₂ substrate and Ag.
4.3. Wettability Experiment

The prepared SnO\textsubscript{2} powder was pressed into a substrate with a diameter of 20 mm and a thickness of 2 mm, and then it was sintered into shapes. In order to reduce the influence of gravity on the experimental results, the weight of the silver was selected as 0.3 g. The silver was placed on the substrate, then it was heated to 1050 °C and held for 0.5 h to make the silver melt into droplets and spread on the substrate. After the sample was cooled, the contact angle measuring instrument was used to measure the wetting angle. Figure 5 is the measurement picture of the wetting angle between the prepared SnO\textsubscript{2} substrate and Ag.

Figure 5. Wetting angle test results: (a) SnO\textsubscript{2}; (b) Y-doped SnO\textsubscript{2}; (c) Mo-doped SnO\textsubscript{2}; (d) Y-Mo co-doped SnO\textsubscript{2}.

The wetting angle is an important parameter to judge the wettability between two phases. The average measured wetting angle of each contact sample is shown in Table 8. According to the data in the table, the average value of the left and right wetting angles of AgSnO\textsubscript{2} was 93.2°, indicating that there was poor wettability between SnO\textsubscript{2} and Ag. The average wetting angle of Y-doped AgSnO\textsubscript{2} was 62.0°, and the average wetting angle of M-doped AgSnO\textsubscript{2} was 68.6°, indicating that Mo and Y can improve the wettability between SnO\textsubscript{2} and Ag. The Y-Mo co-doped AgSnO\textsubscript{2} demonstrated the smallest angle of 31.1°, indicating that Ag is further spread on the Y-Mo co-doped SnO\textsubscript{2} substrate. Therefore, the Y-Mo co-doping can improve the wettability between SnO\textsubscript{2} and Ag.

Table 8. Wetting angles.

| Sample          | Wetting Angle (°) |
|-----------------|-------------------|
| AgSnO\textsubscript{2} | 93.2              |
| Y-AgSnO\textsubscript{2} | 62.0              |
| Mo-AgSnO\textsubscript{2} | 68.6              |
| Y-Mo-AgSnO\textsubscript{2} | 31.1              |

5. Conclusions

In this study, the electrical and mechanical properties of SnO\textsubscript{2}, Y-doped SnO\textsubscript{2}, Mo-doped SnO\textsubscript{2} and Y-Mo co-doped SnO\textsubscript{2} were calculated through the CASTEP module in the Material Studio software. The AgSnO\textsubscript{2} contact materials were prepared by the sol-gel method and powder metallurgy method, and their conductivity, hardness and wettability were tested. The results show the following:

1. The enthalpy change and the impurity formation energy of the models show that doping can improve the stability of the models, with Y-Mo co-doped SnO\textsubscript{2} having the strongest stability and being the easiest to form. It can be seen from band structure...
and density of state that Y-Mo co-doped SnO$_2$ has denser energy levels and has the smallest band gap, reducing the energy required for carrier transition significantly. The atom population and bond population show that the Y-Mo co-doped SnO$_2$ provides more electrons and exhibits a more stable bond. According to all mechanical properties calculated, the Y-Mo co-doped SnO$_2$ is superior.

2. The test results show that doping can increase the conductivity of AgSnO$_2$ and reduce its hardness. The conductivity of Y-Mo co-doped AgSnO$_2$ is the largest and its hardness is the smallest. The wettability test shows that Y-Mo co-doping can improve the wettability best of all samples.

Overall, this study analyzed the influence of doping on the electrical and mechanical properties of SnO$_2$ through simulation. It was shown that Y-Mo co-doping can more effectively improve the performance of SnO$_2$ compared to other doping methods. Additionally, the simulation result was verified through experiments, providing an effective method for the research of AgSnO$_2$ contact material.

Author Contributions: Formal analysis, Y.Z.; investigation, G.Z. and G.H.; project administration, J.W.; writing—original draft, Y.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 51777057.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Li, Z.G.; Zhou, X.L.; Hu, R.M.; Yu, J.; Liu, M.M. A research progress of composite-reinforced silver-based electrical contact materials. Mater. Rep. 2018, 32, 81–85.
2. Jeannot, D.; Pinard, J.; Ramoni, P.; Jost, E. Physical and chemical properties of metal oxide additions to Ag-SnO$_2$ contact materials and predictions of electrical performance. IEEE Trans. Compon. Packag. Manuf. Technol. Part A 1994, 17, 17–23. [CrossRef]
3. Wang, H.T.; Wen, P.L.; Liang, I.; Zhu, Y.; Wang, X.W. Effect of wettability on properties of AgSnO$_2$TiO$_2$ contact material. Electron. Compon. Mater. 2016, 35, 80–83.
4. Francisco, H.A.; Myers, M. Optimization of silver tin oxide chemistry to enhance electrical performance in a.c. application. IEEE Holm Conf. Electr. Contacts 1998. [CrossRef]
5. Chen, H.Y.; Xie, M.; Wang, J.; Yang, Y.; Liu, M.; Chen, Y.; Cui, H.; Liu, J. The advances and developmental trend of Ag/SnO$_2$ electrical contact material. Precious Ment. 2011, 32, 77–81.
6. Zhang, Y.; Wang, J.B.; Li, Y.M.; Chen, L.C.; Yang, M.G.; Ding, B.J. Study of Nanocomposite Silver-based Contact Materials and Additives. Mater. Rep. 2005, 19, 34–37.
7. Li, M.; Huang, F.X.; Li, S.S.; Wang, Z.; Yin, P. Research and Development of Silver-based Electrical Contact Materials with Rare Earth. Electr. Eng. Mater. 2009, 3, 30–35.
8. Wang, J.Q.; Zhang, Y.; Kang, H.L. Study on properties of AgSnO$_2$ contact materials doped with rare earth Y. Mater. Res. Express 2018, 5, 085902.
9. Muto, Y.; Mnakato, S.; Oka, N.; Iwabuchi, Y.; Kotsubo, H.; Shigesato, Y. High-rate deposition of Ta-doped SnO$_2$ films by reactive magnetron sputtering using a Sn-Ta metal-sintered target. Thin Solid Films. 2012, 546, 3746–3750. [CrossRef]
10. Amine, S. Ab initio study on the structural, electronic, optical and electrical properties of Mo-, Nb- and Ta-doped rutile SnO$_2$. Opt Quant Electron. 2016, 48, 160–170.
11. Han, S.; Yan, J.J.; Sun, Y.; Wang, S. The Surface Wettability and Photocatalytic Property of Mo-Doped TiO$_2$ Thin Films. J. Harbin Univ. Sci. Technol. 2020, 25, 1–5.
12. Wang, J.Q.; Liu, Z.; Chen, L.; Yu, S.M.; Zhu, Y.C. Effect of Cu F Co-doping on the Properties of AgSnO$_2$ Contact. Materials 2019, 12, 2315. [CrossRef]
13. Wang, J.; Liu, Z.; Yancai, Z.; Guangzhi, Z.; Zhizhou, B. Effect of Cu, N co-doping on conductive properties of AgSnO$_2$ contact. Mater. Res. Express 2019, 6, 106311. [CrossRef]
14. Hou, Q.Y.; Wu, Y.; Zhao, C.W. Study on the effect of In-2N co-doping at preferential locality on the photoelectric function of ZnO (GGA+U). Acta Phys. Sin. 2014, 63, 334–340.
15. Ghosh, G.; Asta, M. First-principles calculations of structural energetics of Cu-TM (TM = Ti, Zr, Hf) intermetallic. *Acta Mater.* 2005, 53, 3225–3252. [CrossRef]

16. Dolbec, R.; Khakani, M.A.E.; Serventi, A.M.; Trudeau, M.; Saint-Jacques, R.G. Microstructure and physical properties of nanostructured tin oxide thin films grown by means of pulsed laser deposition. *Thin Solid Film.* 2002, 419, 230–236. [CrossRef]

17. Chao, D.; Wei, L.; Ju-Yan, L.; Lin-Lin, W.; Yun, C.; Pei-Feng, P. First principle study of electronic structure of Sb, S Co-doped SnO2. *Acta Phys. Sin.* 2018, 67, 141–147.

18. Xu, S.; Yang, P. Aluminium and Nitrogen Co-doping Effects on the Electrical Structure and Optical Properties of SnO2. *Electron. Sci. Tech.* 2018, 31, 47–51.

19. Zhang, F.C.; Zhang, Z.Y.; Zhang, W.H.; Yan, J.F.; Yun, J.N. The first-principal calculation of electronic structure and optical properties of Ir2O3. *Acta Chim. Sin.* 2008, 66, 1863–1868.

20. Reuss, A. Calculation of the flow limits of mixed crystals on the basis of the plasticity of monocrystals. *Z. Anew. Math. Mech.* 1929, 9, 49–58. [CrossRef]

21. Hill, R. The elastic behaviour of a crystalline aggregate. *Proc. Phys. Soc.* 2002, 65, 349–354. [CrossRef]

22. Ranganathan, S.I.; Ostoja, S.M. Universal Elastic Anisotropy Index. *Phys. Rev. Lett.* 2008, 101, 055504. [CrossRef]

23. Wu, Z.J.; Zhao, E.J.; Xiang, H.P.; Hao, X.F.; Liu, X.J.; Meng, J. Crystal structures and elastic properties of superhard IrN2 and IrN3 from first principles. *Phys. Rev. B* 2007, 76, 054115. [CrossRef]