

Research and Development of Preparation Technology of Strontium Niobate Titanate Single Crystal

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Abstract: With the continuous warming of semiconductor research, sto has become a candidate to construct a new memristor structure due to its resistance switching phenomenon. By doping sto with metal, researchers can replace SR or Ti elements in sto. For example, sto doped with Nb, Nd, La and other elements becomes an n-type semiconductor. More and more researchers have paid attention to metal doped sto materials. Therefore, the preparation process of strontium niobate doped (SND) single crystals is researched and developed in this paper. Firstly, the optimization and mechanism of hydrothermal synthesis of strontium titanate were studied, and then the preparation process of strontium titanate doped with niobium was analyzed; Finally, the sto single crystal samples doped with 0.05%wt and 0.7%wtNb were characterized. Hall test showed that the single crystal was a donor doped semiconductor. The electrical performance test showed that the strontium niobate single crystal had excellent resistance.

1. Introduction

With the rapid development of science and technology and the ever-changing material needs of human beings, the development of information technology is particularly critical. The rapid development of information technology has led to more frequent updates of memory. The existing flash memory has become "powerless" in terms of storage performance. At the same time, the traditional storage technology has encountered the limitations of miniaturization in the industry competition, Therefore, it is urgent to develop the next generation memory with better performance. In order to obtain new storage materials and technologies, researchers have done a lot of research work and found that there is resistance switching phenomenon in oxide materials. When an electrical signal is applied to the resistive memory, the resistance of the memory will suddenly

change. This phenomenon can be observed in metal oxides (such as NiO, TiO₂, Nb₂O₅, strtio_x, etc.). Therefore, the preparation technology of SND single crystals is studied and analyzed in this paper.

Many scholars at home and abroad have studied and analyzed the preparation technology of SND single crystals. Vojisavljevic K studied the effect of strontium doping (0 ~ 2mol%) on the structure, microstructure and functional properties of potassium sodium niobate (KNN) thin films prepared on Pt (111) /tio₂/sio₂/si substrates. The addition of up to 1mol% SR in KNN lattice hinders grain growth and vertical roughness, and helps to form fine-grained dense thin film microstructure with monoclinic system. This effectively reduces the leakage current and improves the ferroelectric characteristics; By successfully in-situ polarization of the selected region using PFM lithography, good ferroelectric domain mobility is proved [1]. Using alumina obtained from alum sludge, rmka prepared EU and Dy doped strontium aluminate persistent luminescent materials by solid-state reaction. The samples were fired under different activated carbons at 1250 °C. The surface morphology, crystal structure, photoluminescence measurement and attenuation characteristics were characterized by SEM, XRD and photoluminescence spectrometer. The results show that the main component of the sample sintered under activated carbon powder is strontium aluminate [2].

In recent years, people have found excellent electrical resistance in SrTiO₃ (STO) doped with many elements. The single crystal doped with strontium niobate (nsto) has stable chemical properties and structure. Among many oxide varistor materials, the single crystal material doped with strontium niobate (nsto) has obvious advantages: its composition and photoelectric properties can be easily modulated by element doping. A relatively simple resistive transformer structure is established to facilitate the analysis of resistive transformer mechanism. By doping with different concentrations, donor or acceptor energy levels can be formed in the forbidden band. Schottky junctions or ohmic junctions can be easily formed by contacting with some metals. Resistive materials are placed in different resistive states by electric pulse excitation. Hall and resistive state tests were carried out on nstos with different doping amounts by means of temperature variation to explore the influence of temperature and doping concentration on resistive change, and it was determined that the region where resistive change occurred was at the Schottky interface [3, 4].

2. SND Single Crystal

In recent years, researchers have developed new memristor materials by doping sto. The most common is 0.7wt%nbsto material. It has obvious high and low resistance states and intermediate resistance states. It is not only used in ordinary resistance switches, but also has the function of multi-level storage. Moreover, its stability and fatigue resistance are also noteworthy. The most important thing is that it is easy to prepare and the process is simple, which also paves the way for its future commercialization.

For sto materials, 0.7wt%nbsto single crystal belongs to high concentration doping, while 0.05wt%nbsto belongs to low concentration doping. Whether the doping concentration will affect the device, and whether the performance of devices with different doping concentrations will be different. At present, there are few reports on the comparison of two concentration single crystals. Semiconductor doped materials similar to nbsto materials also include lasto and ndsto materials. Although these materials all have resistance, their resistance mechanism is still unclear [5]. In addition, nbsto, lasto or ndsto materials are all n-type semiconductors, and there are relatively few reports on p-type semiconductor materials.

Combined with the above analysis, nbsto is used as n-type semiconductor material to discuss the influence of doping concentration and conductivity type on the resistive storage performance of the device, and reveal the resistive storage mechanism and the regulation effect of defects on the

resistive storage performance of the device.

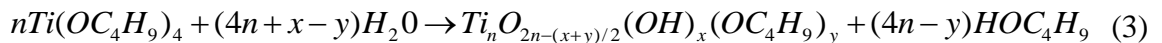
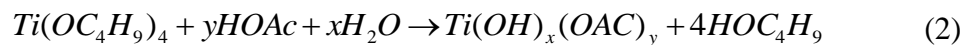
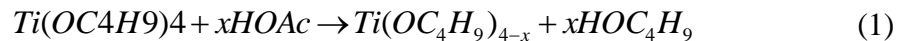
2.1. Process Optimization and Mechanism Study of Hydrothermal Synthesis of Strontium Titanate

2.1.1. High Temperature Solid State Reaction Method

The high-temperature solid-state reaction method usually adopts the reaction of SR or SrCO₃ with TiO₂ to prepare SrTiO₃ at about 1200 °C. The main problems of the solid-state reaction method are that the reaction is insufficient and the product is uneven, and the components are difficult to be mixed evenly when doping, especially when micro doping. High temperature solid state reaction method is a method for preparing SrTiO₃ powder by solid state sintering at high temperature. It can be directly synthesized at high temperature and the process is simple [6].

2.1.2. Sol Gel Method

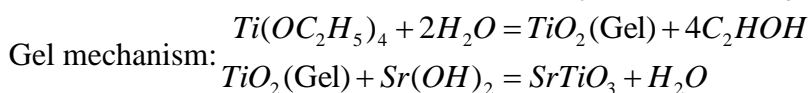
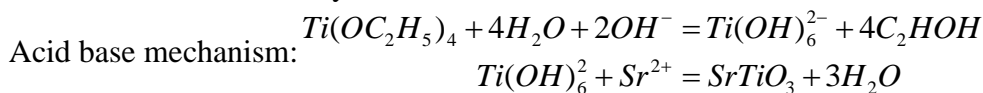
In order to overcome the defects of the solid-state reaction method, a variety of wet chemical methods have been developed to prepare strontium titanate, one of which is the sol-gel method, which uses organic matter as chelating agent and titanium alkoxide and strontium salt as raw materials to prepare homogeneous \wedge colloid, and calcines for several hours to prepare SrTiO₃ powder. The gel preparation mechanism is shown in the following formula:



Impurities are not easy to appear in the process of sol-gel preparation. The SrTiO₃ prepared by this method has small grain size, narrow distribution and high purity. However, as the raw materials used in the sol-gel process are expensive, the organic solvents used are toxic, and the powder is easy to agglomerate after high-temperature treatment, it is not easy to control the process conditions through regulating variables, and the product yield is small, so it is difficult to scale up and realize industrial production [7, 8].

2.1.3. Hydrothermal Method

Hydrothermal reaction is a method to prepare powder in a closed pressure vessel with water as the medium, and the required temperature is generally 100-400° C. The formation mechanism of hydrothermal method usually includes acid-base mechanism and sol mechanism:



The chemical raw materials and reagents selected for the hydrothermal preparation of SrTiO₃ powder and their details are shown in Table 1.

Hydrothermal synthesis has two main advantages: it can prepare very pure and very fine powders with high specific surface area in one step without additional annealing treatment to induce or improve the crystallinity. More importantly, by changing the temperature, reaction time,

precursor properties and precursor concentration, and adding growth regulators such as polar organic molecules and hydrophilic polymers, the particle size and morphology of products can be easily controlled and designed [9]. Hydrothermal method can produce products with different morphological structures, such as equiaxed particles, sheet, rod, linear, mesomorphic, superstructure and heterostructure with sizes ranging from 10 nm to several microns.

Table 1. The list of reagents used in the experiments

Reagent name	Molecular formula	molecular weight	Reagent purity (AR)
Strontium nitrate	Sr(NO ₃) ₂	211.63	99.5%
Lanthanum nitrate	LaN ₃ O ₉ 6H ₂ O	433.01	99%
Niobium pentachloride	NbCl ₅	270.17	99%
Tetrabutyl titanate	C ₁₆ H ₃₆ O ₄ Ti	340.32	98%
glycol	HOCH ₂ CH ₂ OH	62.07	—
sodium hydroxide	NaOH	40.00	96%
Glacial acetic acid	CH ₃ COOH	60.05	99.5%

Hydrothermal synthesis method is the preferred method to prepare pure strontium titanate and doped SrTiO₃ photocatalyst. Strontium titanate photocatalyst can be used to treat water. Firstly, TiO₂ photoelectric electrode is used and external bias voltage is applied to prove that water can be decomposed by UV light. In the laboratory scale, hydrothermal / solvothermal method has been proved to be an effective method to synthesize new compounds. Metastable phases or compound crystals that cannot be prepared by other methods can be prepared by hydrothermal / solvothermal method. Hydrothermal synthesis can provide an alternative route without high-temperature calcination to synthesize nano-sized materials. By adjusting the experimental conditions and adding some organic molecules as surfactants, The particle size and shape can be well regulated [10].

SrTiO₃ powder can be prepared by hydrothermal method from a variety of titanium precursors. The titanium precursor is contained in SrTiO₃ nanoparticles. When PVA was not added, large particles with irregular shape appeared in the product, rather than particles with specific structure, indicating that PVA played an important role in the control of morphology. The results show that the mechanism of the formation process of SrTiO₃ nanostructures with different shapes is directional aggregation. On the one hand, PVA molecules present in the hydrothermal system play a key role in the process of stabilizing nanoparticles, and hinder their growth through the capping effect, thus promoting the directional aggregation process. On the other hand, The morphological change from flower like nanowire superstructure to hyperbranched nanowire network can be realized by adjusting the concentration of reactants from 0.1mol/l to 0.05mol/l and 0.025mol/l. This is because in the early stage of crystal growth, the concentration of reactants has a strong impact on the dispersion of nanoparticles, resulting in polymerization methods, resulting in morphological diversity [11].

2.2. Other Synthetic Methods

In addition to the above detailed synthesis methods of strontium titanate, scientific researchers have developed a variety of methods to synthesize nano strontium titanate powder. The purity of the product obtained by chemical vapor deposition is high (up to 99%), but this method is not suitable for mass production. Microwave synthesis is a method that uses microwave energy to make reactants produce products. SrTiO₃ products with uniform size distribution can be prepared by this method. Microemulsion method is a typical example of microwave synthesis method. Microemulsion lotion synthesis method has the advantages of low cost and less instruments.

Photocatalysis performance of SrTiO₃: SrTiO₃ has the same band gap width as TiO₂, mainly absorbs the ultraviolet light region but not the visible light region, which limits the application of

photocatalysis technology in the visible light region. However, because it is a compound with typical perovskite structure and has a unique crystal structure, it is possible to improve its photocatalysis activity in the visible light region by doping modification [12].

3. Preparation of SND Single Crystals

3.1. Preparation of SrTiO₃ Bulk Samples

SrTiO₃ block is prepared by vacuum hot pressing sintering method. Vacuum hot pressing sintering is a method of preparing block materials by applying certain pressure while sintering at high temperature in vacuum. Micro flow stage: most of the pores are discharged, the powder particles are rearranged, the density increases rapidly, plastic slip and local fragmentation mass transfer occur; The model of vacuum hot pressing sintering furnace used in the experiment is zt-60-20y. Specific experimental steps:

First, put the synthesized powder into a graphite mold with a diameter of 18mm. In order to facilitate demoulding, it is necessary to pad 0.1mm thick graphite foil at the upper and lower gaskets in contact with the powder; Then SrTiO₃ block was prepared by cold pressing and burying sintering method

In the experiment, cold isostatic pressing machine was used to densify the preformed powder block compacts. Because the pressure applied by hydraulic pressure was uniform and equal, more compact and uniform compacts could be obtained. The technology of preparing ceramics by cold pressing and burying firing is easy to operate, efficient, economical and convenient, and is very suitable for mass production. Fig. 1 is the specific experimental flow chart of Nb La Co doped SrTiO₃ powder prepared by hydrothermal method.

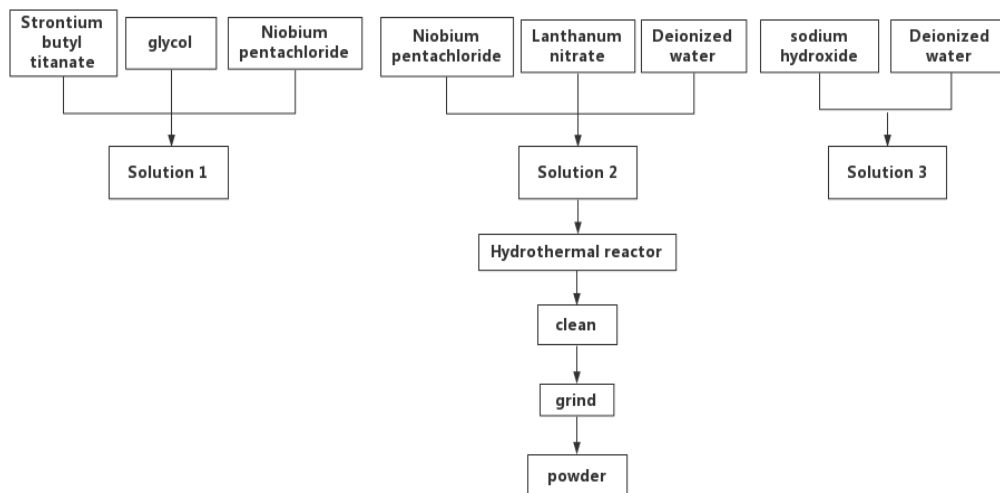


Figure 1. Process flow chart of hydrothermal preparation of SrTiO₃ nano powder

The specific experimental steps are as follows: firstly, the nano powder synthesized by hydrothermal method is loaded into a stainless steel mold with a diameter of 20mm, and pre pressed by means of unidirectional pressure with a desktop electric powder tablet press. The pressure is 4MPa and the pressure holding time is 1min; Secondly, put the preliminarily formed block sample into the hydraulic cylinder of the cold isostatic press for pressurization (250Mpa), and hold the pressure for 1.5min to obtain a more compact block sample; Finally, the samples were put into a

crucible containing carbon powder and sintered in a muffle furnace at 1300 °C for 5h, and then cooled to room temperature with the furnace to obtain black ceramic block samples. Phase and microstructure characterization

3.2. Density Test

In this experiment, Archimedes method is used to test the density of samples ρ , Before measurement, the sample surface shall be polished and polished, and the density measurement component shall be installed in the ohus electronic balance. The density of the sample can be calculated by measuring the mass of the sample in air and distilled water respectively. Its density ρ See formula (4):

$$\rho = \frac{Q}{Q-G}(\rho_0 - \rho_l) + \rho_l \quad (4)$$

For the calculation method of: ρ_0 is the air density, ρ_l is the density of the auxiliary liquid, which can be obtained by checking the table by testing the ambient temperature. Q is the mass of the solid to be tested in the air, G is the mass of the solid to be tested in the auxiliary liquid, and the auxiliary liquid of the sample is distilled water.

3.3. Phase Analysis

X-ray diffraction analysis (XRD for short) is a method for phase analysis, accurate determination of lattice constants and macro stress analysis of materials by using the diffraction phenomenon of X-rays in crystals.

When the wavelength of a beam is λ when the monochromatic parallel X-ray irradiates the crystal, it is scattered by the electrons around the periodically arranged atoms and interferes. Since the scattering lines of the atoms on the same crystal plane are in the same phase in the reflection direction of the crystal plane, it can be strengthened to produce X-ray diffraction rays, that is, it satisfies the Bragg equation formula (5):

$$2d \sin \beta = n\lambda \quad (5)$$

Where D is the crystal plane spacing, β is the grazing angle, and N is the reflection series (integer). The crystal structure and its X-ray diffraction pattern are one-to-one corresponding. Therefore, by analyzing the X-ray diffraction pattern of the crystal, the internal information of the material such as the crystal structure, crystallization degree, lattice constant, phase composition and macro stress can be obtained.

X-ray photoelectron spectroscopy (XPS) can be used to determine the types of elements in materials, as well as the electronic motion, energy state and chemical state of the elements. X-ray is used to irradiate the material to be analyzed. The photoelectron spectroscopy can be obtained by measuring the kinetic energy and quantity of electrons escaping from 1nm to 10nm below the surface of the material.

When the X-ray irradiates the sample surface, the atom will be separated and become a free electron. The change of energy in this process can be expressed by formula (6):

$$E_b = h\nu - E_k - \xi \quad (6)$$

Where E_b is the binding energy of electrons and $h\nu$ is the X photoelectron energy, which is a known quantity, ξ is the work function of the instrument material and is a constant value. E_k is the kinetic energy of electrons. As long as E_k is measured, the electron binding energy E_b of the

sample can be obtained. In order to better understand the influence of the ratio of Ti^{4+} and Ti^{3+} ions and the ratio of Nb^{4+} and Nb^{5+} ions on the thermoelectric transport performance, this paper uses escalab-250xi X-ray photoelectron spectrometer to test the sintered ceramic samples by XPS to obtain the energy spectra of each element, and uses the peak splitting software xpeak to fit the high-resolution spectra of $\text{Ti}2\text{P}$ and $\text{Nb}3\text{d}$.

4. Experimental Test Analysis

Nbsto/zno heterostructures were prepared in this experiment to explore the heterostructure resistance switching effect and negative differential resistance phenomenon due to the mature preparation process of nbsto single crystal and its stable resistance switching characteristics. $\text{Ymno}_3/\text{nbsto}$ devices were fabricated by using 0.7wt% nbsto single crystal. The phenomenon of multi-level resistance switching between ferroelectric layer and interface was found through testing.

In this paper, the sandwich structure of s-in/ nsto /o-in (nsto , SND) is used. Among them, nsto parameters: NB doping concentration is 0.05%wt and 0.7%wt crystal direction [100], specification $5 \times \text{five} \times 0.5\text{mm}$, single crystal. The resistance change of s-pt/ ndsto /o-in devices occurs at the Schottky barrier at the pt/ ndsto interface. Sto doped with different concentrations of Nb was studied

4.1. Preparation and Testing of s-in/ nsto /o-in Devices

The preparation and structure of 0.05%wt NB doped nsto devices are briefly described: it is not clear whether low concentration doped nsto can form ohmic contact with metal, so in the first step, we need to prepare o-in/ nsto devices to ensure good ohmic contact between metal in and nsto . We follow the previous practice, grinding the sample surface and pressing indium manually. The results are obtained after repeated grinding and electrode pressing.

4.2. Comparison of EPR and Raman Signals of Nb Doped Sto Single Crystals with Different Concentrations

With the increase of doping concentration, the defect concentration of STO single crystal also increases. In order to further explore the influence of Nb doping with different concentrations on STO single crystals, I compared their EPR and Raman test results, and also compared the EPR signals of 0.7wt% nbsto single crystals and pt/0.7wt% nbsto devices with upper electrode Pt. The test results are shown in Figure 2.

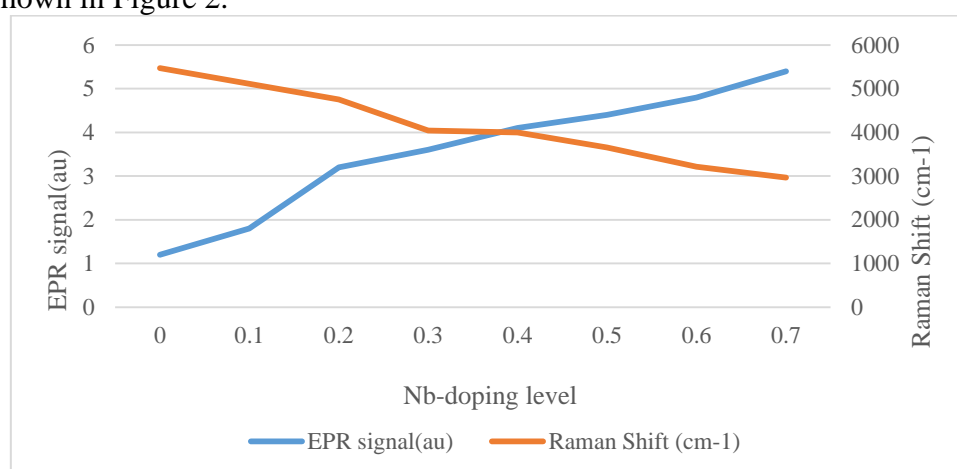


Figure 2. Comparison of EPR and Raman signals of STO single crystals doped with different concentrations of Nb

It can be seen from the figure that the EPR ($g=2.01$) and Raman signal intensity of STO single crystal change with Nb doping concentration. As the Nb doping concentration increases, the EPR intensity gradually increases, while the Raman signal gradually weakens, which indicates that the defect concentration on the surface of STO single crystal gradually increases with the NB doping concentration, and the corresponding EPR active center also gradually increases. According to the size of g factor, the active center is positively charged and can be used as the electron adsorption center.

Next, we used magnetron sputtering to sputter the in electrode on the smooth surface of the sample in order to obtain s-in/nsto. After completing the above work, we obtained s-in/nsto/o-in devices. After tens of weeks of testing, it is found that our devices have good I-V cycle retention and no signs of attenuation. The test results of nsto devices doped with 0.7%wt NB are similar to those of nsto devices doped with 0.05%wt NB.

Hall measurement is one of the best methods to understand the doping type and carrier concentration of samples. In this paper, hms-3000 Hall effect tester is used to test 0.05wt%nbsto single crystal and 0.7wt%nbsto single crystal. In order to ensure the objectivity of the test results, we test each sample for 20 times, and finally take the average as the test result. According to the test, it is verified that both 0.05wt%nbsto single crystal and 0.7wt%nbsto single crystal are n-type. The carrier concentration of 0.05wt%nbsto single crystal is $1.36 \times 10^{18} \text{cm}^{-3}$. The carrier concentration of 0.7wt%nbsto single crystal is $1.06 \times 10^{20} \text{cm}^{-3}$.

It can be seen from the comparison that both of them are n-type semiconductors, but due to the different doping concentration, the carrier concentration is quite different. According to the results of Hall effect test, it is estimated that since the carrier concentration of 0.05wt%nbsto single crystal is low, its resistance in both high resistance state (HRS) and low resistance state (LRs) may be higher than that of 0.7wt%nbsto single crystal in the same resistance state.

5. Conclusion

With the continuous development of science and technology, people have higher and higher requirements for electronic devices. In order to meet people's requirements, researchers are trying to find new materials or develop new functions on the basis of original materials. Sto materials have attracted more and more researchers' attention. In this paper, the preparation process of SND single crystals is developed, and the resistance variation phenomenon of in/nsto/in devices under variable temperature environment is mainly tested. The sto single crystal samples doped with 0.05%wt and 0.7%wt nb were characterized. The experimental results show that the single crystal process has excellent resistance, but there are still shortcomings; For SND single crystals, the metal doped sto should be further studied from the aspects of doping concentration, doping elements, doping types and so on. On this basis, more excellent memristor materials were prepared.

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Data Availability

Data sharing is not applicable to this article as no new data were created or analysed in this study.

Conflict of Interest

The author states that this article has no conflict of interest.

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