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The effect of base pressure and manganese oxidation on preparation of Mn$_3$O$_4$ and higher manganese silicide

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Abstract

In the process of preparing higher manganese silicide (HMS) by magnetron sputtering method, the sputtering base pressure is often a neglected parameter, manganese oxidation is a very difficult problem to avoid. Based on these situations, this paper takes sputtering base pressure as a variable and uses naturally oxidized manganese target as raw material to prepare samples with optimal experimental parameters of HMS, studied the impact of manganese oxidation on the preparation of HMS. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize and analyze the obtained films. It is found that Mn$_3$O$_4$ could be well prepared by MnO and MnO$_2$ on silicon substrate by the same preparation technology to prepare HMS, while control the base pressure higher than $7 \times 10^{-3}$ Pa. The MnO existence will not cause a negative impact to the production of HMS, but MnO$_2$ should be avoided in any process. When MnO and MnO$_2$ exist at the same time, the sputtering base pressure range of $4 \times 10^{-3} - 8 \times 10^{-4}$ Pa should be avoided. The base pressure additionally has a strong regulate effect on the grain size of Mn$_3$O$_4$.

1. Introduction

Higher manganese silicide (HMS) materials have a number of advantages, such as great stability, strong oxidation resistance, environmental protection, and compatible with traditional Si process [1–3]. The study about its thermoelectric properties is quite mature and the band gap of HMS is about 0.83 eV [4, 5], which is corresponding with one of the important wavelength-1.55 $\mu$m (0.8 eV) of fiber optic communication system [6], then HMS has bright research prospect in the optoelectronics [7].

One of the most common preparation method of HMS is high temperature annealing of silicon substrate with manganese films on the surface by magnetron sputtering, in which the base pressure is an necessary parameter that must be considered. However, there are many researchers involved in the preparation of HMS materials by magnetron sputtering method, whose selection of base pressure differs by several orders of magnitude, including $1.7 \times 10^{-3}$ Pa [8], $4.0 \times 10^{-4}$ Pa [9], $6.0 \times 10^{-4}$ Pa [10], $6.3 \times 10^{-4}$ Pa [11], $2.7 \times 10^{-5}$ Pa [12], $10^{-6}$ Pa [13], etc. In general, each parameter has its best value or range. However, there was obviously a great difference in the selection of base pressure for studies of HMS, but the influence of this parameter was ignored.

Oxidation has always been a problem to be considered in the study of active materials such as metals, it occurs during the production, storage and reaction of raw materials. There are different requirements for the oxide content of the sample depending on whether the oxidized substance will affect the expected reaction. According to the experience on the preparations of HMS, manganese oxidation often occurs, at the same time, different phases of HMS are often obtained under the same experimental parameters, which is very puzzling. Therefore, it is necessary to study the effect of oxidation on the preparation of HMS. Besides, in the process of magnetron sputtering, the distance between target and substrate will not be too close due to the factors such as
ignition, which makes the sputtering distance may larger than the mean free path of gas molecules, thus the influence of residual gas in the cavity on the coating process need to be considered. In this paper, by taking the base pressure of magnetron sputtering as variable, and using a natural oxidation high purity manganese target material as raw material, while the other parameters are optimum technology parameter for the preparation of HMS based on the research group’s past experience [12], the research studied the effect of oxidation on preparation of HMS.

2. Experimental

Thin films deposited on P-type Si(111) (resistivity 7–13 Ω cm, purity 99.999%) by high vacuum magnetron sputtering system (model JGP560). The Mn target (diameter 60 mm, thickness 5 mm, label purity 99.95%) for Sputtering, which had been stored in vacuum bag for several years. The substrate Si were decreased by acetone and alcohol for 15 min respectively and then rinsed by deionized water for 15 min before being put into the sputtering chamber. After the substrate was dried, it was fixed in the sample tray and fixed on the sample rack of the sputtering chamber. Close the top cover of the sputtering chamber, and then vacuumed the sputtering chamber, the base pressure was controlled by $6 \times 10^{-3}$, $4 \times 10^{-3}$, $8 \times 10^{-4}$, $5.7 \times 10^{-4}$ and $7 \times 10^{-5}$ Pa, respectively. In order to prevent the influence of accidental factors, the sputtering sequence alternates between low and high vacuum. In all case, the sputtering pressure was 2.0 Pa, the distance between target and substrate is 4.5 cm, the sputtering power was about 110 W, the argon gas flow rate was 20 sccm, the deposition time was 7 min.

After deposition, samples were subsequently annealed at the same time in different ceramic boats under Ar gas ambient in a tubular furnace, to ensure the uniqueness of variables. Before annealing, the whole gas path of tubular furnace was evacuated by vacuum pumps, and then filled the quartz tube with high purity Ar gas. After repeating this operation for 3 times, continue to inject Ar gas, until the pressure in quartz tube was higher than atmospheric pressure, open the exhaust port, in order to prevent reverse suction of external air. The heat treatment temperatures was 700 °C with the heating rate of 6 °C min $^{-1}$. The heat treatment time was 5 h, and then cooled naturally to room temperature.

The phases of synthesized films were analysed by x-ray diffractometer (XRD, PANalytical Empyrean) with CuKα radiation (45 kV, 40 mA). The diffraction patterns were measured in the 0–2θ mode (10–90° 2θ) with a step size of 0.1°, a scan speed of 0.264 s/step, and a wavelength of 1.541 nm. A field emission scanning electron microscopy (FE-SEM, SU8010) was used to examine the microstructure of the films.

3. Results and discussion

3.1. Analysis of reaction materials

XRD pattern of the samples before annealing at base pressure of $7 \times 10^{-3}$ Pa is shown in figure 1. For all cases, the analyses are based on the dates existing in the ICSD Powder Diffraction File [14]. Because the raw materials have not been annealed, there are no reactions between manganese and silicon. Therefore, The main products been detected should be manganese and silicon and their corresponding oxides. The three strong diffraction peaks are observed at $2\theta = 34.75^\circ$, $40.35^\circ$, $58.35^\circ$ can be well corresponding to the pattern (No. 01-077-2363) of MnO. The peak observed at about $56.15^\circ$ could correspond to the strongest peak of MnO$_2$ (No. 00-030-0820) could correspond to this pattern. In addition, the peak at $52.45^\circ$ could be corresponded to one of the three strong peaks of Si (No. 01-079-0613), combined with the XRD pattern of Mg$_2$Si prepared before, there is a peak at the same position which cannot be accurately matched. It shows that the peak is no connection with Mn, therefore, it can be considered that the peak belongs to Si material, which corresponds to the substrate used in the experiment. But there are no matching Mn peak been found. According to the experimental experience of successfully preparing HMS with new target materials, the Mn is impossible been completely oxidized just under this background vacuum degree. Thus, it can be determined that the target was seriously oxidized due to long storage time, and the main product was manganese oxide including MnO and MnO$_2$. The elemental manganese may exist in amorphous or microcrystalline form, so the corresponding peak cannot be detected.

3.2. Effect of base pressure on the crystal structure of Mn$_3$O$_4$

Figure 2 is the XRD pattern of manganese oxide films deposited under different base pressure, then annealed at same time. In order to compare the changes of materials before and after annealing more intuitively, the XRD pattern in figure 1 is also put in the figure. It can be seen that the peaks of MnO$_2$ and Si substrates still correspond to the peaks after annealing, but all the MnO peaks disappear. The results show that MnO participates in the reaction and is completely consumed in the annealing process. The main reaction product after annealing is Mn$_3$O$_4$ (No. 00-001-1127). Mn$_3$O$_4$ has no preferential orientation under this process, and the peak distribution
is uniform. Considering the ratio of oxygen to Mn of Mn$_3$O$_4$ is between MnO and MnO$_2$. Besides, the ceramic tube used for annealing is protected by positive pressure Ar atmosphere after several times of vacuum pumping, so there is no additional source of O$_2$. It shows that Mn$_3$O$_4$ is the product of the reaction between MnO and MnO$_2$, but there may be multiple steps. Before the base pressure reaches $7 \times 10^{-5}$ Pa, no products other than Mn$_3$O$_4$ are produced, which indicates that the process parameters used in these experiment could also be used to prepare Mn$_3$O$_4$.

### 3.3. Effect of base pressure on the crystal structure of MnO$_2$

With the increase of base pressure, in figure 2, the MnO$_2$ peaks present a trend of first increasing and then decreasing. The mean free path during the sputtering process can be calculated according to the following formula:
\[ \lambda = \frac{RT}{\sqrt{2\pi d^2 N_A P}} \]

In this formula: \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( d \) is the diameter of the molecule, \( N_A \) is Avogadro’s constant, \( P \) is the absolute pressure. We can get the mean free path of air molecules is 3.78 mm and that of water molecules is 2.89 mm. They are all obviously smaller than the distance between target and substrate, which proves that the effect of residual gas can not be ignored. Based on this situation, the phenomenon of higher peak value at lower base pressure is considered to be caused by the impurity gases in the tube under lower base pressure. In particular, water vapor and other adsorption particles will affect the trajectory of the particles. When the particles are adsorbed together, the volume of particles increases, thus increasing the probability of collision with other particles. A positive feedback effect is produced, and larger particles are formed when they are finally deposited on the substrate surface. Because these larger particles are relatively independent of each other, they are less restricted in the annealing process, so they are more prone to orientation.

For the initial period of peak increase, because of the increase of base pressure, the particles with adsorption force in the cavity gradually decrease, and then the volume and quantity of atoms deposited on the surface is reduced. As a result, the distribution of particles on the substrate surface becomes relatively sparse, and the independence between particles is stronger, it shows stronger orientation. However, at low base pressure, due to the large number of adherent particles, the particles will be larger and more quantity, which will restrict each other. At the same time, due to the more particles, so there is more chance of contact and even accumulation between particles, which limits the relative independence of particles. Finally, the orientation of the films prepared under lower base pressure is relatively weaker. When the base pressure is higher than \( 4 \times 10^{-3} \) Pa, the residual gas in the chamber decreases obviously, that make the sputtering particles are no longer affected, and the particles deposited on the substrate are more uniform and compact, then the growth of particles is more restricted, so the orientation of materials becomes weaker. Therefore, the MnO2 peak decreases with the increase of base pressure in this period.

On the other side, in the case of lower vacuum, there is residual oxygen in the chamber. The splashed MnO and MnO2 are in the state of tiny particles, and the surface area of the splashed material is increased, that make chance of contact with oxygen increases significantly, which may lead to the oxidation of some MnO to MnO2. Due to its stable properties, MnO2 has no further oxidation occurred. With the increase of base pressure, the effect of oxidation on MnO decreases gradually. This may also be one of the reasons why the MnO2 peak increases significantly at lower base pressure.

When the base pressure reaches \( 7 \times 10^{-5} \) Pa, the MnO2 peak disappears completely. In figure 1, there are MnO2 peaks of the samples not annealed at \( 7 \times 10^{-5} \) Pa, so the disappearance of MnO2 peak after annealing is not due to the complete elimination of MnO2 by increasing the base pressure. The reason of the disappearance is that MnO reacts with MnO2 to produce Mn3O4 during the annealing process, which consumes MnO2. When the base pressure is between \( 5.7 \times 10^{-4} \) Pa and \( 7 \times 10^{-5} \) Pa, MnO2 can be completely consumed in the annealing process. In addition, because the gas is very rare at \( 7 \times 10^{-5} \) Pa, the sputtered films can be considered as unaffected, and the manganese target is oxidized naturally for many years. In this situation, if the oxidation reaction proceeds from Mn to MnO and then to MnO2, the possibility of complete reaction of MnO2 and MnO to produce Mn3O4 with no residual raw materials is very low when the natural oxidation time is uncertain. It is believed that there are other reactions of the residual MnO after completely consumed MnO2.

### 3.4. Effect of base pressure on morphology and stress

Figure 3 is the SEM images of manganese oxide films prepared before annealing under different base pressure. Because the films have not been annealed, the influence of sputtering process on the quality of films can be more directly reflected. It can be observed that the morphology of the films prepared under the base pressure of \( 10^{-3} \) Pa and \( 10^{-4} \) Pa has a great difference, and the particle size changes significantly, showing agglomerated particles. The boundary between the agglomerated particles is clear, which indicates that the agglomerated particles are formed before the deposition on the substrate. If the agglomeration occurs after particles contact with substrate, there will be a large number of continuous boundaries between the particles, because small particles will fill the gap. This is consistent with the previous explanation of the adsorption under low base pressure. It is believes that there is a certain value of the sputtering base pressure between \( 4 \times 10^{-3} \) Pa and \( 8 \times 10^{-4} \) Pa, it is the critical pressure for the positive feedback effect of adsorption and accumulation between the residual gas in the chamber and the splashed particles. From the observation in figure 3(c), it can be found that the morphology of the films obtained by sputtering under higher base pressure, there are some concentration areas of particle distribute, that shows there is still a weak agglomeration phenomenon. Therefore, it can be considered that \( 8 \times 10^{-4} \) Pa is the critical pressure. However, to judge whether the agglomeration is caused by MnO or MnO2 or their mixture, it needs to be further explored by experiments.
Because the raw materials of Mn₃O₄ prepared by this process contain both MnO and MnO₂, the guiding role of this conclusion on the overall process is still adequate.

From the observation in figure 2, it can be found that the Si peak at 10⁻³ Pa has a obvious shift compared with under higher base pressure. In general, the stress may be caused by the lattice mismatch between the film and the substrate. However, the peak shift only occurs in the order of 10⁻³ Pa, and there is no similar phenomenon under other background vacuum levels with the same film structure and compositions, so the peak displacement is not related to the lattice mismatch. Furthermore, the position of other peaks did not change, indicating that there was lattice distortion caused by macro residual stress. Because the peak value is shifted to higher angle, it shows that the residual stress of annealed film is compressive stress. This is because of the change of stress caused by the change of particle size and distribution. By comparing the morphologies in figures 3 and 4, it can be found that the annealing process has an obvious effect on the morphology repair. But the peak shift of XRD is consistent with the time when the particle size changes significantly in figure 3, which is the test data after annealing, it is showed that the residual stress in 10⁻³ Pa sputtered films is not completely eliminated by annealing. This is due to the fact that the particles of the film are larger, and there is more volume after the particles soften and fill the gap in the annealing process, resulting in the mutual extrusion between the original agglomerated particles due to gravity. The annealing time is not enough to release the stress completely, so the final product presents compressive stress. However, this process takes a long time to complete, and it can be considered that the fused agglomerated particles are not affected by external stress before they contact each other, which makes MnO₂ have a preferred orientation. Due to the stronger adsorption and accumulation at 6 × 10⁻³ Pa compared with 4 × 10⁻³ Pa, the contact time between fused agglomerated particles is shortened, that leads to a decrease in the orientation of MnO₂. This is consistent with the previous explanation of MnO₂ orientation.

Table 1 is the particle size statistics of figure 4 by ‘nano measure’ software. Although the mean particle size are the same when the vacuum degree is increased from 6 × 10⁻³ to 4 × 10⁻³ Pa, both the maximum particle size and the minimum particle size increase. Therefore, the particle size increases with the increase of the base pressure, which indicates that the base pressure has a regulatory effect on the grain size in a large range. Under various conditions of base pressure, the main substance is Mn₃O₄, and the main impurity MnO₂ has completely disappeared at 7 × 10⁻⁵ Pa. Therefore, the materials affected by the base pressure should be Mn₃O₄. In figure 3, the morphologies of the films sputtered at 4 × 10⁻³ Pa and 8 × 10⁻⁴ Pa before annealing have little difference compared with those under same vacuum level. However, it can be found that the morphology is affected by the annealing, in figure 4, the sample prepared under 8 × 10⁻⁴ Pa base pressure has obvious holes, and the samples
prepared under \(4 \times 10^{-3}\) Pa have inhomogeneous and slight holes in some regions. This is because the two base pressure parameters are near the critical point where the particle size of sputtered deposition changes dramatically. At this time, both the large and small size of particles are simultaneously exist, which leads to the uneven stress distribution in the annealing process, and finally greatly affects the morphology. Prolonging the annealing time may be beneficial to the stress release, but it is difficult to achieve a balance between the repair effect and annealing time. It is suggested that the range of \(4 \times 10^{-3} - 8 \times 10^{-4}\) Pa should be avoided and appropriate space should be reserved when preparing Mn\(_3\)O\(_4\) by this technology. Additionally, because the sharp change of morphology occurs in the sputtering stage, this vacuum range should be avoided during sputtering thin films when MnO and MnO\(_2\) are contained in the raw material.

### 3.5. Effect of base pressure on preparation of higher manganese silicide

When the background vacuum reaches \(7 \times 10^{-5}\) Pa, in figure 2, a new peak appears which corresponds to the pattern of main peak of Mn\(_{27}\)Si\(_{47}\) (No. 01-073-1312), which belongs to one of the phases of HMS. Because the experimental parameters were originally used to prepare HMS, therefore, the product is in line with the expectation. Mn\(_3\)O\(_4\) and Si exist under different base pressure, which shows that these two substances have no effect on the formation of Mn\(_{27}\)Si\(_{47}\), while the only difference is the presence or absence of MnO\(_2\). This article believes that HMS is obtained by the reaction of MnO and Si, and the results are related to the ratio of MnO to MnO\(_2\). Because MnO reacts with MnO\(_2\) to form Mn\(_3\)O\(_4\), when MnO\(_2\) is present in the results, it indicates that MnO has been totally consumed. So, no MnO reacts with Si to form MnSi, which makes the subsequent
peritectic reaction impossible and prevents the formation of HMS. In addition, because the existence of Mn in the sputtered film cannot be ruled out, if Mn does exist in the reaction raw materials, this situation can prove that the presence of MnO may prevent the reaction of Si and Mn. Therefore, the existence of MnO has no effect on the preparation of higher manganese silicide, but the existence of MnO in raw materials should be avoided. This is consistent with the previous explanation of the complete reaction between MnO2 and MnO.

The original product of this experimental parameter should be Mn11Si19 [12]. Since Mn27Si47 and Mn11Si19 are different phases of HMS, it indicates that the peritectic reaction process, rather than the chemical reaction, is affected, the ratio of MnSi with Si is the main factor affecting the peritectic reaction. Although Mn3O4 does not react with MnSi, its presence hinders the contact between MnSi and Si substrate, thus the ratio of MnSi to Si is affected in other ways, so the products with different phases are obtained. In this process, Mn3O4 actually acts as a buffer layer, which indicates that the study of adding buffer layer may play an important role in controlling the different phases of HMS.

4. Conclusions

1. The experimental parameters can be used to prepare Mn3O4 on silicon substrate from MnO and MnO2, new impurity phase won’t be introduced before MnO2 has been completely consumed.

2. Under the experimental parameters, the growth of MnO2 has a preferred orientation. The effect of base pressure on the orientation of MnO2 is obvious. With the increase of base pressure, the orientation of MnO2 increases first and then decreases. This is related to the distribution of particles, and the stronger the independence of particles, the stronger the preferred orientation.

3. There is a great difference in the morphology of MnO and MnO2 films obtained by sputtering at the vacuum level of 10−3 Pa and 10−4 Pa, which is due to the positive feedback effect of adsorption and accumulation between the residual adsorbed gas and the splashed particles. The critical pressure of the positive feedback effect is 8 × 10−4 Pa. The sputtering of MnO and MnO2 mixture in the range of 4 × 10−3–8 × 10−4 Pa should be avoided.

4. When the sputtering base pressure is in 10−3 Pa magnitude, the XRD peak value of the annealed films are shifted to a higher angle obviously, which is caused by lattice distortion caused by the macroscopic residual compressive stress caused by the abrupt change of morphology. The residual compressive stress is produced after the preferred orientation growth of MnO2.

5. The impurities introduced by natural oxidation of Mn target are MnO and MnO2. MnO impurities do not affect the formation of higher manganese silicide, and even can be used to produce HMS by reaction of MnO and Si. However, if MnO is further oxidized to MnO2, Mn3O4 impurity will be introduced in the process of preparing HMS, and the output of HMS will be reduced because of consumption of MnO. The introduction of MnO2 should be avoided in the preparation of HMS.

6. Mn3O4 and Si do not react with HMS, but the existence of Mn3O4 will affect the peritectic reaction process of HMS, and make the obtained HMS phase change. Mn3O4 acts as a buffer layer in this process. The addition of buffer layer may play an important role in controlling the phase of HMS.

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