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Study on Process Parameters of Magnetron Sputtering Titanium Coating in Deep Porous Structures

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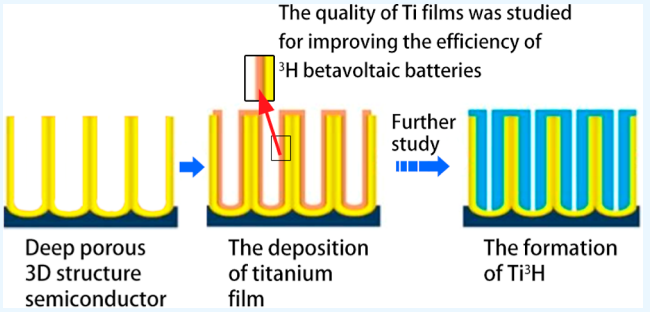
ABSTRACT: In order to improve the energy conversion efficiency and power density of the tritium-powered betavoltaic battery, titanium was deposited on the inner surface of the deep porous three-dimensional structure semiconductor as a tritium absorption material. Therefore, magnetron sputtering technology was used to explore the parameters of titanium coating on the inner surface of a deep porous semiconductor. First, the effects of argon pressure and sputtering power on the properties of titanium films were studied. The properties of the titanium films were characterized by a scanning electron microscope and an atomic force microscope. The optimized sputtering parameters were obtained as follows: argon pressure of 0.5 Pa and sputtering power of 80 W. Based on this parameter, the background vacuum and coating angle were changed, and the titanium film was coated in the deep porous structure. Energy dispersive spectrometry line scan and surface scan were used to analyze the coating results, which showed that these two parameters directly affected the content of titanium in the channel, and the area of titanium in the channel structure accounted for more than 50% under each test condition.



1. INTRODUCTION

Titanium metal is the single metal material with the highest density of hydrogen absorption (and hydrogen isotopes) discovered so far, and the tritiated titanium formed by titanium absorbing the isotope tritium of hydrogen has an extremely low room-temperature equilibrium pressure. Therefore, titanium is commonly used as a tritium storage material.[1] Titanium (chemical symbol Ti) is an IV secondary metal element with an atomic number of 22 and an atomic mass of 47.90. Metal Ti can adsorb and store tritium in solid form at a pressure of about 1.33×10^{-5} Pa, forming metal tritides with high tritium storage density and fast tritium absorption speed. The equilibrium dissociation and decompression at room temperature are about 10^{-5} Pa.[2] Therefore, titanium metal is a suitable material for long-term tritium storage and will not cause tritium leakage.

Titanium, as a cheap tritium storage material with good performance, is often used in various radioactive source products using tritium as a radioisotope source, such as those betavoltaic batteries that generate electrical energy through the betavoltaic effect by using beta particles released from tritium. Particles (usually beta particles) interact with semiconductor materials to generate electron-hole pairs, which are separated and move in a directional direction under the action of the built-in electric field, and the external load can generate current.[3] The traditional tritium betavoltaic battery adopts a planar semiconductor structure,[4,5] but the planar semiconductor has a low collection efficiency of energy-carrying particles emitted by radioisotopes, resulting in relatively poor energy conversion efficiency and other defects.[6] To solve this problem, researchers have proposed a variety of tritium betavoltaic batteries based on three-dimensional structure semiconductors,[6−9] including deep-porous type, shallow-porous type, and grooved devices, to increase the surface area of semiconductor devices with a certain volume, and correspondingly improve the energy conversion efficiency and output power density of the battery. Theoretically, compared with deep porous devices, shallow porous and grooved devices have limited effect on improving the contact area of radioactive sources and the utilization rate of decay particles, so deep porous devices may be more potential device configurations in the future.[10]

In the research so far, tritium is directly loaded in gaseous form (tritium gas) by tritium betavoltaic cells with deep porous devices as energy conversion units,[6] which is not conducive to the practical application of tritium betavoltaic cells in the

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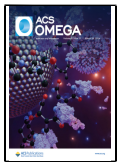

Table 1. Experimental Parameter Conditions and Obtained Film Thickness

test number	p_0/Pa	coating time/min	factor		thickness/nm
			argon pressure/Pa	sputtering power/W	
1	1.1×10^{-3}	30	0.5	80	820
2				100	1030
3				120	1210
4			1.0	80	860
5				100	960
6				120	1150
7			1.5	80	830
8				100	1050
9				120	1170

future. Therefore, it is necessary to obtain a Ti coating with uniform distribution in the deep porous structure.

Magnetron sputtering technology has the advantages of high deposition rate, low substrate temperature,[11] and good film substrate adhesion.[12] It is widely used in the study of preparing titanium films on the surface of single-crystal silicon and glass.[13−16] However, there are few reports on the preparation of Ti films in deep porous device structures. In this article, Ti films were deposited on the surface of deep porous single-crystal silicon semiconductor devices by magnetron sputtering technology. A series of titanium coatings were obtained under different parameters by changing the sputtering power, argon pressure, and other parameters. The morphology, roughness, and other properties of the obtained titanium coatings were characterized by a step tester, scanning electron microscope (SEM), energy dispersive spectrometer (EDS), and atomic force microscope (AFM), and the effect of parameter changes on the properties of titanium films was studied to explore the process of obtaining uniform titanium film on the surface of deep porous devices.

2. EXPERIMENTAL EQUIPMENT AND MATERIALS

The coating process is carried out on the DST3 magnetron sputtering coater. The sample for coating is ⟨100⟩ crystal orientation single-crystal silicon wafer, with a size of 10 mm × 10 mm × 0.6 mm, and the deep porous ⟨100⟩ crystal orientation single-crystal silicon wafer, with the size of 12 mm × 12 mm × 0.5 mm, the size of the perforated part is 10 mm × 10 mm, the hole parameter is Φ6 μm × 30 μm, and the hole spacing is 4 μm. The sputtering target is made of titanium, with a purity of 99.999%, and a size of Φ50.5 mm × 5 mm. The working gas is high-purity argon with a purity of 99.99%.

3. EXPERIMENTAL METHOD

3.1. Preparation of Titanium Thin Films. The coating process is as follows: we should wash the sample with acetone, anhydrous ethanol, and deionized water in the ultrasonic cleaning machine for 1 min, take it out and blow dry the surface with a bulb syringe, adhere the sample to the sample tray of the coating machine with double-sided high-temperature tape, and adhere a small piece of single-sided high-temperature tape on the sample surface as a mask for measuring the thickness of titanium film after coating. For the deep porous sample, we should adhere it to a shim inclined at a certain angle and then adhere the shim to the sample table. We should close the sealing cover of the sputtering chamber, start the mechanical pump to pump the pressure inside the sputtering chamber below 5 Pa, and then start the molecular pump to pump the vacuum inside the sputtering chamber to the required background vacuum level. We should inject high-purity argon gas and maintain a flow rate of 80 sccm for 5 min to blow the surface of the sample; at the same time, we should adjust the voltage and current of the DC power supply to achieve the preset sputtering power. We should then turn on the DC power supply and maintain it for 10 min for presputtering to remove the impurities from the surface of the target. Then, the argon flow was adjusted until the pressure gauge showed the required working pressure. We should set the coating time to 30 min and open the target baffle to start sputtering. During the coating process, the sample disk was rotated at 10 rpm to improve the uniformity of the obtained titanium film. After reaching the set time, the coating machine will automatically turn off the DC power supply, and then we should keep the coated sample in the sputtering chamber for cooling in a vacuum for 5 h and take out the sample.

3.2. Characterization Method. Bruker Dimension Icon AFM was used to observe the two-dimensional morphology of the coating surface, and the average roughness was characterized. The scanning range was 5 μm × 5 μm, and the scanning rate was 1 Hz. A diamond knife was used to draw a center line on the back of the sample and a brittle fracture to obtain the cross-section of the sample. Zeiss GeminiSEM 560 SEM was used to characterize the surface and cross-sectional morphology of the samples, and the voltage was 5−15 kV. The EDS attached to the SEM was used to conduct line scan and surface scan analysis on the cross-section to characterize the changes in element composition and content on the cross-section. A Bruker DektakXT step meter was used to measure the thickness of the titanium film. The scanning length was 2000 μm, and the average value was obtained after measuring five times.

4. RESULTS AND DISCUSSION

4.1. Effect of Coating Parameters on the Properties of Titanium Films. The experimental conditions and obtained film thickness for nine sets of samples are shown in Table 1. The AFM average roughness results of samples numbered 1, 2, 3, 5, and 8 are shown in Table 2. According to the data in Tables 1 and 2, it can be seen that under fixed argon pressure and coating time, increasing the sputtering power leads to an increase in the thickness of the obtained titanium film, which is basically linearly related to the increase in sputtering power. The roughness of the surface morphology of titanium film increases first and then decreases with the increase in sputtering power, but the effect is not significant. The data in Table 2 are summarized in Figure 1; it can be seen that the factor that has the greatest impact on the average roughness of the titanium coating on the sample is argon

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Table 2. Average Roughness of Titanium Film Coating on Samples

test number	position/nm			average result/nm
	1	2	3	
1	3.66	3.80	3.97	3.81
2	3.90	3.98	3.87	3.92
3	3.15	3.18	3.22	3.18
5	15.40	15.90	15.50	15.60
8	25.50	25.80	24.40	25.23

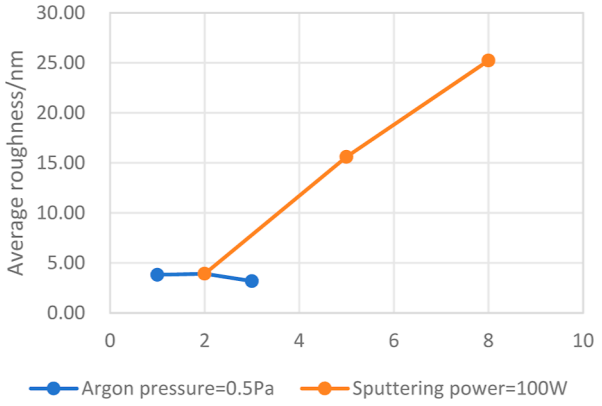

Figure 1. Average roughness variation trend of titanium films.

pressure. Under the condition of determined sputtering power, as the argon pressure increases, the roughness of the titanium film also increases. The average roughness at 1.5 Pa is 6.4 times that at 0.5 Pa.

Figure 2 shows the height maps of samples 1, 2, 3, 5, and 8. From the figure, it can be observed that under low argon pressure conditions, the film tends to grow in an island shape, and the distribution of island-shaped particles on the surface of the titanium film is generally more uniform. In addition, under the same argon pressure, increasing the sputtering power results in a decrease in the density of the island-like structure, and the roughness of the titanium film shows a trend of first increasing and then decreasing. According to the principle of magnetron sputtering growth of thin films, when the deposition thickness is small, many small islands are formed on the substrate surface, and there is a certain distance between the islands. As the thickness of the film increases, the small islands tend to grow longitudinally, and agglomeration occurs between the islands, gradually forming more uniform grains.[17] Besides, under the same sputtering power conditions, increasing the argon pressure resulted in a significant increase in the surface roughness of the titanium film. This is because, as the pressure of argon gas increases, the probability of collision between argon atoms and electrons increases, leading to energy loss. Finally, the energy of particles that interact with the target material decreases, causing poor diffusion of target atoms on the substrate and an increase in roughness.

Figure 3 shows SEM pictures of the surface and cross-section of samples 4, 6, 7, and 9. The large image shows the cross-section, and the small image shows the surface. From the graph, it can be seen that under a constant argon pressure, increasing the sputtering power results in an increase in the average grain size of the titanium film; under a certain sputtering power, increasing the argon pressure results in a decrease in the average grain size of the obtained titanium film. In addition, when the sputtering power is increased, it can be observed from the cross-sectional view that the thin film tends to generate columnar structures. This is because at high sputtering power, the energy of ionized argon ions bombarding the target material increases, resulting in an increase in the kinetic energy of the splashed target atoms, which can migrate

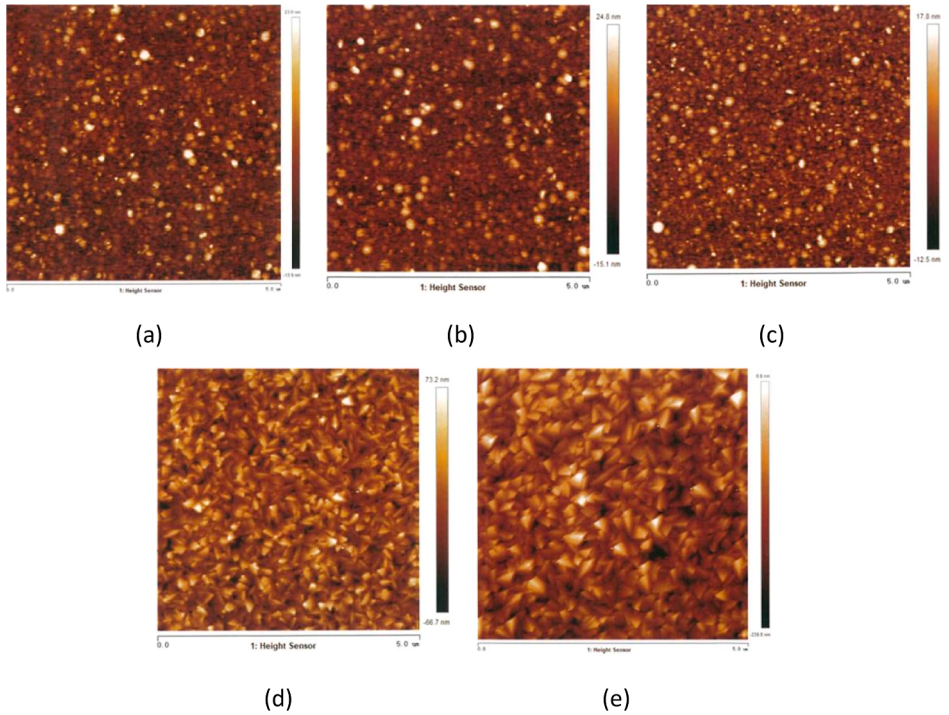

Figure 2. Height maps of titanium films obtained with different sputtering parameters: (a) sample no. 1; (b) sample no. 2; (c) sample no. 3; (d) sample no. 4; and (e) sample no. 5.

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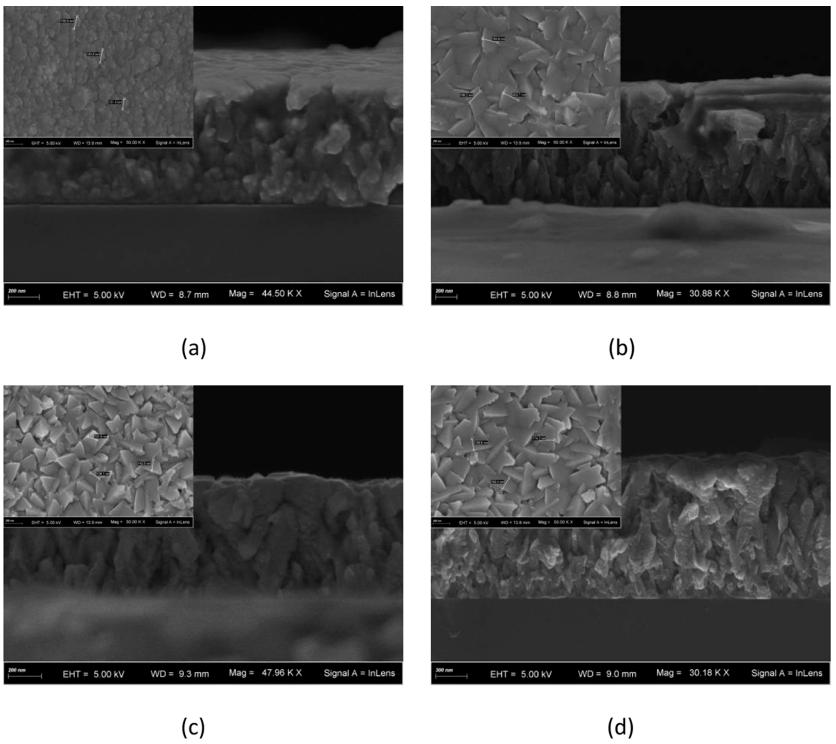

Figure 3. SEM images of the surface and cross-section of titanium thin films obtained with different sputtering parameters: (a) sample no. 4; (b) sample no. 6; (c) sample no. 7; and (d) sample no. 9.

on the substrate surface and occupy an available equilibrium position on the formed titanium film crystal lattice, leading to the formation of a columnar structure in the film.[18] However, the columnar structure will reduce the density of titanium films, leading to the unstable performance of titanium films.[19] To avoid the formation of columnar structures as much as possible, lower argon pressure and sputtering power should be used as the process parameters for sputtering. Based on the above experimental results, a titanium film will be deposited on the surface of deep porous devices using an argon pressure of 0.5 Pa and a sputtering power of 80 W in the future.

4.2. Effect of Changing Coating Conditions on the Distribution of Titanium Thin Films on the Surface of Deep Porous Devices. After the determination of the sputtering power and argon pressure, a titanium thin film is deposited on the inner surface of the holes of deep porous semiconductor devices by changing the background vacuum degree of the sputtering chamber and the tilt angle of the sample. Table 3 shows the parameters for conducting the experiment.

We should select one group of samples with the same background vacuum degree but different inclination angles and one group of samples with the same inclination angle but different background vacuum degrees. We should compare the EDS surface scanning results, as shown in Figure 4. The red color in the figure represents the Si substrate signal, and the green color represents the Ti signal. From the figure, it can be seen that while maintaining the same background vacuum degree and changing the coating angle, titanium can be deposited on the sidewalls of the holes. The deposition of the titanium film is concentrated in the upper half of the holes, and there is also a small amount of titanium deposition at the bottom of the holes. Under a certain tilt angle, increasing the background vacuum degree results in a trend of decreasing and

Table 3. Test Parameters for Titanium Coating in Deep Porous Devices

test number	factor		argon pressure/Pa	sputtering power/W	coating time/min
	p_0/Pa	coating angle/°			
TD-1	9.7×10^{-4}	8.6	0.5	80	30
TD-2		9.6			
TD-3		10.6			
TD-4	8.3×10^{-4}	8.6			
TD-5		9.6			
TD-6		10.6			
TD-7	6.9×10^{-4}	8.6			
TD-8		9.6			
TD-9		10.6			

then increasing the distribution of Ti on the sidewall of the hole. This indicates that an increase in background vacuum does not necessarily lead to an increase in titanium deposition on the sidewalls, but rather, there exists an optimal background vacuum to achieve optimal deposition results for titanium. By adjusting the vacuum degree and tilt angle, the distribution of titanium thin films can be controlled. In addition, according to the proportion of the titanium element signal to pore area, it can be seen that the distribution of Ti in the pores exceeds 50% under each condition.

Two holes from each SEM result were selected, and line scanning from the inlet to the bottom of the holes. We should correspond the Ti signal distribution of the scanning results to the scanning line, and the result obtained is shown in Figure 5. From the figure, it can be seen that for all samples, as the depth of the pore increases, the content of titanium on the sidewall gradually decreases. The distribution of the Ti element is basically not detected in the later part of the pore, while the

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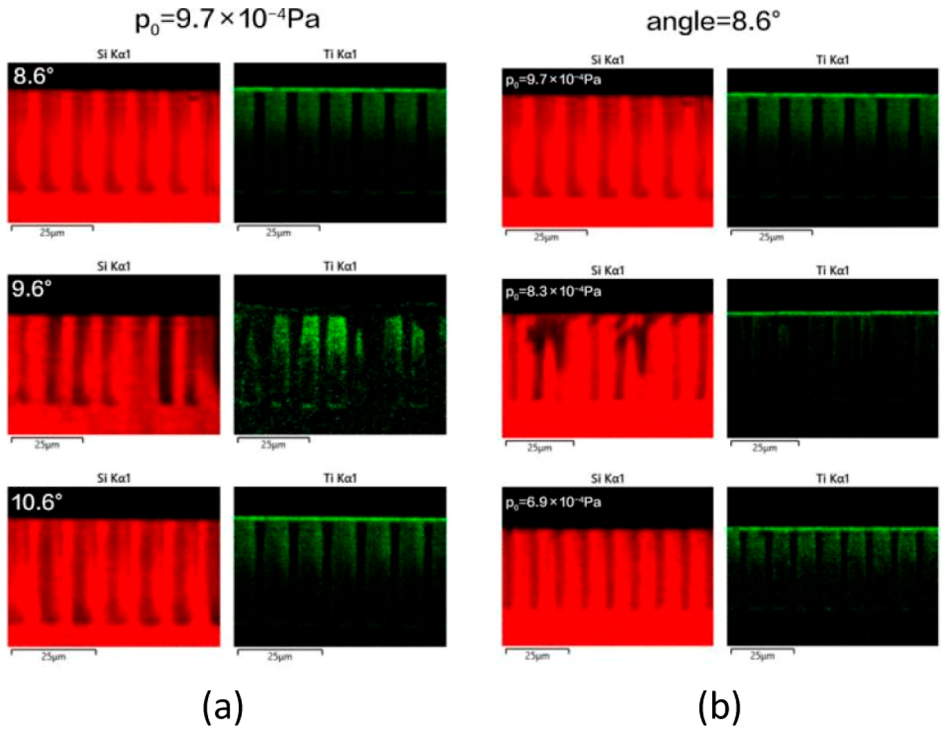

Figure 4. EDS surface scanning results of titanium coating under different initial conditions: (a) p_0 = 9.7 × 10^{-4} Pa with different coating angles and (b) coating angle = 8.6° with different background pressures.

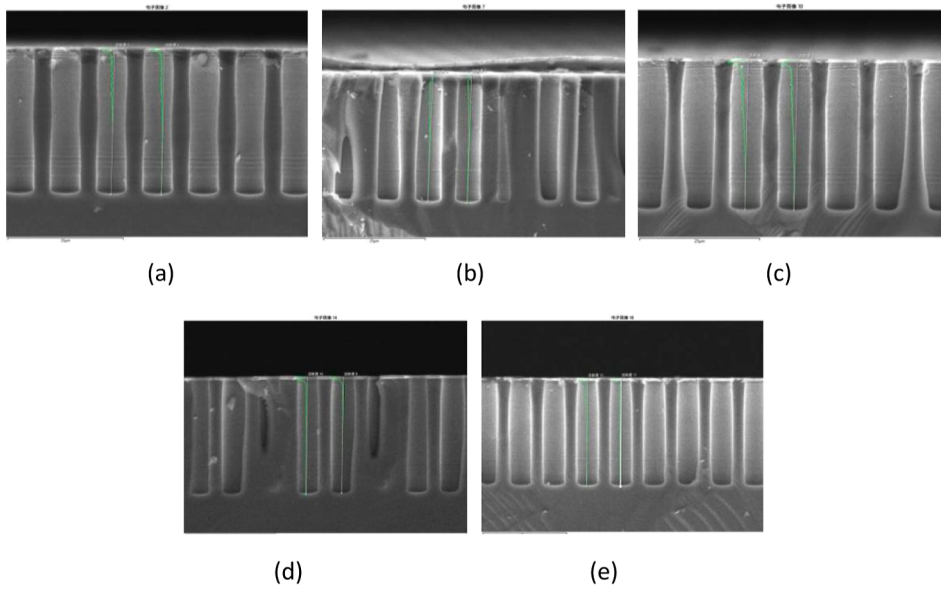

Figure 5. EDS line scan results of titanium coating under different initial conditions (figures a−e show samples TD-1, TD-2, TD-3, TD-4, and TD-7 in sequence).

distribution of Ti at the bottom of the pore slightly increases. Compared with the titanium film obtained by changing the coating angle, the titanium film obtained by changing the background vacuum degree shows a more significant change in content at the same depth position, indicating that the change in background vacuum degree has a direct impact on the deposition of the titanium film. The change in background vacuum degree results in different degrees of argon gas entering the pores during the presputtering stage and thus affects the distribution of target atoms in the pores during the sputtering stage.

The two sets of line scan results for each channel are summarized in Table 4. From the data in the table, it can be seen that as the inclination angle increases, the average distribution of Ti in the pores first decreases and then increases. When the inclination angle is 10.6°, there is the most titanium distribution in the holes. In addition, different coating angles and background vacuum degrees directly affect the average titanium content in deep porous structures. Further exploration of parameters to further increase the titanium content is needed in subsequent research.

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Table 4. Average Titanium Content in Deep Porous Structures

test number	position/wt %		average result/wt %
	1	2	
TD-1	11.4	11.4	11.4
TD-2	8.3	8.0	8.2
TD-3	12.0	13.8	12.9
TD-4	6.5	5.3	5.9
TD-7	8.5	8.2	8.4

4.3. Simulation of Radiation Source Thickness and Energy Deposition. Using the Monte Carlo simulation software MCNP, the energy deposition and deposition ratio of incident particles with different radiation source thicknesses in devices based on Ti^3H radiation sources were simulated, as shown in Figure 6.

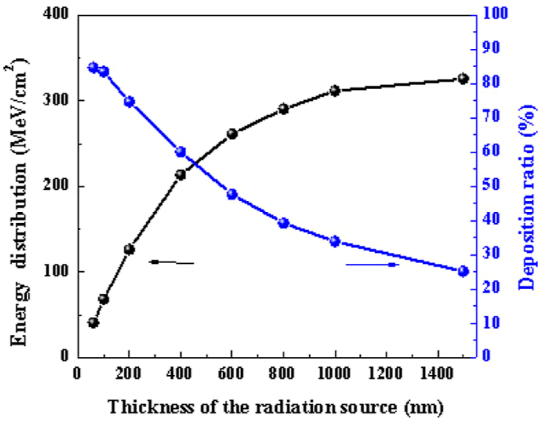

Figure 6. Energy deposition and deposition ratio of incident particles with different radiation source thicknesses based on Ti^3H.

From the figure, it can be seen that the energy deposition rate is at its maximum when the thickness of the radiation source is 100 nm and decreases as the thickness increases to 1500 nm. Therefore, the thickness of the titanium film in the holes of the deep porous structure is most suitable at 100 nm.

5. CONCLUSIONS

(1) When conditions such as argon pressure and coating time are constant, there is a linear relationship between the increase in film thickness and the increase in sputtering power. The factor that has the greatest impact on the surface roughness of titanium thin films is argon pressure. When the argon pressure increases from 0.5 to 1.5 Pa, the average surface roughness of titanium thin films increases by 6.4 times.

(2) Titanium thin films with a dense internal structure and low surface roughness can be obtained by optimizing sputtering process parameters. The optimized process parameters are a sputtering power of 80 W and an argon pressure of 0.5 Pa.

(3) By changing the background vacuum degree and coating angle, titanium thin films with an area ratio of over 50% can be obtained in deep porous semiconductor structures. The titanium content inside the pore is directly affected by two parameters: inclination angle and vacuum degree.

(4) When the thickness of the radiation source (the thickness of the titanium film in the hole) is 100 nm, it has the maximum energy deposition rate.

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Notes

The authors declare no competing financial interest.

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