Effect of annealing process on microstructure and electrical properties of Ni films

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Abstract. By DC magnetron sputtering, the Ni films of 600 nm thickness were successfully deposited on BF33 glass substrates. Then annealing at different temperature from 150 to 450°C and different holding time from 3 to 6 hours under vacuum conditions using bonding machine. The surface morphology and structure of Ni films were analyzed by scanning electron microscopy(SEM), films surface roughness and resistivity were investigated by atomic force microscope(AFM) and four-probe tester respectively. The results show that the annealing process contributes to the refinement of the grains. And the films roughness reaches the best level at the annealing temperature of 300 °C and the roughness data with holding time of 6h is 0.678 nm. Above all, As the annealing temperature increases, the films resistivity decreases significantly. The surface roughness decreases and the resistivity gradually decreases.

1. Introduction

Ni films resistor is a new type of temperature measuring element researched in recent years. It has large temperature coefficient of resistance, low melting point, easy film formation and low price. It has been widely used in various temperature sensors and thermal flow sensors. In addition, the nano-Ni film can be deposited by using a flexible polymer material as a substrate to prepare an ideal polymer materials for developing electromagnetic wave shielding, fiber sensors, solar panel, and so on[1-2].

The film prepared by magnetron sputtering has uniform film structure, compactness and good performance, and the film adheres firmly to the substrate, and has obvious advantages in applications such as conduction, antistatic, radiation protection and electromagnetic shielding. Since the surface morphology of the metal film is very important in the fabrication of some film resistors, it is generally believed that when the thickness of the film can be compared with the mean free path of the electron, the effect of the surface morphology on the resistivity of the metal films has a size effect, but when the film is very thick, the effect is not obvious[3-5]. The surface morphology of the film directly affects its performance. In addition to the macroscopic properties of film thickness and roughness, the microscopic morphology of the film, such as grain size, voids and cracks, and film structure, can better reflect the quality of the film. The effects of annealing temperature and annealing time on the surface morphology, film resistivity and surface roughness of sputtered Ni films were investigated.

In this paper, the Ni films was prepared by DC magnetron sputtering. The film sample was annealed in a vacuum environment of the bonding machine. Different annealing temperatures and holding times were selected for the annealing process. The surface morphology, film resistivity and surface roughness of the Ni films were tested by scanning electron microscope(SEM), atomic force microscope(AFM) and four-probe tester. Then the optimum annealing conditions were obtained.
2. Experiment Procedure

2.1. Sample preparation
In this experiment, the Ni films was prepared by magnetron sputtering. In order to reduce the thermal stress caused by the mismatch of thermal expansion coefficient between the substrate and the film, a BF33 glass with a thermal expansion coefficient close to the substrate material was selected, and a high purity nickel target was used (99.99%). The distance between the target and substrate is 63mm, the sputtering gas is high purity argon (argon purity is 5N), the sputtering pressure is 3*10^{-3}mbar. After wet cleaning process, the substrate should be kept horizontal. Before sputtering, a Pre-sputtering process for 2 min should be done to remove contaminants on the surface of the target, a negative bias is used to enhance the bonding strength between the film and the substrate, and the thickness of the sputtered Ni films is controlled to be about 600 nm.

2.2. Annealing experiment
The prepared films samples were subjected to in a vacuum environment using the bonding machine with the vacuum of 10^{-5} mbar. The experiment is divided into multiple groups. The first group of annealing temperature is set to 150, 200, 250, 300, 350, 400, 450°C. The second group is set to same annealing temperature, but with different holding annealing time of 3, 4, 5, 6h respectively. The principle of the annealing treatment in this experiment is that the particles are re-obtained by thermal annealing to perform grain reconstruction. The grain size and spacing of the film directly affect the temperature coefficient of the film. The annealed experimental samples were tested by SEM, AFM and four-probe tester.

3. Results and Discussion

3.1. Study on Surface Morphology of Ni Films
The film samples before and after annealing were observed by SEM, and the surface morphology of Ni films at different annealing temperatures was taken. From Figure 1(a) we can see before annealing that the Ni films consists of nearly regular block particles, the particle size and distribution are relatively uniform, and the gap is small, so this show that the Ni films belongs to a dense films. Figure 1(b)-(f) shows after different annealing temperature processing that the surface morphology of Ni films. It was found that the films was better than before annealing, and there were no defects such as cracks and voids. It proves that the slow annealing process contributes to the refinement of the grains, resulting in a reduction in the film gap and a more compact structure. Figure 1(f) is the morphology of Ni films in the case of rapid annealing at 450 °C, because rapid annealing accelerates the agglomeration of crystal grains, so this annealing condition resulting in larger grain size, poor compactness of the structure, and cracking in some film regions.
3.2. Study on Surface Roughness of Ni Films

3.2.1. Effect of annealing temperature on roughness. Figure 2 shows the roughness data at different annealing temperatures. The results show that as the annealing temperature increases, the surface roughness decreases first and then increases. The reason is that as the annealing temperature increases, the grain size increases, and after the atoms on the surface of the film gain energy, they migrate from the high potential point to the low potential point, and the defects such as film voids, dislocations, and vacancies are reduced. So the surface is smoother. At the annealing temperature of 300 °C, the atoms get enough energy to fully migrate, at which point the roughness reaches the best level[6].
3.2.2. Effect of annealing time on roughness. Figure 3 shows the roughness data at different annealing holding time. From the figure we can see that the surface roughness continued to decrease with the increase of annealing time. The roughness data with holding time of 6h is 0.678 nm. Figure 4 are the AFM image of the Ni films taken before and after annealing. It can be seen that the zigzag surface of the magnetron sputtered Ni films has a high and low undulating state distribution, which is obviously superior to the undulation state before annealing. It indicating that the annealing process helps to improve the surface morphology, thereby reducing the surface roughness of the film to some extent.
3.2.3. Effect of annealing on film resistivity. According to the electrical characteristics of the sheet resistance, it is generally composed of two parts[7-9]: one part is the resistance generated by the transmission of electrons between the crystal grains, and the other part is the electric resistance generated by the electrons transmitting inside the crystal grains. It is assumed that the inside of the grain is a continuous film transmission, and between the grains is activated tunneling. Resistivity between grains:

\[
\rho_T = \frac{4}{3} \cdot \frac{r}{b^2} \cdot \frac{1}{e} \cdot \exp\left(\frac{E_s}{kT}\right) \cdot \frac{4\pi b}{\sqrt{2m(W-E_k)}}
\]

(1)

In formula (1), \(\rho_T\) is the resistivity between grains, \(E_s\) is the surface activation energy, \(k\) is the Boltzmann constant, \(T\) is the temperature, \(r\) is the grain radius, \(W\) is the tunnel barrier, and \(b\) is the grain. The distance between \(E_k\) is the electron kinetic energy and \(h\) is the Planck constant. Internal resistivity of the grain:

\[
\rho_n = \frac{C}{4\theta_D} \cdot \frac{4\lambda}{3d \ln(\lambda/d)} \quad (d \ll \lambda)
\]

(2)

In the formula (2), \(\rho_n\) is the resistivity between the crystal grains, \(\theta_D\) is the Debye temperature, \(C\) is a constant, \(T\) is the temperature, \(\lambda\) is the electron mean free path, and \(d\) is the film thickness.

It can be seen from the formulas (1) and (2) that the structure, size and spacing between the inside and the grains are different; the resistivity is also different. According to the electrical properties of the film resistor, the resistance increases with the increase of temperature due to the electron scattering inside the grain, and it has a positive temperature coefficient. The electrons are tunneled between the crystal grains, and the resistivity decreases with temperature and is negative coefficient. The final temperature coefficient of the sheet resistance is the result of competition between these two trends.

The resistance of the Ni films is an important parameter in the sensor design. In this paper, the sheet resistance \(R_s\) of the Ni films is measured by a Four-probe tester, and the resistivity of the sputtered Ni films is calculated according to the formula (3). Where \(\rho\) is the film resistivity and \(d\) is the film thickness, and the same film thickness is obtained by controlling the process parameters.

\[
\rho = R_s \cdot d
\]

(3)

![Figure 5. Film resistivity vs temperature.](image1)

![Figure 6. Film resistivity vs surface roughness.](image2)

The annealed samples was then tested. The annealing temperatures were set to 150, 200, 300, 350, 400, and 450 °C respectively. Figure 5 shows the resistivity changes with the annealing temperature changes. From the figure it can seen that the annealing temperature and the resistivity are basically linear. As the annealing temperature increases, the resistivity of the Ni films decreases significantly. Because the metal films is annealed, the higher annealing temperature causes the fine particles in the film to merge into larger grains, the grain size increases, the intergranular area decreases, the degree of crystallization of the film increases, and the crystallization defect decreases. So the internal stress in the
film is reduced, the grain boundary and surface scattering effects was weakened, the scattering effect of the carrier is weakened, the mobility is increased, the resistivity of the film is decreased, then the electrical conductivity is improved.

Figure 6 shows that effect between resistivity and surface roughness of Ni films. As shown, as the surface roughness increases, the resistivity of the film gradually increases. This is related to the growth structure of the Ni films. The magnetron sputtered Ni films grows in a columnar crystal structure, and the particle size is uneven in the direction perpendicular to the surface of the film. The particles of different heights in the longitudinal direction and different sizes in the lateral direction which result in different film surfaces roughness, which affects the transport of electrons in the film, resulting in changes in film resistivity.

4. Conclusions
The Ni films of 600 nm was successfully prepared by magnetron sputtering. The effects of annealing temperature and annealing time on the surface morphology, film resistivity and surface roughness were investigated. The results show that the annealing process contributes to the grain refinement. The Ni films after annealing process is better than before annealing, and there are no defects such as cracks and voids. The grain size increases, the film gap decreases, and the structure is more compact. As the annealing time is lengthened, the surface roughness of the film continues to decrease. When the annealing temperature is 300 °C, the atom obtains sufficient energy to fully migrate. At this time, the roughness data at 6 h of the holding time is 0.678 nm, and the roughness reaches the best level. In addition, the study found that the annealing temperature and resistivity are basically linear. As the annealing temperature increases, the resistivity of Ni films decreases significantly. As the surface roughness increases, the resistivity of the film gradually increases.

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6. References
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