Spark plasma sintering of W-10Ti alloys: microstructure, properties and grain growth kinetics

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Abstract

The microstructure, properties and grain growth kinetics of W-10 wt. % Ti alloys prepared by spark plasma sintering (SPS) method at the temperatures from 1400 to 1700 °C, with the dwelling time from 0 to 30 min and a constant axial pressure of 30 MPa were investigated. The sintered W-10Ti alloys only contained a dominant β-W(Ti) phase and a fractional β-Ti(W) phase. The content of Ti-rich phase declined with the rise of sintering temperatures. In addition, the higher the sintering temperature, the higher the alloy density. When the sintering temperature was constant, the alloy density first increased and then decreased with the increasing dwelling time, and reached the maximum at 15 min. With the increase of the sintering temperature and dwelling time, the thermal conductivity first decreased, then flattened or slightly increased. At low temperatures (1400 °C–1500 °C), the grain growth was not obvious, but at high temperatures (1600 °C–1700 °C), the grain grew rapidly. The grain growth exponent of W-10Ti alloys was found to be \( n = 2 \), suggesting grain boundary diffusion controlled grain growth in the alloys. Activation energy for grain growth was calculated as 49.21–61.46 kJ mol\(^{-1}\).

1. Introduction

With the rapid development of electronic technology, integrated circuit chips, as the core of information products, have higher and higher requirements in terms of integration level, and the number of transistor devices on per unit area silicon (Si) substrate increases exponentially, which requires higher performance of the interconnect metal and barrier film [1–3]. In the manufacture of modern semiconductor devices, Al, Cu and Ag are primarily used as metal interconnection materials. However, Al, Cu and Ag will diffuse into the dielectric layer of Si or SiO\(_2\), to form metal silicates with high resistance, which will substantially reduce the current density in the wires and lead to complete failure of the electrical performance of the entire wiring system. Therefore, a layer of diffusion barrier should be added between the wiring and Si or SiO\(_2\). W-Ti alloy target with Ti mass fraction of 10\%–30\% is prepared by sputtering method as Cu wiring diffusion barrier layer, which cannot only block Cu diffusion but also effectively improve the bonding strength of Cu film and matrix (Si and SiO\(_2\), etc), serving as the leading materials of Cu wiring diffusion barrier layer [4–7]. However, particle contamination on the surface of W-Ti films via magnetron sputtering usually affects the film’s resistance, which is directly related to the characteristics of the target. The low density and purity, eutectoid structure and the Ti-rich phase of W-Ti target are considered as the main pollution sources [8–10]. Due to the enormous difference of the melting point between W (3380 °C) and Ti (1668 °C), W-Ti alloy is usually prepared by powder metallurgy (PM) methods such as hot pressing (HP), hot isostatic pressing (HIP), and thermal explosion consolidation combustion synthesis (CSA-HEC) [11–13]. Therefore, to address these issues, the properties of W-Ti alloy are improved by the treatment and selection of raw material powders, the preparation methods, the cooling condition and the later heat treatment in the past researches [14–19].

SPS technology has been gradually applied in the field of target preparation due to its characteristics such as fast heating rate, short sintering time and low sintering temperature, which can obtain high density of sintered...
body and restrain grain growth \cite{20, 21}. Luo et al \cite{22} successfully prepared W-10Ti alloy with relative density of 96.1\% by SPS using ball-milled W-Ti powders at sintering temperature of 1300 °C and dwelling time of 10 min with the pressure of 30 MPa, and made a characterization of its properties and microstructure. Huang et al \cite{23} mainly demonstrated the densification mechanism of W-10Ti at low temperatures (900 °C–1300 °C) and microstructure evolution with dwelling time of 6 min and fixed pressure of 30 MPa. However, the influence of different dwelling time and sintering temperatures on the microstructure and properties of W-10Ti alloy and the grain growth behavior at high temperature has not been studied systematically.

In this research, the W-10Ti alloy was prepared via SPS method under temperatures ranges of 1400 to 1700 °C with dwelling time ranges of 0 to 30 min and constant pressure of 30 MPa. The objective is to investigate the effects of the dwelling time and sintering temperatures of the SPS method on microstructure, properties and grain growth behavior of W-10Ti alloys.

2. Experiment

2.1. Materials and process

The high purity W-10Ti powders (purity > 99.995\%) with an average particle size of 8.42 μm (mixed by ~3 μm tungsten and ~20 μm titanium particles) were adopted as the raw powders in this study.

The mixed powders were put into a 20 mm inner diameter graphite mold which had been lined with two 0.2 mm thickness graphite foil at both ends and a fitted size graphitic sheet between the die and powder bed previously for easy removal. Besides, the die was encompassed by a graphite felt sized ~10 mm thickness for thermal insulation and reducing the radiation heat loss. The mixed powders were sintered by spark plasma sintering (SPS, LABOX-350, Sinterland, Japan) with a constant axial pressure of 30 MPa forced on punches of the prepared die. Sintering was operated in vacuum with a heating rate of 100 °C min$^{-1}$ during the first six minutes and 90 °C min$^{-1}$ for the rest time until reaching the desire temperature (1400, 1500, 1600 and 1700 °C). And the dwelling time was scheduled as 0, 5, 15 and 30 min respectively. The pressure was maintained at 30 MPa as the furnace cooling to room temperature. The typical sintering curve is reported in figure 1.

2.2. Microstructural characterizations and properties

The surface graphite and any other contaminations were removed by grinding and polishing for all of the sintered specimens. After that, the density of processed specimens was measured via Archimedes method. Thermal conductivity was obtained by Laser thermal conductivity meter (LFA457, Netzsch, Germany) whose sample size is required as ~12.5 mm in diameter and 3–5 mm in thickness. The microstructure of specimens taken from polished plane or fracture surfaces was examined by the scanning electron microscopy (SEM, Sigma, Zeiss, Germany), equipped with an energy-dispersive spectrometer (EDS) analysis system. And the X-ray diffraction (XRD, Smartlab, Riguka, Japan) was utilized to analyze the phase composition of the specimens. The CuKα source was used for radiation. The diffraction angle varied from 10 to 90°, and the scanning speed was 10° min$^{-1}$ with the grating of 5 mm at the test voltage of 40 kV and current of 40 mA. Professional image processing software IPP served to calculate the proportion of Ti-rich phase. A statistical method was used to approximately measure the grain size of each sample by considering at least 180 grains per fracture surface from SEM images.
2.3. Grain growth kinetics analysis

Polycrystalline material’s grain growth kinetics was described by the classical power law expression, which was displayed as equation (1) [24]:

\[ d_0^n - d_t^n = Kt \]  

where \( d_t \) is the average grain size of the material at time \( t \) for a particular temperature, \( d_0 \) is the grain size at time \( t = 0 \) at that temperature, \( n \) is the grain growth exponent, \( K \) is the temperature dependent rate constant, and \( t \) is the dwelling time. The activation energy for grain growth was confirmed under the following Arrhenius equation shown as [25]:

\[ K = K_0 \exp(-Q/RT) \]  

where \( R \) is the gas constant, \( K_0 \) is the pre-exponential constant of the diffusion coefficient, \( T \) is the absolute temperature, and \( Q \) is the activation energy of grain growth.

3. Results and discussion

3.1. Microstructure and properties of the sintered W-10Ti alloys

The scanning electron microscopy morphology and the XRD pattern of original powders are shown in figure 2. It can be seen that the raw W-10Ti powders consisted of \( \alpha \)-Ti and \( \beta \)-W phases.

Figure 3(a) shows the XRD patterns of W-10Ti alloys sintered at different temperatures without dwelling time while figure 3(b) presents these with different dwelling time at 1400 °C. The diffraction peak of \( \beta \)-W(Ti) phase was identified in all the specimens. A weak diffraction peak of \( \beta \)-Ti(W) phase was only observed when the sintering temperature was 1400 °C without dwelling time [26]. As the temperature rose, the solid solubility of Ti...
in W increased, and the corresponding $\beta$-Ti(W) phase decreased, and then disappeared over 1400 °C. As the temperature and dwelling time increased, the diffraction peak of $\beta$-W(Ti) was slightly shifted to a lower angle, for the reason that the atomic radius of Ti was larger than that of W, and the lattice constant of W increased due to the formation of the solid solution.

Figure 4 and table 1 show the surface morphology of W-10Ti alloys sintered with different dwelling time and temperatures and the content of the Ti-rich phase respectively. Less content of Ti-rich phase is pretty beneficial for reducing particle pollution and improving the surface quality of the film during the magnetron sputtering [10]. The brighter phase was dominant, which was identified as $\beta$-W(Ti). The darker phase was $\beta$-Ti(W) which occupied only a small volume ratio and was evenly distributed in the whole sintered body. A rise in temperature from 1400 to 1700 °C resulted in a fall in the content of Ti-rich phase. As the dwelling time increased from 0 to 15 min at 1400 °C, the content of Ti-rich phase decreased from 16.68 ± 2.03% to 3.04 ± 0.65%, nevertheless, it increased to 6.84 ± 0.89% as the dwelling time increased to 30 min. The above results indicated that the mutual diffusion degree of W and Ti can be improved by increasing sintering temperature and extending dwelling time in a certain range.

Table 1. Ti-rich phase content of typical sintered specimens.

| Temperature (°C) | 1400 | 1500 | 1600 | 1700 |
|------------------|------|------|------|------|
| Dwelling time (min) | 0 | 10.17 ± 1.28 | 3.04 ± 0.65 | 6.84 ± 0.89 | 11.34 ± 1.93 |
| Content of the Ti-rich phase (%) | 16.68 ± 2.03 | 3.04 ± 0.65 | 11.34 ± 1.93 | 0.59 ± 0.12 |

Figure 4 and table 1 show the surface morphology of W-10Ti alloys sintered with different dwelling time and temperatures and the content of the Ti-rich phase respectively. Less content of Ti-rich phase is pretty beneficial for reducing particle pollution and improving the surface quality of the film during the magnetron sputtering [10]. The brighter phase was dominant, which was identified as $\beta$-W(Ti). The darker phase was $\beta$-Ti(W) which occupied only a small volume ratio and was evenly distributed in the whole sintered body. A rise in temperature from 1400 to 1700 °C resulted in a fall in the content of Ti-rich phase. As the dwelling time increased from 0 to 15 min at 1400 °C, the content of Ti-rich phase decreased from 16.68 ± 2.03% to 3.04 ± 0.65%, nevertheless, it increased to 6.84 ± 0.89% as the dwelling time increased to 30 min. The above results indicated that the mutual diffusion degree of W and Ti can be improved by increasing sintering temperature and extending dwelling time in a certain range.

W-10Ti alloys usually have a polyphase structure, and their density is directly related to the solid solubility [8], so it is difficult to accurately calculate the theoretical density. Thus, density was used to replace relative density to characterize the W-10Ti sintered body in the present study. Figure 5 shows the density of the specimens sintered at different temperatures with different dwelling time. The density slightly increased from 14.86 to 15.18 g cm$^{-3}$, as temperature increased from 1400 to 1700 °C at a constant dwelling time of 15 min. However, at a constant temperature, the density increased first and then decreased slightly with the longer dwelling time. The threshold was achieved at 15 min of dwelling time. Grain growth occurred at the final stage of sintering where the dominating kinetics of densification shifted from grain boundary diffusion to slow lattice
diffusion responsible for grain boundary migration resulting in grain growth. In this process, the air pressure in the pores increased, and the pores also grew together with the grains. The number of pores remained the same, but the pore volume increased, and the macroscopic density reduced [27].

Figures 6 and 7 show the fracture morphology of typical W-10Ti alloys and the curve of grain size with sintering temperatures and dwelling time respectively. It can be seen that the type of fracture was a mixture of inter and intragranular, and almost no pores can be observed. It is found that the grain size increased with the increase of the sintering temperature, and the grains grew significantly (1.68 to 5.55 μm) in the temperature from 1500 to 1600 °C. Huang et al [23] have proved that densification mainly occurred and grain growth was suppressed below 1300 °C, when the heating rate was 100 °C min⁻¹. In the present work, the heating rate was 90
$119^\circ\text{C}\min^{-1}$ and $1300^\circ\text{C}$ can be approximately used as the critical temperature for grain growth. The grain growth occurred as the sample was overheated ($1400^\circ\text{C}$–$1700^\circ\text{C}$). Therefore, after the densification stage, the rise of sintering driving force resulted in the increase of grain boundary migration rate, so the grain grew with the increase of temperatures.

Figure 8 presents the thermal conductivity of typical W-10Ti alloys sintered at different temperatures: (a) $1400^\circ\text{C}$–$1700^\circ\text{C}$ with no dwelling time and with different dwelling time: (b) 0–30 min at $1400^\circ\text{C}$ measured at different test temperatures. It can be seen that with the increase of the test temperatures, the thermal conductivity of the alloy also increased. According to figure 8(a), thermal conductivity decreased with the rise in sintering temperature. When the test temperature was $25^\circ\text{C}$, the specimen sintered at $1600^\circ\text{C}$ achieved the lowest thermal conductivity. It can be seen from figure 8(b) that thermal conductivity decreased when the dwelling time was below 15 min, however, it rose when the dwelling time reached 30 min. Generally, the thermal conductivity of alloy material occurred through the thermal motion of electrons and phonons in the alloy. If the internal structure of the alloy was very regular, the motion of electrons and phonons was relatively smooth, and the alloy had a good thermal conductivity [28]. Generally, the density, solid solubility and grain size simultaneously affect the thermal conductivity of the samples [29]. However, in this study, the fluctuation in density of test samples was very small (the maximum was 14.95 g cm$^{-3}$ and the minimum was 14.67 g cm$^{-3}$), thus, the density played a minor role in the thermal conductivity among three factors. The content of Ti-rich phase was used to approximately characterize the solid solubility as shown in table 1. The less Ti-rich phase, the better solid solubility degree, the more lattice distortion, and the lower thermal conductivity. At $1400^\circ\text{C}$, the content of Ti-rich phase first decreased then increased as the rise of
dwelling time, and the threshold was reached in 15 min. However, the grain growth was slow at 1400 °C as shown in figure 7. Therefore, the thermal conductivity showed the same trend as the content of Ti-rich phase, shown in figure 8(b). The variation in figure 8(a) can also be based on the same discussion. In conclusion, the solid solubility and grain size were the mainly factors resulting in the variation of the thermal conductivity in this study.

3.2. Grain growth kinetics

According to equation (1), the grain growth exponent \( n \) which characterized the rate controlling process was calculated. The grain growth exponent \( n \) known as the kinetic parameter has been reported to be 2 or 3 in former studies [25], where \( n = 2 \) for grain growth controlled by grain boundary diffusion and \( n = 3 \) for grain growth controlled either by diffusion through the lattice or through the liquid phase at the grain boundary [30]. Therefore, \( n \) can be assumed to be 2 or 3 for sintered W-10Ti alloys. By plotting linear relationship of \( d^2_0 - d^2_n \) verse \( t \), the proper exponent can be confirmed. It can be found that the regression coefficients \( R^2 \) as \( n = 2 \) shown in figure 9(a) was bigger than that as \( n = 3 \) shown in figure 9(b) at temperatures from 1400 to 1700 °C, which can be judged that the \( n \) value was confirmed to be 2 in this study.

Taking the natural log of both sides and rearranging the equation (1) gives:

\[
\ln (d^2_0 - d^2_n) = -\frac{Q}{RT} + \ln (K_0t)
\]

The activation energy of grain growth was calculated from the slope of logarithmic rate constant and inverse absolute temperature shown in figure 10. The grain growth activation energy was calculated to be 57.48 ± 8.42 kJ mol\(^{-1}\) (5 min), 49.21 ± 10.91 kJ mol\(^{-1}\) (15 min) and 61.46 ± 8.17 kJ mol\(^{-1}\) (30 min). This consequence proved that the control mechanism for grain growth of W-10Ti sintered by SPS was grain boundary diffusion.

4. Conclusions

The spark plasma sintering of W-10Ti alloys was studied in the temperatures from 1400 to 1700 °C under a pressure of 30 MPa and the dwelling time from 0 to 30 min.

(1) The W-10Ti alloys were composed of W-rich phase and Ti-rich phase. The rise in temperatures resulted in the fall of the content of Ti-rich phase and rise of density. With the increase of dwelling time, the content of Ti-rich phase firstly decreased and then increased, while the density was opposite, both reaching the threshold value at 15 min.

(2) At low temperatures (1400°C–1500°C), the grain growth was slow, on the contrary, as the temperature exceeded 1600 °C, the grain growth was intense. In this study, the thermal conductivity of the sintered W-10Ti alloy was mainly affected by solid solubility and grain size. Within the dwelling time ranges of 0–15 min, the thermal conductivity decreased continuously, and as the dwelling time continued to increase, the thermal conductivity increased slightly.

(3) The grain growth in W-10Ti alloy was found to follow square growth kinetics over the temperature ranges of 1400 to 1700 °C. The activation energy for grain growth was calculated to be 54.48 ± 8.42 kJ mol\(^{-1}\) (5 min), 49.21 ± 10.91 kJ mol\(^{-1}\) (15 min) and 61.46 ± 8.17 kJ mol\(^{-1}\) (30 min). Thus, the control
mechanism for grain growth of W-10Ti in SPS was grain boundary diffusion based on the above consequences.

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Figure 10. Plot of ln (d2 – d02) verse 1/T for growth of W-10Ti grain.
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