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利用 EBSD 探討奈米銅鍍層之晶體方向性及晶粒尺寸分布

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EBSD Characterization of Twinned Copper Prepared by Pulsed Electrodeposition

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摘　要

研究利用脈衝電鍍法製備具高雙晶密度之奈米純銅晶粒，再藉由 EBSD (Electron Back Scattering Diffraction)來做晶體方向性、晶粒尺寸分布之分析。並比較 EBSD、TEM 以及 XRD 三種分析方法決定晶粒大小之優劣。由 XRD、EBSD 以及 TEM 來決定純銅鍍層的平均晶粒大小分別為 82.9 nm、1.035 μm 和 0.5 ~ 1.0 μm。銅鍍層是由生長雙晶以及具有{220}優選取向的不規則形狀晶粒所組成，且雙晶晶界佔全部晶界的 37.98%。

關鍵字：雙晶；脈衝電鍍；EBSD；奈米晶粒。

ABSTRACT

In this work copper with high density twins was obtained by pulsed electrodeposition technique. The crystallographic parameters and the grain size of the electrodeposited copper were determined using the electron back scattering diffraction (EBSD) technique and were compared with those obtained from transmission electron microscopy (TEM) and X-ray analyses. The average grain sizes of the as-deposited Cu determined from XRD, EBSD and TEM were 82.9 nm, 1.035 μm, and 0.5 μm to 1.0 μm, respectively. There existed a {220} preferred orientation in the as-deposited Cu and the ratio of twin boundaries to total grain boundaries was 37.98%.

Keywords: Twin; Pulsed electrodeposition; BSD; Nano-particle.

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1. Introduction

Due to advantages of lower resistivity, higher thermal conductivity and better electro-migration resistance of copper in comparison with Al, copper has been introduced at the end of the 1990's as an interconnect material for Si microelectronic technology. It is necessary to integrate low-k dielectrics into copper interconnect, in order to reduce the interconnect capacitance and the switching delay and active power consumption. The replacement of the porous low-k by an air gap appears as a solution to low-k dielectrics. For air-gap structures, the mechanical properties of Cu interconnects play a central role on supporting the structures, Therefore, the mechanical and electrical properties of Cu are required for the application in interconnect materials. Recently, electrodeposited nanotwinning copper with high density of twins was successfully synthesized using the pulsed electrodeposition technique[1]. It was found that nanotwinned copper showed ultra high yield strength, ductility and electrical conductivity[1]. In addition to the pulsed electrodeposition technique, nanotwinning copper structure can be fabricated by magnetron sputtering deposition[1-4].

The formation mechanism of nanotwin structure is still not fully understood yet at present. In this study, a pulse electrodeposition technique was used to synthesize nano-twinned Cu because the electrodeposition techniques are widely adopted in the semiconductor industry. In order to know the relationship between the nanotwins and the mechanical and electrical properties, EBSD (Electron Back-Scattering Diffractometer) was utilized to characterize the crystallographic microstructure of as-deposited Cu, and the results were then compared with those from the TEM and XRD analyses.

2. Experimental Procedure

2.1 Sample Preparations

Nano-twinned Cu was directly deposited on a graphite substrate using a pulse electrodeposition technique from a 0.5 M $CuSO_4$ electrolyte and its pH value of 1.0. During the electrodeposition, the temperature of the electrolyte was controlled at 20 °C by water cooling and the electrolyte was mechanically stirred at 200 rpm. The home-designed electrodeposition system consists of an electroplating cell in Figure 1 and an external pulse power supply of Keithley SourceMeter Model 2611. During the electrodeposition, the peak pulse current density (PCD) was 0.5 A/cm^2 with on-time (Ton) of 0.02 seconds and off-time (Toff) of 2.00 seconds as shown in Figure 2. The anode of 99.99% purity copper was prepared into the dimensions of 30 mm x 30 mm x 3 mm and the graphite cathode into a disk with diameter of 11.3 mm and thickness of 2 mm. Then, the anode and cathode were polished with 1500, 2000, 4000 and 0.03 μm grit SiC abrasive papers.

2.2 Microstructure Analysis

X-ray diffraction (XRD) for phase analysis was conducted using a Rigaku diffractometer of Rigaku D-max IIIV with a Cu anode operated at 30 kV and 20 mA.

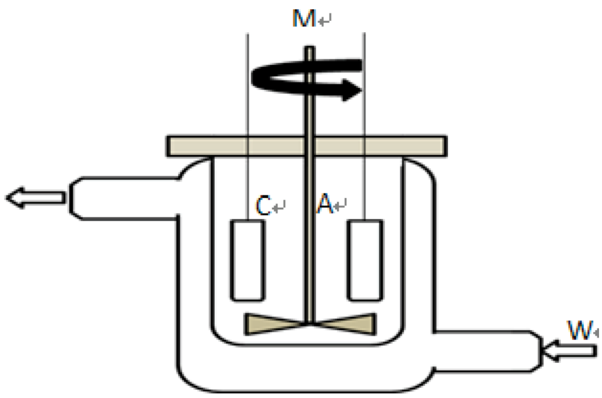

圖 1　脈衝電鍍實驗槽裝置簡圖。(M：攪拌，C：陰極，A：陽極，W：冷卻水)

Figure 1　Schematic illustration of the pulsed electrodeposition setup. (M: stirrer, C: cathode, A: anode and W: water circulation)

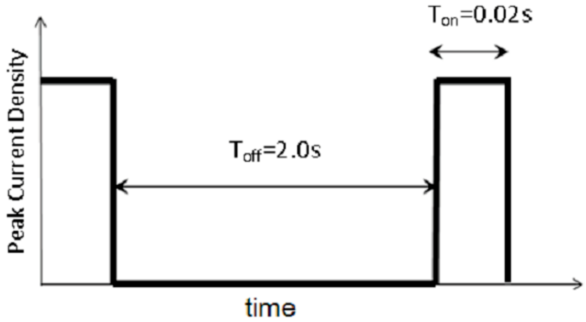

圖 2　脈衝電源之波形示意圖。(Ton and Toff 分別爲脈衝實施的時間和兩個脈衝間隔的時間)

Figure 2　Schematic of the current pulses. (Ton and Toff: ON and OFF durations of periodic current, respectively)

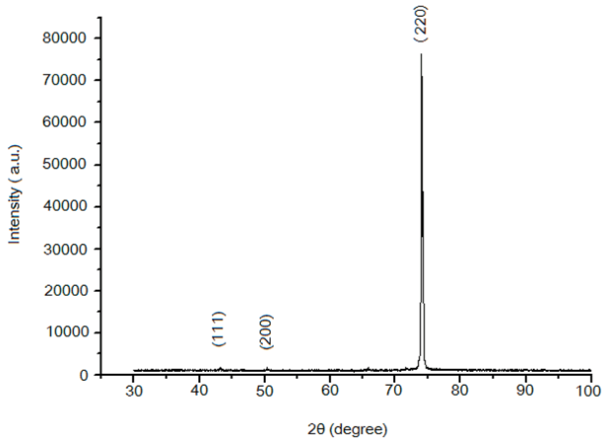

圖 3　電鍍銅之 XRD 繞射圖形。

Figure 3　XRD spectrum of the electrodeposited copper.

EBSD orientation mapping was conducted with an EDAX/TSL Technology EBSD system on a field emission SEM of JEOL 7001F operated at 20 kV with a step size of 50 nm. Sample preparation plays a significant role at the EBSD analysis. Surfaces of the materials were mechanically polished via a standard metallographic procedure to a final level of 0.03 μm, followed by electro-polishing at the voltage of 1.5 V for 60 seconds in a phosphoric acid electrolyte which consisted of 825 mL phosphoric acid and 175 mL de-ionized water. Specimens for TEM were prepared by double-jet electropolishing with a phosphoric acid electrolyte, in which 825 mL phosphoric acid and 175 mL de-ionized water was mixed, at a temperature of 20 °C. TEM was performed using a JEOL model 2010 operated at 200 kV.

3. Results and Discussions

The XRD pattern of as-deposited Cu is shown in Figure 3. The presence of pure copper with a lattice constant of 3.61507 Å can be clearly seen from the diffraction peaks of (1 1 1), (2 0 0) and (2 2 0). In the XRD pattern, copper has a very strong (2 2 0) diffraction peak at 2θ = 74.13°, and the ratio of $I_{(2\,2\,0)}/I_{(111)}$ for as-deposited Cu is 46.15 much stronger than that of I(2 2 0)/ I(111) = 0.02 for powder Cu obtained from ICDD. The high intensity in (220) diffraction peak indicates the deposited copper possessed (220) preferred orientation. The grain size was determined by using the Scherrer equation[5]:

$$\Delta 2\theta = \frac{K\lambda}{L\cos\theta} \qquad (1)$$

where Δ2θ is the broadening of diffraction peak, L is the diameter of grain size, and λ is the wavelength of the incident beam and coefficient K= 0.9.

The full-width at half maximum (FWHM) of the diffraction peak for (1 1 1), (2 0 0) and (2 2 0) was used to determine the broadening of diffraction peak Δ2θ. The measured width of the diffraction peaks for (1 1 1), (2 0 0), and (2 2 0) are 0.221 degree, 0.221 degree, and 0.176 degree, respectively. According to Eq. (1) and the measured widths, the grain size of the diffraction peaks of (1 1 1), (2 0 0), and (2 2 0) is 38.66 nm, 39.72 nm and 56.52 nm, respectively and the average grain size is 44.96 nm.

Figure 4 shows the distribution of grain boundaries obtained from EBSD, where the blue lines indicate grain boundaries with misorientation larger than 5 degrees and the red lines represent twin boundaries with <111> 60 degrees, that is, a 60° rotation about the <111> axe with the {111} twinning

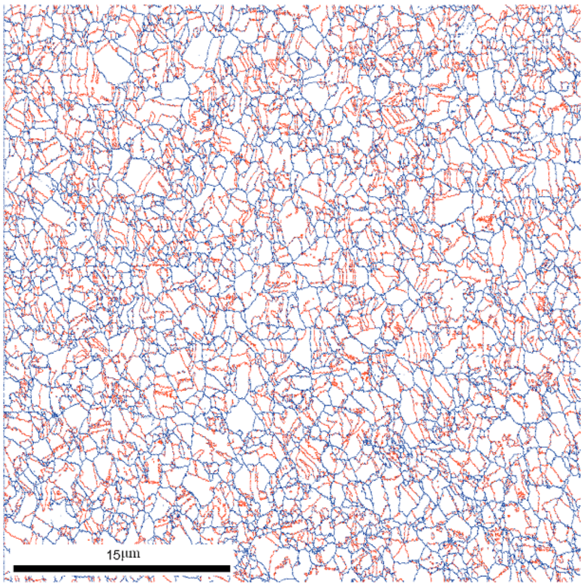

圖 4　電鍍銅之晶界以及雙晶晶界之分佈。(藍：晶體取向角度差小於 5°之晶界；紅：延著 <111>軸旋轉 60˚之雙晶晶界)

Figure 4　Distribution of grain boundaries and twin boundaries the electrodeposited copper. (blue: grain boundaries with misorientation > 5° and red: twin boundaries with <111> 60°)

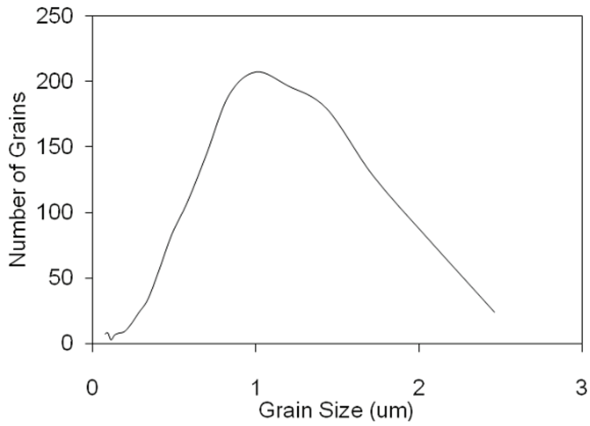

圖 5　晶粒大小分布圖。

Figure 5　Grain size distribution the electrodeposited copper.

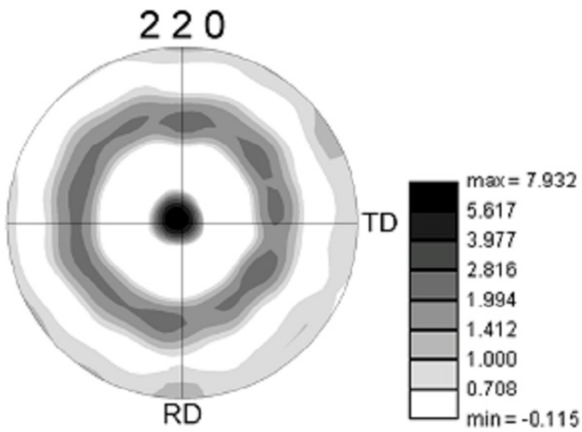

圖 6　電鍍銅之{220}極圖。

Figure 6　{220} pole figure of the electrodeposited copper.

plane. The software, OIM Analysis®, analyzed the orientation information from the raw data and calculates the relation between two neighbor sampling points. The result is the well-known misorientation which is composed of two parts: the misorientation axis and misorientation angle. The OIM Analysis® determines the type of boundaries by this relation. The ratio of twin boundaries to total grain boundaries is 37.98% and the distribution of grain size is shown in Figure 5. The area averaged grain size $\bar{v}$ of 1.035 μm in Figure 4 is determined according to the following equation:

$$\bar{v} = \frac{\sum_{i=1}^{N} A_i V_i}{\sum_{i=1}^{N} A_i} \qquad (2)$$

where A_i is area of grain i and vi is the grain size of grain i.

Considering only the grain boundaries with a misorientation of larger than 5 degrees, the area averaged grain size of 2.43 μm is larger than that of the foregoing 1.035 μm.

The {220} pole figure obtained from EBSD analysis is shown in Figure 6. It is observed a {220} fiber texture in which the {220} pole is parallel to the out-of-plane direction designated as the normal direction (NR) as shown in and in Figure 6. This {220}-fiber texture obtained from EBSD consisted with the high intensity of {220} peak in the XRD pattern as shown in Figure 3. It suggests that the as-deposited Cu possessed a {220}-fiber.

The microstructure of the as-deposited Cu is shown in Figure 7. The grain size was calculated by measuring the width of the TEM image and comparing it with the scale bar on the image. The results showed that the as-deposited Cu is composed of grain size from 0.5 μm to 1.0 μm and a number of twins from 33 nm to 189 nm. Comparing the results, the average grain sizes determined from XRD, EBSD and TEM were 82.9 nm, 1.035 μm and 0.5 μm to 1.0 μm, respectively. The grain size predicted from XRD is smaller than that from EBSD and TEM. It can be attributed to the broadening of diffraction peaks in XRD pattern. The instrument's angle resolution, texture and residual stress affect the results in the peak broadening and it is difficult to distinguish the difference between them. The lateral resolution of EBSD is limited by 20 nm ~ 50 nm dependent on materials. The limit of lateral resolution is the main reason to predict larger grain size than TEM. However, the difference in grain size obtained from EBSD and TEM is quite similar.

4. Conclusions

Copper with high density twins was obtained using a pulsed electrodeposition technique. The average grain sizes of the as-deposited Cu determined from XRD, EBSD and TEM were 82.9 nm, 1.035 μm and 0.5 μm to 1.0 μm, respectively. There existed a {220}-fiber in the as-deposited Cu and the ratio of twin boundaries to total grain boundaries was 37.98%.

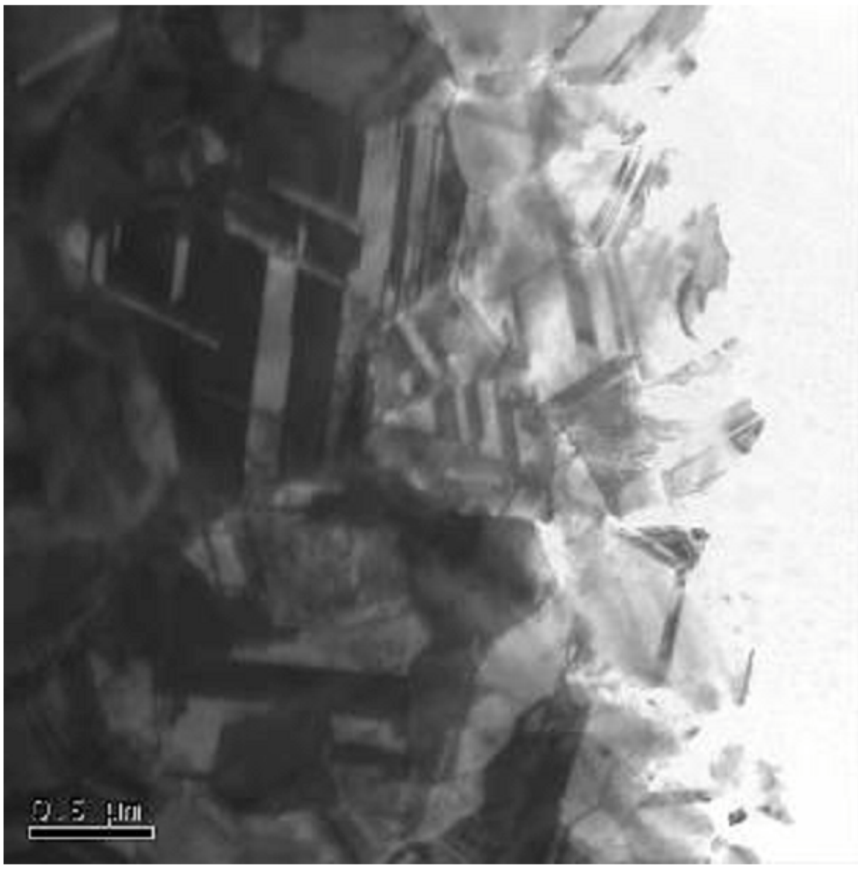

圖 7　電鍍銅之 TEM 影像。

Figure 7　Bright-field TEM image of the electrodeposited copper.

Acknowledgements

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