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Structure-dependent mechanical behavior of copper thin films

Yong-Seok Lee[a], Sangyul Ha[b], Jin-Hyoung Park[c], Soon-Bok Lee[a],*

[a] Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea
[b] Department of Corporate R & D Insititute, Samsung Electro-Mechanics, Maeyoung-ro 150, Yeongtong-gu, Suwon, Gyeonggi 16674, Republic of Korea
[c] Korea Institute of Industrial Technology, Hayang-ro 13-13, Hayang-eup, Gyeongsan-si, Gyeongbuk 38430, Republic of Korea

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ABSTRACT

The mechanical properties of copper foils electroplated with (200) and (220) preferred orientations and thicknesses of 8–24 μm were assessed at various temperatures. It was found that the yield strength and elastic modulus both decrease with increasing temperature to 150 °C, and that the greater susceptibility of a columnar structure to defects makes it more sensitive to temperature than an equiaxed structure. Thus, for a given grain size, a columnar structure has a lower yield strength. A modified Hall-Petch relation was subsequently developed to take into account the effect of micro-structure on material strength by introducing a structure factor $(S): \sigma_y = \sigma_0 + kd^{-1/2} + S$. As the slope ($k$) of this equation is constant, it can be used for copper thin films of any thickness, provided they are at room temperature and above the micro-level in scale. This structure factor concept, however, is only valid at room temperature. In the modified Hall-Petch relation, the new variable related to the equiaxed and columnar structures in the copper thin films was abstracted from the Hall-Petch relation. Then, if the materials are the same, the k value and the σ_0 value are constant regardless of the scale, and the relationship between the grain size and the yield strength can be shown by only changing the structure factor.

1. Introduction

Copper thin films are already widely used as a wiring material in electronic devices, but there has been increased research into the large-scale behavior of films produced from powder or nano crystalline copper [1–3]. The decreasing size of electronic devices has also generated greater interest in the mechanical behavior of thin copper films on substrates, as measurements obtained using the indentation method have revealed an inverse relationship between strength and thickness. This is consistent with the fact that the mechanical behavior of a material greatly changes as its size decreases from a bulk state to a micro/nano scale [4]. A grain boundary effect caused by thermal treatment [5–7] has also been identified, but only limited attention has been given to the high temperature mechanical behavior of thin films [8–10]. Hemker et al. have measured the tensile strength of γ-TiAl micro samples at elevated temperatures [11], but research into the high-temperature behavior of thin films has tended to focus on the effects of recrystallization during heating [12].

Extensive investigations into the room temperature mechanical properties of copper films [13–16] have revealed that 35 and 15 μm-thick films have a much lower elastic modulus (92 and 72 GPa, respectively) than bulk copper (120–130 GPa) [17–19]. The strength of a thin copper film changes with grain size and thickness; i.e., if the grain size is increased by electroplating, then the thickness of the copper thin film can influence the overall strength of the material. Specifically, a decrease in grain size results in an increase in yield strength, as modeled by the Hall-Petch relation [20,21]. This dictates that the yield strength, σ_y, is related to the grain diameter, d, according to [14]:

$$\sigma_y = \sigma_0 + kd^{-1/2} \tag{1}$$

where σ_0 and k are constants. This Hall-Petch relation is valid from the bulk scale to micro/nano-scale, whereas the inverse Hall-Petch relation (i.e., a smaller grain size leads to a lower yield strength) holds true for materials only a few nanometers in thickness [22]. The range of reported Hall-Petch coefficients (k, σ_0) for the same material and thickness is remarkably wide due to the formation of twin boundaries, which can increase the yield strength of copper foils [23]. It is also possible that the growth structure may have some influence on this inconsistency in the Hall-Petch coefficients.

The crystal structure of a copper thin film deposited by electroplating will vary depending on the manufacturing process used [24]. Electro-deposited copper foils that exhibit (200) and (220) preferred orientation are considered to be equiaxed and columnar, respectively.

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* Corresponding author at: Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea.
E-mail address: sblee@kaist.ac.kr (S.-B. Lee).

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Materials with equiaxed structure are considered to have higher mechanical strength than material with columnar structure in bulk size [25]. However, previous studies have shown that copper foils with a columnar structure have a higher yield strength than those with an equiaxed structure [26]. This clearly demonstrates that structure does have an effect on the mechanical strength of thin copper films, and hence, in this study, the effects of columnar and equiaxed structures on the yield strength of thin copper films over a wide range of grain sizes were experimentally investigated. The ultimate aim of this study is to modify Hall-Petch relations that can be used to evaluate the mechanical behavior of copper thin films at room temperature and to investigate the influence on the mechanical characteristics at elevated temperature.

2. Experimental Details

The elastic modulus and yield strength of copper thin films of various thicknesses were measured at elevated temperature using a modified micro-tensile testing machine (Fig. 1(a, b)). The actuating part of this system, which was originally designed to investigate nickel thin films [27], consists of a TST350 stage (Linkam). Strain was measured using a non-contact digital image correlation (DIC) method based on a 1.3 megapixel CCD camera (Manta G-145B PoE). This had an optical magnification of 2.5 × and a field of view (FOV) of 3 × 3 mm, giving a strain resolution of 2 μm. Labview (NI) was used for data acquisition.

The copper foils used were commercially available electro-deposited products of seven different thicknesses: 8, 10, 12, 18, 20, 22 and 24 μm. These thin copper films consisted of a seed layer and electroplating layer, both of which were identical in composition but gave the foils a shiny side and matt side. The thickness of the seed layer with 8, 10, and 12 μm-thick copper thin films is about 0.5 μm. In the case of 18, 20, 22, and 24 μm-thick copper thin films, the thickness of the seed layer was as small as 0.5–1 μm. And it was confirmed that there was no structural difference between the electroplating layer and the seed layer. The influence of the seed layer can be negligibly small in these cases. Specimens thicker than (or equal to) 12 μm were fabricated using a cutting plotter (Graphtec FC8000), whereas those thinner than (or equal to) 10 μm were fabricated by etching. The final dog-bone shape of the specimens, as shown in Fig. 1-(c), measured 40 mm in total length, 20 mm in gauge length and 2 mm in width. Tensile testing of these samples using a strain rate of 5×10^{-5}/s was performed at room temperature and at elevated temperatures of 100 and 150 °C (Fig. 2). A micro heater was used to increase the temperature of the samples and maintain them at the target temperature for 30 min prior to testing. Higher temperatures were avoided so as to prevent the appreciable oxidation that occurs above 200 °C. After heating the copper foil for 30 min at each temperature, component analysis by EDAX showed that the weight percent of oxygen was 1.09% at 70 °C, 1.52% at 100 °C, 1.73% at 200 °C and 5.30% at 300 °C. In other words, the degree of oxidation was found to be large near 200–300 °C. Based on these results, it can be seen that the oxide film is not generated at a temperature below 150 °C.

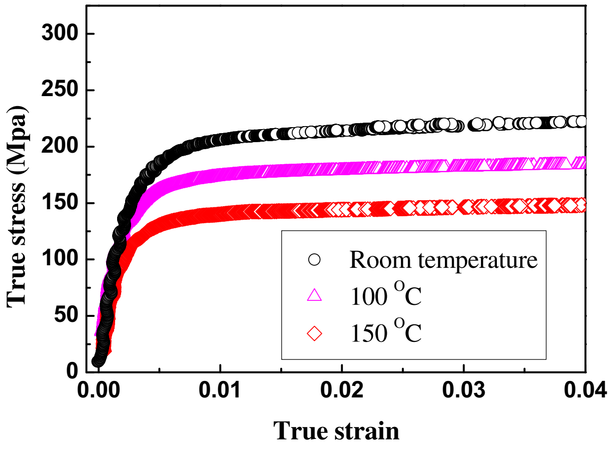

Fig. 2. Stress-strain curves of 10 μm-thick copper at various temperatures.

The mechanical behavior is of course not the same for copper and copper oxide. Moreover, the growth mechanism of copper oxide by thermal oxidation generally occurs by outward diffusion of copper cations to the upper surface. This leads to the formation of Kirkendall porosity in the films which dramatically affects the mechanical properties of copper layer [28]. This point should be clarified to ensure that oxidation is limited even at 150 °C.

To analyze the micro-structure of the thin copper films, cross-sectional images were obtained through exposure to a focused ion beam

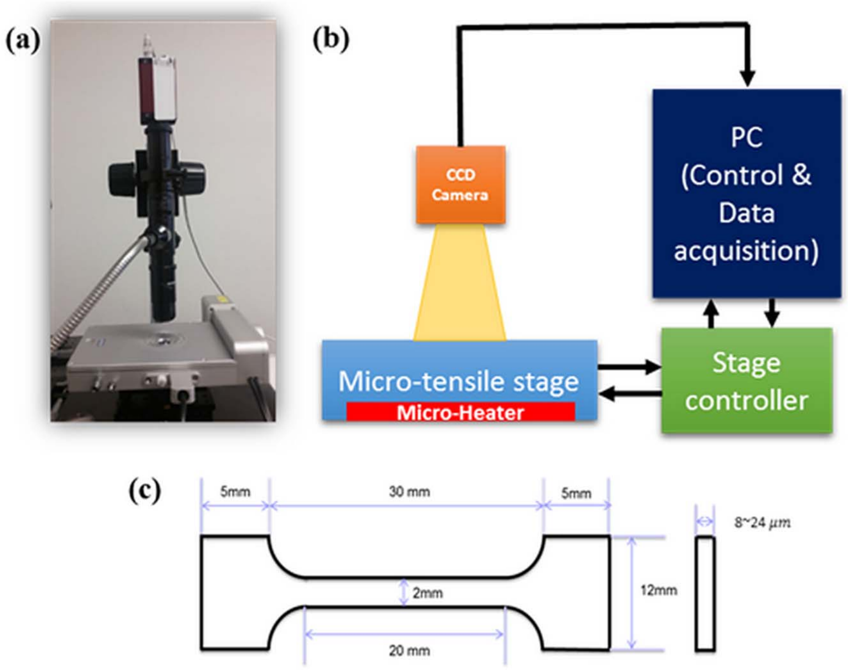

Fig. 1. (a) Photograph and (b) schematic configuration of micro-tensile testing system, and (c) specimen design.