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Nanoscale corrosion behavior of polycrystalline copper fine wires in dilute NaCl solution investigated by *in-situ* atomic force microscopy

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ABSTRACT

In this study, nanoscale corrosion behavior of copper fine wires in dilute NaCl solution is studied by atomic force microscopy and electron backscatter diffraction. The dissolution rate of grains constituting the wires strongly depends on their crystallographic orientation. In pure water, the dissolution rate increases in the order of (111) < (001) < (110). Addition of Cl^- dramatically increases the dissolution rate of the (111) surface to alter the order to (110) ≈ (001) ≈ (111) at 0.1 mM. These results show that the crystallographic orientation dependence is significantly changed by a slight increase of Cl^- concentration in dilute solution.

1. Introduction

Corrosion of copper fine wires during fabrication of semiconducting devices has been a serious problem. To fabricate copper fine wires, a patterned trench structure on a Si wafer is formed by photolithography and a copper thin film is deposited on it. Subsequently, the surface is flattened by chemical mechanical polishing (CMP), where a rotating wafer is pressed against a fixed polishing pad in a slurry solution. The solution contains anticorrosive molecules to form a protective layer on the copper surface. Thus, the polished copper surface is protected during the polishing and subsequent transfer of the wafer to the next process. However, before proceeding to the next process, the protective layer should be removed by gently scrubbing the surface in a cleaning solution. Although the solution contains another anticorrosive component, it is gradually replaced with pure water before drying. During this cleaning process, a copper surface is exposed to a dilute ionic solution and partially dissolves to form defects: locally etched spots showing high electrical resistance in a wire. To prevent such corrosion, it is essential to understand nanoscale corrosion processes of a copper fine wire in a dilute ionic solution.

So far, corrosion behavior of various metals in different solutions has been investigated. Among them, copper corrosion in pure water [1–4] and Cl^- solution [5–10] is one of the most extensively studied examples. This is due to the wide use of copper materials and the ubiquity of Cl^- in an aqueous environment (e.g. sea water and tap water). Macroscopic corrosion behavior is mainly studied by electrochemical measurement techniques while microscopic behavior is analyzed by optical, electron or X-ray beam technologies as well as scanning probe microscopy (SPM) [6–10]. However, microscopic studies on copper fine wires are limited [11]. In addition, previous studies were mainly performed at a high Cl^- concentration [5–10] due to the strong interests in the corrosion caused by sea water. Therefore, microscopic corrosion behavior of copper fine wires in a dilute Cl^- solution has not been well understood in spite of its importance in semiconductor industry.

Recently, SPM techniques such as scanning tunneling microscopy (STM) [12], atomic force microscopy (AFM) [13] and scanning electrochemical microscopy (SECM) [14] have been proven to be a powerful tool for studying microscopic corrosion processes. As they can be operated in liquid, *in-situ* measurements of microscopic corrosion behavior can be performed. Furthermore, when it is used with electron backscatter diffraction (EBSD) measurement technique, crystallographic orientation dependence of corrosion behavior can be studied [6–10]. According to these previous studies, microscopic metal corrosion behavior strongly depends on crystallographic orientation. In addition, Lapeire et al. reported that the crystallographic orientation of the neighboring grains can also influence the corrosion behavior [7]. Copper fine

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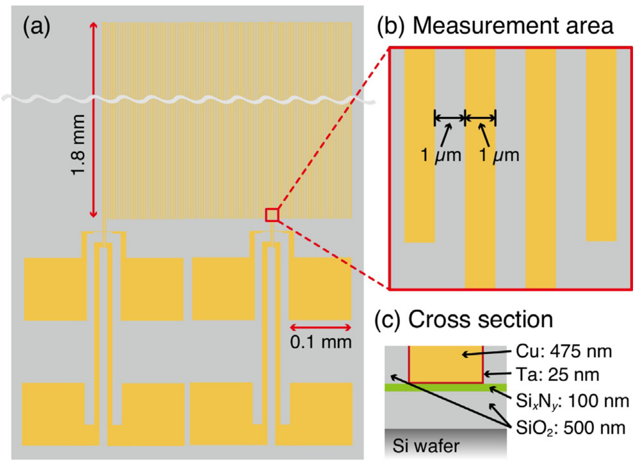

Fig. 1. Schematic illustration of copper fine wires used in this study. (a) A large-scale view. (b) A magnified view of the area measured by AFM and EBSD. (c) Cross sectional view of a copper wire.

wires consist of plated polycrystalline thin film having nanoscale domains with different crystallographic orientations. Therefore, to understand their corrosion behavior, it is essential to use a microscopic technique having a nanoscale spatial resolution in liquid.

In this study, nanoscale corrosion processes of copper fine wires in dilute NaCl solution is studied by *in-situ* AFM and *ex-situ* EBSD measurements. AFM measurements in different NaCl concentration were performed. Comparing the AFM images with inverse pole figure (IPF) maps obtained by EBSD, dependence of the nanoscale corrosion behavior on crystallographic orientation and NaCl concentration is clarified. A possible model to explain the observed corrosion behavior is also presented.

2. Material and methods

2.1. Copper fine wires

For the AFM and EBSD measurements, patterned copper fine wires fabricated on a Si wafer (854 Cu CMPd Wafer, Advanced Materials Technology) was used. Fig. 1(a) shows a large-scale view of the pattern while Fig. 1(b) shows a magnified view of the area that was measured by AFM and EBSD. In this region, the line and space width is 1 μm. The two wires at the center are connected to a 0.1 mm × 0.1 mm copper pad while the others are electrically isolated. Owing to the characteristic wiring pattern in this area, its location can be easily identified either by scanning electron microscopy (SEM) or optical microscopy. This enables to analyze the same area by AFM and EBSD.

Fig. 1(c) shows a cross section of one of the wires shown in Fig. 1(b). As illustrated in this cross section, the copper wires are formed on a 25 nm Ta film and have a depth of 475 nm. The outline of the fabrication process is as follows.

1. A patterned trench structures were formed by etching the SiO$_2$ layer.
2. A 25 nm Ta film was formed on the wafer surface by physical vapor deposition (PVD).
3. A thick copper film was formed on the Ta film by electroplating.
4. The wafer was annealed at 150 °C for 30 min.
5. The surface was polished by CMP to make the SiO$_2$ thickness 500 nm, which corresponds to the copper wire thickness of 475 nm.

In this way, polycrystalline copper fine wires were fabricated. The wires consist of nanoscale grains with different crystallographic orientations. For the AFM and EBSD measurements, the wafer was cut into 10 mm × 10 mm pieces such that each sample should have the same type of copper wire pattern at its center.

2.2. AFM and EBSD measurements

In this study, AFM measurements were performed in pure water and 0.01 mM/0.1 mM NaCl solution. For each experiment, a different piece of sample was used. Before the AFM measurements, an EBSD measurement was performed to obtain an IPF map of the copper wires. For the measurements, field-emission scanning electron microscopy (JIB-4601F, JEOL) and EBSD detector and software (TSL Solutions) were used. The acceleration voltage and current of the electron beam were 20 kV and 1 nA, respectively.

During the EBSD measurements, carbon contaminations were deposited on the surface. To remove such contaminations, the surface was cleaned by Ar plasma cleaner (SC-701, Sanyu Electronics). The Ar plasma cleaning with a typical operating condition can severely damage the copper wires. Thus, the bias voltage and the inlet gas pressure were adjusted to just as high as required for maintaining the plasma. In addition, the sample was covered with a Cu plate to suppress the electric field applied to the sample surface. Under this condition, the damage of the wires caused by the cleaning is negligible.

After the Ar plasma cleaning, the sample was attached onto a sample holder for the AFM used in this experiment. On the fixed sample, a 100 μL 0.5 M citric acid solution was dropped and left it for 1 min to remove organic contaminations deposited on the surface during the sample transfer process. Subsequently, the deposited solution was replaced with pure water by gentle pipetting. This process was repeated for five times not only to completely replace the solution but also to rinse the surface with pure water. Although the copper surface partially dissolves in the citric acid, the created height variations do not significantly influence following discussions, where time-dependent height changes of the copper wires are compared between different solution conditions and crystallographic orientations.

The sample holder was set onto the AFM system. Just before starting the tip coarse approach process, the water on the sample was replaced with an imaging solution, which is either pure water, 0.01 mM or 0.1 mM NaCl solution. Note that the term ‘imaging solution’ is used to refer to ‘solution in which AFM imaging was performed’. This process was repeated twice to completely replace the solution with the imaging solution. The elapsed time was recorded since this replacement as each AFM image was saved.

In this experimental procedure, it is very important to keep the sample surface wet after the cleaning by citric acid. Experiments without a cleaning by citric acid or with an exposure of the surface to the air after the cleaning results in poor reproducibility due to the contaminants deposited on the copper surface during the exposure to the air. This is particularly evident for an experiment in dilute NaCl solution, where relatively minor corrosion processes must be accurately analyzed.

AFM measurements were performed by a custom-built amplitude-modulation AFM (AM-AFM) [15–17] in the imaging solution. AFM images were obtained in the constant amplitude mode, where the tip-sample distance is controlled such that cantilever oscillation amplitude is kept constant. A commercially available AFM controller (RC4/OC4, SPECS) was used for the AFM operation. Si cantilevers (AC55, Olympus) having a spring constant of ∼80 N/m, a resonance frequency (f_0) of ∼1.3 MHz and Q factor of ∼12 in aqueous solution were used.