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Seedless Copper Electroplating on CoW Thin Films in Low pH Electrolye

Early Stages of Formation

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Abstract

The present work sought to study how the electroplating conditions could be tailored to enable the formation of a copper film over a Co-W substrate. An electrolyte solution at 0.5M Cu comprised of sulphuric acid, sodium chloride, polyethylene glycol and copper sulphate was used at two distinct pH values (1.8 and 3.5) to assess the effect of the concentration of H^+ ions on the microstructure. Galvanostatic deposition using direct current (DC) and pulsed current (PC) for equivalent total mass transfer were used to evaluate the effect of different current densities (5mA/cm^2, 10mA/cm^2 and 20mA/cm^2). Solid continuous films were successfully deposited using the higher pH solution at 10mA/cm^2.

Introduction

The continuous decrease in transistor size and related features poses new challenges from a manufacturing technology standpoint, in terms of the technologies and materials being used to allow for the creation of the necessary nanostructures. The electroplating stage is a fundamental step in the currently used dual-damascene technique use for circuit production, and recent developments from a material standpoint are focused on opposing the dewetting of the copper films that comprise the circuits over which the electrons move when a voltage is applied, under normal usage.

One of the areas that is being pursued in an attempt to overcome thin film dewetting is through the use of new barrier layer materials, whose purpose is to prevent copper diffusion during normal operation. Currently there are a number of materials being considered for barrier layer usage as alternatives to the standard Ta/TaN system, such as Ru-W, Ru-Mn or Co-W.

Experimental Procedure

The substrate Co-W layer was co-deposited using physical vapor deposition (PVD), from a cobalt target (99.95% purity) and a tungsten target (99.95%), on top of a SiO_2 layer created over p-type boron doped (100) oriented single crystal Si wafer pieces.

The pieces measured 15 x 15 mm and were mounted on an acrylic container for electroplating. The standard electrolyte used was comprised of 0.05M $CuSO_4{\cdot}H_20$, 0.05M H_2SO_4, 1 mM of NaCl and 300 ppm polyethylene glycol, dissolved in distilled water. The pH of the second analyzed solution was raised through addition of drops of NaOH to a solution similar to the first.

The microstructures were analyzed by scanning electron microscopy (SEM) using a FEI Quanta 400 FEG ESEM, and a digital optical microscope/infinite focus microscope LEICA.

Table 1. Electroplating conditions for the PC samples analyzed.

Current Type	pH	i (mA/cm^2)	Cycles (#)	t_{ON} (ms)	t_{OFF} (ms)
PC	1.8	5	400	20	500
PC	1.8	20	100	20	500
PC	1.8	40	50	20	500
PC	1.8	20	400	20	500
PC	1.8	20	1600	20	500

Table 2. Electroplating conditions for the DC samples analyzed.

Current Type	pH	i (mA/cm^2)	Total Dep. Time (s)
DC	1.8	5	900
DC	1.8	10	225
DC	3.5	5	900
DC	3.5	10	225

The deposition strategies adopted sought to assess how the deposition parameterization was affected by the electrolyte and its pH, as well as the type of current during electroplating, with pulsed-current opposed to direct current.

Pulsed Current

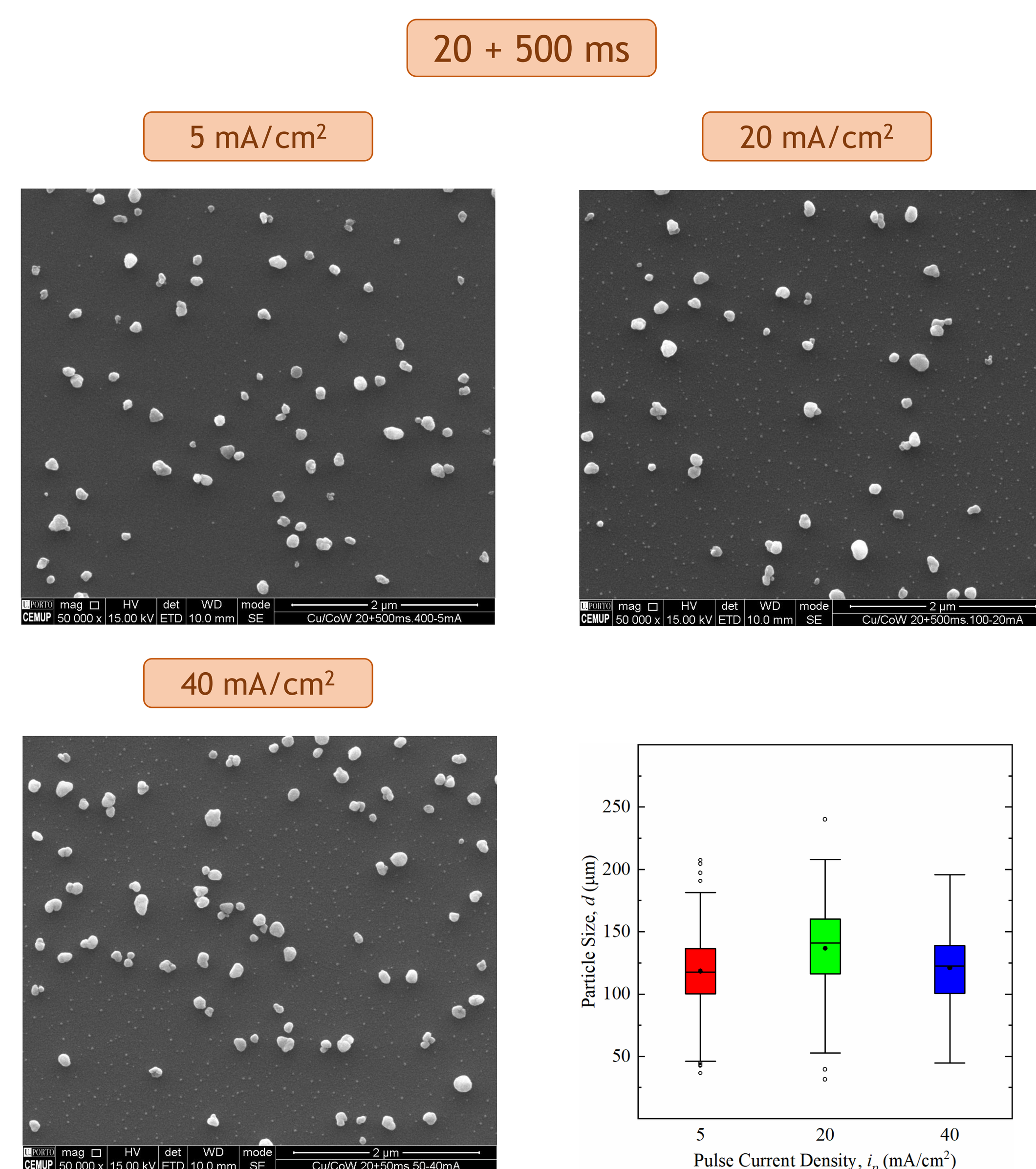

Figure 1. Copper particles obtained after electroplating over a Co-W coated Si wafer piece, at three different current densities at the same duty cycle, and corresponding grain size distribution.

The variation in the current densities applied did not considerably affect the particle size or density.

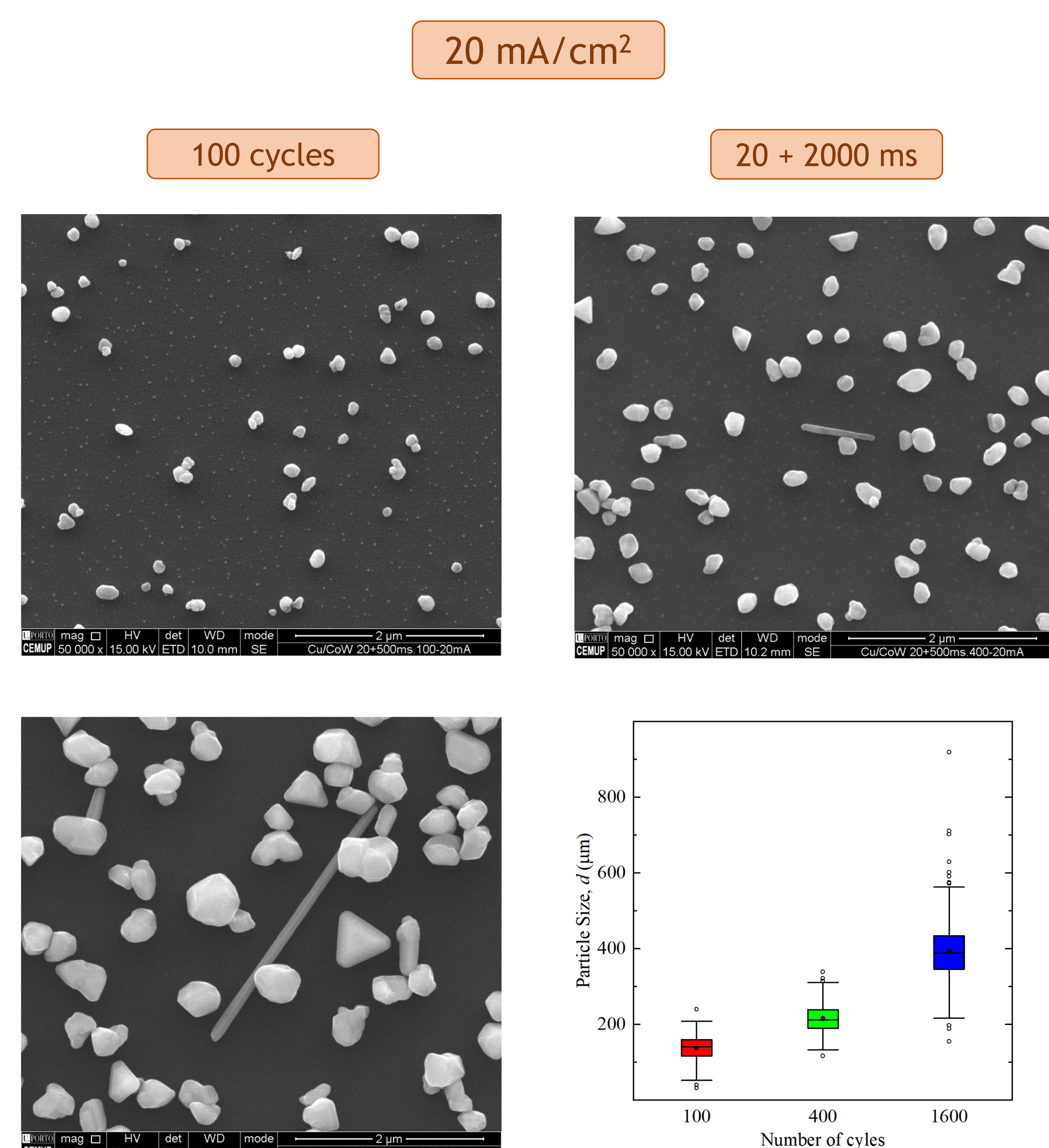

Figure 2. Copper particles obtained after electroplating on CoW with increasing number of cycles at 20 mA/cm^2.

Increasing the number of cycles leads to particle grow, but as the immersion time increases Co-W dissolution prevents a complete substrate coverage.

Direct Current

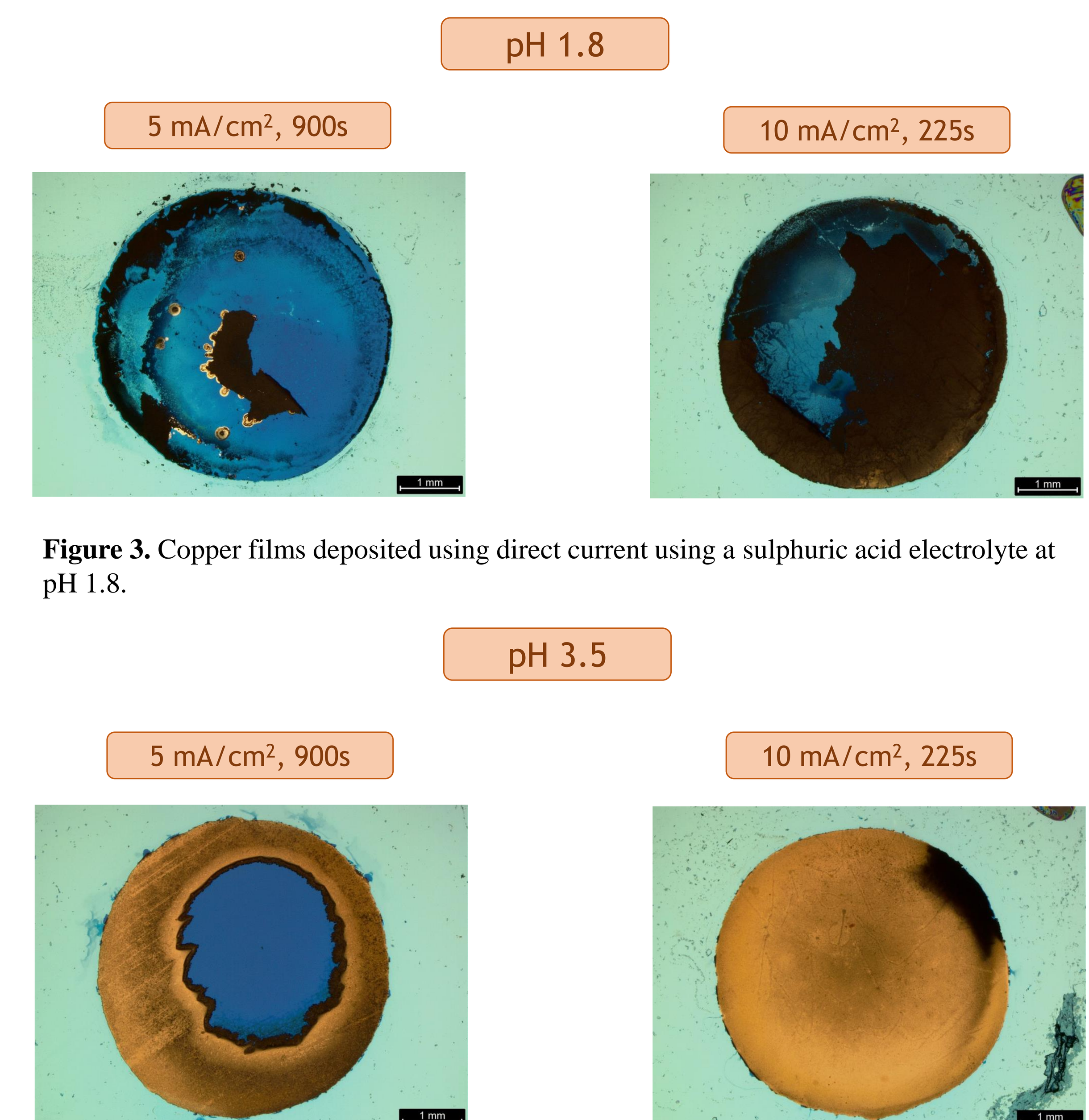

Figure 3. Copper films deposited using direct current using a sulphuric acid electrolyte at pH 1.8.

Figure 4. Copper films deposited using direct current using a sulphuric acid electrolyte at pH 3.5.

Raising the pH value of the electrolyte proved successful in allowing for the creation of a solid film throughout the exposed Co-W surface. Current density needs to be high enough so as to quickly cover the Co-W before the electrolyte etches it completely. But too high currents lead to hydrogen evolution and strong branch-like morphology, destroying the film. As such, the results show that controlling current density and electrolyte pH by is required to control the process and deposit a continuous, compact copper film.

Conclusions

- Co-W thin films are directly electroplated (seed layer not required)
- Co-W undergoes dissolution in acidic electrolyte
- Substrate dissolution prevents complete coverage in low pH
- Increasing pulse-current density does not change substrate coverage
- Higher pH electrolyte are required for a continuous compact Cu film
- Optimum current density is also required for complete substrate coverage

References

1. F. Leroy, et al., How to control solid state dewetting: A short review, Surf. Sci. Rep. 71 (2016) 391-409.
2. Y. Su, et al., Effect of tungsten incorporation in cobalt tungsten alloys as seedless diffusion barrier materials, Microelectron. Eng. 171 (2017) 25-30.

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