

Ruthenium CMP Integration for Dual-Damascene Copper Interconnects

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EXECUTIVE SUMMARY

Continued IC dimensional scaling requires new materials, such as ruthenium thin film barriers for copper interconnects. Fast and reproducible CMP processing of tantalum, ruthenium, and copper dual-damascene interconnects has been developed. Due to the unique materials property challenges of ruthenium, both selective and relatively non-selective CMP slurry sets have been developed to work with soft pads. Through tuning slurry properties to match known topographic variations, negative dielectric “dishing” can be achieved.

The IC manufacturing industry continues to scale device dimensions so as to stay on the Moore’s Law trend line of doubling the number of circuit elements per IC. With 45nm node IC technology now in production, and 32nm to 22nm nodes under development, many of the device structures are approaching atomic limits. Thin films of traditional metals and dielectrics have been reduced in thickness to accommodate scaling demands, to the extent that fundamental materials properties no longer provide minimum functionality.

Many new materials are under investigation as replacements for existing materials. The metal ruthenium (Ru) in particular has been the subject of research for use in multiple electronics applications. Ruthenium is being investigated as a copper diffusion barrier film to replace tantalum and tantalum nitride in interconnect wiring structures. Ruthenium is also being investigated for use as an electrode in advanced capacitor applications for next-generation memory devices. The integration of ruthenium into manufacturing processes for these applications requires significant technical investment.

Dual-damascene (DD) process flows for metal interconnect formation in modern ICs center around the electrochemical deposition (ECD) of copper (Cu). After deposition of a metal barrier layer and a metal “seed” layer inside the dielectric vias and trenches, the Cu is grown from the seed layer using aqueous chemistry. The Cu overgrowth and the barrier/seed thin films must then be cleared from the top of the dielectric using CMP.

Ruthenium (Ru) metal has been investigated as a barrier for Cu DD interconnects for many years (Fig. 1). Ru provides a thin seed layer from which Cu may be directly grown by ECD, and the resulting metal lines tend to show reduced electrical resistance compared to lines grown from PVD Cu seeds.

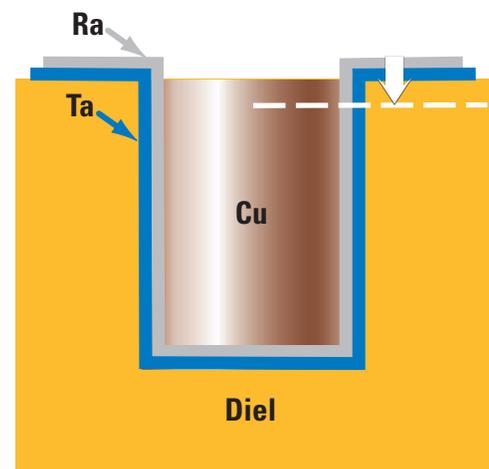


Figure 1. Ruthenium thin-film used as a barrier layer in copper dual-damascene interconnect processing for 45nm node and below ICs.

The development of chemical mechanical planarization (CMP) processes for ruthenium is not a trivial task. Careful consideration must be given to the design of CMP slurries to insure beneficial performance and compatibility with other materials present in the film stack.

The Science of Ru CMP

Ruthenium is a naturally occurring rare metal that serves many roles as an industrial catalyst [1,2]. Ruthenium is sensitive to oxidizers and eight oxidation states have been observed with the +2, +3, and +4 states being the most common. Ruthenium can be deposited with a variety of techniques to yield thin films suitable for electronic applications. Manufacturing facilities around the world are investigating the use of a variety of deposition tools and techniques to yield films of ruthenium via atomic layer deposition (ALD) [3,4], chemical vapor deposition (CVD) [5,6,7,8] or physical vapor deposition (PVD) [9,10,11]. Each of these deposition methods has advantages and disadvantages that must be considered when developing processes that use ruthenium.

Ruthenium is a hard metal with little chemical reactivity. From a CMP perspective, any ruthenium film poses a significant challenge in terms of slurry design and development. Ruthenium films are resistant to chemical attack and traditional CMP slurries yield limited results. The strength and toughness of the ruthenium film is high so pursuit of ruthenium removal with a mechanical approach does not yield high removal rates. Early work on Ru CMP that used almost purely mechanical slurries showed planarization results that were as limited as the sophistication of the approach. Also, without proper control over slurry chemistry, it is known that a toxic oxide byproduct of the process can form.

Of the different stable oxides that may be formed from metallic Ru, only RuO_4 is known to be toxic. RuO_4 gas can form when ruthenium is in contact with an oxidizer under low pH and relatively high electrochemical potential, as

shown in the Pourbaix diagram (Fig. 2). In the known electrochemical region of formation, significant RuO_4 gas can form and travel through the tool to reach fab personnel. However, proper control of the slurry chemistry to hold the pH between 8.4 and 10 ensures that the Ru oxidation reaction is far from the RuO_4 gas generation region, with Ru(OH)_3 and RuO_2 predicted as the main byproducts.

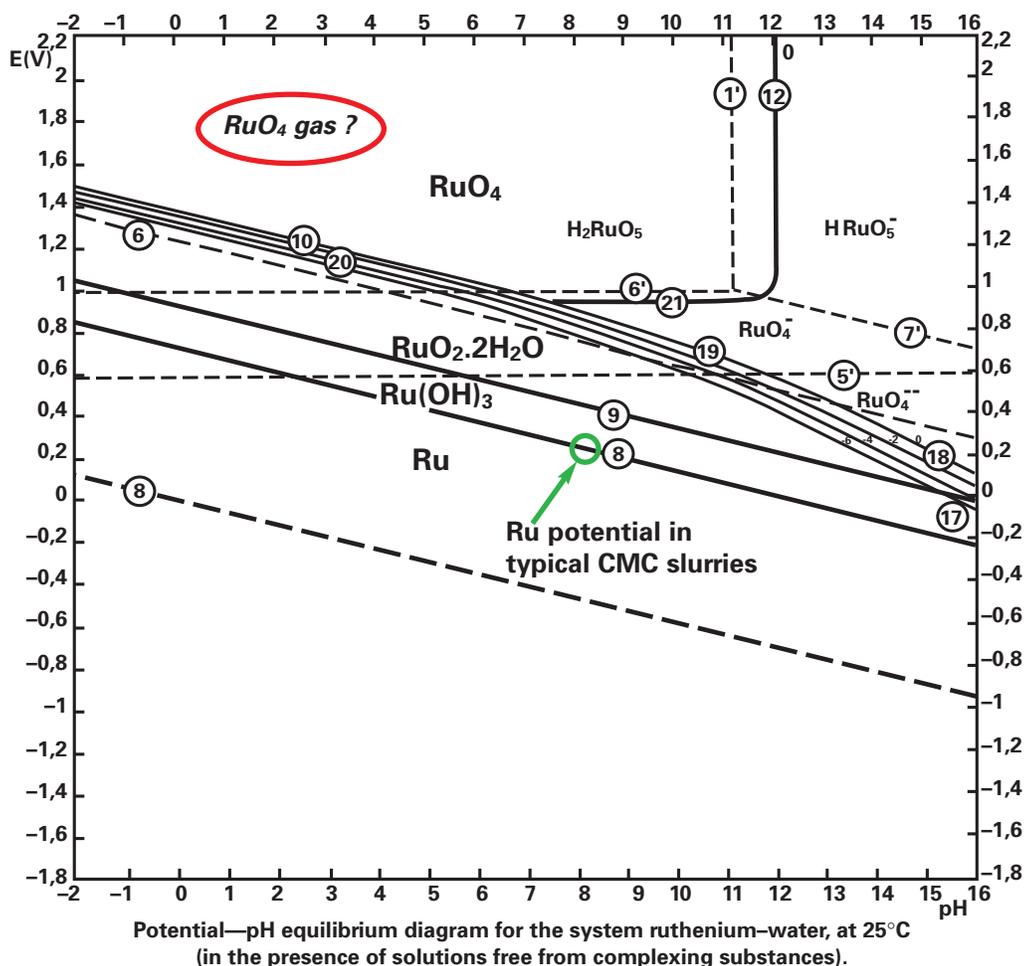


Figure 2. Pourbaix diagram showing that the oxidation region used for Cabot Microelectronics Corporation (CMC) ruthenium slurries is well below the region where toxic RuO_4 forms.

Due to the inherent materials properties of ruthenium, from first principles it is challenging to develop a CMP process that is capable of planarizing even blanket layers. When ruthenium is used as a thin-film within a complex IC device topography, then it is far more difficult to balance the different materials properties. In particular, tantalum (Ta) metal is typically used as the barrier layer in Cu DD structures, and to develop a workable ruthenium CMP slurry set it is essential that a unique abrasive as well as a Ta rate enhancer are both present.

Another unique challenge to the integration of ruthenium into DD copper flows is that the two metals form a galvanic

cell when they are isolated during CMP processing. To offset the galvanic cell effect, a proper oxidizer and Cu film former is needed to adjust the Cu potential and prevent corrosion.

Fundamental research at Cabot Microelectronics led to the development of a number of slurry formulations specifically designed to yield ruthenium removal while maintaining compatibility with copper, dielectrics, and other materials present in the integrated film stack. Abrasive selection required an extensive series of experiments to evaluate the applicability of 12 different particles. Most particles led to tantalum and ruthenium removal rates well below 50Å/min., while only one provided initial favorable removal rates for both metals >200Å/min. Following slurry chemistry development has allowed for removal rates to be increased up to 600Å/min. or higher for these metals, depending upon the desired selectivities to other materials.

The slurries developed by Cabot Microelectronics fall into two categories of performance; dielectric selective and dielectric nonselective. These two slurry families provide the ability to clear patterned ruthenium barrier films quickly and efficiently and together they provide the option to the design engineer to either stop on dielectric (selective approach) or achieve a target of dielectric loss (nonselective approach).

Ru CMP Experiments

Slurry formulations were created through the combination of commercially available chemical reagents and abrasive particles, as previously reported [12]. Slurries were prepared by adding specified amounts of formulation chemicals to deionized water with agitation. The pH of the slurry chemistry was adjusted to insure compatibility with the particle raw material. The particles were added to the slurry with mixing, and potassium hydroxide or nitric acid was used to bring the slurry pH to the final desired value.

New wafers of 200 mm diameter with blanket films were used as received from the various suppliers. Planarization evaluations for blanket wafers were completed using an Applied Materials Mirra 200mm tool. Planarization evaluations for patterned wafer performance were completed using an Applied Materials Reflexion LK 300mm tool. The planarization downforce for all measurements was 1.5 psi with a slurry flow rate of 200mL/min.

Prior to barrier planarization, patterned wafers were planarized to endpoint with Cabot Microelectronics iCue® C8200 copper CMP slurry. For barrier planarization, a Rohm and Haas Politex embossed CMP pad was used for blanket and pattern planarization experiments. Removal rate was determined with the use of a KLA-Tencor RS-100

four point probe resistivity measurement tool. A KLA-Tencor eV300 scanning electron microscope was used to perform EDX analysis for residual ruthenium on pattern wafers. Dishing measurements on pattern wafers were carried out with a Veeco Vx310 Atomic Force Profiler.

Ru CMP Development

One slurry family developed by Cabot Microelectronics, known as Sentinel™ B9000, includes a number of formulations that are designed for performance targets in terms of copper:dielectric:ruthenium selectivity. By taking advantage of a proprietary particle technology invented by Cabot Microelectronics, these slurries have the ability to remove ruthenium at a high rate yet maintain low copper rate which can be tuned with slurry formulations. The unique particle technology of this slurry allows the CMP process to stop on dielectric with only a low level of dielectric removal. Tests show that the removal rates of all tested materials is Prestonian: displaying a direct correlation to the pressure*velocity product (Fig. 3).

Effect of P*V on RR of Tested Materials

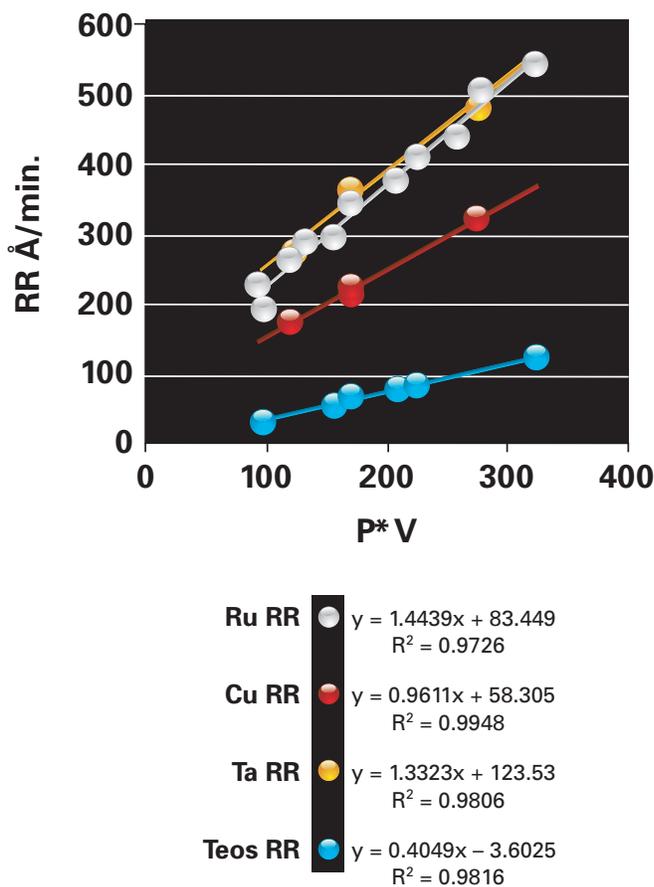


Figure 3. CMC ruthenium slurry family shows purely Prestonian behavior for materials of interest in copper dual-damascene interconnects.

A comparison of the planarization performance of one slurry of the family, Sentinel™ B9003, on representative blanket wafers is shown in Table 1. Multiple planarization experiments on patterned wafers with ruthenium barriers were completed, and the first criterion to be met is whether the ruthenium has been completely removed from the unintended features on the wafer. EDX scans of patterned wafers before and after polish with Sentinel™ B9003 show that CMP for 30 seconds removes all of the ruthenium from the wafer. Further analysis of the wafer at the center, middle, and edges confirm the lack of ruthenium across the wafer at features of all sizes.

With the confirmation of complete ruthenium removal, the question of slurry performance turns to topography change during the final CMP step in the DD flow. Standard Cu DD processing uses different processes and slurry sets on each of three platens in the tool: P1 for bulk Cu removal, P2 for final Cu removal, and P3 for barrier removal. We studied the dishing and erosion of patterned wafers post-P2 using Cabot Microelectronics iCue® C8200 copper CMP slurry, in comparison to the dishing and erosion post-P3 with Sentinel™ B9003 (Fig. 4).

Table 1	
Film	Sentinel™ B9003 Removal Rate (Å/ min)
Copper	50-150
Tantalum	500-600
Ruthenium	300-400
Silicon oxide (TEOS-based)	<50
Silicon oxycarbide (low-k)	50-500

CMP removal rates of Sentinel™ B9003 on 200mm wafers with blanket films at 1.5 psi on Politex pads.

designed to stop on underlying dielectric. The reduction of dishing is positive because that it shows the copper removal rate to be low and under control and slightly lower than the dielectric rate which leads to some correction of the topography.

This type of CMP slurry performance is an ideal fit to emerging three platen recipe schemes where barrier removal at the P2 stage is chosen. In these cases, dielectric thinning and topography correction is completed at P3 with traditional high dielectric barrier slurries [13].

In general, <100Å dishing has been shown on typical features used in 90nm, 65nm, and 45nm node typical features, regardless of the array density. In general the barrier CMP can be tuned with our slurry to correct incoming topography and to yield a targeted dielectric loss.

In contrast to the Sentinel™ B9000 slurry family, Cabot Microelectronics has successfully developed an alternate family of slurries that deliver ‘non-selective’ performance where targeted amounts of dielectric removal are desired. These slurries are designed to deliver ruthenium removal with the ability to correct

incoming topography through tuning and control of film removal rates. For the development of these slurries, the key enabling technology breakthrough was the development of a group of proprietary chemicals that yield ruthenium removal with control of copper removal rates to yield tunability.

Dishing Before & After Polish with Sentinel™ B9003

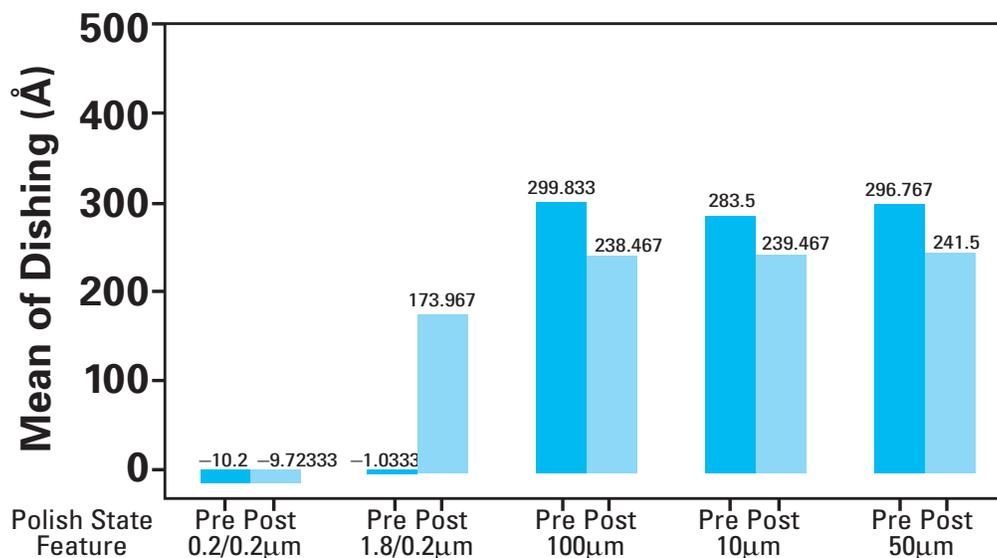


Figure 4. Dishing observed with Sentinel™ B9003 slurry for various pattern feature spacings.

In the analysis of the CMP performance of the Sentinel™ B9003 slurry post-P3, a small change in the dishing can be seen. In general, the copper line dishing is reduced in all features except for the 1.8 micron line. The dishing improvement is in accordance with what is expected from this slurry that has low dielectric removal rates and is

The representative performance of one slurry in this family, Sentinel™ B9515, is illustrated in Table 2. For most of the films planarized, the slurry can be tuned with proper choice of consumables or process conditions. This is advantageous for a wide range of applications when different levels of correction are required. For example, the Sentinel™ B9532 formulation reduces the tantalum removal rate to 600-800 Å/min, while maintaining the same removal rates for other materials as Sentinel™ B9515.

Table 2	
Film	Sentinel™ B9515 Removal Rate (Å/ min)
Copper	100-200
Tantalum	1200-1300
Ruthenium	200-300
Silicon oxide (TEOS-based)	600-800
Silicon oxycarbide (low-k)	100-1000

CMP removal rates of Sentinel™ B9515 on 200mm wafers with blanket films at 1.5 psi on Politex pads.

In a series of experiments similar to those discussed for Sentinel™ B9003, the slurry Sentinel™ B9515 was evaluated in a test where ruthenium patterned wafers were processed with iCue® C8200 to remove copper and to expose the ruthenium barrier. The wafers incoming to the barrier P3 polish were analyzed with a variety of techniques to verify the presence of ruthenium before polish and to assess the incoming topography.

Through EDX analysis, the wafers before Sentinel™ B9515 polish were found to have ruthenium present. After 60 seconds of polish with Sentinel™ B9515 no ruthenium was found to be present on the wafer.

After proving the complete clearing of the ruthenium barrier, the dishing and erosion of a variety of features were measured. Figure 5 shows the dishing of copper features after P1+P2 polish with iCue® C8200 ranges from 200 to 400Å depending on the feature and array size. After processing with Sentinel™ B9515 for 100 seconds, the dishing is significantly reduced on nearly all the features with values close to zero.

These impressive results are from nonoptimized experiments, yet indicate the ability of the Sentinel™ B9515 slurry to correct topography with the appropriate tuning of slurry components and proper selection of polish times. In contrast to Sentinel™ B9003, the ability to clear ruthenium and correct topography in one step is a good fit to traditional two and three platen planarization processes with a stand alone barrier step at the end of the sequence.

The Sentinel™ B9000 slurry family generally improves the surface roughness of deposited thin-films post-CMP. Blanket PVD ruthenium and patterned copper films both with ~1.5 nm average surface roughness showed just ~0.3 nm after CMP.

Galvanic Corrosion

Another important aspect of slurry design is the compatibility of the slurry formulation with regard to ruthenium and copper and the possibility of galvanic corrosion between the two metals. Galvanic corrosion is an electrochemical process that occurs when one metal preferentially dissolves when in electrical contact with another metal. Ruthenium and copper are known to establish galvanic coupling in certain cases; indeed, a critical issue for all semiconductor manufacturing structures, where two or more metals are in contact, is the question of whether galvanic corrosion can occur.

Dishing Before & After Polish with Sentinel™ B9003

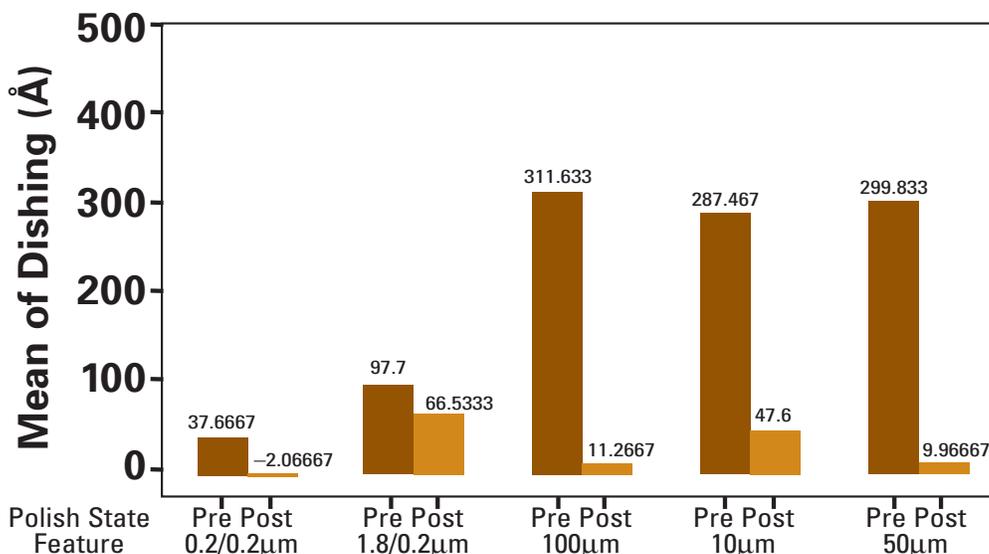


Figure 5. Dishing observed with Sentinel™ B9515 slurry for various pattern feature spacings, showing “negative dishing” over large features to provide for topography correction.

With regard to CMP slurry design, poor choice of slurry formulation ingredients, salts, pH, oxidizers or oxidizer concentration can lead to a situation where copper corrodes which leads to pitting, blisters or in extreme cases complete copper line loss. During the development of Sentinel™ B9003 and Sentinel™ B9515 the slurry formulations were examined via electrochemical testing to determine the possibility of unfavorable galvanic coupling between copper and ruthenium (Fig. 6).

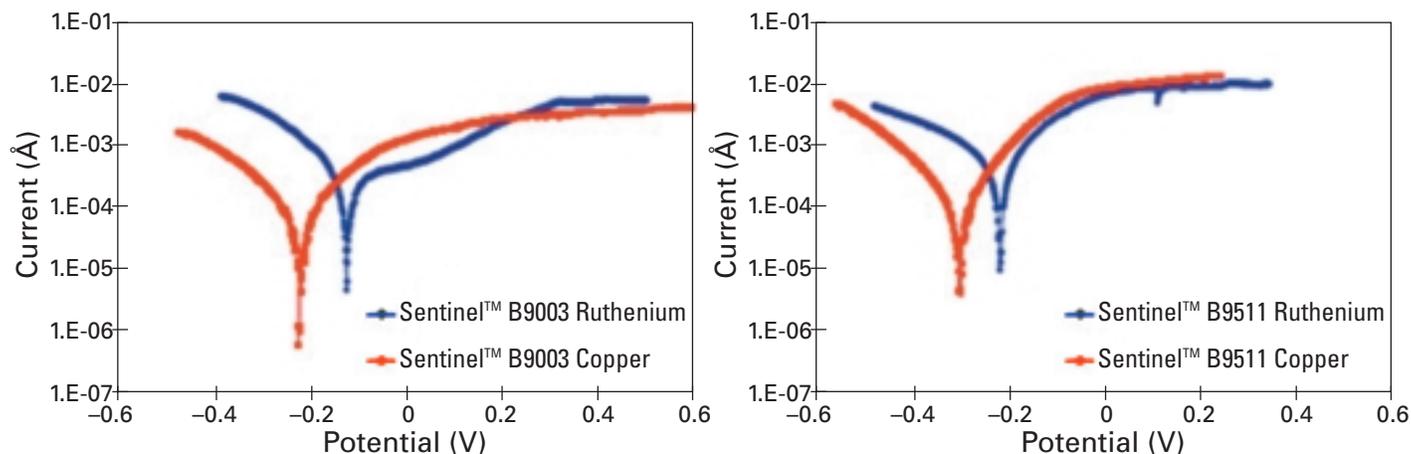


Figure 6. Potential versus Current data for Sentinel™ B9003 and Sentinel™ B9511 slurry formulation showing that unfavorable galvanic coupling between copper and ruthenium does not take place.

The potential versus current data for each slurry indicates that an unfavorable galvanic coupling between the ruthenium and copper does not take place. The location of the intersection of the anodic region of the copper trace and the cathodic region of the ruthenium trace for each slurry indicates that the copper is under slight galvanic attack by

the ruthenium. However, the magnitude of this attack is estimated to be less than 100Å/min. Through proper selection of the oxidizer and copper film former, the copper potential is tuned to be close to that of ruthenium.

Electrochemical testing is generally a good indicator of catastrophic galvanic corrosion, however in cases such as with Sentinel™ B9003 and Sentinel™ B9511 where low levels of corrosion are expected, the best test of compati-

bility is with patterned wafer planarization. Our experiments which have examined copper:ruthenium patterned structures after CMP with Sentinel™ B9003 and Sentinel™ B9511 show no presence or indication of galvanic corrosion, as predicted by the electrochemical data. ■

Ruthenium metal is an important new barrier material being integrated into advanced IC chip manufacturing. CMP of ruthenium presents new challenges due to the unique properties of this refractory material. In particular, proper slurry selection and control is needed to ensure that a toxic oxide of ruthenium does not form during CMP processing.

A novel slurry system capable of removing both ruthenium and tantalum layers, with tunable rates for copper and dielectrics, has been developed. For copper barrier applications, low dielectric removal as well as low dishing have been shown at high removal rates using a soft pad.

CONCLUSIONS

Cabot Microelectronics Corporation has thoroughly explored the ruthenium CMP slurry space, including the use of other particles and chemistry sets, so that uniquely targeted formulations may be developed for applications in the future. In particular, ruthenium is under development as the bottom electrode for future DRAM metal-insulator-metal (MIM) capacitor structures; slurries have already been tuned to provide different material selectivities for high removal rate of the relatively thick ruthenium overburden on the top side of such structures.

ACKNOWLEDGMENTS

iCue is a registered trademark and Sentinel is a trademark of Cabot Microelectronics Corporation. Politex is a trademark of Rohm and Haas (a subsidiary of The Dow Chemical Company). Mirra and Reflexion are registered trademarks of Applied Materials Inc.

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