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Bartlet DeProspo
University at Albany, State University of New York

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Bartlet DeProspo

Professor Dunn

Honors Thesis

11th May 2016

Fundamental Interdiffusion Analysis of Ruthenium and Cobalt Films

Resistance has always had an impact on determining future technology innovations in regard to interconnect technology. As device dimensions continue to shrink past the 10nm technology node the resistance in the back-end-of-line (BEOL) begins to play a more important role in overall device performance. To compensate for the increasing resistivity of Copper lines as dimensions continue to shrink, as shown below in Figure 1, semiconductor companies have been trying to find places to lower resistance elsewhere.

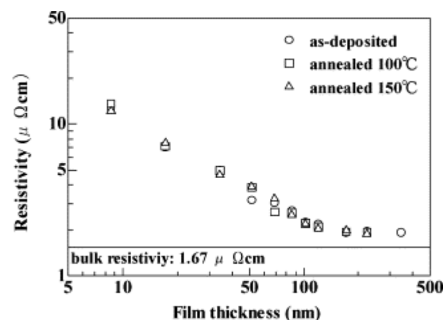

Figure 1 Copper Resistivity vs Film Thickness[6]

One area that has been specifically targeted for resistance compensation is the liner material. Current integration schemes are utilizing Tantalum (Ta) or Tantalum Nitride (TaN) based films to line the trenches. Unfortunately, Ta has a resistivity of 13.1 μΩ*m and this is an area where cutting back on resistivity can greatly enhance device performance and offset the resistivity

increase from copper [4]. Many companies such as Qualcomm, Applied Materials and IBM have publicly disclosed that they are investigating ruthenium and cobalt as a potential liner material [3] [5] [8]. The motivation for investigating ruthenium and cobalt is backed by the lower resistivity values of 7.4 μΩ*m and 5.81μΩ*m respectively [4]. However, IBM has also discussed utilizing cobalt on top of copper interconnects for device performance since around 2010 [2]. In an interconnect technology where there are ultra-thin film thicknesses in contact with each other there is a need to understand the possible interaction that may occur between the films. However, cobalt and ruthenium data is not readily available and most of the systems that are available utilize a third metal such as nickel or copper. Trying to find a publication that focuses just on these two metals proved to be difficult.

The ability to obtain a surface level understanding of how these two metallic films interact with each other is of interest to both industry and academia. More than understanding the interaction, the ability to obtain the activation energy (E_a) and the diffusion coefficient (D_o) values is of more interest. By obtaining these variables, the Arrhenius Equation, shown below, can be evaluated to obtain a diffusion value (D) for any temperature.

$$D = D_o e^{-\frac{E_a}{RT}}$$

After a diffusion value (D) is obtained for a given temperature the distance may then be determined based upon a solution to Fick’s Law shown below.

$$x \cong \sqrt{4Dt}$$

To obtain these variables based upon experimentation we must evaluate the equation for different distances and times. In this equation x, is diffusion distance in meters, D is the diffusion constant in $\frac{m^2}{s}$ and t is time in seconds [1]. In the following experimentation the diffusion distance (x) is determined based upon TOF-SIMS profiles. Given that each sample was annealed for a set time of 1800 seconds we can take our diffusion distance, and our time in seconds, to evaluate a diffusion constant (D).

After obtaining an array of diffusion constants across a temperature range we may then proceed in extracting the necessary activation energy and diffusion coefficient. The specific graph of the natural logarithm of the diffusion constant (D) vs $\frac{1}{T}$ where, T is our temperature in kelvin is attainable. This plot will allow D_o and E_a values to be obtained. From the plot, a linear trend line is fit to the experimental data. The equation of that linear trend line will be in the standard point-slope form. Comparing the point-slope form to the Arrhenius Equation allows for D_o and E_a to be extracted.

$$D = D_o e^{-\frac{E_a}{RT}}$$

$$\ln(D) = -\frac{E_a}{R} * \frac{1}{T} + \ln(D_o)$$

$$y = m * x + b$$

Examining the two equations it is shown that the slope (m) is equal to the $-\frac{E_a}{R}$ and the y-intercept (b) is equal to the $\ln(D_o)$.

$$m = -\frac{Q_d}{R} \ and \ b = \ln(D_o)$$

Utilization of the two above equations allows the activation energy and diffusion coefficient for cobalt diffusing into ruthenium to be obtained from the equation of the best fit linear trend line.

A design of experiments (DOE) was established, as this interaction is not well versed, to deliver an array of understanding for various scenarios.

Wafer	TaN	Ru	Co	Cap
1	60nm	20A CVD Ru	18A CVD Co	100A NBLOK
2	60nm	30A CVD Ru	30A CVD Co	100A NBLOK
3	60nm	30A CVD Ru	100A CVD Co	100A NBLOK
4	60nm	200A CVD Ru	200A PVD Co	10nm TaN Low/No Bias (No Pref)
5	60nm	100A CVD Ru	100A PVD Co	100A NBLOK
6	60nm	100A CVD Ru	30A CVD Co	100A NBLOK
7	60nm	100A CVD Ru	100A CVD Co	100A NBLOK

Figure 2 DOE Split Table with films deposited on 300mm Si Wafers with TaN being the bottom most layer. Where A = Angstroms, nm = nanometers

From the design of experiments we sought to obtain different levels of understanding with specific diffusion data to be obtained from wafer 4. Other wafers in the split table offer valuable insight into the interaction at ultra-thin thicknesses as well as processing comparisons. In standard metal and via BEOL processing conditions a dielectric cap deposition occurs. This deposition is simulated by the NBLOK capped wafers. The NBLOK cap is deposited at 300°C for approximately 60 seconds. Wafer 4 is the condition above that is as close to an initial starting point as possible because the 10nm TaN cap layer is deposited at room temperature. This DOE will provide immense amounts of exploratory data on the interaction between ruthenium and cobalt films.

Typical BEOL processing occurs below 500°C as it is important to the final structure. To best capture the processing below this temperature various anneals were performed on the

samples. After the silicon wafers had finished processing the wafers were diced up and annealed in a tube furnace and then sent for TOF-SIMS analysis. Upon examination of initial results it was noted that a significant level of diffusion did not occur at 100°C and 200°C for the duration of 30 minutes. Also temperatures above 400°C had shown near complete mixing. In order to precisely obtain values for activation energy and diffusion coefficient the temperature between 300°C and 400°C was focused on and anneals were added in 25°C increments. These increments allowed for us to extract the best possible diffusion data scenario.

For the TOF-SIMS analysis two beams are utilized. One is for analysis purposes and the other is for sputtering through the material. The analysis beam scatters secondary ions from the surface as the beam is pulsed at the sample. These secondary ions are then accelerated into a flight path. The time-of-flight (TOF) is measured and the time the ions are in flight is directly related to their respective mass. The mass can then be correlated to a specific element for quantitative studies. The sputter beam allows for the analysis to slowly progress through the sample. The output of a standard TOF-SIMS analysis is shown graphically in counts vs seconds. Where counts is how many atoms of a specific element were observed and seconds is how long the material has been sputtered through. In the analysis of these thin-film samples a Bi^{+} beam was utilized at 25 keV and the angle of incidence of the beam to the sample surface was set to 45°. The sputter beam that was utilized was a 1 keV Cs^{+} beam also at a 45° angle of incidence. This methodology was chosen because of its extremely high sensitivity and well resolved mass resolution.

Since the output of our SIMS data does not directly give us distance, high-resolution TEM's were taken of neutral conditions for calibration purposes.

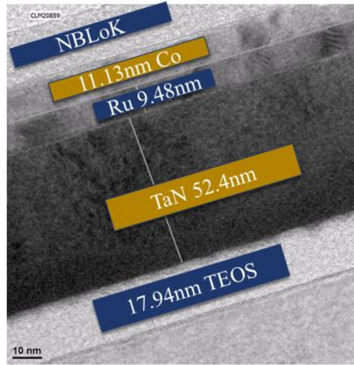

Figure 3 High-Resolution TEM of neutral condition

As shown in figure 3, actual thicknesses can be obtained for each of the deposited layers. A sputter rate can also be extracted from the TEM's in conjunction with our SIMS analysis on the neutral conditions. Since the SIMS profile displays how long it takes to get through a certain layer, and we now know how thick that layer is from the TEM. A sputter rate in $\frac{m}{s}$ can be obtained. This sputter rate is then utilized to calculate a diffusion distance (x) from the SIMS profiles. This is done by taking our calculated sputter rate and multiplying the time from the SIMS profile, in seconds, to achieve a distance in meters.

In order to ensure that we extract the most precise diffusion values possible; the 200Å Ru / 200 Å Co sample was specifically selected for extraction. This sample is chosen due to the room temperature cap that is deposited on top of the cobalt. Examining a snapshot of the plots below, it is apparent that with temperature as well as time the cobalt diffuses farther into the ruthenium.

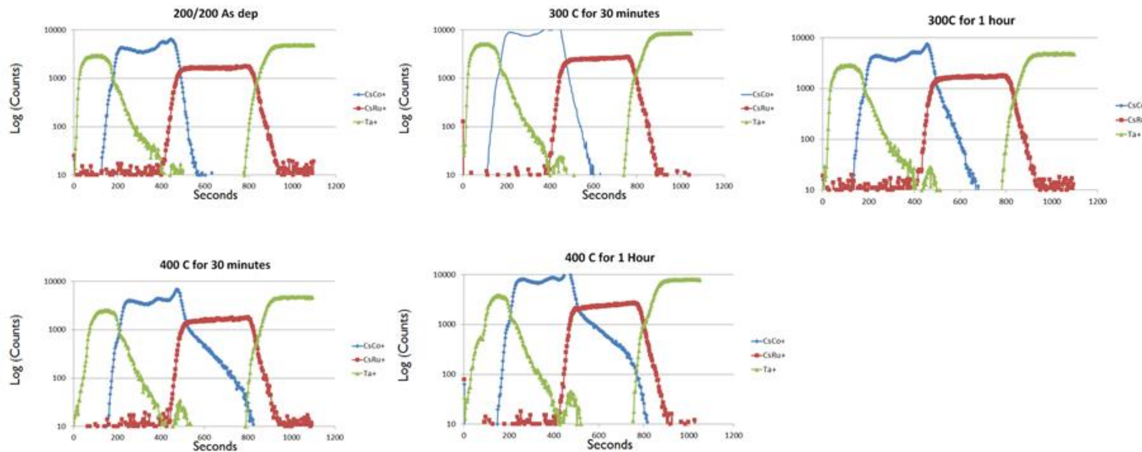

Figure 4 SIMS profile snapshot of 200A Ru and 200A Co Samples where a) is the as deposited condition b) 300C anneal for 30 minutes c) 300C anneal for 1 hour d) is a 400C anneal for 30 minutes and e) is a 400C anneal for 1 hour

This snapshot displays the rationale on the chosen time of 30 minutes ensuring that we were not measuring build up at the ruthenium and tantalum interface but rather cobalt's diffusion into ruthenium. The snapshot also shows consistent diffusion both with time and with temperature into the ruthenium. We see a consistent shift in the end of the cobalt peak inside of the ruthenium peak when we examine the SIMS profiles for 30 minute conditions in 25°C increments from 300°C to 400°C. Using the methodology explained the peak end time can be converted to a distance by utilizing the sputter rate obtained from the TEM. After obtaining the diffusion distances from the SIMS profile, the solution to Fick's Laws from above allows for us to evaluate a diffusion value (D) for each temperature.

$$x \cong \sqrt{4Dt}$$

After calculating each D value, the graph of the $\ln(D)\ vs\frac{1}{T}$ was evaluated and a linear trend line was fitted to the graph.

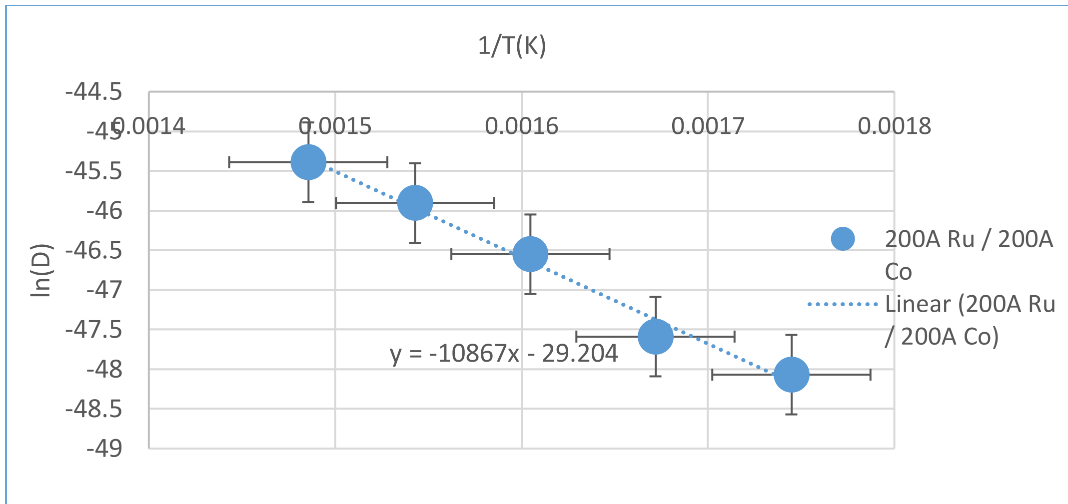

Figure 5 Graph of Ln(D) vs 1/T for 200A Ru - 200A Co Sample

Utilizing the above plot for the calculation of the E_a value can be seen below.

$$-10867\frac{J}{Kmol} = -\frac{E_a}{R}\, E_a = 90.348\frac{kJ}{mol} = 0.9363\frac{eV}{atom}$$

The D_o value was also calculated from the linear trend as well.

$$\ln(D_o) = -29.204\; D_o = 2.074E - 13\frac{m^2}{s}$$

When compared to other metal systems it appears that the energy for activation for cobalt to diffuse into ruthenium is rather low. However, the low activation energy is offset by the diffusion coefficient value being small. The E_a represents the ability for cobalt to easily diffuse into ruthenium. However, D_o represents that cobalt does not attempt to diffuse into ruthenium as frequently as some other metal systems. These values are consistent with the amount of diffusion that is observed at the given temperatures and over the respective time.

Alternative data from other wafer splits was also obtained. If we examine first the ultra-thin film results it is observed that the films are almost completely mixed after processing.

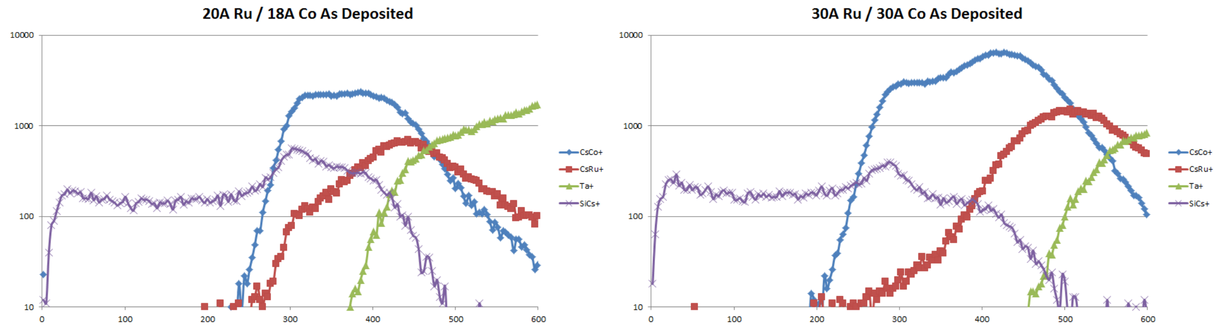

Figure 6 As deposited SIMS profiles for a) 20A Ru and 18A Co b) 30A ru and 30A Co

This mixing is due in part to the thickness of the films and also the dielectric cap deposition. This cap deposition takes place at approximately 300C for 1 minute. In figure 6a and 6b it should be noted that the SIMS sputtering rate through the samples was drastically reduced in an attempt to capture the cobalt-ruthenium interface as best as possible. For future experimentation at ultra-thin film thicknesses such as these; it is necessary to utilize a cap material that deposits at room temperature such as TaN. The annealing conditions for these samples showed minor changes from the deposited conditions that are displayed above.

Examining the next set of SIMS profiles in figures 7a and 7b the assumption that Co diffuses into Ru was verified.

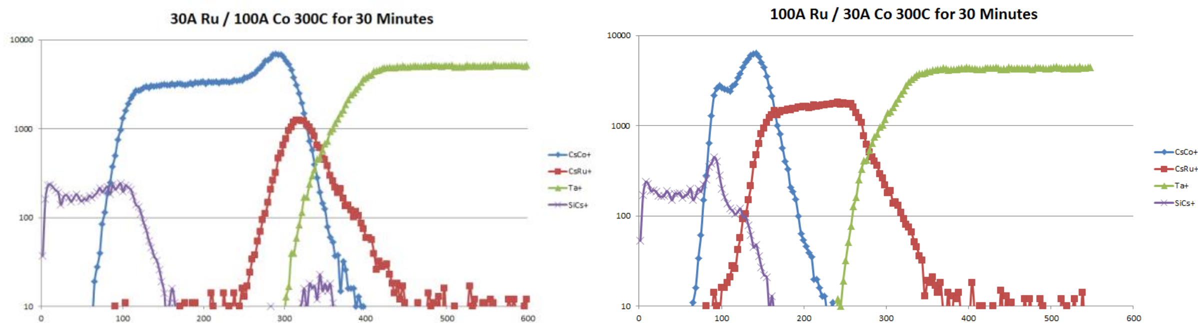

Figure 7 a) 30A Ru/100A Co for 300C at 30 minutes b) 100ARu/30A Co for 30 minutes

It is observed that in figure 7a after annealing the sample that the cobalt has completely mixed into the ruthenium layer. This is due to the low activation energy for cobalt to diffuse into ruthenium. In figure 7a the lack of available ruthenium sites means that the overabundance of cobalt at the interface will lead to faster diffusion into the ruthenium layer. The reciprocal condition in figure 7b shows that the cobalt only slightly enters the ruthenium at this condition. This is due to the lack of cobalt at the interface meaning that there are fewer atoms trying to successfully mix with the ruthenium.

The final observation this work sought to understand was the difference between physical vapor deposition (PVD) cobalt films as compared to chemical vapor deposition (CVD) based cobalt films. In figure 8 the comparison is depicted via SIMS profiles. Examination of figure 8a and 8c depicts that CVD cobalt diffuses faster into ruthenium than PVD cobalt does. Comparison of figures 8b and 8d expresses the same result. However, more experimentation is needed to draw a final conclusion as our data set is limited to 1 cycle of experimentation. This preliminary conclusion can possibly be explained by the excess precursor gas that would be left over from

the CVD process. Depending on the gas it could potentially enhance cobalt's ability to diffuse into the ruthenium layer.

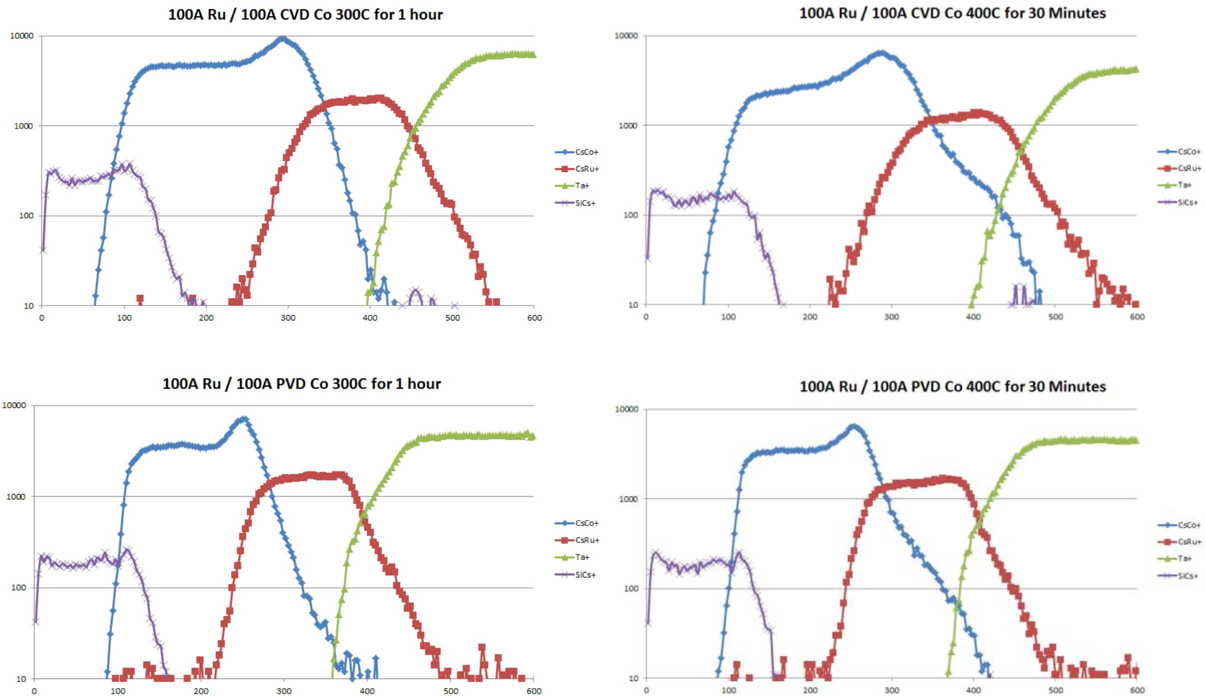

Figure 8 Comparison of PVD Co vs CVD Co a) CVD Co at 300C for 1 Hour b) CVD Co at 400C for 30 minutes c) PVD Co at 300C for 1 hour d) PVD Co at 400C for 30 minutes

In order to draw finalized conclusions from these preliminary results that were obtained a second cycle of experimentation is necessary. A reported activation energy of 0.93 $\frac{eV}{atom}$ appears to be consistent with the amount of diffusion that was observed across the array of experiments as is the D_o value of 2.074E-13 $\frac{m^2}{s}$. The repeatability of these values is of extreme importance and is a requirement for this work in the future. However, it is beyond apparent that these two metal films have a high tendency to intermix with one another. This tendency to mix must be evaluated further to understand if this issue is of concern to BEOL process integrators. It is expected that any cobalt and ruthenium that comes into contact in an interconnect environment will likely continue to mix as subsequent metal and via levels are fabricated. This mixing is assumed to

result in an increase in liner resistivity which would negatively impact the overall semiconductor technology.

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