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Atomic layer deposited ultra-thin metal nitride barrier layers for ruthenium interconnect applications

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RC-time delay in Cu interconnects is becoming a significant factor requiring further performance improvements in future nanoelectronic devices. Choice of alternate interconnect materials, as for example, refractory metals, and subsequent integration with underlying barrier and liner layers are extremely challenging for the sub-10 nm nodes. The development of conformal deposition processes for alternate interconnects, liner, and barrier materials are crucial in order for implementation of a possible replacement for Cu interconnects for narrow line widths. In this study we report on ultra-thin (~3nm) chemical
vapor deposition (CVD) grown ruthenium films on 0.5 and 1 nm thick metal nitride (TiN, TaN) barrier layers deposited via atomic layer deposition (ALD). Using scanning electron microscopy, we determined the effect of the underlying barrier layer on the coverage of the ruthenium overlayer. We utilized synchrotron x-ray diffraction with in-situ rapid thermal annealing to investigate the thermal stability of the barrier layers and determine the effective activation energies of barrier failure leading to ruthenium monosilicide formation. For Ru films deposited directly on Si and on 0.5 nm MN (M=Ti, Ta) covered Si substrates, silicide formation proceeds via a two-step crystallization process involving lateral nucleation above ~ 440 °C followed by thickening of the ruthenium monosilicide layer above ~520 °C. This silicidation temperature of ~ 440 °C could be potentially problematic in back-end-of-the-line (BEOL) processing since it is close to the typical thermal budget used. However ~1 nm thick ALD MN (M=Ti, Ta) was found to be adequate to block silicide formation up to ~ 580 °C and ~ 620 °C for TiN and TaN, respectively, and also aided in superior coverage of the CVD ruthenium overlayer (>90%). The results reported here might be useful to ascertain annealing temperature and time for BEOL process and integration optimization without reaching a state where ruthenium silicides start forming.

I. INTRODUCTION

The widths of metal interconnect lines in semiconductor devices are now at sub-10 nm scales for advanced technology nodes. At this small length scale, the combined resistance of the copper interconnect, adhesion liner, and the barrier layer is becoming the dominant obstacle to the RC time-delay. For suppressing Cu diffusion at the typical
thermal budgets encountered during back-end-of-the-line (BEOL) processing, a minimum physical thickness of the barrier and adhesion liners is required. Because of physical constraints on barrier/liner layer thicknesses, the actual volume of the metal component of interconnects becomes an even smaller fraction of the total interconnect width as the linewidth dimensions are further reduced. Due to increasing surface and grain boundary scattering effects\(^3\), the resistivity of copper also increases significantly in these narrow lines. In addition, issues related to electromigration in Cu will also become more significant at these nanodimensions\(^4\). The performance improvement in future nanoelectronic devices will depend heavily on the choice of alternate interconnect materials and process development for conformal deposition of barrier and interconnect layers.

Refractory metals are promising candidates for alternate interconnect materials because they possess higher melting temperatures, relatively small bulk resistivity values, and shorter inelastic mean free paths (IMFPs) for electrons as compared to the IMFP in Cu\(^5\). Ruthenium has already found use as the seed layer for electroplating of Cu\(^6,7\). Ruthenium, being a refractory metal, is stable in contact with SiO\(_2\) and may offer pathways for barrierless metallization. However, ultra-thin metal nitride-based barrier layers may still be necessary from an adhesion standpoint during the subsequent chemical mechanical planarization step in the interconnects\(^8\).

Thermal stability is a critical property for a good barrier layer. In addition, a denser barrier layer will contain fewer defects, voids and loosely packed grain boundaries. The microstructure of the barrier layer also plays a critical role for minimizing the grain boundary diffusion paths. Although a defect-free single crystalline barrier layer would be ideal, it is not practical to include such a process in the high
volume manufacturing environment in a semiconductor foundry due to constraints related to thermal budget and materials choice. Polycrystalline films are undesirable as barrier layers, while films with columnar grain structure are particularly problematic as the grain boundaries could extend throughout the entire thickness of the film giving connected pathways for diffusion across layers. Accordingly, either amorphous films or films with nanocrystallites in an amorphous matrix are the most desirable diffusion barriers. Barrier layers based on refractory metal nitrides are among the leading candidates because they possess relatively low chemical reactivity and high melting points. The choice of the material and determination of a suitable conformal deposition process is essential for integrating barrier materials that could sustain the typical thermal budget, mechanical stress, and electrical stress encountered during fabrication and operation of a semiconductor chip. A line-of-sight technique like physical vapor deposition (PVD) for metal nitride layer deposition could be replaced by a more conformal deposition technique like ALD, resulting in a denser and more uniform barrier layer.

In this work, we have grown 0.5 and 1 nm thick ALD metal nitride barrier layers on chemically cleaned Si <100> substrates followed by chemical vapor deposition (CVD) of ~3 nm thick ruthenium layer, and evaluated the effect of underlying barrier layers on the properties of the CVD Ru overlayer. Using a series of in-situ rapid thermal annealing (RTA) x-ray diffraction (XRD) experiments performed at synchrotron facilities, we have determined the temperature at which silicides formed and calculated the effective activation energy of the silicidation. There also exist other techniques, as for example, bias-temperature-stressing, for assessing barrier effectiveness. We have used the RTA XRD method since this method could be corroborated with the thermal budget requirements during the film deposition steps of a manufacturing process. Although CVD of ruthenium is possible at relatively low
temperatures, annealing at higher temperatures may be necessary for filling of future interconnect lines to avoid pinholes and seam voids in the structure. A recent study by Wen et al.,\textsuperscript{11} has shown seamless filling of conformally deposited Ru into 9.5 nm wide interconnect lines owing to recrystallization of Ru into larger grains at slightly higher annealing temperatures.

II. EXPERIMENTAL

A. Film Deposition

The film stacks were deposited on 300 mm bare Si <100> wafers using a TEL Trias Tandem\textsuperscript{TM} cluster tool. Prior to loading the wafers in the cluster tool, an ex-situ native oxide removal was performed on the Si wafers to form H-terminated Si.\textsuperscript{12,13} After loading in the cluster tool, a degas/pre-cleaning step was performed and the wafers were moved to another deposition chamber without any vacuum break for ALD of TiN and TaN layers using TiCl\textsubscript{4} and Ta(NCMe\textsubscript{3})(NEtMe\textsubscript{3}) (Me=CH\textsubscript{3} and Et=C\textsubscript{2}H\textsubscript{5}) precursors, respectively, with NH\textsubscript{3} used as a co-reactant. The steady-state growth per cycle (GPC) of ALD TaN was \textasciitilde 0.7 Å/cycle at 350 °C as described previously\textsuperscript{14,15} and the steady-state GPC of ALD TiN was \textasciitilde 0.35 Å/cycle at 430 °C. The deposition of the metal nitride layer was followed by CVD of \textasciitilde 3 nm ruthenium using a Ru\textsubscript{3}(CO)\textsubscript{12} precursor\textsuperscript{16}. A control stack of CVD Ru (3 nm)/Si was also studied for barrierless metallization. For comparison purposes, a second control stack of PVD Cu (25 nm)/Si was also measured. In total, six films were studied, namely, CVD Ru (3 nm)/ALD MN (x nm)/Si (M = Ti, Ta; x = 0, 0.5, 1) and PVD Cu (25 nm)/Si. The thicknesses of the films were measured using inline X-ray Fluorescence and also corroborated with spectroscopic ellipsometry measurements.
B. **Scanning Electron Microscopy (SEM)**

To determine the Ru film coverage with or without the under-layer of ALD metal nitride (TiN, TaN), SEM images of the as-deposited ruthenium films were collected using a Hitachi S-5500 SEM operated at 4 keV. The SEM images presented in Figure 1 were collected in secondary electron mode, which is more surface sensitive and provides greater resolution than backscattered electron mode. The fractional coverage of the Ru overlayer covering the underlayer was estimated using ImageJ software\textsuperscript{17}. For automated boundary-detection around the pin-holes with arbitrary shapes, the SEM images were processed using the *Trainable Weka Segmentation* plugin\textsuperscript{18} in ImageJ software.

C. **Rapid Thermal Annealing (RTA)**

In-situ rapid thermal annealing (RTA) X-ray diffraction was done in order to determine the effectiveness of the ultra-thin ALD metal nitride layers as diffusion barriers for potential application in advanced interconnects. Repeat measurements of some of the film-stacks were done to check reproducibility. The first set of experiments was done at the A2 beamline of the Cornell High Energy Synchrotron Source (CHESS) using a Dectris Pilatus 300K area detector and x-rays of energy 8.02 keV. A custom made portable heating stage fitted with a beryllium dome was used for sample mounting and annealing at CHESS. The second set of experiments was done at the IDEAS beamline of the Canadian Light Source (CLS) using a remote-controlled robotic sample changer, a beryllium-window-fitted chamber with a heating stage capable of reaching 1200 °C, a custom linear detector (8 cm Si strip detector, 640 pixels)\textsuperscript{19}, and x-rays of energy 8.02
keV (1.5% bandpass in energy; flux $\sim 10^{13}$ photons/sec) selected by a W-Si multilayer monochromator. A $K$-type thermocouple, calibrated using melting points of 3 different eutectic metals (Ag, Au, Al) in contact with silicon, was used for calibrating the temperature with an accuracy of $\pm 3$ °C$^{20}$. The linear detector is capable of collecting data in 100 ms intervals. The detector was placed at 110 mm from the sample, allowing it to collect diffracted x-rays spreading $\sim 40\degree$ in $2\theta$ from the sample kept at the center of the goniometer circle. The diffracted x-rays are emitted radially while the linear detector is located in a vertical line tangential to the detector arm’s $2\theta$ position. In this geometry, only the central pixel of the linear detector is right on the diffraction circle and both $2\theta$ and intensity corrections are required for all the other pixels$^{21}$. This geometrical correction has been applied to the diffraction data reported in this work. The rapid thermal annealing of the samples was done as follows. The samples were cut into small coupons of dimension 16 mm x 13 mm. The coupons were held by molybdenum based clamps onto a molybdenum block which is in contact with a pyrolytic boron nitride resistive heater. To prevent any unwanted oxidation during the rapid thermal annealing process, the heating chamber was evacuated twice to below $2\times10^{-3}$ Torr and then slowly filled with ultra-high purity He. The reading on a zirconia O$_2$ sensor in the exhaust path was below the detection limit in the parts-per-billion (ppb) range throughout the RTA experiments. The films were annealed at multiple ramp rates in the range 0.3 – 13.5 °C/s up to $\sim 900$ °C while the detector was kept fixed with the center at $2\theta = 45\degree$, covering a range of $d$-spacing where XRD peaks from metallic ruthenium and ruthenium silicides (RuSi, Ru$_2$Si$_3$) co-exist. The data was normalized with respect to the peak intensity of a silicon diffraction peak (at $T = 30$ °C) which is also present in the $d$-spacing range.
covered during the experiment. In this manner, it was possible to investigate the failure of the barrier layers \textit{in-situ} by monitoring the formation of ruthenium silicides with increasing temperature.

\textbf{D. Pole Figure Measurements}

In order to investigate the film texture before and after the thermally assisted failure of the metal nitride barrier films via silicide formation, x-ray diffraction pole figure data were collected at the A1 beamline at CHESS using a Pilatus Eiger area detector on a Huber 4-circle diffractometer and x-rays of energy 19.9 keV.

\textbf{III. RESULTS AND DISCUSSION}

\textbf{A. Controlling pinhole density with choice of barrier layer}

The left column of fig. 1 shows the SEM images of the as-deposited ruthenium films (~ 3 nm) studied in this work. The right column of fig. 1 shows the processed images highlighting the pinhole formation in the films where the Ru islands and the visible areas of the substrates are colored in green and red, respectively. We also calculated the percentage area of the underlayer covered by the Ru overlayer using pixel quantification in the ImageJ software\textsuperscript{17}. These values are summarized in table 1. For the films directly deposited on the Si substrate, fig. 1a, ruthenium coalesces into large island-like patches due to surface energy effects, covering 52 ± 2% of the underlayer. For the 3 nm ruthenium films deposited on 0.5 nm of ALD TiN and TaN, figs. 1b and 1c, better surface coverage (70 ± 2% and 81 ± 2% respectively) could be achieved although
multiple pinholes are present. This implies a lower density of the pinholes for films grown on 0.5 nm TaN as compared to TiN films of similar thickness. Figures 1d and 1e show 3 nm ruthenium films deposited on 1 nm thick ALD TiN and TaN films, respectively. The film deposited on 1 nm TiN still shows the presence of a few pinholes (underlayer coverage: 90 ± 2%) whereas the pinholes are virtually nonexistent for the ruthenium film deposited on 1 nm TaN (underlayer coverage: 97 ± 2%).

For effective integration of ruthenium as an alternate interconnect material in devices, a chemical mechanical polishing (CMP) step is required. Recently Wen et al.\textsuperscript{8} reported weak adhesion of ruthenium with silicon (adhesion energy = 1.5 Jm\textsuperscript{-2}), which is at least 3 times smaller than the minimum adhesion energy of ~ 5 Jm\textsuperscript{-2} required for successful CMP of single damascene structures. In their study, they found that incorporation of even a 0.25 nm thick TiN liner significantly increased the adhesion energy (~ 7 Jm\textsuperscript{-2}) for the conformally deposited ruthenium films. We have found that ~ 1 nm thick TaN is necessary for the growth of a Ru film with more or less uniform surface coverage. Pull test experiments\textsuperscript{22} done on the CVD Ru (3 nm)/ALD MN (x nm)/Si (M = Ti, Ta; x = 0, 0.5, 1) films showed that the Ru film strongly adheres to the underlayers when x = 1 (the tool reached its limit of the pulling force to be applied) but the films separate relatively easily for x = 0 and 0.5.

**B. Barrier failure via silicide formation**

In order to study the effect of thermal annealing on the thin film stacks, in particular the effectiveness of the 0.5 nm and 1 nm ALD TiN and TaN layers as diffusion barriers, *in-situ* XRD measurements were conducted at a fixed ramp rate of dT/dt ~
4.5°C/s. Throughout the thermal annealing experiments, the linear detector was centered at a 2θ angle corresponding to \( d \sim 2.4 \text{ Å} \), covering a range of \( \sim 0.9 \text{ Å} \) on either side of the central \( d \)-spacing value. For brevity, we will describe the results obtained from the Ru/Si thin-film stack (fig. 2) although the same discussion is valid for all the thin film stacks studied in this work. Figures S1-S5 in the supplementary material show the results for all the remaining thin-films, viz., CVD Ru (3 nm)/ALD MN (x nm)/Si (M = Ti, Ta; x = 0.5, 1) annealed at \( dT/dt = 4.5 ^\circ C/s \) and PVD Cu (25 nm)/Si annealed at \( dT/dt = 3.0 ^\circ C/s \).

A data analysis routine, RTAPYLYSIS, has been developed in the python programming language for the analysis of rapid thermal annealing data reported here and made available for downloading at GitHub for other researchers doing similar kinds of measurements at synchrotron facilities.

Figure 2(a) shows the x-ray intensity map versus temperature (rapid thermal annealing or RTA plot in short) for the Ru/Si film stack. Three different XRD plots are shown in figs. 2(b-d) corresponding to the three Ru containing phases present at three selected temperatures (100, 580, and 800 °C corresponding to hexagonal Ru, cubic RuSi, and tetragonal Ru\(_2\)Si\(_3\), respectively). The XRD peaks from Ru containing phases in fig. 2(a) are overshadowed by the high intensity of the tail of the Si(311) XRD peak which becomes broader due to increased Si lattice vibrations at higher temperatures. The peaks corresponding to Ru containing phases become more prominent after a polynomial background is subtracted from the XRD plots at all temperatures. Figure 2(e) shows the background subtracted RTA plot for \( 1.95 \text{Å} \leq d \leq 3.3 \text{Å} \) where the peaks corresponding to the different Ru containing phases can be seen more clearly. With increasing temperature, multiple XRD peaks appear and disappear at different \( d \)-spacing values representing three
different Ru containing phases. In order to determine the phase transition temperatures, a narrow $d$-spacing range was chosen around each XRD peak and the integrated peak area is plotted in fig. 2(f). The transition temperatures were determined from the maximum rate of change of the peak area with temperature (fig. 2(g)) and marked by vertical dotted lines in figs. 2(e-g).

For $T < T_c = 439^\circ$C, the Ru film is found to be in its hexagonal phase ($P6_3/mmc$) with $a = 2.71$ Å and $c = 4.28$ Å (PDF #6-663)$^{26}$. All of the XRD peaks appear rather broad due to both the nanoscale nature of the film thickness and the use of a wide energy bandpass monochromator to obtain the necessary x-ray flux for the measurements. Nevertheless, the relative intensities of the observed peaks in fig. 2(b) for $d \sim 2.3$ Å and $d \sim 2.1$ Å indicate that the 3 nm CVD Ru film possesses a random nanocrystalline grain orientation. The intensity of both XRD peaks increases with rising temperature indicating possible crystallization into larger grains of Ru.

At $T = 439$ °C, the peak near $d = 2.3$ Å starts to disappear while the peak near $d = 2.1$ Å shifts slightly towards a higher $d$-spacing value and also becomes more intense. In addition, a new peak starts to appear near $d = 2.9$ Å. On optical inspection, the films become darker in color when heated above $T = 439$ °C. This is the temperature range at which silicon atoms react with the ruthenium to start forming a metal silicide phase. The XRD peak positions match closely with the cubic ruthenium monosilicide (RuSi) phase ($Pm\bar{3}m$) with $a = 2.91$ Å (PDF #01-083-0144)$^{27}$. One of the primary reasons to study such thin Ru films (~ 3 nm) in this work was to identify how the ruthenium silicide phase(s) evolve with temperature, which was at first observed optically in our annealing experiments performed inside a vacuum chamber. Initially both the Ru and silicide
phases are expected to coexist with the fast growing silicide phase eventually consuming all of the Ru. In this case, a portion of Ru is still in the hexagonal phase and slowly converts to RuSi as the Si becomes sufficiently mobile to diffuse through the formed RuSi phase. The peaks corresponding to cubic RuSi near $d = 2.9$ Å and $d = 2.1$ Å persist for $439 \, ^\circ\text{C} < T < 622 \, ^\circ\text{C}$, although the peaks intensify after $T = 524 \, ^\circ\text{C}$. We initially suspected a preferential grain growth of the RuSi phase at $T \geq 524 \, ^\circ\text{C}$ and proceeded with pole figure measurements as shown in fig. S6 in the supplementary file. No signature of preferential orientation of the RuSi phase was observed in the pole figures. This two-stage silicide reaction phenomenon could be understood after Coffey et al. The first stage between $439 \, ^\circ\text{C} < T < 524 \, ^\circ\text{C}$ in fig. 2 could be interpreted as the nucleation and lateral growth of a very thin layer of the RuSi phase in the plane of the substrate. At $T \geq 524 \, ^\circ\text{C}$, the thermal energy is high enough for Si to diffuse across the formed RuSi phase and consume the remaining Ru leading to thickening of the RuSi layer for $524 \, ^\circ\text{C} < T < 622 \, ^\circ\text{C}$ and increased signal intensity as shown in fig. 2. Similar two-step crystallization, first via lateral nucleation followed by thickening, could be found in several thin film silicide and aluminide forming systems.

For $T \geq 622 \, ^\circ\text{C}$, a second phase transition takes place. The XRD peaks near $d = 2.9$ Å and $2.1$ Å disappear and new XRD peaks appear near $d = 2.8$ Å, $2.15$ Å, and $2.0$ Å. These peak positions and intensities are consistent with a more silicon-rich silicide Ru$_2$Si$_3$ phase with random orientation of the nanocrystallites. The XRD peak positions match well with a tetragonal structure ($P4c2$) with $a = 5.53$ Å and $c = 8.82$ Å (PDF #01-070-9281). The structure of Ru$_2$Si$_3$ may equally well be explained by an orthorhombic unit cell (Pbcn) with $a = 11.06$ Å, $b = 8.93$ Å and $c = 5.53$ Å (PDF #32-0978) which is
approximately half of the tetragonal structure (with \(P\bar{4}c2\))\textsuperscript{37}. But that orthorhombic phase is usually observed at lower temperatures\textsuperscript{37}.

The CVD Ru (3 nm)/ALD MN (x nm)/Si (M = Ti, Ta; x = 0, 0.5) film-stacks studied in this work showed similar phase transitions with thermal annealing\textsuperscript{23}: the silicidation reaction proceeds via formation of a cubic ruthenium monosilicide phase followed by the formation of a more stable silicon-rich Ru\(_2\)Si\(_3\) in tetragonal phase at higher temperature. The RuSi to Ru\(_2\)Si\(_3\) transition in these thin films is believed to proceed via “nucleation-controlled silicide reactions”\textsuperscript{37} possibly controlled by stress or surface effects\textsuperscript{38}. The larger density of pinholes in these films (fig. 1) also points towards Ru and Si being in direct contact in many places, which could potentially aid the RuSi nucleation process. For the CVD Ru (3 nm)/ALD MN (x nm)/Si (M = Ti, Ta; x = 1) film-stacks, a better coverage of the Si substrate could be achieved. As such, this two-step process of RuSi formation is not observed as can be seen in fig. 3 for the plots of rate-of-peak-area-change vs. temperature for the 5 sets of Ru film-stacks reported in this work. The metal nitride barriers in these two films fail at a much higher temperature compared to the films with no metal nitride barrier and sub-nm thick metal nitride barriers.

**C. Kinetics of silicide formation with and without a barrier layer**

at different ramp rates \(dT/dt\)

All the CVD Ru (3 nm)/ALD MN (x nm)/Si (M = Ti and Ta; x = 0, 0.5, 1) thin-film stacks, along with a control film of PVD Cu (25 nm)/Si, were studied for metal silicide formation indicating barrier failure with thermal annealing at different ramp rates \(dT/dt\). The onset of silicide formation was used to determine the barrier failure
temperature \((T_c)\) as shown in fig. 2. The total thermal budget largely depends on the ramp rate during the RTA process, which in turn affects the transition temperature. The dependence of the value of \(T_c\) on the ramp rate \((dT/dt)\) is shown in fig. 4 for the Ru/Si thin-film stack annealed at four different ramp rates: \(T_c\) is higher for films annealed at higher \(dT/dt\).

The kinetics of thermally driven metal silicidation can be described using the Kissinger equation\(^{39,40}\) which assumes the diffusion limited growth of the metal silicide phase\(^{41,42}\). In this analysis the Arrhenius plot is used in order to determine the reaction rate and effective activation energy of thermally driven processes from time and temperature dependent changes in the system\(^{43}\). We performed in-situ RTA XRD experiments, where various annealing ramp rates were used for experimental determination of the RuSi formation temperature \(T_c\) at different \(dT/dt\), as shown in fig. 4. Colgan and d'Heurle\(^{41,42}\) have shown the applicability of the Kissinger equation in RTA studies of thin film silicidation where an equation of the form: 
\[
\ln\left(\frac{(dT/dt)}{T_c^2}\right) = -\frac{E_a}{kBT_c} + C,
\]
+ \(k_B\) being the Boltzmann constant, and C being the intercept term, has been used in order to determine the effective activation energy \(E_a\) of silicide formation. In this form of the Kissinger equation, the value of \(E_a\) is determined from the slope of the linear fit between \(y = \ln\left(\frac{(dT/dt)}{T_c^2}\right)\) and \(x = 1/k_BT_c\). The intercept term C is assumed to be independent of the ramp rate\(^{44}\) and may be used to extract information regarding the rate constant of the diffusion-controlled reaction\(^{41}\).

Figure 5 shows the results of the Kissinger analysis for all the film stacks studied in this work. The values of \(E_a\) and \(T_c\) (at a single \(dT/dt\)) are summarized in table I. Cu is highly diffusive, reacts very easily with Si, and forms a Cu2Si phase at \(T = 245\) °C for
\( \frac{dT}{dt} = 3 \, ^\circ C/s \). This observation is consistent with previous measurements on Cu\(^{45}\). A Kissinger analysis by repeating the RTA measurement at 3 different ramp rates yields \( E_a \sim 1.6 \, eV \) which is close to the value reported earlier\(^{46}\). Similar kinetics studies on CVD Ru (3nm)/ALD MN (x nm)/Si (M=Ti, Ta; x = 0, 0.5) film stacks yields \( E_a \sim 2.1 - 2.3 \, eV \) which is consistent with previous measurements\(^{37}\). Although significant improvement in surface coverage for Ru was achieved after incorporation of 0.5 nm of TiN and TaN layers (fig. 1), it does not show any measurable improvement in barrier properties as evident by the \( E_a \) and \( T_c \) values measured here (table I and fig. 5). This is most likely due to still incomplete coverage of the under-layer when 0.5 nm metal nitride films were used as barrier layers. Where the metal nitride coverage is incomplete, the overlying Ru is in direct contact with Si and these areas can act as silicidation nucleation points. For the film stacks with 1 nm ALD TiN as the barrier layer, \( T_c \) increases significantly and the value of \( E_a \) is found to reach 2.6 ± 0.3 eV. The values of \( T_c = 621 \, ^\circ C \) (at \( dT/dt = 4.5\,^\circ C/s \)) and \( E_a (2.9 \pm 0.3 \, eV) \) are even higher for the film stack with 1 nm ALD TaN as the barrier layer. A higher value of \( E_a \) indicates a higher resistance towards Si diffusion along the grain boundaries of the barrier layer and into the Ru layer of the film stack. ALD TaN of \( \sim 1 \, nm \) thickness appears to serve as a good barrier layer and also leads to more or less uniform coverage for Ru films on top as shown in the SEM images of fig. 1. The \( \sim 1 \, nm \) thick TaN films outperform the TiN counterparts possibly because of having a superior density and higher melting point temperature.

**IV. SUMMARY**
Ultra-thin film stacks of CVD Ru (3 nm) /ALD MN (x nm)/Si (x = 0, 0.5, 1; M=Ti, Ta) have been investigated by SEM and in-situ rapid thermal annealing synchrotron XRD measurements. The thickness of the ALD metal nitride barrier layer significantly affects the Ru film coverage and the Si diffusion through the formation of silicides during rapid thermal annealing tests. Approximately 1 nm thick ALD TaN is found to be adequate in providing good Ru film coverage and acts as a good diffusion barrier for Si diffusion in stacked planar structures. With thermal annealing, the Ru and Si react via silicide formation according to the sequence Ru – RuSi – Ru2Si3. The formation of the first silicide in the sequence, ruthenium monosilicide, proceeds via a two-step crystallization process of lateral nucleation followed by layer thickening for the film-stacks of CVD Ru (3 nm) /ALD MN (x nm)/Si (x = 0, 0.5; M=Ti, Ta). No such effect is observed for the film-stacks of CVD Ru (3 nm) /ALD MN (x nm)/Si (x = 1; M=Ti, Ta) where a more or less uniform substrate coverage was achieved. As semiconductor devices become even smaller at sub-7 nm nodes, Ru may be a strong candidate for replacing some of the back end and middle of the line Cu as the interconnect material. Since literature on experimental studies of ruthenium silicide formation in thin and ultra-thin films is very limited, the detailed study of barrier failure via ruthenium silicide formation reported in this work is highly relevant for barrier and interconnect process development for sub-7 nm technology nodes. In the future, the properties of the barrier layer may be tailored in order to see how it affects the microstructure of the ruthenium overlayer in high aspect ratio structures with ALD TaN liner and CVD Ru and its relationship to device performance.
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19 D.P. Siddons, HERMES ASIC-Based Photon-Counting Si Microstrip Detector (Brookhaven National Laboratory, Upton, NY, USA, Private Communication).
23 See Supplementary Material at Http://Dx.doi.org/1x.xxxx/X.xxxxxx for Additional Results Pertaining to in-Situ Rapid Thermal Anneal X-Ray Diffraction Experiments and Pole Figure Measurements; Figures S1-S6 (2016).
FIG. 1. (Color online) (a-e) left column: SEM images of the as-deposited thin films collected using secondary electrons. The right column highlights the differences in pinhole density in the films after the respective SEM images were processed using the Trainable Weka Segmentation plugin in the ImageJ software.
FIG. 2. (Color online) RTA experiment done on Ru/Si film stack at a ramp rate of 4.5 °C/s. Before subtraction of a polynomial background: (a) RTA plot; (b-d) XRD plots for hexagonal Ru at T<439°C, cubic RuSi at 439°C<T<622°C, and tetragonal Ru₂Si₃ at T>622°C. After subtraction of a polynomial background: (e) RTA plot; (f) peak areas under individual peaks; (g) the rate of change of peak areas with temperature.
FIG. 3. (Color online) Plots of rate of change of XRD peak areas (background subtracted) vs. temperature for the CVD Ru (3 nm) /ALD MN (x nm)/Si (x = 0, 0.5, 1; M=Ti, Ta) film-stacks at a ramp rate of 4.5 °C/s. The vertical dotted lines show the transition temperatures.
FIG. 4. (Color online) Representative RTA plots (background subtracted) for Ru/Si film stack at four different ramp rates annotated in figure. The vertical dotted white lines show the transition temperatures calculated from the maximum rate of change of peak areas as described in fig. 2(g).
FIG. 5. (Color online) Kissinger plots for CVD Ru (3 nm)/ALD MN (x nm)/Si (x = 0, 0.5, 1; M=Ti, Ta) film stacks and a comparison of activation energy ($E_a$) of silicide formation with a film stack of PVD Cu (25 nm)/Si.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Si</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>Ru/Si</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>Ru/5Å TiN/Si</td>
<td>2.2 ± 0.3</td>
</tr>
<tr>
<td>Ru/5Å TaN/Si</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>Ru/10Å TiN/Si</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>Ru/10Å TaN/Si</td>
<td>2.9 ± 0.3</td>
</tr>
</tbody>
</table>
TABLE I. Summary of Ru fractional coverage and effective activation energy for silicidation from Kissinger analysis. $T_c$ has an error of ± 3 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area coverage by Ru overlayer (%)</th>
<th>$E_a$ (eV)</th>
<th>$T_c$ (°C) at $[dT/dt$ (°C/s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVD Cu (25nm)/Si</td>
<td>--</td>
<td>1.6 ± 0.3</td>
<td>245.3 [3.0]</td>
</tr>
<tr>
<td>CVD Ru (3nm)/Si</td>
<td>52 ± 2</td>
<td>2.1 ± 0.3</td>
<td>439.3 [4.5]</td>
</tr>
<tr>
<td>CVD Ru (3nm)/ALD TiN (5Å)/Si</td>
<td>70 ± 2</td>
<td>2.2 ± 0.3</td>
<td>439.4 [4.5]</td>
</tr>
<tr>
<td>CVD Ru (3nm)/ALD TaN (5Å)/Si</td>
<td>81 ± 2</td>
<td>2.3 ± 0.3</td>
<td>439.0 [4.5]</td>
</tr>
<tr>
<td>CVD Ru (3nm)/ALD TiN (10Å)/Si</td>
<td>90 ± 2</td>
<td>2.6 ± 0.3</td>
<td>578.0 [4.5]</td>
</tr>
<tr>
<td>CVD Ru (3nm)/ALD TaN (10Å)/Si</td>
<td>97 ± 2</td>
<td>2.9 ± 0.3</td>
<td>621.1 [4.5]</td>
</tr>
</tbody>
</table>
Supplementary Information:
Atomic layer deposited ultra-thin metal nitride barrier layers for ruthenium interconnect applications

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Figures S1 – S4 show the analysis of the rapid thermal annealing (RTA) data for the film stacks of CVD Ru (3 nm) / ALD MN (x nm)/Si (x = 0.5, 1; M=Ti, Ta)/Si. Figure S5 shows the RTA data analysis for PVD Cu (25 nm)/Si. Figure S6 shows the pole figure measurements done on one set of the CVD Ru films.
FIG. S1. (color online) RTA experiment done on 3nm Ru/5Å TiN/Si film stack at a ramp rate of 4.5 °C/s. Before subtraction of a polynomial background: (a) RTA plot; (b-d) XRD plots for hexagonal Ru, cubic RuSi, and tetragonal Ru₂Si₃ at three different temperatures. After subtraction of a polynomial background: (e) RTA plot; (f) peak areas under individual peaks; (g) the rate of change of peak areas with temperature.
Fig. S2. (color online) RTA experiment done on 3nm Ru/5Å TaN/Si film stack at a ramp rate of 4.5 °C/s. Before subtraction of a polynomial background: (a) RTA plot; (b-d) XRD plots for hexagonal Ru, cubic RuSi, and tetragonal Ru₂Si₃ at three different temperatures. After subtraction of a polynomial background: (e) RTA plot; (f) peak areas under individual peaks; (g) the rate of change of peak areas with temperature.
FIG. S3. (color online) RTA experiment done on 3nm Ru/10Å TiN/Si film stack at a ramp rate of 4.5 °C/s. Before subtraction of a polynomial background: (a) RTA plot; (b-d) XRD plots for hexagonal Ru, cubic RuSi, and tetragonal Ru$_2$Si$_3$ at three different temperatures. After subtraction of a polynomial background: (e) RTA plot; (f) peak areas under individual peaks; (g) the rate of change of peak areas with temperature.
Fig. S4. (color online) RTA experiment done on 3nm Ru/10Å TaN/Si film stack at a ramp rate of 4.7 °C/s. Before subtraction of a polynomial background: (a) RTA plot; (b-d) XRD plots for hexagonal Ru, cubic RuSi, and tetragonal Ru2Si3 at three different temperatures. After subtraction of a polynomial background: (e) RTA plot; (f) peak areas under individual peaks; (g) the rate of change of peak areas with temperature.
FIG. S5. (Color online) RTA experiment done on PVD Cu (25nm)/Si control film stack at a ramp rate of 3.0 °C/s. Before subtraction of a polynomial background: (a) RTA plot; (b-c) XRD plots for cubic Cu (space group #225) and cubic RuSi (space group #220). After subtraction of a polynomial background: (d) RTA plot; (e) peak areas under individual peaks; (f) the rate of change of peak areas with temperature.
FIG. S6. (Color online) Pole figure collected at $d \sim 2.91 \text{ Å}$ for one set of CVD Ru films, i.e., at (100) for cubic RuSi phase. (a) Si reference; (b) as deposited film (Ru); (c) annealed at $T = 600 \degree C$ and cooled to room temperature (in RuSi phase); (d) annealed at $T = 850 \degree C$ and cooled to room temperature (in Ru$_2$Si$_3$ phase). The four intense reflections are from the tail of Si {111}. No texturing could be seen in the Ru-film except an overall, albeit small, increase in intensity for (c) RuSi phase.