Plasma Enhanced Atomic Layer Deposition of Ruthenium Films Using Ru(EtCp)$_2$ Precursor

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Abstract: Ruthenium thin films were deposited by plasma-enhanced atomic layer deposition (PEALD) technology using Ru(EtCp)$_2$ and oxygen plasma on the modified surface of silicon and SiO$_2$/Si substrates. The crystal structure, chemical composition, and morphology of films were characterized by grazing incidence XRD (GXRD), secondary ion mass spectrometry (SIMS), and atomic force microscopy (AFM) techniques, respectively. It was found that the mechanism of film growth depends crucially on the substrate temperature. The GXRD and SIMS analysis show that at substrate temperature $T = 375$ $^\circ$C, an abrupt change in surface reaction mechanisms occurs, leading to the changing in film composition from RuO$_2$ at low temperatures to pure Ru film at higher temperatures. It was confirmed by electrical resistivity measurements for Ru-based films. Mechanical stress in the films was also analyzed, and it was suggested that this factor increases the surface roughness of growing Ru films. The lowest surface roughness ~1.5 nm was achieved with a film thickness of 29 nm using SiO$_2$/Si-substrate for deposition at 375 $^\circ$C. The measured resistivity of Ru film is 18–19 $\mu$Ohm·cm (as deposited).

Keywords: PEALD; ruthenium; ruthenium oxide; ruthenium films

1. Introduction

Thin ruthenium films are highly demanded in a wide range of applications. Ruthenium is a leading candidate for next-generation integrated circuit (IC) interconnection [1–4], as an ultra-thin layer of ruthenium has an electrical conductivity higher than other competing metals [5], does not require special barrier layers, and can be deposited in narrow trenches by atomic deposition (ALD) [6,7]. Ruthenium is also a promising candidate for the electrodes of the dynamic random-access memory (DRAM) capacitors [8], gate electrodes in metal oxide semiconductor transistors (MOSFETs) [9], and high conductive coating for MEMS devices [10,11]. It is also widely used in heterogeneous catalysis [12]. For example, it acts as a catalyst in Fischer Tropsch [13] and ammonia decomposition reactions [14,15]. Thin ruthenium films are also essential for soft X-ray [16–18] and extreme ultraviolet (EUV) optics [18,19]. To a large extent, considerable interest in ruthenium can be explained by comparably low prices for this noble metal.

There are a few articles about the chemical vapor deposition (CVD) of ruthenium [20–24]. However, the most interest is concentrated on conformal thin and ultrathin Ru and RuO$_2$ films, and the best way to get them is an atomic layer deposition (ALD) technique [25–31]. A lot of organometallic precursors have been developed for ruthenium deposition [32]. The most frequently used precursors are bis(cyclopentadienyl)ruthenium(II) (or RuCp$_2$) [25,33] and bis(ethylcyclopentadienyl)ruthenium(II) (or Ru(EtCp)$_2$) [8,18,34]. Ru(EtCp)$_2$ is a relatively inexpensive, commercially available liquid precursor. Thermal and plasma-enhanced ALD (PEALD) processes have been presented for this precursor. Moreover, a wide variety of co-reactants can be selected for Ru(EtCp)$_2$, such as O$_2$ [6,33], O$_3$ gases [8], and
NH₃ plasma [33]. Using Ru(EtCp)₂, it is possible to get high density (12.3 g·cm⁻³) [18] ruthenium thin films with low surface roughness (0.9 nm) and low resistivity (up to 16 μOhm·cm) [33].

This article presents the investigations of structural and electrical properties of ruthenium-based thin films deposited by PEALD on silicon and silicon dioxide in the extended range of substrate temperature (200–400 °C). The influence of post-process annealing at 400 °C on film properties is also analyzed. The maximum process temperature of 400 °C seems to be the typical thermal budget for most applications.

2. Experimental

Atomic-layer deposition of films was carried out on the substrates of p-type boron-doped monocrystalline silicon wafers (10 Ohm·cm) with a diameter of 100 mm, a thickness of 460 μm, with a surface orientation of (100). In other sets of experiments, Ru-based films were also deposited on the same silicon wafers with a preliminary deposited by PECVD SiO₂ layer of 300 nm thick for electrical measurements and comparison of PEALD growth features with deposition on a bare silicon surface.

The deposition process was carried out on a commercial FlexAl system (Oxford Instruments Plasma Technology, Yatton, UK) in a plasma-enhanced mode using a 13.56 MHz ICP remote plasma source. The chamber was evacuated with the turbo-molecular pump to a base pressure of 1.2 × 10⁻⁶ Torr.

The process was performed in the range of growth temperature of 200–400 °C using an alternating dosage of Ru(EtCp)₂ and O₂ plasma into the chamber. Argon and oxygen used in the process were 99.9999% quality grade. Chamber walls and precursor feeding pipes, as well as the vacuum system, were pre-heated to 100–120 °C to prevent precursor condensation. The chamber pressure was kept at 65 mTorr during the plasma step in the PEALD cycle. Ru(EtCp)₂ was contained in a bubbler, which was pre-heated to 70 °C. Its saturated vapor was delivered to the reactor chamber by argon carrier gas at the flow rate of 150 sccm.

One deposition cycle of PEALD for Ru-films consisted of six steps: (i) dosage of Ru(EtCp)₂ during 2 s; (ii) pump out the chamber during 1 s; (iii) purge pulse with 150 sccm of Ar for 4 s; (iv) 2 s step of oxygen pressure stabilization in the chamber; (v) O₂ plasma ignition and exposure during 1 s, and (vi) another chamber purge with 150 sccm of Ar for 4 s. The remote ICP plasma was powered at 75 Watt with 60 sccm of oxygen flow.

The bare silicon wafer with native oxide or silicon oxide surface ruthenium growth started from the formation of random nuclei instead of normal monolayer-by-monolayer mode, and therefore a growing film had no integrity at the beginning of growth and large roughness after the process was complete. Since it is known [33] that the introduction of sub-layers of transition metal nitrides can significantly improve nucleation of Ru, the possibilities of using the underlying sub-1 nm TiN and TaN layers were previously investigated. The material of the sub-layers, their thickness (as minimal as possible), and the resulting roughness of the layers were optimized. It was found that the best nucleation condition for Ru film at the first PEALD cycle is provided by a surface with tantalum nitride interlayer (IL) applied in the same chamber without breaking the vacuum [35]. The dependence of the stack Ru/IL TaN roughness on the thickness of TaN sub-layer was separately investigated. The tantalum nitride layer obtained at five cycles is sufficient enough for good Ru-nucleation, and the resulting roughness of 0.4 nm was obtained, which is comparable to the substrate surface roughness. A further increase in the thickness of the tantalum nitride interlayer leads to a rise in the surface roughness.

In this study, PEALD of tantalum nitride IL employed organometallic precursor tertiary-butylimido-tris-(diethylamino)-tantalum (TBTDET) with the linear formula Ta [N(C₂H₅)₂]₃[=NC(CH₃)₃]. The bubbler was heated to a temperature of 70 °C. It is known that plasma-enhanced ALD of tantalum nitrides from organometallic precursors makes it possible to obtain a range of nitrides of different stoichiometry and conductivity (from metallic TaN to dielectric Ta₃N₅) [36,37]. Our goal was to deposit the conducting seed layer.
Therefore, the optimization of the PEALD reaction of TBTDET with hydrogen plasma was aimed at obtaining the stoichiometric composition of sub-layer TaN. Increasing the plasma exposure time for adsorbed TBTDET provides the decline of the specific film resistance due to the removal of the excess of nitrogen; however, the ALD cycle duration significantly increases. The resistivity of tantalum nitride obtained in optimized PEALD process was about 2–3 m$\Omega$·cm (measured by the four probe method) that correspond with literature data [38].

Summarizing, we note that all films of ruthenium and its oxide studied in this work were deposited on samples with 0.3 nm tantalum nitride sub-layer which was pre-deposited using the recipe for ALD cycle as follows: (i) dosage of TBTDET for 3 s with 200 sccm of Ar as carrier gas through bubbler; (ii) chamber purge step with 200 sccm of Ar flow during 5 s; (iii) pump out the chamber during 2 s; (iv) hydrogen chamber pressure stabilization for 2 s; (v) H$_2$ plasma ignition and exposure at the pressure 15 mTorr and RF power of 100 Watt with 40 sccm of gas flow for 30 s, and (vi) another purge with 200 sccm of Ar flow for 2 s. The chamber pressure was kept at 80 mTorr, excluding plasma steps (15 mTorr). Tantalum nitride was always deposited at 400 °C, and the substrate temperature for subsequent ruthenium layer growth was varied. Such extremely small thickness of sub-layer can be described as a delicate surface modification for Si or SiO$_2$/Si substrates.

The thickness of the deposited Ru-based films was measured ex-situ using spectroscopic ellipsometry (Woollam M-2000X, Lincoln, NE, USA), scanning electron microscopy (SEM, Carl Zeiss Ultra-55, Oberkochen, Germany), and X-ray reflectometry (XRR, SmartLab, Rigaku, Tokyo, Japan). SEM images were obtained on cross-sections made by scribing hand tools used for manual cleaving of silicon wafers. The measurements demonstrate reproducible results with high uniformity of Ru films over the area of a 100 mm wafer. The difference in thicknesses was ±5% on a sample with 70 nm film (1500 ALD cycles).

Some samples were additionally post-annealed at 400 °C for 1–3 h in N$_2$ using rapid thermal processing (RTP) system Annealsys AS-One 100 (Montpellier, France). The base vacuum of the RTP system was 10$^{-2}$ Torr. Annealing processes were carried out in the N$_2$ (99.999%) at atmospheric pressure. The samples were annealed in the graphite container covered with CVD SiC.

The crystal structure, chemical composition, and morphology of films were characterized by grazing incidence XRD (GXRD, SmartLab, Rigaku, Tokyo, Japan), secondary ion mass spectrometry (SIMS) at TOFSIMS$^5$ tool, and by atomic force microscopy (AFM, Nanopics 2100, SII Nanotechnology Inc, Chiba, Japan). All results on film electrical resistivity present in the paper were obtained by four-probe method (Cascade Alessi four-probe station at Keithley 4200-SCS) on the films deposited SiO$_2$(300 nm)/Si-wafer.

X-ray diffraction studies were performed to investigate the phase composition of samples and the evolution of film crystallinity by using copper radiation with SmartLab (Rigaku) diffractometer. To suppress the signal from a substrate, the incoming X-ray beam was directed at a grazing angle $\theta_i = 0.5$ deg to the film surface (a little more than the critical angle for total external reflection). Scattering X-ray intensity at large in-plane diffraction angles $2\theta = 10–80$ degrees (GID-scheme) were studied. The scattered signal was collected by scintillation counter with Soller slit 0.114 degrees.

Stress analysis of samples with Ru-based films was carried out using a Zygo New view 5000 interference microscope (Zygo Corporation, Middlefield, CT, USA). At the first step, the pristine substrates were checked for deflection parameter within tolerance. Then, after applying the film, the deflection of the films on the substrates was measured. The mechanical stress in the film of ruthenium or its oxide was calculated using the Stoney formula [39]:

$$\sigma = \frac{E_s}{6(1 - \nu_s)} \frac{h_f^2}{h_s} \left( \frac{1}{R} - \frac{1}{R_0} \right),$$

where $E_s$ is Young’s modulus, $\nu_s$ is the Poisson’s ratio, $h_s$ is the thickness of the substrate, $h_f$ is the thickness of the film, and $R$ and $R_0$ isthe curvature radii of the substrate after and before deposition, respectively.
SIMS analysis was performed by TOF-SIMS\(^5\) system utilizing the Cs\(^+\) ions (1 keV, 75 nA, 300 × 300 \(\mu\)m\(^2\)) for sputtering. For probing, pulsed Bi\(^+\) ion beam was used (25 keV, 50 × 50 \(\mu\)m\(^2\)). A pulsed e-beam (20 eV) was used for charging compensation. Film morphology was characterized by contact-mode AFM technique with SII Nanopics 2100.

3. Results and Discussion

3.1. Influence of Substrate Temperature on ALD

On bare silicon and silicon oxide surface, 3D growth of ruthenium films was observed in the PEALD process and was attributed to poor nucleation. It was observed that, island growth of Ru films on untreated Si or SiO\(_2\) surface continues for the thickness of a few dozen nanometers. Earlier, we have found that the tantalum nitride underlayer obtained after five ALD cycles is optimal for the nucleation process of ruthenium on it [35]. The estimate of the thickness of such a layer from the known growth rate of a tantalum nitride film in the ALD process is about 0.3 nm, which is, in order of magnitude, one monolayer. It is possible to consider this as a surface modification leading to more efficient nucleation for Ruthenium film.

After ALD of Ru-based films, all the samples were comprehensively characterized. The thickness and electrical resistivity of the samples of films are presented in Table 1.

| Sample # | # of TaN Cycles | # of Ru Cycles | Dep Temp, °C | Thickness, nm | Resistivity, \(\mu\)Ohm cm |
|----------|----------------|---------------|--------------|--------------|--------------------------|
| 1        | 5              | 750           | 200          | 6 ± 1 \*     | 652.6 ± 1.5             |
| 2        | 5              | 750           | 250          | 9 ± 1 \*     | 508.5 ± 1.5             |
| 3        | 5              | 750           | 300          | 17 ± 2       | 288.0 ± 1.0             |
| 4        | 5              | 750           | 325          | 20 ± 2       | 200.2 ± 1.0             |
| 5        | 5              | 750           | 350          | 25 ± 2       | 130.5 ± 1.0             |
| 6        | 5              | 750           | 375          | 27 ± 1 \**  | 18.2 ± 0.8              |
| 7        | 5              | 750           | 400          | 33 ± 1 \**  | 19.1 ± 0.8              |

\* Measured by spectroscopic ellipsometry on Si; \** Measured by scanning electron microscopy (SEM) and X-ray reflectometry (XRR).

To obtain reliable results on all samples, thickness measurement methods based on different principles were applied. Samples 1 and 2 could not be measured in SEM with acceptable accuracy due to low contrast; the thickness of the films on them was determined by spectral ellipsometry. For samples 3–7, SEM measurements on cross-section made it possible to obtain accurate estimates of the thickness and resolve their polycrystalline morphology. On samples 3–5, the films had the grain size of the order the film thickness, while on samples 6 and 7, the films had a columnar structure, and the lateral grain size was about 10–15 nm. For samples 6 and 7, it was possible to obtain accurate results when simulating the XRR curves, making it possible to estimate the roughness (root mean square (RMS) = 1.5 nm) and density of the deposited ruthenium (12.0 ± 0.2 g·cm\(^{-3}\)). At 375–400 °C, the growth rate per ALD cycle was about 0.045–0.050 nm.

The electrical resistance of films thinner than 10 nm is influenced by low-dimensional effects [2] and does not allow estimating the bulk resistivity of the material; therefore, the values presented for the resistivity of the film on samples 1 and 2 should be considered as an upper estimate.

In Figure 1a, the scatterplot of the resistivity vs. deposition temperature is presented. It appears that the resistivity linearly decreases with deposition temperature growth. At the deposition temperature of 375 °C, it reaches the minimum.
Figure 1. (a) Resistivity vs. deposition temperature; (b–d) secondary ion mass spectrometry (SIMS) yield of $^{18}$O, $^{102}$Ru, and carbon-containing ions in the coatings deposited at different temperatures, respectively.

In Figure 1b–d, the SIMS yield of $^{18}$O, $^{102}$Ru, and C-containing ions from the coatings deposited at different temperatures are presented. For the oxygen yield, it can be seen that there are two temperature ranges for the composition of the film (1) rich in oxygen at 200–350 °C samples and (2) having an oxygen yield at the detection limit of the SIMS technique at 375–400 °C samples. It can be concluded that pure ruthenium film is formed only at $T > 350$ °C, and at lower temperatures, a film enriched with oxygen is deposited. The reduced yield of oxygen and ruthenium for samples deposited at very low substrate temperatures can be attributed to an ion yield dependence on matrix material (pure metal or oxide) in SIMS analysis. The yield for carbon, as seen from the graph, decreases with increasing temperature. This confirms the assumption about the incomplete reaction of the deposited material with oxygen plasma; apparently, the films, in this case, contain organic residues along with oxygen.

The GXRD spectra obtained for the coatings deposited at the temperatures 300–400 °C and reference peak positions (vertical lines) for Ru [40] and RuO$_2$ [41] in the randomly oriented powders are presented in Figure 2. It can be seen that the spectra of samples 3–5 contain only the peaks that are in line with the randomly oriented tetragonal RuO$_2$ phase (P4$_2$/mm). On the other hand, the spectra of samples 6 and 7 contain the peaks that coincide only with the randomly oriented hexagonal Ru phase (P6$_3$/mmc). It shows that...
at a deposition temperature of 375 °C, an abrupt change in surface reaction mechanisms takes place, leading to the changing in film composition and structure from polycrystalline RuO₂ at low temperatures to pure Ru film at higher temperatures. However, it should be noted that the resistivity of our RuO₂ films is significantly larger than the values reported earlier [42]. The possible reason is the noticeable carbon contamination of ruthenium oxide. All the peaks of RuO₂ are displaced to higher angles. This can be explained by the compressive stress in the coatings. The mechanical stress analysis will be presented in the next section.

![Grazing incidence XRD (GXRD) spectra obtained for the coatings deposited at temperatures 300–400 °C.](image)

**Figure 2.** Grazing incidence XRD (GXRD) spectra obtained for the coatings deposited at temperatures 300–400 °C.

### 3.2. Mechanical Stress

Comparison of the X-ray diffraction curves (Figure 3) on films deposited on Si-wafer and on SiO₂(850 nm)/Si-wafer shows a different state of the crystal lattice deformation in the films. The shift of the peaks relative to the reference values shows that Ru film on silicon is in a stressed state. On a sample with an SiO₂ film as a surface for Ru deposition, ruthenium film is relaxed with a layer of silicon oxide. The shift in the position of the peaks makes it possible to estimate the Ru lattice deformation on SiO₂ of about 0.0039. These data are confirmed by observing the deflection of the substrates under the action of stress in the film. Profilometry of deflection for all films gives stress values of 2.8–4.6 GPa (on Si).

The mechanism of relaxation of the ruthenium film on a single-crystal silicon surface is associated with the formation of blisters. We have observed such ruthenium films blistering on Si-substrate (Figure 4a). It allows us to conclude that the compression stress in these films relaxes significantly, and since no blister of Ru-film is formed on the silicon oxide layer (Figure 4b), the films Ru/SiO₂/Si-substrate remains stressed with compression. It is consistent with GXRD data (Figure 3) where Ru-peaks from the films on Si has a smaller shift than ones on SiO₂/Si. This different behaviour can be attributed to the different adhesion of films on Si and SiO₂ surfaces.

Mechanical stress data are also consistent with the roughness of the films. According to the AFM data, the samples with silicon substrates have a very high surface roughness (RMS = 17.1 nm), due to the formation of blisters (Figure 5a). On samples where there is an upper layer of silicon oxide, the blistering is much less (Figure 5b,c). As was found, the optimal substrate temperature in the ALD process for minimizing the blister formation is 375 °C. In this case, the absence of blistering manifests itself in the minimum surface roughness (RMS = 1.48 nm). It should be noted that blistering also decreases with decreasing film thickness and does not occur at any thickness lower than 10 nm.
Figure 3. GXRD pattern of as grown Ru deposited at substrate temperature 400 °C on Silicon and SiO₂(850 nm)/Si substrates.

Figure 4. SEM image of ruthenium film on Silicon (a) and SiO₂(850 nm)/Si (b) substrates.

Figure 5. Atomic force microscopy (AFM) images of the surface of (a) ruthenium film deposited at 400 °C on silicon (vertical scale—90 nm, surface roughness RMS = 17.1 nm); (b) ruthenium film deposited at 400 °C on SiO₂ (vertical scale—12 nm, blisters are out of scale, surface roughness RMS = 5.05 nm); (c) ruthenium film deposited at 375 °C on SiO₂ (vertical scale—8 nm, blisters are out of scale, surface roughness RMS = 1.48 nm).
3.3. Post Annealing of Films

The deposition of 33 nm thick Ru film by PEALD at 400 °C takes about 3 h. The thermal budget of some applications (for example, interconnects of ICs) is not high enough for such a process. It looks attractive to deposit the film at a lower temperature and then modify it by post-annealing. Samples 3–5 were annealed at 400 °C for 1–2 h. It was found that the thickness of the Ru-based films deposited at low temperature by PEALD reduces substantially during post-annealing (Table 2). This effect was not observed for films produced by PEALD at 375–400 °C.

Table 2. Thicknesses of the films immediately after deposition and after annealing at 400 °C in N₂ for 2 h.

| # of Sample | Thickness after Deposition, nm | Thickness after Annealing, nm |
|-------------|--------------------------------|-------------------------------|
| 3           | 17 ± 2                         | 9 ± 2                         |
| 4           | 20 ± 2                         | 10.7 ± 2                      |
| 5           | 25 ± 2                         | 14.7 ± 2                      |

In Figure 6a, GXRD spectra of sample 3 before and after annealing at 400 °C in N₂ for 1 h are presented. It can be seen from the graph that during annealing, the composition and the structure of the coating remarkably changed. Polycrystalline tetragonal RuO₂ structure changed to a polycrystalline hexagonal Ru film. It appears that during annealing, RuO₂ decomposes. The disproportionation reaction with the formation of volatile RuO₄ also appears to be possible.

![Figure 6a](image-url)

Figure 6a. GXRD spectra obtained for the film, deposited at 300 °C, before and after additional annealing at 400 °C in N₂ for 1 h; (b) resistivity of the samples before and after post-annealing at 400 °C in N₂ for 2 h vs. deposition temperature.

This phase transition was accompanied by electrical resistivity reduction. In Figure 6b, the samples’ resistivity before and after annealing at 400 °C in N₂ for 2 h is presented. Nevertheless, in all the cases, the films’ resistivity after annealing remains higher than one for high-temperature samples 6 and 7. For some low-temperature samples, post-annealing led to a resistivity decrease up to 50–60 μΩ·cm. These values are close to the values reported for RuO₂ earlier [42].
4. Conclusions

It is possible to deposit ruthenium using both thermal and plasma-enhanced ALD, but almost all authors noted that using PEALD with oxygen plasma leads to lower GPC or absence of the growth at all [18]. This can be explained by oxygen plasma competitive etching of ruthenium in the ALD process producing volatile RuO\(_4\) oxide. On the other hand, using PEALD with NH\(_3\) plasma, where such mechanism of etching is excluded, amazingly smooth ruthenium films were formed [33].

In a remote plasma ALD system, we have fabricated Ruthenium thin films by PEALD technology using Ru(EtCp)\(_2\) and oxygen plasma on silicon and SiO\(_2\) surfaces modified by TaN 0.3 nm sub-layer. High uniformity and integrity of films as well as reasonable GPC rate were achieved over the area of 100 mm silicon wafer. Two different ALD regimes of surface reaction between precursors were observed: uniformity and integrity of films were achieved at temperatures below 375 °C. At temperatures above 400 °C, polycrystalline ruthenium oxide films were grown. At a higher temperature, pure polycrystalline metal ruthenium coatings were formed.

For 29 nm thick ruthenium coating, it was possible to obtain the surface roughness with RMS = 1.48 nm. It is much lower than films formed by thermal ALD from popular precursors (RMS = 2.6–3.5 nm). To a great extent, the surface roughness of ALD ruthenium films with thickness more than 10 nm can be explained by consequences of mechanical stress in the films.

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