Properties of plasma enhanced atomic layer deposited ruthenium thin films from Ru(EtCp)$_2$

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Abstract. Ruthenium thin films were deposited by plasma enhanced atomic layer deposition using bis(ethylcyclopentadienyl)ruthenium(II) or Ru(EtCp)$_2$ and oxygen plasma. The growth characteristics have been studied on a silicon substrate with different interfaces in a wide temperature range. On Si and SiO$_2$, a nucleation delay period has been observed, which can be substantially reduced by the use of a tantalum nitride underlayer of $\sim 0.3$ nm. The surface analysis shows that the substrate’s temperature strongly affects the composition of the film from ruthenium oxide at low temperatures to pure ruthenium film at higher temperatures.

1. Introduction
The development of deposition techniques for thin good-quality ruthenium films has recently become an actual and popular problem due to the prospects for its application in metallization systems of integral systems [1-5]. The interest in ruthenium is partly due to its high technological properties of the noble metal at a relatively low cost, which makes it possible to use it in the mass production of integrated circuits. Ultrathin continuous films without any voids are needed when Ru is used as a diffusion barrier for Cu interconnects. The application of Ru as a conducting interconnection material requires Ru with low resistivity and low impurity contents.

Particular interest in the development of the use of ruthenium as a metal for an IC interconnect system is due to the fact that processes for plasma etching of ruthenium are well known, with the possibility of obtaining a good vertical profile at room temperature and without redeposition [6]. Such processes open up the prospect of abandoning the damascene process, which is used to create copper metallization. In the process of damascene, due to the impossibility of proposing an adequate etching process for copper, it is necessary to use plasma etching of the dielectric, which inevitably causes its degradation, which could not be completely eliminated despite great efforts [7].

There are a few approaches for deposition of metallic films: physical deposition (i.e. magnetron sputtering), chemical vapour deposition (CVD), thermal atomic layer deposition and plasma enhanced atomic layer deposition (PEALD). Although physical deposition methods are the easiest to implement, they cannot be applied to some applications where conformal coating and filling of thin trench and holes is required, which is especially important in IC metallization systems where ruthenium can be applied at levels with a minimum critical size.

PEALD is one of the most attractive methods for producing films with these characteristics, given its inherent ability to easily transition to three-dimensional structures.
A typical ALD process consists of the alternating dosing of precursor and coreactant gas that interact with a substrate through self-limiting surface reactions. In this work, we examine the growth and nucleation of Ru thin films deposited using bis(ethylcyclopentadienyl)ruthenium(II) precursor in PEALD process that includes an oxygen plasma pulse. In particular, we look at how the substrate temperature influences the growth and nucleation of the film and how it can be used to manipulate the material properties.

It was shown earlier [8] that one of the main problems of film growth is also delamination, which is apparently associated with mechanical stresses in the film. This becomes especially critical for films with a thickness of more than 50 nm.

The research of the resistance of Ru-based films obtained in the optimal mode is presented in the previous work [9].

2. Experiment
ALD processes were performed in a commercial FlexAl system (Oxford Instruments Plasma Technology) with a base pressure of $10^{-6}$ Torr, using a 13.56 MHz ICP remote plasma source. Ru(EtCp)$_2$ was contained in a bubbler, preheated to 70°C and delivered to the reactor by argon flow gas at a flow rate of 150 sccm. The manifold lines were heated to 100 °C and the reactor walls to 120 °C to prevent the condensation of the precursor. The recipe for Ru ALD (Table 1) consisted of a 2 s Ru(EtCp)$_2$ dosing, 1 s pumping, 4 s Ar purge, 2 s step of oxygen pressure stabilization in the chamber, 1 s O$_2$ plasma ignition and exposure (O$_2$ pressure of 0.065 Torr), and 4 s Ar purge. In the work, we used gases of a semiconductor grade.

| Table 1. Conditions at each step of a single PEALD cycle for deposition of Ru films |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Flow, sccm                      | Dose Ru         | Ru Purge        | Plasma Gas      | Plasma           | Post Plasma     |
|                                 | 150 Ar          | 150 Ar          | Stabilization   | 60 O$_2$         | 60 O$_2$        | 150 Ar          |
| Pressure, mTorr                 | 80              | 80              | 65              | 65              | 80              |
| ICP RF power, W                 | -               | -               | -               | 75              | -               |
| Time, s                         | 2               | 4               | 2               | 1               | 4               |

Depending on the thickness of the films, adequate ex situ methods were used to measure the growth rate: for films with a thickness of less than 10 nm, spectroscopic ellipsometry (Woollam M-2000X) was used, and for thicker films, a cross-section scanning electron microscopy (Carl Zeiss Ultra-55). To apply the ellipsometry method, the dependence of $k$ and $n$ on the wavelength was determined experimentally from a thick ruthenium film obtained by our method (> 30 nm). In this case, it can be assumed that the light reflected from the lower boundary does not leave the sample and the calculation is carried out as for bulk ruthenium. The dependencies were approximated by a B-spline.

Stress analysis of samples was carried out using a Zygo New View 5000 interference microscope.

3. Results and Discussion
We examine the range of growth temperature of 200–400 °C and it turned out that the substrate temperature plays a critical role in determining whether Ru or RuO$_2$ is deposited. It was noticed that at 375 °C an abrupt change in surface reaction mechanisms takes place, leading to the changing in film composition and structure from polycrystalline RuO$_2$ at low temperatures to pure Ru film at higher temperatures.

Figure 1a shows how ruthenium is deposited onto an unprepared silicon surface. It can be seen that the growth has an insular character. Even if, during long-term deposition, the islands close together giving a continuous layer, its roughness will be higher than the permissible values. Then we used
prepared wafers with a tantalum nitride underlayer of $\sim 0.3$ nm. Figure 1b shows the character of growth on prepared silicon. Blistering can be seen, which means that the film has significant compressive stresses, and the adhesion to the surface is insufficient. Figure 1c shows the growth of a film on a SiO$_2$ layer deposited on silicon. In this case, it can be seen that the film is continuous without visible roughness within the resolution of the scanning electron microscope. AFM measurements confirmed this with a roughness of about 1.5 nm.

![Figure 1](image)

**Figure 1.** Cross-sectional image of the samples obtained with a scanning electron microscope. a) Island growth of a film on unprepared silicon, b) on a prepared silicon surface, c) on a prepared SiO$_2$ surface.

For estimation of Ru film stress on the silicon surface, the deflections of single-crystal silicon wafers with a thickness of 380 $\mu$m were measured with films deposited on them. The measurement was carried out in a field of 5 mm x 5 mm; the vertical measurement accuracy was about 1 nm. Figure 2 shows the distribution of heights on the investigated central part of the silicon wafer (the arrow shows the section along which the approximation was carried out). Figure 3 shows a cross-sectional profile that was then approximated by a circle giving the radius of curvature of the surface.

![Figure 2](image)

**Figure 2.** Dependence of the surface stress of the films on the deposition temperature.

![Figure 3](image)

**Figure 3.** Dependence of the surface stress of films grown at a temperature of 375°C on the number of PEALD cycles.
The obtained distributions were approximated by a spherical profile, and the mechanical stress in the film was calculated using the Stoney formula:

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

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 $R_0$ are the curvature radii of the substrate after and before deposition, respectively.

The application of this approach will allow optimizing the stresses in the films by varying the deposition modes and plasma treatment, which will make it possible to obtain films of metallic ruthenium with better quality.

Mechanical stress data are consistent with the roughness of the films. The mechanism of relaxation of the ruthenium film on a single-crystal silicon surface is associated with the formation of blisters. Stress values of 2.8–4.6 GPa (on Si) were measured.

4. Results and Discussion

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 with and without modification by TaN 0.3 nm sub-layer (5 cycles). High uniformity and integrity of films as well as reasonable GPC rate were achieved over the area of 100 mm silicon wafer on SiO$_2$ layer modified by TaN deposition. The fact that such a result was achieved on the silicon oxide layer is explained by the fact that, in contrast to crystalline silicon, it makes it possible to reduce the stresses of the film. For interconnection technology, this is permissible since in it the metal is always deposited on an intermediate dielectric layer. In the future, it is of interest to study the deposition of ruthenium on stop SiOC layers on the surface of a low-k dielectric.

Acknowledgments

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