Atomic layer deposition of Ruthenium on different interfaces for an advanced metallization system of ICs

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Abstract. Nucleation effects were experimentally studied for ruthenium thin films grown by plasma-enhanced atomic layer deposition (PEALD) using O₂ plasma. Bis(ethylcyclopentadienyl)ruthenium (II) (Ru(EtCp)₂) was used as Ru precursor. The films with the thickness 10 nm on different underlying thin layers (interfaces), including Si, SiO₂, Ta₂O₅, TiN, and TaN were deposited to investigate the effects of interfaces for nucleation of the Ru in ALD process. Some of the samples were previously processed in ammonia and oxygen plasma to enhance nucleation. The processes of forming barrier layers based on titanium and tantalum nitrides by plasma-enhanced atomic layer deposition were also studied. Films properties were evaluated by spectral ellipsometry, scanning electron microscopy and atomic force microscopy.

1. Introduction
Highly conformal Ruthenium thin films have many applications in microelectronics; for example, as a gate electrode for p-FET [1], capacitor electrodes in new generation dynamic random access memories (DRAMs) [2], and capacitor electrode for ferroelectric random access memories (FRAMs) [3]. The other promising application is the advanced interconnections of first levels of ICs [4,5].

Thermal and plasma-enhanced atomic layer deposition Ruthenium were reported by several groups [6]. At dimensions smaller than 10 nm, the Ruthenium effective resistance depends less on the scaling than that of Cu/barrier systems. These extremely scaled Ruthenium lines show excellent electromigration behavior. Time-dependent dielectric breakdown measurements reveal negligible Ruthenium ion drift into low-κ dielectrics up to 200 °C, demonstrating that ruthenium can be used as a barrierless metallization in interconnects [7].

Cobalt and Ruthenium are the two leading materials to replace copper at small dimensions. The advantage of Ruthenium is the possibility to use it without diffusion barriers or apply Ru as a barrier for other metals [8,9]. One of the main disadvantages of the thin Ruthenium film growth process is the effect of delayed nucleation.

It manifests itself in the presence of idle cycles at the beginning of the ALD process. In the case of incomplete nucleation, this results in island growth on the surface, which leads to the high roughness of the films. The present paper performs research on the initial stages of Ruthenium growth on surfaces coated with different interfaces and subjected to various pretreatments. The processes of forming barrier layers based on titanium and tantalum nitrides by plasma-stimulated atomic layer deposition were also developed.

2. Experiment
Ru films were deposited on different substrates by PEALD at a growth temperature of 400 °C using an alternating supply of Ru(EtCp)₂ and O₂ plasma. The deposition pressure was kept at 65 mTorr during
plasma steps and 80 mTorr in others. Ru(EtCp)$_2$ was contained in a bubbler, which was heated to 70°C and delivered to the reactor by argon carrier gas at a flow rate of 150 sccm. The feeding line and chamber were heated to 120 °C to prevent the condensation of the Ru(EtCp)$_2$ precursor.

There were 300 deposition cycles for each sample. One deposition cycle of PEALD-Ru consisted of six steps: (i) dose of Ru(EtCp)$_2$; (ii) pump during 1 s; (iii) purge pulse with 150 sccm of Ar; (iv) plasma gas stabilization; (v) O$_2$ plasma exposure and (vi) another purge with 150 sccm of Ar. During the plasma pulse, the radio-frequency plasma was operated at 75 W with 60 sccm of gas flow.

The growth was performed on bare silicon wafers and on different underlying thin layers (interfaces), including Ta$_2$O$_5$, TiN, and TaN to investigate the effects of interfaces for nucleation of the Ru in the ALD process.

All processes of preliminary preparation of the samples considered in this article were carried out in situ without breaking the vacuum.

The roughness was measured with the help of AFM Nanopics. Images of the surface were also obtained on an electron scanning microscope Supra 55.

3. Results and discussion

On untreated silicon, Ruthenium growth originated from the sites of the formation of random nuclei, and therefore a non-continuous film was formed, scattered hemispheres (Figure 1). Even if they merged with further growth, the film was very rough (up to 20 nm).

![Figure 1. SEM Si surface after 400 ALD cycles.](image)

To stimulate nucleation, the possibilities of the formation of oxide sublayers were considered. A variant of the formation of a oxygen-saturated surface was considered. For this, a process similar to the formation of ruthenium, but with an elongated plasma step, was used. It was assumed that this gives rise to the formation of Ruthenium oxide. Another option is to use tantalum oxide as the underlying layer, which was also formed by the ALD method. The argument in favor of using the oxide sublayer was its possible use as a barrier. The last option for surface preparation is plasma treatment. Treatment in oxygen plasma was applied to saturate the porosity with oxygen (O$_2$ plasma, 50 mTorr, 400 W, 3 min). In addition, the possibility of processing in ammonia plasma (NH$_3$ plasma, 50 mTorr, 400 W, 3 min), which could form a layer of the nitridized surface saturated with hydrogen bonds, was considered separately.
Atomic force microscopy was used as an express method for analyzing film quality, in which roughness served as an indicator of poor nucleation.

Figure 2 shows the difference of the surfaces of Ru films deposited on RuO₂ (a), Ta₂O₅ (b) substrate. Two samples were previously processed in oxygen Figure 2 (c) and ammonia Figure 2 (d) plasma. The high values of the obtained roughness indicate that the surface prepared by methods higher, remains unfavorable for nucleation.

**Figure 2 (a, b, c, d).** AFM of ALD Ru film on RuO₂ (a), Ta₂O₅ (b) substrate. AFM of ALD Ru film, the substrate was previously processed in oxygen (c) and ammonia (d) plasma.

Figure 3 demonstrates SEM images showing how the growth pattern of metallic Ruthenium in a plasma stimulated process depended on the material of the sublayer. The application of a scanning electron microscope makes it possible to more accurately understand the causes of roughness. The sample on the Figure 3 (a) first of all was covered with Ta₂O₅ film in 10 cycles of ALD. It can be seen that in this case the roughness is caused by the blistering of the film due to poor adhesion to the substrate. Figure 3 (b) shows Ru film on a pre-applied layer of 20 ALD cycles TaN. On the Figure 3 (c) the underlying interface was TiN film (200 ALD cycles). For tantalum nitride and titanium nitride as the underlying layers, it can be seen that blistering is much less pronounced.
Figure 3 (a, b, c). SEM of ALD Ru film on Ta₂O₅ (a), TaN (b), TiN (c) surface.

Further optimization of the process, carried out below, will completely eliminate it. For optimization, it was decided to use a tantalum non-nitride sublayer. As can be seen from Figure 3, its surface is much smoother in comparison with titanium nitride, which has a roughness caused not only by blistering, but also by the crystal structure obtained at 400 °C.

The roughness of a stack of ruthenium films (10 nm) on tantalum nitride was studied depending on the number of TaN deposition cycles. Figure 4 represents the results of optimizing the tantalum nitride sublayer thickness for roughness. A more detailed analysis showed that if the tantalum nitride sublayer is no more than 5 layers thicker, which corresponds to a thickness of about 0.25 nm, then the roughness of the resulting stack is minimal and is close to the roughness of the silicon wafers of the batch used. With an increase in the number of nitride layers (10-100), blistering begins, which leads to an uncontrolled increase in roughness up to the range of nanometers.

Figure 4. The dependence of roughness of TaN/Ru stacks on the number of TaN ALD cycles.

Since it was shown that the optimal film stack from the point of view of the considered applications tasks is (TaN (5 cycles)/ Ru), the dependences of the thickness of the obtained Ruthenium film on the number of cycles were additionally investigated (Figure 5 a). It can be seen that the growth rate in the investigated range (300-1500 cycles) is linear, but a nucleation delay of about 100 is also evident. On the one hand, this delay is suboptimal, since it implies idle cycles. On the other hand, the presence of a nucleation delay opens up opportunities for ASD with further optimization of the cycle [10]. We also studied the dependence of the film growth rate on the substrate temperature during deposition (Figure 5 b). It can be seen that in this temperature range, a decrease in the growth rate is observed with decreasing
temperature, which apparently means a decrease in the reactivity of the precursor adsorbed on the surface upon interaction with oxygen plasma particles.

![Graph](image)

**Figure 5 (a,b).** The dependence of Ru film thickness on the number of ALD cycles at 400°C on the pretreated surface (a), and temperature dependence of the growth rate of ruthenium (b).

4. Conclusion

It was shown that the nucleation delay during the deposition of Ruthenium could be up to several hundred cycles, and it significantly depends on the interface material. It also determines the roughness of the resulting films. It was found that the nucleation rate for Ruthenium in a plasma-stimulated deposition process substantially depends on the surface of the substrate. Measurements by atomic force microscopy showed that the formed films have a characteristic roughness, which occurs due to the gradual formation of nuclei on the surface. An analysis of the performed experiments on the deposition of ruthenium on Ta₂O₅, TiN, and TaN showed that total nucleation is observed on tantalum nitride. Thus, the stimulation of nucleation leads to a decrease in the roughness of the films. It has been established that films of metals deposited by plasma-stimulated deposition - (TiN and TaN) of a second precursor compositionally optimized to produce films with minimal electrical resistance - are favorable for deposition.

The tantalum nitride layer obtained at 5 cycles is sufficient for high-quality nucleation and the resulting roughness of 0.4 nm, which is comparable to the initial roughness of the silicon substrate. A further increase in the thickness of the tantalum nitride layer leads to an increase in the roughness due to the blistering of the film.

It was shown that even on a prepared surface, on which 5 cycles of tantalum nitride were preliminarily deposited, a delay in the nucleation of ruthenium is observed up to 100 cycles. The temperature dependence of the growth rate of ruthenium has been established, which grows with a temperature from 0.023 nm per cycle to 0.044 nm per cycle in the temperature range of 300-400°C.

The results can be used to develop ruthenium deposition processes in trench coats in ICs metallization systems, as well as to develop promising area selective deposition processes.

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