Atomic layer deposition of Ti and its deposition method

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Abstract. Atomic layer deposition (ALD) is a very popular thin-film technique, and it is considered to be a method with great potential because it can produce conformal thin film with control of the thickness of layers and composition of the films at the nano-scaled level. In fact, there are other two types deposition techniques: Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD), which are also commonly used in surface treatment. However, the treatment conditions are different as CVD requires up to 1000°C while PVD requires lower than 500 °C. However, because of the self-controllability in ALD, this technique is widely applied in the fields including semiconductors, nanotechnology, and catalysts. In our current knowledge, substantial numbers of element could be used for ALD to form substrate layers. Some notable elements are carbide, Nitride, oxide, metal and so on. Among all kinds of possible deposited materials, titanium contained precursor are special and they receive tremendous attention because they could strengthen the base materials or protect the base materials from oxidization so that they improve the mechanical or chemical properties of pristine materials. Specifically, it could improve the properties of base materials such as reducing the work function, which is discussed in the passage. The purpose of this review is to provide an overview of current technology of deposition titanium contained chemicals and point out possible research topics in the future.

Keywords: Atomic layer deposition; thin-film; Ti.

1. Introduction
Generally, PVD is a process in which the material goes from a condensed state to a vapor phase and then goes back to a thin film state. PVD is commonly used in the manufacture of items such as thin film solar panels [1], aluminized PET film for food packaging and balloons [2], and titanium nitride coated cutting tools for metalworking. CVD is highly used in semiconductor industry to produce thin films. In typical CVD, the substrate is exposed to one or more volatile precursors and the precursors would react and/or decompose on the surface to produce the desired deposit. The application of CVD could be found almost anywhere. Commonly, CVD can be used to deposit conformal films in ways that traditional surface modification techniques are not capable of. Some examples are CVD of metal-organic frameworks, amorphous polysilicon, and membrane coatings [3,4]. Speaking of “Atomic Layer Deposition” (ALD), it is also a thin-film deposition technique which is actually a subclass of chemical vapor deposition. Generally, the ALD reactions has two chemical called precursors. These precursors react with the surface of a material one at a time in a sequential, self-limiting, manner [5]. The thin film will then gradually deposit on the surface of the base material. Semiconductor processing has been one of the main applications. One of main specific examples is that ALD has been included for high
dielectric constant gate oxides in the MOSFET Structure and copper diffusion barriers in backend interconnects [6]. All three methods play a very important role in current industrial field. Depending on the requirements of a component, different deposited methods can be applied. However, ALD has the edge of thickness control and uniform distribution. As mentioned above, depending on the number of precursors, ALD could stop by itself.

2. Literature review of ALD of Ti

Among several elements, titanium is widely used as thin film deposited on the surface of other materials because its ability to provide outstanding properties on base materials. In the followings, several methods in different parameters of depositing Ti contained thin film are classified. For example, various precursors could make a huge difference and play an important role in determining the properties of thin film [7]. In addition, it is highly used in work function engineering. The work function of a metal gate material could be tuned by manipulating TiC or TiN thin film [8, 9, 10]. Furthermore, it is learned that the TiN thin film could possibly be deposited by plasma assisted atomic layer deposition for copper metallization. Its plasma pulse time, power, and composition will have a huge effect on the electrical properties of TiN [11]. Sometimes, in order to produce highly conformal TiN thin film. The combination of thermal and plasma-enhanced atomic layer deposition can be applied [12, 13]. Coatings are another common usage for ALD of Ti, which acts as an adhesion layer and promotes the bonding [14, 15].

2.1. Effect of Precursors on ALD of Ti

To make titanium thin-film, ALD technique is commonly used. However, different treatment methods will meet different requirements and properties of materials for various usages. Namely, different kinds of precursors could be a factor on changing properties of materials. In Gihee Cho and Shi-Woo Rhee’s paper, they used three types of titanium precursors: tetrakis dimethyl amido titanium (TDMAT), tetrakis ethylmethyl amido titanium (TEMAT), and tetrakis diethyl amido titanium (TDEAT) and compared them in growth rate, resistivity, and the composition as function of substrate temperature. According to the result, the TDMAT, TEMAT and TDEAT had different ALD window. TDMAT has a range of 125-175 ℃, and TEMAT has range between 175-200 ℃ while TDEAT is between 175-250 ℃. Specific growth rate data is shown below in Figure.1. The plot has shown that the TDMAT presents much faster growth rate at any temperature from 100 -300 ℃ range, TEMAT is not far behind and TDEAT has the slowest growth rate.

![Figure 1. The growth rate for TDMAT, TEMAT and TDEAT precursors](image-url)
Figure 2. Resistivity changes for TDMAT, TEMAT and TDEAT at different temperatures

Figure 2 shows the resistivity changes as function of substrate temperature. The graph shows resistivity decreases with temperature going up with TDMAT having the lowest resistivity across the temperature range and TDEAT presenting the highest resistivity. Therefore, it illustrates the higher thermal stability will increase resistivity because TDEAT is the most stable one among all three according to the ALD temperature windows range.

Finally, the paper reveals composition of film of three precursors as function of temperature. TDMAT and TEMAT both showed decomposition of carbon content as the composition of carbon increases, resulting in the reduction of oxygen and forming in TiC phase filling in the vacancy. However, the temperature in the project is only up to 300 °C. How will things change above that temperature is still unknown.

Figure 3. composition of thin films by using (a)TDMAT, (b)TEMAT and (c)TDEAT at different temperatures
2.2. Effect of ALD on work function
ALD process of titanium also plays a very important role in tuning work function. It is proved that TiN is suitable for metal gate material. However, there is no such a technique to develop it in a conformal film growth, which is required for 3D devices. In Sanghun Jeon and Sungho Park’s paper [8], they adjusted deposition temperature, the carbon content could be altered. More specifically, they changed deposition mode from ALD mode to CVD like mode at temperature above 200 °C which increased bonding concentration and lower the work function of metal gate. The range of work function they focused on was 5.0 eV, where it is suitable for a p type FET, to 4.6 eV where it is suitable for a fully depleted silicon-on-insulator FET. Similarly, there is another TiC film which is almost as important as TiN. Choong-Ki Kim and his company used slightly different temperatures which ranged from 250°C to 500°C [9]. It was discovered that work function of TiC was affected by crystal orientation and determined by the average WF of each oriented sub-plane.

![Figure 4](image)

**Figure 4.** Work function and summary of atomic percentages of C, Ti and Al.

The previous two papers are both related to temperature. There is another one published by JinJun Xiang and Tingting Li regarding thickness changes on work function [10].

![Figure 5](image)

**Figure 5.** The EOT and \( J_g \) values of the capacitors with different TiN thickness.
The trend shows the thickness would initially increase the current density $J$ and lower the EOT. With the thickness becoming thicker, the EOT goes up and current density goes down. The result shows that metal-oxide-semiconductor (MOS) without TiN barrier exhibits lower $J$ and higher EOT. They argued that was due to the TiN could suppress Al diffusion and boost Ti diffusion into substrate. However, the sample pool was not quite substantial enough as they only tested four points. In order to make more convincing conclusion, more data points should be expected.

2.3. Effect of plasma on ALD of Ti
Sometimes, plasma could be helped to prepare Titanium ALD. Do-Hyeoung Kim, Young Jae Kim and others introduced plasma method because the traditional metalorganic TiN ALD method, high resistivity remains a problem of the sample [11].

![Figure 6](image.png)

**Figure 6.** Top left: The effect of plasma treatment on film growth rate and resistivity.
Top right: The effect of plasma power on film growth rate and resistivity.
Bottom: The effect of plasma gas composition on film growth rate and resistivity.

From those diagrams, it mainly illustrates plasma treatment time, power and the ratio of Nitrogen over hydrogen could be a factor on the resistivity, growth rate and stability of TDMAT-based PAALD TiN films. Based on the graphs, the resistivity goes down as a longer plasma treatment time while the growth rate doesn’t change significantly. Also, as the plasma power increases, the resistivity goes down. The higher hydrogen percentage could lower the resistivity as well. The method really showed a big improvement on electrical properties of thin films.

Some scientists such as Delphine Longrie and his research group, and Loic Assaud tried combination of plasma and thermal ALD methods [12,13]. According to Delphine and his company, they used a rotary reactor to deposit TiN on ZnO powder. The most important takeaway from this article is the resistivity decreases and the conductivity increases with the increasing power of plasma-enhanced ALD shown in Figure 7.
Figure 7. Resistivity of the AnO powder coated with 100 cycles of TiN using PE-ALD process with 200W and 350W plasma power.

Figure 8. Resistivity as function of thickness deposited by Thermal-ALD and plasma-enhanced ALD.

Figure 8 also clearly showed that both Thermal and Plasma-enhanced ALD would lower the resistivity value as layers become thicker, but the plasma-enhanced ALD shows a significantly better performance. Therefore, it is declared that plasma-enhanced ALD has an edge over Thermal-ALD.

2.4. Effect of ALD on mechanical properties

Lastly, there are a couple of articles describing Ti coating to improve the mechanical properties. J.B Zang and J. Lu used ALD method to deposit Titanium on Nanocrystalline which they employed hydrogen gas and TiCl$_4$ binary reaction sequence to react with diamond matrix and form TiC in coating [14,15]. They suggested the formation of TiC could improve the internal bonding of nanocrystal diamond. Tommi O.Kaariainen has used ALD of Ti to improve the adhesion to PMMA substrate. TiO$_2$ and Al$_2$O$_3$ were used for two deposition processes, and ozone was used as a source of oxygen for both. Then, the deposition of the metal/metal carbide layer was followed by using pulsed DC reactive magnetron sputtering. The fracture strength prior to sputtered Ti is shown in Figure 9:
Figure 9. The relationship between fracture strength and deposition thickness

Clearly, we can see that the thickness of Al₂O₃ reaches 33 nm and TiO₂ reaches 50 nm, the fracture strength is significantly better than original PMMA, suggesting a big improvement on mechanical properties and adhesion.

3. Conclusion
The purpose of this review is to get an idea on how Ti ALD is currently used in application and method. To summarize, Ti ALD is heavily used in semiconductor devices such as metal gate materials. They could also be prepared by thermal and assisted by plasma pulse. Sometimes, they could be used as a coating method to improve the internal bonding and enhance mechanical properties of base materials. Sometimes, different precursors could also have a completely different performance as well. Therefore, in future, several research topics could be made based on this review. For instance, it could be test other precursors and compare their electrical properties. Some notable materials are Titanium diisopropoxidebis, Titanium isopropoxide. Also, regarding on the papers about work function, all the treatment temperatures were above 200°C. How is work function going to change under 200°C could be an interesting topic. Also, plasma assisted properties is proved to be competent on improving electrical properties. But some topic such as whether there will be any effect on mechanical properties of the materials and how mechanical properties of materials would change with plasma power and power time as well as the stability of the Ti coating applied by ALD method, such as corrosion resistance. Those can all be problems to be solved.

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