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Review of plasma-enhanced atomic layer deposition: Technical enabler of nanoscale device fabrication

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With devices being scaled down to the nanometer regime, the need for atomic thickness control with high conformality is increasing. Atomic layer deposition (ALD) is a key technology enabler of nanoscale memory and logic devices owing to its excellent conformality and thickness controllability. Plasma-enhanced ALD (PE-ALD) allows deposition at significantly lower temperatures with better film properties than in conventional thermal ALD. These benefits make PE-ALD more attractive for nanoscale device fabrication. In this paper, the basic characteristics and film properties of PE-ALD processes will be reviewed, focusing on the application of PE-ALD in key components of nanoscale device fabrication: gate oxides, Cu interconnects, and nanoscale contacts. © 2014 The Japan Society of Applied Physics

1. Introduction
As devices are scaled down to the nanometer regime, the need for excellent conformality and atomic thickness controllability becomes immense. Because of the recent implementation of three-dimensional devices with the critical dimension less than 20 nm, this need is becoming even greater. Atomic layer deposition (ALD) is expected to play an important role in future device fabrication, owing to its atomic level thickness control and excellent conformality.1

1.1 History and current trends of ALD
ALD originated from experiments carried out in the 1960s and the 1970s.2,3 Interest in ALD gradually increased in the early 1990s and 2000s, as indicated by the large number of scientific publications on ALD.4 In 1996, the surface chemistry of ALD was reviewed by George et al.5 For different points of view on the history and current trends of ALD over the years, many reviews have been reported.6–9 Additionally, ALD has emerged as an important technique for depositing thin films for a variety of applications. It has recently been described in several reviews focusing on different areas: catalyst,10 nanotechnology,11 and electronic and optoelectronic materials.12,13

Among the various applications, semiconductor processing has been one of the main motivations for the recent development of ALD. The International Technology Roadmap for Semiconductors (ITRS) has included ALD for the fabrication of high dielectric constant gate oxides in the MOSFET structure and for copper diffusion barriers in backend interconnects.4 In addition, ALD has met challenging requirements in other areas, including the deposition of high-quality dielectrics to fabricate trench capacitors for dynamic random access memory (DRAM).14

1.2 Overview of science and technology around ALD
A major driving force for the recent interest in ALD is a critical difference from conventional chemical vapor deposition (CVD). ALD is a CVD process based on the self-limited adsorption of vapor molecules only by surface reaction. It differs from the conventional CVD process in the way that it is carried out, as shown in Fig. 1. The CVD process shown in Fig. 1(a) is based on one or more volatile precursors that react and/or decompose on the substrate. Meanwhile, for the ALD process shown in Fig. 1(b), the precursor and reactant are alternately exposed to the surface and the process is based only on surface reactions. Thus, the sequential cycle in ALD
employs the better thin-film growth characteristics of ALD, such as excellent step coverage and large-area uniformity as well as atomic-scale thickness and composition controllability, than CVD. Thus, ALD has been a key technical enabler of high-density memory device fabrication for more than 10 years now.

In contrast to conventional thermal ALD, in which the necessary energy for the surface reaction is provided entirely by thermal energy from the heating of the substrate, additional chemical energy is provided to carry out plasma-enhanced ALD (PE-ALD). In other words, radicals with high reactivity facilitate the chemical reaction, which allows deposition at significantly lower temperatures than conventional in thermal ALD. Moreover, the existence of ions and electrons in the plasma produce different film properties, sometimes resulting in enhanced device properties. In addition, since ALD is a surface-sensitive deposition technique, surface modification by plasma exposure can be used to alter nucleation and adhesion. These make PE-ALD attractive as an alternative method for nanoscale semiconductor device fabrication. Recently, we reviewed the basic aspects and characteristics of PE-ALD.15) In this paper, we describe the characteristics and film properties of PE-ALD, focusing on nanoscale semiconductor devices: gate oxides, Cu metallization, and nanoscale contacts.

2. Characteristics of PE-ALD

The detailed characteristics of PE-ALD compared with those of conventional thermal ALD were reported previously.15) Here, we briefly summarize the essential characteristics of PE-ALD, in contrast with those of the conventional thermal ALD process. Figure 1 shows the PE-ALD process schematically. The overall process sequence of PE-ALD is similar to that of thermal ALD. The process sequence is composed of four steps: precursor exposure, purging, reactant exposure, and purging. Detailed reviews of the ALD process can be found in the literature.1) In PE-ALD, however, plasma is generated during the reactant exposure sequence. The generation of radicals in the plasma provides high reactivity. It should be noted that the plasma should not be turned on during the precursor exposure step, because it would disturb the self-limited adsorption of the precursor molecules.

Owing to the enhanced reactivity caused by the radicals, PE-ALD has several benefits over conventional thermal ALD, such as a reduced process temperature, improved film properties, and versatile reactions. Because of the lower growth temperature, the “process window” is effectively widened to a lower temperature region. Figure 2 shows examples of the PE-ALD of Ta-based materials.16) Usually, the reactivity of hydrogen molecules is too low to reduce a Ta precursor such as TaCl5. Thus, an unacceptably high deposition temperature (for example, over 400 °C for a metallization process) is required in conventional thermal ALD. However, in PE-ALD Ta, a low deposition temperature (below 200 °C) is possible owing to the high reactivity of the H radical. In addition, if a nitrogen source, such as a nitrogen radical, is provided with the hydrogen, TaN ALD becomes feasible.17) If a nitrogen containing precursor such as pentakis(dimethylamido)tantalum(V) [Ta(NMe2)5] is used, TaN is deposited by the incorporation of nitrogen from precursor molecules.18) Thus, PE-ALD allows versatile reactions that would not be possible with conventional thermal ALD.

Another noteworthy feature of PE-ALD is its ability to modify the surface by exposure to plasma. When plasma is induced, discharge ions and electrons are generated. These ions are accelerated by biased voltage toward the surface of the substrate. Then, the accelerated ions are physically sputtered or chemically react with substrate materials on the surface, resulting in damage.19) Although there is a possibility of damaging the substrate, proper control of the process parameters can allow for the enhancement of surface properties without creating significant problems. In particular, plasma usually promotes nucleation behavior during ALD resulting in improved growth characteristics. Figure 3 shows the thickness of Ru deposited by PE-ALD using NH3 plasma as the reactant on various substrates. It is well known that Ru deposited by thermal ALD using O2 has significant nucleation delay on Si and oxide surfaces.20) However, Fig. 3 shows that no significant nucleation delay was observed on various surfaces when using PE-ALD, indicating its usefulness. In addition, since plasma is composed of radicals, ions, electrons and neutral molecules, the properties of PE-ALD thin films can be modified by the interactions of these various species with the deposited thin films. For example, while radicals mainly contribute to improved reactivity, ions can contribute to the modification of film properties by providing kinetic energy to the deposited films. However, a difficult task is to establish a method of estimating the contribution of ions because the rates of ion-molecule reactions are too fast.21) Meanwhile, the radicals arrive on the film surface where they react to form the film. If the radicals are reactive, they undergo insertion reactions at the landing site. If such radicals are dominant, columnar growth occurs and the surface is rough. Less reactive radicals do not form bonds at the landing site, and are physisorbed on the surface. These physisorbed radicals can then hop from site to site until they finally react. This process of surface diffusion is essential to the formation of dense films having smooth surfaces.22) This can enhance film properties such as density, as we will describe later. However, deposition can cause damage to the surface, but can be avoided by careful control of the process.
Meanwhile, when using PE-ALD, there exists the possibility of limited step coverage compared with thermal ALD. Figure 4(a) shows a scanning electron microscopy (SEM) image of Ru deposited with PE-ALD using the NH$_3$ plasma. It can be seen that the Ru deposition was limited to the top part of the nanoscale via, which is due to the recombination of radicals inside the via. Thus, careful monitoring of the process is required to assure good conformality. However, PE-ALD does not always show poor conformality. Figure 4(b) shows a SEM image of PE-ALD Ga-doped ZnO grown by using oxygen plasma. As can be seen, good conformality comparable to that of thermal ALD was obtained. Thus, it appears that the conformality of PE-ALD is critically dependent on the choice of radicals as well as other process parameters. In fact, step coverage by ALD is determined by three separate conditions, which must be met for ALD reaction to give 100% step coverage. First, the chemistry of the two reactants must be suitable for undergoing a self-limiting reaction with the surface. Second, a sufficiently large dose of each reactant must be supplied to obtain stoichiometric films over the entire surface, including in the conformal surface in the substrate. Third, the doses of each reactant vapor must be present inside the via for a time long enough for reactants to react with the entire interior surface of via. However, systematic study of the conformality of PE-ALD process is yet to be performed.

In this study, we used different PE-ALD tools with a direct or remote plasma system, and are connected them to a radio-frequency (RF) plasma generator with a matching network. The tool with a direct plasma system has double showerheads, which help to realize uniform deposition by enabling different ways of exposing precursor and reactant. The use of remote plasma generated outside the deposition chamber, which results in only the radicals being directed into the system, can reduce unwanted defects related to ion bombardment during deposition. Details about these were presented in our previous report. In addition, tools for oxide deposition are equipped with oxidant plasma sources but those for metal or silicide deposition are equipped with reducing plasma sources with the base pressure of 10 mTorr.

3. Scaling down of semiconductor devices and applications of PE-ALD

ALD plays an important role in the fabrication of semiconductor devices. For example, ALD is an indispensable technology for the fabrication of nanoscale MIM capacitors, which are the key component in high-density DRAM devices. The overall application of ALD in nanoscale device fabrication and in other emerging applications was reviewed by us several years ago. Here, we will focus only on the applications of PE-ALD which exploit the benefits of plasma in key components of semiconductor devices: gate oxides, Cu metallization, and nanoscale contacts, as shown schematically in Fig. 5. Since the PE-ALD process for various applications requires the optimization of many parameters,
their proper selection including those of the precursor, the process temperature, the plasma power, and source, is strongly related to the target application. However, it is worth noting that three applications in this review require low deposition temperature to reduce thermal damage to devices.

3.1 PE-ALD for formation of gate dielectric

With device scaling, the gate oxide thickness should decrease accordingly. However, if SiO₂ is used, the physical thickness becomes too small, resulting in unacceptably large gate leakage. Thus, high-k materials such as HfO₂ should be used in nanoscale devices. HfO₂-based gate oxides have been implemented in high-performance logic devices since 2007.²⁶) ALD is a key technology for the formation of gate oxides, since the gate oxide thickness is only a 3 to 4 nm and an areal uniformity over a 300-mm-diameter wafer can only be achieved by ALD. With further scaling down of semiconductor devices, gate oxide technology is expected to present more challenges. Figure 6 summarizes some of the technical issues related to gate oxides that will emerge in coming years. Since the physical thickness of the gate oxide will decrease, ALD is expected to play an important role.

For now, thermal ALD is used for the formation of HfO₂-based gate oxides and PE-ALD is considered to be problematic owing to the potential for damage. However, if the process is carefully controlled, improved device properties can be realized by using plasma. Figure 7 shows the electrical properties of thermal ALD and PE-ALD HfO₂ deposited using an HfCl₄ precursor. After deposition, metal oxide semiconductor (MOS) capacitors were fabricated by sputtering of Ru. Prior to the electrical measurements, the MOS capacitors were subject to nitrogen annealing at 400 °C. Capacitance–voltage (C–V) measurements [Fig. 7(a)] show that the interface defect density (Dᵢ) of the PE-ALD HfO₂ was lower than that of the thermal ALD HfO₂ (1.7 × 10¹¹ vs. 1.8 × 10¹¹). Thus, in contrast to the belief that there is always plasma damage when using PE-ALD, a carefully controlled process could even improve some device properties. Also, the leakage current of the PE-ALD HfO₂ was almost one order of magnitude lower than that of the thermal ALD HfO₂, as shown in Fig. 7(b). Usually, the density of a PE-ALD film is higher than that of a thermal ALD film, which is often attributed to the energy transferred to the film from the species in the plasma.²⁷)

As mentioned above, with further device scaling, stringent requirements are expected for gate oxides. Thus, the use of additional elements may be necessary to solve potential technical issues. Rare earth oxides could be good candidates for this purpose. However, it should be noted that, owing to the limited availability of a proper precursor, it is often difficult to deposit rare earth oxides with good properties by ALD. As an example of the use of a rare earth oxide, we developed a La₂O₃ PE-ALD process using tris(isopropylcyclopentadienyl)lanthanum(III) [La(iPr₅Cp)₃] to produce a highly pure oxide.²⁸) La₂O₃ capping controls the flat voltage shift caused by Fermi level pinning of the high-k-based gate oxide.²⁹) Since the capping layer thickness is only several mono layers, ALD is the only viable technical option. Figure 8 shows the X-ray photoelectron spectroscopy (XPS) data of ALD La₂O₃/HfO₂ laminates with different compositional profiles, demonstrating the ability of PE-ALD to form a nanoscale gate oxide with controlled compositional profiles.

Additionally, the doping of rare earth elements in HfO₂ and other high-k materials can modify their physical properties. Ce- or Y-doping stabilizes the metastable cubic phase of HfO₂, resulting in a significant increase in the dielectric constant.³⁰) Figure 9 shows the leakage currents of MOS capacitors made with PE-ALD Dy₂O₃, HfO₂, and Dy-doped HfO₂. It can be seen that Dy-doped HfO₂ had a significantly reduced leakage current.³¹) Microstructure analyses showed the formation of epitaxial-like HfO₂ films caused by Dy-doping and subsequent annealing at 600 °C. In this work, a newly synthesized Dy precursor was utilized. Here, thermal ALD did not produce films because of the low reactivity of water molecules. Only PE-ALD successfully deposited films,
which indicates the importance of PE-ALD in the exploration of the incorporation of various elements for device performance enhancement.

3.2 PE-ALD for Cu metallization in BEOL

In this section, we summarize the potential technical benefits of PE-ALD for Cu metallization. An overall review of the application of ALD for Cu metallization can be found in our previous report.32) The Cu interconnect was introduced in the late 90s because of its low resistivity and good electromigration, which were promising for reducing RC delay and improving device reliability. To fabricate Cu interconnects, owing to the difficulty of Cu etching, the damascene process shown in Fig. 10 is employed. Besides the introduction of a novel integration process, Cu introduces additional difficulties when used as a wiring metal since Cu is a very fast diffuser. To prevent the diffusion of Cu, a diffusion barrier having good adhesion is needed. The gap filling of nanoscale vias and trenches is achieved by Cu electroplating, which requires the deposition of a conducting seed layer. Because of the aggressive scaling down of the interconnect structure, ALD is expected to be a promising technique for the deposition of the diffusion barrier and the seed layer.32)

Usually, ALD of metals is considered to be more difficult than that of oxides owing to the lack of a good reducing agent. H₂, which is a typical reducer, does not have sufficient reducing power to deposit metal thin films. The ALD of transition metals is particularly difficult to carry out. Thus, PE-ALD is a valuable tool for depositing very thin metal layers with good properties, including short nucleation delay and high purity. A potential deposition scheme of Ta-based materials was already discussed in Sect. 2. Figure 11 shows the Cu interconnect structure enabled by the use of an ALD barrier and seed layer. Here, a TaN diffusion barrier was deposited by the PE-ALD process mentioned above using a metal organic precursor, and it provided an effective diffusion barrier with a thickness of only 2 nm.18) In this example, Ru seed layer was deposited by PE-ALD with oxygen plasma.20) However, potential oxidation of the TaN barrier layer may be prevented by the use of Ru formed by PE-ALD with NH₃ plasma.20)

With the use of Cu, porous low-k materials should be implemented to further reduce RC delay. However, there is a technical issue related to metal penetration when using
porous low-k materials. As we previously reported, PE-ALD of a barrier could be a solution but there is a limited conformality of PE-ALD. In addition, a penetration sealing layer can be formed by PE-ALD. Figure 12 is a cross-sectional image of a PE-ALD SiNxCy layer deposited using bis(dimethylamino)dimethylsilane (BDMADMS) and a hydrogen plasma, and shows good conformality.

3.3 PE-ALD for silicidation on Si substrate

The contact resistance between the metal interconnects and the device becomes more severe with device scaling. Thus, it is essential to use a proper contact layer, that is, a silicide compound. Since, with device scaling, the “narrow-line-width-effect” of TiSi2 becomes a serious problem for the source/drain contact in MOSFETs, CoSi2 and NiSi have been studied as alternative contact materials. Generally, metal silicides are formed through physical vapor deposition (PVD) of a metal film followed by annealing. However, some nanoscale devices, especially memory devices, require the formation of contacts inside deep contact holes. ALD might be a promising deposition technique for this purpose. However, the ALD of most transition metals is difficult. Oxygen-based thermal ALD, which is a useful process for refractory metals such as Ru and Pt, cannot be applied to the deposition of transition metals such as Co and Ni because of their tendency to oxidize. Thus, transition metal ALD with a proper reactant is required for nanoscale contact formation. In the ALD of these transition metals, PE-ALD could be a viable solution. We developed various PE-ALD processes for Co and Ni, and the silicidation of PE-ALD metals. A detailed review of ALD and PE-ALD Co and Ni and processes for silicidation can be found in Ref. 36. Thus, here we include only a brief summary.

PE-ALD of Co and Ni was carried out using appropriate metal organic precursors and NH3 plasma. Under optimal conditions, highly pure Co films with resistivity as low as 10 Ω cm were deposited. Instead of NH3 plasma, a mixture of N2 and H2 can also be used. Figure 13 shows the XPS compositional depth profile of PE-ALD Co deposited using CoCp2 and N2/H2 plasma. A highly pure Co film was deposited with almost no contamination. The lowest resistivity was obtained at a N2/H2 flow ratio of 1:3, indicating the significant role of the NH3 radical. Similarly, highly pure Ni deposition is possible using NH3 plasma.

During PE-ALD of Co or Ni using NH3 plasma, the underlying Si substrate is subject to nitridization owing to the high reactivity of the N and NH3 radicals. Thus, a SiNx interlayer is formed between the PE-ALD Co or Ni and the Si. Figure 14 is a cross-sectional transmission electron microscopy image of PE-ALD Ni showing nm-thick interlayers. The existence of interlayers alters the silicidation process carried out by thermal annealing. The interlayer retards the diffusion of elements during annealing, resulting in an increased silicidation temperature and process time. However, as a result of the change in the diffusion rate, an epitaxial CoSi2 layer can be formed through interlayer mediated epitaxy, as we reported previously. Thus, in the fabrication of nanoscale contacts using Co or Ni, PE-ALD may play an important role in solving technical issues.

4. Summary and prospects

As described in this article, the use of plasma during PE-ALD could lead to various beneficial effects in the deposition of nanoscale thin films and their physical properties. The versatility of PE-ALD with highly reactive radicals will be extremely valuable considering the requirements for the deposition of novel materials in emerging applications. Compared with thermal ALD, there may be additional issues
to be solved for PE-ALD in addition to the complexity of the equipment and process. However, compared with thermal ALD, which has been studied for over thirty years, only a small number of reports is available regarding PE-ALD. Thus, more intensive study should be carried out on PE-ALD as a technical enabler of the fabrication of nanoscale semiconductor devices.

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