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<th>A Brief Review of Plasma Enhanced Atomic Layer Deposition of Si₃N₄</th>
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A Brief Review of Plasma Enhanced Atomic Layer Deposition of Si₃N₄

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ABSTRACT

Silicon nitride (Si₃N₄) thin films have attracted considerable interest as an important material for use in next-generation devices such as a gate spacer in 3D fin field-effect transistors (finFETs), charge trap layers, etc. Many studies using the Si₃N₄ plasma enhanced atomic layer deposition (PEALD) method have been conducted, owing to its advantages over other Si₃N₄ deposition methods. In this review, the recent studies on PEALD of Si₃N₄ thin films are summarized, and the effects of some process parameters including plasma power, frequency, and process temperature on the material properties of Si₃N₄ are discussed. In addition, some properties of Si₃N₄ thin films such as conformality, wet etch rate, and others are reviewed.

Keywords: Silicon nitride (Si₃N₄), Plasma enhanced atomic layer deposition (PEALD), Process temperature, Step coverage, Wet etch rate

I. Introduction

Recently, silicon nitride (Si₃N₄) has attracted considerable interest owing to its diverse range of applications [1–10]. For instance, Si₃N₄ is used as a permeation barrier for flexible organic light emitting devices [7–10] or as a charge trap layer for logic and memory devices [4]; Si₃N₄ gate spacers have also been studied extensively [1–6]. High quality and excellent conformality are critical requirements for various applications of Si₃N₄ thin films. In addition, lowering the deposition temperature is an important factor for devices employing low temperature substrates such as polymer substrates. To satisfy such a requirement for employing Si₃N₄ thin films, many studies have used various deposition techniques such as chemical vapor deposition (CVD), low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD), atomic layer deposition (ALD), plasma enhanced atomic layer deposition (PEALD), and so on [11–43].

Low pressure chemical vapor deposition is the most common technique used to fabricate Si₃N₄ thin films because of its simple method and low cost. However, it is difficult to achieve a conformal layer on a high aspect ratio substrate. In addition, the deposition needs to be conducted at high temperature (> 700 °C) [17,18]. Plasma enhanced chemical vapor deposition can deposit films at temperatures lower than that by using thermal LPCVD. Unfortunately, this leads to poor step coverage and low film quality [3,15,16]. To address issues related to conformality, the ALD technique has been studied extensively [19–26]; ALD is a cyclic process that offers atomic scale thickness control of the material that is being deposited. In addition, ALD methods can deposit thin films with high quality in terms of low wet etch rate and high conformality at low process temperatures [25,26]. However, ALD methods have several challenges such as a relatively high thermal budget for actual device application and low throughput (GPC > 2 Å/min) that hinders the industrialization of ALD methods [22,26]. By assisting with a plasma for dissociating reactive gases during ALD with PEALD processes, a thin film with a good step coverage on a high aspect ratio structure can be deposited at low temperatures. A plasma with reactive molecules can be used instead of exposure to reactant molecules only during the reactant exposure step; highly reactive species are formed during the reactant exposure step, which allows the deposition of high quality films with a high growth rate while lowering deposition temperatures [15,27–42].

In this paper, we briefly reviewed the recent work of PEALD Si₃N₄ and related process parameters that could determine film characteristics. Furthermore, this review will discuss properties of the film that are dependent on deposition conditions. A schematic of a PEALD cycle is shown in Fig. 1. Each Si₃N₄ PEALD cycle can be divided into four steps. In the first precursor adsorption step, similar to ALD, a Si precursor is introduced into the deposition chamber. Si precursors are chemisorbed on the surface through self-limiting reactions followed by a purge step. In the following plasma exposure step (for ALD, reactant exposure step), plasma-generated reactive species react with the adsorbed precursor on the surface. As a plasma source, capacitively coupled plasma (CCP) or inductively coupled plasma (ICP) sources are commonly used along with N₂, NH₃, or N₂/H₂ to generate reactive plasmas [5,15,27–40]. To optimize PEALD processes, various parameters should be adjusted to meet the material properties of Si₃N₄ required for the application.

II. Process parameters

As mentioned above, in PEALD, there are various process parameters including reactant gas, plasma source, precursor, precursor...
dose time, purge time, process temperature, and others. In this section, the effects of some process parameters influencing SiNₓ deposition are briefly discussed.

1) Precursors
Many kinds of precursors such as trisilylamine (TSA), diisopropyldiaminosilane (DIPAS), bis(tertiary-butyl-amino)silane (BTBAS), trisdimethylaminosilane (3DMAS), dis(sec-butylamino)silane (DSBAS), hexachlorodisilane (HCDS), pentachlorodisilane (PCDS), dichlorosilane (DCS), and tetramethylsilane (TMS) have been reported as Si sources of SiNx PEALD [5,27–30,32–36,38–40]. Table 1 summarizes studies on SiNₓ PEALD in recent decades; it also provides details on Si precursors, reactant gas, plasma source, deposition temperature, and growth rate.

2) Plasma conditions
Plasma characteristics such as density of radicals, energy, and density of electrons and ions have a considerable influence on SiNₓ PEALD processes. Therefore, controlling plasma conditions such as rf frequency is important.
power and frequency is important.

Weeks et al. [32] reported PEALD SiN, using a precursor of neopentasilane (NPS) and N₂ plasma by using a CCP source at the temperature of 275 °C. They determined the effects of plasma power on the wet etch rate, hydrogen concentration, and film density. A high plasma power resulted in more energetic ions that could damage the depositing film. Therefore, as shown in Fig. 2, the wet etch rate of the SiN films in a 100:1 HF solution (HF: deionized water = 1:100) decreased when the plasma power decreased from 750 to 250 W, which was consistent with the results of low hydrogen contents and high film density, as summarized in Table II. With a decrease in the power from 750 to 250 W, the H concentration decreased while the film density increased. The wet etch rate is closely related to the H concentration in the film and film density [30].

Park et al. [31] also investigated the effect of RF power on film property. Charge trap density, wet etch rate, N/Si ratio, carbon concentration, and oxygen concentration were measured for SiN film deposited by PEALD using DTDN2-H₂ and N₂ plasma with various plasma powers ranging from 75 to 400 W. As shown in Fig. 3, the carbon and oxygen concentrations of the film increased with increasing RF power; however, the N/Si ratio decreased. This can be attributed to the dissociation of precursor ligands that desorbed from the surface because of the high RF power of the plasma. Owing to the deposition of the carbon impurity, the wet etch rate of the film was also increased with increasing RF power.

Another important parameter influencing plasma properties such as electron density and electron temperature is the frequency of plasma generation. Thus, the plasma generation frequency also needs to be controlled to improve SiN thin film quality. King et al. compared the Fourier-transform infrared spectroscopy (FTIR) results for SiN, deposited using SiN₄ and N₂ plasma with different source frequencies [15]. As shown in Fig. 4, PEALD SiN film using a frequency of 13.56 MHz showed a high intensity of the Si-N stretching mode. In contrast, the peak intensities of the Si-H and N-H stretching modes were lower than those obtained from films deposited using a frequency of 200–400 kHz. A higher plasma frequency can achieve the effective decomposition of N₂ gas, thus allowing a higher density of N and N⁺ ions. Reactive species such as N and N⁺ ions can react with the Si-H surface bonds and form a bond with Si by replacing the H atom. Therefore, PEALD SiN films deposited using higher frequency showed less Si-H and N-H bonding compared to those using lower frequency.

3) Process temperature

PEALD methods can lower the deposition temperature compared to other deposition techniques. However, a considerably lower process temperature is still required for SiN, PEALD for various applications of SiN, films. For example, in the case of polymer or flexible substrates, very low process temperatures are required. The effect of the substrate temperature on the surface reaction mechanism...
in SiN, PEALD systems has been studied. Results showed that the PEALD process could lower the process temperature compared to other deposition techniques (LPCVD and ALD, etc.). However, the quality of SiN thin films is still temperature dependent.

Park et al. investigated the effect of process temperature on step coverage and wet etch rate [37]. They deposited SiN films on trench patterned wafers (aspect ratio (AR) of 5.5) using 1,3-di-isopropylamino-2,4-dimethylcyclosilazane (CSN-2) precursor and N$_2$ plasma (27.12 MHz) at temperatures between 250 and 500 °C. As shown in Fig. 5, SiN thin films grown at 500 °C showed a high step coverage of 98% at the center of the trench. With increasing temperature, the step coverage of the middle and bottom side walls showed substantial enhancement in conformality. In addition, the wet etch rate of a silicon nitride film in a diluted HF solution (300:1 diluted HF solution) decreased with an increasing process temperature as shown in Fig. 6. Differences in the wet etch rates of the bottom and lower sidewalls also decreased for films deposited at 500 °C. These results indicate that a higher process temperature offers more reactions between N radicals of the plasma and the precursor ligands on the surface. At a high process temperature, N radicals can reach the lower sidewall of the trench and effectively remove ligands from the surface, which results in excellent step coverage and wet etch rate.

Similarly, Jang et al. studied the temperature dependency of SiN thin film properties such as surface roughness and refractive index [27]. Their results revealed that SiN thin films deposited at lower temperatures showed lower defect density caused by high hydrogen content.

High defect density is the common reason for hysteresis in a capacitance–voltage (C–V) curve. Therefore, as shown in Fig. 7, the SiN thin film deposited at 250 °C showed a considerably lower hysteresis curve. Although lower hysteresis was observed at lower PEALD temperature because of the high hydrogen content, crystallographic defects were found to be higher at lower deposition temperatures. In addition, hydrogen could be removed during processes such as annealing. Therefore, the deposition of SiN at the lower PEALD temperature tends to cause more defect formation in the film.

Figure 5. (Color online) (a) Step coverage of PEALD SiN thin film deposited by PEALD at various process temperatures. Cross-sectional TEM images of SiN thin films deposited by PEALD consisting of CSN-2 exposure and N$_2$ plasma at (b) 250, (c) 350, and (d) 500 °C after wet etch in a 300:1 diluted HF solution. Reproduced with permission from [37], Copyright 2018, American Chemical Society.

Figure 6. (Color online) (a) Wet etch rate of PEALD SiN depending on process temperature. Cross-sectional TEM images of SiN films deposited by PEALD consisting of CSN-2 exposure and N$_2$ plasma at (b) 250, (c) 350, and (d) 500 °C after wet etch in a 300:1 diluted HF solution. Reproduced with permission from [37], Copyright 2018, American Chemical Society.

Figure 7. (Color online) C–V curves of SiN films deposited by PEALD as a function of process temperature. Reproduced with permission from [27], Copyright 2014, John Wiley and Sons.
III. Properties of SiNₓ

In this section, we discuss common properties of SiNₓ thin films. These properties are important for applications of the film.

1) Step coverage

When the feature size of a semiconductor device decreases, high conformality on high aspect ratio structures is a critical requirement. Studies on SiNₓ PEALD focusing on the conformality of the film have been reported. For example, Faraz et al. deposited a SiNₓ layer on trench-patterned wafers with an aspect ratio of 4.5 using a PEALD method [33]. Films were deposited by alternating the exposures of di(3-sec-butylamino)silane (DSBAS) precursor and N₂ plasma at 13.56 MHz at 500 °C. The step coverage of SiNₓ film was examined. As shown in Fig. 8, a bottom coverage of 69% and sidewall coverage of 50% were observed using PEALD. The step coverage was not as good as that in ALD processes. However, several reports on SiNₓ thin films deposited by the PEALD method showed a good step coverage of above 90%.

Ovanesyan et al. [36] reported SiNₓ thin films with ~95% conformality on patterned structures (aspect ratio of 5). Figure 9 is a TEM image for a ~25-nm-thick SiNₓ thin film deposited from SiCl₄, CH₃NH₂, and N₂ plasma at 400 °C. In this case, Ovanesyan et al. [36] suggested a novel three-step PEALD process. By adding a CH₃NH₂ exposure step in the PEALD cycle, conformality and growth rate per cycle (GPC) were increased compared to those with the PEALD method using aminosilanes and N₂ plasma. Park et al. [37] also reported that SiNₓ thin films deposited by PEALD at 500 °C showed a high conformality of ~95% on patterned wafers of AR 5.5. Thus, PEALD methods can be used to deposit SiNₓ thin films with high conformality on trench structures. However, to achieve higher conformality on a high aspect ratio structure (AR > 6) with low process temperature, various attempts such as using a novel Si precursor or additional steps in PEALD process are required.

2) Wet etch rate

The wet etch rate is highly correlated with the integrity and density of the film. Kim et al. [5] demonstrated the relationship between film density and wet etch rate and suggested a SiNₓ etching mechanism. They investigated the effects of plasma gas composition and process temperature on wet etch rates of SiNₓ deposited by PEALD. The SiNₓ thin films deposited using hexachlorodisilane (HCDS) precursor and Ar/NH₃ plasma at 300 °C showed a wet etch rate of 1.2 nm/min in a 500:1 HF solution. By comparing the wet etch rates of SiNₓ deposited at various conditions, Kim et al. [5] found that the densification of the SiNₓ thin film is caused by increased Si-N bonds, which eliminate hydrogen and result in low wet etch rates.

In another study, Knoops et al. [29] deposited SiNₓ thin films on planar substrates using bis(tertiary-butyl-amino)silane (BTBAS) and N₂ plasma at 400 °C, and they investigated the wet etch rate of the films before and after a dip in a 7:1 HF solution (H₂O : HF = 7:1). A low wet etch rate (~0.1 nm/min) was obtained because of the low hydrogen concentration in the films. This result is comparable to the wet etch rate of the SiNₓ thin film deposited by chemical vapor deposition (CVD) at high temperature.

Besides studies on the wet etch rate of SiNₓ thin films on planar surfaces, the wet etch rate has also been studied for high aspect ratio structures. However, most studies showed different wet etch rates for the sidewall, bottom, and top surface of 3D trench patterns [36]. The poor wet etch rate at the bottom sidewall is problematic in silicon nitride PEALD processes.

IV. Concluding remarks

This brief review examined not only the deposition of SiNₓ thin films using the PEALD process, but also summarized the characteristics of SiNₓ thin films. Compared to other deposition methods, the PEALD process provides atomic scale thickness control and excellent conformality with a lower process temperature. Various SiNₓ PEALD processes have been studied, and some results have shown excellent film properties such as good step coverage and low wet etch rate. However, for device applications, several issues need to be solved. To address these issues, the effect of each PEALD process parameter (temperature, plasma power, exposure time, and gas composition) on the film growth mechanism needs to be understood in detail. Further, new plasma sources and precursors that can deposit highly conformal and dense thin films at low process temperatures for a variety of state-of-the-art devices, which require SiNₓ thin films, must be developed. Further studies on the deposition mechanism are required to enhance the quality of the deposited SiNₓ thin films.
References