A Brief Review of Plasma Enhanced Atomic Layer Deposition of Si\textsubscript{3}N\textsubscript{4}

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ABSTRACT

Silicon nitride (Si\textsubscript{3}N\textsubscript{4}) thin films have attracted 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 Si\textsubscript{3}N\textsubscript{4} plasma enhanced atomic layer deposition (PEALD) method have been conducted, owing to its advantages over other Si\textsubscript{n} deposition methods. In this review, the recent studies on PEALD of Si\textsubscript{n} thin films are summarized, and the effects of some process parameters including plasma power, frequency, and process temperature on the material properties of Si\textsubscript{n} are discussed. In addition, some properties of Si\textsubscript{n} thin films such as conformality, wet etch rate, and others are reviewed.

Keywords: Silicon nitride (Si\textsubscript{3}N\textsubscript{4}), Plasma enhanced atomic layer deposition (PEALD), Process temperature, Step coverage, Wet etch rate

I. Introduction

Recently, silicon nitride (Si\textsubscript{n}) has attracted considerable interest owing to its diverse range of applications [1–10]. For instance, Si\textsubscript{3}N\textsubscript{4} 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]; Si\textsubscript{n}, gate spacers have also been studied extensively [1–3,6]. High quality and excellent conformality are critical requirements for various applications of Si\textsubscript{n}, 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 Si\textsubscript{n} 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 Si\textsubscript{n} thin films because of its simple method and low cost. However, it is difficult to achieve a conformal layer on a high aspect ratio structure. 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 A/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 reactant 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 Si\textsubscript{n}, 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 Si\textsubscript{n} 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 N\textsubscript{2}, NH\textsubscript{3}, or N\textsubscript{2}/H\textsubscript{2} to generate reactive plasmas [5,15,27–40]. To optimize PEALD processes, various parameters should be adjusted to meet the material properties of Si\textsubscript{n} 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), disopro-
pylaminosilane (DIPAS), bis(tertiary-butyl-amino)silane (BTBAS), tris-
dimethylaminosilane (3DMAS), di(sec-butylamino)silane (DSRAS), hexa-
chlorodisilane (HCDS), pentachlorodisilane (PCDS), dichlorosilane (DCS), and tetrachlorodisilane (TMS) have been reported as Si sources of SiNx PEALD [5, 27–30, 32–36, 38–40]. Table I 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...
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 SiNₓ 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 SiNₓ 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 SiNₓ thin film quality. King et al. compared the Fourier-transform infrared spectroscopy (FTIR) results for SiNₓ deposited using SiNₓ and N₂ plasma with different source frequencies [15]. As shown in Fig. 4, PEALD SiNₓ 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 SiNₓ 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 SiNₓ, PEALD for various applications of SiNₓ 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-dimethylcyclasilazane (CSN-2) precursor and N₂ plasma (27.12 MHz) at temperatures between 250 and 500 ºC. As shown in Fig. 5, SiN thin films grown at 500 ºC 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 ºC. 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 ºC 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.
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(tert-butylamino)silane (DSBAS) precursor and N₂ plasma (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 Si₂Cl₆, 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 (~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.
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