

HfO₂ Film Formation by Metal-Organic Chemical Vapor Deposition

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Abstract

We synthesized highly pure (>99.99999%) liquid CVD precursor tetrakis-diethylamido hafnium (TDEAH:Hf(NEt₂)₄) for HfO₂ thin film formation. TDEAH was a colorless liquid at room temperature. It had a moderate vapor pressure (7.5 torr at 80°C). And it was stable at 80°C for 180 days. So we tried to deposit HfO₂ film by LPCVD using TDEAH and investigated its properties. The film included the impurities C and N. Increasing the additional O₂ flow rate decreased the amount of residual C. Increasing the deposition temperature decreased the amount of N. As the result, we obtained a stoichiometric HfO₂ film with low impurity concentrations. We also investigated the quality of step coverage, and obtained good coverage and smooth surface morphology at high temperature (450°C). Deposited films had a polycrystalline structure and an amorphous layer 2 nm thick at the Si interface.

Introduction

A new insulator material with higher permittivity than SiO₂ is required for fabricating future metal-oxide-semiconductor (MOS) devices, because the conventional SiO₂ gate will be too thin to prevent current leakage. HfO₂ and its silicate have high dielectric constants and good thermal stability. Therefore, they have been considered as promising materials for future gate dielectrics [1-4]. These films have usually been deposited by physical vapor deposition (PVD), such as reactive sputtering. However, the step coverage quality of the deposited film is not good enough. These are factors that deteriorate the device performance. From this point of view, chemical vapor deposition (CVD), which can provide high-quality step coverage and good-quality thin films with uniform thickness, could improve the device characteristics. Despite these advantages, only a few results of using CVD for HfO₂ film have been reported, because many kinds of Hf source, such as (EtO)₄Hf, DPM₄Hf and HfCl₄ are solid at room temperature and do not have sufficient vapor pressure for supplying them into the deposition chamber [5,6]. Therefore, a direct vaporization system has been used to obtain the Hf source. However, this system may cause the Hf source gas to decompose before it is injected into the deposition chamber. These problems may deteriorate the quality of the film, including its thickness and crystalline structure.

In this paper, we describe the Hf source gas tetrakis-diethylamido-hafnium (Hf(NC₂H₅)₄:Hf(NEt₂)₄:TDEAH) (Fig. 1), which was liquid at room temperature and had moderate vapor pressure, meaning that it is appropriate as a CVD precursor. We synthesized this precursor, investigated its chemical properties, and deposited HfO₂ film on a Si substrate by low-pressure CVD (LPCVD) using the TDEAH/O₂ gas system. In particular, we analyzed the amounts of residual impurities in the films and the step coverage quality of films deposited on substrates with trenches.

Hf precursor TDEAH (Hf(NEt₂)₄)

All manipulations were carried out under an inert atmosphere using conventional Schlenk tube techniques. Solvents were purified by standard methods. We used n-BuLi, Et₂NH, and HfCl₄ as purchased. TDEAH:Hf(NEt₂)₄ was prepared from HfCl₄ + Et₂NLi partially according to a published procedure [7] (yield: 60%, b.p.: 117°C at 0.04 torr). ¹H-NMR (benzene-d₆) 1.15 (t, -CH₃), 3.35 (q, -N-CH₂-).

We investigated its metal impurity (by inductively coupled plasma mass spectroscopy (ICP-MS)), Cl purity (by titration), vapor pressure, and chemical reactivity with air and water. The metal purity of this compound was 99.99999% up (except for Zr). And the amount of residual Cl in it was less than 80 ppm. This compound was not pyrophoric in air, but was sensitive to moisture, in particular, it reacted violently with water. And it had moderate vapor pressure of 7.5 torr at 80°C (Fig. 2), which is appropriate for a CVD precursor. Moreover, to confirm the stability of this precursor, we kept the TDEAH at 80°C for 180 days and measured its nuclear magnetic resonance (NMR) spectroscopy before and after. There was no change between the two spectra. From the stability viewpoint, this precursor for CVD process was stable at 80°C. In addition to these, to investigate the reaction mechanism, we carried out a forced thermal decomposition test. The vessel was filled with TDEAH, which was kept at 150°C for 3 days. The generated gases were collected and analyzed by gas chromatograph mass spectrometry (GC-MS). This analysis revealed the species of these gases, which were CH₃-CH₃ (ethane), CH₃-CH₂-CH=CH₂(butene), and HN-(NC₂H₅)₂ (diethylamine). This means that the Hf-N bond could be cleaved even at 150°C and that we think this precursor is suitable for oxide film formation.

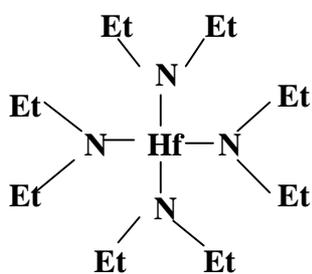


Fig. 1. Structure of TDEAH.

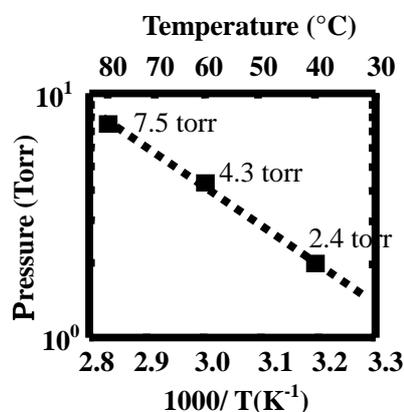


Fig. 2. Vapor pressure of TDEAH.

HfO₂ deposition by LPCVD

● Experimental

A schematic diagram of the CVD apparatus used in this study is shown in Fig. 3. The system uses a cold-wall-type LPCVD and the chamber is made of stainless steel. The system was pumped out using a turbo molecular pump and films were deposited under reduced pressure (1 torr). The substrates were of two types: Si (100) without and with a trench 1 μm wide and 2.5 μm deep. The substrate with the trench was prepared to investigate the quality of coverage. The substrate was heated by a heating element mounted below it. The TDEAH/O₂/N₂ gas system was used for the deposition.

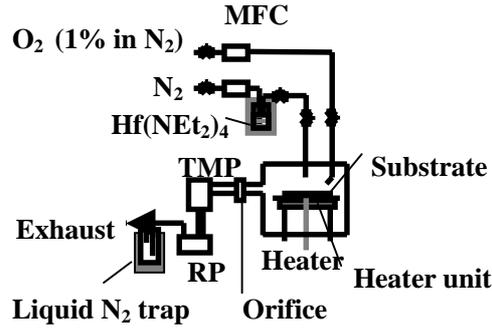


Fig. 3. CVD apparatus.

TDEAH gas was introduced into the deposition chamber by a bubbling system and N_2 was used as the carrier gas. To prevent liquefaction of the source before it entered the deposition chamber, the line from the bubbler to the chamber was maintained at 85°C . Changing the bubbler temperature and the carrier N_2 flow rate controlled the amount of TDEAH vapor introduced into the reactor. The N_2 gas flow rate was changed with a mass flow controller. During the deposition, O_2 gas (1%) diluted by N_2 gas (99%) was injected to obtain the HfO_2 film. This oxygen source was introduced into the chamber through a separate gas-supplying nozzle from that of TDEAH, because oxygen causes TDEAH to decompose. Before the deposition, the substrate was etched with a diluted HF solution to remove the native oxide on the surface, and rinsed with de-ionized water. After that, the substrate was placed into the chamber, and then heated to the deposition temperature. Thus the film was deposited. The typical deposition temperature, total pressure, diluted O_2 gas flow rate, N_2 carrier gas flow rate, and bubbling system temperature were $300\text{--}450^\circ\text{C}$, 1 torr, 0–20 sccm, 40 sccm, and 80°C , respectively. The atomic concentrations of C, N, O and Hf in the deposited film were determined by x-ray photoemission spectroscopy (XPS). The step coverage quality of the film deposited on the substrate with the trench was evaluated by scanning electron microscopy (SEM). The film structure was observed by transmission electron microscopy (TEM).

● Results and discussion

We confirmed that the deposited film contained Hf and O by XPS, but found that it also contained C and N (Fig. 4).

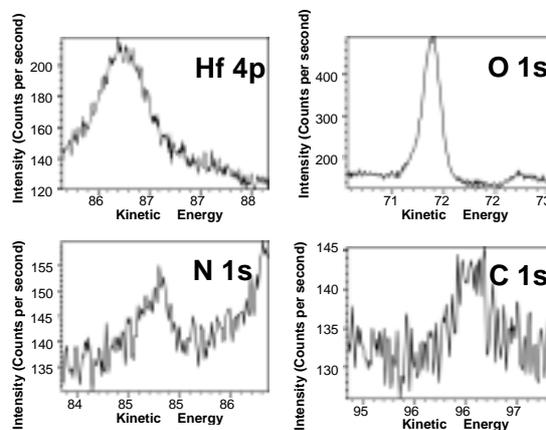


Fig. 4. XPS signals of the deposited film.

The effects of the diluted O₂ gas injection on the amounts of residual C and N are shown in Fig. 5. The deposition temperature was 300°C. The amount of residual C decreased dramatically as the O₂ gas flow rate increased. Possibly C atoms on the growing surface film reacted with O₂ during the deposition and were desorbed as CO or CO₂. On the other hand, the amount of residual N was almost constant independent of the O₂ gas flow rate. This indicates that the Hf-N chemical bond of this precursor cannot be broken through reaction with O₂, so the injection of O₂ gas during deposition was not able to reduce the amount of residual N in the film. The effects of the deposition temperature on the amounts of residual C and N are shown in Fig. 6. The O₂ gas flow rate was 10 sccm. The amount of residual C decreased as the deposition temperature increased, which indicates that the rate of chemical reaction of C and O₂ increased at higher temperatures. The amount of N also decreased as the deposition temperature increased, indicating that the Hf-N chemical bond of this compound was directly broken due to the thermal energy.

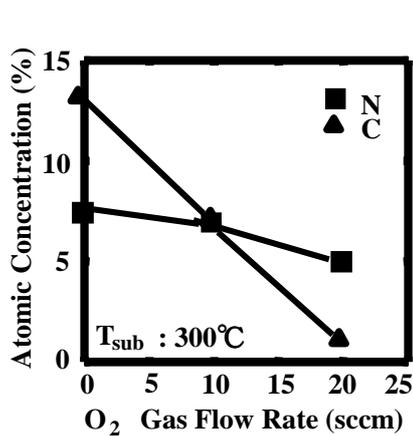


Fig. 5. Amounts of C and N in the film (O₂ gas flow rate).

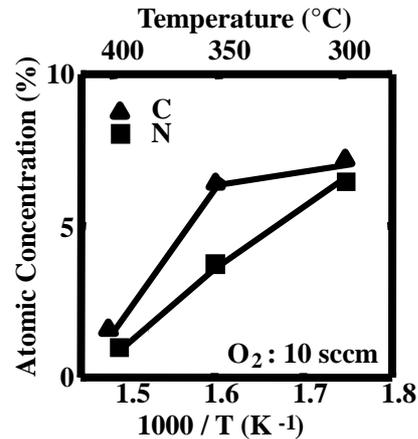


Fig. 6. Amounts of C and N in the film (deposition temperature).

The atomic concentration ratio of O to Hf is shown as functions of deposition temperature and O₂ gas flow rate in Fig. 7. With decreasing concentrations of C and N impurities, the atomic concentration ratio of O to Hf became saturated at the stoichiometric composition of 2. When the deposition temperature was 300°C, the ratio (O/Hf) was less than 2, independent of the O₂ gas flow rate. This means that it is difficult to obtain a stoichiometric HfO₂ film with low impurity concentrations at low temperature even with an O₂ supply. In the result above 350°C, on the other hand, the amounts of residual C and N in the film decreased, and the ratio became saturated at 2 under a relatively low O₂ gas flow rate. The effect of deposition conditions on the step coverage quality of the HfO₂ film deposited on the substrate with trench is shown in Fig. 8. Obviously, good step coverage quality was obtained at higher temperatures. When the deposition temperature was 350°C, the step coverage quality was poor (Fig. 8(a)). In contrast, at 450°C, the step coverage quality was significantly better (Fig. 8(b)).

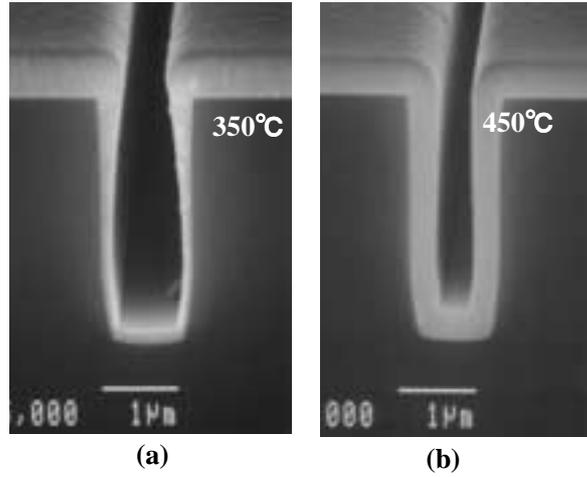
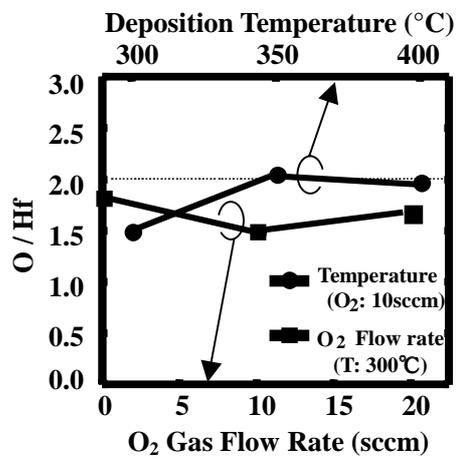


Fig. 7. O/Hf ratio of the deposited film. Fig. 8. Cross-sectional SEM images of the film.

A typical cross sectional TEM image of the deposited film is shown in Fig. 9. Regardless of the deposition conditions, all the films in this study had a polycrystalline structure and an amorphous layer 2 nm thick at the Si interface. The grain boundaries of the poly-crystals may affect the properties of the film, such as leakage current. We need to investigate the correlation between these electric properties and the film structure.

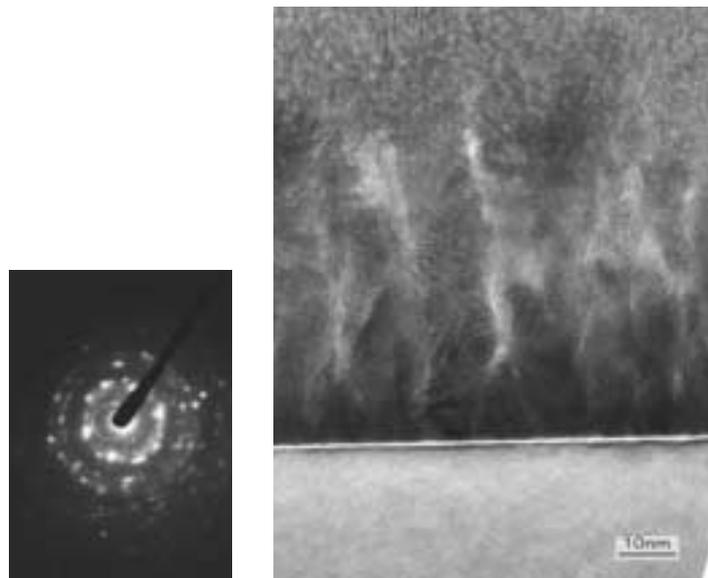


Fig. 9. Cross-sectional TEM image of the film.

Conclusion

We synthesized TDEAH as a precursor of HfO₂ film for CVD. We also investigated the metal impurity, Cl impurity, vapor pressure, chemical reactivity with water and air, and thermal stability. We deposited HfO₂ films using this precursor by LPCVD and found that the deposited film included C and N. However, we succeeded in reducing the amounts of these impurities to obtain a stoichiometric HfO₂ film with low impurity concentrations. We investigated the step coverage quality and found that deposition at higher temperature (450°C) produced good step coverage quality. The HfO₂ films deposited under present conditions using TDEAH had a poly-crystalline structure and an amorphous layer 2 nm thick at the Si interface.

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