Materials Research Express

PAPER

Growth of hafnium dioxide thin films via metal-organic chemical vapor deposition

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Keywords: hafnium(IV) acetylacetonate, hafnium dioxide films, MOCVD

Abstract

Metal-organic chemical vapour deposition (MOCVD) is a key technique for depositing thin solid film materials for use in important technological applications. To obtain thin films of the desired standard, it is essential to design volatile, reactive and thermally stable precursors. A metal-organic precursor consisting of Hf with excellent vaporization characteristics and low decomposition temperature has been reported. Hafnium dioxide thin films on a Mo substrate were obtained via thermal MOCVD using Hafnium(IV) acetylacetonate(Hf(acac)₄) in a horizontal cold-wall reactor. The Hf(acac)₄ precursor was synthesized from HfCl₄ and Hthd in methanol. Hf(acac)₄ was characterized using elemental analysis and infrared spectroscopy. The thermal decomposition properties were studied using thermogravimetric analysis under a nitrogen atmosphere. The results showed that Hf(acac)₄ was completely volatised at 245 °C. The thin films products were investigated using x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The results from these measurements revealed that the main crystalline phase was the monoclinic phase, the surface consists of hafnium and oxygen and the morphology was densely packed and composed of visible grains.

1. Introduction

Thin films of hafnium dioxide (HfO₂) have a number of important technological applications, such as protective coatings, optical coatings, mirrors, sensors and dielectric films in microelectronics [1–7]. HfO₂ exhibits a high dielectric constant, wide band gap, high melting point, thermal and chemical stability [8–11]. The main methods used to prepare HfO₂ films include atomic layer deposition (ALD) [5, 6], ion beam-assisted deposition (IBAD) [10, 12] and metal organic chemical vapor deposition (MOCVD) [1–3, 7, 13]. Some new methods to prepare HfO₂ films have been proposed, such as laser chemical deposition [14] and plasma-enhanced atomic layer deposition (PEALD) [15, 16]. Besides the development of new methods, some chemical elements have been added to improve the quality of HfO₂ films, such as the addition of lanthanum [17], zirconium [18] and yttrium [19].

MOCVD is an attractive technique used for the deposition of high-quality films HfO₂, offering the potential for large area growth, good control of film thickness, film uniformity and excellent conformal step coverage on non-planar device geometries. An essential requirement for a successful MOCVD process is the availability of precursors with appropriate physical properties and decomposition characteristics. The availability of volatile metal-organic precursors possessing sufficient vapor pressure, thermal stability during the evaporation process, and low temperature of decomposition are some of the features desired. It is also an advantage if the precursor is unreactive toward water, giving it a good ambient stability and long shelf-life [20].

A wide variety of precursors have been used for the MOCVD of HfO₂, many of which have a number of drawbacks associated with them. For instance, alkoxides have poor thermal stability and their self-limiting...
growth has been limited to temperatures well below 300 °C. Alkoxide ligands reach a relatively large volume to achieve sufficient volatility, but bulky alkoxide ligands will cause carbon contamination [21]. The majority of [Hf(OR)₄] complexes are dimeric or polymeric with limited volatility [20], [Hf(OtBu)₄] and [Hf(OiPr)₄] are highly reactive and moisture-sensitive, therefore, they have a short shelf-life and a tendency to block the MOCVD reactor inlet lines [22–24]. The amide precursors decompose at relatively low temperature (∼300 °C), resulting in the incorporation of a high amount of impurities such as carbon and poor film density [25]. The metal alkylamides are highly reactive, not very stable in solution and highly air and moisture sensitive, which can lead to difficulties in handling and storage [26, 27]. The relatively low coordination number of five of the Hf centre makes [Hf(NMe₂)₄₂] difficult to handle without suitable inert atmosphere techniques, which decreases its shelf-life [28]. Films grown using [Hf(ONE₂)₄] generally contain lower levels of carbon impurities [2]. β-diketonates have high stability and, in most cases, are solids with low volatility, but there will be carbon residues in their films, affecting the film performance [21]. Hf(tmhd)₄ decomposes at relatively high temperature, therefore, HfO₂ deposition cannot occur at temperatures below 600 °C [13]. Hf(thd)₄ and Hf(tod)₄ are also relatively involatile and require high substrate temperatures for oxide growth. The carbon content in HfO₂ films deposited with Hf(tod)₄ and Hf(thd)₄ is 31 and 41%, respectively [29]. Acetylacetonate precursors are commercially available and inexpensive with low toxicity and exhibit low evaporation temperatures and easily controlled purity [30].

Herein, we report the synthesis and characterization of Hf(acac)₄ and its application toward the thin film deposition of HfO₂ via MOCVD. We have analysed the properties of HfO₂ films deposited on a Mo substrate. The purpose of this study was to investigate the application of hafnium acetylacetonate in MOCVD and provide reference for the deposition parameters of HfO₂ thin films.

2. Experimental

Hf(acac)₄ was synthesized from acetylacetonate and HfCl₄. The general reaction for the synthesis is illustrated in figure 1. The structure of the precursor was confirmed using nuclear magnetic resonance (NMR) spectroscopy. The structure of the precursor is shown in figure 2. The molecular structure of Hf(acac)₄ was formed by 1 hafnium atom and 4 acetylacetone ligands. The central hafnium atom coordinates with eight oxygen atoms of
four acetylacetone ligands to form four stable six-membered chelating rings. The Hf–O bond lengths vary in the range of 2.09–2.225 Å and the average bond length is 2.173 Å.

Thermogravimetric and differential thermal analysis measurements were carried out on a Netzsch STA 409 PG/PC Jupiter thermoanalytical instrument under a nitrogen atmosphere (flux rate: 40 cm$^3$ min$^{-1}$, heating rate: 10 °C min$^{-1}$, temperature range: 25 °C–800 °C).

The gas decomposition products were analysed using GC-MS connected to the outlet of the thermal reactor. GC-MS analysis was performed on a gas chromatograph 2000 series instrument equipped with a Finnigan MS mass spectrometer (HP6890N/5972) using nitrogen as the carrier gas (1 ml min$^{-1}$) and a HP-5MS column (30 m × 0.25 mm × 0.25 μm). The deposition parameters are shown in Table 1. The chromatographic peaks were identified upon comparison with the instruments mass spectra library.

A schematic diagram of the MOCVD system used in this study is shown in Figure 3.

### Table 1. Deposition conditions used for HfO$_2$ films.

| Parameter                  | Value                  |
|----------------------------|------------------------|
| Precursor Hf(acac)$_4$     |                        |
| Vaporizer temperature ($T_{vap}$) | 170 °C–190 °C        |
| Carrier gas flow rate (N$_2$) | 100 ml min$^{-1}$     |
| Substrate temperature ($T_{sub}$) | 220 °C–250 °C       |
| Deposition time            | 2–5 h                  |

3. Results and discussion

3.1. Structural characterization

The Hf(acac)$_4$ sample was treated in the solution to be measured. The hafnium content was determined using coordination titration. A hydrochloric acid solution of HfCl$_4$ was used as the standard solution, EDTA as the standard titration solution and xylenol orange solution as an indicator. The hafnium content in the sample was 31.59%, which was consistent with the theoretical value of hafnium acetylacetonate (31.05%). The results obtained using elemental analysis were in good agreement with the molecular formula of Hf(C$_5$H$_7$O$_2$)$_4$, indicating that the as-prepared compound was the target compound. The infrared spectra of the compound is
shown in figure 4. The vibrational spectra of the ligands change after the formation of the coordination compound. This was because after the formation of coordination bonds, the chemical environment of the coordinated atoms changes, resulting in changes in the original frequency of the chemical bond vibrations. After complexing acac$^-$ with Hf$^{4+}$, a six-membered chelating ring was formed. The π electron cloud on the chelating ring was attracted by Hf$^{4+}$ and moved toward the central metal ion. The contractive vibration peak of the C=O bonds in Hf(acac)$_4$ shifts $\sim$74 cm$^{-1}$ toward the low wavenumber region. At the same time, two different C=O bonds in the original resonant ligands were identical and became two C=O bonds due to the formation of large delocalized π bonds. The infrared spectra of Hf(acac)$_4$ showed a strong absorption peak at 1595.30 cm$^{-1}$. The
absorption peaks of Hf(acac)_4 include CH_3, C=O, C=C, C–CH_3, C=C=O and CH groups, which is consistent with the theoretical chemical formula. A moderate absorption appeared at 425 cm\(^{-1}\), which belongs to the stretching vibrations of the Hf–O coordination bonds.

3.2. Thermogravimetric analysis

Figure 5 shows Hf(acac)_4 loses weight slowly upon increasing the temperature under a nitrogen atmosphere. From room temperature to 190 °C, the weight loss was 2.03%. After that, the TG curve decreases sharply and the sample began to lose a lot of weight. At the same time, the DTA curve shows an obvious endothermic peak at 194 °C, which indicates that Hf(acac)_4 absorbs heat, melts and begins to decompose slowly. When the temperature reached 245 °C, the weight loss was 31.70%. When the temperature was further increased, the complex undergoes a thermal decomposition reaction to form a stable new substance. After 550 °C, the mass of the complex remains unchanged.

The specific thermal decomposition reaction is outlined in figure 6. The analysis results obtained from GC-MS and TG-DTA showed the target compound Hf(acac)_4 was volatile. Hf(acac)_4 melts and decomposes slowly at \( \sim 190 \) °C. A large amount of thermal decomposition begins at 245 °C. The main decomposition products were HfO_2 and the acetacetone ligands. Further increasing the temperature decomposes the acetylacetone into many large and small fragments, which were further reconstituted into other compounds.

3.3. Phase analysis of HfO_2 film

The XRD diffraction pattern of the hafnium oxide thin film prepared via MOCVD is shown in figure 7. Hafnium oxide films are known to exist as monoclinic, tetragonal, cubic and amorphous structures [31]. The crystal structure depends on the growth method and experimental conditions used to prepare the hafnium oxide film. It was found that there was only the monoclinic phase in our hafnium oxide films prepared via MOCVD using Hf(acac)_4 as the precursor. It can be seen from the XRD curve that each diffraction peak was sharp with no obvious broadening and correspond to the standard pattern of hafnium oxide. No other impurity peaks were found in the diffraction pattern. Narrow and sharp peaks indicate the good crystallization of the hafnium oxide phase. The results show that a hafnium oxide thin film with high purity was prepared.

3.4. Chemical composition analysis of HfO_2 film

The chemical composition of the HfO_2 film was analysed using XPS. Figure 8 shows the wide survey scan of the film reveals that the only elements present were hafnium and oxygen in addition to adventitious carbon. The main carbon source was contact with the outer atmosphere or sample manipulation. No molybdenum was detected, indicating that the substrates were completely obscured by the HfO_2 film. The core level spectra for Hf 4f and O 1s are shown in figure 9.

The XPS spectra of Hf 4f shown in figure 9(a) exhibits a doublet peak due to the spin–orbit coupling with peak positions at 18.7 and 17.0 eV corresponding to Hf 4f_{5/2} and 4f_{7/2}, respectively. The feature peaks in the range of 16–19 eV stipulate the formation of Hf–O bonds in HfO_2 [32, 33] and the binding energies match well with those previously reported. In the O 1s core level spectrum shown in figure 9(b), O peaks are observed at
532.6 and 530.9 eV, which correspond to the Hf—O—H and Hf—O bonds in HfO$_2$, respectively. The inclusion of hydroxyl species was partly attributed to the incomplete reaction of the precursor molecules.

3.5. Microstructural analysis of HfO$_2$ film

The surface morphology of the as-deposited HfO$_2$ film was investigated using SEM. Figure 10(a) shows the surface morphology of the hafnium oxide films. The appearance of the film is grey–black. It can be seen the film surface was smooth without any obvious cracks. The high magnification image shows that the film surface was closely stacked by fine hafnium oxide grains (figure 10(b)). The grain size was in a range of 200–300 nm. In addition, there were no obvious boundaries between adjacent grains. Figure 10(c) shows the cross-sectional morphology of the HfO$_2$ film on the Mo substrate. The morphology was very dense and uniform, and mainly comprised of a granular structure. The film consists of uniform-sized fine grains with average dimensions of 30 $\mu$m.
4. Conclusions

A new precursor has been designed for the chemical vapor deposition of smooth and dense thin films of HfO₂. Hf(acac)₄ is an ideal precursor for the preparation of hafnium oxide film via MOCVD due to its thermal stability and good volatility. The HfO₂ thin film was only comprised of a monoclinic phase and the films were prepared

Figure 10. SEM images of HfO₂ films: (a) Surface (b) high-magnification surface and (c) cross-sectional images.
with high purity. The surface of the films was continuous and compact, and the crystallite size was in the range of 200–300 nm.

Acknowledgments

This work was supported by the National Science Foundation of China (Grant No. 51361014 and 51661014) and Excellent Youth Project of Yunnan Basic Research Program (Grant No. 2019FI020).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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