



Optimization of parameters, characterization and thermal property analysis of hafnium ethoxide synthesized by electrochemical method



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Abstract: Hafnium ethoxide was synthesized using electrochemical method. Optimization experiments were used to optimize various parameters namely Et_4NBr concentration (c): 0.01–0.06 mol/L, solution temperature (t): 30–78 °C, polar distance (D): 2.0–4.0 cm and current density (J): 100–400 A/m². The electrolytic products obtained under optimum conditions of $c=0.04$ mol/L, $t=78$ °C, $D=2.0$ cm and $J=100$ A/m² were further isolated by vacuum distillation under 5 kPa. The product was characterized by Fourier transform infrared (FT-IR) spectra, nuclear magnetic resonance (NMR) spectra. The results indicated that the product was hafnium ethoxide. ICP analysis suggested that the content of hafnium ethoxide in the final product exceeded 99.997%. Thermal properties of the product were analyzed by TG/DTG. The vaporization enthalpy of hafnium ethoxide was found to be 79.1 kJ/mol. The result confirmed that hafnium ethoxide was suitable for the preparation of hafnium oxide by atomic layer deposition.

Key words: hafnium ethoxide; electrochemical synthesis; parameter optimization; characterization; thermal analysis

1 Introduction

Hafnium ethoxide is mainly used for the deposition of hafnium oxide (HfO_2) layers by atomic layer deposition (ALD), and deposited in this manner, the hafnium-based high- k dielectrics show much more stable electrical characteristics in comparison with the ones formed by sputtering or chemical vapors [1]. As the semiconductor industry ushered in nanometer era, a gate dielectric thickness in the field effect transistor (FET) reached its physical limits because of an increase in leakage currents due to tunneling effects [2–4]. Therefore, it is necessary to replace SiO_2 with a high- k gate dielectric. HfO_2 layers are amongst the most promising high- k candidates to meet the requirements for replacing the traditional SiO_2 gate oxide in complementary metal–oxide–semiconductor devices [4,5].

In recent years, the most common method of preparing hafnium alkoxides ($\text{Hf}(\text{OR})_4$) has been based on the halide synthesis [6]. This method has the disadvantage that HCl gas is liberated, because an apparatus in which the reaction is carried out is subjected to severe corrosion. And the reaction is performed using large amounts of organic solvents which are harmful to

the environment. In addition, the necessary reagents are scarce and the reactions involve various side processes which contaminate the products and decrease their yields [7].

For these reasons, the direct electrochemical synthesis of metal alkoxides by anode dissolution of metals in absolute alcohols in the presence of a conductive admixture seems a very promising method. The electrochemical method has great promise for the direct conversion of the less electropositive metals to their alkoxides owing to its simplicity and high productivity as well as its continuous and non-polluting character (with hydrogen as the major by-product) [6]. In our earlier works, we prepared several tantalum and niobium alkoxides by electrochemical method [8–10]. Many metal alkoxides, such as Y, Ti, Nb, Ta, Mo, W, Cu, Ge, Sn and other metals were also produced by this technique [6,11–13]. Some hafnium alkoxides, such as $\text{Hf}(\text{OMe})_4$, $\text{Hf}(\text{O}i\text{Bu})_4$, $\text{H}(\text{OC}_5\text{H}_{11})_4$ and $\text{Hf}(\text{OEt})_4$, were prepared using electrochemical method [6]. In 1995, hafnium ethoxide was obtained for the first time by TUREVSKAYA et al [14] with the electrochemical method involving electrolysis of an ethanol solution containing tetrabutylammonium bromide with a platinum cathode and a hafnium anode. However, parameter

optimization in the electrochemical synthesis, characterization and thermal property analysis of hafnium ethoxide have not been undertaken so far.

In the present study, optimization experiments for electrochemical synthesis of hafnium ethoxide were carried out to study the effect of various experimental parameters. Hafnium ethoxide synthesized under optimum conditions was further characterized by FT-IR, NMR and thermal analysis techniques.

2 Experimental

Anhydrous ethanol was supplied by Tianjin Hengxing Chemical Preparation Corporation, China. Tetraethylammonium bromide (Et_4NBr) was purchased from Sinopharm Chemical Reagent Corporation Limited. All reagents were used without further purification.

The electrolytic cell was made of polypropylene and its dimensions were 15.1 cm (length) \times 7 cm (width) \times 24 cm (height). A stainless steel plate was used as cathode, and its working area was 19.0 cm \times 12.0 cm. Hafnium plate (2.0 kg), purchased from Zhuzhou Cement Carbide Group Limited Corporation, China, was employed as anode, and its working area was 17.0 cm \times 12.0 cm. The hafnium plates were made from hafnium powders of metallurgical grade with self-resistance sintering, electron bombardment and rolling treatment. The chemical composition of hafnium plate is shown in Table 1.

Table 1 Chemical compositions of hafnium anode (mass fraction, %)

Zr	Cr	Fe	K	Mg	
0.0015	<0.0003	0.0005	<0.0002	<0.0007	
Na	Mo	Si	Ni	W	Hf
<0.0005	<0.0004	<0.0003	0.0002	0.0036	Bal.

The basic experimental conditions were anhydrous ethanol of 2.2 L, conductive agent of 0.04 mol/L, solution temperature of 78 °C (boiling temperature), polar distance of 2 cm and applied current of 2 A (current density of 100 A/m²). The effects of Et_4NCl , Et_4NBr or Et_4NHSO_4 as supporting electrolytes on the cell voltage with time were studied. The effects of solution temperature, concentration of Et_4NBr and polar distance on the cell voltage with current density were investigated, respectively. The effect of current density on the current efficiency was studied.

The hafnium ethoxide and ethanol solution synthesized under optimal condition was distilled at ambient pressure to separate redundant ethanol at temperature above 78 °C. Then, the distillation temperature was raised to 150 °C gradually, and a little

amount of ester was removed. Finally, the crude hafnium ethoxide solution was distilled at a pressure of 5 kPa and an oil bath temperature of 210–230 °C. The condensate was preserved in a dry nitrogen-sealed glass bottle to keep it from moisture.

FT-IR spectrum was measured with a Nicolet Avatar 360 IR spectrometer operating in the region of 4000–400 cm⁻¹. The ¹H-NMR spectrum was recorded with an Inova-400 (Varian) nuclear magnetic resonance spectroscope, and chloroform-d was adopted as the dilute reagent. Thermogravimetric measurements were carried out in nitrogen atmosphere using a SDT Q600 V8.0 Build 95 thermoanalytical equipment (flux rate of 200 cm³/min, heating rate of 10 °C/min, temperature interval of 25–800 °C, sample mass of 20.6 mg, and surface area of 0.227 cm² (the TG crucible)). In order to determine impurity contents of hafnium ethoxide, some amount of water was added into hafnium ethoxide solution for hydrolysis reaction. After desiccation in desiccator at 100 °C for 12 h, the sample was calcined in muffle furnace at 800 °C for 2 h. The impurity contents were obtained by ICP-Mass Agilent 7500a analyzer. And then the impurity content of hafnium oxide was converted into that of hafnium ethoxide.

3 Results and discussion

3.1 Electrochemical synthesis of hafnium ethoxide

Figure 1 shows the cell voltage–time (E_c – t) curves in anhydrous ethanol using Et_4NCl , Et_4NBr or Et_4NHSO_4 as electrolytes at a polar distance of 2 cm and an applied current of 2 A. At the beginning of the electrolysis, E_c decreases steeply to a minimum at a certain time (t_i), probably corresponding to the rapid increase in the temperature and the dissolution of the surface oxide film. After t_i , it is worth noting that E_c values of Et_4NCl and Et_4NBr begin to increase slightly whereas E_c of Et_4NHSO_4 increases rapidly. The increase in E_c can be explained by the following points: on the one hand, after t_i , as the electrolysis continues to carry out, the polar distance gradually increases and the anode working area slowly shrinks, leading to the increase of the solution resistance; on the other hand, the continuous electrolysis gives rise to the formation of increasing amounts of soluble product in the solution, contributing to the increase in the viscosity, resulting in precluding the migration rate of supporting electrolyte. At a fixed applied current, E_c values are found to be enhanced in the order: $\text{Et}_4\text{NCl} > \text{Et}_4\text{NBr} > \text{Et}_4\text{NHSO}_4$, among which E_c values of Et_4NCl and Et_4NBr are relatively very close. In addition, it is found that there is only one step for preparing Et_4NBr , which is favourable to a significant reduction in the cost. In contrast, the preparation of Et_4NCl and Et_4NHSO_4 needs three steps, in which the

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