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Thermal Properties and Gas Decomposition Products of Hafnium(IV) Acetylacetonate

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Thermal properties and gas decomposition products of hafnium(IV) acetylacetonate, $Hf(acac)_4$, were investigated by TG-DTA in conjunction with GC-MS, in nitrogen and air atmosphere, respectively. The results indicate that the complex is readily volatile and shows similar thermal decomposition behaviour and products under inert and oxidative atmosphere. The evaporation begins at about 190 ºC, followed by decomposition from 245-250 ºC, forming HfO_2 and gas products. The gas products are acetylacetone and its thermal reaction species including acetone, 4,6-dimethyl-2*H*-pyran-2-one and 4-methyl-2-pentanone.

Key Words: Hafnium(IV) acetylacetonate, Thermal properties, Gas decomposition products.

INTRODUCTION

Thin films of hafnium dioxide (HfO_2) have a verity of important technological applications, such as protective coating, mirrors, sensors and dielectric films in microelectronics[1,2]. In particular, HfO_2 has a high permittivity and is relatively stable in contact with silicon, making it a promising candidate to replace SiO_2 as the gate dielectric material for Sb-0.1 μm complementary metal-oxide-semiconductor (CMOS) technology[3,4]. Metal-organic chemical vapour deposition (MOCVD) is an attractive technique for the deposition of HfO_2[5,6], offering the potential for large area growth, good composition control and film uniformity and excellent conformal step coverage on non-planar device geometries. The problem of controlling the deposition processes of film materials, however, is often solved on the basis of the information on precursor used. An essential requirement for a successful MOCVD process is the availability of precursors with the appropriate physical properties and decomposition characteristics. $Hf(acac)_4$ has considerable potential as MOCVD precursor for the deposition of HfO_2 thin films[7,8]. It is extremely important, therefore, to obtain detailed information on the set of thermal properties and decomposing products of $Hf(acac)_4$, which could form the basis for choosing the precursor and for optimizing the film-deposition regimes. Recently, Zherikova *et al.*[9] reported data of the thermogravimetry and differential thermal analysis on $Hf(acac)_4$ in helium atmosphere. However, thermochemical properties of the complex in other atmosphere and decomposition products remains unavailable. To obtain more physical and chemical properties for $Hf(acac)_4$, we have investigated the thermal behaviour and decomposition products of $Hf(acac)_4$ by TG-DTA along with GC-MS in nitrogen and in oxygen atmosphere.

EXPERIMENTAL

Hafnium(IV) acetylacetonate was synthesized as per reported method[10,11]. An excess of acetylacetone (10.0 g, 99.8 mmol) was added to a methanol solution of anhydrous $HfCl_4$ (3.3 g, 20.6 mmol). Sodium hydroxide was added in small portions with heating for 5 h until pH reached 5-6. The complex was purified according to literature[12]. The crude product was dissolved in sufficient benzene to give complete solution and the pure complex was reprecipitated by the addition of petroleum ether.

Thermogravimetric and differential thermal analysis measurements were carried out with a Netzsch STA 409 PG/PC Jupiter thermoanalytical equipment in nitrogen and oxidative (20 % O_2 and 80 % N_2) atmosphere (flux rate: 40 cm^3 min^{-1}, heating rate: 10 ºC/min, temperature interval: 25-800 ºC; sample mass: 46-48 mg).

Gas decomposition products were analyzed by GC-MS connected to the outlet of the thermal reactor. GC-MS analysis were performed in a gas chromatograph 2000 series equipped with a Finnigan MS mass spectrometer (HP6890N/5972), using nitrogen and oxidative atmosphere as carrier gas (1 mL/min) equipped with a HP-5MS (30 m × 0.25 mm × 0.25 µm). The chromatographic peaks were identified by comparison of their mass spectra with the equipment's mass spectral library.

RESULTS AND DISCUSSION

The thermal behaviour of $Hf(acac)_4$ was studied by TG/DTA in air and nitrogen atmosphere. The TG-DTA curves in air environment for $Hf(acac)_4$ are shown in Fig. 1, from which it can been seen that weight loss begins apparently at about 190 ºC, accompanied by an intense endothermic DTA peak at 194 ºC. This indicates that $Hf(acac)_4$ absorbs heat at 194 ºC, leading to the phase conversion of $Hf(acac)_4$ from solid to gas state. With the temperature going up, a large exothermic curve was observed between 245-580 ºC, suggesting that thermal decomposition of $Hf(acac)_4$ is taking place and more stable compounds are being produced. The solid product remaining at the inner wall of the thermal decomposition chamber was collected and determined by XPS analysis to be HfO_2. No sharp loss in weight can be found above 600 ºC.

The thermal decomposition products of $Hf(acac)_4$ in the gas phase were sampled at 250-400 ºC and analyzed by GC-MS. The main products are listed in Table-1. Acetylacetone, the ligand of the complex, accounted for more than 50 % of the total products at 250 ºC and only about 33 % at 400 ºC. In addition to acetylacetone, acetone, 4,6-dimethyl-2*H*-pyran-2-one and 4-methyl-2-pentanone were found in the gas phase. It is believed that they are derived from acetylacetone through thermal decomposition and recombination reactions, as shown in **Scheme-I**. More acetylacetone underwent these thermal reactions at 400 ºC, producing 30 % of 4,6-dimethyl-2*H*-pyran-2-one. Atmosphere seems to have no apparent influence on the thermal decomposition of $Hf(acac)_4$.

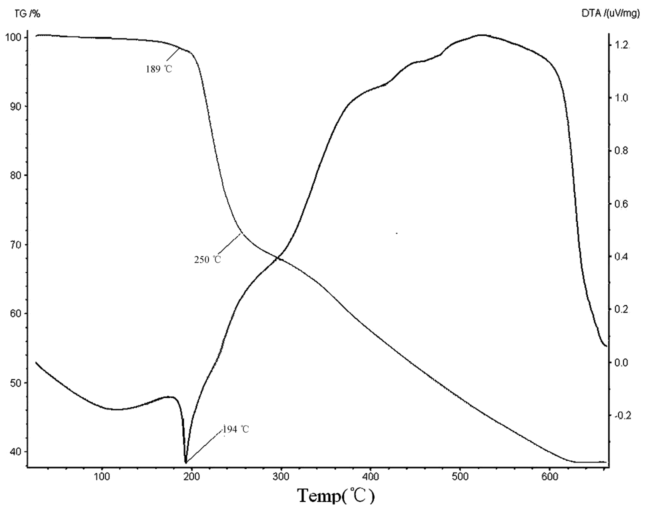


Fig. 1. TG and DTA curves of $Hf(acac)_4$ in oxidative environment

TABLE-1
MAIN DECOMPOSING PRODUCTS OF $Hf(acac)_4$ IN THE GAS PHASE

Products	Content (%)			
	Air		Nitrogen	
	250 ºC	400 ºC	250 ºC	400 ºC
Acetone	7.020	7.380	10.08	7.780
Acetylacetone	55.40	33.65	58.70	36.54
4,6-Dimethyl-2*H*-pyran-2-one	21.33	39.33	23.28	39.27
4-Methyl-2-pentanone	6.830	7.010	–	7.150

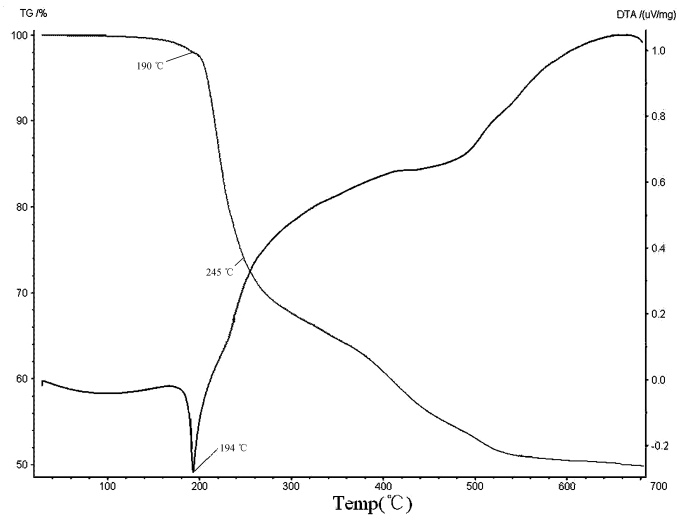
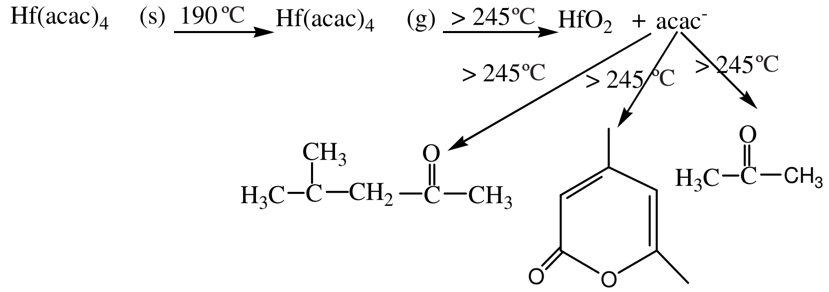


Fig. 2. TG and DTA curves of $Hf(acac)_4$ in nitrogen atmosphere



Scheme-I Possible formation mechanism of main gas decomposition products for $Hf(acac)_4$

Conclusion

The thermal properties and decomposing products of hafnium(IV) acetylacetonate have been investigated by TG-DTA along with GC-MS under nitrogen and air atmospheres. The results show that the complex is volatile and begin to evaporate at about 190 ºC, followed by thermal decomposition at 245 ºC, producing HfO_2 and acetylacetone. Acetylacetone further undergoes thermal decomposition and recombination, leading to the formation of other gas products such as acetone, 4,6-dimethyl-2H-pyran-2-one and 4-methyl-2-pentanone. The atmosphere has no apparent effects on the thermal properties of $Hf(acac)_4$, which implies that the HfO_2 films can prepared by MOCVD either under air or N_2 environment. The best evaporating temperature range for MOCVD is 190-245 ºC and the depositing temperature should be above 250 ºC.

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