

Fourier Transform Infrared Spectroscopy Studies on Thermal Decomposition of Tetrakis-dimethyl-amido Zirconium for Chemical Vapor Deposition of ZrN

Ihl-Woo Kim, Sung-Jae Kim, Do-Heyoung Kim[†], Heegwon Woo*, Man-Yong Park** and Shi-Woo Rhee**

Faculty of Applied Chemistry and Research Institute for Catalysis,

*Department of Chemistry, Chonnam National University, 300 Yongbong-dong, Gwang-Ju 500-757, Korea

**Department of Chemical Engineering, Pohang Institute of Science and Technology # San 21 Hyoja-dong, Pohang, Gyeongbuk 790-784, Korea

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Abstract—The decomposition behavior of tetrakis (dimethylamido) zirconium (TDMAZ) under various ambient gases was studied by using in-situ Fourier transform infrared spectroscopy (FTIR) aimed at understanding the gas phase reactions and also at selecting the appropriate process conditions for ZrN chemical vapor deposition (CVD). The infrared absorbance of the stretching vibration at 933.37 cm^{-1} was employed to monitor the degree of dissociation of the gaseous TDMAZ. In the case of argon and nitrogen atmospheres, TDMAZ starts to decompose at above $300\text{ }^{\circ}\text{C}$, while in a hydrogen atmosphere it starts to decompose at above $350\text{ }^{\circ}\text{C}$. To evaluate the effect of the decomposition behavior of the precursor on CVD ZrN, the ZrN films were grown at $150\text{--}375\text{ }^{\circ}\text{C}$ under Ar, N_2 , and H_2 . A clear difference in transition temperature of controlling from surface reaction to gas phase mass transfer was observed: The ZrN growth rate decreased rapidly at above $300\text{ }^{\circ}\text{C}$ under Ar or N_2 atmospheres, and increased continuously with increase of the deposition temperature under an H_2 atmosphere.

Key words: Thin Films, Zirconium Nitrides, CVD, FTIR

INTRODUCTION

Because of their high physical/chemical stability and good electrical properties, transient metal nitride thin films are of great interest in a wide range of industrial areas, such as microelectronics, for diffusion barriers, hard coatings, and coatings for corrosion resistance. Among various transition metal nitrides, relatively fewer studies have been performed on ZrN than other popular transition metal nitride films such as TiN and TaN, in spite of its comparable physical, chemical, and electrical properties required for industrial applications [Murarka, 1993; Yun and Rhee, 1996; Yong and Jeong, 2002]. Various techniques of physical vapor deposition (PVD) [Östling et al., 1984; Jin et al., 1993; Sproul, 1986; Krusin-Elbaum and Wittmer, 1983; Puclin and Kaczmarek, 1996; Dauchot et al., 2000; Chou et al., 2003; Spillmann et al., 2001] and chemical vapor deposition (CVD) can be used to form ZrN films. However, very few reports exist on CVD ZrN [Motojima et al., 1979; Fix et al., 1991; Hoffman, 1994; Berndt et al., 1995; Sugiyama et al., 1975; Wendel and Surh, 1992]. Furthermore, there are no reports on the study of the gas phase reactions of tetrakis (dimethylamido) zirconium (TDMAZ) for the CVD ZrN process, although it has been shown that gas-phase chemistry greatly affects the deposition characteristics in the CVD processes [Weiller, 1996; Yun and Rhee, 1998; Yun et al., 1998; Dubois et al., 1992]. J.-Y. Yun and S.-H. Rhee reported that ambient gases in the CVD process for TiN significantly affected the film growth mode due to intrinsic transport properties, such as thermal and mass diffusivity, of ambient gases [Yun and Rhee, 1998; Yun et al., 1998].

Therefore, we investigated the thermal decomposition behavior of the TDMAZ under various ambient gases, aiming to relate the gas-phase chemistry and the growth characteristics of CVD ZrN films. The gas phase chemical reactions were studied by using in-situ Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTS

The precursor, TDMAZ, was purchased from Strem Chemicals, Inc. and used without any further purification. There were no detectable impurities in H-NMR spectra of the as-received TDMAZ. The compound is a light-yellow crystalline solid with molecular weight of 267.53 g. Melting temperature was estimated to be $58\text{ }^{\circ}\text{C}$. The vapor pressure of TDMAZ is known to be about 1 torr at $120\text{ }^{\circ}\text{C}$. The decomposition behavior of the precursor was studied by Fourier transform infrared spectroscopy (FTIR, Jasco 430) by monitoring of the specific chemical bonds. A schematic drawing of the experimental apparatus is described elsewhere [Yun et al., 1998]. The mixture of carrier gas and vaporized precursor was introduced into a specially designed quartz gas cell (volume: 141.4 cm^3), which was covered with a heating block. The precursor container was kept at $50\text{ }^{\circ}\text{C}$. During the experiment, the gas line from the bubbler to the inlet of the cell was heated at $70\text{ }^{\circ}\text{C}$ to prevent precursor condensation. A collimated infrared beam (IR bands of $400\text{--}4,000\text{ cm}^{-1}$) was irradiated from the FTIR spectrometer through the quartz cell equipped with two KBr windows, and the passed IR beam was analyzed with a liquid-nitrogen-cooled MCT (Hg-Cd-Te) detector. Each IR spectrum was collected with 8 cm^{-1} resolution and 50 scans were averaged. The gas temperature of the cell, which was measured by K-type thermocouple, varied from $25\text{ to }400\text{ }^{\circ}\text{C}$ under various ambient gases, Ar, N_2 , and H_2 . The deposition of ZrN was also carried

[†]To whom correspondence should be addressed.

E-mail: kdhh@chonnam.ac.kr

out on the (100) *p*-type silicon covered by SiO₂ in a low pressure CVD reactor to investigate the effects of ambient gas on the CVD ZrN process. The films were deposited in a range of 250–375 °C at 1 torr total pressure, 50 °C precursor temperature, and 60 sccm carrier gas volumetric flow rate. Film growth rate was calculated by dividing the film thickness by reaction time, and the thickness of the films was evaluated by using SEM (Hitachi 5000).

RESULTS AND DISCUSSION

Fig. 1 shows the IR absorption spectrum of gas phase TDMAZ, obtained at room temperature. The vibration spectrum was shown to be similar to that of other pure metal alkyl amido compounds [Weiller, 1996; Yun and Rhee, 1998; Dubois et al., 1992]. The degree of thermal decomposition of TDMAZ was monitored by using the intensity of NC₂ symmetric stretch at 933.37 cm⁻¹, because the relatively intense NC₂ stretch is known to be a good signature for the metal-(NMe₂)₄ bond [Weiller, 1996; vab der Vis et al., 1994]. Fig. 2 shows the IR spectra of TDMAZ at cell temperatures of 150, 300, and 350 °C under an Ar atmosphere. As can be seen in this

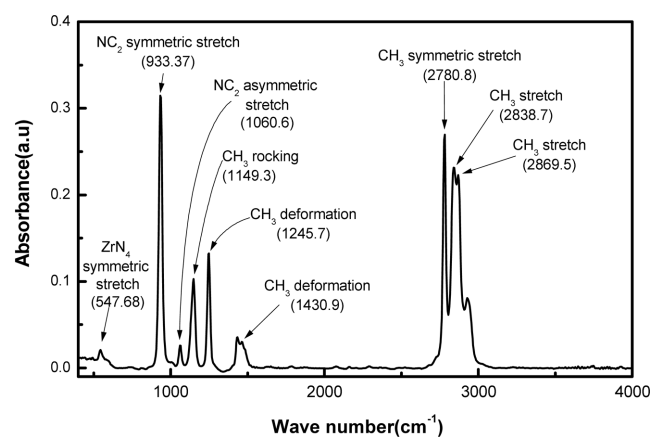


Fig. 1. FTIR spectrum of TDMAZ at room temperature under an Ar atmosphere.

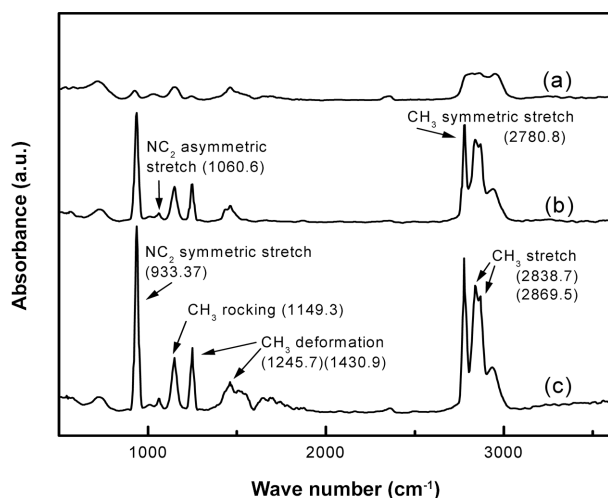


Fig. 2. FTIR spectra of TDMAZ at different cell temperatures under an Ar atmosphere (a) 150 °C (b) 300 °C and (c) 350 °C.

figure, the peak intensity of C-N at 933.37 cm⁻¹ decreased with increasing the cell temperatures, and only amine-related peaks eventually appeared at 350 °C.

As the types of carrier gases were reported to profoundly affect the gas-phase reactions [Yun and Rhee, 1998; Yun et al., 1998], we evaluated the effect of carrier gas on the decomposition of Zr(NMe₂)₄, using three types of carrier gases, H₂, N₂ and Ar. Fig. 3 shows the IR spectra of the TDMAZ obtained at 325 °C under these gases. As can be seen in Fig. 3, the shape of the IR clearly depended upon the type of carrier gas. In particular, it is interesting to note that the spectra obtained when using hydrogen are far different compared with those of other carrier gases.

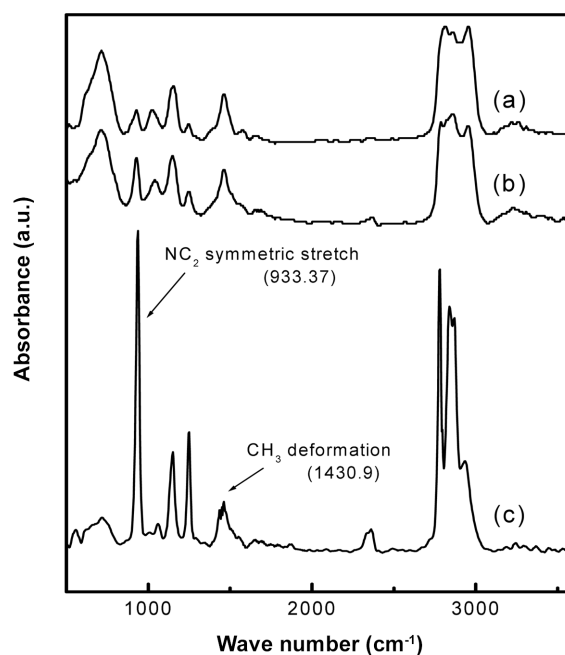


Fig. 3. FTIR spectra of TDMAZ at cell temperature of 325 °C under (a) N₂ (b) Ar and (c) H₂.

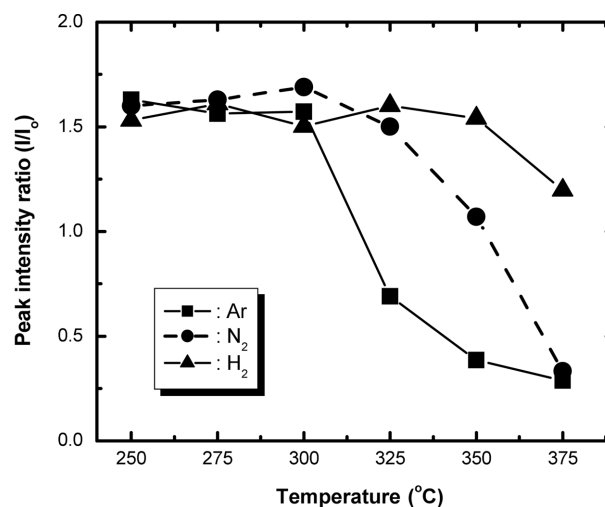


Fig. 4. Absorption intensity ratio of the peak intensity of NC₂ stretch (I) to CH₃ deformation (I₀) under Ar, N₂ and H₂ atmospheres.

To investigate quantitatively the degree of the decomposition of TDMAZ at the various gas phase temperatures using H_2 , N_2 and Ar gases, the ratio of the peak intensity of NC_2 stretch (I) to CH_3 deformation (I_0) was employed. The reason we adopted the $1,430\text{ cm}^{-1}$ peak of CH_3 deformation peak as a standard was due to the near-insensitivity of this peak under the conditions investigated. The peak intensity was obtained by the integration of the peak area, and Fig. 4 shows the variation of the peak intensity ratio of I to I_0 at the cell temperatures of $250\text{--}375^\circ\text{C}$. For all gases, there was no significant change in the ratio of peak intensity upon increasing the temperatures up to 300°C . However, the ratio was greatly decreased at above 300°C for the case of N_2 and Ar atmospheres, suggesting that the dissociation of dimethylamido groups from Zr became significant at above 300°C . From this result, one may know that the gas phase temperature should be kept below 300°C with N_2 and Ar gases to avoid particle generation or a starved-reaction regime in $Zr(NMe_2)_4$ -based CVD.

However, there was no significant change in the ratio of peak intensity upon increasing the temperature up to 350°C for the case of hydrogen gas, and slight decrement of the ratio with increasing the temperature was observed at above 350°C . This indicates that hydrogen suppresses the dissociation reaction of dimethylamido groups from $Zr(NMe_2)_4$. Therefore, usage of hydrogen would be beneficial for reducing the particle generation in the gas phase as well as extension of the kinetic-controlled regime in a $Zr(NMe_2)_4$ -based CVD system. A kinetic-controlled regime is known to be very important to obtaining a conformal deposition in various CVD systems [Kim et al., 1999].

To clearly confirm the effect of carrier gases on the film growth, ZrN has been grown at $250\text{--}375^\circ\text{C}$ in the ambients of Ar, N_2 , and H_2 . The deposition rate as a function of the substrate temperature is shown in Fig. 5. Different transition temperatures, from surface reaction to gas-phase mass transfer, depending on the ambient gases for the ZrN film growth, can be seen in Fig. 5. The growth rate of ZrN increased with increasing the deposition temperature below 300°C in all gases. This indicates that the substrate temperature below 300°C is the surface reaction-limited regime in TDMAZ-based CVD ZrN. However, at substrate temperatures above 300°C , the

film growth rate decreased rapidly with further increases in substrate temperature for the cases of Ar and N_2 atmospheres, supporting that the film growth was controlled by gas-phase mass transfer at above 300°C .

The film growth rate increased continuously with further increase in substrate temperature in a H_2 atmosphere, indicating an extension of a kinetic-controlled regime compared to that of Ar and N_2 atmospheres.

Under the various ambient gases, the trends of dependence of ZrN film growth on the substrate temperatures are well consistent with the effects of cell temperatures on the degree of the decomposition of TDMAZ. Thus, it is believed that the decrement of the film growth rate with increased substrate temperature under N_2 and Ar is caused by the precursor depletion near the substrate surface resulting from the gas phase dissociation of $Zr(NMe_2)_4$. Also, it is thought that H_2 somehow suppresses the dissociation of dimethylamido groups from Zr, which leads to the extension of the regime of the surface reaction control in the CVD ZrN process. It is well known that H_2 has higher thermal diffusivity compared with N_2 and Ar [Yun et al., 1998]. As thermal boundary layer thickness is proportional to the square root of thermal diffusivity, the high temperature zone could be extended further from the substrate surface by using a gas which has a higher thermal diffusivity. This means that the usage of a higher-thermal-diffusivity gas leads to more decomposition of the precursor above the substrate than a lower-thermal-diffusivity gas. In other words, if the ZrN CVD system is dominantly affected by the different transport property, i.e. diffusivity, a relatively lowered film growth rate or a shortening of the kinetic-controlled regime should appear with H_2 compared with N_2 and Ar, because the depletion of the precursors would occur significantly with H_2 .

However, in our experiment, the usage of H_2 did not result in decrement of the ZrN growth rate in the surface reaction regime compared to that with N_2 and Ar gases. Rather, inversely, the film growth rate of ZrN in a H_2 atmosphere increased continuously with increment of the deposition temperatures up to 375°C , in spite of decrements of the film growth rate appearing in both N_2 and Ar atmospheres even above 300°C . Therefore, it is believed that H_2 suppresses the dissociation reactions of TDMAZ in the gas phase, which avoids the situation of precursor depletion even above 300°C under our investigated CVD conditions. We did not understand how H_2 is involved in the dissociation reactions. More sophisticated experiments would be required to elucidate clearly this phenomenon. The overall activation energy for the ZrN film growth under H_2 , N_2 and Ar was 7.05, 8.63, and 8.97 kcal/mol, respectively, in the surface reaction-controlled regime.

CONCLUSION

As a baseline study for TDMAZ-based ZrN CVD systems, an FTIR study was conducted at the cell temperatures of $150\text{--}375^\circ\text{C}$. It was found that ambient gases strongly affect the degree of precursor dissociation, and thus the film growth characteristics. Hydrogen was found to be more effective in suppressing the gas phase dissociation of TDMAZ, compared with nitrogen or argon. This was confirmed by changes of transition temperature, from surface reaction to gas-phase mass transfer in the film growth experiments. With H_2 ambient gas, the transition temperature appeared higher

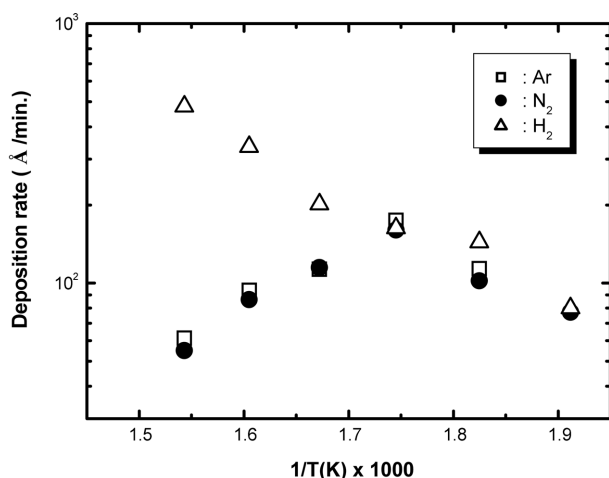


Fig. 5. The effect of the substrate temperature on the deposition rate under different ambient gases.

(about 350 °C) than that with Ar and N₂ atmospheres (about 300 °C).

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