

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

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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  $933.37\text{ cm}^{-1}$  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  $300^\circ\text{C}$ , while in a hydrogen atmosphere it starts to decompose at above  $350^\circ\text{C}$ . To evaluate the effect of the decomposition behavior of the precursor on CVD ZrN, the ZrN films were grown at  $150\text{--}375^\circ\text{C}$  under Ar,  $\text{N}_2$ , and  $\text{H}_2$ . 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  $300^\circ\text{C}$  under Ar or  $\text{N}_2$  atmospheres, and increased continuously with increase of the deposition temperature under an  $\text{H}_2$  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  $58^\circ\text{C}$ . The vapor pressure of TDMAZ is known to be about 1 torr at  $120^\circ\text{C}$ . 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:  $141.4\text{ cm}^3$ ), which was covered with a heating block. The precursor container was kept at  $50^\circ\text{C}$ . During the experiment, the gas line from the bubbler to the inlet of the cell was heated at  $70^\circ\text{C}$  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  $8\text{ cm}^{-1}$  resolution and 50 scans were averaged. The gas temperature of the cell, which was measured by K-type thermocouple, varied from  $25$  to  $400^\circ\text{C}$  under various ambient gases, Ar,  $\text{N}_2$ , and  $\text{H}_2$ . The deposition of ZrN was also carried

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out on the (100) *p*-type silicon covered by SiO<sub>2</sub> 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 NC<sub>2</sub> symmetric stretch at 933.37 cm<sup>-1</sup>, because the relatively intense NC<sub>2</sub> stretch is known to be a good signature for the metal-(NMe<sub>2</sub>)<sub>4</sub> 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

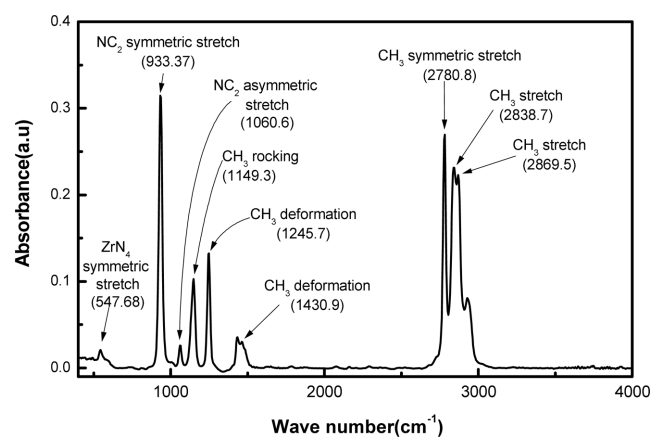


Fig. 1. FTIR spectrum of TDMAZ at room temperature under an Ar atmosphere.

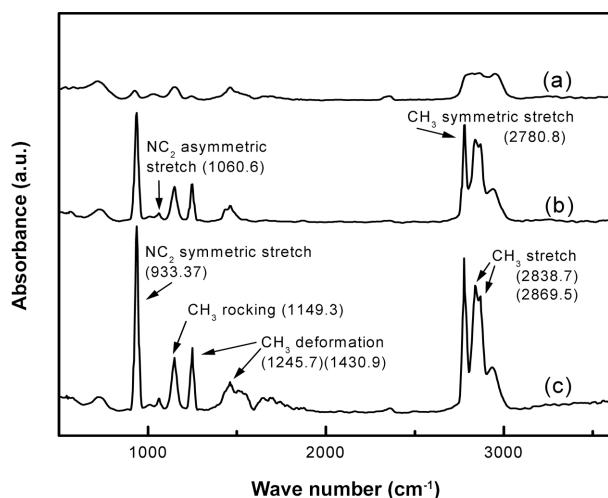


Fig. 2. FTIR spectra of TDMAZ at different cell temperatures under an Ar atmosphere (a) 150 °C (b) 300 °C and (c) 350 °C.

figure, the peak intensity of C-N at 933.37 cm<sup>-1</sup> 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(NMe<sub>2</sub>)<sub>4</sub>, using three types of carrier gases, H<sub>2</sub>, N<sub>2</sub> 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.

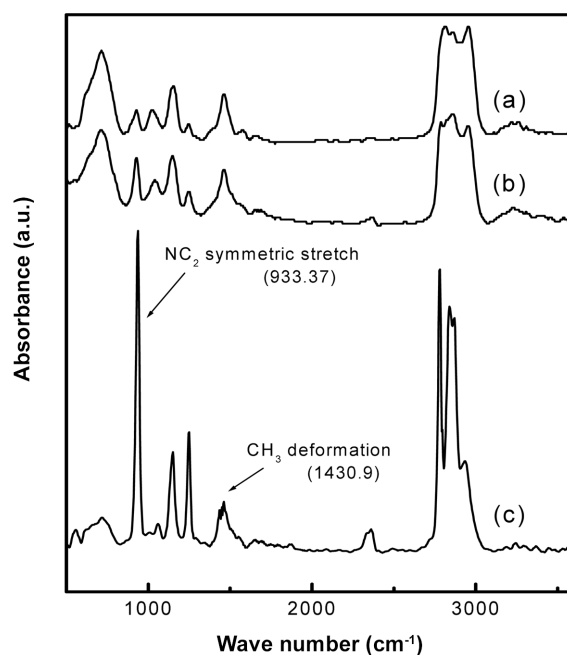


Fig. 3. FTIR spectra of TDMAZ at cell temperature of 325 °C under (a) N<sub>2</sub> (b) Ar and (c) H<sub>2</sub>.

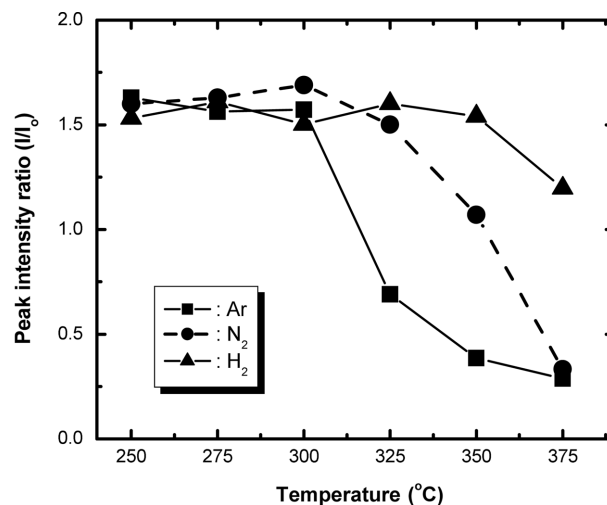


Fig. 4. Absorption intensity ratio of the peak intensity of NC<sub>2</sub> stretch (I) to CH<sub>3</sub> deformation (I<sub>0</sub>) under Ar, N<sub>2</sub> and H<sub>2</sub> atmospheres.

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  $300^\circ\text{C}$ . However, the ratio was greatly decreased at above  $300^\circ\text{C}$  for the case of  $N_2$  and Ar atmospheres, suggesting that the dissociation of dimethylamido groups from Zr became significant at above  $300^\circ\text{C}$ . From this result, one may know that the gas phase temperature should be kept below  $300^\circ\text{C}$  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  $350^\circ\text{C}$  for the case of hydrogen gas, and slight decrement of the ratio with increasing the temperature was observed at above  $350^\circ\text{C}$ . 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  $300^\circ\text{C}$  in all gases. This indicates that the substrate temperature below  $300^\circ\text{C}$  is the surface reaction-limited regime in TDMAZ-based CVD ZrN. However, at substrate temperatures above  $300^\circ\text{C}$ , 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  $300^\circ\text{C}$ .

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  $375^\circ\text{C}$ , in spite of decrements of the film growth rate appearing in both  $N_2$  and Ar atmospheres even above  $300^\circ\text{C}$ . 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  $300^\circ\text{C}$  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

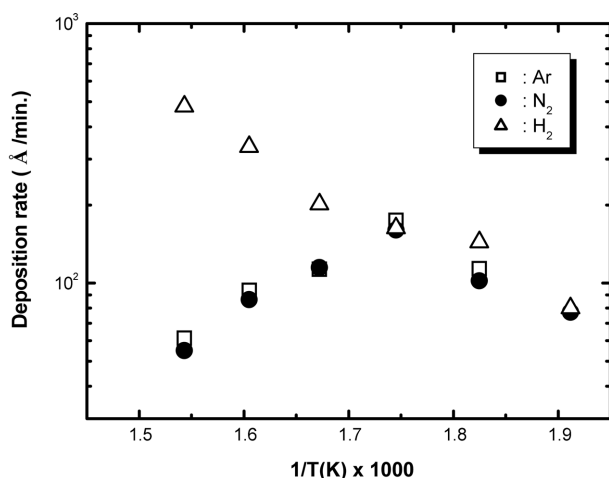


Fig. 5. The effect of the substrate temperature on the deposition rate under different ambient gases.

(about 350 °C) than that with Ar and N<sub>2</sub> atmospheres (about 300 °C).

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