REAL TIME EVALUATION OF VACUUM PROCESS FOR THIN FILM ALUMINUM DEPOSITION

Sang-Woo Kang, Ju-Young Yun, Jin-Tae Kim, Yong-Hyun Shin, Jong-Yeon Lim

Vacuum Center, Korea Research Institute of Standards and Science, Deajeon, S. Korea, swkang@krissr.re.kr

Abstract: The chemical species in gas phase and on the surface of aluminum precursor (boro-hydride trimethyl-amine (ABHTMA)) for aluminum deposition process with the vacuum level and the hot wall temperature were studied using two kinds of Fourier transform infrared (FT-IR) spectroscopes which was installed at the end of the chamber. The absorbance of Al-H, B-H, C-H and C-N stretching features of the chemical species in the gas phase and on the surface was sensitive to the variation of analysis conditions. From those results, the temperature dependence of the film composition and quality could be explained.

Keywords: **real time, vacuum process, CVD, FT-IR.**

1. INTRODUCTION

Aluminum (Al) has been used widely as interconnect materials in the fabrication of integrated circuit devices [1]. Physical vapor deposition (PVD) techniques are often used to deposit Al films. However, successful Al interconnection becomes extremely difficult because the size of the vias is becoming smaller and the aspect ratio is becoming larger. So the chemical vapor position (CVD) of Al has attracted considerable attention as an alternative physical vapor deposition (PVD) metallization process. The Al CVD process must have a suitable metal organic precursor, that is, a new precursor has to be designed for deposition. A variety of metal organic precursors for Al CVD have been developed over the past two decades. Trimethylaluminum (TMA) and triisobutylaluminum (TIBA) were among the early Al precursors and were abandoned due to the impurity like carbon incorporated to films, low deposition rate and low reflective index. Dimethylethylamine (DMEAA), methylpyrrolidine alne (MPA) [3] and triemthylamine alane (TMAA) including the amine-alane adduct have been found and those are expected to yield high purity (carbon-free) films due to no direct Al-C bonds in there molecular structures. However, DMEAA and MPA have a low stability, and TMAA is a solid precursor. Normally the solid precursor was making it difficult to control the vapor flow in terms of maintaining a constant surface area in the source.

In order to study a developed precursor (ABHTMA) for novel device manufacturing, investigating chemical species under various conditions is important. Researchers worked in this field were being interested in the FT-IR system because it can monitor concentration accurately in real time, is non-invasive to the process chamber and is low maintenance cost.

The real-time studies of the gas phase species and adsorbed species on the surface have been reported using FT-IR spectroscopy for the Cu deposition from (hfac)Cu(VTMS) (hfac : hexafluoroacetylacetonate, VTMS: vinyltrimethylsilane) $Cu(DPM)_2$ (DPM: bis-dipivaloyl-methanato) and $Cu(hfac)_2$, Al deposition from TMMA (TMMA : trimethylamine alane) – NH_3 system, AlGaAs deposition from trimethyl-aluminum (TMA) – TMG (trimethylgallrium)-AsH_3 system, SiO_2 deposition from the TEOS (tetraethylortho-silicate)-ozone system and diamond from a CH_4-H_2-O_2 gas mixture. In-situ real-time FT-IR spectroscopy is the most useful and proper technique for monitoring the process and diagnosing a mechanism.

In this work, we have studied the behavior of ABHTMA at the gas phase and on the surface as a function of the temperature and the pressure of a hot wall reactor with modified FT-IR spectroscopy after dosing ABHTMA for chemical vapor deposition (CVD) process. We also performed density-function-theory calculations to show the stable species and by-products during the Al CVD process in various process conditions. The ABHTMA is found to be a stable precursor for the Al CVD in the trimethylamine-rich and the near-stoichiometric condition of alane and borane. By the dissociation and reaction of the ABHTMA, the borane-trimethylamine complex can be produced.

2. EXPERIMANTAL

The FT-IR system was installed at the end of the hot wall reactor chamber to investigate gas species coming out from the chamber during Al deposition (Fig. 1) with the variety of deposition temperature and chamber pressure. The modified gas cell and the tube of the FT-IR system was heated up to 40 ^oC in order to avoid contamination of the gas cell, potassium bromide (KBr) windows and pumping lines. A collimated IR beam from FT-IR spectrometer (Nicolet Avata 360) is passed through the gas cell with two KBr windows and liquid nitrogen cooled MCT (Hg-Cd-Te) detector was used. The IR band under examination covered wavenumbers range from 400 to 4000 cm^{-1}, and each IR spectrum was collected at 2 cm^{-1} resolution using 62 scans to allow a good signal to noise ratio. The gas cell pressure was controlled by the throttle valve. And we used another FT-IR system called transmission FT-IR spectroscope to obtain the information on the species adsorbed on the surface. The system requires the high surface area particles. The ZrO_2 nanoparticles were obrained from Nanomaterials Research Corporation (Longmont, CO) and were spherical with an average diameter of 50 nm. The ZrO_2 nanoparticles were supported by a photoetched tungsten grid. Before taking a spectrum of adsorbed species, the Al film was deposited on the pressed ZrO_2 nanoparticles for 10 min at

150°C with ABHTMA because of changing ZrO_2 surface to Al metal surface. The transmission FT-IR spectroscope system was already reported in previous studies [2]. The precursor was evaporated from a stainless steel bubbler maintained at appropriate temperature of 25°C and transported to the reactor by Ar carrier gas at a rate of 20 sccm. The temperature of feeding lines between chamber and bubbler is 40 °C which is same as the exhaust line temperature.

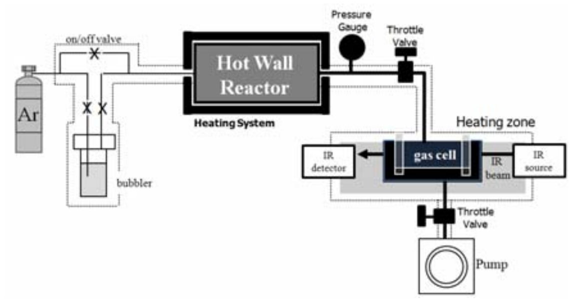

Figure 1. Schematic of diagram of diagnosis system.

3. RESULTS AND DISCUSSION

We first investigate the stabilities of molecules composed of the alane, borane, and trimethylamine molecular components. As important stable species, the molecular structures of ABHTMA and borane-trimethylamine complexes are shown in Fig. 2. The calculated formation energies for various molecules are plotted in Fig. 3 as a function of the alane chemical potential. The high (AlH_3) represents the alane-rich condition in the chamber, while the low (AlH_3) is the borane-rich condition. When the trimethylamine concentration is rich (Fig. 2(b)) and the concentrations of alane and borane are similar, the ABHTMA molecule is found to be the most stable among those composed of the alane, borone, and trimethylamine components. Thus, with the trimethylamine-rich and near the stoichiometric condition of the alane and borane, the ABHTMA can be a stable and proper precursor for the Al CVD process. As the ABHTMA molecules are consumed during the Al CVD, the concentration of the alane component can become reduced, leaving the chamber with the borane-rich condition. As shown in Fig. 2(b), the most stable species in such borane-rich condition is the borane-trimethylamine complex. Thus, the ABHTMA precursors used can be degraded by the formation of the borane-trimethylamine complex.

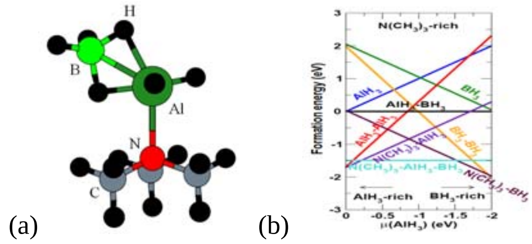

Figure 2. (a) Structural formula of ABHTMA
(b) Calculation results

Figure 3 shows the measured IR absorption spectrum for the chemical species coming out of the reactor at 40 °C wall temperature. The stretch modes of Al-H (1844, 1793 and 1007 cm^{-1}), Al-N (746 cm^{-1}), B-H (2485 and 2443 and 2169 cm^{-1}), C-N (2828 and 2775 cm^{-1}) and C-H (2927, 2988 and 1484cm^{-1}) from ABHTMA are clearly detected. Those peaks have been identified from similar molecules elsewhere. In this spectrum, we found the other B-H peaks (2394, 2382 and 2374 cm^{-1}) related with the borane- trimethylamine complex, which can be generated during the dissociation and recombination of ABHTMA passing the hot wall reactor. The assignment of the borane-amine complex lines were confirmed by the IR spectrum library supported from the Nicolet Avata software (OMNIC™).

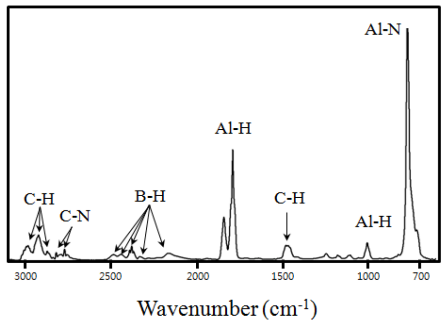

Figure 3. The IR absorption spectrum of molecules coming out from the hot wall reactor at 40°C.

Figure 4 shows the change of the C-H, C-N and Al-H stretch modes as a function of the reactor wall temperature at the reactor pressure of 0.95 Torr. The C-H stretch modes located in the range of 1420 ~ 1520 cm^{-1} and 2850 ~ 3100 cm^{-1} were decreased gradually with the increase of the reactor wall temperature. However, the C-H stretch mode at 2964 cm^{-1} (CH_2 asymmetric stretch) was increasing with increasing the temperature over 175 °C due to the decomposition of CH_3 groups at trimethylamine ligand in ABHTMA. In case of the C-N stretch modes, the intensities of peaks at 2834 and 2775 cm^{-1} were increasing with the increase of the temperature up to 200 °C. To investigate the reason, we have taken the infrared spectrum of the similar molecules, dimethylethylamine alane (DMEAA) (Fig. 4(a)) and trimethylamine (Fig. 4(b)). In case of the two molecules, the intensity of the C-N stretch mode is similar to that of the C-H stretch mode. However, after the trimethylamine was bonded with the alane-borane molecule, the intensity of the C-N stretch mode of ABHTMA shown in Fig. 4 is much lower than that of the C-H. It is believed that the bonding with borane makes the intensity of the C-N stretch modes in range of 2750 ~ 2850 cm^{-1} be lower. So, breaking the bond between alane and borane by the thermal energy would be making the intensity of C-N stretching features higher. It was also identified by the results shown in Fig 4(b).

Figure 4(c) shows the variation of peak intensity (1793 (peak A) and 1844 cm^{-1} (peak B)) and generation of the peaks (1892 and 1882 cm^{-1}) related to Al-H stretching features over the reactor wall temperature of 150°C. It means that thermal energy from the hot wall has an effect on the dissociation and decomposition of ABHTMA and the Al-H stretching features are sensitive to the transmission of thermal energy controlled by the wall temperature and the reactor pressure. The peak A only gives information about the Al-H vibrational feature of alane bonded with borane and trimethylamine. The peak B gives mixed information about Al-H features of alane itself and oligomerized forms of alane. And the new generated two peaks only give the information about oligomerized forms of alane. The alane dissociated from ABHTMA are easily oligomerized due to the high degree of intermolecular association of Al-H molecules. When observing the two main peak related to Al-H vibrational feature, the peak A was decreased and the peak B was fluctuated as the deposition temperature was increasing. The peak B showed a decline up to 140^{o}C and at 150^{o}C, the intensity was getting higher than that observed at 140^{o}C. In the temperature range of 160 ~ 200^{o}C, the intensity was decreased again. Only at 150^{o}C, the abnormal behavior of peak B was observed. It is because that the peak B is correlated with the Al-H stretching feature related to the oligomerized forms of the Al-H stretching feature. We found that over 150^{o}C, new peaks at 1882 and 1892 cm^{-1} started to be generated and then the intensity of the peak B was increased. So, it is believed that the new generated peaks are related with the oligomerized forms of Al-H molecules dissociated. The intensity of the new peaks is much smaller than that of the peak A and B. It means that the amount of the oligomerized forms of alane is small.

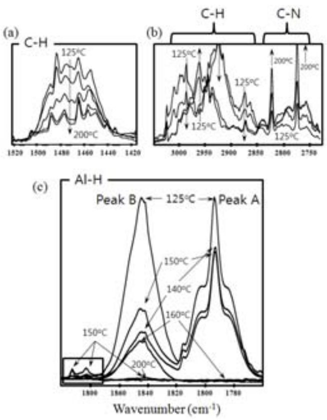

Figure 4. FT-IR spectra of (a & b) C-H, (b) C-N and (c) Al-H stretching features as a function of the hot reactor wall temperature

Figure 5 shows the B-H stretching features as a function of the pressure at the fixed temperature. At the temperature as low as 125^{o}C, the pressure increase results in an increase in absorbance for B-H of ABHTMA (Peak C) and borane-trimethylamine (peak D). The increase rate of the integrated absorbance ratio was increased slightly with the increase of pressure as shown in Fig. 10. It is not owing to additional decomposition with increasing the pressrue, but to the additional recombination between borane and trimethylamine. If additional decomposition of ABHTMA were happening, the intensity of Al-H stretching features should be decreased together. At 140^{o}C, peak C was decreased by lowering the ABHTMA concentrations. Meanwhile, peak D was increased rapidly by the recombination of borane and trimethylamine. In case of B-H stretching features observed at 175^{o}C, the B-H peaks related with a borane-trimethylamine complex only remained in the full pressure range. Over 175^{o}C, the ABHTMA was fully dissociated and recombined. So, the Al-H and B-H stretching features of ABHTMA located at the original position were disappeared and then generated at the new position related with oligomerized forms of alane and borane-trimethylamine complex over 175^{o}C, respectively.

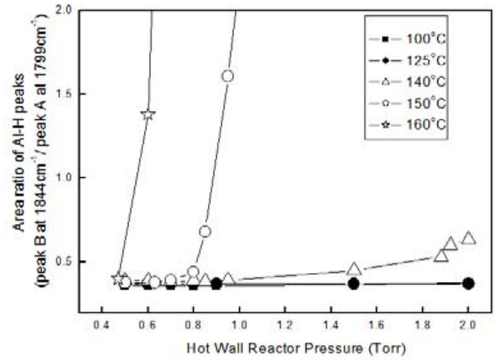

Figure 5. Area ratio of integrated absorbance of Al-H stretching features (peak B at 1844cm^{-1}/peak A at 1799cm^{-1})
.

Figure 6 shows FT-IR spectra of ABHTMA adsorbed on the W grid surface coated with Al metal deposited by CVD process as a function of the temperature and dosing time. At the temperature as low as 80^{o}C (Fig. 6(a)), ABHTMA dosed to the grid was stacked on the surface. Though the intensity of peaks was increased with dosing time, the peaks were disappeared after 12 min without dosing. It is because any ABHTMA formed no chemical bonds with the Al metal surface. So the absorbance peaks of adsorbed ABHTMA are similar as the ABHTMA in gas phase as shown in Fig. 7. Figure 7(b) and 7(c) show the IR spectra of ABHTMA adsorbed on the surface at 80^{o}C and ABHTMA taken in gas cell at 80^{o}C, respectively. Compared with two spectra, main peaks (Al-H, C-H and C-N) were located at the similar position. Especially, the B-H stretching features were shifted to lower frequencies and the ratio of intensity of B-H and Al-H stretching features was bigger than the ratio in Fig. 7(c). We believed that it is on account of the interaction among the borane, trimethylamine and Al metal surface and the interaction is making the change of frequencies and intensities. When ABHTMA was dosed at 125^{o}C, the Al-H stretching features in the range of 1795 ~ 2000 cm^{-1} and C-H stretching features in the range of 1400 ~ 1500 cm^{-1} were only observed. The Al-H and C-H stretching features remained on the surface due to the incomplete reaction of ABHTMA dosed and those are representing the source of the carbon contamination incorporated into the films. Meanwhile, the peak related to B-H was not observed. It is because of the high vapor pressure (0.8 Torr at 23^{o}C) and high stability of borane complex (easy desorption). The decomposition characteristics of borane-triethylamine were already reported. The borane-trimethylamine complex had used to deposit the boron carbonitride films in the temperature range of 500 to 700^{o}C. When the ABHTMA was dosed at 150^{o}C (Fig. 6(c)) no peaks were observed. It means the all kinds of molecules were adsorbed and then desorbed at this temperature. It is affecting the film quality.

The film deposited in this region (around 150°C) has the best film properties with respect to the surface roughness, reflectance and resistance. It is a good evidence that there is strong relations between deposition characteristics and the inspection result of molecules adsorbed on surface.

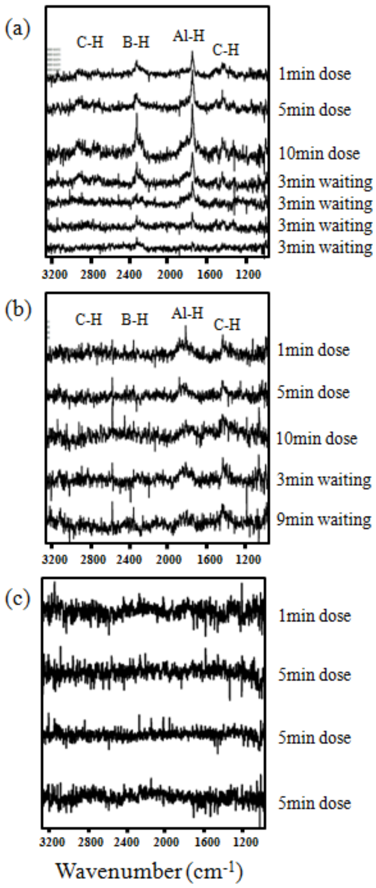

Figure 6. IR spectra of ABHTMA adsorbed on the Al metal surface (a) at the surface temperature of 80^{o}C, (b) 125^{o}C and (c) 150^{o}C

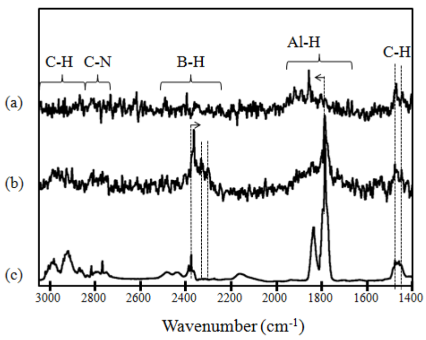

Figure 7. Comparison of spectrum taken (a) at the surface temperature of 125^{o}C, (b) at the surface temperature of 80^{o}C and (c) gas cell temperature of 80^{o}C.

4. CONCLUSION

The study on the behavior diagnosis of ABHTMA in the gas phase and on the surface was successfully carried out using FT-IR spectroscopy. The alane-borane-trimethyl-amine complex is found to be the most stable, when the trimethylamine concentration is high and the alane and borane concentrations are similar to each others. Thus the ABHTMA is a stable and proper precursor for the Al CVD in those conditions. By reducing the alane concentrations, the borane-trimethylamine complex can be generated as a by-product, as observed in the FT-IR measurements. It is observed that the C-H, C-N, Al-H and B-H stretching features were sensitive to changing the measurement conditions such as how wall temperature and the pressure. The intensity of most of C-H stretching features was decreased with the increase of the wall temperature due to the partial decomposition of ligand. The intensity of C-N stretching features was showed the different behavior with the temperature change compared with that of C-H features. The intensity of C-N peaks was increased with the increase of the temperature by the dissociation of borane. Especially, the B-H and Al-H stretching features gave information about the status of ABHTMA.

5. REFERENCES

[1] T. T. Kodas and M. J. Hampden-Smith, The Chemistry of Metal CVD. VCH, Weinheim, 1994.

[2] S. W. Kang, S. W. Rhee and S. M. George, “Infrared spectroscopic study of atomic layer deposition mechanism for hafnium silicate thin films using $HfCl_2[N(SiMe_3)_2]_2$ and H_2O,” J. Vac. Sci. Technol. A, vol 22, no 6, pp 2392-2397, 2004.