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The Study on the Precursor Adsorption using *in-situ* Nanoparticle-assisted Attenuated Total Reflectance Infrared Spectroscopy

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The adsorption behavior of tris (dimethylamino)-cyclopentadienyl-zirconium (Cp-Zr) precursor using an *in-situ* attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FT-IR) was studied. In attempt to improve the detection intensity of an adsorbed precursor, nanoparticles were uniformly distributed on the Ge ATR crystal surface employing the spray method. The absorption characteristics studies were carried out over the Ge crystal temperature in the range of 30～50°C. Upon increasing the temperature, a reduction of absorption was observed. Based on the peak intensities of ATR-FT-IR spectroscopy, higher-ZrO_2 absorption efficiency occurs when the nano-particles are utilized compared to pure Ge crystal.

Keywords : ATR, Crystal, Nanoparticle, FT-IR

I. Introduction

Many researchers have investigated the properties of precursor in the liquid or gaseous state using gas chromatography, mass spectrometry, and infrared spectrometry, in order to develop high-performance evaporation materials [1]. However, there are few prior achievements of the adsorption behavior in precursor deposited on wafer surfaces using chemical vapor deposition (CVD) and atomic layer deposition (ALD) [2]. In particular, several studies have been conducted to investigate the physical and chemical properties of precursor in an effort to select the most suitable for semiconductor [3]. Cp-Zr is one of the attracting precursor for the high dielectric film and nanoelectronics devices. It has high evaporation rate and thermal stability [7]. Several crystals have been pursued to be integrated into attenuated total reflectance (ATR). In order to testing high refractive index materials, Ge crystal which allows for the measuring polymers in expanded spectral range is suitable candidates for ATR application [8].

In this paper, we report on the absorption behavior of the precursor on the substrate surface. Attenuated total reflectance-Fourier transform infrared (ATR-FT-IR) spectroscopy was performed under high vacuum

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conditions. Nanoparticles coated on Ge crystal surface enhance the absorption of the precursor. In attempt to analyze characteristics of adsorption and decomposition using modified ATR-FT-IR spectroscopy, Cp-Zr precursor was deposited on Ge crystal at temperature in the 30～50°C range to absorb high dielectric film. Changes in the FT-IR peak intensity of the FTIR were monitored in situ, which reveals the changes in the absorption of precursor on Ge crystal surface.

II. Experimental Section

To analyze the absorption behavior of the Cp-Zr precursor, an ATR spectrometer is installed in an FT-IR spectrometer, which is a device for analyzing molecular structures. The FT-IR spectrometer employed in this study was a Nicolet 6700 (ThermoFisher Scientific). The light source of 400～4000 cm^{-1} wavenumber in the mid-IR range was measured by using a Hg-Cd-Te (MCT) detector. Data collected from detector was analyzed by OMNIC software installed on PC. A multi-bounce ATR spectrometer (VeeMax II) was used. To adsorb the gaseous Cp-Zr precursor on the crystal surface of the ATR spectrometer, a gaseous system was set up by improving the ATR structure. Fig. 1 shows each part of the structurally improved ATR spectrometer and the assembled ATR spectrometer. This device was modified to investigate the surface adsorption behavior by injecting the gaseous precursor. It consists of a multi-bounce crystal used in the VeeMax II ATR, a heating module to heat the crystal surface directly, a vacuum sealing module to create a vacuum state at the crystal surface, and a device for generating plasma.

Fig. 2 indicates the modified ATR spectrometer installed in a FT-IR spectrometer. It consists of a vacuum gaseous system for injecting the gaseous precursor, a pump for maintaining vacuum level and a heating device. Since the infrared spectrum in mid-IR range includes strong absorption wavelengths

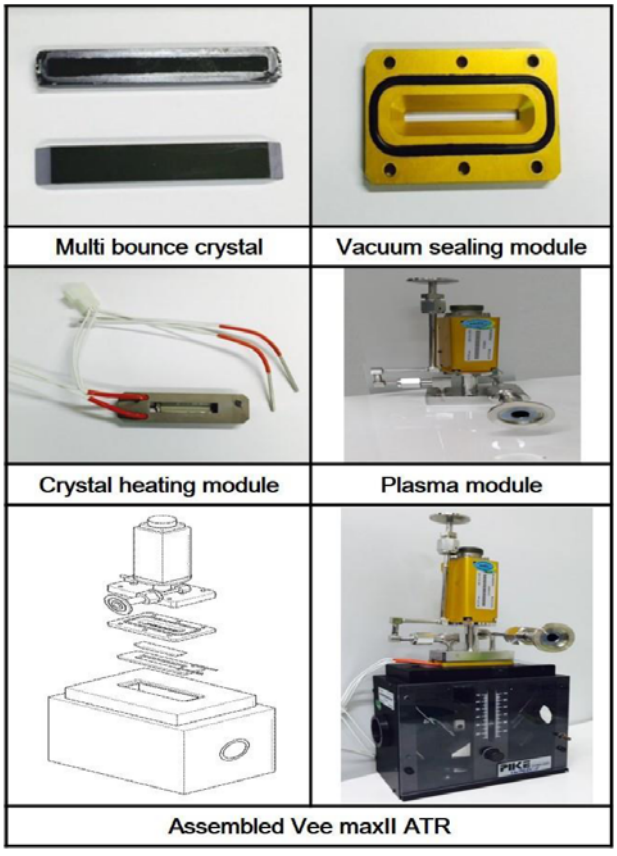

Figure 1. The parts of the modified ATR system.

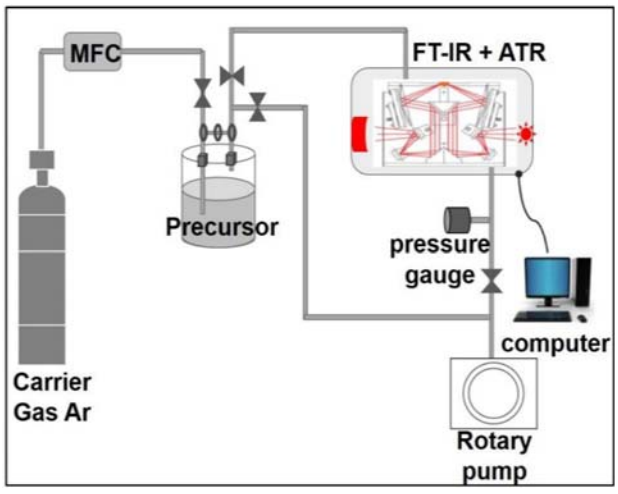

Figure 2. The multi-bounce ATR system installed in the FT-IR spectrometer.

of H_2O and CO_2, The spectrometer was installed inside an acrylic box so that a N_2 atmosphere has been obtained. It is possible to obtain an accurate IR spectra from blocked external elements (H_2O, CO_2, etc.).

To improve absorption of Cp-Zr precursor, as shown in Fig. 3, the nanoparticle solution was applied to the Ge crystal surface. Using a syringe with a mixture of deionized water solution and 1 mole ZrO_2, ZrO_2 nanoparticles were dispersed thinly and uniformly on the crystal surface by spraying method. Also, the ozone gas was injected on the Ge crystal to investigate the reaction of oxidizer and adsorbed precursor.

III. Results and Discussion

When infrared ray passes from a dense medium to a less dense medium the light is refracted inside a crystal. When an angle of incidence increases, the reflectivity increase. The penetration depth is changed according to wavelength of incidence light, refractive index and angle of incidence. The radiation is called the evanescent wave. If the less dense medium absorbed evanescent wave, intensity of wavelength of absorption band is attenuated. At this time, the attenuated infrared beam is detected by the detector and recorded absorption of wavelength. In general, an ATR spectrum exhibits a band identical to that of an IR spectrum but the intensity is different. In addition, in the ATR spectrum, radiant rays can penetrate only a few millimeters into a sample. Accordingly, spectral absorbance depends on the incidence angle, irrespective of the sample's thickness. The effective penetration depth is depends on wavelength of infrared ray, refractive index of the sample and angle of light [4,5]. The effective penetration depth is as follow equation.

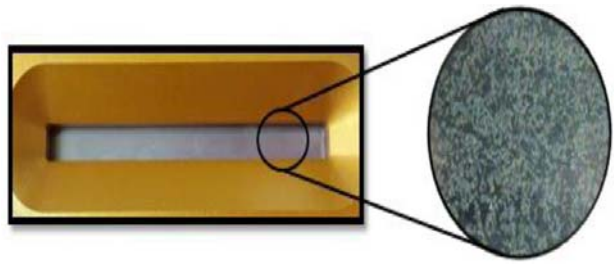

Figure 3. Distribution of ZrO_2 nano particles above the crystal surface.

$$d_p = \frac{\lambda_c}{2\pi[sin^2\theta - (n_s/n_c)^2]^{1/2}} \quad (1)$$

Where λ_c is the wavelength of the crystal, θ is the angle of incidence, n_s is the refractive index of the sample and n_c is the refractive index of the crystal. To examine the spectrum of the structurally modified ATR-FT-IR, we comparatively analyzed the data spectrum measured using a gas cell. As shown in Fig. 4(a), the band of the Cp-Zr spectrum in the gas phase is identical to that of the spectrum measured by adsorbing the Cp-Zr precursor on the Ge crystal surface, but peak intensity is different. Fig. 4(b), 4(c) shows several peaks in the 500~1300 cm^{-1} and 2700~3500 cm^{-1} ranges. The surface of ATR exhibits spectral responses up to 938 cm^{-1}, 1142 cm^{-1}, 1241 cm^{-1}, 2764 cm^{-1} (and 2862) cm^{-1}, and 2960 cm^{-1}, due to NC_2 symmetric stretching vibratory motion, CH_3 rocking, CH_3 deformation, CH_3 symmetric vibration motion, CH_3 stretching, and CH_3 asymmetric stretching, respectively. These data represent that a peak shift in the range of 2700~3000 cm^{-1} may originate from broadening effect [6].

Fig. 5 shows ATR-FT-IR measured from adsorbed Cp-Zr precursor for 2 minute on the general Ge crystal (Ge ATR) and employed ZrO_2 nano particle Ge crystal (NP ATR) at the various temperature (30, 40 and 50°C). According to the spectra responses of Ge ATR and NP ATR, crystal surfaces of both Ge ATR and NP ATR with increased temperature reveal a

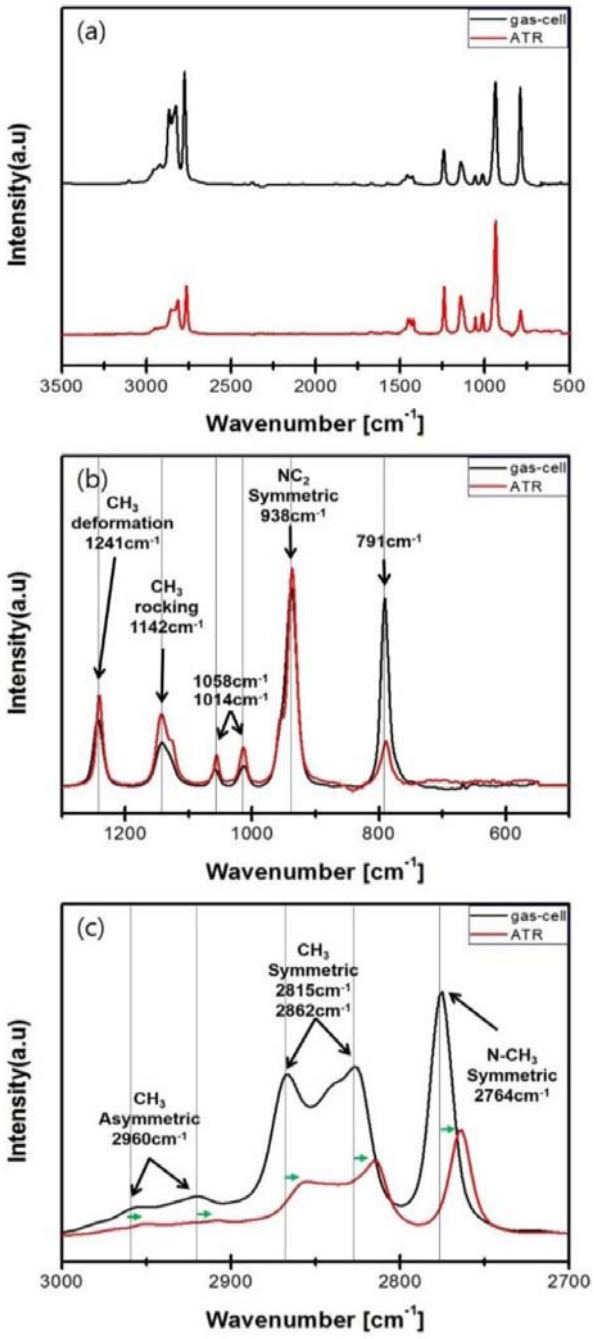

Figure 4. The comparison on precursor spectra measured at the gas phase and ATR surface (a) full range of 500~3500 cm^{-1}, (b) range of 500~1300 cm^{-1}, (c) range of 2700~3500 cm^{-1}.

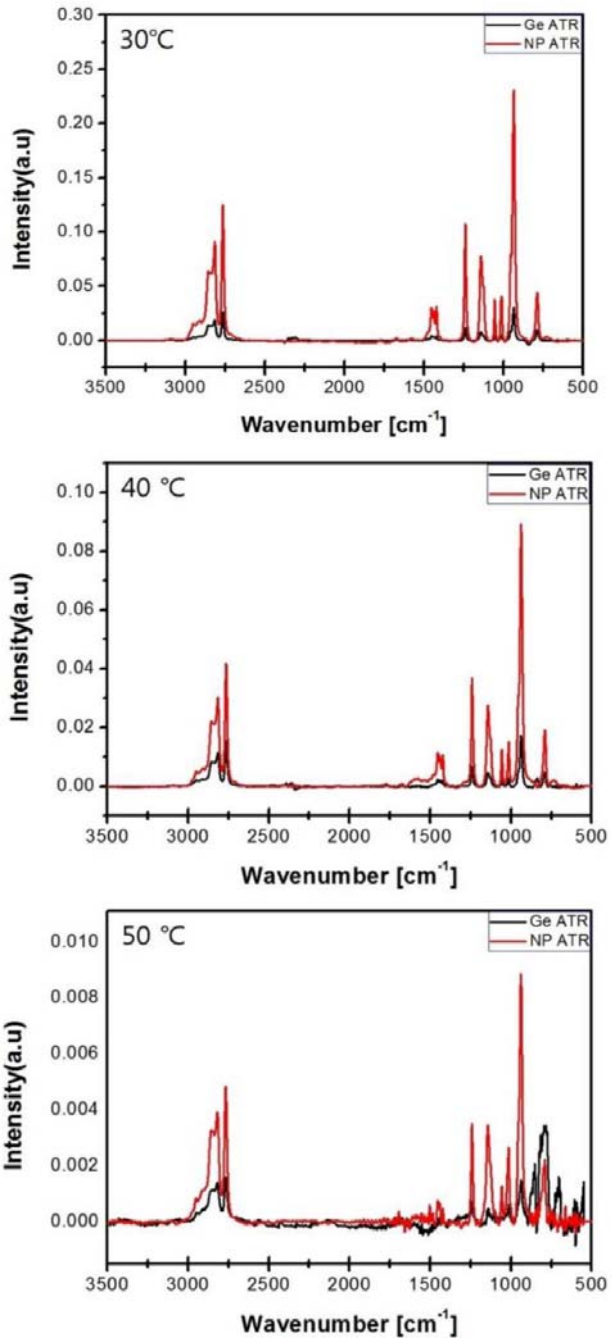

Figure 5. The comparison on the spectrum of the Cp-Zr precursor adsorbed (for 2 min) on the Ge crystal surface (Ge ATR) and employed ZrO_2 nanoparticles Ge crystal (NP ATR) at 30, 40, and 50°C temperature.

reduction in the absorption. This behavior is thought to be result of improvement physical desorption at higher temperature. NP ATR enhance the spectra responses for comparison to Ge ATR at 30 and 40°C owing to the stronger absorption with a large surface, while the presence of NP does not significantly affect to the absorption at relatively high temperature (50°C) as shown in Fig. 6.

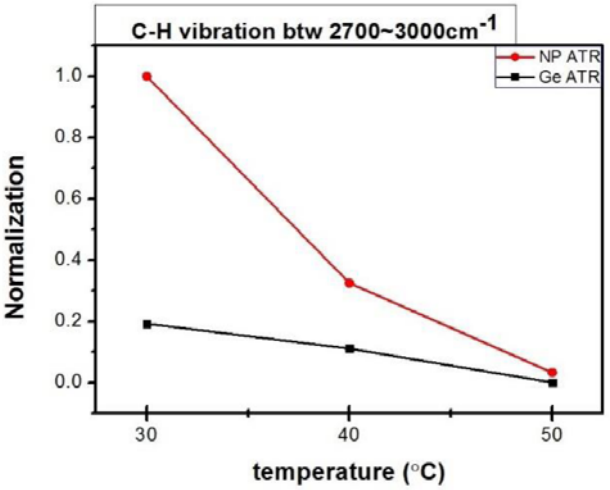

Figure 6. Normalized peak intensity about C-H vibration area range of 2700~3000 cm^{-1}.

ATR-FT-IR was used to investigate in situ the reaction of O_3 over Cp-Zr precursor on Ge crystal. The precursor was adsorbed for 1 min at a Ge crystal surface temperature of 30°C. Fig. 7 reveals ATR-FT-IR spectra of absorbed O_3 on Cp-Zr precursor for 1 minute at 30°C. The intensity of peaks at 938 cm^{-1}, 1142 cm^{-1}, 1241 cm^{-1}, 2764 cm^{-1}, 2815 cm^{-1}, and 2960 cm^{-1} are attenuated, which was attributed to the presence of absorbed ozone on the surface. This method is a promising development for *in-situ* monitoring of deposition equipment such as CVD and ALD in real time.

IV. Conclusions

Characteristics of absorption and reactivity of adsorbed Cp-Zr with ozone gas were monitored by *in-situ* vacuum ATR-FT-IR system. Higher temperature leads to decreased absorption of Cp-Zr precursor on Ge crystal. The Ge crystal employing ZrO_2 nanoparticles plays a pivotal role to an increase absorption of Cp-Zr precursor at 30°C.

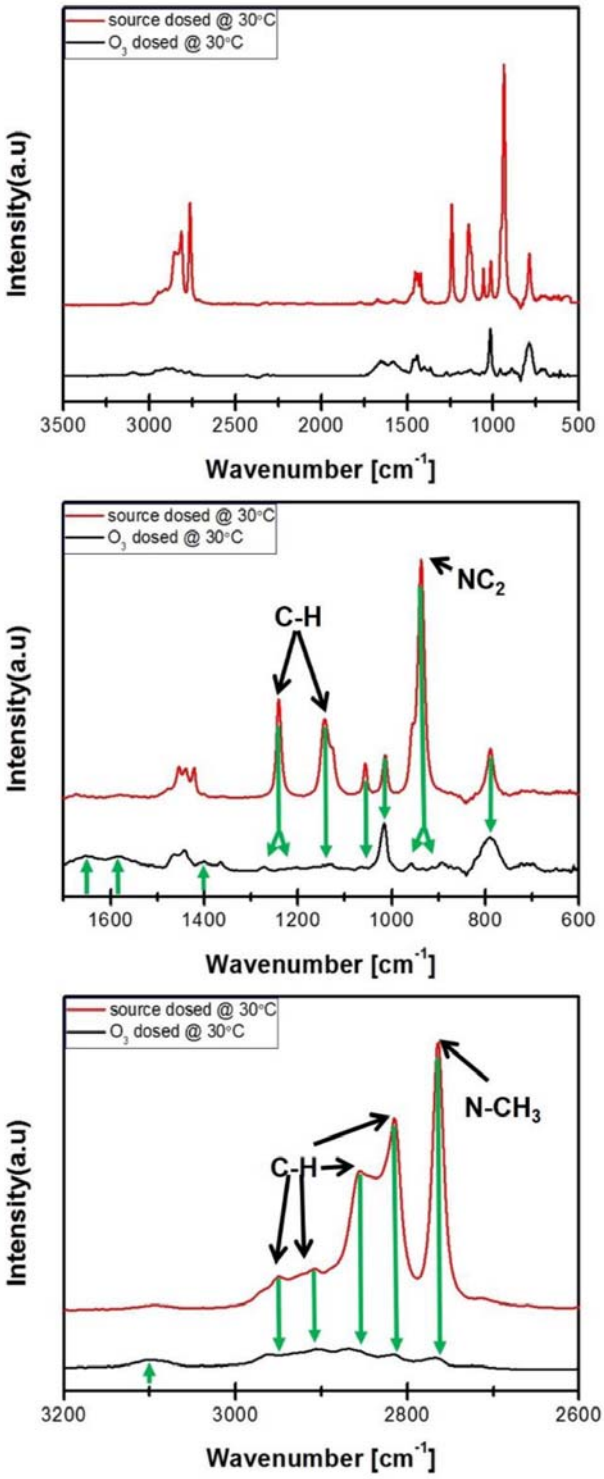

Figure 7. The reactivity of the Cp-Zr precursor adsorbed on Ge crystal with O_3 at surface temperature 30°C. (a) full range of 500~3500 cm^{-1} (b) range of 600~1700 cm^{-1} (c) range of 2600~3200 cm^{-1}.

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