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High Sensitivity Compact Gas Concentration Sensor with Heating Function for High Precision Trimethyl Aluminum Gas Supply System

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Abstract

This work presents a high sensitivity, real-time and compact gas concentration sensor using time-sharing dual wavelength ultraviolet (UV) light absorption method developed for high precision Trimethyl Alminum (TMA) gas supply system. By controlling the sensing temperature to increase the ratio of monomer TMA with higher UV absorbance, a high resolution of 62.7ppm was achieved.

1. Introduction

In the semiconductor manufacturing scenes, TMA is the most widely used MO gas as aluminum precursors for high-k dielectric formation and AlGaAs epitaxial growth and so on [1-2]. In general, bubbling method is employed to supply MO gases including TMA that have low vapor pressure for manufacturing equipment. Fundamentally by this method, gas concentration varies temporally during the process. Thus, in-line gas concentration sensors shown in Fig.1 is required for precise control of MO gases. Some sensors using near-infrared light absorption based or ultrasonic based methods have been proposed for this purpose [3-4]. However, the sampling speed and resolution of concentration of the current sensors are not sufficient for precise control of TMA gas.

Various MO gases have relatively high light absorbance in the UV waveband. Focusing on this characteristics, we have been researching on the development of high sensitivity MO gas concentration sensor using UV light absorption measurement method [5-6]. *Lambert-Beer Law* (1) is a relational expression between attenuation and concentration when irradiating a target gas with light.

$$A = -log\frac{I}{I_0} = \beta cd \qquad (1)$$

where, A is the absorbance of the gas to be measured, I_0 is the incident light intensity, I is the transmitted light intensity, β is the molar absorption coefficient [M^{-1}], c is the concentration [$mol{\cdot}l^{-1}$], And d is the optical path length[cm]. As concentration unit, it is necessary to measure the change in absorbance. A high SN ratio is critically important to improve measurement accuracy, thus concentration resolution. By using a charge amplifier circuit to integrate photo charge for higher SN ratio, 10ppm order resolution has been achieved for several MO gases [5-6]. However, the previously developed sensor is not sufficient to measure TMA gas concentration below about 300ppm due to its low UV light absorbance.

In this work, in order to improve the TMA concentration resolution below 100ppm, we newly introduced a temperature heating system to the gas cell unit for controlling the TMA phase based on the gas characteristic analyses, as well as, changed the LED wavelength, and the obtained performance is reported.

2. Gas Concentration Sensor with Heating Function

Figure 2 shows the picture and schematic diagram of the gas concentration sensor unit with heating function developed in this work. The gas cell optical path length is L50 mm, collimated light is irradiated in parallel to the gas flow path, and the light amount is measured by the photodiode. As the light source, a λ 368 nm LED (SETi: UV TOP) was selected as the reference light without absorption, and a λ 252 nm LED (Crystal IS: OPTAN) was selected for light absorption by TMA. A Si photodiode (Hamamatsu Photonics K.K.: S1336) was utilized as photodetector. For heat protection, light sources, photodiode and the readout circuit board were separated from the gas cell with heating unit in this work. The measuring light was introduced and received by heat resistant optical fibers.

The charge amplifier based photodetector circuit and timing diagram for signal sampling are shown in Fig.3. Differential signal voltage by switching two wavelength LEDs with and without light absorption are amplified by differential amplifier and sampled by 16bit A/D converter. The sampling period is 2s and it can be even shorter by optimizing light intensities and so on. This sampling speed is beneficial for real-time control of gas concentration.

3. Temperature Characteristics of TMA

Fig. 4 shows the UV light absorption spectrum of TMA at elevated temperature. As the temperature rises, an increase in the absorbance is confirmed, which is advantageous for sensitivity improvement. It is known that TMA is not a monomer at room temperature but a dimer is a stable three-center two-electron bond state [7-8]. The relationship between the change of absorption and the phase of TMA was analyzed as follows. Fig.5(a) shows the Fourier-transform infrared (FT-IR) spectrum of TMA at various temperature, and Fig.5(b) shows the behavior of the dimer peak 565cm^{-1}, respectively. The phase change from dimer to monomer of TMA was confirmed at elevated temperature with a good agreement of a report [9]. This indicates the increase of UV light absorbance at elevated temperature is due to the phase change from dimer to monomer. Knowing that the thermal decomposition temperature of TMA is at 336°C, we chose 140°C for sensing temperature of TMA.

4. TMA Concentration Measurement Results

TMA concentration was measured by the developed sensor at various conditions. Here, TMA concentration was controlled by changing the mixing ratio of 1% TMA/Ar and 100% Ar. Fig.6(a) shows the temporal output of the gas concentration sensor when 1% TMA and 100% Ar were switched at intervals of about 5 min by valve operation. It is confirmed that the concentration is stably monitored with good repeatability. Fig.6(b) shows the correlation between TMA concentration and measured sensor output. A good linearity was obtained. If the resolution is set at the 5 times of standard deviation of signal output during 0% TMA (100% Ar), the obtained resolution by the developed sensor is 62.7ppm. A sub 100ppm resolution is successfully obtained which is promising for precise control of TMA gas supply for various process scenes.

5. Conclusions

A compact gas concentration sensor using time-sharing dual wavelength UV light absorption method with heating function was developed for TMA. By controlling the phase change of TMA from dimer to monomer by raising sensing temperature at 140°C, UV light absorbance was found to be large. Consequently, a very high resolution of 62.7ppm was achieved for TMA. The developed sensor is promising for a real-time, precise control of TMA gas supply for various semiconductor manufacturing equipment.

References

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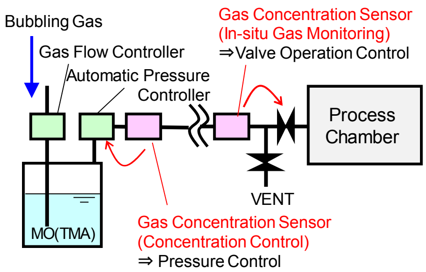

Fig. 1 Targeted MO gas supply system with gas concentration sensor.

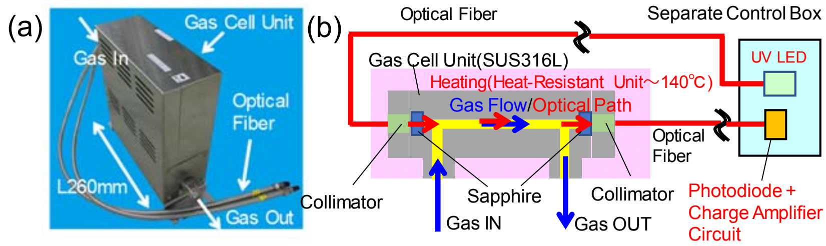

Fig. 2 (a) Picture and (b) schematic diagram of fabricated gas concentration sensor.

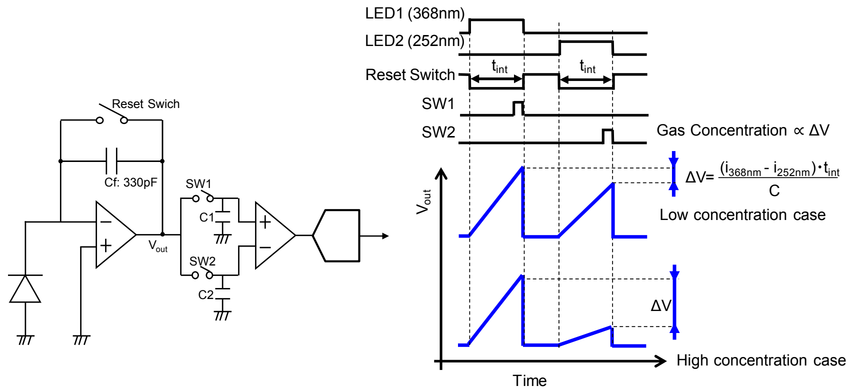

Fig. 3 The charge amplifier based photodetector circuit and timing diagram for signal sampling (Using time-sharing dual wavelength UV light absorption method).

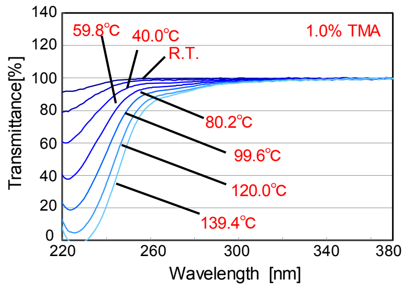

Fig. 4 Change in transmission spectrum of 1.0%TMA at elevated temperature.

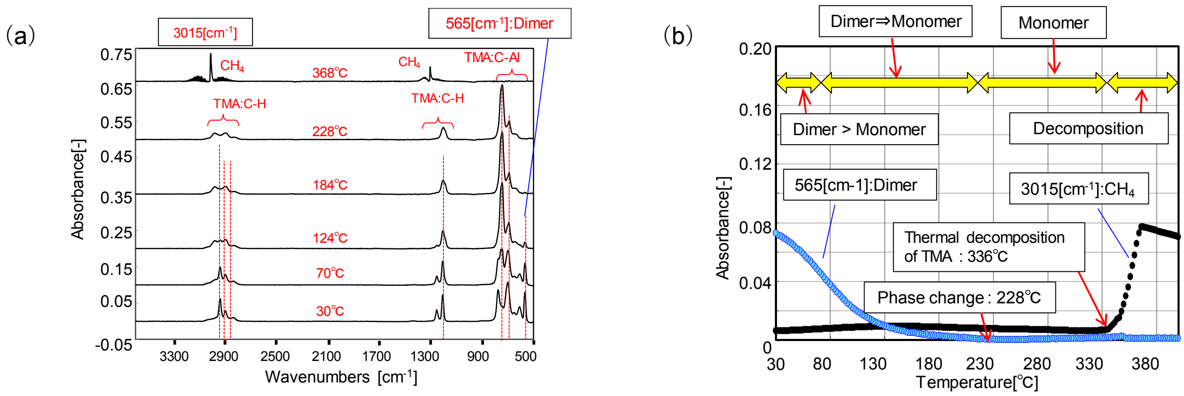

Fig. 5 (a) IR Spectral change of TMA at elevated temperature. (b) IR Absorbance change of TMA at elevated temperature.

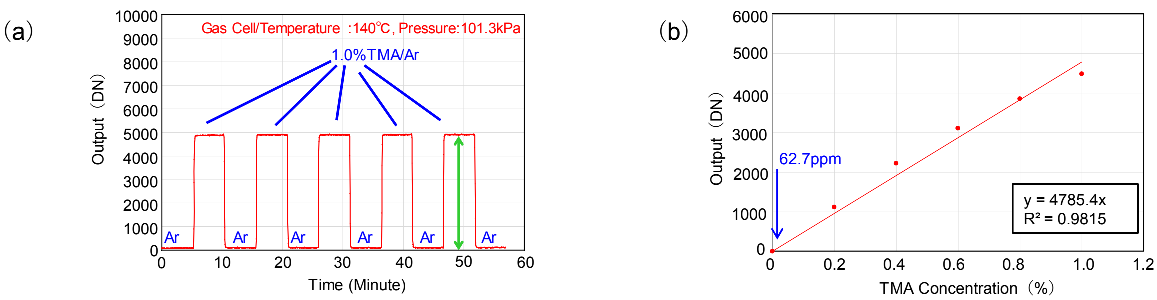

Fig. 6 (a) Fluctuation in output value of the concentration sensor unit when 1% TMA and 100% Ar were switched and (b) TMA concentration calibration curve.