Investigation of Thin Film for High Emissivity Infrared Micro Emitter

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Summary

A platinum infrared emitter by Joule's heat, about $0.5 \times 0.5 \text{ mm}^2$ of a pattern size, has been fabricated with micro lithography process of the platinum film on a quartz glass substrate. A hafnium oxide buffer film was used. The heat characteristics of the emitter were examined with thermography and a spectroradiometer. The maximum temperature of the heating emitter is confirmed to be 600°C at least. The platinum film emitter has the emissivity less than 0.1 and is nearly equivalent to gray body in wavelength $4\text{--}14 \mu\text{m}$. The emissivities of ceramics films on the platinum film were investigated to obtain the higher emissivity. The emissivities of oxide ceramics thin films are different from that of bulk targets and less than them. In Corning 7059 thin films, however, the higher emissivity values rather than that of the target is obtained at film thickness $6.7 \mu\text{m}$ in wavelength $7\text{--}11 \mu\text{m}$. The highest value of emissivity of the thick film was 0.96 at wavelength $9.5 \mu\text{m}$.

Keywords: Infrared emitter, Emissivity, Thin film, Laser ablation, Ceramics

1. INTRODUCTION

There is a need for portable and inexpensive detection systems to monitor pollutant or hazardous gases. Gases of particular interest include hydrocarbon, hydro-sulfur and the oxide of nitrogen and carbon. One method of detecting these gases makes use of the infrared vibrational absorption of the particular gases. The infrared source of gas detection system is needed to tune the emission wavelength to the infrared vibration of the particular gas. The attenuation of this emission which passes through a sample of the atmosphere is a direct measure of the concentration of the gas. The emitter has been made of metal wire till now. In order to obtain the smaller infrared emitter, we adapted the technique of micro fabrication process of thin film pattern. The infrared rays are emitted by the Joule's heat of the thin film pattern. The feature of the thin film emitter is suitable for the designs of various radiant powers. We used platinum thin films, because of high melting point (1772°C), chemical stability and confidence in industry. However, Pt film has low emissivity. The high emissivity coating films are necessary for the infrared micro emitter. The high emissivity of ceramics coating on metal was reported by the investigation for oxide films [1-3].

The purposes of this investigation are the production of infrared micro emitters and the high emissivity thin films

suitable for gas detection. One points of this paper is production and estimation of Pt film resistive heater for the micro infrared emitter. Another point is high emissivity of Corning 7059 glass film.

2. EXPERIMENT

A) Production of micro infrared emitter

We used a quartz glass as a substrate. A hafnium oxide film was deposited on the glass substrate. Next a Pt film was deposited on the Hf oxide film. The Hf oxide film adhered the Pt film to the substrate, as a buffer layer. Moreover, this Hf oxide film was used as an insulator. The pre-treatment of the substrate was 5 minutes ultrasonic cleaning with trichloroethylene, acetone and ethanol, respectively.

The Hf film was made with electron beam vacuum deposition. The back pressure of this deposition was in 2×10^{-5} Torr. The temperature of the substrate during deposition was 300°C . The source voltage of electron beam was 10 kV. The source current was 180 mA. The deposition time was 120 sec. The thickness of Hf film was 80 nm. This Hf film was oxidized under the thermal treatment of 700°C and O_2 gas flowing, for 2 hours. The Pt film was made with RF magnetron sputtering deposition. The back pressure of this deposition was 2×10^{-6} Torr. The temperature of the deposition was 250°C .

°C. The RF source voltage was 0.7 kV. The RF source current was 40 mA. The RF power was 10 W. The Argon gas pressure was maintained 3×10^{-3} Torr. The deposition time was 2 hours. The thickness of the Pt film was about 200 nm.

The Pt film emitter pattern was produced with electron beam lithography and a negative resist. The Pt film was etched with ECR microwave plasma etching. The patterned negative resist was used as an etching mask. The etching conditions were 34 A of magnetic current, 200 W of microwave power and 20 W of RF power. The flow rate of argon gas was 10 sccm. The etching time was 10 minutes, next 10 minutes for cooling of the resist mask. The etching speed of the Pt film was 12.5 nm/min. The etching speed of the resist pattern was 5 nm/min. The pattern size of the Pt film emitter was about 0.5×0.5 mm². The width of the Pt pattern line was 20 μ m.

The distribution of temperature for the heated emitter was measured with thermography. The our necessary heating temperature for the emitter is 500 °C at least by Planck's law. The measuring system of thermography was Infra Scope, which made by Barnes Engineering Division.

B) Production and estimation of ceramics films

We investigated the emissivities of ceramics films to obtain the higher emissivity. The ceramics thin films were deposited on Pt film/ Hf film buffer/ quartz glass substrate with laser ablation method. The size of the substrate was $25 \times 25 \times 1$ mm³.

The ceramics targets of excimer laser ablation were barium borosilicate glass (Corning 7059), alumina, yttria-stabilized zirconia (YSZ), SrTiO₃ (STO) and 6H silicon carbide. The substrate temperatures during depositions were 300 °C. The back pressure was several 10^{-6} Torr. In the case of oxide films, the O₂ gas pressure was maintained 10 mTorr during deposition. In SiC film deposition, the pressure was 2×10^{-6} Torr with no gas introduced. The KrF excimer laser with 248 nm wavelength, 100 mJ energy, and 24 ns pulse width was focused to a spot size of 1×3 mm² on respective targets in a vacuum chamber. The power density was 3 J/cm². The substrate was located 4 cm from the targets. Depositions of Corning 7059 glass, alumina and YSZ were performed for 15-30 minutes at a laser repetition rate of 10 Hz. Depositions of SiC and STO were performed for 20 minutes at a laser repetition rate of 2 Hz. In order to investigate for the effect of emissivity on film

thickness, the films of Corning 7059 glass and alumina were deposited with varying film thickness; The deposition time of Corning 7059 thick film was 40 minutes and the laser repetition rate of alumina thick film was 15 Hz.

The infrared radiances and spectral emissivity of the ceramics films were measured with spectroradiometer, which made the model SA-200 by Barnes Engineering Division. This detector was a sandwich construction detector, consisting of InSb and HgCdTe photo diodes. The wavelength range covered was from 1.35 to 14.49 μ m. The samples were heated up to 500 °C. These samples were joined to a resistive heater with Ag paste. The temperatures of samples ($25 \times 25 \times 1$ mm³) were measured with thermocouple touched on the surface of films, which was made of wires of 0.2 mm in diameter.

3. RESULTS AND DISCUSSION

A) Results of infrared micro emitter

Figure 1 is a thermograph of heating emitter at 300 °C at the part of Pt emitter pattern by electric power 465 mW. The figure shows that the left part of a pattern is heating. This heating element has 22 Ω of resistance, about 1/3 value of whole pattern (0.5×0.5 mm²). This figure shows that a quartz glass substrate became an infrared emitting element. The white line shows the pattern of the platinum film in the figure. The white part means highest temperature.

Fig. 1 Thermograph of a heating emitter at 300 °C.

Figure 2 shows a correlation between temperature at a heating Pt pattern and electric power. The temperature of a heating Pt pattern was measured with Infra Scope. The measurement range of Infra Scope was until 600 °C. The temperature of a heating Pt element was over range on electric power 652 mW. The temperature of a heating element is confirmed to be 600 °C at least on electric power 652 mW.

Figure 3 shows the spectral radiances of a infrared micro emitter. These radiances are weak, because of small square of heating element. The thermal time constant of the infrared micro emitter was 17 msec. That of minimum coil heater of Pt wire (length: 0.4 mm, diameter: 0.09 mm, 14 turns, diameter of wire: 0.02 mm) was 28 msec. The response of this micro emitter was faster than that of Pt coil heater.

Fig. 2 Correlation between temperature and electric power of a heating emitter.

Fig. 3 Spectral radiances of a heated infrared emitter. The electric powers are 42, 123, 228, 465 and 652 mW, from the bottom.

B) Emissivities of ceramics films

The thicknesses of deposited thin films of Corning 7059, alumina, YSZ, silicon carbide and STO are 2 μm , 400 nm, 850 nm, 100 nm and 100 nm at least, respectively. The thicknesses of deposited thick films of Corning 7059 and alumina are 6.7 μm and 600 nm, respectively. These films have thickness variation. The emissivities of all films are higher than one of the Pt film. The emissivities of films are less than that of targets, according to results

of the measured emissivities at 500 °C.

Figure 4 shows the spectral emissivities of a silicon carbide film, a STO film and a Pt film. The Pt film has the emissivity less than 0.1 and is nearly equivalent to gray body in wavelength 4-14 μm . The spectral emissivity of a STO thin film has three peaks, wavelength of about 3.5, 7 and 14 μm .

Figure 5 shows the spectral emissivities of a YSZ thin film and a YSZ bulk target. This film has a peak at wavelength of about 2.8 μm . In the case of wavelength over 10 μm , the emissivity of a YSZ target has over 1. We think that this error is caused of two reasons. One reason is that those radiant intensities from the samples and a standard black body radiator are smaller in longer wavelength range. As a result, the ratio of signal and noise is a low value. Another reason is the influence of error for the temperature measurement of the samples.

Fig. 4 Spectral emissivities of a SiC film, a STO film and a Pt film at 500 °C.

Fig. 5 Spectral emissivities of a YSZ thin film and a YSZ target at 500 °C.

Figure 6 shows the spectral emissivities of an alumina thin film (200nm), an alumina thick film (600nm) and an alumina target. The thin film has a broad peak at about 3.7 μm . The relation between the emissivities and thicknesses for alumina film was investigated by T.S.Eriksson et al. [1]. They reported that the low emissivity of the alumina film was obtained for the film thicknesses lower than 0.8 μm , whereas rather high emissivity could be obtained for films thicker than 3 μm .

Fig. 6 Spectral emissivities of an alumina thin film, an alumina thick film and an alumina target at 500 °C.

Fig. 7 Spectral emissivities of a Corning 7059 glass target, a thin film and a thick film at 500 °C.

Figure 7 shows the spectral emissivities for a target, a thin film (2 μm) and a thick film (6.7 μm) of Corning 7059 glass. The profiles of films have two peaks at wavelength of about 7 and 9.5 μm . In particular, the emissivity of the thick film is higher than that of the target in the range from 8.5 to 10.5 μm . The highest value of emissivity of the thick film is 0.96 at wavelength 9.5 μm . The same two peaks of emissivity for the glass film were reported by K. Kusabiraki et al. [2]. The wavelength of the reported main peak, however,

was about 12 μm . We think that the reason of wavelength difference is caused in the film deposition and the concentration of impurity. The influence of impurities for glass coating was reported [3]. The glass reported by of K. Kusabiraki et al. [2] was molten $\text{Na}_2\text{O}-2\text{SiO}_2$. The sodium impurity in the Corning 7059 glass, however, was less than 1 %, and more than one in quartz glass with flame reaction. The absorption wavelengths for SiO_2 were 7.46, 9.04, 12.4 and 21.3 μm . The highest absorption was 9.04 μm . The mentioned above, this wavelength difference of the peaks is dominated by the impurity.

4. CONCLUSIONS

The platinum infrared micro emitter shows that the temperature raised up to 600 °C at least. The emissivities of ceramics thin films on the platinum film are different from one of bulk targets and less than them. In Corning 7059 thin films, however, the higher emissivity of the film rather than the target emissivity is obtained at film thickness 6.7 μm in wavelength 7- 11 μm . The highest value of emissivity of the thick film is 0.96 at wavelength 9.5 μm . The Corning 7059 thin film emitter is suitable for gases detection in wavelength 7-11 μm . The infrared vibrational absorption wavelengths for the pollutant gases are 7.20 and 7.78 μm of CO_2 , 7.25 and 10.07 μm of C_2H_6 , 7.58 μm of NO_2 , 7.66 μm of CH_4 and 9.35 μm of SO_3 .

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