Photocatalytic Application and Preparation of Several Metal Oxide Films from Precursor Solutions Shigehiro MIYAMOTO^a, Yuuko NAKAMURA^b, Seichi RENGAKUJI^a, and Akifumi YAMADA^c

^aDepartment of System Engineering of Materials & Life Science, Faculty of Engineering, Toyama University ^bCenter for Instrumental Analysis, Toyama University, ^cDepartment of Chemistry, Nagaoka University of Technology,

^b 3190 Gofuku, Toyama 930-8555, Japan,

^c1603-1 Kamitomioka, Nagaoka 940-2137, Japan

INTRODUCTION: TiO₂ thin film prepared by advanced sol-gel method has a high performance, i.e. a high photocatalytic ability, and its thickness can easily be controlled to several tenths of a nanometer, etc. This process is based on the hydrolysis and polymerization of metal alkoxide in hydrophilic and hydrophobic mixed solvents, such as butanol and toluene. The obtained precursor solution is transparent without any precipitates, and stable. The high performance of the thin film obtained from the precursor solution may be caused by the selforganizational property of the solution itself. It is thought that the metal oxide cluster present in the solution has a small size and amphiphilic property. To clarify this property, we will present the gel structure change during film formation using IR measurement. We applied this film to evaluate the photocatalytic ability of TiO_2 film. Quartz crystal microbalance (QCM), which is a gravitation method, was employed instead of the conventional absorption method. This method was also tested in application to an organic gas sensor

EXPERIMENTAL: Titanium tetra n-butoxide (monomer) was used as the starting material. A small amount of H_2O was added to the dissolved titanium alkoxide solution in a mixed solvent, which was then refluxed, concentrated and diluted with solvent. Other metal oxide precursor solutions were prepared by the same method. After the TiO₂ thin film was coated on the QCM element, India ink was coated on the QCM element as the experimental material for the photodecomposition. The amount of decomposition during UV light irradiation was detected by the frequency-shift.

RESULTS and DISCUSSION: Figure 1 shows the IR data for SiO₂ film formation. Thin film(c) is prepared: precursor solution was dropped on the IR card and measured immediately, and (d) is measured after being dried with an infrared ray lamp. Vibrational frequencies of about 3300 and 3400cm⁻¹ were assigned to the OH group from butanol and the OH group from the metal oxide cluster, respectively. It is considered that the metal oxide cluster may contain a OH hydrophilic group in the cluster, which acts as a binder for self-organization. More obvious results were obtained for ZrO₂ precursor solution.

As the small amount of India ink on the TiO_2 coated on the QCM element decomposed by photocatalysis could be directly measured as frequency-shift, this method is useful to shorten the time for detection of, and to give an accurate evaluation of, photocatalytic ability. The relation between the frequency-shifts caused by the decomposition of India ink during UV light irradiation and the various TiO_2 film thicknesses is shown in Fig.3. The frequencyshifts become higher as the film thickness of the TiO_2 becomes thicker. When this film is applied to an organic gas (acetaldehyde and toluene) sensor, quick response was observed. The frequency-shift corresponded to the concentration of acetaldehyde gas (Fig.4). Therefore, it is thought that this method is also applicable to other gases.

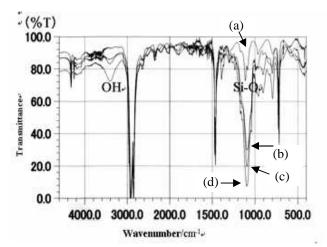


Fig.1 IR spectra for (a) tetraethoxysilane, (b) SiO2 precursor solution, and (c), (d) SiO₂ thin film.

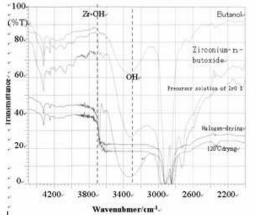


Fig.2 IR spectra for Zr alkoxide, precursor solution, and films.

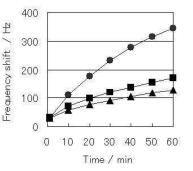


Fig.3 Frequency shift by the photocatalyst for the India ink decomposition. The TiO_2 thin films are of film thicknesses 136nm(O), 58nm(A), 81nm(O).

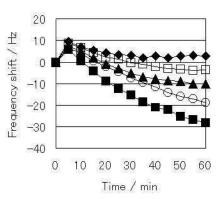


Fig.4 Changes in frequency shift of QCM element in various concentrations of acetaldehyde gas under irradiation of UV. Gas concentration is $500ppm(\spadesuit)$, $300ppm(\Box)$, $100ppm(\spadesuit)$, $10ppm(\bigcirc)$, $blank(\blacksquare)$.