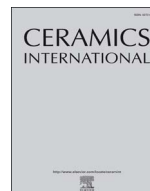




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# Solid conversion behaviors of indium oxide gel consisting of hybrid clusters with thermal- and/or ultraviolet-treatments for low temperature processing

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## ABSTRACT

Herein, the thermal and ultraviolet (UV)-irradiation solidification of indium-oxide (In-O) cluster gel, which is made from an indium acetylacetonate solution using propionic acid as a solvent, is reported. The cluster gel is an assembly of hybrid clusters, which has In-O cores coordinated with organic ligand molecules. It is confirmed that the well-defined structure of the cluster gel enables us to have a predictable solidification in the thermal treatment. Hence, we are able to understand what happens in each temperature stage from solution to solid, which can be strictly defined. It is observed that even the amount of the residual solvent in the gel is a function of temperature. The limitation of thermal pyrolysis is also clarified in the carbon-based solution. Some amounts of hybrid clusters remain even after annealing at 500 °C, leading to a carbon content that is higher than 10 at% and large  $V_{th}$  shift due to many defects in the fabricated thin-film transistors. As for the UV treatment, it is confirmed that the UV irradiation solidifies the gel even at room temperature (RT). Moreover, it is found that the UV reactions generate new carbon bonds, which have a higher binding energy than those in the starting gel. Although the residual organics in the gel prevent the growth of the In-O core in the case of UV irradiation at RT, the combination of thermal and UV treatments makes possible the growth of fine In-O crystals with reduced (2 at %) and stabilized carbon elements. As a result, it can be stated that a good semiconductor film is developed even at a temperature as low as 200 °C by using this combined treatment.

## 1. Introduction

The development of electronics has made our daily lives convenient. Thin film transistors (TFTs) are used in various electronic devices and have become indispensable in modern society. Recently, oxide-semiconductor TFTs have begun to be used as driving elements for organic electronic luminescent displays and high-definition liquid crystal displays [1–3]. The general method used for manufacturing oxide TFTs is a vacuum process, which yields a high-quality film but has problems in terms of efficient material usage and energy efficiency. Recently, a solution process has been proposed to address these problems [4–8]. In this process, a desired solid thin film is formed from the solution materials.

We have studied the formation of functional oxide thin films using a solution process, especially by using a solution that is composed of solutes having core-shell clusters dispersed in the solvent. The core and shell consist of metal-oxide and organic ligands coordinated to the core, respectively. We named such solution a “hybrid cluster solution,” which indicates that each cluster-like solute is a hybrid of inorganic and

organic components. When the solvent dries, the solution becomes a gel, which preserves the structure of the hybrid cluster in the solution. As the gel is completely constructed from the hybrid clusters, we refer to it as a “cluster gel.” The cluster gel is a physical gel mainly aggregated by van der Waals (vdW) interaction [9], such that when the cluster gel material is put into an original solvent, it easily dissolves into the solution again. This type of gel occurs in systems such as InO, InSnO, InZnO, InGaZnO, ZrO, and LaZrO [10]. Such cluster gel structures can be widely found in metal-oxide precursor materials. The hybrid cluster solution and cluster gel have several advantages. Since the structures are well-understood and well-defined, issues related to the solution process, such as wetting, coating, and pyrolysis, can be theoretically handled. Improvements in the properties of oxide materials become possible through the cluster structure design. In addition, we can imprint the cluster gel on a substrate to form solid patterns; we have successfully accomplished this using the above systems.

In this study, we apply the cluster gel concept for the conversion of gel to solid, in order to add value in the solution processes of an In-O material. The cluster structure of In-O from the solution, which is

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synthesized using In-acetylacetonate (acac) dissolved in propionacid (PrA), has been well studied by us. Using high-energy X-ray diffraction (HEXRD) at the SPring8 facility (Hyogo, Japan), a pair distribution analysis of an In-O gel annealed at 100 °C shows clear evidence of a cluster structure, with the diameter of each cluster being around 1 nm (Supplementary materials: Fig. S1) [11]. A typical composition of the cluster is  $\text{In}_7\text{O}_5(\text{acac})_2(\text{PrA})_6$  (Supplementary materials: Fig. S2) [11]. In this case, the shell consists of two acac molecules and six PrA molecules, which are coordinated to the  $\text{In}_7\text{O}_5$  core, whose structure is very similar to that of an InO crystal. In synthesizing the solution, ligand exchange occurs from acac to PrA. Based on this structure, a rough image of the thermal pyrolysis process can be easily understood. Through thermal treatment, the organic shells are decomposed and desorbed, while the adjacent cores start to show necking, form metal-oxide networks, become condensed, and finally, are solidified. Generally, if we can precisely characterize the physical and chemical properties of shells and cores, we can establish the conditions and process for developing metal-oxide thin films.

With respect to the conversion process from gel to solid, ultraviolet (UV) light irradiation, along with thermal processing of gels, is an attractive option. We have demonstrated that UV irradiation adds value to the solution process by improving film properties, direct patterning of metal-oxide patterns, and lowering the process temperature. In our previous work, we confirmed that the semiconductor properties of an InGaZnO film improved dramatically after annealing by UV/O<sub>3</sub> treatment of the InGaZnO gel [12]. A second advantage of UV irradiation is that it introduces a new direct patterning method by changing the re-dissolving ability of the gel against the original solvent [13]. Since the UV-irradiated regions of the gel tend to solidify, making it more difficult for the regions to dissolve in the solvent, compared to the easily dissolvable non-irradiated regions, the half-solidified gel patterns remain on the substrate after dissolving. Another advantage of UV irradiation is that it is a novel, eco-friendly patterning technique that does not require resist materials or vacuum systems. Finally, we succeeded in lowering the process temperature of film production with thermal UV irradiation, which is a combination of thermal and UV pyrolysis. Good-quality In-O and LaZrO films were formed at a process temperature of 200 °C. TFTs with mobility of around 2 cm<sup>2</sup>/(Vs) were successfully developed at this temperature [14,15].

UV irradiation has proven to be very effective for the solidification of gels, especially cluster gels. However, the mechanisms of UV solidification of cluster gels are not fully understood. Thus, the current study aims to investigate the solidification processes of InO cluster gels by both thermal pyrolysis and UV irradiation, and to better understand how thermal and UV solidification enables low-temperature fabrication of InO films with good properties.

## 2. Experiment details

### 2.1. Preparation of InO precursor solution

For the InO precursor solution, Tris-In-acac (Wako Pure Chemical Industries) was dissolved in PrA (Kanto Chem.) at a molar concentration of 0.2 mol/kg for the re-dissolving ability experiment and TFT fabrication and 0.4 mol/kg for the other experiments. The mixture was stirred at 110 °C/1000 rpm for 1 h, after which the solution was filtered using a polytetrafluoroethylene (PTFE) filter (0.2- $\mu\text{m}$  pore).

### 2.2. Preparation of InO films

For the film thickness measurement, FT-IR measurement, and XRD measurement, a Pt (200 nm)/Ti (2 nm)/Si substrate having an area of 20 mm  $\times$  20 mm was used. For the re-dissolving ability measurement, TFT fabrication, composition analysis, and thermal desorption spectrometry (TDS) analysis, a SiO<sub>2</sub> (100 nm)/Si substrate having an area of 20 mm  $\times$  20 mm was used. For the UV/VIS measurement, a synthetic

quartz substrate was used. These substrates were cleaned by ultrasonic cleaning for 5 min with immersion in acetone, ethanol, and deionized water, respectively. After the substrate was cleaned, the solution was spin-coated on it and dried at room temperature (RT) to obtain the gel films, which were then used for the various measurements.

In the thermal pyrolysis experiments, the thin films were fabricated as follows: 1) samples processed between 100 and 200 °C were annealed on a hot plate for 1 min at each temperature; 2) samples processed between 250 and 325 °C were dried at 100 °C for 30 s and annealed on a hot plate for 5 min at each temperature; and 3) samples processed at 350 °C or higher were dried at 100 °C for 30 s, pre-baked at 150 °C for 30 s, and annealed using a rapid thermal annealing system (RTA SSA-P 610CP, ULVAC-RIKO, INC.) for 5 min in ambient environment at each temperature. For UV irradiation experiments, a UV treatment system (UV300H-E, SAMCO) was used, which had a low-pressure mercury lamp generating UV light including the wavelengths of 185 nm and 254 nm, of which the intensity ratio was  $I_{185\text{ nm}} / I_{254\text{ nm}} = 2/8$ . The film dried on a hot plate at 100 °C for 1 min was used as the starting film for all UV irradiation experiments. UV irradiation was performed at RT and 200 °C. Hereafter, UV irradiation at RT is RT-UV, and UV irradiation at 200 °C is 200 °C-UV. The experimental conditions for each experiment are described below.

### 2.3. Thermogravimetry-differential thermal analysis (TG-DTA)

To observe the thermal behavior of the InO precursor solution, TG-DTA measurement was performed. The temperature ranged from RT to 1000 °C with a scanning rate of 10 °C/min in air flow. The test solution was packed in a Pt pan (TG-DTA 6200, SII).

### 2.4. Film thickness measurement

The thicknesses of all sample films were measured by ellipsometry (GES 5 E, SEMILAB). Film thicknesses were measured after the samples were annealed. The thermally treated samples were prepared by annealing at each temperature ranging from RT to 800 °C. The RT-UV- and 200 °C-UV-treated samples were prepared by UV irradiation of the starting films for 5, 15, 30, and 60 min at each temperature under N<sub>2</sub> atmosphere.

### 2.5. Re-dissolving ability measurement

The re-dissolving ability of a gel film indicates how much of its volume dissolves in an original solvent when immersed. This property indicates the type of interaction occurring inside the gel. When the re-dissolving ability is high, i.e., the gel film is soluble in the solvent, the gel's cohesion force is characterized by a vdW interaction. A gel in this state is called a "physical gel." On the other hand, when the re-dissolving ability is low, the cohesion force of the gel is defined by chemical bonding, such as covalent bonding, and the gel becomes insoluble. A gel in this state is called a "chemical gel."

Thermally treated samples were prepared by drying the gel film at 100 °C, 150 °C, 170 °C, 180 °C, 190 °C, 200 °C, and 250 °C for 1 min on a hot plate. RT-UV-treated samples were prepared by RT-UV treatment of the starting film for a period ranging from 4 to 32 min under N<sub>2</sub> atmosphere. Afterwards, the samples were immersed in PrA for 1 min. Following immersion, the film thickness was measured by ellipsometry. Using pre-immersion film thickness (Thickness 1) and post-immersion film thickness (Thickness 2) values, the re-dissolving ability was evaluated as follows:

$$\text{Re-dissolving ability (\%)} = \frac{\text{Thickness1} - \text{Thickness2}}{\text{Thickness1}} \times 100$$

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