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A new photocatalyzer InN_xO_{1-x} film

grown by ArF excimer laser-induced MOCVD at low temperature (RT~200°C)

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ABSTRACT

Using the ArF excimer laser-induced MOCVD method, $InN_{1-x}O_x$ thin films are grown on a glass substrate. The photolytical decomposition of NH_3 enables to grow them even at room temperature. It is found that the $InN_{1-x}O_x$ thin films grown at a temperature less than 250˚C show an excellent photocatalytic decomposition of H_2S under UV irradiation, while the activity of the films grown at a temperature higher than 300˚C is very small, less than 1/4 of that for the low-temperature films. The excellent photocatalytic activity for the low-temperature films is closely related to the amorphous phase of the films.

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1. INTRODUCTION

The major problem in the conventional metalorganic chemical vapor deposition (MOCVD) of InN is the low thermal decomposition rate of NH_3 at a growth temperature around 600˚C. For example, the decomposition rate is as low as 3.8% even at 700˚C [1]. In order to solve this problem, we have developed the laser-induced MOCVD technique of InN [2,3], where an ArF excimer laser (λ=193 nm) is employed to dissociate NH_3 photolytically. NH_3 has an absorption coefficient as high as 100-1000 $cm^{-1}atm^{-1}$ for ultraviolet light with a wavelength 180-200 nm [4], and can be easily decomposed into NH_2 and H by absorbing photons with such a high energy [5]. We have shown that the laser-induced MOCVD enables to grow InN-based films in a wide range of growth temperature, from RT to 700ºC. The films grown at a temperature less than 450°C were found to contain a large amount of oxygen and to have a lattice constant larger than that of the pure InN [3]. Therefore, such a film is concluded to be an alloy of InN and In_2O_3, $InN_{1-x}O_x$.

It is known that In_2O_3 has a photocatalytic activity [6,7]. According to Fujii et al. [8], the energetic position of the valence band top in In_2O_3 is very low compared with other semiconductors. This means that holes in In_2O_3 have an oxidation power higher than those for other semiconductors including TiO_2. Therefore, we are very interested in photochemical and/or photocatalytic behavior of $InN_{1-x}O_x$.

In this paper, we report the photocatalytic H_2S decomposition of the $InN_{1-x}O_x$ thin films grown at a low temperature (RT ~ 250˚C). The excellent photocatalytic activity of the films is found to be related to the amorphous phase of those films.

2. EXPERIMENTAL

Figure 1 schematically shows the ArF laser-induced MOCVD system used to grow $InN_{1-x}O_x$ films. Trimethylindium (TMI) and NH_3 are used as sources and they are introduced perpendicularly to the substrate surface. As substrates, 10 x10 mm^2 size (0001) sapphire and 18 x18 mm^2 size glass sheet are used. The ArF excimer laser beam (wavelength 193 nm, energy 50 mJ and repetition rate 20 Hz) is passed parallel to the substrate surface (2 mm above the substrate). The pressure in the chamber is kept at 1-2 Torr during the growth. Substrate temperature is varied from RT to 600°C. The thickness of grown films is approximately 1 μm. Figure 2 shows the schematic drawing of the setup for photocatalytic H_2S decomposition experiment. For the photocatalytic experiments, a glass substrate with an $InN_{1-x}O_x$ film is set in a sealed UV-transparent container with the 500 cc-air containing 40 ppm H_2S, as shown in Fig. 2. UV light with 300-400 nm wavelength and 600 $\mu W/cm^2$ intensity is irradiated to the film surface in the container for 0-4 hours. A 10 x10 mm^2 size piece of a wet paper is included in the container to supply water vapor. To compare the photocatalytic activity of $InN_{1-x}O_x$ films, polycrystalline TiO_2 and In_2O_3 films are also prepared. Polycrystalline TiO_2 films are obtained by the sol-gel method using P-cat MIX® (TiO_2: 0.8~0.9 wt%). Films of polycrystalline In_2O_3 are obtained by annealing $InN_{1-x}O_x$ films at 400 ºC in the air.

3. RESULTS AND DISCUSSION

Figure 3 shows the photographs of $InN_{1-x}O_x$ films grown at a different temperature. The color of the film is changed from black for the 600°C-grown film to yellow for the RT-grown one. The color change is due to the change in composition of the films; In_2O_3 content is increased with decreasing deposition temperature [3]. The sources for oxygen seem to be H_2O and/or O_2 incorporated into the chamber during the substrate loading. Figure 4 shows the results of the photocatalytic experiments. Concentration of H_2S in the container is plotted with time. The $InN_{1-x}O_x$ films grown at 200°C are used here. First, no or very small change in H_2S content is confirmed when no catalyzer is contained or UV is not irradiated. In the case of the $InN_{1-x}O_x$ films under UV illumination, as seen in Fig. 4, H_2S concentration becomes to zero after 4 h. This reduction of H_2S concentration is due to a photocatalytic effect. Data for other photocatalyzers, TiO_2 and In_2O_3, are also shown for comparison. The results in Fig.4 show that the $InN_{1-x}O_x$ films have an excellent photocatalytic activity compared with the other photocatalyzers. Figure 5 shows the results of the repeatability check of photocatalytic activity of $InN_{1-x}O_x$. In this case, the same $InN_{1-x}O_x$ film is used four times; the 1st in the dark and the 2nd to 4th with UV irradiation. The sample shows the excellent repeatability. Figure 6 shows the growth temperature dependence of H_2S concentration in the container after 2 or 4 hours UV irradiation. It is clearly found that the excellent photocatalytic activity is obtained only for films grown at a temperature less than 250°C. On the other hand, the activity of the films grown at a temperature higher than 300˚C is very small, less than 1/4 of that for the low-temperature films. It is noted that the change in the activity with growth temperature is very drastic. Figure 7 shows the X-ray diffraction spectra for $InN_{1-x}O_x$ films grown at a different temperature. One can see that the diffraction peak from the film is shifted to a lower angle with decreasing growth temperature. This is due to the increase in In_2O_3 component in the films. As can be seen in this figure, the films grown at a temperature less than 250°C show no diffraction peak, indicating that such films are of amorphous phase. Therefore, the excellent photocatalytic activity seems to be closely related to the amorphous phase of the films.

4. CONCLUSION

Thin films of $InN_{1-x}O_x$ are grown on a glass substrate at a temperature in the range from RT to 600˚C using the ArF excimer laser-induced MOCVD method. The photocatalytic H_2S decomposition experiment is performed in a sealed UV-transparent container with 500 cc-air containing 40 ppm H_2S. It is found that the $InN_{1-x}O_x$ thin films grown at a temperature less than 250˚C can reduce H_2S content to almost zero ppm after 4 h UV irradiation. The excellent repeatability of the photocatalytic activity is also confirmed. The activity of the films grown at a temperature higher than 300˚C is very small, less than 1/4 of that for the low-temperature films. The X-ray diffraction analysis indicates that the excellent photocatalytic activity is closely related to the amorphous phase of the low-temperature films.

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FIGURE CAPTIONS

Fig. 1. The ArF laser-induced MOCVD system used for $InN_{1-x}O_x$ thin film growth.

Fig. 2. Schematic drawing of the setup for photocatalytic H_2S decomposition

Fig. 3. $InN_{1-x}O_x$ films grown on sapphire substrate (10 x 10 cm^2) at a different temperature.

Fig. 4. Changes in H_2S concentration with time under UV irradiation. The $InN_{1-x}O_x$ films grown at 200°C are used here. Data for other photocatalyzers are also shown for comparison.

Fig. 5. Reproducibility check of photocatalytic H_2S decomposition of an $InN_{1-x}O_x$ film. The $InN_{1-x}O_x$ films grown at 200°C are used here.

Fig. 6. The growth temperature dependence of H_2S concentration in the container after 2 or 4 hours UV irradiation.

Fig. 7. X-ray diffraction spectra for $InN_{1-x}O_x$ films grown at a different temperature.

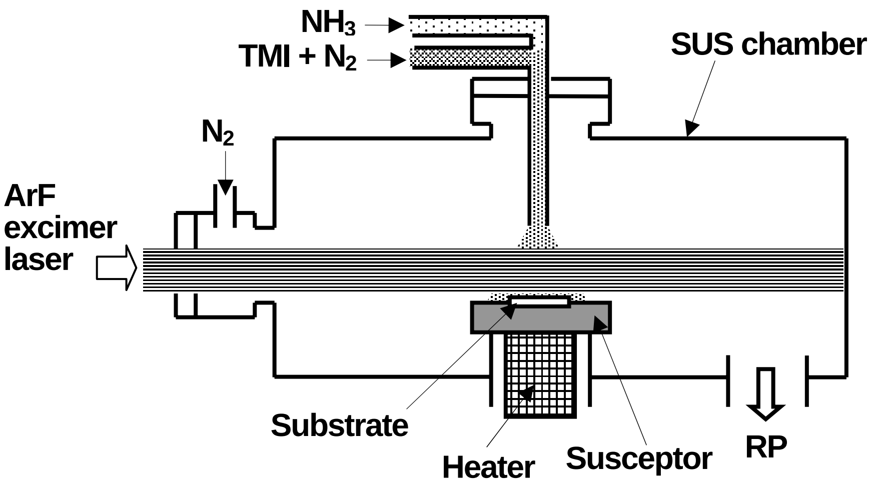


Fig. 1 A. Yamamoto et al.

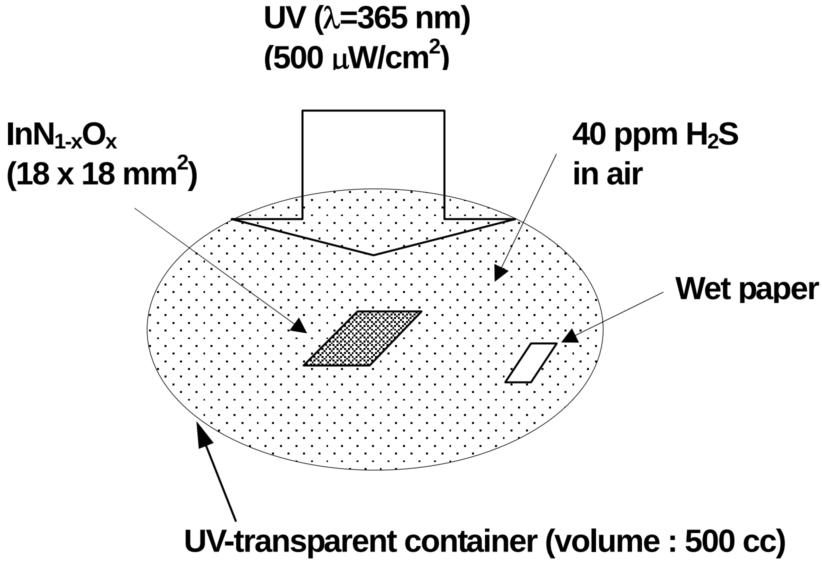
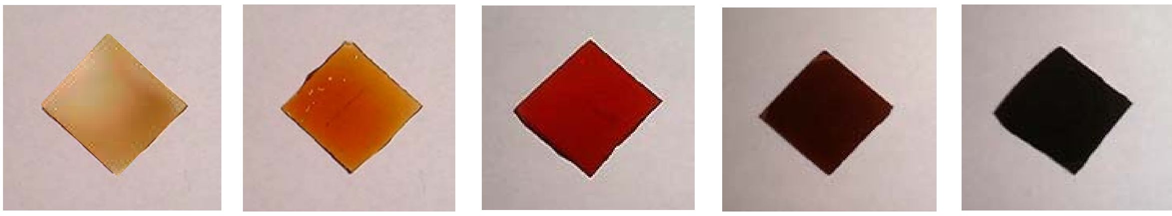
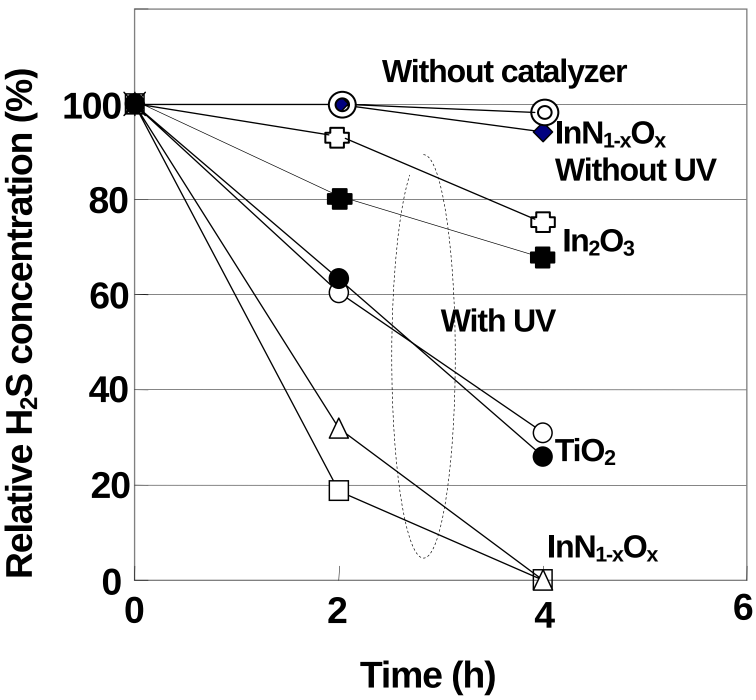


Fig. 2 A. Yamamoto et al.



RT 100°C 200°C 400°C 600°C

Fig. 3 A. Yamamoto et al.



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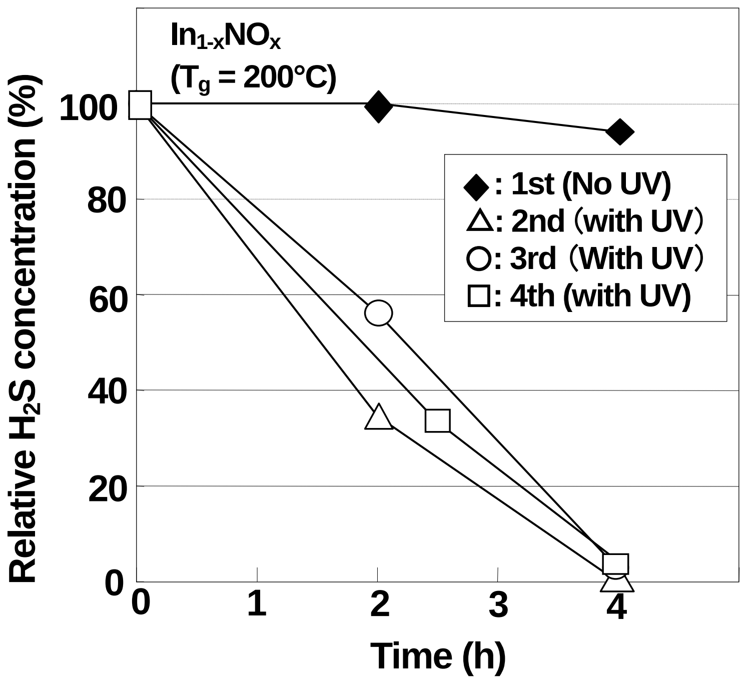

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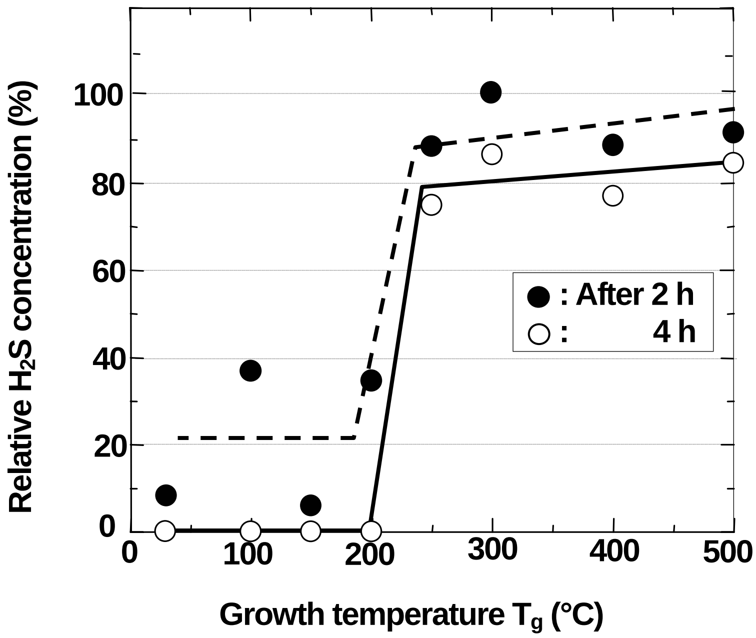

Fig. 6 A. Yamamoto et al.

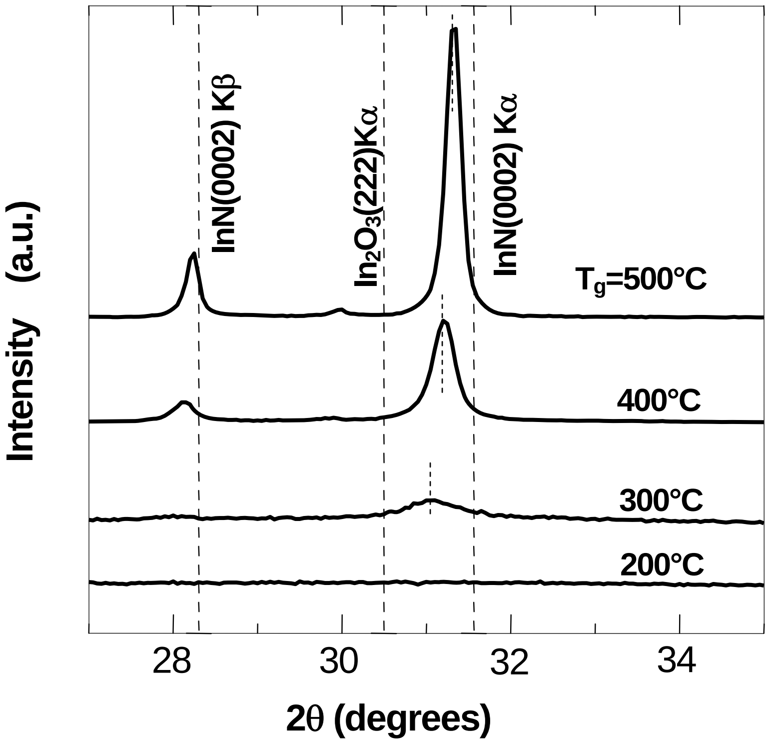

Fig. 7 A. Yamamoto et al.