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Catalytic decomposition of NH$_3$ on heated Ru and W surfaces

Hironobu Umemoto[1,*], Yuta Kashiwagi[1], Keisuke Ohdaira[2], Hiroyuki Kobayashi[2], Kanji Yasui[3]

[1] *Faculty of Engineering, Shizuoka University, Johoku, Naka, Hamamatsu, Shizuoka 432-8561, Japan*

[2] *School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Nomi, Ishikawa 923-1292, Japan*

[3] *Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan*

ABSTRACT

The catalytic decomposition processes of NH$_3$ on heated W and Ru-coated W wires were examined by employing laser spectroscopic and mass spectrometric techniques. Laser spectroscopic measurements show that more H atoms are produced on uncoated W wires, while the NH-radical densities are higher for Ru-coated wires, at the same wire temperatures. Mass spectrometric measurements show that the decomposition efficiencies are nearly the same in both systems. The main products on heated W wires must be NH$_2$ and H, while the production of NH should also be important on Ru-coated W wires.

Keywords: Catalytic decomposition, NH$_3$, Ru, W, Laser spectroscopy, Mass spectrometry

[*] Corresponding author.

E-mail address: thumemo@ipc.shizuoka.ac.jp (H. Umemoto).

1. Introduction

Recently, Yasui and coworkers have shown that GaN films can be grown from NH_3 and trimethylgallium by employing a hot-mesh chemical vapor deposition method [1,2]. They used W and Ru-coated W meshes and found that the crystallinity of GaN films grown using the Ru-coated W mesh was better than that grown using the W mesh at low catalyst temperatures. They estimated the H-atom densities in the gas phase during the deposition based on the measurements using tungsten phosphate glass plates, and have concluded that the decomposition efficiency of NH_3 on the heated Ru-coated W mesh must be higher than that for the uncoated W mesh [1].

Tungsten oxide doped in phosphate glass can be reduced by H atoms, but is not reduced by H_2 molecules at moderate temperatures [3]. This is why this glass plate can be used to estimate the H-atom densities. The degree of reduction can easily be measured by its change in optical transmittance in the visible region. The problem is that tungsten oxide may also be reduced by NH_2 or NH radicals. Then, it is desired to measure the radical densities directly during the decomposition of NH_3 to elucidate the cause of the change in GaN film qualities when a Ru-coated mesh was used.

In the present work, the absolute densities of H atoms and NH radicals produced by the catalytic decomposition of NH_3 on heated W and Ru-coated W wires were evaluated by laser spectroscopic techniques. Mass spectrometric studies were also carried out to evaluate the decomposition efficiencies of NH_3.

2. Experimental Details

The experimental apparatus and the procedure were similar to those described

previously [4-7].   A cylindrical reaction chamber made of stainless steel, 10 cm in internal diameter, was used.   Two equal-length wires, one was uncoated W and another was Ru-coated W, were installed in this chamber and the radical densities produced on these wire surfaces were measured without breaking the vacuum.   With this procedure, it is possible to compare the radical densities without changing the wall conditions.   The wire length was 30 cm while the diameter was 0.38 mm.   The wires were resistively heated by using a DC power supply.   The wire temperatures were estimated from the electric resistivity [8].   The gas flow rates were controlled by using a mass flow controller.   The inner walls of the chamber were coated with SiO_2 in order to reduce the removal rates of radical species [9].   The procedure to prepare a Ru-coated wire was the same as that reported elsewhere [1].   It was prepared by radio-frequency (rf) magnetron sputtering using a Ru target (Nilaco, 99.99%) in the presence of 0.8 Pa of Ar.   The rf power was 20 W.   The deposition time was 5 min and the distance between the sample and the target was 4 cm.   The expected thickness of the Ru layer is 20 nm.   The W surface was not completely covered with Ru judging from the X-ray photoelectron spectroscopy (XPS) measurements, but the situation must have been the same in the previous studies on hot-mesh CVD [1,2].   Ru makes an alloy with W when heated.   The temperature of the Ru-coated wire was kept below 1660 K in order to avoid alloying.   No changes were observed in the XPS spectra below this temperature.

H atoms produced on heated wires were detected by a vacuum-ultraviolet (vuv) laser absorption technique and a vuv laser-induced fluorescence (vuv LIF) technique at 121.6 nm [5-7].   The distance between the wire and the detection zone was 9 cm. The vuv laser pulse was generated by tripling the frequency doubled output of a Nd:YAG pumped dye laser by using a mixture of Kr and Ar.   In the absorption measurements, the transmitted laser intensity was measured by monitoring the NO^+ ion

current. The absolute densities can be determined by this technique. In the LIF measurements, the induced fluorescence was detected at an angle perpendicular to the laser beam with a solar-blind photomultiplier tube through an MgF_2 collimating lens and an interference filter. The photomultiplier signal was processed with a digital oscilloscope or a gated boxcar averager. At 1490 K for W and at 1570 K for Ru, the atomic hydrogen densities were determined by both techniques. Since the absorption of the vuv laser cannot be ignored at these temperatures, this contribution was corrected in the LIF measurements. The relative values obtained by the LIF technique were scaled to the absolute ones by comparing the signal intensities at these temperatures.

NH radicals were detected by employing a laser-induced fluorescence (LIF) technique around 336 nm, which corresponds to the (0,0) band of the A $^3\prod_i$ – X $^3\Sigma^-$ transition. The procedure was the same as that described elsewhere [4]. The absolute densities were evaluated by comparing the time-integrated LIF intensity for the $R_1(N"=3)$ line at 334.6 nm with the intensity of the Rayleigh scattering caused by Ar. This rotational line is not overlapped with other lines and this transition system can be regarded as a two-level one. The plane of polarization was rotated to be perpendicular to the observation direction with a double-Fresnel rhomb after passing through a Glan-laser prism in these absolute density measurements.

Mass spectrometric analysis was also carried out to measure the decomposition efficiency [4-7]. A quadrupole mass-spectrometer was attached to the chamber through a sampling hole (0.1 mm in diameter). The flight tube was differentially pumped down to 5×10^{-4} Pa with a turbo molecular pump.

NH_3 (Takachiho, 99.999%), H_2 (Japan Air Gases, 99.999%), NO (Nihon Sanso, 99%),

Ar (Japan Air Gases, 99.999%), and Kr (Nihon Sanso, 99.995%) were used from cylinders without further purification.

3. Results

3.1. Detection of H atoms

Fig. 1 shows the relationship between the H-atom density and the reciprocal of the catalyst temperature.   The NH_3 flow rate was 50 sccm and the pressure was 6.8 Pa when the catalyst was not heated.   The plots are Arrhenius-type, both for W and Ru, but the apparent activation energies are different.   The activation energy for W was 133 ± 6 kJ mol^{-1}, while that for Ru was 173 ± 3 kJ mol^{-1}.   The error limits are the standard deviations.   The H-atom density when a Ru-coated wire was used was less than that for W, at least below 1660 K.   The activation energy for W is a little smaller than the result of our previous study, 150 kJ mol^{-1} [4].   A similar result has been obtained for H_2 [10].   The H-atom density depends not only on the formation rate but also on the removal rate, which increases with the wall temperature.   A large reaction chamber was used in our former measurements.   The wire temperature dependence of the wall temperature may be different for different chambers.   In addition, in our previous study, the temperature range was rather small; between 1270 and 1570 K since only vuv absorption technique was employed.   The temperature range in the present work is wider and the result should be more reliable.   It should be noted that the H-atom density in the presence of H_2 was almost independent of the choice of the wire materials; W or Ru-coated W.

3.2. Detection of NH radicals

It was possible to identify NH when the catalyst temperature was over 1600 K.   The relative population when a Ru-coated wire was used was 4 times larger than that for W

at 1660 K. The NH_3 pressure dependence was minor between 24 and 120 Pa. The absolute densities were evaluated under two conditions. In one case, W was used as a catalyst and the temperature was 2060 K. The NH_3 pressure was 50 Pa when the catalyst was not heated. The absolute density was 5.9×10^{10} cm^{-3}. The density was 1.8×10^{10} cm^{-3} when a Ru-coated wire was used and the temperature and the pressure were 1660 K and 120 Pa, respectively.

In our former work, we have found that the catalyst temperature dependence of the NH density is not Arrhenius-type and the apparent activation energy is small when the temperature is high (unpublished). However, below 2100 K, it was possible to assume a linear relationship between the logarithm of the NH density and the reciprocal of the catalyst temperature. This result was confirmed in the present study and the apparent activation energy between 1600 and 2070 K was 310 kJ mol^{-1} when W was used. We have also found that the NH density increases nonlinearly with the increase in NH_3 flow rate [4]. This was also confirmed in the present study as is shown in Fig. 2.

3.3 Mass spectrometric measurements

Fig. 3 shows the catalyst temperature dependence of the mass spectrometric signals of NH_3, N_2, and H_2, both for coated and uncoated wires. The detection sensitivities were evaluated by measuring the signal intensities in the NH_3, N_2, and H_2 flows. The typical NH_3 flow rate and the pressure were 20 sccm and 4.0 Pa, respectively. The results for the uncoated wire are very similar to those reported previously [4] and also very similar to the results for the Ru-coated wire. In other words, although the product yields are different for W and Ru-coated W wires, the overall decomposition efficiencies are similar. The leveling off of the NH_3 decomposition efficiency at high catalyst temperatures can be explained by the production of NH_3 from NH_2 and H,

produced from H_2, on chamber walls, as has been discussed in our previous paper [4]. The decomposition efficiency of NH_3 did not change when N_2 or Ar was added to the flow, but that decreased when H_2 was added.   This supports the above explanation that NH_3 is reproduced from NH_2 and H, since H atoms are produced efficiently from H_2.

4. Discussion

Yasui and coworkers have demonstrated that tungsten oxide doped in phosphate glass is reduced more when a Ru-coated mesh was used [1].   This may seem in contradiction to the present result that less H atoms are formed when a Ru-coated wire is used.   However, it should be noted that tungsten oxide may be reduced not only by H atoms but also by NH and NH_2 radicals.   If NH radicals reduce tungsten oxide more efficiently than H atoms, the contradiction may be resolved.

The NH-radical density increases nonlinearly against the NH_3 pressure.   One of the causes should be the suppression of the diffusional loss, but it should be remembered that NH_2 density increases more linearly [4].   The nonlinear pressure dependence suggests that NH is not produced directly on the catalyst surfaces.   Reactions between radical species adsorbed on the catalyst, such as $SNH_2+SH \rightarrow SNH+H_2+S^*$ and $SNH_2+H \rightarrow SNH+H_2$, must be involved.   Here, SNH_2, SH, and SNH represent chemisorbed NH_2, H, and NH, respectively, while S^* stands for a vacant site on the catalyst.   In our previous report [4], we have mentioned that bimolecular process in the gas phase, $NH_2+H \rightarrow NH+H_2$, should be important to produce NH.   However, the present results suggest that NH should be formed on the catalyst surfaces.   If NH is produced only in the gas phase, the amount of NH must be larger when an uncoated W wire is used.   The more efficient production of NH on Ru surfaces suggests that the

residence time of NH$_2$ on Ru is longer than that on W.

It is not easy to explain why better crystallinity of GaN films was obtained when more NH radicals were present.   In general multivalent radicals do not have good effects on the film properties because they insert into single bonds [11].   However, it should be remembered that triplet radicals, such as NH(X $^3\Sigma^-$), are less reactive than singlet bivalent radicals, such as NH(a $^1\Delta$), and do not insert into single bonds [12]. According to the measurements by Fisher et al., the surface loss probability of NH on a-SiN$_x$ surfaces is less than 0.1 [13].   In other words, NH radicals may migrate on the film-growing surfaces to find the energetically favorable sites.   This may be why better crystallinity was obtained when Ru-coated catalysts were used.

References

1. Y. Fukada, K. Yasui, Y. Kuroki, M. Suemitsu, T. Ito, T. Endou, H. Nakazawa, Y. Narita, M. Takata, T. Akahane, Jpn. J. Appl. Phys. 47 (2008) 573.

2. Y. Komae, T. Saitou, M. Suemitsu, T. Ito, T. Endoh, H. Nakazawa, Y. Narita, M. Takata, T. Akahane, K. Yasui, Thin Solid Films 517 (2009) 3528.

3. T. Morimoto, H. Umemoto, K. Yoneyama, A. Masuda, H. Matsumura, K. Ishibashi, H. Tawarayama, H. Kawazoe, Jpn. J. Appl. Phys. 44 (2005) 732.

4. H. Umemoto, K. Ohara, D. Morita, T. Morimoto, M. Yamawaki, A. Masuda, H. Matsumura, Jpn. J. Appl. Phys. 42 (2003) 5315.

5. H. Umemoto, M. Moridera, J. Appl. Phys. 103 (2008) 034905.

6. H. Umemoto, H. Kusanagi, K. Nishimura, M. Ushijima, Thin Solid Films 517 (2009) 3446.

7. H. Umemoto, H. Kusanagi, Open Chem. Phys. J. 2 (2009) 32.

8. R.T. Wimber and J. J. Halvorson, J. Mater. 7 (1972) 564.

9. S.G. Ansari, H. Umemoto, T. Morimoto, K. Yoneyama, A. Masuda, H. Matsumura, M. Ikemoto, K. Ishibashi, J. Vac. Sci. Technol. A 23 (2005) 1728.

10. M. Yamamoto, T. Maruoka, A. Kono, H. Horibe, H. Umemoto, Appl. Phys. Express 3, (2010) 026501.

11. A. Matsuda, Jpn. J. Appl. Phys., 43 (2004) 7909.

12. R.F.W. Bader, R.A. Gangi, J. Am. Chem. Soc. 93 (1971) 1831.

13. E.R. Fisher, P. Ho, W.G. Breiland, R.J. Buss, J. Phys. Chem. 96 (1992) 9855.

Figure Captions

Fig. 1 H-atom density as a function of the reciprocal of catalyst temperature. The open symbols represent the results for Ru while the closed symbols represent the results for W. The circles represent the results of vacuum-ultraviolet laser absorption measurements while the triangles represent those of laser induced fluorescence measurements. The NH_3 flow rate was 50 sccm and the pressure was 6.8 Pa when the catalyst was not heated.

Fig. 2 NH_3 flow rate dependence of NH densities. Triangles represent the results for Ru at 1660 K, while closed circles represent those for W at 1770 K. The result for W at 1660 K is represented by an open circle. The NH_3 pressure was 120 Pa at 50 sccm when the catalyst was not heated.

Fig. 3 Catalyst temperature dependence of the H_2(circle), N_2(triangle), and NH_3(square) densities measured mass spectrometrically. The open symbols represent the results for Ru while the closed symbols represent the results for W. The flow rate of NH_3 was 30 sccm while the pressure was 4.1 Pa when the catalyst was not heated.
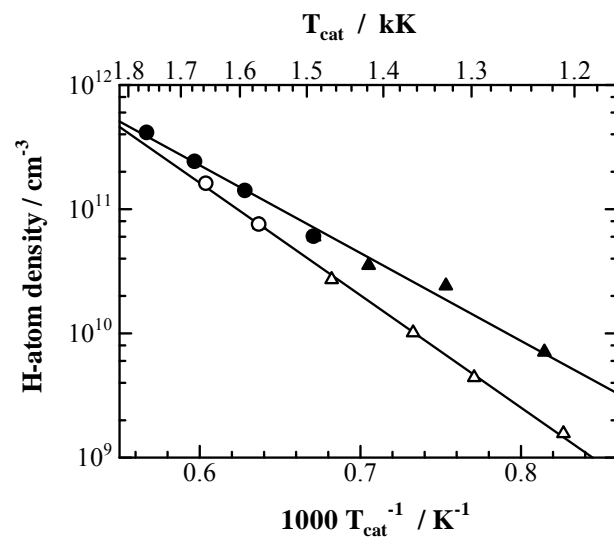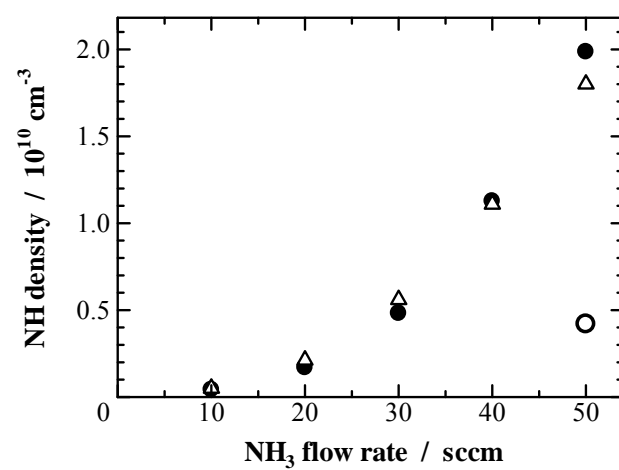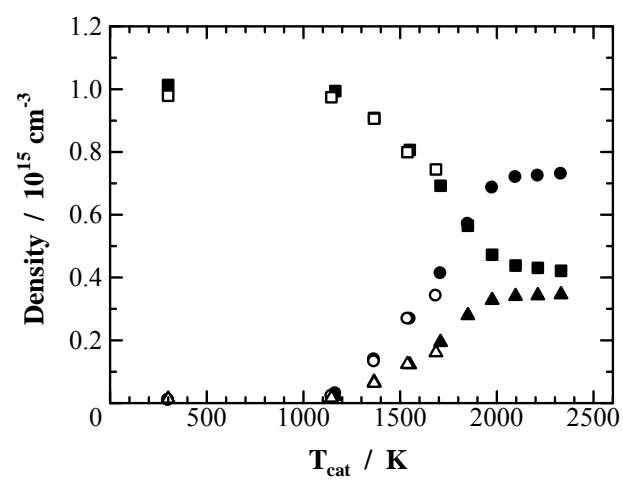
Fig. 1 (Umemoto)

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