Title	触媒化学気相堆積法の酸化性気体への応用拡大
Author(s)	瀬戸口，将太
Citation	
Issue Date	2007-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/3670
Rights	
Description	Supervisor:梅本　宏信，材料科学研究科，修士

Extension of catalytic chemical vapor deposition technique to oxidizing species

by

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A thesis submitted to

School of Materials Science,

Japan Advanced Institute of Science and Technology,

In partial fulfillment of the requirements

for the degree of

Master of Materials Science

Graduate Program in Materials Science

Written under the direction of

Professor Hironobu Umemoto

February , 2003

1. Introduction

In catalytic chemical vapor deposition (Cat-CVD, often called Hot-Wire CVD) processes, thin films without plasma damages can be prepared because charged species such as electrons and ions do not exist in the vapor phase. On the other hand, in Cat-CVD, it has been difficult to use oxidizing species as a material gas. This is because tungsten, one of the most widely used catalyzer materials, is easily oxidized and the vapor pressure of tungsten oxide is much higher than that of tungsten meal. This problem can be avoided by using Ir instead of W. However, Ir is more expensive, and that will be a barrier for the spread of this technique to the industrial world.

In order to avoid the oxidization of W catalyzers, Izumi proposed the addition of H_2 [1]. However, no systematic studies have been carried out to investigate the conditions not to oxidize catalyzers. In the present study, the conditions not to oxidize tungsten catalyzers were looked for by using O_2, NO, and N_2O as oxidizing materials. H_2 and NH_3 were used as reductive dilutants. In addition, the decomposition efficiencies of oxidizing species were measured using a quadrupole mass spectrometric technique, under various conditions including the deposition conditions of SiO_xN_y, which is known to be used as passivation films of organic light emitting diodes.

2. Experimental

Two kinds of measurements were carried out. In the first, the time dependence of the resitivity of W catalyzers was measured under various catalyzer temperatures and the mixing ratios in the H_2/O_2, H_2/NO, and H_2/N_2O systems. When the catalyzer is oxidized, there must be a variation in resistivity. The DC voltage applied to the filament was fixed and the current was monitored as a function of time. A power supply made by Takasago Ltd. (EX-1125H2)

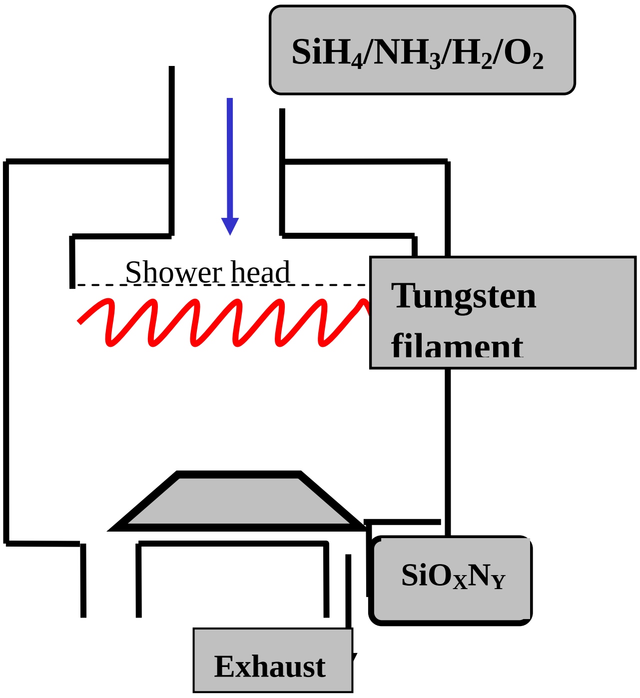

Fig.1 Schematic diagram of the CVD chamber

was used to apply the voltage and to monitor the current. A tungsten wire, 0.5 mm in diameter and 20 cm in length, was used as a catalyzer.

In the second measurement, the consumption efficiencies of the material gases in the $SiH_4/NH_3/O_2/H_2$ system, were measured by using a quadrupole mass-spectrometer (Anelva, M-QA200TS). The diameter and the length of the W wire were 0.4 mm and 120 cm, respectively. The mass spectrometer was attached to the chamber through a sampling hole (0.4 mm in diameter), and was differentially pumped. Similar experiments were performed for NO and N_2O.

3. Results and Discussion

Figs. 2 and 3 show the time dependence of the currents when the applied voltages were fixed. The flow and voltage conditions are summarized in table. 1. The partial pressures of O_2 were the same under all conditions. The voltages were adjusted to hold the initial filament temperatures constant. The initial temperatures estimated from the resistivities were 1990 and 2340 K, respectively.

At 1990 K, the current is constant when the H_2/O_2 mixing ratio is larger than 18, while at 2340 K, it was impossible to keep the current constant even when the mixing ratio is as large as 100. Similar results were obtained for H_2/NO and H_2/N_2O mixtures. In the H_2/NO system, the oxidization could be ignored when the mixing ratio was over 38 at 1960 K. As for O_2 and NO, the oxidization was more remarkable when the catalhyzer temperature was high. On the other hand, the opposite was true for N_2O. The oxidization was less remarkable at higher temperatures. Here, it may seem that N_2O is a better oxidization material because it is possible to increase the catalyzer temperature. However, as Fig. 4 shows, the decomposition efficiency of N_2O is much lower than those of O_2 and NO. Since two O atoms can be produced from O_2, it can be concluded that O_2 is the best source gas and the catalyzer temperature may be increased up to 2000K.

The above results on the H_2/O_2 system are consistent with those of Ogawa et al. who have shown that oxidization is minor when the flow rates of $SiH_4/NH_3/H_2/O_2/He$ are 10/20/400/6/294 sccm at a catalyzer temperature of 2020 K [2]. In order to evaluate the consumption efficiencies under the above conditions, mass-spectrometric measurements were carried out. The results are given in Fig. 5. According to Fig 5, the consumption efficiency of O_2 increases rapidly by the introduction of SiH_4. Similar results were obtained in the $SiH_4/NH_3/H_2/NO/He$ and $SiH_4/NH_3/H_2/N_2O/He$ systems. Two explanations may be possible for these results. In the presence of an excess amount of H_2, SiH_4 can easily be converted to SiH_3 radicals by the reaction with H atoms produced from H_2 [3,4]. SiH_3 may react with O_2 rapidly to produce SiO [5,6]. Under such situation, SiO may be one of the major deposition species in this system. Another possible consumption path is the reactive processes of O_2 on chamber walls and substrate surfaces activated by the deposition of SiH_3.

The consumption efficiency of NH_3 decreases with the introduction of both SiH_4 and O_2. This can be explained by the poisoning of the catalyzer surfaces. The residence time of O_2 and SiH_4 on the W surfaces may be longer than that of NH_3. The decomposition of NH_3 is obstructed by adsorbed SiH_4 or O_2, but there are no synergistic effects.

4. Conclusions

The oxidization of tungsten catalyzers by O_2, NO, and N_2O can be prevented if these species are used in the presence of an enough amount of hydrogen. As for O_2 and NO, the catalyzer temperature should be kept below 2000 K, while that should be kept over 2160 K for N_2O. Among them, O_2 is the best oxygen source because the decomposition efficiency is the highest. This was further confirmed under the actual deposition conditions of SiO_XN_Y films. The consumption efficiency of O_2 was the highest even in the presence of SiH_4 and NH_3

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Table 1 Flow and applied voltage conditions for the measurements in the time dependence measurement of the current.　The oxygen partial pressure was constant at 0.43 Pa.

Hydrogen dilution rate	Hydrogen flow rate ／sccm	Oxygen flow rate ／sccm	Total pressure ／Pa	initial temperature of the catalyzer	
				1990/K	2340/K
				voltage /V	voltage /V
100	1000	10	45	5.1	7.5
80	800	10	34	5.0	6.9
60	600	10	26	4.9	6.6
38	300	8.0	16	4.8	6.4
18	100	5.5	8.0	4.8	5.9
0	0	1.0	0.43	4.7	5.5

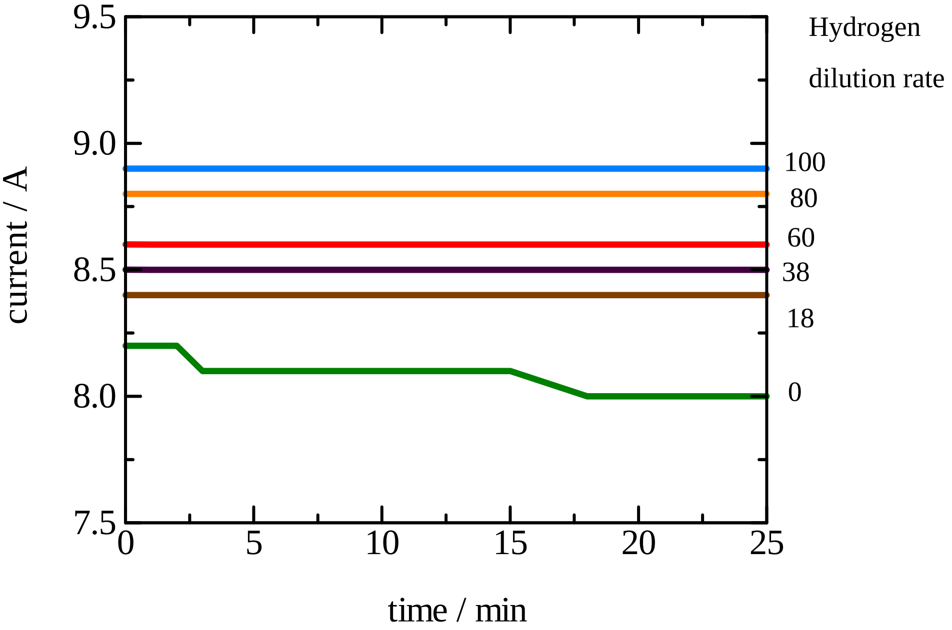

Fig. 2 Filament current in the H_2/O_2 system as a function of time. The initial temperature was 1990 K and the O_2 partial pressure was 0.43 Pa.

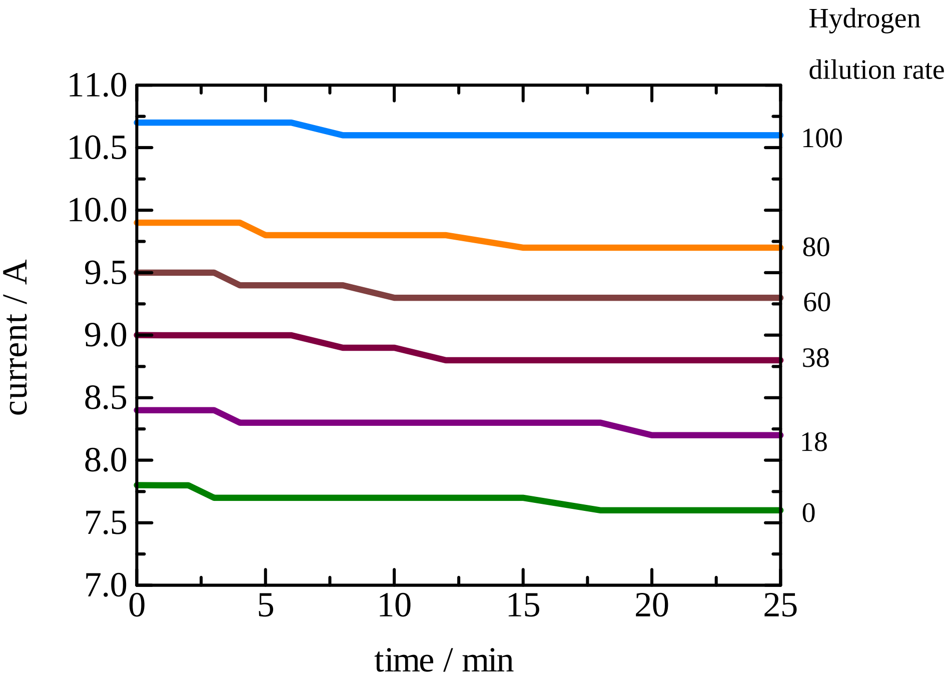

Fig. 3 Filament current in the H_2/O_2 system as a function of time. The initial temperature was 2340 K and the O_2 partial pressure was 0.43 Pa.

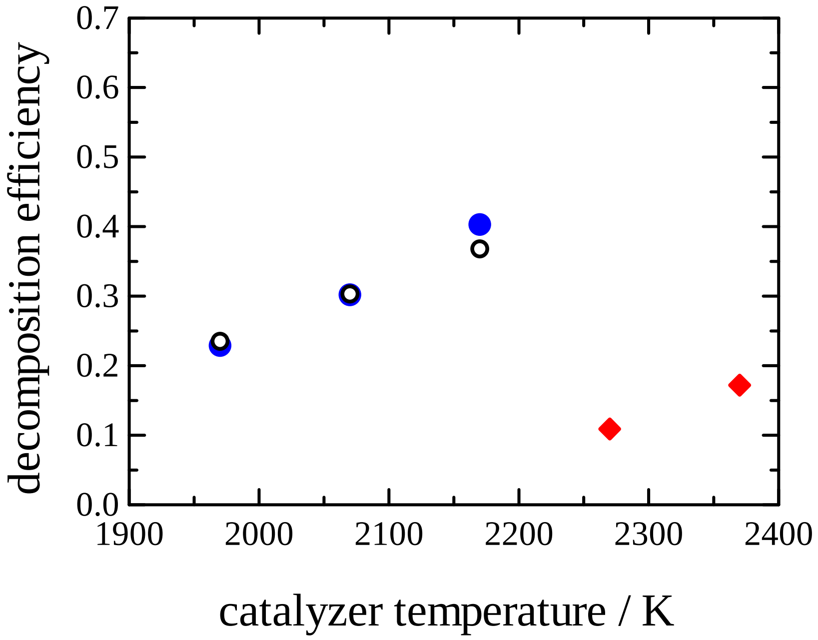

Fig. 4 Catalyzer temperature dependences of the decomposition efficiencies of O_2, NO and N_2O.

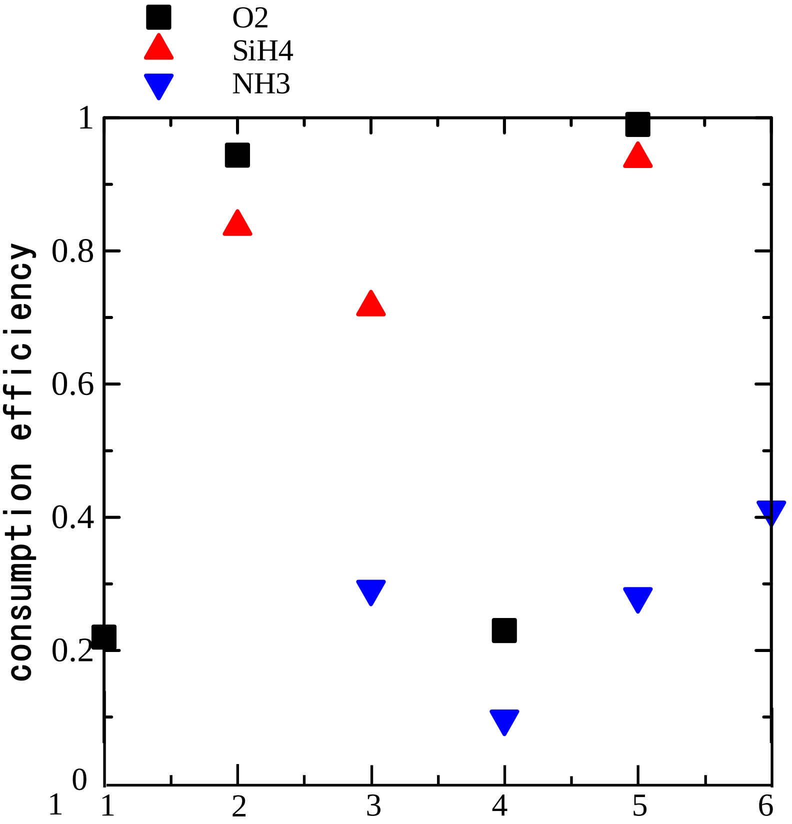

Fig. 5 Consumption efficiencies in the $O_2/H_2/NH_3/SiH_4$ system