Catalytic CVD processes of oxidizing species and the prevention of oxidization of heated tungsten filaments by H₂

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ABSTRACT

The catalytic decomposition conditions of O₂, N₂O and NO were investigated to avoid oxidization of heated tungsten filaments. It was confirmed that no oxidization takes place in the presence of an excess amount of H₂ or NH₃; for example, when the catalyzer temperature is 1990 K and the H₂/O₂ flow rate ratio is more than 18. These results are consistent with the recent results that no oxidization is observed in the SiH₄/NH₃/H₂/O₂/He system to deposit SiO_xN_y films as long as the O₂ flow rate is low. In addition, it was revealed that in this SiH₄/NH₃/H₂/O₂/He system, O₂ is not only decomposed on the catalyzer surfaces but also is consumed in homogeneous and/or heterogeneous reactions. One of the consumption paths in the gas phase should be the reaction with SiH₃ to produce SiO

Keywords

Catalytic chemical vapor deposition, Cat-CVD, Hot-Wire CVD, Oxygen, Oxidization, SiO_xN_y

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1. Introduction

One of the weak points in catalytic chemical vapor deposition (Cat-CVD, often called Hot-Wire CVD) processes compared to plasma-enhanced CVD (PECVD) is that it is 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 metal. According to Ogita and his coworkers, the typical lifetime of tungsten catalyzers used in the presence of trimethyl aluminum and O_2 to deposit Al_2O_3 is as short as 25 min [1,2]. This problem can be avoided by using Ir instead of W [3,4]. However, Ir is much more expensive than W. In addition, in the presence of SiH_4 , Ir can make a low-melting-point alloy with Si [3].

In order to avoid the oxidization of W catalyzers, Izumi proposed the addition of H_2 [5]. He tried to oxidize Si surfaces by the decomposition products of a H_2/O_2 mixture on heated W catalyzers. In order to avoid metal contamination, he carried out the oxidization with a H_2/O_2 flow rate ratio as large as 2000. However, it is not certain if this ratio is the critical one. More recently, Matsumoto et al. used a mixture of $\text{SiH}_4/\text{H}_2/\text{O}_2$ to prepare SiO_2 films [6,7]. The H_2/O_2 ratio was between 0.25 and 1.5 [8]. Although Matsumoto stated that the catalyzer lifetime was not changed by the introduction of O_2 , his reported lifetime, 8 h, seems to be much shorter than that under typical deposition conditions of

a-Si:H and poly-Si:H, which is more than 1000 h [7,9].

Recently, Ogawa et al. have reported that SiO_xN_y films prepared from a mixture of $\text{SiH}_4/\text{NH}_3/\text{H}_2/\text{O}_2$ can be used as a buffer layer to reduce the stress in SiN_x films and to prevent the formation of cracks in the passivation films [10]. The typical flow rates were 10 sccm for SiH_4 , 20 sccm for NH_3 , 400 sccm for H_2 , and 300 sccm for 2% He-diluted O_2 . The total pressure was kept at 20 Pa while the catalyzer temperature was 2020 K. Under such conditions, no oxidization of W filaments was observed after several hours' use.

In the present work, the effect of H_2/O_2 and NH_3/O_2 flow rate conditions on preventing the oxidation of W filaments was investigated systematically. Both H_2 and NH_3 are known as reducing agents and by mixing these gases it should be possible to avoid oxidation. In addition, the consumption efficiencies of O_2 were measured using a quadrupole mass spectrometric technique under various conditions including the deposition conditions for SiO_xN_y . The catalytic decomposition processes of NO and N_2O were also examined.

2. Experimental

Two kinds of measurements were carried out. In the first, the DC voltage applied to the filament was fixed and the current was monitored as a function of time. When the filament is oxidized, there must be a variation in resistivity. A power supply made by Takasago Ltd. (EX-1125H2) 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, a quadrupole mass-spectrometer (Anelva, M-QA200TS) was used to monitor the steady-state densities of the stable molecules, such as O_2 and SiH_4 . The consumption efficiency of the material gas molecules can be obtained by comparing the signal intensities under catalyzer-heated and unheated conditions. 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. The CVD chamber and other experimental apparatus were similar to those described elsewhere [11-13].

3. Results and Discussion

Figures 1 and 2 show the time dependence of the current when the applied voltage was fixed. The flow and voltage conditions (a)-(f) 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. The stepwise behavior is due to the limited resolution of the digital ammeter used.

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. Intermediate results were obtained at intermediate temperatures. At 2160 K, the current was constant when the ratio was over 60. Similar results were obtained for H_2/NO and NH_3/O_2 mixtures. In the H_2/NO system, the oxidization could be ignored when the mixing ratio was over 38 at 1960 K. As for the NH_3/O_2 system, the oxidization was minor when the catalyzer temperature was 2150 K and the mixing ratio was over 22. In these systems, oxidization is minor when the mixing ratio is large and when the catalyzer temperature is low. On the other hand, in the H_2/N_2O system, the oxidization was less efficient at higher temperatures. When the catalyzer temperature was 2000 K, it was necessary to increase the mixing ratio up to 60 to avoid the oxidization, while oxidization could be ignored at 2340 K when the ratio was 18. The situation for N_2O is similar to the silicidation of tungsten. Silicidation by neat SiH_4 can be ignored when the catalyzer temperature is over 1900 K. Here, it may seem that N_2O is a better oxidization material because it is possible to increase the catalyzer temperature. However,

quadrupole mass spectrometric measurements showed that the decomposition efficiency of N_2O is much lower than those of O_2 and NO . When the flow rate ratio of H_2/oxides is fixed at 60 and the total pressure at 26 Pa, the decomposition efficiencies of O_2 and NO were 30 % at 2070 K, while that for N_2O was only 17 % at 2370 K. The catalyzer temperature dependences of the decomposition efficiencies are plotted in Fig.3.

The above results on the H_2/O_2 system is consistent with those of Ogawa et al. who have shown that oxidization is minor when the flow rates of $\text{SiH}_4/\text{NH}_3/\text{H}_2/\text{O}_2/\text{He}$ are 10/20/400/6/294 sccm at a catalyzer temperature of 2020 K [10]. In order to evaluate the consumption efficiencies of the material gases under these conditions, we carried out mass-spectrometric measurements under the same conditions. The results are illustrated in Fig. 4. It should be noted here that the consumption efficiency of O_2 in this system is more than that in H_2/O_2 system. The direct reaction of O_2 with SiH_4 is not the cause of the decrease. The O_2 signal did not decrease unless the catalyzer was heated. Table 2 lists the consumption efficiencies of the material gases under various flow conditions. The total pressure and the catalyzer temperature were kept at 20 Pa and 2020 K, respectively. According to table 2, the consumption efficiency of O_2 increases rapidly by the introduction of SiH_4 . Similar results were obtained in the $\text{SiH}_4/\text{NH}_3/\text{H}_2/\text{NO}/\text{He}$ and $\text{SiH}_4/\text{NH}_3/\text{H}_2/\text{N}_2\text{O}/\text{He}$ systems. 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 [14,15]. SiH_3 may react with O_2 rapidly to produce SiO [16,17] and SiO may be one of the major deposition species in this system. Another possible consumption path is the reaction on chamber walls and substrate surfaces activated by the deposition of SiH_3 . The recombination processes of O atoms on chamber walls may also be suppressed by the deposition of Si compounds. Finally, as is shown in table 2, the consumption efficiency of NH_3 decreases with the introduction of both SiH_4 and O_2 . The decrease caused by SiH_4 has been explained as the poisoning of the catalyzer surfaces [12,13]. A similar mechanism may be assumed for O_2 . It should be noted, however, that there are no synergistic

effects.

4. Conclusions

The catalytic decomposition processes of O_2 , NO and N_2O were examined, paying special attention to the deposition of SiO_xN_y films. The oxidization of the W catalyzer can be avoided by introducing an excess amount of H_2 or NH_3 . These results will make it possible to increase the lifetime of W as a catalyzer material. The consumption efficiency was the highest for O_2 among the oxidizing species, exceeding 90 % in the presence of SiH_4 and H_2 . O_2 is not only decomposed on heated catalyzer surfaces, but also is lost in reactions in the gas-phase or on surfaces activated by the deposition of Si-related compounds.

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Table 1 Flow and applied voltage conditions for the measurements in Figs.1 and 2

Table 2 Gas consumption efficiencies in the $\text{SiH}_4/\text{NH}_3/\text{H}_2/\text{O}_2/\text{He}$ system. The total pressure and the catalyzer temperature were 20 Pa and 2020 K, respectively.

Fig. 1 Filament current in the H_2/O_2 system as a function of time. The applied voltage was fixed. The initial filament temperature was 1990 K.

Fig. 2 Filament current in the H_2/O_2 system as a function of time. The applied voltage was fixed. The initial filament temperature was 2340 K.

Fig.3 Catalyzer temperature dependences of the decomposition efficiencies of O_2 , NO and N_2O .

Fig. 4 Mass spectrometric spectra in the $\text{SiH}_4/\text{NH}_3/\text{H}_2/\text{O}_2/\text{He}$ system.

Table 1

	Flow rate / sccm		Total pressure / Pa	Applied voltage in Fig.1 / V	Applied voltage in Fig.2 / V
	H ₂	O ₂			
(a)	1000	10	45	5.1	7.5
(b)	800	10	34	5.0	6.9
(c)	600	10	26	4.9	6.6
(d)	300	8.0	16	4.8	6.4
(e)	100	5.5	8.0	4.8	5.9
(f)	0	1.0	0.43	4.7	5.5

Table 2

Flow rate / sccm				Consumption efficiency / %		
SiH ₄	NH ₃	H ₂	O ₂	SiH ₄	NH ₃	O ₂
		400	6			22
	20	400	6		10	23
10		400	6	84		94
10	20	400	6	94	28	99
10	20	400		72	29	
	20	400			41

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