Catalytic CVD processes of oxidizing species and the prevention of oxidization of heated tungsten filaments by H$_2$

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ABSTRACT

The catalytic decomposition conditions of O$_2$, N$_2$O 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 H$_2$ or NH$_3$; for example, when the catalyzer temperature is 1990 K and the H$_2$/O$_2$ flow rate ratio is more than 18. These results are consistent with the recent results that no oxidization is observed in the SiH$_4$/NH$_3$/H$_2$/O$_2$/He system to deposit SiO$_x$N$_y$ films as long as the O$_2$ flow rate is low. In addition, it was revealed that in this SiH$_4$/NH$_3$/H$_2$/O$_2$/He system, O$_2$ 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 SiH$_3$ to produce SiO
Keywords

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

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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 O₂ to deposit Al₂O₃ 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 SiH₄, 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 H₂ [5]. He tried to oxidize Si surfaces by the decomposition products of a H₂/O₂ mixture on heated W catalyzers. In order to avoid metal contamination, he carried out the oxidization with a H₂/O₂ 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 SiH₄/H₂/O₂ to prepare SiO₂ films [6,7]. The H₂/O₂ ratio was between 0.25 and 1.5 [8]. Although Matsumoto stated that the catalyzer lifetime was not changed by the introduction of O₂, 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\textsubscript{x}N\textsubscript{y} films prepared from a mixture of SiH\textsubscript{4}/NH\textsubscript{3}/H\textsubscript{2}/O\textsubscript{2} can be used as a buffer layer to reduce the stress in SiN\textsubscript{x} films and to prevent the formation of cracks in the passivation films [10]. The typical flow rates were 10 sccm for SiH\textsubscript{4}, 20 sccm for NH\textsubscript{3}, 400 sccm for H\textsubscript{2}, and 300 sccm for 2% He-diluted O\textsubscript{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\textsubscript{2}/O\textsubscript{2} and NH\textsubscript{3}/O\textsubscript{2} flow rate conditions on preventing the oxidation of W filaments was investigated systematically. Both H\textsubscript{2} and NH\textsubscript{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\textsubscript{2} were measured using a quadrupole mass spectrometric technique under various conditions including the deposition conditions for SiO\textsubscript{x}N\textsubscript{y}. The catalytic decomposition processes of NO and N\textsubscript{2}O 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\textsubscript{2} and SiH\textsubscript{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 O2 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 H2/O2 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 H2/NO and NH3/O2 mixtures. In the H2/NO system, the oxidization could be ignored when the mixing ratio was over 38 at 1960 K. As for the NH3/O2 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 H2/N2O 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 N2O is similar to the silicidation of tungsten. Silicidation by neat SiH4 can be ignored when the catalyzer temperature is over 1900 K. Here, it may seem that N2O 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$_2$O 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$_2$O 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 SiH$_4$/NH$_3$/H$_2$/O$_2$/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 SiH$_4$/NH$_3$/H$_2$/NO/He and SiH$_4$/NH$_3$/H$_2$/N$_2$O/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$_2$O were examined, paying special attention to the deposition of SiO$_x$N$_y$ 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 catalyst 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 catalyst surfaces, but also is lost in reactions in the gas-phase or on surfaces activated by the deposition of Si-related compounds.
References

[8] Y. Matsumoto, private communication
List of table and figure captions

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

Table 2 Gas consumption efficiencies in the SiH₄/NH₃/H₂/O₂/He system. The total pressure and the catalyzer temperature were 20 Pa and 2020 K, respectively.

Fig. 1 Filament current in the H₂/O₂ system as a function of time. The applied voltage was fixed. The initial filament temperature was 1990 K.

Fig. 2 Filament current in the H₂/O₂ 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 O₂, NO and N₂O.

Fig. 4 Mass spectrometric spectra in the SiH₄/NH₃/H₂/O₂/He system.
Table 1

<table>
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<th>Flow rate / sccm</th>
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<th>Applied voltage in Fig.2 / V</th>
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<tr>
<td>(f) 0</td>
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<td>Flow rate / sccm</td>
<td>Consumption efficiency / %</td>
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Fig. 3 H. Umemoto et al.
Fig. 4 H. Umemoto et al.