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ScienceDirect
Thin Solid Films 516 (2008) 687–690
www.elsevier.com/locate/tsf

Fabrication of PTFE thin films by dual catalytic chemical vapor deposition method

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Available online 10 July 2007

Abstract

Dependence of catalyzing materials on deposition of polytetrafluoroethylene (PTFE = "Teflon" in commercial) films by catalytic chemical vapor deposition (Cat-CVD) method is investigated. It has been clarified that Ni-containing catalyzers has a catalyzing effect that can decompose hexafluoropropylene-oxide (HFPO) to form PTFE films. A novel method named Dual Cat-CVD is also proposed. In the method, carbonized and fluorinated surface of Ni-containing catalyzer is removed and refreshed using atomic hydrogen generated by additionally introduced tungsten (W) catalyzer in the same chamber. This Dual Cat-CVD method enables to recover the deposition rate of PTFE films drastically.

Keywords: Catalysis; Chemical vapor deposition (CVD); Polytetrafluoroethylene (PTFE); Hexafluoropropylene-oxide (HFPO); Catalyzer; Catalyst

1. Introduction

Polytetrafluoroethylene (PTFE) has many excellent characteristics such as low permittivity, high heat resistance, high chemical resistance and high water repellency. Since there is no suitable solvent for PTFE, formation of PTFE films in industry have been usually performed by spraying or dipping of liquid emulsions. The disadvantage of this method is that post sintering process at more than 300 °C is required, which is not applicable for substrates with poor heat resistance. Therefore, formation of PTFE films by deposition techniques at low temperature is required. Recently, it has been reported that high quality PTFE films can be deposited at 25 °C by catalytic chemical vapor deposition (Cat-CVD) method using NiCr catalyzers and hexafluoropropylene-oxide (HFPO) gas [1]. For further development of their pioneer work, we studied the effect of catalyzing materials and the factor deciding deposition rate for PTFE preparation. However, the exposure of catalyzer to HFPO gas brings about rapid and drastic changes of deposition rate after several minutes. Such a catalyzer surface is carbonized and fluorinated after deposition. For practical industrial application demanding long continuous operation, carbonized and fluorinated catalyzer surface, which causes significant reduction of deposition rate, should be effectively removed and refreshed. For such a purpose, the effect on addition of another catalyzing material is investigated to clarify the decomposition mechanism of HFPO as well as to improve the deposition rate. Finally, we propose a novel method named Dual Cat-CVD. In the method, the carbonized surface of catalyzer, used for HFPO decomposition, is removed by atomic hydrogen generated at tungsten (W) catalyzer which is additionally installed in same chamber. Continuous high deposition rate is achieved by this Dual Cat-CVD.

2. Experimental details

As catalyzing materials, NiCr, Ni, Fe, Inconel 600, Mo, W, Pt, Ti, Ta and SUS 304 wires were used to know the dependence of catalyzing materials in deposition of PTFE films by Cat-CVD. Deposition conditions are shown in Table 1. Film properties were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) to confirm the deposition of PTFE films. Level of carbonization and fluorination of catalyzer surface was also examined by using XPS. For investigation of the cleaning process for carbonized catalyzer surface, we installed additional tungsten (W) catalyzer in the same Cat-CVD apparatus. Such an additional

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doi:10.1016/j.tsf.2007.06.185

Table 1
Deposition conditions by Cat-CVD method

Catalyzer materials	NiCr, Inconel600, Ni, W, Ta, Ti, Mo, Fe, 2%ThO_2W, SUS304, Pt
Catalyzer temperature	600–1200 °C
Substrate	Si
Substrate temperature	R.T. (<30 °C)
Total pressure	0.05–1 Torr
Feed gas	HFPO (hexafluoropropylene oxide)
Flow rate	8, 16 sccm

catalyzer could be separately heated from the other catalyzer used for decomposition of HFPO and was used to generate atomic hydrogen by decomposing newly introduced H_2 gas. The schematic of this Dual Cat-CVD method is shown in Fig. 1. W catalyzer was heated at up to 1800 °C in order to generate high density atomic hydrogen [2]. Both simultaneous and alternative supplies of gases were attempted. Deposition condition with mixing gas is shown in Table 2. Hydrogen radical flashing condition is summarized Table 3.

3. Results

3.1. Catalyzing material dependence

FT-IR spectra for the films deposited with various catalyzing materials are shown in Fig. 2(a). Four clear characteristic absorption peaks originating from CF_2 bonds (CF_2 rocking mode at 513/530 cm^{-1}, CF_2 wagging mode at 641/629 cm^{-1}, CF_2 symmetric stretching mode at 1155 cm^{-1}, and CF_2 asymmetric stretching mode at 1215 cm^{-1}) are observed only from the films deposited using Ni-containing metals as catalyzers, while the catalyzing effect hardly occurs in case of the other materials even if they are heated at more than 1000 °C [3,4]. Therefore, it can be concluded that Ni atoms play an important role to decompose HFPO molecules. This result also shows that decomposition of gas molecules in Cat-CVD is not due to pyrolytic cracking but due to catalytic reaction. It can not be decided that whether these deposited films are PTFE only from this FT-IR spectra, because CF_2 bonds can be also observed in other fluorinated films. Fig. 2(b) shows XPS spectra for deposited films using NiCr, Inconel 600 and Ni catalyzing wires. The inset of Fig. 2(b) shows the high resolution spectrum of a C_{1s} peak (CF_2 at 292 eV) [5]. Since the peak position in energy axis and relative intensities of the peaks in the observed spectra exactly agree with those for bulk-PTFE shown in Fig. 2(c), the deposited films can be finally identified as PTFE with consideration of the results of FT-IR.

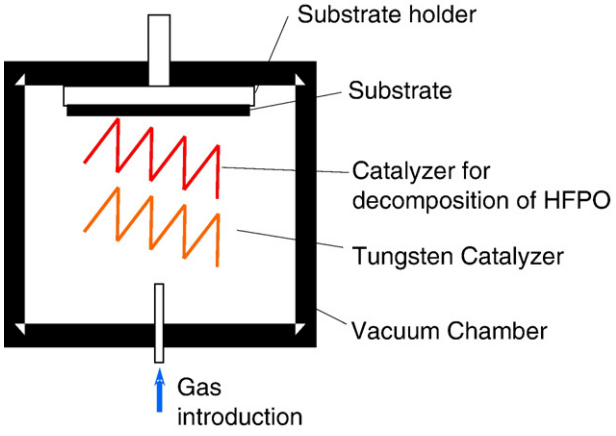

Fig. 1. Schematic diagram of Dual Cat-CVD apparatus.

Table 2
Deposition condition to introduce HFPO and hydrogen gas into Dual Cat-CVD chamber at the same time

Catalyzer material	NiCr, W
Catalyzer temperature	800 °C (NiCr) 1800 °C (W)
Substrate	Si
Substrate temperature	R.T.
Total pressure	0.2 Torr
Feed gas	HFPO
HFPO flow rate	8 sccm
Deposition time	30 min

3.2. Dual Cat-CVD

At first, HFPO and hydrogen gases were introduced and two catalyzers were heated. However, the deposition rate could not be increased, as shown in Fig. 3. This is probably because the CF_2 radicals react with H_2 to form stable gas molecule and a large amount of hydrogen atoms occupy the surface of NiCr or Inconel and prevents the cracking of HFPO. Therefore, next, we attempted to investigate the effect of interval hydrogen flashing, that is, only HFPO gas is supplied during deposition and after stopping the deposition only hydrogen gas is introduced. Fig. 4 represents XPS spectra of Inconel 600 catalyzers. Peaks from Ni and Cr contained in Inconel 600 are observed before exposure to HFPO, whereas they disappear and the peaks originating from C start to appear after deposition of PTFE. This indicates that the catalyzer surface has been completely carbonized and fluorinated. After the atomic hydrogen treatment, Ni- and Cr-related peaks are observed again as shown in Fig. 4. This clearly shows that carbonized and fluorinated layer on the catalyzer surface has been successfully removed by atomic hydrogen. Fig. 5 shows deposition rate of PTFE films as a function of total deposition time. Without atomic hydrogen treatment, the deposition rate drastically decreases as deposition time increases, because of the carbonization and fluorination of the catalyzer surface as discussed above. In contrast, the deposition rate has been kept over 100 nm/min if atomic hydrogen treatment is

Table 3
Hydrogen radical flashing condition

Catalyzer material	Inconel600, W
Catalyzer temperature	900 °C (Inconel600) 1800 °C (W)
Total pressure	0.5 Torr
Feed gas	H_2
Flow rate	30 sccm