催化增强化学蒸气沉积法在聚酰亚胺上沉积钯-铂合金薄层

俞开潮[1]　Yousef Hamadan[1]　程银华[1]　周锦兰*,[1]　李正佳[2]　于澍燕[3]　焦　庆[3]
([1]华中科技大学化学系;[2]武汉光电国家实验室,武汉　430074)
([3]中国科学院化学研究所,高分子物理与化学国家重点实验室,北京　100080)

摘要: 以 N_2,O_2 作载气,通过催化增强化学蒸气沉积(CECVD)分别制得在聚酰亚胺上的金属铂、钯及其合金薄层。铂、钯配合物的共同沉积可生成 Pt-Pd 合金薄膜。在 Pd-Pt 合金的沉积过程中,Pd/Pt 的原子数比率随共同沉积的条件改变而变化。O_2 为载气、300 ℃条件下,用 Pd(η^3-allyl)(hfac)和 Pt(COD)Me_2 作前驱体共沉积制备 Pd-Pt 合金,得到含 Pd 37.2%,Pt 62.8%且不含碳和氟的合金。

关键词: 催化增强化学蒸气沉积; 聚酰亚胺; 钯-铂合金
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Formation of Palladium-Platinum Alloy Films on Polyimide by Catalyst-Enhanced Chemical Vapor Deposition

YU Kai-Chao[1]　Yousef Hamadan[1]　CHENG Yin-Hua[1]　ZHOU Jin-Lan*,[1]
LI Zheng-Jia[2]　YU Shu-Yan[3]　JIAO Qing[3]
([1]*Department of Chemistry*; [2]*Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan* 430074)
([3]*State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing* 100080)

Abstract: Pd, Pt and their alloy films on polyimide were prepared by Catalyst-Enhanced Chemical Vapor Deposition (CECVD) under the carrier gas (N_2, O_2). Co-deposition of Pd and Pt complexes was used for deposition of alloy film. During the CVD of palladium-platinum alloy, the Pd/Pt atomic ratios varied with co-deposition conditions. Co-deposition of Pd(η^3-allyl)(hfac) and Pt(COD)Me_2 under O_2 at 300 ℃ produced palladium-platinum alloy containing palladium of 37.2% and platinum of 62.8%, respectively without the contamination of carbon and fluorine.

Key words: catalyst-enhanced chemical vapor deposition, polyimide (PI), palladium-platinum alloy

0 Introduction

As integrated-circuit structures become more complex, the increasing constraints on deposited layers require deposition over range of conditions. Chemical vapor deposition (CVD)[1~4] provides the needed flexibility. Catalyst-enhanced chemical vapor deposition (CECVD) is a kind of enhancement methods developed recently for chemical vapor deposition [5,6]. During CECVD process, a noncatalytic metal is deposited when catalyzed by another catalytic metal. It has the advantages of lowering the deposition temperature, improving the purity of the deposited films. CECVD is especially useful for CVD on polymer sur-

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*通讯联系人。E-mail:jlmtt@163.com
第一作者:俞开潮,男,49 岁,博士,教授;研究方向:光谱分析、复合材料化学。

face due to the low melting point of polymer compared to glass or silicon.

Polyimide (PI) is very useful in microelectronic devices (e.g., IC packaging) because of its advantageous physical properties and chemical inertness. Polyimide films have excellent thermal and dielectric properties with applications as planarized insulation layers and protective barriers for integrated circuits[7,8a]. Compared with metal films deposited on glass substrate, the films deposited on organic substrates have advantages such as light, convenient for fabrication. For polyimide, besides thermal stability, it has good adhesive property with metal because of the metal-polymer interaction[8b,9]. Palladium and platinum metal are very oxidation-resistant and good conductors. Other metallization method for polyimide such as laser-induced chemical liquid-phase deposition (LCLD)[10,11] or electrolessplatity[8c] have been reported. CVD of these two metals on polyimide has advantage over other deposition methods due to mild operation conditions and the availability of thicker films. Such metallized PI may find their new application as novel opto-electronic materials as well as catalyst system. We report here our work on CECVD of palladium, platinum, and alloy films on the polyimide surface.

1 Experimental

1.1 Materials

The polyimide (poly(*N*,*N*′-(1,4-phenylene)-3,3′,4,4′-benzophenone-tetra-carboxylic imide/amic acid)) was purchased from Sigma-Aldrich Company. Complex $PtMe_2$(COD) (**1**) was purchased from Strem Chemicals and was sublimed prior to use. Complexes Pd(η^3-allyl)(hfac) (**2**)[12], Pd(3-2-methylallyl)(hfac) (**3**)[12] and Pd$(hfac)_2$ (**4**)[13], Pd(3-2-methylallyl)(acac) (**5**)[12] were synthesized according to the literature procedure and used as the precursors. Abbreviations: COD=1,5-cyclooctadiene, hfac=1,1,1,6,6,6-hexafluoro-2,4-pentanedionate ($CF_3COCHCOCF_3$), and acac=2,4-pentanedionate ($CH_3COCHCOCH_3$).

1.2 Substrate preparation

A 3%~5% solution of the polyimide in dimethylsulfone (DMSO), was added on top of a thin disk of Al foil (0.5 mm thick and 1 cm in diameter). The disk was placed on the hot plate, heated to 120 ℃ to allow the solvent to evaporate. The thickness of the film was about 75 μm.

1.3 Chemical vapor deposition

Chemical vapor deposition was performed in a vertical cold wall reactor under atmospheric pressure. The reactor consists of a Pyrex reaction chamber with a gas inlet. The top lid consists of a substrate probe into which a heater coil can be inserted and a vacuum fed through. The two sections, when bolted with an O-ring in between, provided a vacuum tight seal. The substrate was fixed to the CVD reactor probe using high purity silver paint. The precursor was kept at a certain temperature stated as above while the substrate was maintained at a temperature ranging from 180~300 ℃ using an external heating rod.

1.4 CVD of Palladium-Platinum Alloy

Polyimide substrate was mounted on the reactor, platinum precursor **1** (8 mg, 0.024 mmol) was added to the main chamber and palladium precursor **3** (8 mg, 0.022 mmol) was added to the side chamber. N_2 carrier gas (50 mL·min^{-1}) was introduced to the main chamber and O_2 carrier gas (50 mL·min^{-1}) was introduced to the side chamber. The main chamber and side chamber were heated to 65 ℃ and 45 ℃, respectively, using oil baths. The reactor was heated to 280 ℃ using a heating rod. After 4 h, the reactor was cooled down, the substrate with deposited palladium-platinum alloy was removed from the reactor and stored in vacuum for XPS and SEM analysis.

1.5 Analysis

The prepared films were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The XPS experiments were carried out using an SSX-100 X-ray photoelectron spectrometer with a monochromatized Mg $K\alpha$ small-spot size X-ray source (1 253.6 eV). [This an operation rutine, no need for detailed description]. All spectra were obtained with a 300 nm spot size providing an overall spectrometer resolution of ~0.6 eV. A minimum pressure of 5.7×10^{-7} Pa inside the spectrometer was maintained during analysis and a pressure of 2.7

$\times 10^{-5}$ Pa was used when sputtering. Top and cross-sectional view SEM images of the films obtained with Hitachi S-4500 microscope operation at an acceleration voltage of 5.0 or 15.0 kV at a magnification of 50 K, 60 K or 300 K. (See each separate imaging).

2 Results and discussion

2.1 Catalyst

Precursors **4**[14] and **5**[15] have been shown particular usefulness for CECVD under oxidative or reductive conditions, respectively. In addition to these two catalysts, **2** and **3** were also used as catalyst for CVD of palladium and platinum. During CVD, the molar ratio of precursor/catalyst was 2~4:1.

2.2 Pd, Pt CVD

The condition for CVD of palladium on polyimide substrate was similar to glass substrate. All palladium and platinum films prepared were shiny, mirrorlike.

The binding energy of Pd3$d_{5/2}$ level appeared at 335.4 eV from XPS analysis and was assigned to Pd^0, in agreement with that obtained for a sputter-cleaned palladium foil[16]. Palladium 3$d_{3/2}$ peak appeared at 340.18 eV. Pure palladium was obtained when precursor **2** was used as precursor, O_2 as carrier gas, at 300 ℃.

The deposition conditions for CVD of platinum as well as the results of XPS analysis of the thin films are listed in Table 1. When there was no palladium catalyst, the deposition of platinum failed in 4 h. During deposition of platinum using the mixture of **4** and **1** at 250 ℃, platinum only was obtained. Therefore, the catalytic reactions can be presumed as follows[14b,17,18]:

$$Pd(hfac)_2 \rightarrow Pd + 2hfac;$$

$$hfac \rightarrow CF_3COF,\ COCF_3,\ CF_3,\ CO\ (fragments);$$

$$Pt(COD)Me_2 \xrightarrow{Pd} Pt + COD + CH_4$$

Table 1　CVD Conditions and XPS analysis of Pt film on polyimide[a]

CVD condition for Pt (Pd precursor is used as catalyst)			XPS analysis/atomic ratio / %				
Precursor	Substrate temp. / ℃	Carrier gas	Pd	Pt	C	F	O
1, **2**	250	O_2, N_2	—	87.3	6.5	—	6.2
1, **3**	250	O_2, N_2	—	26.0	54.1[b]	—	19.9
1, **4**	250	O_2, N_2	—	45.7	40.6[b]	—	13.7
1 + **4**	250	O_2	—	65.0	27.6	—	7.4

[a] O_2 was for palladium precursor, N_2 for platinum precursor.

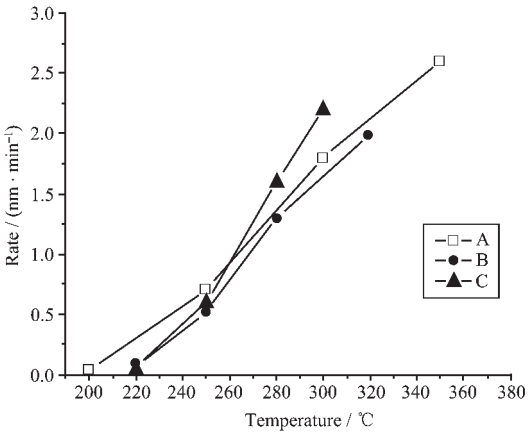
[b] There was no sputtering before XPS measurement.

1, **4**: **1** and **4** in separated chambers; **1** + **4**: mixture of **1** and **4** in the same chamber.

The peak at 284.2 eV in XPS is assigned to carbon 1s. Carbon impurities on the surface arise both from the CVD process itself (mainly from hfac ligand) and from subsequent exposure to the atmosphere. It was reported that the three distinct peaks at 293.2, 288.1 and 285.2 eV for C1s spectrum were assigned to CF_3, C=O, and CH groups of the hfac ligand, respectively[17]. The binding energy for the carbon from the substrate is 289.34 eV. For the thin film, the carbon from the substrate may be observed for XPS analysis. From SEM result, as the content of the carbon increase, the particle sizes of the metals increased. The film with lower carbon is bright and adhesive very well on the substrate, the film with higher carbon is less bright and the adhesive is not very good.

The thickness of the films was investigated by the cross sectional scanning electron microscope (SEM). It is found that the rate of film growth increased with the substrate temperature (Fig.1). From Fig.1, one can see that the film growth rate of single metal is almost the same (A, B), and is slower than that of bimetal (C). The growth rate on polyimide for platinum is 75 $nm \cdot h^{-1}$ that is much slower than that on glass substrate (200 $nm \cdot h^{-1}$). For palladium, the precursor (**2**) gaves the fastest growth rate.

Fig.2 and 3 show some SEM images of the thin films for top view or cross-sectional view. The particle size of the top layer of Pd is in about 100 nm. The particle size of Pt is in the region of 100~150 nm (The distance between left point to right point).



A: Pd; B: Pt; C: Pd-Pt

Fig.1 Dependence of the rate of films growth on the substrate temperature

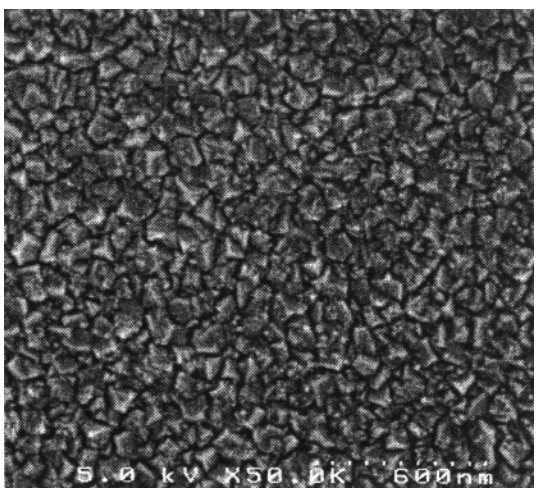


Fig.2 SEM of Pd on polyimide surface (CVD at 300 ℃, top view)

2.3 Pd-Pt alloy CVD

Palladium-platinum alloy films were prepared by co-deposition of Pd-Pt in the same chamber or in the different chambers. When CVD was run at the same chamber, precursor **1** and **4** were used due to their close sublimation temperature. Palladium precursors were used as reactive precursors as well as catalysts. During CVD, the molar ratio of precursor: catalyst (reactive precursor) was 1:1. The experimental conditions used for CVD of alloy films are summarized in Table 2.

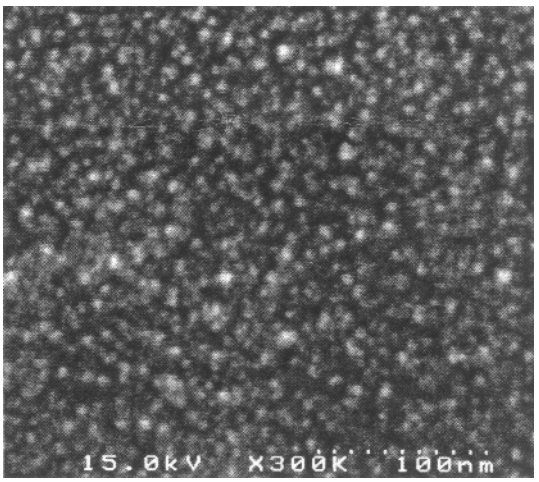


Fig.3 SEM of Pt on polyimide surface (top view)

The atomic ratios of Pd/Pt in the Pd-Pt alloys vary with CVD conditions. Under 220 ℃, only platinum was deposited on polyimide surface during the co-deposition. Precursor **2** is the most volatile precursor among the palladium precursors **2**~**5**. Pure Pd-Pt alloy only was produced by co-deposition of precursor **2** with **1** at 300 ℃, under O_2 carrier gas. The content of palladium and platinum are 37.2% and 62.8%, re-

Table 2 CVD conditions and XPS analysis of Pd-Pt alloy films

CVD condition for Pd-Pt alloy			XPS analysis/atomic ratio / %				
Precursor	Substrate temp. / ℃	Carrier gas	Pd	Pt	C	F	O
1, **2**	300	O_2, O_2	37.2	62.8	—	—	—
1, **2**	280	O_2, O_2	24.1	29.8	46.1[a]	—	—
1, **4**	300	N_2, N_2	23.4	23.0	47.6[a]	5.0	—
1 + **4**	300	N_2	—	26.2	29.4	44.4	—
1, **4**	280	N_2, O_2[b]	19.4	14.9	53.0[a]	2.7	—
1, **5**	280	N_2, N_2	18.5	10.3	71.2[a]	—	—

[a] Without sputtering before XPS measurement.

[b] O_2 is for palladium precursor, N_2 for platinum precursor.

1, **4**: **1** and **4** in separated chambers.

1 + **4**: mixture of **1** and **4** in the same chamber.

spectively.

For Pd-Pt alloy, a decrease in the Pd3$d_3$2 signal together with a positive binding energy shift to 341.15 eV (Pd(0) is 340.4 eV[19]) was observed (Fig.4). The positive shift may arise from the change in the electronic relaxation energy of palladium *d*-level in the presence of platinum, since electron transfer from palladium to platinum *d*-level is possible[20,21]. The intimate Pt-Pd contact also accounts for the observed decrease in the surface exposure of palladium due to the dilution effect of platinum on the bimetallic particles.

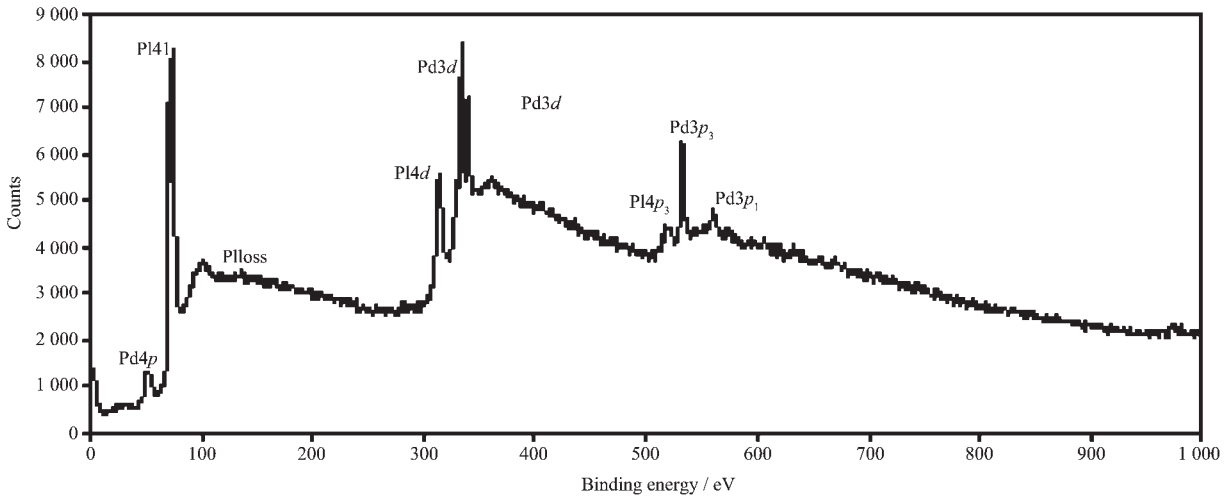


Fig.4　XPS spectrum of Pd-Pt alloy on polyimide

Fig.5 shows the SEM image of the thin film for top view. The film conformity is very good from the SEM of palladium-platinum alloy. The thickness of film is about 250~300 nm.

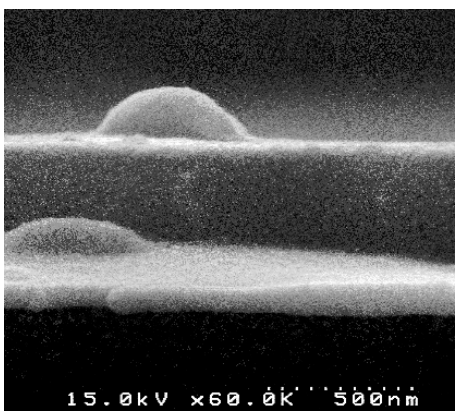


Fig.5　SEM of Pd-Pt alloy on polyimide surface (cross section)

2.4　Conductivity

The conductance of the film was measured by the four-point probe method. The electrical resistivity of palladium, palladium-platinum alloy and platinum film on polyimide varied from 21.6~45.2, 28.2~43.3, 20.4~31.8 mΩ·cm, respectively, which are higher than bulk Pd (electrical resistivity 9.93 mΩ·cm at 0 ℃) and Pt (electrical resistivity 9.85 mΩ·cm at 0 ℃). It still indicates that these films are of high metallic quality.

2.5　Adhesion test

Adhesion test was conducted using a Scotch tape. All of the films grown on polyimide at 250 ℃ or above remained intact as the tape were peeled away from the palladium, platinum, and their alloy films. The adhesion of the palladium and platinum films to polyimide was very good.

3　Conclusions

With Catalyst-Enhanced Chemical Vapor Deposition, Palladium, platinum and their alloy films grow on the polyimide substrate in the rate of 70~80 nm·h^{-1} in the carrier gas (O_2, N_2) atmosphere at 220~300 ℃ under reduced pressure or normal pressure.

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