Synthesis of Novel Platinum Precursor and Its Application to Metal Organic Chemical Vapor Deposition of Platinum Thin Films

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A novel platinum aminoalkoxide complex, $Pt(dmamp)_2$ has been prepared by the reaction of *cis*-$(py)_2PtI_2$ with two equivalents of Na(dmamp) (dmamp = 1-dimethylamino-2-methyl-2-propanolate). Single-crystal X-ray crystallographic analysis shows that the $Pt(dmamp)_2$ complex keeps a square planar geometry with each two nitrogen atoms and two oxygen atoms having trans configuration. Platinum films have been deposited on TaN/Ta/Si substrates by metal organic chemical vapor deposition (MOCVD) using $Pt(dmamp)_2$. As-deposited platinum thin films did not contain any appreciable amounts of impurities except a little carbon. As the deposition temperature was increased, the films resistivity and deposition rate increased. The electrical resistivity (13.6 $\mu\Omega$cm) of Pt film deposited at 400 °C is a little higher than the bulk value (10.5 $\mu\Omega$cm) at 293 K. The chemical composition, crystalline structure, and morphology of the deposited films were investigated by X-ray photoelectron spectroscopy, X-ray diffraction, and atomic force microscopy.

Key Words : Platinum, Precursor, MOCVD, Aminoalkoxide, Thin films

Introduction

Platinum is a material that has low resistivity, high thermal stability, corrosion resistance, high melting point, oxidation resistance, and catalytic activity.[1] These physical and chemical properties afford a variety of important technological applications for platinum thin films, such as microelectronic device processing,[2] buffer layer in the fabrication of high-T_c superconducting tapes,[3] electrochemical and catalytic applications, etc.[4] In particular, platinum films have been tested as top and/or bottom electrode material in many semiconductor devices, specially due to their large work function, anti-oxidation, and no inter-diffusion properties. Therefore, the successful development of platinum thin films will provide electrodes for complementary metal-oxide semiconductor (CMOS) gate dielectrics and perovskite-based capacitors in random access memories (RAMs) and high-frequency phase-array devices.[5-7]

Until now, physical vapor deposition (PVD) methods, such as RF-sputtering and thermal evaporation, were usually used to prepare the Pt films. However, as the substrate structures become more complicated with successive scale-down and a new three-dimensional device concept, the requirement of the film uniformity and conformality can not be satisfied by the physical deposition methods.

MOCVD has been regarded as a promising technique for high quality platinum thin films because it has some advantages over other methods such as good uniformity, controllability of thickness with a low defect density, and better step coverage.[8]

In MOCVD method, proper choice of precursors is important to get good quality thin films. Many platinum complexes have been used as precursors for the MOCVD of platinum films. Examples include platinum(II) and platinum(IV) complexes such as $CpPtMe_3$ (Cp = cyclopentadienyl),[9] $(MeCp)PtMe_3$ (MeCp = methylcyclopentadienyl),[1] $(EtCp)PtMe_3$ (EtCp = ethylcyclopentadienyl),[10] $Pt(acac)_2$ (acac = acetylacetonate),[11] $Pt(CO)_2Cl_2$,[12] $Pt(PF_3)_4$,[13] $Pt(hfac)_2$ (hfac = hexafluoroacetyl-acetonate),[14] *cis*-bis(η^2,η^1-pent-4-en-1-yl)platinum.[15]

Recently we have been interested in the development of new MOCVD and atomic layer deposition (ALD) precursors which have high applicability in microelectronic area. During the course of these investigations, we developed some metal precursors containing donor-functionalized alkoxide as ligands and applied them to prepare metal or metal oxide thin films by MOCVD and ALD.[16-19] The main skeleton of the ligands has an ethylene linkage with one dialkylamino and sterically crowded alkoxde. Two alkyl substituents on the α-carbon atom from the oxygen atom act as sterically hindered group to keep monomeric structure instead of dimer or trimer by prohibiting the oxygen atom approaching the neighboring metal when the ligands form the complex with transition metal. In our continuous and concentrated efforts to develop new metal precursors of high volatility and good stability for thin film deposition process, we report the synthesis and characterization of novel platinum precursor, in addition its application to MOCVD to prepare the platinum thin films. A novel platinum precursor, $Pt(dmamp)_2$ [dmamp = 1-dimethylamino-2-methyl-2-propanolate, $(CH_3)_2$-$NCH_2C(CH_3)$-$(C_2H_5)O$], was prepared by the reaction between *cis*-$(py)_2PtI_2$ with two equivalents of Na(dmamp) and

characterized by analytical methods. Single-crystal X-ray crystallographic analysis of the compound $Pt(dmamp)_2$ is also reported. In addition, platinum thin films were deposited on TaN/Ta/Si substrates using the precursor synthesized in this work by low-pressure metal-organic chemical vapor deposition (LP-MOCVD). The platinum thin films were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and X-ray diffraction (XRD) measurements. Moreover, electrical property of the films was also investigated.

Experimental Section

Synthesis and Characterization of the Precursor $Pt(dmamp)_2$. *Cis*-diiodobis(pyridine)platinum [*cis*-$Pt(py)_2I_2$][20] and two equivalents of Na(dmamp) which was prepared by the reaction of 1-dimethylamino-2-methyl-2-propanol (dmamp)[16] and sodium metal in THF, were placed in a 125 mL of Schlenk flask filled with argon. Toluene (70 mL) was added to the stirred mixture. The reaction mixture was refluxed for 2 days. After cooling to room temperature, the reaction mixture of the black solution was filtered, and the volatile organic materials of the filtrate were evaporated under vacuum to produce yellow solids. Purification of the crude product was conducted by sublimation (at 45 °C, 10^{-2} torr). The yield was 0.28 g (33%). MS (m/z^{-}, %): 427 [$Pt(dmamp)_2$, 70], 415 [$Pt(dmamp)_2$-CH_3, 65], 310 [$Pt(dmamp)_2$-dmampH, 45], 116 [dmamp, 35], 58 [acetone, 100]. ^{1}H NMR ($CDCl_3$, 20 °C): δ 2.93 (s, 12H, $C(C\underline{H}_3)_2$-CH_2), 2.33 (s, 4H, $C\underline{H}_2$), 1.39 (s, 12H, $N(C\underline{H}_3)_2$). Anal. Calc. for $C_{12}H_{28}N_2O_2Pt \cdot \frac{1}{2} H_2O$: C, 33.02; H, 6.70; N, 6.42. Found: C, 33.05; H, 6.88; N, 6.22. IR (cm^{-1}): 2900 (s, ν_{C-H}); 535 (m, ν_{Pt-O}).

A thermal analysis was also conducted to investigate the thermal behavior of $Pt(dmamp)_2$ by using a simultaneous thermogravimetric/differential thermal analysis (TG/DTA) apparatus (Perkin-Elmer TGA7). Single crystals of $Pt(dmamp)_2$ suitable for X-ray crystallography could be obtained during the sublimation of the crude products for purification.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. is CCDC-661333). The data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

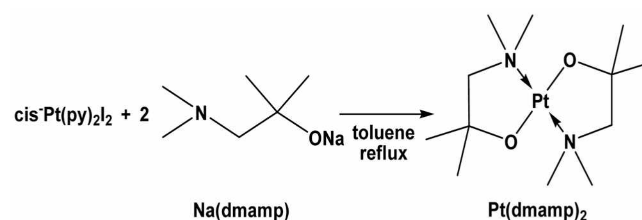
Chemical Vapor Deposition and Characterization of Platinum Thin Films. A horizontal, stainless steel low vacuum chamber was used to grow the Pt films. Pt films were deposited onto TaN/Ta/Si substrates. TaN/Ta/Si substrate was chosen to enhance adhesion between Pt films and substrate. The substrate temperature was varied in the range of 300-500 °C. The base pressure of the deposition chamber was 15-20 mTorr and the pressure was increased to 300-400 mTorr during the film deposition with Ar carrier gas and H_2 reactant gas. The temperature of precursor vessel and all dosing lines was maintained at 80 °C. Each deposition was carried out for 2 h.

The thickness of the Pt films was measured by an ellipsometer using a He-Ne laser. The surface morphology of the films was characterized by atomic force microscopy (AFM, Nanoscope IV, Digital Instrument). Chemical compositions and impurities of the films were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB MK II, VG Scientific, Ltd., using the Al Kα radiation with the energy 1483.6 eV) after Ar ion sputtering. X-ray diffraction (XRD) with the Cu Kα radiation (λ = 1.541838 Å) was employed to investigate the crystallinity of the films. The electrical resistivity was measured by the four-point probe method.

Results and Discussion

Synthesis and Characterization of the Precursor. As shown in Scheme 1, the novel platinum complex, $Pt(dmamp)_2$ was easily prepared by a metathesis reaction (salt elimination reaction) between *cis*-diiodobis(pyridine)platinum [*cis*-$Pt(py)_2I_2$] and two equivalents of sodium aminoalkoxide, $Na(dmamp)_2$ in toluene solution. However, the yield of the reaction product was low. The other possible starting reagent of platinum, *cis*-diaminedichloroplatinum(II) could not give a successful reaction either. The new compound is a light yellow solid at room temperature, quite stable in air, and highly soluble in common organic solvents such as toluene, ether, and THF.

Thermal analysis was carried out to investigate the thermal behavior of the platinum precursor with a heating rate of 10 °C/min under argon atmosphere (Figure 1). The TG result revealed that the compound underwent a very



Scheme 1. Synthetic scheme of $Pt(dmamp)_2$.

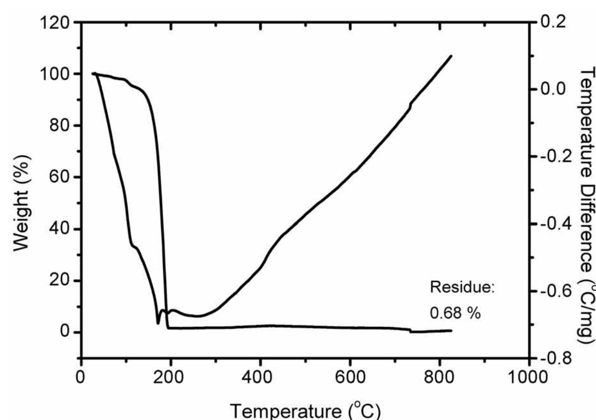


Figure 1. TG/DTA of of $Pt(dmamp)_2$. Heating rate = 10 °C/min, argon atmosphere.

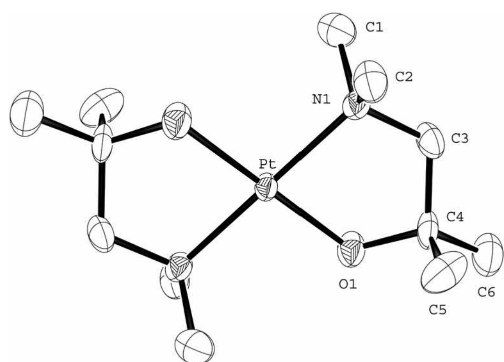


Figure 2. ORTEP drawing of $Pt(dmamp)_2$ with thermal ellipsoids at 50% probability without hydrogen atoms and solvent water molecules for clarity.

rapid and one-step weight loss in the temperature range from 125 to 190 °C upon heating. The DTA curve revealed an endothermic peak at 162.5 °C, attributed to the melting point of the platinum complex. The weight loss of the precursor reached almost zero around 190 °C after thermal treatment with a remaining residue of only 0.68%. These results suggest that the $Pt(dmamp)_2$ precursor vaporizes intact in the temperature range 125-190 °C without visible thermal decomposition during the TG/DTA.

The platinum complex, $Pt(dmamp)_2$ crystallizes in a symmetric space group C2 with two fold rotation axis and no inversion center as shown in Figure 2. The results of X-ray crystal structure analysis of the platinum compound are

Table 1. Crystallographic Data for $Pt(dmamp)_2$

Empirical formula	$C_{12}H_{32}N_2O_4Pt$
Formula weight	463.49
Space group	monoclinic, C2/c
a (Å)	18.646(3)
b (Å)	10.8209(9)
c (Å)	9.2290(10)
α (°)	90
β (°)	113.740(10)
γ (°)	90
Volume (Å^3)	1704.5(4)
Z	4
Dc (g cm^{-3})	1.806
μ (cm^{-1})	82.43
F(000)	912
Crystal size (mm)	0.12 × 0.11 × 0.11
h range	−22/22
k range	0/12
l range	−10/10
Reflections collected / unique	2986 / 1497 [R(int) = 0.0385]
Completeness to theta = 24.99	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1497 / 0 / 94
Goodness-of-fit on F^2	1.154
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0782
R indices (all data)	R1 = 0.0438, wR2 = 0.0842
Largest diff. peak and hole	1.447 and −1.838 e.A^{-3}

Table 2. Selected Bond Distances (Å) and Angles (°) for $Pt(dmamp)_2$

Pt-O(1)	2.002(6)
Pt-O(1_1)	2.002(6)
Pt-N(1)	2.049(6)
Pt-N(1_1)	2.049(6)
O(1)-Pt-O(1_1)	180.0(3)
O(1)-Pt-N(1_1)	95.3(2)
O(1_1)-Pt-N(1_1)	84.7(2)
O(1)-Pt-N(1)	84.7(2)
O(1_1)-Pt-N(1)	95.3(2)
N(1_1)-Pt-N(1)	180.0(3)

summarized in Table 1. Selected bond lengths and bond angles for $Pt(dmamp)_2$ are also shown in Table 2. The platinum(II) atoms lies in a center of a square planar coordination geometry of two 1-dimethylamino-2-methyl-2-propoxide chelate ligands which are trans-arranged each other. To our best knowledge, this crystal structure is the first example that the platinum compound of aminoethoxide moieties has trans geometry of the ligands, although the *cis* complexes of platinum of those ligands have been known for the investigation of their antitumor activity.[21,22] The corresponding distances of Pt-O(1) and Pt-N(1) are 2.002(6) and 2.049(6), respectively, showing comparable distances found in *cis*-platinum complexes of aminoethoxide derivatives.[21,22] Bond angles of O(1)-Pt-N(1) and O(1)-Pt-N(1_1) are 84.7(1), and 95.3(2), respectively. These values are in the range of the bond angles of *cis*-complexes.

Chemical Vapor Deposition of Pt Films. XPS analysis was performed to determine the composition of Pt films deposited on TaN/Ta/Si substrate at 500 °C. Figure 3 shows the XP spectra of before and after Ar^+ ion sputtering. The spectra clearly display the photoelectron and Auger electron peaks for Pt. Besides the Pt relevant peaks, there also appear O 1s peak, C 1s peak, and their Auger peaks that are attributed to surface contamination of the newly formed films by air and/or moisture during sample transfer to the XPS analysis chamber. For the elimination of surface contamination, the surface of the deposited films was sputter

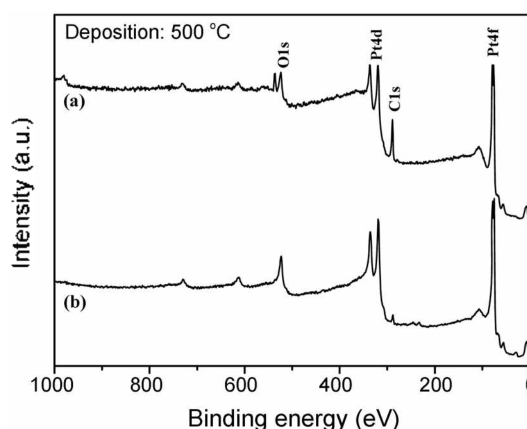


Figure 3. XP spectra of the Pt film deposited at 500 °C: (a) Before Ar^+ supttered; (b) After Ar^+ sputtered.

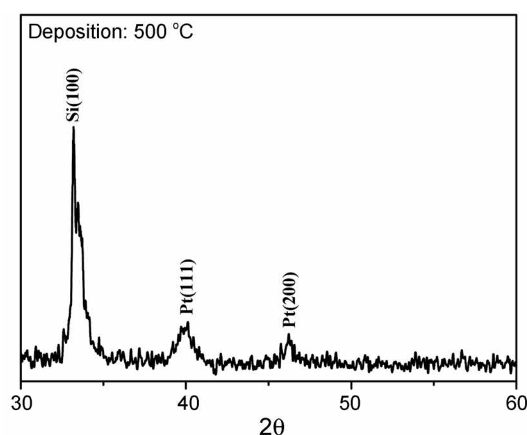


Figure 4. X-ray diffraction pattern of Pt film deposited at 500 °C.

etched by an Ar^+ beam of 5 keV. After etching the O 1s peak almost disappeared but C 1s peak remained below 9%. It indicates that the oxygen exists mostly in the surface region of the films and a little amount of carbon is contained in Pt films. As a result, the XPS analysis evidently shows that the Pt films have low levels of impurities.

Figure 4 shows the X-ray diffraction patterns of the Pt films deposited at 400 °C. These films do not have a clearly preferred orientation, but we have observed that the Pt films are crystalline and slightly (111), (200) oriented at 2θ = 39.765, 46.244, respectively. The XRD intensity is very low due to the thin thickness of Pt thin film.

AFM image of the surface of Pt films grown onto TaN/Ta/Si substrate at 500 °C showed that the root-mean-square (rms) roughness value for the area 1 μm × 1 μm was found to be ~2.4 nm. The films display homogeneous and smooth and dense morphologies.

The growth rates of the Pt films at various temperatures were calculated from thickness measurements. The maximum growth rate was achieved at 400 °C, which was 0.35 nm/min. The activation energy which calculated from an Arrhenius plot of the deposition rate was 2.22 kcal/mol. The value is less higher than that of $Pt(C_2H_5C_5H_4)(CH_3)_3$ (1.58 kcal/mol). This may be explained by the increased stability of the $Pt(dmamp)_2$ precursor due to the presence of the bulky ligand dmamp. The film deposition rate increased with increasing the deposition temperature.

We also measured the resistivity of Pt films deposited at 400 °C. The bulk value of the electrical resistivity (ρ) of Pt at 293 K is 10.5 $\mu\Omega$m.[3] The electrical resistivity of the Pt films deposited at 400 °C was measured to be 13.6 $\mu\Omega$cm a little higher than the bulk value. But the resistivity of Pt films increased as the deposition temperature was increased, because the hole in the films can interrupt the conducting carriers.[2]

Conclusions

We prepared a new platinum aminoalkoxide complex $Pt(dmamp)_2$ by the reaction between *cis*-$(py)_2PtI_2$ and Na(dmamp) for a potential precursor of platinum thin films. $Pt(dmamp)_2$ keeps a square planar geometry with each two nitrogen atoms and two oxygen atoms having trans configuration. Platinum films have been deposited on TaN/Ta/Si substrates by MOCVD using a newly synthesized $Pt(dmamp)_2$. As-deposited platinum thin films did not contain any appreciable amounts of impurities except a little carbon. The electrical resistivity (13.6 $\mu\Omega$cm) of Pt films deposited at 400 °C was slightly higher than the bulk value (10.5 $\mu\Omega$cm) at 293 K.

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