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Full Paper

Plasma-Enhanced Atomic Layer Deposition of Palladium on a Polymer Substrate

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In this paper, a method for the plasma-enhanced (PE) atomic layer deposition (ALD) of palladium on air-exposed, annealed poly(*p*-xylylene) (Parylene-N, or PPX) is presented. Palladium is successfully deposited on PPX at 80 °C using a remote, inductively coupled, hydrogen/nitrogen plasma with palladium (II) hexafluoroacetylacetonate ($\text{Pd}^{\text{II}}(\text{hfac})_2$) as the precursor. By optimizing the mixture of hydrogen and nitrogen, the polymer surface is modified to introduce active sites allowing the chemisorption of the $\text{Pd}^{\text{II}}(\text{hfac})_2$. In addition, enough free hydrogen atoms are available at the surface for ligand removal and Pd reduction, while at the same time, enough hydrogen atoms are consumed in the plasma to ensure there is no visible degradation of the PPX. X-ray photoelectron spectroscopy (XPS) measurements of the substrate after hydrogen/nitrogen plasma treatment at 50 W clearly show the presence of nitrogen bound to the substrate surface. XPS measurements of the deposited Pd films indicate good quality for both substrates, suggesting that the substrate temperature was low enough to prevent dissociation of the hfac ligand and adequate scavenging of the hfac ligand by the available atomic hydrogen. The remote hydrogen/nitrogen plasma enables Pd film deposition on polymer surfaces, which do not typically react with the Pd precursor, and are not catalysts for the dissociation of molecular hydrogen.

Keywords: Amine, Palladium, Parylene-N, PEALD, Polymer

1. Introduction

ALD has been actively investigated for use in integrated circuit (IC) manufacturing,^[1–4] and is becoming a clear candidate for applications where high surface area and conformal coverage is critical. Although there are many and varied techniques for ALD in terms of the chemistries and process conditions used, metal-organic precursors are popular because of their good stability, low deposition temperature requirements, and concerns with residues from halide chemistries.^[5,6] Pd and its alloys have recently been investi-

gated for a variety of applications, including acting as a seed layer for both electroless plating^[7] and electroplating^[8] in IC interconnect applications, hydrogen storage,^[9,10] and hydrogen detection.^[11]

Surface modification of polymers has been thoroughly investigated over the past two decades, with techniques including mechanical treatments, wet-chemical treatments, and plasma treatments.^[12] Plasma treatment of parylene has recently been investigated using microwave NH_3 treatment,^[13] O_2 plasma treatment,^[14,15] and atmospheric plasma treatment.^[16] In addition, Riley et al. examined Ar/ O_2 plasma treatments to improve the adhesion between parylene and a variety of metal and dielectric substrates.^[17] Other polymer modifications have been investigated including work done by Park and Inagaki using remote Ar, H_2 , and O_2 plasmas,^[18] He/ NH_3 studies by Arefi-Khonsari et al.,^[19] and tailored H_2/N_2 plasmas by Chen et al. for low-*k* passivation.^[20] Excellent summary information is also available on nitrogen grafting for surface functionalization.^[21–25]

ALD metals and metal nitrides can be utilized as a barrier and/or seed layer for interconnect metallizations, but obtaining good adhesion to the interlayer dielectrics (ILD) may be an issue. Work to develop pore-sealing technologies^[26,27] to prevent ALD precursor penetration into porous ILDs during metallization, is underway, but this can make the adhesion, and even the ALD process, much more difficult. Dielectric or polymer pore sealants may require the use of a plasma to generate species required for reduc-

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tion and ligand removal for metal-organic precursor-based ALD. However, in the case of hydrogen plasmas, the reactive species tend to attack organic surfaces,^[28,29] and in the case of a polymeric pore sealant, this attack can completely etch away the material.

Previous work with a plasma reduction scheme has been undertaken by this group^[30] and others^[1,31–34] to enable deposition on various substrates, including oxidized metals, at relatively low temperatures. However, the use of hydrogen plasma eliminates the use of these processes for depositing metals onto polymer surfaces. Work done by Kim et al. on the PE-ALD of TaN made use of H₂/N₂ plasma,^[32] but in that case the inclusion of the N₂ species was aimed at the addition of N to the film, not for substrate modification. The present work demonstrates the ability to deposit Pd with a PE-ALD approach on Parylene-N by tailoring the plasma species to enable ALD, while at the same time not attacking the substrate. To the authors' knowledge, this is the first demonstration of PE-ALD on a polymer substrate. Parylene-N was chosen because it is a material that could be encountered in the back end of the line (BEOL) for advanced logic devices since it can act as a pore sealant for porous low-*k* materials.^[26] The Pd surface is an excellent seed layer for the electrochemical deposition of Cu, or as a catalyst for electroless deposition of Cu, as demonstrated previously.^[7] The results of these PE-ALD depositions, including H₂/N₂ plasma characterization, PPX surface modification, and Pd film quality, are presented in this paper.

2. Results and Discussion

Pd was successfully deposited on annealed PPX and air-exposed Si at 80 °C with thicknesses of 25 Å and 38 Å, respectively, during the same deposition using 100 cycles ALD with a 50 W 1:1.5 ratio H₂:N₂ plasma. The H₂/N₂ plasma was able to reduce the Pd and remove the hfac ligand, and did no visible damage to the PPX surface. In this case, the H₂/N₂ plasma creates reactive surface sites of NH₂ groups that enable the chemisorption of the precursor which, in turn, enables growth. In contrast, all attempts to deposit Pd on PPX using only H₂ as the feed gas for the plasma resulted in the complete etching of the PPX film, and only after the PPX film was removed to expose the Si substrate was Pd deposition successful.

The specific plasma chemistry and power used for the depositions were chosen after analyzing the NH₃, NH₂, NH, H₂, N₂, H, and N signals in the chamber before, during, and after the plasma was struck. Shown in Figure 1a are the quadrupole mass spectrometry (QMS) data taken for the percentage change in species concentration in the chamber when the plasma was struck for various ratios of H₂ to N₂ feed rates. Because the goal was to graft NH₂ groups onto the surface, the H₂:N₂ feed ratio chosen was 1:1.5 which, as shown, optimized the generation of NH₃ species in the chamber suggesting the most NH₂ generation. Shown in

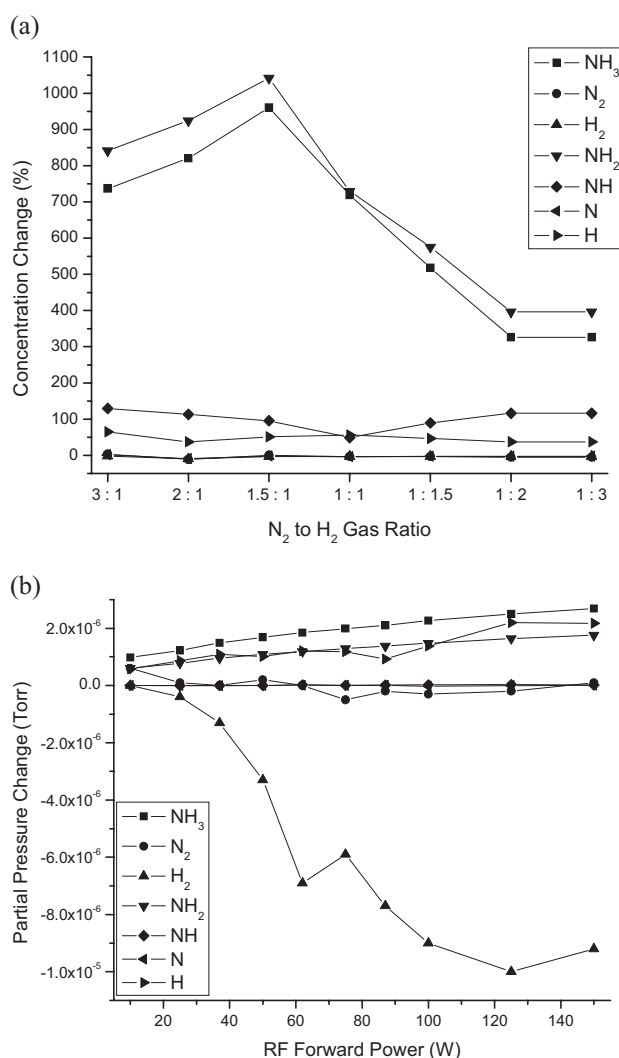


Fig. 1. QMS scans of the gas species in the chamber. a) The gas species concentration change as a function of the N₂:H₂ inlet ratio. b) Partial pressure change of the gas species in the chamber as a function of applied RF power for the 1:1.5 H₂:N₂ plasma case. In both cases it should be noted that the absolute value of the measurement could be skewed as a result of QMS location and gas recombination, but the ratios are self-consistent and correspond to established cracking patterns. The plasma pressure was 75 mTorr.

Figure 1b are the QMS data taken for the partial pressure change in the chamber when the plasma was struck for various applied levels of RF power, at the established 1:1.5 H₂:N₂ feed ratio. As shown, the higher power applied tends to consume the available H₂, while the other species remain largely unaffected. This was deemed desirable based on conclusions drawn by Favia et al. that increased H₂ content lowers the N:C grafting ratio.^[25] It should be noted, however, that the H species partial pressure did increase as a function of forward power, suggesting that a low power process would reduce the impact of reactive species on the PPX surface. In addition to the results shown in Figure 1, other data were taken to observe the species changes as a function of system pressure, which showed an inverse relationship between the pressure and NH_x generation. In con-

trast, experiments with NH_3 plasmas tended to produce H_2 , N_2 , N , and H species proportionally with applied power, and had an inverse relationship between H_2 and N_2 generation and system pressure. As a result, only H_2/N_2 plasmas were used for the deposition experiments.

2.1. Substrates and Deposition

In order to determine the effect of the H_2/N_2 plasma on the PPX substrate, an annealed PPX sample was subjected to a 10 min plasma that mimicked the deposition conditions. The surface chemistry of the treated film was then analyzed using ex-situ XPS, and the results for the N 1s and C 1s spectra are shown in Figures 2 and 3, respectively. The

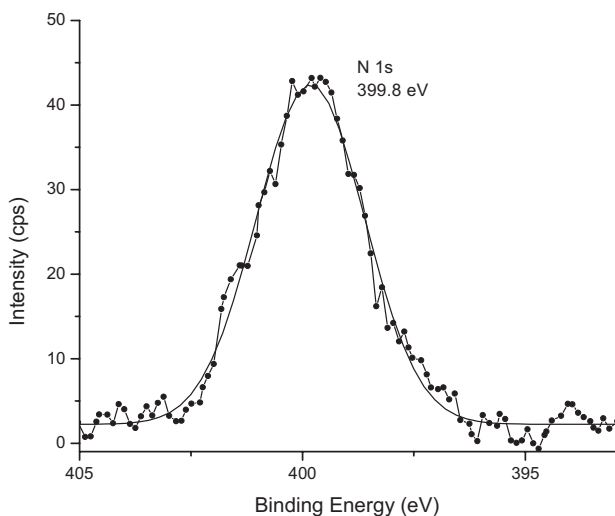


Fig. 2. The N 1s XPS spectra for the PPX substrate after 10 min of exposure to the 50 W H_2/N_2 plasma used for subsequent deposition. The peak position is shifted by +1.7 eV relative to established values. This peak location corresponds to NH_2 groups on an organic surface [35].

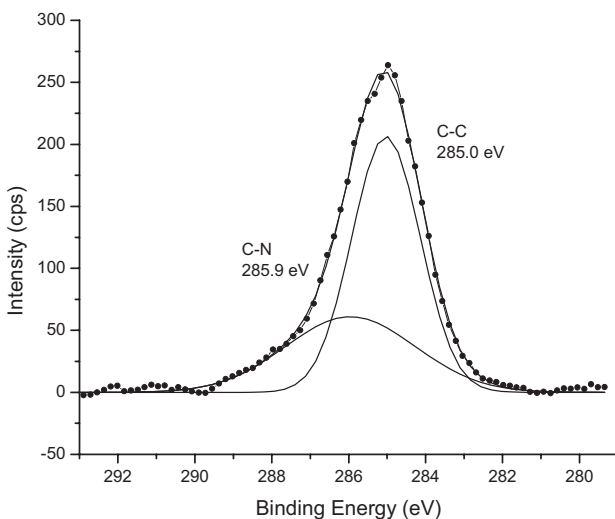


Fig. 3. The C 1s XPS spectra for the PPX substrate after 10 min of exposure to the 50 W H_2/N_2 plasma used for subsequent deposition. The peak at 285.9 eV corresponds to carbon-nitrogen bonding [35].

N 1s peak shown is shifted by 1.7 eV relative to established values, corresponding to NH_2 bound to carbon.^[35,36] That the film has a clear N 1s signal indicates grafting of N-containing species during the plasma treatment. It has been established^[21,37,38] that the grafting of N-containing groups during plasma treatment is a difficult process, with surface site concentrations of the order of 5–10%. Examination of the relative intensities of the N 1s and C 1s signals gives a N:C ratio of 17%, which is above reported values. In addition, because the current process is cyclic, a synergy exists between the N group grafting to the surface and the Pd growth. As sites are grafted, the Pd is able to chemisorb, and during the reduction and ligand removal (the plasma pulse) additional N-containing sites can be formed. As shown in Figure 3, the C 1s energy scan results in a convolution of 2 peaks, corresponding to C–C or C–H bonding (285.0 eV) and C–N bonding (285.9 eV).^[35]

Once the PPX substrate was characterized, a 100 cycle Pd deposition was performed on annealed PPX and air-exposed Si substrates. Rutherford backscattering spectrometry (RBS) data measured 25 Å and 38 Å for the annealed PPX and air-exposed Si samples, respectively. The deposition rate on air-exposed Si was significantly higher than reported previously using H_2 plasma.^[30] This variance was not expected, but it can be attributed to an increase in chemisorption sites for the precursor that resulted from the use of the H_2/N_2 plasma. The variance in deposition rate between the PPX and air-exposed Si substrates was expected because, without the surface treatment, all attempts to adsorb even a monolayer of $\text{Pd}^{\text{II}}(\text{hfac})_2$ onto PPX failed, therefore the deposition on PPX would be limited to available nucleation sites generated by the plasma. Additional study of the morphology of the film will be necessary to gain a better understanding of the nucleation densities achieved with this approach.

The chemical composition of the Pd films was analyzed with ex-situ XPS and the results are shown in Figure 4. For each substrate there exist clear Pd 3d_{5/2} and Pd 3d_{3/2} peaks at 335.5 eV and 340.8 eV, respectively, with the associated PdO₂ and shake-up peaks typical for these films. As can be seen in the figure, the peak positions for Pd are shifted by approximately 0.4 eV relative to the XPS analysis on Pd films performed by Militello and Simko.^[39] The peak separation was consistent at 5.3 eV, but the carbon content was slightly elevated compared to prior PE-ALD results using H_2 plasma.^[30] Part of this carbon can be attributed to adventitious carbon present on all samples measured using ex-situ XPS, but there remains some concern that the ligand removal for this deposition was incomplete. Further supporting this is the fact that there was a measurable F 1s signal, and although the F:Pd ratio for both films was very low (F:Pd = 0.04 for Pd on PPX and F:Pd = 0.03 for Pd on SiO₂), that there was any measurable F signal confirms incomplete ligand removal. This, again, is in contrast to prior work using H_2 plasma where no measurable F was present.^[30] It should also be noted that there was no measur-

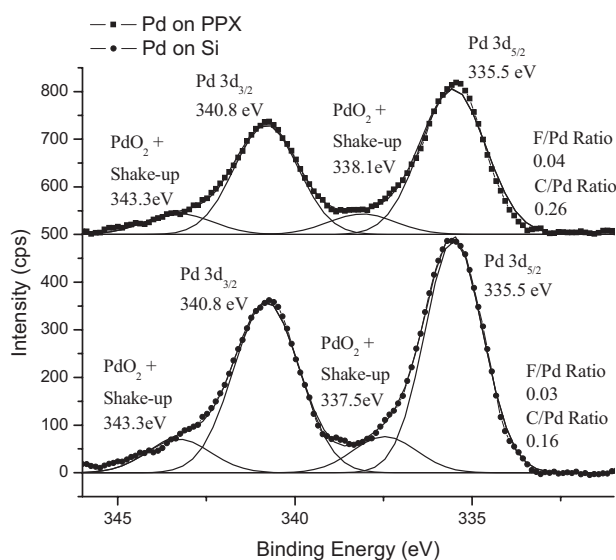


Fig. 4. The Pd 3d XPS spectra for 25 Å of Pd deposited on PPX (top) and 38 Å of Pd deposited on air-exposed Si (bottom). The peak position of the Pd 3d_{5/2} and Pd 3d_{3/2} curves have the 5.3 eV separation expected, and in both cases are shifted by -0.3 eV relative to the literature data [39].

able N 1s signal present in data taken for these Pd films, indicating no adverse affect on the films from the N₂ addition to the plasma.

2.2. Ultrathin Pd on PPX

In order to better understand the chemistry at the Pd/PPX interface, a separate deposition was undertaken with identical conditions to those discussed above, but with only 35 cycles. This resulted in only 2 Å of Pd on the PPX surface, allowing the chemistry of the interface to be examined using ex-situ XPS. Presented in Figure 5 are the Pd 3d peaks from the resultant film. Again, the Pd 3d_{5/2} and Pd 3d_{3/2} peaks are clearly defined and are located at 336.3 eV and 341.6 eV, respectively, with a separation of 5.3 eV. In addition, the measurable F 1s signal corresponded to a F:Pd ratio of 0.04, indicating incomplete ligand removal. Because of the ultra-thin nature of the film, the XPS was able to measure a significant C 1s signal from the underlying PPX, resulting in an extremely large C:Pd ratio of 0.77. Of particular interest in these Pd peaks is the 0.8 eV shift relative to the peak locations noted in Figure 4 for the thicker Pd films. This Pd 3d peak shift is indicative of Pd bonding to the substrate surface rather than bonding to underlying Pd, as is the case for thicker films. This shift can be attributed to Pd bonding with either nitrogen or oxygen groups on the surface, but it is not possible to say with certainty which is the dominant mechanism. Recently, Crowhurst et al. demonstrated the synthesis of noble metal nitrides,^[40] and their XPS results show a positive binding energy shift of 3.2 eV and 1.1 eV for Pt and Ir, respectively, in conjunction with the N 1s shift of +0.9 eV. They attribut-

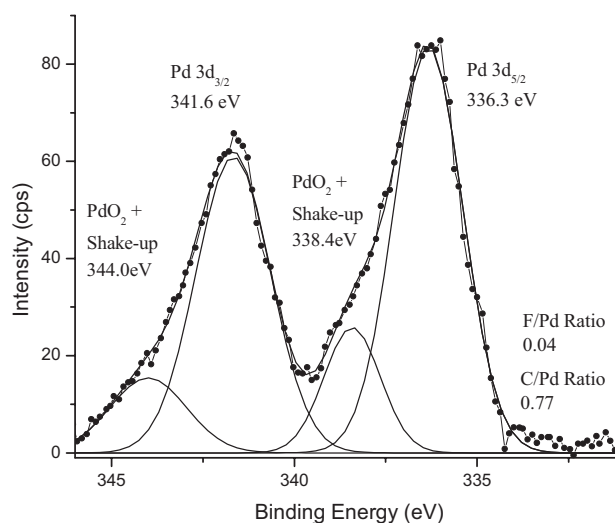


Fig. 5. The Pd 3d XPS spectra for 2 Å (35 ALD cycles) of Pd deposited on PPX. The peak position of the Pd 3d_{5/2} and Pd 3d_{3/2} curves have the 5.3 eV separation expected, but are shifted by +0.8 eV relative to the peaks in Figure 4. This peak shift is attributed to the interface bonding between Pd and surface N and/or O species. The high C/Pd ratio is attributed to the underlying C in the PPX, clearly visible for such a thin film.

ed these shifts to nitride compound formation, and the similarities to the current work suggest that this is a reasonable hypothesis to explain the present results. On the other hand, the deposition chamber maintains a water vapor partial pressure of the order of 1×10^{-5} Torr, which allows for some surface oxidation during the deposition. In this case, O could bond to the N attached to the substrate, and provide a nucleation site for the Pd^{II}(hfac)₂. Examination of the O 1s peak for this film does show a significant peak shift of +1.6 eV relative to the established value of 531.0 eV, which could suggest O bound to both N and Pd at the surface.

3. Conclusions

A method was presented for the low temperature PEALD of Pd on Parylene-N using a combined H₂ and N₂ plasma. The H₂/N₂ plasma enabled both the surface modification of the polymer surface (allowing chemisorption of the precursor) and also the reduction and ligand removal of the Pd^{II}(hfac)₂ precursor. The Pd films showed clean Pd 3d peaks, suggesting that the Pd films are of similar quality to those previously obtained using all-H₂ plasma.^[30] Examination of an ultra-thin Pd layer provided information on the chemical bonding at the interface, and the data suggest Pd is bonded to nitrogen groups grafted to the surface, or to oxygen bound to these grafted nitrogen groups.

4. Experimental

In order to obtain reproducible deposition, the as-received Pd^{II}(hfac)₂ powder (Aldrich, Milwaukee) was re-crystallized. The re-crystallization was

undertaken by dissolving the Pd^{II}(hfac)₂ into dried, heated (40 °C) hexane (HPLC Grade, Fisher Scientific, Pittsburg), and sealing the glassware to minimize the evaporation rate. The hexane was dried by pouring through a filter containing magnesium sulfate anhydrous powder.

Two surfaces were used for the ALD of Pd. 1000 Å of Parylene-N was deposited onto a Si(100) wafer, and the second substrate was intrinsically oxidized Si(100). Parylene-N thin films were deposited using the Gorham method [41]. The reactor consisted of a sublimation furnace, a pyrolysis furnace, and a bell jar-type deposition chamber. A detailed description of the reactor and deposition process has been given elsewhere [42,43]. The Pd film deposition was carried out through a four pulse cycle. First, the precursor flooded the system depositing a monolayer on the surface, and the system was then purged with Ar. Next, reactive H was introduced (via the remote plasma) to dissociate the precursor, forming volatile compounds and reducing the Pd, leaving behind the pure metal atom. During this step, the presence of nitrogen in the plasma also leads to the formation of NH and NH₂ species, believed to be responsible for the chemisorption sites on the PPX. The system was again purged with Ar, and the cycle repeats.

A custom-built vacuum chamber with computer-controlled gas flow was used for the ALD of Pd via Pd^{II}(hfac)₂, as described previously [30,44]. The depositions were undertaken at a deposition temperature of 80 ± 5 °C, and a Pd^{II}(hfac)₂ sublimation temperature of 47.5 ± 0.2 °C. Pd^{II}(hfac)₂ is known to show volatility at temperatures above 42 °C [45,46]. The deposition chamber walls were kept at 85–90 °C, and the lines between the sublimation tube and the deposition chamber at 95 °C, to ensure no cold spots existed to condense Pd^{II}(hfac)₂. Prior to each deposition, a 2 h 200 °C in-situ anneal in Ar was performed. During each experiment, 50.0 sccm Ar (99.999% Air Products) was flowed as a purge gas, 13 sccm Ar as a carrier gas for Pd^{II}(hfac)₂, and 30.0 sccm H₂ as a reducing gas with 45.0 sccm N₂. The pulse sequence was 10 s of Pd^{II}(hfac)₂ followed by 10 s of 'dead time' with just 50.0 sccm Ar flowing as a purge gas, then 7 s of H₂/N₂ to allow for steady state in the plasma, and then 15 s of remote H₂/N₂ plasma with 30.0 sccm H₂ and 45 sccm N₂ flow and 50 W net forward power. The RF power was supplied by an ENI OEM-12A 13.56 MHz power supply, applied to a 3.5 turn water-cooled coil as described previously [30]. Unless noted, the number of cycles for each deposition was 100. No throttle valve was used to control the pressure and, in fact, the initial instability of the mass-flow controllers aided in the purging of the system before each portion of the cycle (MFCs were behind the valve, so they went to a fully open state when the valve was closed).

The gas species in the chamber were analyzed using an in situ Stanford Research Systems RGA-300. The Pd deposition was characterized by RBS with the 4.0 MV Dynamitron accelerator at the Ion Beam Laboratory, Department of Physics, University at Albany. Measurements were made using 2.0 MeV ⁴He⁺ particles. RBS-determined areal density was converted into an equivalent thickness by dividing it by the bulk atomic density of Pd (6.77 × 10²² atoms per cm³). Spectra were collected with a 20 mm² area beam spot, 4 μC of charge, and 10 nA of current. The surface chemical structure of each sample was analyzed using XPS. The samples were loaded into the XPS chamber with a chamber base pressure about 1–2 × 10⁻⁹ Torr, and during a spectrum collection, the pressure was raised to about 3–4 × 10⁻⁹ Torr. The X-ray Mg Kα source (PHI model 04-151) used in this experiment has a primary energy of 1253.6 eV, and a cylindrical energy analyzer controller (PHI Model 15-255G) with a passing energy of 50 eV used for high-resolution scans. In all cases, the signals were referenced to the C 1s peak at 285.0 eV.

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