Full Paper

Plasma-Assisted Atomic Layer Deposition of Palladium


A method is presented for the atomic layer deposition (ALD) of palladium using remote hydrogen plasma as the reducing source and agent. Palladium was deposited on iridium, tungsten and silicon at 80 °C using a remote inductively coupled hydrogen plasma with palladium(II) hexafluoroacetacyletacetonate as the precursor. In the case of the Pd film grown on Ir, the carbon and fluorine content were significantly reduced compared to previous thermal ALD results. Use of remote plasma eliminated the noble metal substrate requirement needed for thermal ALD, enabling films to be grown on W and Si. Ultra-thin Pd films grown on W and Si possessed a nearly random texture from reflection high-energy electron diffraction (RHEED) measurements. Atomic force microscopy (AFM) images showed very different surface morphologies for the different substrates suggesting very different substrate film interactions. X-ray photoelectron spectroscopy (XPS) measurements indicate high quality Pd films for all substrates, suggesting the substrate temperature was low enough to prevent dissociation of the hfac ligand and adequate C and F scavenging by the atomic hydrogen. The remote hydrogen plasma source results in the loss of selectivity but growth is evident on every surface used including surfaces that do not react strongly with the Pd precursor and are not catalytic towards the dissociation of molecular hydrogen.

Keywords: ALD, H₂ plasma, Metal–organic, Palladium, Plasma-assisted

1. Introduction

Self-limiting chemistries that result in atomic layer control of deposited films are becoming popular due to their conformality with thickness control and control of interface chemistry. Coordination-compound-based precursors for ALD are attractive because their chemical bonding can be tailored to yield stable ALD precursors with controlled vapor pressure, condensation temperature, and precursor-substrate interaction.[1] ALD is a viable deposition technique for future ultra-large scale integrated devices since sputtering techniques have limited deposition conformality for high aspect ratio trench/via structures. Palladium and its alloys are potential replacements for gold electrical contacts[2,3] in gas sensors[3] and as ‘seed’ layers for electroless plating.[4]

ALD is defined by its utilization of self-limiting chemistry via the alternating pulses of source materials to generate layer-by-layer growth on a substrate that favors the chemisorption of the precursors.[5] There are many coordination compounds based on the β-diketone chemistries that are suitable for metal ALD.[6] Further, β-diketones are known to have a high vapor pressure,[7] and have been utilized for the CVD of metal.[8–10] However, for ALD these precursors often require high substrate temperatures or specific surface compositions for metal reduction and organic ligand removal.[1,2,11] Metal–organic compounds based on acetylacetonato and dipivaloylmethanato chemistries can exist in the solid state at room temperature and have been shown to be suitable for plasma CVD.[12] however each of these has a volatility at temperatures high enough that alternative chemistries were investigated. Of the various β-diketone derivatives of Pd available, Pd(hfac)₂ has been shown to have the highest vapor pressure, and can therefore be implemented at the lowest process temperature.[6]

To date, Pd ALD has not achieved success on oxide-terminated surfaces primarily due to the lack of chemisorption of palladium(II) hexafluoroacetacyletacetonate, Pd(II)(hfac)₂.[12,13] Additionally, there has been a lack of suitable reducing agents. Senkevich et al.[12] successfully demonstrated the use of thermally cleaved glyoxylic acid as a reducing agent for Pd ALD, but this technique required substrate temperatures in excess of 200 °C, which only yielded a monolayer ‘seed’ layer whereupon hydrogen could be used at 80 °C. Hydrogen can only be utilized with thermal ALD when a catalytic surface is present for the dissociation of molecular hydrogen to atomic hydrogen. Other methods of substrate-independent Pd ALD have been explored, including the use of sulfur to enhance the chemisorption of the Pd coordination compound.[11]
The use of remote H₂ plasma for atomic hydrogen generation is well established, and its use in the ALD of metals such as Ta, Cu, and Ti has also been reported. This strategy has been employed here to successfully grow Pd films on three different substrates. In the present work, Pd is deposited on an Ir substrate, an oxidized metal (W with native oxide), and on a dielectric (Si with native oxide). The Ir substrate provides a growth rate comparison to previous ALD work in the same system. The W substrate is an ideal choice since it readily oxidizes and is currently used in IC fabrication. The Si substrate is chosen because it is believed that its native oxide coupled with a toluene dip treatment will approximate the surface of typical low-κ silicon oxycarbide films found in current IC fabrication. Though a simpler thermal ALD approach exists for Pd growth on Ir, the addition of a remote plasma source eliminates the need for a catalytic surface for H₂ dissociation and low-temperature growth on oxidized surfaces is enabled through its use.

2. Results and Discussion

Pd was successfully deposited on Ir, W, and Si surfaces at 80 °C with thicknesses of 20.6 Å, 38.7 Å, and 16.6 Å, respectively, under the same conditions using 150 cycles of pulsed ALD. The noble metal Ir will chemisorb Pd(hfac)₂ and dissociate molecular hydrogen to atomic hydrogen, and was therefore used to compare the remote plasma-assisted ALD to previous thermal ALD work. Because oxide-terminated W has a low surface reactivity with H₂,[21] no dissociation of H₂ is expected until the oxide is removed. Similarly, the Si surface with its native oxide present and having been treated with a controlled hydrocarbon contamination, also provides no H₂ dissociation. The variation in chemisorption of Pd(hfac)₂ can be indirectly measured by Rutherford backscattering spectrometry (RBS). In comparison to a separate deposition of thinner films using only 100 cycles of pulsed ALD (14.5 Å on Ir, 27 Å on W, and 5.8 Å on Si), the effective growth rate for each surface, estimated by subtracting the 100 cycle thickness from the 150 cycle thickness, was approximately uniform after an initial Pd “seed” layer was grown. The approximated growth curves are shown in Figure 1, for 100 cycle and 150 cycle deposition on each substrate. The exact number of cycles required to obtain this “seed” layer was not determined in this work, but the data indicates that it does occur in the first 100 cycles. Once this Pd layer is formed, growth rates on each substrate approach those found by Senkevich et al.[12]

2.1. Remote Plasma-Assisted ALD of Pd

To achieve ALD, it is necessary to successively remove the hfac ligand from Pd(hfac)₂, and reduce Pd²⁺ to Pd. It has been previously established that dissociated H₂ can accomplish this, but early work has required catalytic substrates, typically noble metals.[23] The use of remote high-density inductively coupled plasma (ICP) enables ALD of Pd independent of the starting substrate, provided that there is at least some interaction between the Pd(hfac)₂ molecule and the surface. This is critical in the cases of oxide-terminated W and dielectric surfaces where no dissociation of H₂ is expected.[21] The active atomic hydrogen from the plasma serves as the reducing agent during the initial Pd monolayer growth. Once a monolayer of Pd has formed, the situation becomes one of Pd–Pd interaction, which facilitates deposition much more readily. This is enhanced due to the high rate of molecular hydrogen dissociation on Pd.[23] Caution must be exercised in the experimental procedure when the pulse separation is not long enough, which leads to parasitic CVD rather than ALD. Figure 2 shows the ICP setup used for the experiments. A similar setup has been demonstrated by Kim et al. to enable the ALD of amorphous Ta films, with atomic hydrogen as one of the reaction precursors.[20] Low pressure (≤1 torr) ensures that the dissociated H₂ and Pd(hfac)₂ pulses both operate in the molecular regime. The substrate temperature is also important in this growth. Pd(hfac)₂ has been shown to

Fig. 1. Growth data for 100 cycle and 150 cycle depositions on Ir, W, and Si substrates.

Fig. 2. Experimental ICP setup.
decompose at 230 °C[13,24] above which it no longer exhibits self-limiting chemistry, leading to parasitic CVD.[13,25] This mode of CVD is not desirable since the decomposition of Pd(II)(hfac)_{2} can give rise to various fluoride species and organics.[21] A low deposition temperature additionally minimizes ligand dissociation leading to higher quality Pd films with minimum carbon and fluoride contamination. Additionally, the low substrate temperature is important to minimize the desorption of Pd(II)(hfac)_{2} from the surface due to its weak chemisorption.

Depending on the substrate, the remote H_{2} plasma will either enable deposition (as in the cases of the oxidated W and Si) or may enhance deposition by providing reactive H species to the surface which scavenge the organic ligand and also reduces the Pd(II). Once a uniform catalytic Pd is deposited on the surface, the deposition per cycle will stabilize since the new Pd surface is catalytic and will also dissociate H_{2} molecules and only Pd(II)(hfac)_{2}-Pd interaction is occurring. To minimize the hydrogen ion bombardment of the substrate surface, the plasma is struck remotely and at a power just sufficient to achieve a sustained ICP.

### 2.2. Palladium ALD on Ir, W, and Si (XPS)

Ex-situ XPS was used to assess the chemical quality of the Pd films. Specifically, Pd films grown on Ir, W, and Si were used. In all cases clear peaks were obtained for the Pd_{3d_{5/2}} and Pd_{3d_{3/2}} energies. The peak positions for each sample were referenced to carbon at 285.0 eV. As can be seen in Figure 3, the peaks for each sample are shifted by about 0.4 eV from established values,[20] but the 5.3 eV peak spacing is consistent in all samples. The carbon present on or in the films was also analyzed and is presented in Figure 4. As can be seen, there is a clear C–C or C–H peak present in each sample, and a careful examination of the data revealed the presence of C–O peaks for each film. The C/Pd signal ratios for each sample were compared and found to be significantly reduced in the Pd on Ir and Pd on W films when compared to thermal ALD results for Pd on Ir. For the Pd film on Ir, C/Pd = 0.04, compared to the thermal ALD result of 0.09. Interestingly, the Pd on Ir sample also shows noticeable C=O energies. This carbon signal is consistent with adventitious carbon indicating the C/Pd ratio may be even lower than originally calculated.

Initially, the W and Si substrates were analyzed to determine the surface oxidation. For the W substrate, clear W_{4f_{7/2}} and W_{4f_{5/2}} peaks were obtained, along with strong WO_{x} peaks as shown in Figure 5. The Si substrate has a clear layer of SiO_{2}, as seen in Figure 6. These peaks are indicative of a surface oxide, and it was expected that the Pd growth on W would occur at a rate similar to the growth on the Si.
WO$_3$ will not contribute to H$_2$ dissociation. However, the growth on the W substrate was higher than that of both Ir and Si, suggesting that the remote H$_2$ plasma was able to at least partially reduce the WO$_3$. The C/Pd ratio for the films grown on the W substrates was found to be C/Pd = 0.06, which is comparable to the Pd on Ir film, and still an improvement over the thermal ALD results.

For the Si sample, the carbon ratio was found to be C/Pd = 0.21; however, due to the low thickness (16.6 Å) and high roughness (21.25 Å) of the film, it is believed that this measurement includes the carbon measured on the surface of the substrate, as shown in Figure 7. Taking this into consideration, the carbon levels measured for the surface shown in Figure 7 suggest an actual C/Pd ratio for the Si film closer to C/Pd = 0.10. This indicates a reduced carbon level in the film given similar conditions for adventitious carbon to form. The relative intensity of the Pd on Si sample is lower due to the reduced film thickness on this sample. Because there is only limited interaction between the Pd$^{11}$(hfac)$_2$ precursor and the Si surface, the nucleation phase of the growth was likely extended beyond that of either W or Ir. Without the use of a remote plasma source there is no growth on the oxide-terminated W and Si substrates, indicating that the contribution of H radicals from the plasma is essential.

Another significant result of the XPS measurements was the insignificant F levels in each film. Previous work$^{[12]}$ with thermal ALD on Ir had measurable F levels in the films, indicating an incomplete removal of the hfac ligand. It is believed that the increased level of H radicals due to the remote plasma both allowed for more efficient removal of the ligand and also helped to scavenge any residual F present on the surface.

2.3. Interfacial Interactions between Pd$^{11}$(hfac)$_2$ and the Ir, W, and Si Surfaces

It has been shown by this group that palladium metal–organicss do not interact well with oxide-terminated surfaces. Senkevich et al. successfully demonstrated a method of surface modification to create a sulfur-terminated Si surface that had favorable interaction with Pd$^{11}$(hfac)$_2$. It was further shown that little to no Pd could be grown on hydroxyl-terminated Si surfaces using thermal ALD. Surface chemistry plays an important role in the film characteristics, and the present work suggests that the remote H$_2$ plasma successfully modified the Si surface to promote Pd surface wetting since measurable Pd films were obtained. Similarly, the plasma appears to have reduced the WO$_3$ on the surface, resulting in improved Pd interaction with the W substrate. In addition to the improved Pd surface interaction, the reduction of WO$_3$ exposes elemental W, known to dissociate H$_2$ which leads to enhanced scaving of the hfac ligand and Pd reduction. In fact, the RBS data obtained indicate that the Pd growth rate on W is nearly double that of Pd on Ir, and 3–4 times that of Pd on Si during the initial growth phase. Further data indicate that the growth rate for Pd on Ir, W, and Si was almost equal after the first 100 cycles of deposition, which is to be expected since the rate should stabilize once a complete Pd layer exists on the surface. Based on the Pd$^{11}$(hfac)$_2$ structure, the theoretical maximum growth rate is estimated to be 0.4 Å per cycle, and the post-monolayer growth obtained was approximately 0.22 Å per cycle. The overall growth rate on the W substrates was ~0.3 Å per cycle, compared to the growth on the Ir sample of ~0.14 Å per cycle, and on the Si sample of ~0.11 Å per cycle. Interestingly, the growth rate for the Ir and Si substrates increased after the initial monolayer of growth, while the growth on the W substrate decreased. It has been shown that there is a complex bonding mechanism between Pd and W, where the binding energy for the W/Pd bimetallic layer has been shown to be enhanced relative to Pd(111), which may explain the experimental results obtained.
2.4. Atomic Force Microscopy (AFM)

The surface morphology of the Pd films on both W and Si substrates was studied. As shown in Figure 8, the surface roughness of the Pd on the W film has a very small grain structure, indicating good surface wetting on the W film, whereas the grain size on the Si sample is much larger, indicating poor wettability of the Si surface. Given the layer-by-layer growth mechanism, surface roughness is representative of the type of nucleation. Higher surface roughness indicates preferential chemisorption on existing Pd atoms relative to the substrate and can be correlated to the reduced overall deposition rate. The surface roughness measured for the Si substrate was $5.32 \pm 0.1$ Å. A 16.6 Å Pd film deposited on that Si substrate had a measured roughness of $21.25 \pm 1.0$ Å. In contrast, the W substrate was measured to have a roughness of $4.29 \pm 0.41$ Å and the subsequent 38.7 Å Pd film had a roughness of $4.22 \pm 0.07$ Å. This result is to be expected assuming the WO$_2$ reduction, given that noble metals tend to have strong attractive interaction with W surfaces, leading to the formation of close-packed islands.\cite{31} This result is clearly visible in the AFM image. Although larger grain sizes are desirable in thicker films, these data suggest that the larger grain sizes correspond to poor surface wettability of the Si but excellent wettability on the W substrate. It is believed that this strong surface reaction with the treated W surface allows growth to initiate more rapidly and produce much smoother films.

2.5. Reflection High-Energy Electron Diffraction (RHEED)

The structure of the Pd films can be obtained by using a RHEED camera under ultra-high vacuum conditions. Figure 9 shows the RHEED images taken for the Pd films grown on W and Si. In both cases, the films appear to be amorphous, which parallels the results obtained by Kim et al. from their ALD of Ta.\cite{17} Previously reported ALD growth of Pd\cite{12} has shown a definitive texture, so amorphous structures were not expected, especially given the reduced levels of C and F in the films. The small grains structure of the Pd on W shown in Figure 8 could account for the amorphous nature of the RHEED data, but the Pd on Si has much larger grain sizes, approximately equal to the film thickness, so a clear texture was expected. Prior work\cite{12} indicates that Pd has a strong growth preference in the (111) direction, but the RHEED data in the present work suggest amorphous film growth, possibly resulting from the more uniform distribution of nucleation sites on the surface. Current work by Tang et al., studying the evolution of grain size in Cu film growth, has shown a random distribution of grain orientation for

---

Fig. 8. The AFM surface scan images for Pd deposited on W and Si. 38.7 Å of Pd on 120 Å of W had a surface roughness of $4.22 \pm 0.072$ Å. 16.6 Å of Pd on Si had a surface roughness of $21.25 \pm 1$ Å.
films below 100 Å.\textsuperscript{[32]} Given the preference for (111) growth in both Pd and Cu films these results may explain the absence of a clear ring pattern for the Pd films in Figure 9.

3. Conclusions

A method was presented for the low temperature ALD of Pd on oxidized substrates using remotely generated, inductively coupled plasma. The primary goal was to use a remote hydrogen plasma to enable the reduction of the hfac ligand, thereby enabling growth on hydrocarbon and oxidized surfaces. The ALD method employed used a substrate temperature of 80°C, and growth rates of close to 50% of the theoretical maximum were obtained. This method has a broad range of applications, given its low temperature and substrate-independent nature.

In all cases negligible F levels were measured, and the carbon levels in each film were significantly improved over prior thermal ALD work. The surface morphology suggests strong wettability on the W substrate, and relatively poor wettability on the Si surface, requiring longer nucleation times for stable growth. The lack of a strong crystal orientation preference is a deviation from established thermal growth\textsuperscript{[32]} and this will be examined in future work.

4. Experimental

In order to obtain reproducible deposition, the as-received Pd\textsuperscript{0}(hfac)\textsubscript{2} powder (Aldrich, Milwaukee WI) was re-crystallized. The recrystallization was done by dissolving the Pd\textsuperscript{0}(hfac)\textsubscript{2} into dried, heated (40°C) hexanes (HPLC Grade, Fisher Scientific, Pittsburgh, PA), and sealing the glassware to minimize the evaporation rate. The hexanes were dried by pouring through a filter containing magnesium sulfate anhydrous powder.

Three surfaces were used for the atomic layer deposition of palladium. 110 Å of Ir (99.95 % Alfa Aesar, Ward Hill, MA) was electron-beam deposited onto a Si(100) wafer. 120 Å of W (99.95 % Plasmaterials, Inc., Livermore, CA) was sputter deposited onto a Si(100) wafer. The third surface was a toluene (CMOS Grade, J. T. Baker, Phillipsburg, NJ) dipped Si(100) wafer with native oxide used to approximate typical low-dielectric Si wafer. The Si wafer was cleaned using the standard RCA clean 1 and 2 prior to the toluene dip. The Pd film growth was carried out through a four pulse cycle. First the precursor floods the system depositing a monolayer on the surface, and the system was then purged. Next, the reactive H was introduced (via the remote plasma) to dissociate the precursor forming volatile compounds and reduce the Pd, leaving behind the pure metal atom. 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 palladium via Pd\textsuperscript{0}(hfac)\textsubscript{2}. The base pressure of the vacuum system was 5.0 \times 10^{-7} torr with the use of a roots blower/direct drive roughing pump (Leybold RUVAC WS/WSU 151 and TRIVAC D25 BCS (hydrocarbon precoated)) and a 3.7 L foreline trap (bronze gauze) to prevent
oil backstreaming. The vacuum chamber was warm walled to prevent condensation of the Pd(hfaca)2 precursor. Further, pneumatic valves could turn off or turn on the gas flow and mass flow meters could control the flow of gases into the system under steady state conditions. Three types of depositions were undertaken, one (on), one on a W/WO3 surface, and one on a controlled hydrocarbon contaminated Si surface with native oxide.

The depositions were undertaken at a deposition temperature of 80±5 °C, and a Pd(hfaca)2 sublimation temperature of 47.9±0.2 °C. Pd(hfaca)2, is known to show to volatility at temperatures above 42 °C [6,25]. The depositions were made in 1 or 2 mmol of H2, 105.00 cc/m of H2, 99.999 % Air Products) and 65 W net forward power in a three-turn inductively coupled plasma. The plasma was struck and maintained at ~ 120 mtorr. During each experiment, 55 cc/m Ar (99.999 % Air Products) was flowed as a purge gas, 13 cc/m Ar as a carrier gas for Pd(hfaca)2, and 105.00 cc/m H2 as a reducing gas. The pulse sequence was 15 s of Pd(hfaca)2, followed by 8 s of ‘dead time’ with just 55 cc/m Ar flowing as a purge gas, then 7 s of H2 to allow for steady state in the plasma, and then 15 s of remote H2 plasma with 105.00 cc/m H2 flow and 65 W net forward power. The number of cycles for each deposition was 150. 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 Pd growth was characterized by RBS with the 4.0 MV Dynamiton accelerator at the Ion Beam Laboratory: Department of Physics, University at Albany. Measurements were made with 2.0 MeV 4He particles. RBS determined areal density was converted into an equivalent thickness by dividing by the bulk atomic density of palladium, 6.77×1022 atoms cm–2.

Spectra were collected with a 20 mm2 area beam spot, 2–4 nC of charge, and 3 nA of current.

The surface chemical structure on each sample was analyzed by using XPS. The samples were loaded into the XPS chamber with a chamber base pressure of about 1×10–9 torr, and during a spectrum collection the pressure raised to about 3×10–7 torr. The X-ray Mg Kα source (PHI model 04-151) used in this experiment has a primary energy 1253.6 eV, and a cylindrical energy analyzer controller (PHI Model 15-255G) with a passing energy 50 eV used for high-resolution scans.

The AFM images were taken using an AutoProbe CP (Park Scientific Instruments, TM Microscope). A triangular silicon cantilever with silicon conical tip (Veeco Metrology Group) is used in non-contact mode to measure the surface topography. The tip radius of curvature is < 10 nm. The root-mean-square (rms) roughness is given by the standard deviation of the data, determined using the standard definition:

$$R_{\text{rms}} = \sqrt{\frac{\sum_{n=1}^{N} (z_n - \bar{z})^2}{N-1}}$$

(1)

where $\bar{z}$ = mean z height. The rms roughness refers only to the included areas within a mask. The measurement is referenced to the mean height of the data within that mask.

The RHEED images were taken with a 15 keV electron beam source that produces a 100 μm diameter spot size. The pressure of the stainless steel chamber was ~1×10–10 torr. The high-energy electron beam was incident at 1° from the sample plane. The diffracted electrons pass through two metal retarding grids before striking the phosphor-coated screen, which is imaged using a 16-bit Princeton Instruments CCD camera.

Received: March 15, 2004
Final version: June 1, 2004