Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2017 April 6; 121(13): 7240–7247. doi:10.1021/acs.jpcc.6b12896.

Silver Deposition onto Modified Silicon Substrates

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Abstract

Trimethylphosphine(hexafluoroacetylacetonato)silver(I) was used as a precursor to deposit silver onto silicon surfaces. The deposition was performed on silicon-based substrates including silica, H-terminated Si(100), and OH-terminated (oxidized) Si(100). The deposition processes at room temperature and elevated temperature (350 °C) were compared. The successful deposition resulted in nanostructures or nanostructured films as confirmed by atomic force microscopy (AFM) and scanning electron microscopy (SEM) with metallic silver being the majority deposited species as confirmed by X-ray photoelectron spectroscopy (XPS). The reactivity of the precursor depends drastically not only on the temperature of the process but also on the type of substrate. Density functional theory (DFT) was used to explain these differences and to propose the mechanisms for the initial deposition steps.

Graphical Abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b12896.

Additional XPS and AFM investigations, DFT predictions with B97D3/LANL2DZ, complete ref 29 (PDF)

density functional theory (DFT). These results suggest that by using selected deposition conditions and appropriately prepared substrates, a considerable amount of silver can be delivered in a single deposition cycle. At room temperature, the process investigated is self-limiting, depending on the availability of surface sites available to react with a precursor molecule and to stimulate ligand removal. At elevated temperature, however, thick silver films can be grown based on the same precursor. Both the morphology of the nanostructures/films deposited and the efficiency of the deposition depend on the type of the substrate and surface chemical functionality used to react with the precursor. These parameters may in turn affect a wide range of properties of the resulting materials, including, for example, their optical signatures.^{21,22} In these experiments, silica, hydroxyl-terminated silicon (HO-Si(100)), and hydrogen-terminated silicon (H-Si(100)) were used as the substrates to demonstrate these differences and to test the mechanistic steps leading to silver deposition.

Trimethylphosphine(hexafluoroacetylacetonato)silver(I) ($\text{Ag}(\text{hfac})\text{P}(\text{CH}_3)_3$) was used throughout the experiments because of its unique physical and chemical properties. In particular, the phosphine ligand was reported to play important roles in both antioligomerization and deoxygenation,²³ resulting in the decrease of the oligomerization reactions and the oxygen contaminations in the product. In addition, this precursor was proved to be stable in air, moisture, and ambient light²⁴ while still sufficiently volatile for deposition to occur.²⁵

2. EXPERIMENTAL DETAILS

2.1. Materials

Trimethylphosphine(hexafluoroacetylacetonato)silver(I) (Strem Chemicals, Inc., 99%) was used as purchased as the silver deposition precursor (Figure 1). This compound is a light yellow powder at room temperature and can be introduced into the high-vacuum system via an organometallic precursor doser described below. P-type double-side polished Si(100) wafer (Virginia Semiconductor) was used as the substrate. In particular, the out-of-the-box Si(100) wafer following only the cleaning with deionized water (first-generation Milli-Q water system (Millipore) with 18 M Ω cm resistivity) and ethanol (200 proof, Decon Laboratories, Inc.) in this paper is referred to as “silica”. Without additional cleaning, a native oxide layer is covering this substrate. The OH-terminated silicon substrate (HO-Si(100)) and the H-terminated silicon substrate (H-Si(100)) are prepared from the same wafer following the corresponding etching process (modified RCA procedure) described in detail elsewhere^{26,27} to introduce functional groups onto the silicon surface. Briefly, following the cleaning of the Teflon beakers, the as-received Si(100) samples were kept in a mixture of Milli-Q water, hydrogen peroxide, and ammonium hydroxide (4:1:1 in volume) for 10 min at 80 °C in a water bath. After that, the samples were cleaned with Milli-Q water again and then kept in HF buffer solution for an additional 2 min. Then a mixture of Milli-Q water, hydrogen peroxide, and hydrochloric acid (4:1:1 in volume) was used to react with the samples for an additional 10 min to grow the silicon oxide layer terminated predominantly with Si–OH. Placing these samples in the HF buffer solution again for 1 min would lead to the formation of Si–H functionality as the predominant surface termination.

2.2. Dosing Process

An organometallic precursor doser (McAllister Technical Services) was used to introduce the silver precursor into the high-vacuum system. The detailed description of the doser can be found in ref 28. The precursor was loaded directly into the doser without any further treatment since it is stable under ambient environment.²⁴ During the deposition, the precursor was heated to 100 to 110 °C and introduced into the high-vacuum chamber with a pressure of 2.0×10^{-5} Torr. Depending on the type of the experiments, either a cold substrate (room temperature) or a hot substrate (350 °C) was utilized. For all the experiments performed at room temperature, the dosing time was kept at 1 h. For these experimental conditions, the room-temperature dosing resulted in a self-limiting deposition, as the amount of material deposited and the morphology of the substrates produced did not change if the same dosing procedure was repeated multiple times. For the experiments at 350 °C, different dosing times were used as indicated below to deposit substantially more silver than could be deposited in room-temperature experiments. For each experiment recorded, only one dose was applied and no samples were reused.

2.3. Computational Details

Density functional theory (DFT) calculations were performed using the Gaussian 09 suite of programs²⁹ and GaussView 5 interface. B3LYP functional^{30,31} and LANL2DZ basis set^{32–35} were used to optimize selected structures. B97D3^{36–38} functional was also used to optimize these structures in order to illustrate the dispersion contribution into the calculations. For silica, a $\text{Si}_{22}\text{O}_{38}\text{H}_{20}$ model³⁹ was used with four hydroxyl groups on the topmost surface sites. The bottom layer was fixed for this model in order to avoid unrealistic distortions during structure optimization process. $\text{Si}_9\text{O}_2\text{H}_{14}$ was used to represent the OH-terminated silicon substrate with two neighboring hydroxyl groups on the topmost layer of the surface. Si_9H_{14} cluster was used to represent the H-terminated silicon surface.^{26,27,40}

2.4. Characterization Methods

Atomic force microscopy (AFM) images were acquired under tapping mode with a J-scanner scanning probe microscope (Multimode, NanoScope V). The sensing tips (aluminum coated, Budget Sensor) have a resonant frequency of 300 kHz and 40 N/m force constant. The images were processed with Gwyddion software.

XPS studies were performed using the K-Alpha⁺ X-ray photoelectron spectrometer system from Thermo Scientific. Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) with a 35° takeoff angle was used for all the measurements. The resolution was set to be 0.1 eV. The data were processed by CasaXPS software,^{28,41} version 2.3.17. The carbon 1s peak at 284.6 eV^{28,41} was selected to calibrate all the spectral features.

A Zeiss Auriga 60 FIB/SEM at the W. M. Keck Electron Microscopy facility at the University of Delaware was used to perform all the SEM, focused ion beam (FIB), and energy-dispersive X-ray spectroscopy (EDX) measurements. In-lens detector was used to collect all the images with an accelerating voltage of 6 keV and a working distance of 5.0 mm. FIB was done at a 54° angle with 120 pA current.

3. RESULTS AND DISCUSSION

To verify the successful deposition of silver on the surfaces as well as to probe the chemical state of this element in structures deposited, XPS was utilized. As shown in Figure 2, photoelectron spectra of the silver precursor itself and the silver structures deposited on different surfaces (silica, HO–Si(100), and H–Si(100)) were recorded. In particular, the Ag 3d_{5/2} peak centers at 368.9 eV for the silver precursor itself. In contrast, the Ag 3d_{5/2} peaks from both silica and HO–Si(100) surfaces shift to a lower binding energy to 368.3 eV, indicating the presence of metallic silver.^{42–45} Compared with these substrates, there is virtually no silver signal recorded on the H–Si(100) surface. This significant difference implies that the H–Si(100) surface can be very inert to the silver deposition process at room temperature. The similar Ag 3d_{5/2} intensities on silica and HO–Si(100) surfaces may suggest similar reaction mechanisms for the surface deposition processes on these substrates. The full XPS survey spectra of the samples studied are provided in the Supporting Information section (Figure S1) to show the similarity in terms of the signal intensities, specifically for the two surfaces where efficient deposition has occurred.

To compare the surface morphology of the different substrates, AFM investigation was performed, and the key results are presented in Figure 3. Consistent with the XPS results, there are very few nanoparticles visible on the H–Si(100) surface (Figure 3A). This, again, suggests that the reactivity of the Si–H surface can be the lowest among all the surfaces studied. As for HO–Si(100) and silica surfaces, both of them are clearly decorated with nanoparticles (Figure 3B,C) with a very similar surface particle density. Moreover, according to the particle height distribution shown on the right panel of Figure 3, the average height of the few particles observed on the H–Si(100) surface is approximately 2.6 nm while those on HO–Si(100) and silica surfaces are nearly identical, 6.2 and 5.5 nm, respectively, with very similar size distributions. Considering the fact that the deposition was performed at room temperature, the formation of the nanoparticles on the surface is quite consistent with the results reported previously, suggesting a Volmer–Weber (VW) growth mode.^{46,47} To confirm that the formation of silver nanoparticles is a result of the deposition process, the AFM images of the silica, HO–Si(100), and H–Si(100) surfaces before the silver deposition were also recorded and exhibited no nanoscale features, as shown in the Supporting Information section (Figure S2).

Based on the AFM images, the number of silver atoms deposited on the hydroxylated surface can be estimated by assuming that all the nanoparticles on the surface are hemispheres and by fitting the volume of a unit cell of the silver lattice into the volume of the hemispheres.⁴⁸ Admittedly, this is only an estimate, but it does provide some useful information about the deposition efficiency. For the HO–Si(100) surface, for example, the theoretical number of surface –OH species is calculated to be $9.6 \times 10^{14}/\text{cm}^2$ while the number of silver atoms on the surface is calculated to be $2.6 \times 10^{15}/\text{cm}^2$, suggesting a high reaction efficiency even at room temperature.²⁶ At the same time, based on the high-resolution XPS spectra of P 2p and Ag 3d spectral regions, the atomic ratio of Ag/P is calculated to be 1.2 for the HO–Si(100) surface and 1.6 for the silica surface. It is worth noting that the Ag/P ratio is quite low, close to 1.5 in both cases, and that the binding energy observed for the deposited silver (Ag 3d) corresponds to the metallic silver. Thus, it is very

likely that the resulting surface represents metallic silver nanoparticles covered with $\text{P}(\text{CH}_3)_3$ ligands, and judging by the Ag/P ratio, some of the ligands may spill over to the substrate surface. However, the quantitative analysis based on these XPS measurements alone is quite difficult, since this technique does not necessarily probe the entire volume of the nanoparticles formed and the results are definitely affected by the morphology of the samples formed.

Thus, according to both XPS and AFM results, there is a similarity in terms of the surface particle size as well as the density of the deposited silver nanoparticles for HO–Si(100) and silica surfaces. On the other hand, the H–Si(100) surface shows very different results compared to these two surfaces. Along with a very weak silver signal in XPS, only a few nanoparticles, likely nucleated at the surface defect sites, can be observed in the AFM investigation. This comparison strongly implies that the silver precursor has a very different reactivity toward the H–Si(100) surface compared to the other two surfaces (HO–Si(100) and silica). At the same time, the precursor exhibits very similar reactivities on HO–Si(100) and silica surfaces. The nature of the similarities and differences should originate from the surface reaction mechanism, which will be discussed in detail later.

To test the surface morphology, SEM images were also recorded to show the differences among the substrates. As illustrated in Figure 4A, only a few nanoparticles can be observed on the H–Si(100) surface, which is consistent with the XPS and AFM results discussed previously. In comparison, the nanoparticles cover most of the HO–Si(100) and silica surfaces (Figure 4B,C). It is worth noting that the HO–Si(100) surface seems to lead to some agglomeration not observed on silica, as a number of larger particles are shown in Figure 4B.

Judging from the XPS, AFM, and SEM data, it is reasonable to assume that the particle morphology is related to the functionalization of the surface. Hence, computational calculations following possible surface reactions of silver precursor molecule with these functionalities should be helpful in explaining these differences. One observation that can be helpful in designing appropriate surface reaction pathways is provided by XPS. Careful examination of the XPS spectra suggested that following the deposition, no F 1s signal is recorded for any of the surfaces studied. On the other hand, the P 2p signal was clearly detected (Figure S3). This may suggest that following the silver deposition, the hfacH moiety is removed, very likely by forming a hfacH molecule that desorbs from the surface, leaving the $\text{AgP}(\text{CH}_3)_3$ moiety attached. Based on this observation, DFT calculations were performed for the interactions between different substrates (H–Si(100), HO–Si(100), and silica) and the silver precursor leading to the removal of the hfacH molecule to address two major questions: why were fewer particles observed on the H–Si(100) surface compared to other two surfaces, and what was the driving force of the deposition process?

Figure 5 illustrates the simulations of the reactions between the precursor studied and the differently functionalized solid substrates. For the interaction between the precursor and H–Si(100) surface (Figure 5A), a very weak adsorption (E of -4.8 kJ/mol) is predicted. However, when it comes to HO–Si(100) and silica, the adsorption energy becomes much more substantial, -93.7 and -114.5 kJ/mol, respectively. For the last two cases, the oxygen

atoms in the hydroxyl groups play a critical role in stabilizing the precursor on the surface by forming hydrogen bonds as shown in Figure 5B,C. For H–Si(100) surface, however, the absence of the oxygen atoms in the topmost layer makes the surface less “attractive” to the precursor; hence, less metal is deposited, and fewer nanoparticles are formed on the surface as a result. Also, both HO–Si(100) and silica surfaces follow a very similar energetic diagram, indicating a similar reaction mechanism and similar adsorbed moieties for both surfaces. In order to take dispersion force into consideration, B97D3 functional was also used instead of B3LYP for each structure shown above, and the results followed a very similar trend (Figure S4).

The results above show that the silica and HO–Si(100) surfaces exhibit very similar behavior with respect to silver deposition leading to very similar surface morphology. It is expected since both surfaces are covered with OH-functional groups. On the other hand, however, the H–Si(100) surface shows a very different chemical reactivity toward the precursor leading to a very different surface morphology following the deposition at room temperature. Thus, following this initial assessment, most of the comparisons in the remaining experiments will be between silica and H–Si(100) surfaces. In order to test the influence of the substrate temperature on the deposition process, the silica substrate was heated to 350 °C to perform the deposition. The high temperature is expected to accelerate the deposition process and lead to a higher deposition rate. Figure 6 unveils the resulting XPS spectra of the samples deposited at room temperature and at 350 °C. Compared to the room-temperature experiment, the Ag 3d signal increased dramatically in the survey spectra (Figure 6A) after the deposition at 350 °C, indicating a significant increase of the amount of silver on the surface. Also, the intensity of Si 2p and O 1s plummeted after the high-temperature deposition, implying again that the surface is dominantly covered with silver. As for the Ag 3d spectra (Figure 6B), the binding energies at 368.3 eV for Ag 3d_{5/2} and 374.3 eV for Ag 3d_{3/2} again suggest the existence of metallic silver on the surface.

To further confirm the existence of silver deposition on the surface, SEM and EDX were performed to the silica surface after the high-temperature deposition. As shown in Figure 7, nanoparticles are clearly deposited on the silica surface with a fairly high surface coverage. The observed width of the nanoparticles is about 20–30 nm. To investigate the chemical composition of the particles, EDX was performed at two different locations shown in the figure (A (area EDX) and B (single point EDX)). Consistently 7.2% and 6.1% of silver were observed at A and B regions, respectively.

AFM was also performed to interrogate the topography of the resulting surfaces. In particular, silica and H–Si(100) surfaces are compared after the deposition of silver at 350 °C as shown in Figures 8A and 8C, respectively. As discussed previously, the absence of oxygen atoms on the H–Si(100) surface makes it very inert to react with the silver precursor. Only a few nanoparticles, similarly to the room-temperature process, can be observed on the surface after the deposition at 350 °C (Figure 8C). On the other hand, the silica surface is packed with nanoparticles (Figure 8A) with an apparent height of 3–5 nm (Figure 8B). This difference is consistent with the deposition results acquired at room temperature. Namely, compared to the other types of surfaces, the H–Si(100) surface is less reactive to the silver precursor, even as the surface temperature is increased substantially.

To further compare the differences between silica and H-Si(100) surfaces with respect to silver deposition, XPS was also performed for the two surfaces (Figure 9). Consistent with the AFM images, there is virtually no silver signal from the H-Si(100) surface after the deposition while a strong signal of silver is recorded for the silica surface.

From the previous discussion, it is obvious that high temperature (350 °C) deposition can lead to denser surface nanoparticles, but it is still not clear if this would result in the formation of a continuous thin film on the surface. To answer this question, a different set of experiments were performed. The deposition pressure was increased from $\sim 10^{-5}$ to $\sim 10^{-2}$ Torr, and the duration of the deposition process was changed to 2 or 4 h instead of 1 h while the temperature was still kept at 350 °C.²⁵ The increased pressure and deposition time should affect the deposition efficiency and thus the film thickness and surface morphology. Figure 10 presents the AFM image and the corresponding surface particle height profile following silver deposition under these conditions. Compared to the previous samples, the particles acquired under this condition appear to be much larger (in apparent height) and yield a much denser structure. Overall, this deposition protocol favors columnar growth, although it is not clear if there is 2D silver film formed beneath the columnar structures. Based on these results, it appears that the growth at these conditions still follows the Volmer–Weber mode; however, the Stranski–Krastanov mode also cannot be ruled out.

To better understand the factors that may affect the growth of the silver nanostructures as well as to unveil the film-growth mode, another experiment was also performed. This time, the silver precursor was dosed at $\sim 10^{-2}$ Torr for 4 h with the substrate temperature of 350 °C. SEM and FIB were utilized to follow the morphology of the surface as well as to follow the profile of the film deposited. As shown in Figure 11, compared to the lower pressure deposition, Figure 11B shows a thicker, approximately 75 nm, layer of deposited silver. Based on the image presented in Figure 11B, it appears that at these conditions Stranski–Krastanov growth mode for the silver nanoparticles can be achieved, similarly to the previous investigations.^{49–51} For the surface treated with lower pressure and shorter time (Figure 11A,C), there is no continuous layer deposited. Hence, by increasing the dosing time and the pressure, a thicker layer of silver is proved to grow on the silica substrate; however, the structure of this film suggests that additional treatments may be necessary depending on the potential applications of this system.

4. CONCLUSIONS

The reactivity of three different types of surfaces (H-Si(100), HO-Si(100), and silica) toward trimethylphosphine(hexafluoroacetylacetonato)silver(I) ($\text{Ag}(\text{hfac})\text{P}(\text{CH}_3)_3$) was examined at room temperature and at 350 °C. The results prove that compared to the HO-Si(100) and silica surfaces, H-Si(100) surface is very inert to the silver precursor. Basically no deposition, except for a few particles likely formed at defect sites, can be observed either at room temperature or at 350 °C for this surface. On the other hand, the HO-Si(100) and silica surfaces have a very similar reactivity toward the precursor. The silver nanoparticles formed on those surfaces also have a very similar morphology. With increased vapor pressure of the precursor molecule in the gas phase and deposition time, the silver film can be formed on silica surface at 350 °C. DFT calculations explained the reason for this

difference based on the initial surface reactivity. Namely, the oxygen atoms of the hydroxyl groups on the topmost layer of the surface play a critical role in the reaction process. By forming hydrogen bonds, the HO–Si(100) and silica surfaces are very “attractive” to the precursor, so the reaction is more likely to occur. The absence of hydroxyl groups on the H–Si(100) surface results in the poor reactivity toward the silver precursor and virtually inefficient deposition even at the deposition temperature of 350 °C.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also partially supported by the National Science Foundation (CHE1057374 and DMR1609973 (GOALI)). Additional partial support was provided by the University of Delaware Research Foundation Strategic Initiatives (UDRF-SI) Grant. The authors acknowledge the NSF (9724307; 1428149) and the NIH NIGMS COBRE program (P30-GM110758) for partial support of activities in the University of Delaware Surface Analysis Facility.

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Figure 1.

Structure of the silver precursor trimethylphosphine(hexafluoroacetylacetonato)silver(I).

Black = carbon, cyan = fluorine, red = oxygen, blue = hydrogen, green = silver, and yellow = phosphorus.

Figure 2.

XPS spectra of the silver precursor $\text{Ag(hfac)P(CH}_3)_3$ powder (A) and the deposited silver following the deposition on different substrates (from top to bottom: silica (B), HO-Si(100) (C), and H-Si(100) (D)) at room temperature.

Figure 3. AFM images of the different surfaces (A: H-Si(100); B: HO-Si(100); C: silica) following the deposition of silver from the $\text{Ag}(\text{hfac})\text{P}(\text{CH}_3)_3$ precursor at room temperature and the corresponding particle height distribution.

Figure 4. SEM images of the surfaces (A: H-Si(100); B: HO-Si(100); C: silica) following the deposition of silver from the $\text{Ag}(\text{hfac})\text{P}(\text{CH}_3)_3$ precursor at room temperature.

Figure 5.

DFT predictions of the reactions between the $\text{Ag(hfac)P-(CH}_3)_3$ silver precursor studied and H-Si(100) (A), HO-Si(100) (B), and silica (C). Gray = silicon, cyan = fluorine, red = oxygen, blue = hydrogen, green = silver, yellow = phosphorus, and black = carbon.

Figure 6.

XPS spectra showing the comparison of (A) the survey spectra of the silica surface after the deposition process with the $\text{Ag(hfac)P(CH}_3\text{)}_3$ precursor at room temperature and at 350 °C and (B) the silver (Ag 3d spectral region) spectra of the silica surface after the deposition at room temperature and at 350 °C.

Figure 7.

SEM image of the silver nanoparticles on the silica surface following the deposition process with the $\text{Ag(hfac)P(CH}_3)_3$ precursor at 350 °C. The white box (A) and the white arrow (B) indicate the locations where EDX was taken.

Figure 8. AFM image of the silver nanoparticles on the silica surface after the deposition from $\text{Ag(hfac)P(CH}_3)_3$ at 350 °C (A) and the corresponding line profile for the surface indicated by the white line in part A (B). (C) AFM images of H-Si(100) surface after the deposition at 350 °C.

Figure 9. XPS spectra of silver after the deposition at 350 °C for silica surface (top) and H-Si(100) surface (bottom).

Figure 10.

AFM image (top) of the silica surface after the silver deposition from $\text{Ag}(\text{hfac})\text{P}(\text{CH}_3)_3$ precursor at $\sim 10^{-2}$ Torr at 350 °C for 2 h and the corresponding line profile (bottom) indicated by a white line in the image.

Figure 11.

SEM images of the silica surfaces after depositions from $\text{Ag(hfac)P(CH}_3)_3$ precursor under different conditions. For (A) and (C), the deposition was performed at 350 °C with $\sim 10^{-5}$ Torr pressure for 1 h. For (B) and (D), the deposition was performed at 350 °C with $\sim 10^{-2}$ Torr pressure for 4 h. (A) and (B) were recorded at a 54° angle in order to estimate the thickness of the deposited silver layer. The cavities in (A) and (B) are the results of FIB (focused ion beam) application.