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Atmospheric pressure plasma enhanced spatial ALD of silver

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The authors have investigated the growth of thin silver films using a unique combination of atmospheric process elements: spatial atomic layer deposition and an atmospheric pressure surface dielectric barrier discharge plasma source. Silver films were grown on top of Si substrates with good purity as revealed by resistivity values as low as 18 μΩ cm and C- and F-levels below detection limits of energy dispersive x-ray analysis. The growth of the silver films starts through the nucleation of islands that subsequently coalesce. The authors show that the surface island morphology is dependent on surface diffusion, which can be controlled by temperature within the deposition temperature range of 100–120 °C. © 2014 American Vacuum Society.

I. INTRODUCTION

Silver thin films can have many potential applications, for instance, in nanoscale lithography, single-biomolecule detection, and high-efficiency photovoltaics. As with most thin metal films, silver films have been reported to have a nanocrystalline morphology, and potentially uncoalesced and nanoparticulate morphologies at early stages of the film growth. Accurate control of film morphology, thickness, and conformality over large areas of these metal films is key in tailoring the film parameters for each specific application. Atomic layer deposition (ALD) is a technique with potential to meet these challenges, and recently, the deposition of silver films using conventional, vacuum-based ALD has been described in literature. However, for applications in high-volume and low-cost manufacturing, such as thin film photovoltaics, conventional ALD has some drawbacks in terms of upscaling and throughput due to its low deposition rate. In the last few years, spatial atomic ALD has shown to enable the same high level of control as conventional ALD at industrial scales. Hence, spatial ALD is also an interesting candidate for large area and high throughput silver thin film deposition.

The silver ALD processes reported in literature requires plasma activation of the silver precursor. Yet, plasmas used in conventional plasma enhanced (PE-)ALD are typically low-pressure plasmas that can contain quite different physicochemical species than those at atmospheric pressures. In the past 20 years, the number of publications about atmospheric plasma-enhanced deposition has grown explosively as pointed out in a recent review by Merche et al. So far, only a few studies on PE-ALD of silver have been published, all of them involving conventional ALD using a remote low-pressure plasma source. Only recently, atmospheric pressure plasmas have been used in (spatial) ALD of oxides.

In this paper, we demonstrate for the first time spatial atmospheric plasma enhanced ALD of silver films from Ag(fod)(PET3), triethylphosphine(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) silver(I), and an N2–H2 plasma. This process combination allows us to accurately control film morphology at processing speeds up to 0.8 nm/min for all atmospheric conditions compared to a maximum of 0.15 nm/min as reported by Kariniemi et al. for the case of conventional plasma-enhanced ALD. Films with a morphology ranging from low-coverage islands to high-coverage conductive and coalesced films have been deposited. We show that the spatial ALD deposition process is strongly determined by the growth temperature. Thus, the surface morphology of the silver film (especially, island size and nucleus density) can be carefully controlled by this parameter.

II. EXPERIMENT

Plasma enhanced spatial ALD based on a dielectric barrier discharge was carried out at atmospheric pressure in a rotary reactor as described in Refs. 12 and 13. The plasma source design is derived from a surface dielectric barrier discharge (SDBD) design. In our design, both electrodes are in contact with the dielectric barrier, the dielectric used...
being sintered alumina.\textsuperscript{15} This electrode configuration creates a homogeneously distributed plasma over large areas and high plasma power density (typically, 5–10 W/cm\textsuperscript{2}). A cross-section of the setup including the electrode configuration is schematically shown in Fig. 1.

The active surface plasma has an elongated rectangular shape, characterized by a typical width and length of 7 and 30 mm, respectively. The SDBD plasma is operated in an N\textsubscript{2}-H\textsubscript{2} gas mixture supplied at both sides of the linear source. The transport of the N\textsubscript{2}-H\textsubscript{2} gas to the plasma region depends on the diffusion as well as the flow of the gas underneath the active plasma zone due to movement of the substrate.

The SDBD plasma is operated with a home-built alternating high-voltage pulsed power supply providing pulses with an amplitude of 5 kV, 5 \(\mu\)s pulse width, and 50 kHz pulse repetition frequency. At these electrical settings, the typical power dissipation in the above described SDBD plasma source amounts 22.5 W.

The SDBD plasma is created parallel to the horizontally rotating substrate in a high electric field (typically, 5–25 kV/mm) between a high voltage electrode, which is covered by the dielectric barrier, and a pair of grounded exterior electrodes. The alternating high electric field is concentrated on the dielectric barrier surface and sufficiently high for ionization of the gas at atmospheric pressure, the degree of ionization is typically 0.5 \(\times\) 10\textsuperscript{-4}.

The setup comprises a gas injector head with various gas inlets and outlets. The substrate is transported along the gas injector head and repetitively exposed to the coating precursor, nitrogen purging, plasma treatment, and again nitrogen purging. The gas in- and outlets serve additionally as gas bearing providing a thin gas layer between the gas injector head and the substrate. The gas bearing gap is in 20–40 \(\mu\)m range. Si wafers of 150 mm with a native oxide layer on top were used as a substrate. Triethylphosphine(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) silver(I) \([\text{Ag(fod)}(\text{PET}_{3})]\) supplied by Strem Chemicals was used as the silver containing precursor.

The exposure time \(t\) to the silver precursor of a point at a specific radius \(r\) on the rotating sample is directly related to the width of the gas injector head \((w = 12 \text{ mm})\) and the angular frequency \(\omega\) as \(t = w/(\omega r)\). Typically, the exposure time of the precursor was varied between 25 and 150 ms.

\(\text{Since the ratio of the plasma width and the gas injector head width is fixed at } 0.6, \text{ the plasma exposure time cannot be varied independently of the precursor exposure time.}\)

The precursor was evaporated by flowing argon gas over the liquid precursor at the same temperature as that of the reactor. Deposition temperatures used are 100 and 120 \(^\circ\)C. The lower temperature limit was determined by the low vapor pressure of the precursor. The instability of the precursor gas\textsuperscript{4} limits the temperature window with a higher limit of 120 \(^\circ\)C. To prevent the influence of light and temperature induced aging of the Ag-precursor at these temperatures, fresh precursor was loaded into the evaporation vessel prior to each set of experiments. The typical value for the Ar carrier gas flow through the silver precursor container was 1500 sccm Ar and for the plasma gas 600 sccm N\textsubscript{2}/800 sccm H\textsubscript{2}.

The thickness of the deposited films was determined by profilometry (Dektak) using a stylus with 5 \(\mu\)m diameter and 3 mg force. The composition of the silver films was measured by energy dispersive x-ray analysis (EDX). The structure was imaged with high resolution scanning electron microscopy and analyzed using the free image processing software ImageJ.\textsuperscript{16} The resistivity of the films was measured with a four-point-probe. Optical characterization was done with spectroscopic ellipsometry using a J.A. Woollam M2000 rotating compensator ellipsometer in the 300–1000 nm range at an angle of incidence of 75.06\(^\circ\).

\section*{III. RESULTS}

Silver films were successfully deposited on silicon wafers. For the silver films deposited at 120 \(^\circ\)C, we have studied the effect of the exposure time of the precursor on film growth (Fig. 2). Due to the fixed reactor head design this is automatically coupled to a fixed plasma exposure time. The layer thicknesses and the corresponding data for the growth per cycle could not be measured unequivocally by spectroscopic ellipsometry, because of the complex optical behavior caused by the silver film morphology that makes it difficult to model the SE measurements. The optical

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(Color online) Schematic representation of gas injector head used for spatial ALD with plasma enhancement by an interrupted surface dielectric barrier discharge. The N\textsubscript{2} inlets depict the gas bearing and the two sections depict the inlets for the reactive species (on the left, the metal precursor and on the right, the plasma source with N\textsubscript{2}-H\textsubscript{2} supply).}
\end{figure}

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(Color online) Step height of silver layer after 2250 cycles at 120 \(^\circ\)C as a function of exposure time of the silver precursor. Note that the reaction time of the plasma scales linearly with the silver precursor exposure time, and cannot be varied independently for our setup due to the fixed configuration of the injector head.}
\end{figure}

The response of the silver films is however in accordance with literature. A typical spectrum of a deposited silver film is shown in Fig. 3. Here, a volume plasmon resonance peak at 3.8 eV and a localized surface resonance plasmon peak are visible around 2.2 eV. We have used the step height measured by profilometry as an indication for the growth rate of silver deposited per cycle. The step height values in the graph were measured using profilometry perpendicular to a scratch in each thin film. Forces as low as 3 mg were used to prevent the profiler stylus from scratching the ductile deposited material. As long as the separation between the grown islands is smaller than the diameter of the tip (<5 µm), the step height can be taken as a measure of island thickness, i.e., vertical growth. Figure 2 shows that the step height (which we take as a measure for growth rate) increases with increasing exposure times, which is typical for the subsaturated regime. However, it does not reach the saturated regime for longer exposure times and the GPC remains below the values reported elsewhere. This limitation might be caused by the maximal dose that we can supply with our evaporation system size, which may have been designed too small to accomplish full saturation. For the even higher exposure time, a drop in step height was observed. SEM images of these layers confirmed that indeed the amount of material deposited was lower and the sudden drop in growth rate was not an artifact caused by the measurement method. The lower growth rate for higher exposure times can be explained by several effects on the surface, including (1) surface poisoning by NH3, (2) the redeposition and poisoning or etching effects of precursor fragments, and (3) the H2 gas diffusion and dosing under the plasma source influencing the rotation speed. The hydrogen gas is dosed next to the source (Fig. 1) and is transported through diffusion and laminar flow caused by the rotation. This laminar flow reduces with decreasing rotation speed. For low rotation speeds (larger exposure times), the H2 supply to the source will be diffusion limited, thus decreasing the amount of active species for reaction.

The purity of the silver films was investigated by EDX. The silver films and Si-wafers were shown to contain Si, Ag, and O, with silicon being the main contributor to the EDX signal. The O/Ag ratio was determined to be approximately 0.3. This relatively high oxygen-content can be expected because of the presence of a native oxide on the Si-wafers and on the silver films itself formed during storage. No additional contamination such as fluorine or carbon was detected using EDX.

Resistivity measurements on a closed layer (>95% coverage) of 50 nm film thickness grown at 100°C gave a resistivity value of 18 µΩ cm as best result, i.e., roughly 10 times higher than that of bulk silver. The resistivity for thinner and, therefore, less coalesced layers quickly increased because these layers contain more limited percolation paths. SEM images of this high-coverage layer show a layer built up from coalesced islands (bright parts of the image) with multiple conduction pathways present (Fig. 4) and dark worm-shaped interspacing areas between the coalesced islands. Because these interspacing areas prevent current to percolate through the shortest distance these are expected to cause the increase in resistivity relative to the bulk value for silver.

A. Surface morphology

Figures 4 and 5(a) show the stages of deposition after 2250 and 4500 cycles in the growth of the silver layer. Figure 4 shows an almost fully covering layer (4500 cycles). When carefully examined one can see that this layer consists of smaller islands coalesced together. Silver growth is known to proceed through Volmer–Weber island growth and this is caused by the high surface energy of most metals, that of silver being 1.25 J m⁻². Figure 5(a) represents an earlier stage in the growth of this layer (2250 cycles). The micrograph
shows bright rounded islands on a darker background (Si wafer). We have studied this island growth regime in more detail and found the surface morphology, i.e., density of island nuclei and distribution and size of nuclei, is changing for different temperatures and exposure times.

At 100 °C and 57 ms exposure time, we found a large amount of small islands (average of 22 nm in diameter, bright round shapes on a black background) closely packed together [nucleation density of 18/100 nm², Fig. 5(a)]. At a higher temperature of 120 °C and 57 ms exposure time, we found a smaller amount of islands per 100 nm² (12.5/100 nm²) with a larger diameter (average of 28 nm) and a larger inter-spacing between these islands for the same amount of ALD cycles [Fig. 5(b)]. Not only the diameter of these islands is different at different temperatures but also the 3D shape. At 100 °C, the ratio between average diameter and height of the islands is >1 which results in a flattened shape. At 120 °C, this ratio is close to 1 resulting in more isometric shaped islands. The corresponding statistical particle size distribution of the islands grown at 100 and 120 °C for three exposure times is shown in Fig. 6. As we are mainly interested in the size of single particles, the coalescence was taken into account for the measurement of the particle size by only measuring the width and not the length of the very elongated wormlike structures. The particle size distribution shows a log-normal distribution in agreement with literature. Two trends can be recognized in these plots: increasing islands size with increasing temperature and increasing islands size with increasing exposure time [illustrated in Fig. 7(a)]. This graph shows a nonlinear increase for the 120 °C dataset, which can be explained by a sudden increase of particle size upon coalescence. The 120 °C dataset shows a higher degree in coalescence, which could be the reason for the influence on the particle size. The coverage of the surface [Fig. 7(b)], however, shows a linear trend for both temperatures, which agrees with conformal deposition of material. The increase of the coverage with exposure time points to deposition in the undersaturated regime.

Next to the island size we also investigated the amount of nuclei per 100 nm² [Fig. 7(c)]. The error bar for these measurements increases with increasing coalescence of islands as
it becomes harder to distinguish between individual nuclei. However, this graph shows clearly that the number of nuclei does not depend on exposure time. It does depend on the temperature and it decreases with increasing temperature.

IV. DISCUSSION

As the results show, one of the parameters influencing the surface morphology is the deposition temperature. A change in temperature influences both (1) the deposition rate and (2) the surface diffusion rate of deposited silver atoms or clusters. In turn, these two parameters influence the nucleation and growth kinetics and, consequently, the surface morphology. The exposure time on the other hand does also influence the deposition rate, yet it does not influence the surface diffusion rate. The surface morphology is determined by the nucleation density of islands and the amount of material deposited, which are influenced by these two parameters.

From mean-field nucleation theory as described by Brune, the nucleation island density, \( n_x \), depends on three parameters: (1) the flux rate \( F \) at which atoms arrive from the gas phase (in atoms per surface unit cell and per second, i.e., in monolayers per second, ML s\(^{-1}\); (2) the critical cluster size \( i \) dynamically defined as the size at which cluster growth is larger than cluster decay rate; and (3) the surface diffusion rate \( D \) at which an adatom meets a second diffusing atom to create a dimer. It can be derived that the expression for the island density \( n_x \) and for the case of such stable and larger clusters is

\[
    n_x = \eta(\Theta, i) \left( \frac{D}{F} \right)^{-\chi} \exp \left( \frac{E_i}{(i + 2)kT} \right),
\]

with the scaling factor \( \chi \) being \( \chi = \frac{i}{i + 2} \),

\[
    \eta(\Theta, i) = \Theta \frac{i}{i + 2} \exp \left( \frac{E_i}{(i + 2)kT} \right) - \frac{1}{i + 2} \exp \left( \frac{E_i}{(i + 1)kT} \right).
\]

In our experiments, both the deposition rate and surface diffusion coefficient increase with increasing deposition temperature and we observe a decreasing nucleation density with increasing temperature. From Eq. (2), it follows that the nucleation density scales positively with the deposition rate and inversely with the surface diffusion rate. The silver flux rate \( F \) increases with temperature, because the precursor dosing is dependent on the temperature while the system is not saturated. This is related to the placement of the Ag precursor evaporator inside the convection furnace, which heats the ALD reactor. Consequently, the nucleation density will scale positively with temperature if it was deposition rate dependent. Yet, it scales inversely with temperature. Thus, we can conclude that the nucleation density and, consequently, the morphology of the silver films is determined by surface diffusion. Figure 7(c) shows that the nucleation density is only influenced by the temperature. This indicates that the temperature influences the surface diffusion to a far larger extent than it does influence the growth rate.

As Eq. (2) shows there should also be a regime possible where an increase in flux rate should cause accelerated nucleation, but this regime is not reached in this study. This indicates that the flux rates are too low to affect the nucleation rate. Although one might expect the growth rate to play a larger role in the kinetics for spatial ALD where the shorter exposure times and process times might prevent atoms from diffusing over their full temperature dependent diffusion lengths. As is illustrated in Figs. 2, 7(a), and 7(b), the growth rate, linked to island height (vertical growth rate), diameter, and surface coverage (lateral growth rate), largely depends on the exposure time. Especially at short exposure times in the undersaturated regime the overall growth rate is strongly determined by exposure time. With larger exposure times, the saturated regime is not reached (Fig. 2). This could be due to the causes mentioned earlier in this article (NH\(_3\),...
poisoning, precursor fragment effects, and plasma gas diffusion. The influence of these growth limiting factors increases with increasing plasma exposure time. One can expect that with longer silver precursor exposure times and shorter/intermediate plasma exposure times it would be possible to achieve saturation. However, to verify this, we would need a more flexible design of the injector head than we used so far in our rotary reactor. The present injector had a design with fixed, thus coupled areas for precursor injection and plasma exposure. This coupling excludes an easy mutual variation of exposure times. However, more flexible injector designs with optimized dimensions for the respective exposure zones can certainly be made to overcome this restriction.

To be able to grow an as thin as possible closed silver film, one would like to combine high growth rate and low surface diffusion in the most effective way. For future work, it would therefore be interesting to use a precursor with a higher vapor pressure (with similar reactivity and stability) in order to enable deposition at even lower temperatures and to suppress the surface diffusion even more, without reducing the growth rate. Another application of the temperature dependence of the surface morphology that we found is the possibility to deposit films with specific (tailor-made) island distributions. These island structures might be preferred over silver films because of their high surface-to-volume ratio tailored for catalysis, sensors and photothermic processes, and/or specific plasmonic properties that enhance the optical performance of devices.

V. SUMMARY AND CONCLUSIONS

For the first time, silver thin films have been deposited using spatial atomic layer deposition combined with an atmospheric surface DBD plasma source. We have deposited silver films with several different surface morphologies, such as island structures and largely closed films at speeds of up to 0.8 nm/min. The best coalesced silver film showed a resistivity of 18 μΩ cm. In the temperature range of 100–120 °C, we have shown a surface diffusion limited process regime with the nucleation density decreasing with increasing temperature. The surface diffusion can be used to control the film morphology by adjusting the deposition temperature within this temperature regime.

10S. M. Prokes and O. J. Glembocki, ECS Trans. 64, 279 (2014).