Epitaxially aligned submillimeter-scale silver nanoplates grown by simple vapor transport†

Youngdong Yoo,†a Si-in Kim,b Sol Han,b Hyoban Lee,b Jihwan Kim,b Han Sung Kim,c Jae-Pyoung Ahn,c Taejoon Kang,c d,e Jaebum Choo e and Bongsoo Kimf K

Epitaxially aligned large silver (Ag) nanoplate arrays with ultraclean surfaces are very attractive for novel plasmonic applications. Although solution-phase methods have been extensively employed to synthesize Ag nanoplates, these cannot be used to grow epitaxial large Ag nanoplates on substrates. Here we report a vapor-phase synthetic strategy to epitaxially grow submillimeter-scale Ag nanoplates on a variety of substrates. By simply transporting Ag vapor to the substrates at an optimal temperature (820 °C), we synthesize ∼100 μm-sized Ag nanoplates with atomically clean surfaces, which are three-dimensionally aligned on the substrates. We demonstrate that both the type of supported seed and their interfacial lattice matching with the substrates determine the epitaxial growth habit of the nanoplates, directing their crystallinity, shape, and orientation. (i) On r-cut sapphire substrates, twinned pentagonal nanoplates grow vertically from twinned triangular seeds through a seed → nanoplate process. (ii) On m-cut sapphire substrates, twinned trapezoidal Ag nanoplates grow slantingly from twinned decahedral seeds through a seed → NW → nanoplate process. (iii) Interestingly, twin-free single-crystalline trapezoidal Ag nanoplates grow from twin-free square pyramidal seeds on STO (001) substrates through a seed → NW → nanoplate process. The epitaxially aligned Ag nanoplate arrays could serve as a new platform for two-dimensional (2D) guiding of surface plasmons as well as for hierarchical 3D plasmonic nanoarchitecturing.

Introduction

Silver (Ag) nanostructures have been widely utilized for various applications, including optical sensing, biological imaging, medical therapy, catalysis, and surface-enhanced Raman scattering (SERS) sensing.1–7 The physical and chemical properties of the Ag nanostructures can be tailored by controlling their shape (e.g., nanoparticles, nanowires, or nanoplates).8–12 Ag nanoplates are two-dimensional (2D) plasmonic nanostructures that show unique optical properties, such as their intense quadrupole resonance, which are not observed in structures that show unique optical properties, such as their nanoplates are two-dimensional (2D) plasmonic nanoarchitecturing.

Received 24th May 2019,
Accepted 11th September 2019
DOI: 10.1039/c9nr04422a
rsc.li/nanoscale

†Electronic supplementary information (ESI) available: Fig. S1–S3. See DOI: 10.1039/c9nr04422a
tional vapor–liquid–solid (VLS) growth and because fcc metals do not have any particular driving force for 2D growth in vapor phase due to their isotropic crystal structure.

In this work, we report the epitaxial growth of submillimeter-scale Ag nanoplates in selective orientations on various substrates through a simple vapor transport method. The nanoplates synthesized by this method are much larger than those obtained using other techniques and their surface is uniquely clean and perfect at the atomic level. In addition, we show how an fcc metal, silver (Ag) can grow in two dimensions in vapor phase starting from supported seeds in diverse shapes. The geometry and orientation of seeds, together with their interfacial matching with the substrate, determine the growth mechanism of the nanoplates. We investigate the epitaxial growth of Ag nanoplates from twinned triangular seeds, twinned decahedral seeds, and twin-free square pyramidal seeds respectively formed on r-cut sapphire, m-cut sapphire, and SrTiO$_3$ (STO) (001) substrates.

Results and discussion

Vertical growth of twinned pentagonal Ag nanoplates on r-cut sapphire: seed $\rightarrow$ nanoplate process

To synthesize Ag nanoplates, we used a simple vapor transport method employing an Ag slug as a precursor, which was heated to 820 °C. We employ a variety of substrates to investigate how the growth habit of the Ag nanoplates changes depending on the kind of substrates employed. We first discuss the growth of Ag nanoplates on an r-cut sapphire substrate. After 2 h of reaction, pentagonal Ag nanoplate arrays grow vertically over a large area on an r-cut sapphire substrate, as shown in the 45° tilted-view and top-view scanning electron microscopy (SEM) images (Fig. 1a–d). The vertical nanoplates, grown in a single direction, have bottom side lengths of 30–80 μm and thicknesses of 180–230 nm. Fig. 1e shows a transmission electron microscopy (TEM) image of a relatively small and thin nanoplate, clearly showing its pentagonal geometry. The inset in Fig. 1e shows a selected area electron diffraction (SAED) pattern obtained from the nanoplate. All the diffraction spots are indexed to {220} planes of a fcc Ag structure, and the zone axis is along a $<111>$ direction, which is perpendicular to the main large plane of the nanoplate. Thus, the main plane of the nanoplate is {111}. The direction of the bottom side of the pentagonal nanoplates interfaced to the substrate is $<211>$ and the directions of the other four sides are $<110>$. Fig. 1f shows a high-resolution TEM (HRTEM) image corresponding to the red square area in Fig. 1e. This image confirms that the lattice spacing of the planes perpendicular to the side direction of the nanoplate is 0.145 nm, which agrees with the spacing of the {220} planes of the fcc Ag structure.

Fig. 1. Ag nanoplates grown vertically on an r-cut sapphire substrate. (a and b) 45° tilted-view and (c and d) top-view SEM images of the nanoplates at low and high magnifications, respectively. (e) TEM image and SAED pattern of the nanoplate. (f) HRTEM image of the red square in (e). (g) Cross-sectional TEM image of the nanoplate, which was cut along the plane perpendicular to the side of the nanoplate. (h) HRTEM image and FFT patterns of the cyan square in (g). Regions A, B, and C are distinguished by two twin planes. All zone axes of the three FFT patterns are $<110>$ directions. Yellow and cyan circles indicate the {200} and {111} reflections, respectively.
We performed cross-sectional TEM measurements to examine the crystallinity of the nanoplates. The cross-sectional specimen was prepared using a focused-ion beam (FIB) technique after the nanoplate was transferred onto a Si substrate. The nanoplate was cut along the plane perpendicular to the side of the nanoplate. The cross-sectional TEM image of the nanoplate shown in Fig. 1g and the HRTEM image in Fig. 1h, which corresponds to the cyan square in Fig. 1g, clearly show that the nanoplate possesses two twin planes parallel to its main planes. The twin planes not only act as internal confinement in the crystal growth process but also form reentrant grooves on the side planes of the crystals, facilitating their 2D growth. These reentrant grooves are also clearly observed on the side planes of the Ag nanoplates vertically grown on the substrate (Fig. 1d). The zone axis is along the (110) direction in this cross-sectional TEM measurement. The three fast Fourier transform (FFT) patterns in the insets of Fig. 1h correspond to three different twin regions (A, B, and C). Yellow and cyan circles in these patterns indicate the (200) and (111) reflections, respectively. They also show that the direction perpendicular to the twin planes is the (111), indicating that these two twin planes are (111). The FFT pattern of region A is equivalent to that of C but different from that of B, demonstrating that there are two parallel twin planes in the nanoplate.

To investigate the early stage of the pentagonal nanoplate growth on the r-cut sapphire substrates, we cooled the furnace rapidly by opening its lid after 2 min of reaction at 820 °C. In this experiment, we observed twinned triangular seeds that are grown vertically on the substrate, and also found twinned pentagonal seeds that are slightly larger than the triangular seeds (Fig. 2a). This suggests that, on an r-cut sapphire substrate, Ag nanoplates grow as follows; twinned triangular seeds → twinned pentagonal seeds → pentagonal nanoplates (Fig. 2a). When the reaction time was 5, 15, 30, 60, and 90 min, the average bottom length of the nanoplates was 3.6, 13.3, 24.4, 33.1, and 38.6 μm and the average area of the main plane was about 15, 179, 607, 1105, and 1469 μm² (Fig. 2b–f), respectively. Fig. 2g shows the plot of (average area of the main plane of nanoplates)²/3 as a function of the reaction time, which indicates that the volume of as-grown nanoplates increases linearly with the reaction time if we assume that the nanoplate thickness increases at a similar rate toward other directions.

Tilted growth of twinned trapezoidal Ag nanoplates on m-cut sapphire: seed → NW → nanoplate process

On m-cut sapphire, the growth of unidirectional twinned Ag nanoplates proceeds as follows: seed → nanowire → nanoplate. To investigate the growth on this substrate, we compared two different reaction times, 1 and 2 h. All other reaction conditions were the same.

When the reaction proceeds for 1 h, horizontal and parallel Ag nanowire (NW) arrays are synthesized on the m-cut sapphire, as shown in a top-view SEM image (Fig. 3a). The length and diameter of NWs are of 30–50 μm and of 80–180 nm, respectively. A magnified top-view SEM image shows a thick faceted Ag NW and a five-fold twinned decahedral nanocrystal (Fig. 3b, inset). The close correlation of the geometry and orientation between the NW and the five-fold twinned decahedral nanocrystal indicates that NWs grow from this nanocrystal seed.

Cross-sectional TEM and HRTEM images of the NW confirm that it is five-fold twinned with five domains and no defects in the interior (Fig. 3c–e). A cross-sectional HRTEM image of the interface between the NW and the substrate shows that two twinned regions, α and β, and the substrate...
have epitaxial relations of (111) Ag//(101¯0) sapphire and (113) Ag //[(1010) sapphire, respectively (Fig. 3d). The zone axes of FFT patterns of α and β regions are all <110> directions, confirming that the NW grows along these directions. Additionally, along the five-fold symmetry axis where five twin boundaries cross, the twinned decahedral seeds can grow and become NWs under the confinement of five twin planes. Note that this growth mechanism is quite similar to that of the Ag NW in solution.49–51 Fig. 3f shows the lattice arrangement of the interface between the NW and the substrate in (d).

When we increased the reaction time from 1 to 2 h, we found that many free-standing trapezoidal Ag nanoplates grow tilted on the substrates (Fig. 4a and b). The nanoplates have long sides of ~100 μm. Top-view SEM images (Fig. 4c and d) show that the free-standing nanoplates are not vertical but tilted toward the substrate. Based on the above, the growth process is likely as follows. At an early reaction stage, twinned decahedral seeds grow along the five-fold symmetry axis to form a parallel NW array. As the reaction proceeds, the parallel NW arrays grow and fill most of the substrate surface. Then, the axial growth of the Ag NWs is practically finished because the surface-diffusing Ag atoms cannot reach the NW tip since they are caught in another part of the NW, which probably contributes to the radial growth. Now, Ag atoms arriving to the NWs by direct impingement from the vapor contribute mostly to the vertical growth of the horizontal NWs, because the radial growth, perpendicular to the NW axis, has a poor lattice match with the
substrate. This finally results in the 2D crystal growth and the formation of free-standing Ag nanoplates.

The bottom side of the nanoplates has lengths over 100 μm because the NWs have a good lattice match along the horizontal growth direction and grow rapidly from twinned seeds at an early reaction stage. The nanoplates have a truncated equilateral triangular shape. As seen in Fig. 4d, the nanoplates have four orientations. An orthogonal projection calculation of the nanoplates in these top-view SEM images indicates that the angle between the nanoplates marked with A and B and the substrate is ~64° and ~135°, respectively. The nanoplates marked with the red A and B are mirror-symmetric to those with blue A and B.

From these observations, it is likely that the horizontal NWs grow along one of the {111} twin planes marked with A and B in Fig. 3c and d, and become nanoplates with major planes of {111}. From Fig. 3c, we measured the tilt angle of A and B to the substrate; the obtained values (64° and 135°) support our suggestion. Growth in other directions would be thermodynamically less favorable. This growth mechanism results in four orientations (two mirror-symmetric pairs) because of the 2-fold symmetry of substrate.

**Tilted growth of twin-free trapezoidal Ag nanoplates on STO (001): seed → NW → nanoplate process**

On SrTiO3 (STO) (001) substrates, Ag nanoplates grow through seed → NW → nanoplate process. To investigate the growth process, we performed reaction-time-dependent experiments (1 and 2 h).

Ag NWs grow along two directions, perpendicular to each other, on STO (001) with 1 h of reaction (Fig. 5a) from the Ag slug at 820 °C. The length and diameter of the NWs are 20–50 μm and 100–250 nm, respectively. Fig. 5b and c shows magnified 45° tilted-view SEM images, which indicate that the NWs are well-faceted and have an elongated square pyramidal shape. From the top-view SEM images (Fig. 5d and e), a square pyramidal seed and a slightly elongated seed are respectively observed on the same substrate. These images demonstrate that the geometries and orientations of square pyramidal seeds are strongly correlated to those of NWs, thus suggesting that the NWs grow from these seeds.

A cross-sectional TEM image of the NW shows that the horizontal Ag NW is twin-free single-crystalline and possesses an isosceles triangular cross-section (Fig. 5f). Fig. 5g corresponds to an HRTEM image and the FFT patterns of the interface between the Ag NW and the STO (001) substrate, confirming that the horizontal NW has a <110> growth direction. The Ag NW has {111} side facets and a (001) bottom plane sitting on a (001) STO plane. The two angles measured between the side plane of the NW and the substrate surface are both 55° (Fig. 5f and g). This value is consistent with the angle between a (001) bottom and {111} side planes (54.74°) obtained by calculating the angles between the planes in an fcc crystal structure. This further confirms that the horizontal Ag NW is an elongated square pyramid. According to the Wulff construction, in these nanostructures, truncated square pyramids with a (001) top plane are thermodynamically more favorable than square pyramids. However, our experiment is a kinetically controlled process, inducing a faster growth of [001] facets. Thus, square pyramidal nanocrystals and NWs enclosed by only {111} side facets are obtained.

The orientational relation between Ag and STO zone axes is Ag/[110] STO, indicating that the growth direction of horizontal Ag NWs is along a <110> direction of STO. Since there are two perpendicular and equivalent <110> directions on the substrate surface, the NWs grow horizontally along two <110> directions perpendicular to each other from square pyramidal seed (Fig. 5h).

When the reaction time increased to 2 h under the same experimental conditions, tilted Ag nanoplate arrays were obtained in two orthogonal directions on the STO (001) substrate. The top-view and 45° tilted-view SEM images of these arrays (Fig. 6a and b) show that trapezoidal nanoplates grow tilted, not vertical, in four orientations. The bottom sides of the nanoplates in two orientations, which are about 20–50 μm long, are parallel to each other and perpendicular to those in the other two orientations. To investigate the crystallinity of the nanoplate, we carried out cross-sectional TEM measurements on the nanoplate (Fig. 6c). The cross-sectional specimen was prepared by cutting the nanoplate that was transferred onto a Si substrate. Fig. 6d shows the HRTEM image corresponding to the cyan square section in Fig. 6c. The FFT pattern of the HRTEM image shows a single set of spots, confirming that the nanoplate has single crystallinity without any twin boundaries (inset of Fig. 6d).
We believe that single-crystalline Ag nanoplates are synthesized through a seed-initiated growth mechanism. Ag atoms arriving at the substrate from the vapor migrate and nucleate to form single-crystalline square pyramidal seeds on the STO (001) substrate. The seeds grow in a single direction to form elongated square pyramidal NWs on the substrate. Note that both the seeds and the NWs have thermodynamically the most favorable \{111\} side facets. In the beginning, surface-diffusing Ag atoms mostly contribute to the axial growth of NWs. As the reaction proceeds, the NWs grow and fill most of the substrate. When the surface-diffusing Ag atoms cannot migrate to the NW tip due to being caught in other parts of the NWs, the surface-diffusing Ag atoms contribute to the radial growth of NWs. After a certain time, the radial growth is also terminated due to the sizable lattice mismatch of 4.57% between NWs and the substrate (Fig. 5h). Then, Ag atoms colliding with the NWs by direct impingement from the vapor contribute mostly to the vertical growth of the horizontal NWs, leading to the formation of free-standing single-crystalline Ag nanoplates that are enclosed by thermodynamically the most favorable \{111\} facets.

To further characterize as-synthesized nanoplates, we performed X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements. The XRD patterns confirm that as-synthesized nanoplates possess a fcc Ag structure (Fig. S1†), and the AFM data shows that the Ag nanoplates have atomically flat and clean surfaces without any contamination (Fig. S2†). To demonstrate the applicability of Ag nanoplates, we measured field emission (FE) properties of gold-coated Ag nanoplate arrays (Fig. S3†).

Mechanisms of seed formation on various substrates

We have demonstrated that the growth of Ag nanoplates is strongly affected by the type of the seeds nucleated on substrates. The key to the control over the nanoplate growth is the control of the seed formation. Ag atoms colliding with the substrate migrate as small clusters, which nucleate to form seed crystals on the substrate. The geometry, orientation, and crystallinity of the seed crystals are determined by the surface energies of the facets of the seeds, the interface energy between the seeds and the substrate, and the surface energy of the substrate.52,58,59 Thus, the substrate plays a crucial role in the seed formation process. The lattice match between the seeds and the substrate strongly affects the interface energy between the seeds and the substrate, determining the crystallinity of the nanoplates. While the seeds and the nanoplates are aligned in a single direction on the r-cut and m-cut sapphire substrates due to the 2-fold symmetry of the substrates, the seeds and the

We believe that single-crystalline Ag nanoplates are synthesized through a seed-initiated growth mechanism. Ag atoms arriving at the substrate from the vapor migrate and nucleate to form single-crystalline square pyramidal seeds on the STO (001) substrate. The seeds grow in a single direction to form elongated square pyramidal NWs on the substrate. Note that both the seeds and the NWs have thermodynamically the most favorable \{111\} side facets. In the beginning, surface-diffusing Ag atoms mostly contribute to the axial growth of NWs. As the reaction proceeds, the NWs grow and fill most of the substrate. When the surface-diffusing Ag atoms cannot migrate to the NW tip due to being caught in other parts of the NWs, the surface-diffusing Ag atoms contribute to the radial growth of NWs. After a certain time, the radial growth is also terminated due to the sizable lattice mismatch of 4.57% between NWs and the substrate (Fig. 5h). Then, Ag atoms colliding with the NWs by direct impingement from the vapor contribute mostly to the vertical growth of the horizontal NWs, leading to the formation of free-standing single-crystalline Ag nanoplates that are enclosed by thermodynamically the most favorable \{111\} facets.

To further characterize as-synthesized nanoplates, we performed X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements. The XRD patterns confirm that as-synthesized nanoplates possess a fcc Ag structure (Fig. S1†), and the AFM data shows that the Ag nanoplates have atomically flat and clean surfaces without any contamination (Fig. S2†). To demonstrate the applicability of Ag nanoplates, we measured field emission (FE) properties of gold-coated Ag nanoplate arrays (Fig. S3†).

Mechanisms of seed formation on various substrates

We have demonstrated that the growth of Ag nanoplates is strongly affected by the type of the seeds nucleated on substrates. The key to the control over the nanoplate growth is the control of the seed formation. Ag atoms colliding with the substrate migrate as small clusters, which nucleate to form seed crystals on the substrate. The geometry, orientation, and crystallinity of the seed crystals are determined by the surface energies of the facets of the seeds, the interface energy between the seeds and the substrate, and the surface energy of the substrate.52,58,59 Thus, the substrate plays a crucial role in the seed formation process. The lattice match between the seeds and the substrate strongly affects the interface energy between the seeds and the substrate, directing the process of the seed formation. By using various substrates with different surface atomic arrangements, we can select the geometry, orientation, crystallinity of the seed crystals and control those of the resulting Ag nanoplates.

The seeds are mostly enclosed by thermodynamically the most favorable \{111\} side facets, though the bottom of the seeds could have another facet depending on the lattice match between the seeds and the substrate. As a result, Ag nanoplates grown from the seeds are mainly enclosed by the \{111\} facets. We have formed twinned seeds which subsequently grow into twinned nanoplates on r-cut and m-cut sapphire substrates, while we have synthesized twin-free single-crystalline seeds which grow into twin-free nanoplates on STO (001) substrates. As discussed above, the surface and interface energies of the seed and the substrate determine whether the twin formation occurs in the seeds, determining the crystallinity of the nanoplates. While the seeds and the nanoplates are aligned in a single direction on the r-cut and m-cut sapphire substrates due to the 2-fold symmetry of the substrates, the seeds and the
nanoplates are aligned in two perpendicular directions on the STO (001) substrate due to the 4-fold symmetry of the substrate.

Conclusions
We have grown submillimeter-scale Ag nanoplates with atomically clean surfaces on various substrates using a simple vapor transport method. The nanoplates are grown epitaxially on the substrates and also aligned three-dimensionally. We have demonstrated that the growth mechanism of stereoaigned Ag nanoplates can be determined from the geometry and orientation of seeds that are selected by the substrates. While the nanoplates grow directly from seeds through seed \( \rightarrow \) nanoplate process on r-cut sapphire, they grow \textit{via} seed \( \rightarrow \) NW \( \rightarrow \) nanoplate process on m-cut sapphire and STO (001). Twinned triangular seeds grow and become vertical twinned nanoplates on r-cut sapphire. Twinned decahedral seeds grow into tilted twinned nanoplate arrays on m-cut sapphire. Finally, twin-free square pyramidal seeds grow into tilted twin-free nanoplate arrays on STO (001). These large Ag nanoplate arrays can be employed in many novel applications, including their potential use as advanced plasmonic platforms for hierarchical 3D metal–semiconductor hybrid nanoarchitecturing.

Experimental section

Synthesis
Ag nanoplates were synthesized using a horizontal hot-wall single-zone furnace equipped with pressure and mass flow controllers. A 1 inch diameter quartz tube was placed in the furnace. Ar gas was used as the carrier gas at a rate of 100 sccm. The chamber pressure was 5–15 Torr. To maintain an inert atmosphere, the system was purged with Ar for 30 min before each reaction. An Ag slug (silver, evaporation slug, 99.99%, Aldrich) was placed in an alumina boat at the center of the heating zone and was heated from room temperature to 820 °C for 20 min. The temperature of the Ag slug was maintained at 820 °C for 1 or 2 h to synthesize the Ag NWs or nanoplates, respectively. The vapor pressure of Ag at 820 °C is \( 10.13 \text{ mP} \). The Ar gas transports the Ag vapor to the lower temperature region to form the Ag NWs or nanoplates on the 5 \( \times \) 5 mm\(^2\) substrates.

Characterization
SEM images were obtained using a Phillips XL30S SEM operated at an accelerating voltage of 10 kV. Samples were coated with gold to avoid a charging effect during the SEM observation. TEM and HRTEM images, and SAED patterns were acquired with a TECNAI F30 TEM operated at 300 kV. After the nanoplates were dispersed in ethanol, a drop of the solution was put on a holey carbon coated copper grid for the TEM analysis. Cross-sectional TEM specimens were prepared employing a dual-beam FIB (FEI Nova 600 NanoLab) equipped with a nanomanipulator (Kleindick MM3A).

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT) (2019R1C1C1008070 and 2018R1C1B5044670). This work was supported by the new faculty research fund of Ajou University. This work was supported by KIRIBB Initiative Research Program.

Notes and references