Full Length Article

Wafer-scale high-quality Ag thin film using a ZnO buffer layer for plasmonic applications

Bo-Gwang Jung, Miyeon Cheon, Su Jae Kim, Alexander Gliserin, Soo Hoon Chew, Chae Ryong Cho, Seong-Gon Kim, Young Hee Lee, Seungchul Kim, Se-Young Jeong

Department of Cogno-mechatronics Engineering, Pusan National University, Busan 46241, Republic of Korea
Center for Integrated Nanostructure Physics, Institute for Basic Science, Sungkyunkwan University Suwon 16419, Republic of Korea
Department of Nanoenergy Engineering, Pusan National University, Busan 46241, Republic of Korea
Department of Physics and Astronomy, Mississippi State University, Mississippi State, MS 39762, USA
Department of Energy Science, Sungkyunkwan University, Suwon 16419, Republic of Korea
Department of Optics and Mechatronics Engineering, Pusan National University, Busan 46241, Republic of Korea
Department of Physics and Astronomy, Mississippi State University, Mississippi State, MS 39762, USA
Center for Integrated Nanostructure Physics, Institute for Basic Science, Sungkyunkwan University Suwon 16419, Republic of Korea

Abstract

Realizing laterally continuous, ultraflat silver (Ag) single-crystal films is a significant technological challenge. Ag thin film grown on various hetero-substrates has been used in numerous applications, due to its superior electrical and optical properties. To exploit these properties without degradation and apply these films to high-precision patterning, surface plasmonics, and so on, a high-quality thin film having an ultraflat surface and few grain boundaries is needed. A zinc oxide (ZnO) buffer layer can be used to facilitate the growth of a single-crystalline Ag thin film on a sapphire (Al₂O₃) substrate. ZnO films deposited on Al₂O₃ substrates have grain boundaries; however, Ag films grown on ZnO are nearly grain-free and close to single-crystalline quality. This can be explained by the exceptionally small extended atomic distance mismatch, of ~0.08%, between Ag and Al₂O₃, in which the ninth Ag atom and the eighth Al atom are matched in terms of coherence and periodicity. A modified radio frequency sputtering system with a single-crystal Ag target enabled wafer-scale growth of ultraflat, grain-free Ag films. The proposed approach using a ZnO buffer provides a new method for fabricating Ag films with high adhesion, anti-oxidative stability, and superior optical properties, and allows for easy nano-patterning.

1. Introduction

Noble metal films, such as gold (Au) and silver (Ag) films, have attracted considerable interest in optical nano-circuitry, next-generation photovoltaic devices, and surface plasmonic resonance [1–4]. Ag-coated mirrors are ideal for observing a wide range of light wavelengths, having high reflectivity and low emissivity that is especially useful in infrared applications for astronomy [5]. Because electromagnetic coupling between light and free electrons at metal surfaces is important in surface plasmons, surface roughness and other inhomogeneities of the metal that limit surface-plasmon propagation are a major barrier to efficient plasmonic devices [6–9].

In a study comparing the optical response of two plasmonic nanoantennae, distinct differences between two structures, where one had an idealized geometry and the other a realistic geometry, resulted in approximately 1.4-fold differences in the near-field properties, polarization, and spectral behavior [10]. Deep subwavelength integration of high-definition plasmonic nanostructures, which is of key importance in the development of future optical nanocircuitry, depends on commonly used thermally evaporated Au layers. Evaporated Au layers tend to have structural imperfections that appear in individual circuit elements, resulting in a drastic reduction in the yield of integrated nanocircuits.

Chemically grown single-crystalline Au flakes have been shown to provide an ideal basis for focused ion beam (FIB) milling and other top-down nanofabrication techniques, to produce high-definition, ultra-smooth Au nanostructures with superior optical properties [11]. Although the fabrication of single-crystalline metallic nanostructures using chemical processing methods has been reported [12,13], a physical technique, such as vaporization or sputtering, is preferred, because chemical processing methods make it difficult to control uniformity due to
to the metallic nanoclusters that form and subsequently complicate the synthesis process [14,15]. Extremely flat, single-crystalline Ag films with a root mean square (RMS) roughness of 0.7 nm and grain size of several hundred nanometers have been obtained using a standard direct current magnetron sputtering system; the films possessed several key properties necessary for plasmonics applications [7]. A single-crystalline Ag film grown on a SiO₂ substrate was used to obtain a Ag nanoparticle structure by FIB milling; [16,17] observation of the crystal orientation of the Ag films using an electron backscatter diffraction (EBSD) method confirmed grain growth, achieved by adjusting the film deposition conditions. However, the grain size under the optimum conditions was no more than ~200 nm. Thus, growth of grain-boundary-free single-crystalline metal films and replacement of Au film with copper or Ag single-crystalline film remains challenging. Sputtering is expected to provide an innovative solution to the aforementioned problems and enable wafer-scale production.

In our previous studies, we introduced a method to obtain high-quality wafer-scale grain-boundary-free single-crystalline copper thin films on a sapphire (Al₂O₃) substrate using a sputtering method [18,19]. However, Ag films grown by the same method showed unexpectedly poor adhesion to the Al₂O₃ substrate due to the large atomic distance mismatch (ADM), which led to film delamination from the substrate. In this letter, we introduce the growth of ultraflat, wafer-scale single-crystalline Ag thin films by incorporating a zinc oxide (ZnO) buffer layer on the Al₂O₃ substrate. We describe how the Ag atoms overcome the large ADM, with the substrate using the ZnO buffer layer to relieve the large strain induced by heteroepitaxy, thus resulting in single-crystalline film with an ultraflat surface and high crystallinity.

2. Materials and methods

Ag thin films were fabricated using a modified radio frequency sputtering method. The single-crystal Ag target used in the sputtering process was prepared as 2-inch-diameter disks derived from single-crystal Ag ingots grown by the Czochralski method, supported by the process was prepared as 2-inch-diameter disks derived from single-crystalline Ag thin films equipped with a Cu-Kα radiation source and the electrical power supply and mechanical vibrations. Ag thin films were grown on 5 nm thick ZnO thin film sputtered on a 2-inch Al₂O₃ (0001) substrate under various conditions. The base pressure was ~10⁻⁶ Torr, and the working pressure, of 10⁻³ Pa, was adjusted by high-purity Ar gas (99.999%). The growth rate was 1 Å/s.

The 0-2θ XRD measurements were performed using an Empyrean Series 2 instrument (PANalytical B.V., Almelo, The Netherlands) equipped with a Cu-Kα source (40 kV, 30 mA). Data were collected within the range of 20° < 2θ < 80°, with a step size of 0.0167°. AFM measurements were carried out using an XE-100 instrument (Park Systems, Inc., Suwon, Korea). AFM images of the Ag thin films (10 × 10 µm²) were obtained in non-contact mode (cantilever: PPP-NCHR). The SEM and EBSD images were obtained using a SUPRA40 VP system (Carl Zeiss AG, Oberkochen, Germany).

The PF represents the spatial orientation of grains and the orientation distribution of crystallographic lattice planes in stereographic projection. The IPF shows the pole that is parallel to a given thin film direction. The IPF represents only a unit triangle, as opposed to a full circle, due to crystal symmetry. The IPF map combines the locally detected orientation with the crystallographic data. The color coding is in accordance with the reduced size of the IPF.

The electrical resistivity of the Ag thin film was measured using the van der Pauw method (HMS-3000; ECOPIA, Anyang, Korea) and the diffuse reflectance was measured using an ultraviolet-visible spectrometer (V-770; Jasco Inc., Easton, MD, USA) equipped with a 60-mm Φ integrating sphere. The reflectivity was measured over the range 180–1000 nm. The baseline correction procedure used a reference white plate (barium sulfate). The incident angle of the beam was set at 5°.

3. Results and discussion

Ag has a large ADM of 4.9% or 5.1% with respect to the Al₂O₃ substrate, varying depending on the growth direction. Despite efforts to optimize film growth conditions, Ag film on the Al₂O₃ (0 0 6) substrate is still of poor quality, and separates easily from the substrate. The quality of Ag films grown on a Al₂O₃ (0 0 6) substrate with previously reported conventional methods was not sufficient for plasmonic applications.

The typical crystalline properties of our Ag film grown on Al₂O₃ are presented in Fig. S1 (Supporting Information). The EBSD orientation map (Fig. S1a, Supporting Information), its inverse pole figure (IPF) (Fig. S1b, Supporting Information) [3], pole figure (PF) with respect to the normal direction, i.e., || {1 1 1} of Ag (Fig. S1c, Supporting Information), and X-ray diffraction (XRD) pattern (Fig. S1f, Supporting Information) show the polycrystalline nature of the Ag thin film on Al₂O₃, despite the use of a modified sputtering method. Every grain in the polycrystalline Ag was aligned in an arbitrary direction, and the grain size was, on average, several tens of nanometers.

Scanning electron microscopy (SEM) images obtained under low (Fig. S1d, Supporting Information) and high magnification (Fig. S1e, Supporting Information) confirmed the EBSD results, i.e., that the grains of the Ag film are deposited in arbitrary directions with a grain size of several tens of nanometers. The surface roughness obtained from atomic force microscopy (AFM) measurements (Fig. S1g, Supporting Information) indicated an RMS value of 5.9 nm, which increased over time due to further oxidation in a normal laboratory environment. Based on these results, we concluded that the Al₂O₃ (0 0 6) substrate was not satisfactory for Ag film growth, and we proceeded to identify a reasonable buffer layer to reduce lattice mismatch and release the strain induced by the large ADM.

Given that we could not improve the crystallinity of the Ag film using a Si substrate, we chose Al₂O₃ as the substrate material. ZnO was determined to be the best candidate as a buffer layer for the Al₂O₃ substrate, as it shows a good structural match with Al₂O₃ and is chemically stable.

ZnO film has been grown on Al₂O₃ (0 0 6) substrates for light-emitting diode (LED) and dilute magnetic semiconductor applications, and is well known to be compatible with Al₂O₃ (0 0 6) substrates [20,21]. The schematic structure of an Ag thin film, on a ZnO buffer layer on a Al₂O₃ (0 0 6) substrate, and an actual photograph of a 50-nm-thick Ag thin film grown on a ZnO buffer layer are shown in Fig. 1a. XRD images were taken of the areas marked by the colored squares in Fig. 1a; the color of the curves in Fig. 1b corresponds to the area marked by the same color in Fig. 1a. The similar XRD results among the different areas prove the wafer-scale homogeneity of the Ag thin film on the ZnO buffer layer. The peaks at 34.4°, 38.2°, and 41.7° correspond to those of ZnO (0 0 2), Ag(1 1 1), and Al₂O₃ (0 0 6), respectively.

An AFM image of the Ag film (Fig. 1c) shows a very flat surface in the vertical scale of a full height of 20 nm; for the 10 μm × 10 μm area; the RMS surface roughness value was 0.73 nm, slightly larger than the RMS roughness (~0.26 nm) of the Al₂O₃ substrate. The right upper inset shows an AFM image of a 2 μm × 2 μm area with a higher contrast in the vertical scale of 5 nm, which was acquired to better resolve the surface roughness. The Al₂O₃ substrate-ZnO buffer layer-Ag film interfaces were characterized using cross-sectional high-resolution transmission electron microscopy (HR-TEM). The cross-sectional HR-TEM images with different resolutions reveal epitaxial growth of the Ag film (Fig. 1d–f). The fast Fourier transform (FFT) patterns of the areas in Fig. 1f marked with rectangular boxes are shown in Fig. 1g–i. The orientation of the Al₂O₃ substrate parallel to the electron beam direction is (1 1 0), whereas the orientations of the ZnO buffer layer and the Ag film are (2 1 0) and (1 1 0), respectively. The (0 0 6) planes of Al₂O₃, ZnO...
(0 0 1), and Ag (1 1 0) are normal with respect to the interfaces; the respective normal values for these directions, (2 1 0) of Al₂O₃, (0 0 1) of ZnO and (1 1 0) of Ag, are also parallel to each other. Thus, HR-TEM analysis supports the observed growth in the (1 1 1) direction of the Ag thin film on a Al₂O₃ substrate.

We attempted to grow the ZnO buffer film on Al₂O₃ substrates under various growth temperatures, ranging from 200 °C to 500 °C, to determine the optimum growth conditions based on XRD and SEM measurements. The films were adjusted to have the same thickness, of ~100 nm. The XRD results for the ZnO buffer films are presented on a linear scale; the intensities of ZnO peaks were normalized with respect to the Al₂O₃ (0 0 2) and Al₂O₃ (0 0 6) peaks at 34.4° and 41.7°, respectively, which indicates that the ZnO films were well aligned in the [0 0 1] direction along the Al₂O₃ (0 0 6) plane. The two samples grown at 400 °C and 500 °C showed a single phase and high crystallinity. However, SEM revealed larger grains in the sample grown at 500 °C (Fig. 2a). Low-magnification SEM images of the ZnO (insets in Fig. 2b) confirmed that the grown ZnO films were of good quality and uniform, regardless of the growth temperature over the range 200–500 °C. High-magnification SEM images clearly revealed grain growth (20–50 nm in size), where grain size increased with growth temperature up to 500 °C. At temperatures higher than 500 °C, the film quality of ZnO deteriorated (not shown here).

Based on these results, we limited the growth temperature of the ZnO film to below 500 °C. Notably, the ZnO film grown at 500 °C showed the best crystallinity and largest grain size among the film samples; additionally, the ZnO films grown at different temperatures showed no clear difference in RMS roughness (Fig. 2a, Supporting Information). Thus, 500 °C was chosen as the optimal growth temperature of the ZnO buffer layer with a thickness of 5 nm for Ag film growth; all other growth conditions, such as the initial pressure, working pressure, Ar flow, and film thickness were held constant during Ag film growth.

Once again, we varied the growth temperature of the Ag film over the range of 200–500 °C to identify the optimal Ag film growth conditions. Notably, Ag film grown above 600 °C showed oxidation and exhibited a dark gray color. The XRD and SEM results of the Ag thin films grown on the ZnO buffer layer deposited at 500 °C are shown in Fig. 2c and d, respectively. The thickness of Ag films was adjusted to ~100 nm during the optimization process. In the XRD data presented at the linear scale (Fig. 2c), only three peaks appeared, corresponding to the ZnO (0 0 2) buffer layer, Ag (1 1 1) film, and Al₂O₃ (0 0 6) substrate at 34.4°, 38.2°, and 41.7°, respectively. The intensity of XRD for each sample was normalized with respect to the Al₂O₃ (0 0 2) intensity, to estimate the crystallinity of the Ag (1 1 1) peak. The intensity of the Ag (1 1 1) peak for all samples was at least three-fold higher than the peak intensity of the Al₂O₃ (0 0 6) substrate itself, whereas the Ag (1 1 1) peak of the polycrystalline Ag film grown directly on the Al₂O₃ (0 0 6) substrate (Fig. S1f, Supporting Information) was almost hidden by the Al₂O₃ (0 0 6) substrate peak, and was not observed at all at the linear scale. Considering the highest peak intensity and smallest full width half maximum of the Ag (1 1 1) (0.18°) peak, the optimum condition for Ag film growth on ZnO was taken to be 400 °C in this study. Fig. 2d shows SEM images of the samples grown at 200 °C, 300 °C, 400 °C, and 500 °C.

Considering that the ZnO buffer layer was aligned with the [1 0 0] direction, but was still polycrystalline, the smooth surfaces of all four samples observed in low-magnification SEM images (1-μm scale; insets in Fig. 2d) were surprising. A clear grain boundary could not be identified for the sample grown at 400 °C, even under high magnification. This suggests that the Ag film was nearly single-crystalline.

We examined the RMS values of Ag films as a function of growth temperature (Fig. S2b, Supporting Information), where the RMS value was 1.50 nm for the sample grown at 200 °C and 0.73 nm for that grown at 400 °C. The right panel of the AFM images indicates the line profiles across the AFM surface images, and the RMS surface roughness values calculated for a 10 μm × 10 μm area of the thin film. These images further confirmed the single-crystal-like growth structure on the polycrystalline substrate, for which heteroepitaxy is very unusual.

To understand the growth mechanism, it is necessary to investigate the crystallographic structure of the grown Ag film in detail. To determine the crystal orientation in the plane, and to understand the grain growth process, we examined coincident site lattice (CSL) boundary

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Fig. 1. Structural details of a single-crystalline silver (Ag) thin film (thickness: 50 nm) grown on a 5 nm zinc oxide (ZnO) buffer film. (a) Schematic diagram and photographic images of an Ag film on ZnO/sapphire (Al₂O₃). (b) X-ray diffraction (XRD) patterns corresponding to the areas marked in (a). (c) Atomic force microscopy (AFM) images of a single-crystalline Ag thin film on the ZnO buffer layer with the vertical scale of the full height of 20 nm (inset with 5 nm). (d–f) Cross-sectional high-resolution transmission electron microscopy (HR-TEM) images, under different magnifications, of a single-crystalline Ag thin film on a ZnO buffer layer. (g–i) Fast Fourier transform (FFT) patterns of Al₂O₃, ZnO, and Ag, corresponding to the areas in the HR-TEM image (f) marked by rectangular boxes.
line maps of Ag thin films using EBSD. Crystallographic characterization of Ag thin films was performed. The CSL boundary lines in the EBSD maps of Ag thin films, grown on a \( \text{Al}_2\text{O}_3 \) substrate using a ZnO buffer layer, showed the changes in film crystallinity with growth temperature. (Fig. 3a) with respect to the normal direction, i.e., \( \parallel [1 1 1] \), should have three-fold symmetry; however, the six-fold symmetry of the \( \phi \)-scan XRD pattern of the Ag (1 1 1) plane (Fig. 3d) implies 60° rotation of two types of grains in the thin film. The peaks marked by ▲ and ▽ on the XRD \( \phi \)-scan represent the two grain types; the equivalent markers in the EBSD map obtained under the 400 °C condition indicate the cause of the six-fold symmetry in the (1 0 0) PF in Fig. 3c, and the XRD peaks in Fig. 3d, respectively. The formation of the two kinds of grains rotated by 60° was attributed to the two stacking orders, ABC... and ACB... stacking order [19].

Ideally, the (1 0 0) PF of the cubic structure with respect to the normal direction, i.e., \( \parallel [1 1 1] \), should have three-fold symmetry; however, the six-fold symmetry of the \( \phi \)-scan XRD pattern of the Ag (1 1 1) plane (Fig. 3d) implies 60° rotation of two types of grains in the thin film. The peaks marked by ▲ and ▽ on the XRD \( \phi \)-scan represent the two grain types; the equivalent markers in the EBSD map obtained under the 400 °C condition indicate the cause of the six-fold symmetry in the (1 0 0) PF in Fig. 3c, and the XRD peaks in Fig. 3d, respectively. The formation of the two kinds of grains rotated by 60° was attributed to the two stacking orders, ABC... and ACB... stacking order [19].

The CSL boundary lines in the EBSD maps showed that the sample grown at 200 °C had relatively smaller grains. The grains of samples grown at 300 °C and 500 °C were larger, but showed a slight difference in degree of tilt from the (1 1 1) plane; thus, the spots in IPF show a wide dispersion. The six-fold symmetry in the EBSD (1 0 0) PF with respect to the normal direction, i.e., \( \parallel [1 1 1] \) (Fig. 3c), arises from the two grains rotated by 60° with an ABCABC...- and ACBACB...- stacking order [19]. Although the spots in PF (Fig. 3c, insets) were located within a small area, the spots in the IPF were widely dispersed or separated into two clusters, as each of the three originates from two grain types of different stacking orders. The IPF under the 400 °C condition was better aligned in the (1 1 1) direction; two grain types (same color on the EBSD map) were well aligned in the (1 1 1) plane. The CSL boundary lines in the EBSD maps are represented in red, and the rotation angle between the two grains ranged between 59° and 60°. Parts of the red CSL boundary lines were larger than 99.5% for the sample grown at 400 °C (see the rotation angles below the corresponding EBSD map in Fig. 3), which implies that two grain types were typically rotated by nearly 60° with respect to the other.

Ag film growth on the ZnO buffer layer of an Al\(_2\)O\(_3\) substrate involved two types of heteroepitaxy. The ZnO film worked well as a buffer; however, it retained a polycrystalline form and, thus was not single-crystal in nature to the same extent as the Al\(_2\)O\(_3\) substrate. Furthermore, the large ADM between Ag and ZnO makes it difficult to explain how Ag thin film of single-crystalline quality can grow on the polycrystalline ZnO buffer layer. Thus, we used an EADM model to determine whether there was extended periodicity of the lattice match between the two materials. The structural relations among the substrate, buffer, and final growth material are illustrated by the superposition of atomic layers in Fig. 4a. According to the Moiré pattern observed with lattice superposition, overlayer growth can be predicted.
Generally, oxides such as Al$_2$O$_3$ are ionic crystals, in which small-size cations, such as Al$^{3+}$, with larger valences easily attract and retain oxygen ions. The surface of Al$_2$O$_3$ consists only of oxygen ions [22]. Thus, the lattice mismatch can be calculated with respect to the change in Ag-O atomic distances between Ag and Al$_2$O$_3$. The O-O distance of Al$_2$O$_3$ in the [1 0 0] direction was 2.753 Å, and that of Ag in the [1¯ 10] direction was 2.889 Å. The degree of ADM was 4.9%, with 20:21 being the smallest integral ratio (2.889:2.753). Twenty times the Ag-Ag distance of Ag is nearly equal to twenty-one times that of the O-O distance of Al$_2$O$_3$, as shown in Fig. 4a. The EADM for large lattice mismatch epitaxial growth can be calculated as follows:

$$EADM = \frac{I'}{I},$$

where $I$ and $I'$ are integers and $d$ and $d'$ are atomic distances of the epilayer and substrate, respectively. $I$ and $I'$ are determined as follows: $d' \sim I$, where $I$ is the smallest integral ratio for $d'd'$. The difference between $I$ and $I'$ introduces a periodic edge-type dislocation [23–25]. Although the EADM for Ag and Al$_2$O$_3$ is small (0.08%), $I$ and $I'$ are 20 and 21, respectively. This period length in Ag in the [110] vertical direction is about 5.0 nm, which is much smaller than that between Ag and Al$_2$O$_3$. The small EADM, $I$ and $I'$ values promote ultraflat growth of Ag film on ZnO with single-crystalline quality. All results of ADM and EADM are summarized in Table 1.

The electrical conductivity and optical reflectivity are representative physical quantities sensitive to grain boundary formation. The scattering of electrons at grain boundaries and rough surfaces is the main cause of resistivity and deterioration of electric properties. The reduction in resistivity achieved by eliminating grain boundaries amounts to about 13% in bulk copper and Ag substrates [26,27]. The

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**Fig. 3.** Crystallographic orientations of Ag films grown on a ZnO buffer film under various temperatures: (a) coincident site lattice (CSL) boundary line maps of electron backscatter diffraction (EBSD) measurements of Ag thin films. All scale bars are 1 µm; (b, c) inverse pole figure (IPF) corresponding to the EBSD orientation maps of (a) (b) and EBSD [4] pole figure (PF) with respect to the normal direction, i.e., || Ag [1 1 1] (c). (d, e) φ-scan XRD pattern of the Ag (1 1 1) plane (d) and an atomic model showing two possible stacking configurations on the hexagonal basal plane, in which a grain is rotated by 60° (e).

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**Fig. 4.** Extended atomic distance mismatch between the film and substrate lattice: superposition of (a) Ag in Ag (1 1 1) on O in Al$_2$O$_3$ (0 0 1), (b) Zn in ZnO (0 0 2) on O in Al$_2$O$_3$ (0 0 1), and (c) Ag in Ag (1 1 1) on O in ZnO (0 0 2).
minimum resistivity that can be achieved in a copper single-crystal film was reported as 1.61 μΩ·cm, which is 7% lower than the resistivity of Cu bulk according to the International Annealed Copper Standard (IACS: 1.7241 μΩ·cm), and 6% higher than that of single-crystal Cu bulk (1.52 μΩ·cm at 293 K) [18]. For our Ag thin films deposited on ZnO, no clear grain boundaries were observed. The film surface was ultraflat, with an RMS roughness nearly a quarter of that of polycrystalline Ag films (Fig. S2a, Supporting Information). In this study, the measured resistivity of the single-crystalline Ag thin films (thickness: 50 nm) was < 3 μΩ·cm; the resistivity of the samples grown under 400 °C and 500 °C was ~1.87 μΩ·cm, which is close to that of Ag bulk (1.6 μΩ·cm); the typical resistivity of polycrystalline Ag is 2.61 μΩ·cm) [28] (Fig. 5a).

These results suggest that the mean free path of electrons was increased by the absolute decrease in electron scattering seen at the grain boundaries and on rough surfaces.

The reflectivity of the single-crystalline 50-nm-thick Ag thin film was compared to that of a commercial polycrystalline 150-nm-thick Ag thin film (G-mek, Inc., Gyeonggi, Korea). The single-crystalline Ag thin film showed clearly superior reflectivity over the measured wavelength range. To determine the chemical stability of the single-crystalline Ag thin film, its reflectivity was measured again 6 months later and similar results were obtained [Fig. 5(b) and Supplementary Fig. S3]. The fact that the reflectivity of our Ag film was maintained even after several months indicates the chemical stability of the film; notably, a protective layer for commercial Ag mirrors is mandatory.

Surface plasmon resonance (SPR) curves were obtained for single- and polycrystalline Ag films using a coherent 632.8-nm light source (Fig. 5c). In the single-crystalline Ag film, a deeper and sharper resonance curve was obtained compared to that for the polycrystalline Ag film, with the same film thickness. The position and depth of the dip in SPR well-matched that obtained with numerical simulations of a single-crystalline Ag film (Supplementary Fig. S4). This implies that the single-crystalline film should have a higher real permittivity and lower imaginary permittivity. The width of the plasmonic dip depends on the imaginary part of the dielectric constant of the metal. Such an SPR angle mismatch between single- and polycrystalline films may originate from the ZnO interlayer film below the single-crystalline Ag film. However, numerical simulations showed that the ZnO buffer layer did not affect the SPR curve (Supplementary Fig. S4). The chemical stability of the single- and polycrystalline Ag films was evaluated based on the SPR curve, after exposing the samples to ambient conditions for 2 months (Fig. 5d and e). The shift in SPR curve of the single-crystalline

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic distance (Å)</th>
<th>ADM</th>
<th>1</th>
<th>1′</th>
<th>EADM</th>
</tr>
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<tr>
<td>Ag(1 1 1)/Al2O3(0 0 6)</td>
<td>D1 = 2.889 D2 = 2.753</td>
<td>4.9%</td>
<td>20</td>
<td>21</td>
<td>0.08%</td>
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<tr>
<td>D1′ = 5.004 D2′ = 4.761</td>
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<td>20</td>
<td>21</td>
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<tr>
<td>ZnO(0 0 2)/Al2O3(0 0 6)</td>
<td>D3 = 3.248 D2 = 2.753</td>
<td>18.0%</td>
<td>6</td>
<td>7</td>
<td>0.51%</td>
</tr>
<tr>
<td>D3′ = 5.625 D2′ = 4.761</td>
<td>18.1%</td>
<td>5</td>
<td>6</td>
<td>1.5%</td>
<td></td>
</tr>
<tr>
<td>Ag(1 1 1)/ZnO(0 0 2)</td>
<td>D1 = 2.889 D2 = 3.248</td>
<td>11.1%</td>
<td>9</td>
<td>8</td>
<td>0.07%</td>
</tr>
<tr>
<td>D1′ = 5.004 D2′ = 5.625</td>
<td>11.0%</td>
<td>9</td>
<td>8</td>
<td>0.08%</td>
<td></td>
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</table>

D1, D2, and D3 are the vertical atomic distances of Ag-Ag, O-O in Al2O3, Zn(O)-Zn(O) respectively. D1′, D2′, and D3′ are the horizontal atomic distances of Ag-Ag, O-O in Al2O3, Zn(O)-Zn(O), respectively. The mean distance of vertical direction oxygen atoms at Al2O3 was calculated as (2.868 × 2 + 2.524)/3 = 2.753 (Å).

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Fig. 5. Physical properties of Ag single-crystalline film grown using a ZnO buffer layer. (a) Resistivity of the Ag films as a function of growth temperature. (b) Reflectivity of the Ag thin film as a function of wavelength compared to a commercial Ag thin film. (c) Surface plasmon resonance (SPR) reflectivity of the single-crystalline Ag film with a ZnO buffer layer of 5 nm thickness as a function of incident angle just after deposition compared to a polycrystalline Ag thin film without a ZnO buffer layer. (d, e) SPR reflectivity of a polycrystalline Ag thin film without a ZnO buffer layer (d) and a single-crystalline Ag film after 2 months (e).
To grow single-crystalline Ag film on Al2O3 substrate that had better adhesion to the substrate, we used a ZnO buffer layer based on crystallographic structure and EADM predictions. The ZnO film showed optimized growth under the 500 °C condition on the Al2O3 substrate, and was aligned epitaxially along the c-axis with grain sizes of ca. 40–50 nm. The growth of Ag film on 5 nm ZnO was optimized at 400 °C, and exhibited an ultraflat surface with an RMS value of 0.73 nm. The XRD peak intensity of the as-grown 100-nm-thick Ag film was five-fold larger than that of the Al2O3 single-crystal substrate, and its EBSD image indicated crystallographic alignment in the [1 1 0] direction. The resistivity of the single-crystalline Ag film was only about half that of the polycrystalline Ag film, and the reflectivity of the single-crystalline film was enhanced. Besides the choice of a ZnO buffer layer, the remarkable improvement in the quality of the Ag film is attributable to the modified sputtering system with a single-crystal Ag target, which enables 2- and 4-inch wafer-scale growth via the stacking of atomic layers. Thus, the results of this study provide a route to simple fabrication of materials requiring ultrahigh adhesion, anti-oxidative stability, and good optical properties for nano-patterning of Ag.

CRediT authorship contribution statement


