Inverse Stranski–Krastanov Growth in Single-Crystalline Sputtered Cu Thin Films for Wafer-Scale Device Applications

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Supporting Information

ABSTRACT: The single-crystalline copper (Cu) thin film is a platform substrate for the growth of numerous materials and has been a significant issue for the scientific community. The primary concern is the inevitable presence of stacking faults and twin boundary formation in inherent face-centered-cubic (FCC) structures. Here, we report a method for growing single-crystalline Cu(111) thin films on an Al₂O₃ substrate using conventional sputtering deposition. The desired growth configuration is induced by hidden incoherent twin boundaries (HITBs) embedded during the early growth stages. Two possible FCC stacking orders of Cu atoms, A-B-C-A and A-C-B-A rotated by 60°, give rise to HITBs between islands, as confirmed by X-ray diffraction phi-scan mapping. Such islands merge every three layers, triggering layer-by-layer growth that subsequently leads to an inverse Stranski–Krastanov growth mode. Single-crystalline Cu(111) thin film growth is confirmed by high-resolution transmission electron microscopy and electron backscatter diffraction mapping. Our approach paves the way for mass production of single-crystalline metal thin film and thus leads to substantial advanced research and electronic device application.

KEYWORDS: sputtering system, copper thin film, single-crystalline thin film growth, grain-free, incoherent twin boundary

INTRODUCTION

Metal thin films are key components of microelectronic devices and have been used in a variety of applications such as metallization, optical coatings, catalyst, and plamonics.1,2 Copper (Cu), in particular, has numerous advantages, such as high electrical and thermal conductivities as well as a low cost.3 However, Cu has crucial weaknesses with regard to its practical application, mainly its vulnerability to oxidation. Oxygen penetrates the Cu surface through grain boundaries, resulting in a degradation of the physical properties of Cu and its performance reliability.4–6 Cu has recently been revisited due to its availability as a practical substrate for graphene synthesis via low carbon solubility,7–10 however, the inevitable grain boundary formations and rough surfaces in Cu foil remain as obstacles to achieving high-quality graphene.11 Therefore, the growth of single-crystalline Cu thin films has been a significant issue, given that this film is used as a platform substrate for the growth of numerous materials. There have been various attempts to understand the epitaxial growth mode of Cu thin films and to improve the crystallinity of the film structure.12–28 The face-centered cubic (FCC) structure of Cu is inherently susceptible to stacking-fault and twin-boundary formations, in addition to point and line defects, during thin film growth.29–31 In this regard, the formation of...
twin boundaries and their effects on the physical properties of Cu thin films have been intensively investigated.32−44 Wafer-scale single-crystal-like Cu thin films have been grown by precisely controlling the plasma in a conventional sputtering process employing a single-crystal Cu target;45 this approach allows precise control over the size and homogeneity of sputtered specimens. The extremely flat surface and high crystallinity of Cu have allowed successful constructions of flexible transparent conducting electrode via microsize patterning46 and single-crystalline monolayer graphene.47 Here, our objective was to realize ultraflat, grain-free Cu films with low synthesis temperature, which meets the practical demand for mass production. We observed inverse Stranski−Krastanov (ISK) growth at the atomic scale by resolving the formation of unique hidden incoherent twin boundaries (HITBs) in wafer-scale and single-crystalline sputtered Cu thin films.

■ EXPERIMENTAL SECTION

Cu thin films were fabricated using an rf-sputtering method. The single-crystal Cu target used in the sputtering process was prepared from a single-crystal Cu ingot grown by the Czochralski method, which was supported by Crystal Bank, Pusan National University, Korea. A 2-in. disk-shaped target was prepared by electron discharge machining. The optimal growth parameters for Cu thin films grown on a 2-in. Al₂O₃ (0001) substrate were secured by adjusting various parameters, such as the temperature, rf-power, and working pressure. We first adjusted the rf-power and working pressure, which provide a stable plasma during deposition, and the distance between the Al₂O₃ substrate and the single crystal Cu target, and the rf-power was further adjusted to set the growth rate ∼1 Å/s. The film thickness was fixed to be 200 nm for measurements. The optimal growth temperature was investigated in a systematic manner (from room temperature (RT) to 200 °C). The base pressure was fixed at ∼10⁻⁶ Torr, and the working pressure was 10⁻³, adjusted by high-purity argon gas (99.999%). The growth rate was 1 Å/s. The fabricated thin films were kept in an air atmosphere; over a 2−3 year time period, no changes in surface quality were visible to the naked eye (see Figure S1, Supporting Information).

The θ−2θ X-ray diffraction (XRD) measurements were performed using a PANalytical Empyrean series 2 instrument equipped with a Cu−Kα source (40 kV, 30 mA). Data were collected within the range 20° < 2θ < 90°, with a step size of 0.0167° and a dwell time of 0.5 s per point in all cases. Synchrotron φ-scan XRD measurements were performed at the BL1D of the Pohang Light Source (PLS), Korea, operating at 3.0 GeV with a maximum storage current of 300 mA. The X-ray beam was focused using a toroidal mirror and monochromatized to 8.0495 keV (0.154027 nm) using a double-bounce silicon (Si) (111) monochromator. Atomic force microscopy (AFM) measurements were carried out using a PANalytical Empyrean series 2 instrument equipped with a Cu−Kα source (40 kV, 30 mA). Data were collected within the range 20° < 2θ < 90°, with a step size of 0.0167° and a dwell time of 0.5 s per point in all cases. Synchrotron φ-scan XRD measurements were performed at the BL1D of the Pohang Light Source (PLS), Korea, operating at 3.0 GeV with a maximum storage current of 300 mA. The X-ray beam was focused using a toroidal mirror and monochromatized to 8.0495 keV (0.154027 nm) using a double-bounce silicon (Si) (111) monochromator. Atomic force microscopy (AFM) measurements were carried out using a Nanonics Instrumentation system (Park Systems, Inc.). Scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and pole figure measurements were performed with a Zeiss SUPRA40 VP with a scanning electron microscope. High-resolution transmission electron microscopy (HR-TEM) analyses were performed using an FEI Titan3 G2 60−300 equipped with double aberration correctors (image and probe) and a monochromator operating at an acceleration voltage of 200 kV. Transmission electron microscopy (TEM) samples were prepared with a focused ion beam (Helios450F1; FEI).

Figure 1. Schematic diagram of the growth mechanism of single-crystalline copper (Cu) thin films: several stages of (a) early formation of Cu islands with designated stacking layers A−C on the basal plane, adding (b) the first layer with a vacant gap between layers B and C. (c) Second layer with an Σ3{112} incoherent twin boundary (ITB) along the vacancy line (thick orange line). (d) Third layer relaxed to the basal plane, and (e) the kink denoted by long-dashed lines and repeated stacking, consequently resulting in inverse Stranski−Krastanov (ISK) growth and (f) layer-by-layer (LbL) growth (from red dashed line, indicated by arrow), at which the Σ3{111} coherent twin boundary forms (thick blue line).
RESULTS AND DISCUSSION

ISK growth mode is observed in the single-crystalline Cu thin films fabricated using a modified sputtering system equipped with a single-crystal Cu target. Stranski–Krastanov (SK) growth can be described as initially two-dimensional layer-by-layer growth and subsequent three-dimensional island growth (Frank–van der Merwe mode + Volmer–Weber mode, respectively), as determined by the competition of cohesive forces between adatoms and the surface.48,49 Figure 1 depicts the ISK growth mode of HITBs experimentally observed. As the surface plane of the Al2O3(0001) substrate is analogous to the cubic close packing structure of the Cu FCC structure above the basal plane (Figure 1a). Initially, due to the lower interfacial tension energy of the Al2O3 substrate compared to that of the Cu plane (Figure 1a). Initially, due to the lower interfacial tension energy of the Al2O3 substrate compared to that of the Cu plane, Cu atoms begin to continue to build up on the basal plane, a small vacant gap less than 0.2 nm (Figure S3). Therefore, the thin film growth initially follows the three-dimensional Volmer–Weber growth mode.49 Under epitaxial growth, the island should have one of two possible FCC stacking orders, ABCABC····· and ACBACB·····, as depicted in Figure 1a. When two islands (ABC·····/ACB·····) with different stacking orders form next to each other, Cu atoms begin to fill the lateral spaces between them (Figure 1b). As Cu atoms continue to build up on the basal plane, a small vacant gap less than the size of an atom is inevitably left over. To insert one Cu atom, the gap requires twice the d-spacing of the (110) plane (i.e., \( \sqrt{2} a = 5.08 \) Å), which is wider than the spatial distance between layers B and C above the basal layer (3.69 Å), denoted by “v”. The adatoms in the second layer denoted by “i” are placed on top of the vacant gap in the first layer with sufficient space (5.16 Å) at the boundary between the two stacking configurations, i.e., \( \Sigma 3\{112\} \) ITB (Figure 1c). The

atoms in the third layer relax fully to form atoms identical to the basal plane by merging two islands (Figure 1d). ITBs in the kink region are repeated several times to resolve strain due to the lattice misfit and recover to an ideal boundary-free lattice (Figure 1e) which triggers subsequent layer-by-layer growth with the formation of a \( \Sigma 3\{111\} \) coherent twin boundary (CTB) (the thick blue line in Figure 1f).

We first investigated an optimal growth temperature in a systematic manner and show that the growth temperature of 190 °C is one of the key parameters to achieve the single-crystalline Cu thin film. Figure 2a shows the \( \theta-2\theta \) XRD patterns of the sputtered Cu thin films deposited at RT, 100, 180, and 190 °C; the patterns exclusively exhibited a Cu(111) peak, regardless of the deposition temperature. Notably, the deposition temperature had a significant influence on the peak intensity (Figure 2a). We emphasize that the 100 nm-thick Cu thin film deposited at 190 °C had a full-width half-maximum (fwhm) of 0.025°, much narrower than that of Al2O3 (0.048°) (Figure S2). From AFM measurements, the line profile of the film deposited at 190 °C in the bottom panel of Figure 2e revealed a root-mean-square (RMS) surface roughness of less than 0.2 nm (Figure 2e), which was markedly reduced (by ~15 times) compared with that (3.2 nm) of the film deposited at RT. To further confirm the smooth surface observed in the sputtered Cu thin film deposited at 190 °C, we measured the RMS surface roughness of Cu thin films of varying thicknesses (20–600 nm); our results revealed a narrow thickness dependence of 0.4 ± 0.2 nm (Figure S3).

Normal direction (ND) EBSD measurements were conducted to further investigate the crystalinity of the sputtered Cu (111) thin films at various temperatures (Figure 3a–d); the radio frequency (rf) dependence is shown in Figure S4. At RT, the EBSD mapping in the (111) direction was dominant; however, inverse pole figures (IPFs) revealed a blurred (111)
and additional (001) or (101). Similar {100} pole figures were visible with six primary spots accompanied by various, less obvious speckles. The spots other than those in the (111) direction indicated the presence of polycrystalline regions in the film (Figure S5 shows additional IPF data). As the temperature increased, the EBSD spots other than the (111) direction became less prominent. The sole spots associated with the (111) direction were distinct at 190 °C. The {100} pole figure holds an ideal cubic 3-fold symmetry; however, the 6-fold symmetry of the {100} pole figure in Figure 3d implies the presence of twin boundaries in the sputtered Cu thin film.

To elucidate the rotation angle of the twin boundary, we examined the distribution of the misorientation angle in the EBSD (rolling direction (RD) mode) mappings, as shown in Figure 4a−d, in which the rotation angle between grains is indicated by color. The occurrence of grain boundary angles in the sputtered Cu thin film deposited at RT was widely distributed (lower panel). The grain boundary occurrence at 60° became more prominent at high deposition temperatures, reaching nearly 100% at 190 °C, whereas the occurrence of grain boundaries at angles other than 60° was negligible (Figure 4d). Two grains rotated by 60° were identified, each with an ABCABC⋯ (white) and ACBACB⋯(gray) stacking order in 3-fold symmetry; the boundary lines of the misorientation angle (red) formed at the interface between the two stacking orders (Figure 4d and Figure S6).

Two regions with ABC and ACB stacking orders are schematically depicted in Figure 4e. The 6-fold symmetry observed in the ϕ-scan synchrotron XRD data on Cu (111) (Figure 4f) can be explained in terms of the overlap of the two 3-fold symmetries of ABC and ACB stackings, which is in good agreement with the 6-fold symmetry from EBSD pole measurements (the bottom figure of Figure 3d). Figure S7
shows scanning electron microscopy (SEM) images of the Cu(111) film deposited at various temperatures. High-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations were conducted near the Al2O3 interface in an attempt to identify, at the atomic scale, the thin film growth mode in the Cu thin film prepared at 190 °C. A kink in the rectangular box near the Al2O3 substrate was observed by two adjacent stacking orders in different [111] orientations, denoted by A and B (Figure 5a). Fast Fourier transform (FFT) electron diffraction patterns for regions A and B (Figure 5b,c) clearly show the twin boundary with respect to the [110] zone axis. The folded diffraction pattern for the full regions of A and B confirmed the twin boundary, with precise 2-fold symmetry of the spots (Figure 5d).

To clarify the nature of the twin boundary, an atomic-resolution image was extracted from inverse fast Fourier transform (IFFT) data, as shown in Figure 5d. Three layers were continuously repeated from the bottom substrate, with two stacking orders of ABCABC··· to the left of the kink and ACBACB··· to the right (Figure 5e); the two stacking orders assumed a disordered arrangement in the kink region. Remarkably, the two emergent stacking orders recovered from the kink disorder and merged to form epitaxial single-crystalline Cu layers by the 22nd layer (from the basal substrate) or equivalently at ≈6 nm from the substrate. The magnified region in Figure 5f shows the disorders at the kink site as vacancies and strained atoms, resulting in an ITB with two stacking orders. Given that disorders at a kink site are embedded by subsequent epitaxial layers, this feature is defined as a HITB which is not the ITBs observed in Figure 4d since such thin layers (≈6 nm) are unlikely to produce strong diffraction.

To investigate the film growth mode of sputtered Cu thin film (because real-time observation is not available), we measured cross-sectional TEM images of Cu thin films prepared with different deposition times (Figure 6), which directly evinces the suggested growth mechanism depicted in Figure 1. From the cross-sectional TEM image of a sample prepared with a short deposition time (note that the growth rate that we estimated from a thick and complete thin film form was ≈1 Å/s), one can identify the initial growth mode: if the thin film growth indeed follows two-dimensional layer-by-layer growth even in the early growth stage (i.e., Frank–van der Merwe mode), the cross-sectional image is expected to show a complete thin-film form with a uniform thickness. However, as shown in Figure 6a, the sputtered Cu specimens form Cu islands (6 nm height with 5 nm spacing, i.e., not a complete thin film form) on the Al2O3 substrate after 20-s deposition, which is indicative of three-dimensional island growth, namely, Volmer–Weber growth mode in the early stage. The TEM image of the sputtered Cu specimens after 30-s deposition still shows a similar island form on the substrate, but the spacing between islands becomes narrower and more obscure (Figure 6b), and the complete thin-film form (6 nm thick) is observed for the sputtered Cu thin film after 50-s deposition (Figure 6c). Undoubtedly, the series of TEM measurements reveal that the spaces between the initially formed Cu islands are filled by additional sputtering, and the islands become merged in this stage. It is worthy of note that the thickness of the primary thin-film form is consistent with the thickness of 22 layers in [111] FCC stacking (see Figure 5e), which accounts for the presence of the incoherent twin

Figure 5. Hidden incoherent twin boundary (HITB) formation near the bottom substrate. (a) High-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the kink in the A and B regions consisting of different stacking orders deposited at 190 °C. (b–d) Corresponding fast Fourier transform (FFT) images of regions A and B and the full region in part a. (e) Inverse FFT (IFFT) image of the square region marked by the white dashed square in part a. The white lines denote the atomic layer shared by regions A and B. From the red line, a single stacking ordering is observed. (f) Magnified ITB of the square region in part e. Vacancies and strained atoms are represented as white dotted circles and red solid circles, respectively.
Figure 6. ISK growth of an epitaxial single-crystalline Cu thin film: cross-sectional HAADF-STEM images of the sputtered Cu thin film deposited at 190 °C with varying deposition times: (a) Cu islands at 20 s and (b) coalescence stage of two islands at 30 s and (c) ISK growth observed at 30 min in the ≈6 nm-thick Cu thin film. (d) Epitaxial single-crystalline growth was observed at 30 min in the ≈100 nm-thick film. The insets show the corresponding magnified images.

boundaries near the substrate. Once sputtered Cu forms a complete thin film form, the interfacial tension initially present between Al2O3 and Cu vapor is significantly reduced, and the two-dimensional layer-by-layer growth mode can be triggered, which is supported by the extremely smooth surface of the sputtered Cu thin films (rms roughness ≈4 Å; note that the thickness of a layer in [111] FCC stacking is expected to be ≈2 Å) regardless of the film thickness (see Figure S3, Supporting Information). A homogeneous lattice pattern is indeed observed in Figure 6d, which is a cross-sectional TEM image of a 100 nm thick sputtered Cu thin film above the interface region between the substrate and thin film. More detailed information on the sputtered Cu thin film and a comparison with polycrystalline Cu thin film can be found in the Supporting Information (Figures S10–S12).

CONCLUSIONS

The primary achievement of our work is the wafer-scale single-crystalline Cu thin film growth by using a conventional sputtering system with the single-crystal Cu target; the very low deposition temperature (= 190 °C) is highly adequate for practical industrial application, which will also boost many advanced researches. ISK growth was observed at the atomic scale by resolving the unique HITB formation, which is the key mechanism in the single-crystalline Cu thin film growth. While gold films have been the film of choice in the fields of metallic nanostructure and nanopatterning of meta-materials, surface plasmonics, and nano-optical device applications, the ability to produce high-quality single-crystalline Cu thin films, as presented in this research, provides a low-cost, reliable alternative to Au films for long-term use.

ASSOCIATED CONTENT

Supporting Information

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Notes

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