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# Fabrication of high-quality single-crystal Cu thin films using radio-frequency sputtering

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**Copper (Cu) thin films have been widely used as electrodes and interconnection wires in integrated electronic circuits, and more recently as substrates for the synthesis of graphene. However, the ultra-high vacuum processes required for high-quality Cu film fabrication, such as molecular beam epitaxy (MBE), restricts mass production with low cost. In this work, we demonstrated high-quality Cu thin films using a single-crystal Cu target and radio-frequency (RF) sputtering technique; the resulting film quality was comparable to that produced using MBE, even under unfavorable conditions for pure Cu film growth. The Cu thin film was epitaxially grown on an Al<sub>2</sub>O<sub>3</sub> (sapphire) (0001) substrate, and had high crystalline orientation along the (111) direction. Despite the 10<sup>-3</sup> Pa vacuum conditions, the resulting thin film was oxygen free due to the high chemical stability of the sputtered specimen from a single-crystal target; moreover, the deposited film had >5× higher adhesion force than that produced using a polycrystalline target. This fabrication method enabled Cu films to be obtained using a simple, manufacturing-friendly process on a large-area substrate, making our findings relevant for industrial applications.**

Sputtering is an inexpensive, efficient, highly reproducible thin-film growth technique that has been widely adopted in many industrial applications, including semiconductor chip fabrication. Although extremely diverse thin-film materials have been successfully fabricated by sputtering processes, the most straightforward application of sputtering is metal film deposition by direct-current (DC) sputtering using a metal target under high vacuum conditions<sup>1</sup>. Al and Cu may be the most widely studied sputtered metal films, and they have been extensively used as interconnection wires in semiconductor chips<sup>2-6</sup>. However, it can be quite difficult to produce high-quality films of Al and Cu, because the sputtered metal atoms (and metal clusters) in the sputtering chamber and on the film surface are highly vulnerable to oxidation by the presence of residual oxygen in the chamber<sup>6-8</sup>. The equilibrium partial pressure of oxygen at 150°C, which is the main growth temperature in this work, can be as low as  $2.52 \times 10^{-114}$  Pa and  $9.98 \times 10^{-27}$  Pa for Al<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O, respectively<sup>9,10</sup>, suggesting that achieving high-purity (oxidation-free) films depends on the kinetic aspect of the film growth process<sup>9</sup>. The growth rate must be higher than the oxidation speed of the metal atoms on the film surface<sup>8</sup>. Therefore, an exceedingly high growth rate (1–10 nm s<sup>-1</sup>) has been adopted in mass production lines, using high sputtering power (several kW) under very low base-pressure conditions (<10<sup>-6</sup> Pa)<sup>11-14</sup>. Note that 10<sup>-6</sup> Pa does not correspond to extraordinarily ultra-high vacuum conditions compared with those used in various areas of physics. Nonetheless, significant effort is required to maintain vacuum in commercial sputtering systems due to cyclical loading/unloading of samples (i.e., opening/closing of the vacuum chamber and re-establishing high vacuum conditions). Thus, more expensive sputtering systems with higher throughput have been one of the main reasons for rising fabrication costs.

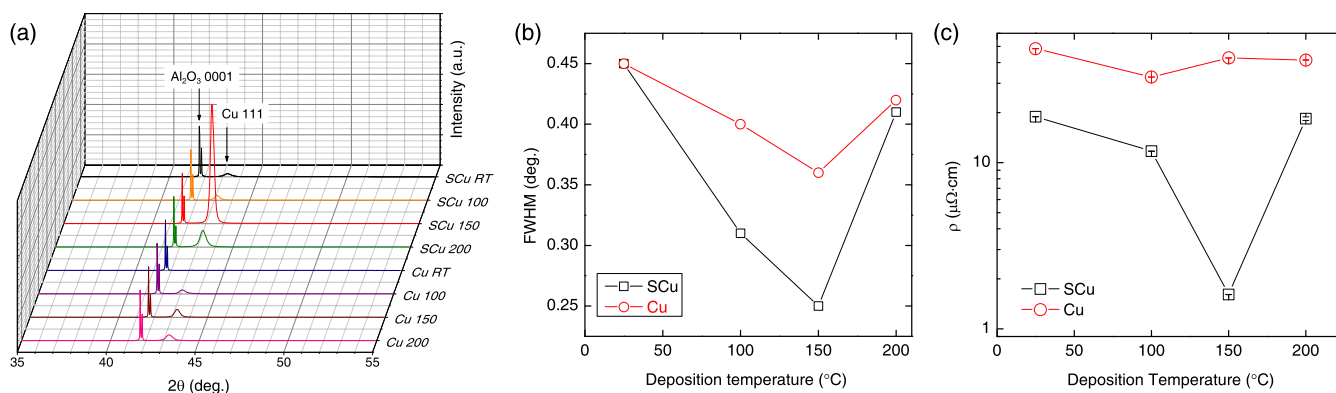
SUBJECT AREAS:

ELECTRONIC DEVICES

ELECTRONIC PROPERTIES AND  
MATERIALSReceived  
22 April 2014Accepted  
5 August 2014Published  
29 August 2014

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**Figure 1** | (a) X-ray diffraction (XRD) patterns, (b) The full width at half maximum for Cu (111) peak and (c) electrical resistivity of Cu thin films as a function of deposition temperature and target type. “Cu” represents the thin films fabricated using a commercial Cu target. “SCu” represents thin films produced using a single-crystal Cu target grown via the Czochralski method.

In contrast, the quality of the metal film produced by sputtering may be improved without adopting a (relatively) high-vacuum system if the target material condition is carefully considered. The target quality in the volume production of metal films has been tightly controlled to obtain very low-impurity concentrations and uniform grain structure, resulting in highly reproducible, uniform film growth over a large area<sup>1</sup>. However, the targets are generally polycrystalline in nature and are limited by the presence of grain boundaries that are difficult to control, especially in mass production.

A viable and intriguing proposal is the use of single-crystal targets, even under non-optimal conditions, to improve the quality of metal films produced by sputtering. In this work, we used a single-crystal Cu target and radio-frequency (RF) sputtering technique to produce high-quality Cu thin films on an Al<sub>2</sub>O<sub>3</sub> substrate. The resulting film quality was comparable to that of an epitaxial film. Moreover, these films were produced under sputtering conditions known to produce inferior quality thin films using polycrystalline targets, albeit identical purity.

To check the feasibility of producing a high-quality Cu thin film with a single-crystal Cu target and sputter deposition, we deliberately adjusted the sputtering pressure and growth rate to extremely unfavorable conditions for general metal film production (i.e., a relatively high base pressure and extremely low growth rate). Specifically, a base pressure of  $10^{-3}$  Pa and growth rate of  $\sim 0.1$  nm s<sup>-1</sup> were used, which would normally result in excessive oxidation of the metal atoms undergoing deposition. Additionally, an RF sputtering technique was adopted, although this approach is generally not used for metal film deposition.

We attempted to grow epitaxial Cu films under the highly unfavorable conditions specified above. Epitaxial films are highly favored as conductor wires because they are free from deleterious grain boundary effects<sup>6</sup>; the epitaxial film structure is also desirable for catalyst layer formation (e.g., growth of graphene layers via chemical vapor deposition (CVD))<sup>15</sup>. It should be emphasized that few researchers in the chemical processing field have access to high-vacuum systems for catalytic metal-film growth; thus, it would be highly desirable to have a method to achieve high-quality epitaxial films using more common (lower quality) vacuum processes by adopting a single-crystal target.

## Experimental procedures

A 2-inch-diameter single-crystal Cu target was obtained from a single-crystal Cu ingot by cutting via electron discharge machining. Cu thin films were grown on a sapphire (Al<sub>2</sub>O<sub>3</sub>) (0001) substrate under various temperature conditions using a radio-frequency (RF) sputtering technique. The base pressure was kept at  $\sim 10^{-3}$  Pa, and the deposition process was performed under  $10^{-1}$  Pa (i.e., working pres-

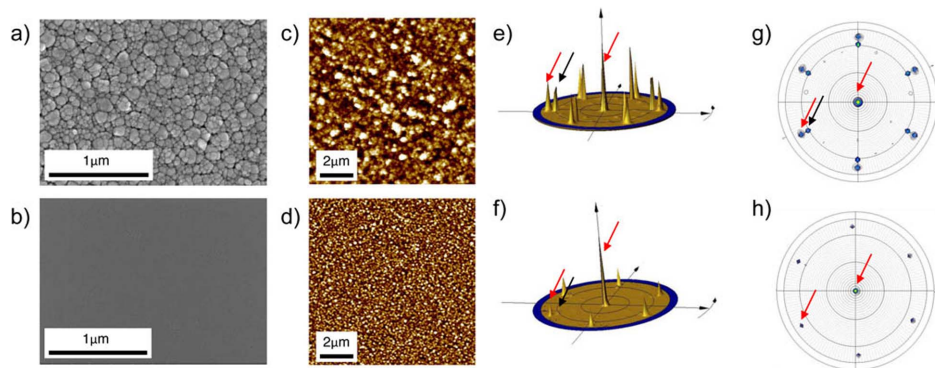
sure) with Ar gas (99.999%). An RF power of 40 W was applied to grow the thin films, resulting in a growth rate of  $0.1$  nm s<sup>-1</sup>. No post-deposition annealing was performed.

X-ray diffraction (XRD) was performed using the  $\theta/2\theta$  geometry on a PANalytical Empyrean Series2 instrument equipped with a Cu-K $\alpha$  source (40 kV, 30 mA); diffraction data were collected within the range  $20^\circ < 2\theta < 90^\circ$  with a  $0.0167^\circ$  step size, and a dwell time of 0.5 s per point in all cases. The pole figures were measured using high-resolution XRD in step-scan mode with  $3^\circ$  intervals and dwell time of 0.5 s for the tilt and azimuth angles. A total measuring time of  $\sim 3$  h was invested for each pole figure. To measure the surface roughness of the Cu thin films and Cu targets, atomic force microscopy (AFM) measurements were carried out using a commercial AFM system (XE-100, Park Systems, Inc.). AFM images for the Cu thin films (size:  $10 \times 10 \mu\text{m}^2$ ) and Cu target ( $30 \times 30 \mu\text{m}^2$ ) were obtained using non-contact mode. Scanning electron microscopy (SEM) was used to estimate the thicknesses of samples, surface images and electron backscatter diffraction (EBSD) patterns. High-resolution transmission electron microscopy (HR-TEM) measurements were performed using a Tecnai TF30 ST (FEI) system operating at an acceleration voltage of 300 kV and focused ion beam (Helios, 450 F1) was used for TEM sample preparation. The electrical resistivity of the Cu thin films was measured using the Van der Pauw method and the ECOPIA 3000 system.

## Results and Discussion

The quality of the Cu thin films was assessed with respect to the sputtering deposition temperature: room temperature, and  $100^\circ\text{C}$ ,  $150^\circ\text{C}$ , and  $200^\circ\text{C}$ . Figure 1a shows the X-ray diffraction (XRD) patterns of Cu thin films sputtered onto Al<sub>2</sub>O<sub>3</sub> (0001) substrates using single-crystal and polycrystalline Cu targets. The single-crystal Cu targets were sliced from a Czochralski-grown ingot. Polycrystalline Cu targets were purchased from RND Korea (purity: 99.997%).

All XRD patterns exhibited two peaks corresponding to the Al<sub>2</sub>O<sub>3</sub> (0001) plane ( $41.675^\circ$ ) and the Cu (111) plane ( $43.295^\circ$ ). For comparison of the diffraction peaks of Cu, we normalized the XRD intensity using the Al<sub>2</sub>O<sub>3</sub> substrate as a reference. The Cu thin films deposited using polycrystalline Cu targets under various temperature conditions (room temperature and  $100^\circ\text{C}$ ,  $150^\circ\text{C}$ , and  $200^\circ\text{C}$ , denoted as Cu RT, Cu100, Cu150, and Cu200, respectively) indicated a peak for Cu (111); this peak was  $10\times$  smaller than the intensity of the peak associated with the Al<sub>2</sub>O<sub>3</sub> substrate. However, the XRD patterns corresponding to a single-crystal Cu target (room temperature and  $100^\circ\text{C}$ ,  $150^\circ\text{C}$ , and  $200^\circ\text{C}$ , denoted as SCu RT, SCu100, SCu150, and SCu200, respectively) demonstrated better film quality; additionally, the Cu (111) peak intensity for SCu150 was twice as large as the Al<sub>2</sub>O<sub>3</sub> substrate intensity, comparable to bulk single-



**Figure 2** | Scanning electron microscopy (SEM) surface images of (a) Cu150 and (b) SCu150 grown on Al<sub>2</sub>O<sub>3</sub> (sapphire) substrates. Atomic force microscopy (AFM) surface images of (c) Cu150 and (d) SCu150. A 2D (projection view) pole figure image of (e) Cu150 and (f) SCu150 and a 2.5D (cylindrical view) pole figure images of (g) Cu150 and (h) SCu150. The notation “150” corresponds to a deposition temperature of 150°C.

crystal Cu. Note that the sample thicknesses were  $\sim 800$  nm for all samples; thus, the peak intensity observed for SCu150 could not be attributed to the sample thickness. Furthermore, the full width at half maximum (FWHM) of Cu (111) also showed a strong dependency on the target and the deposition temperature (Fig. 1b); the FWHM was minimum at the deposition temperature of 150°C, and SCu150 exhibited smaller FWHM of Cu (111) than Cu150, indicating larger grain size of SCu150 than that of Cu150.

Figure 1b shows the electrical resistivities of both SCu and Cu as a function of deposition temperature. As the deposition temperature increased, no significant change was observed in the electrical resistivity of the Cu/Al<sub>2</sub>O<sub>3</sub> samples. In contrast, we observed a remarkable reduction of the resistivity at SCu150. Because the resistivity depends strongly on the grain boundaries, these results do not simply reflect the enhancement of the crystallinity, but also reflect near-perfect film fabrication. We used the single-crystal target for three other deposition temperatures: room temperature, 100°C, and 200°C; however, only the sample produced using a deposition temperature of 150°C demonstrated a significant reduction in resistivity. This result emphasizes the importance of the fabrication conditions, despite the type of target used (i.e., single-crystal versus polycrystalline). The minimum achievable resistivity of the film grown under optimal conditions was 1.61  $\mu\Omega$  cm, even slightly lower than the resistivity of International Annealed Copper Standard (IACS: 1.7241  $\mu\Omega$  cm) Cu bulk and slightly higher than that of single crystal Cu bulk (1.52  $\mu\Omega$  cm at 293 K<sup>16</sup>). The other films exhibited resistivity values as high as 30  $\mu\Omega$  cm, suggesting that the growth conditions adopted to produce high-quality Cu films in this study were quite harsh.

To better understand the dependence of Cu thin-film quality on deposition temperature, we set the deposition temperature to 150°C and compared the structural properties of Cu150 and SCu150. Figure 2 shows scanning electron microscopy (SEM) and atomic force microscopy (AFM) images and pole figure data for both Cu150 and SCu150. The SEM images of Cu150 (Figure 2a) show the characteristic surface of the thin film consisting of numerous grains and grain boundaries, which is common with RF sputtering. In contrast, SEM images of SCu150 (Figure 2b) showed no distinguishable grains; instead, a very clean surface, similar to that of a polished bulk single crystal, was observed. The film quality of Cu150 and SCu150 was examined using AFM (Figure 2c and 2d); the surface roughness of Cu150 and SCu150 corresponded to 45.1 and 9.1 nm, respectively. Pole figure results supported the observed difference in crystalline quality for the two representative samples, Cu150 and SCu150. The term crystalline quality (or quality) refers to the perfectness of the crystallinity of the Cu thin film, which implies low impurity, low point defects (vacancy, interstitial atom) and extended defects (dislocations, boundaries), and smooth surface. Figures 2e

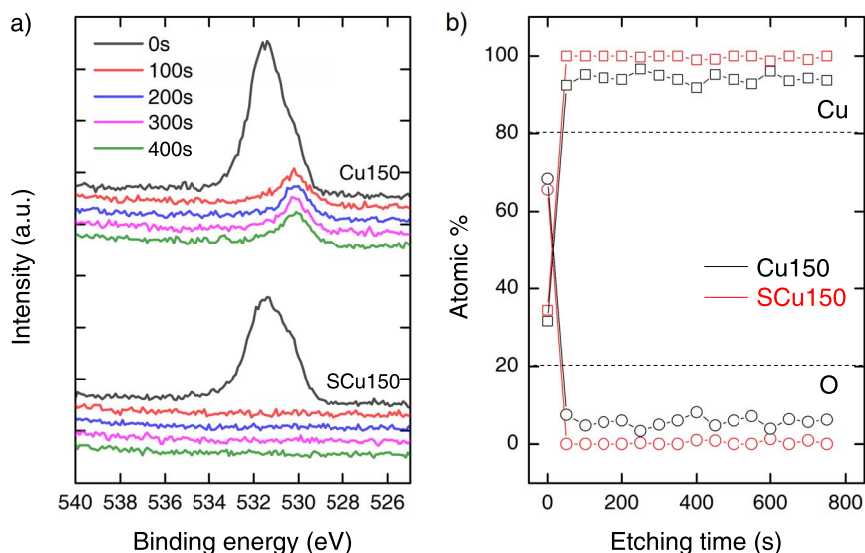
and 2g correspond to the 2D (projection view) and 2.5D (cylindrical view) pole figure images of Cu150, respectively, and Figure 2f and 2h correspond to the 2D and 2.5D pole figures for SCu150, respectively.

The six-fold symmetry peaks (marked with a black arrow) on the inner circle in Figure 2e–h are of the (0001) peak of the Al<sub>2</sub>O<sub>3</sub> sapphire substrate. The three-fold symmetry pair on the outer circle and center (marked with red arrows in Figure 2e–h) corresponds to the (111) plane of the Cu thin film. The intensities for the sapphire substrate for both samples are similar; however, the intensities of the Cu (111) peaks of SCu150 were  $\sim 20\times$  larger than those of Cu150.

X-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation and purity of the Cu thin films for two representative samples, SCu150 and Cu150. Figure 3a shows the XPS spectra of O 1s for SCu150 and Cu150 as a function of etching time. Both SCu150 and Cu150 exhibited an O 1s peak at the surface (i.e., without etching), indicating the existence of a native oxide layer at the surface, similar to the silicon dioxide layer observed for a silicon surface. After the etching process for Cu150, the intensity of the O 1s peak became smaller; however, the peak did not disappear, despite 400 s of etching. This indicates that the polycrystalline Cu films are easily oxidized at the grain boundary. However, the O 1s peak of SCu150 completely disappeared after etching for only 100 s. For clarification, we examined changes in the atomic concentration of Cu and O as a function of the etching time for both films, as shown in Figure 3b. Whereas the atomic concentration of Cu in SCu150 remained close to 100% over the entire etching duration, that in Cu150 changed by  $\sim 4$ –6%, reflecting the change in the O content in Cu150. The atomic percent of O in Cu150 was observed to be  $\sim 4$ –6%. In contrast, the atomic percent of O in SCu150 was observed to be close to zero over the entire film. SCu150 contained almost no oxygen; moreover, no oxygen-related species was observed at the surface. Thus, the difference in the oxygen content in the two samples despite similar fabrication conditions was attributed to the difference in target crystallinity (i.e., polycrystalline target (Cu150) versus a single-crystal target (SCu150)). Also, the chemical stability of Cu films sputtered from a polycrystalline target was much lower than that from a single-crystal target, i.e., the Cu specimen sputtered from a single-crystal target had superior anti-oxidative characteristics.

The SCu150 film quality was verified using electron backscatter diffraction (EBSD) and high-resolution transmission electron microscopy (HR-TEM). Figure 4a shows an EBSD inverse pole figure (IPF) image of the surface of SCu150, which was measured along the normal direction of the thin film (i.e., transverse direction//((0001) Al<sub>2</sub>O<sub>3</sub>)). For comparison, it was also attempted to achieve the EBSD pattern for Cu150 but it was failed because of its high roughness and small grain size causing an energy loss scattering and inaccessible area (i.e., shadowing effect) of electron beam<sup>17</sup>. We speculate that the





**Figure 3** | (a) X-ray photoelectron spectroscopy (XPS) O 1s peaks for SCu150 and Cu150 as a function of etching time. (b) Change in the atomic concentration of Cu and O as a function of etching time (i.e., depth profiling).

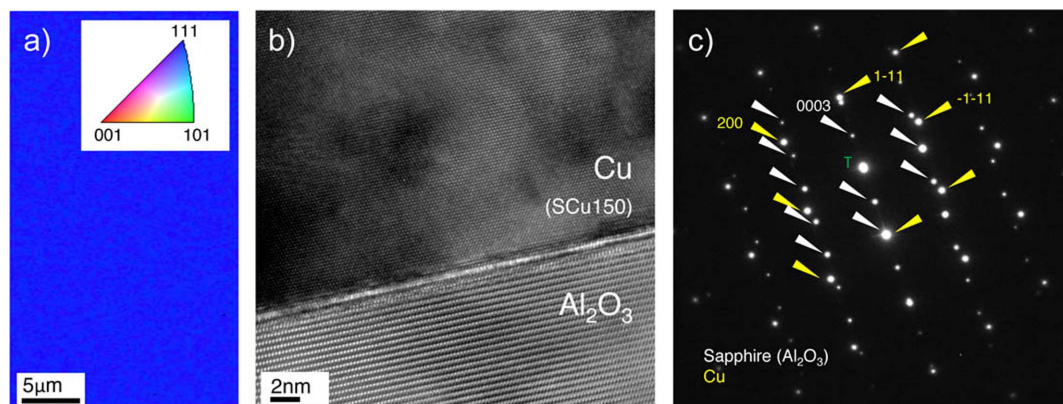
oxygen-related species (e.g., copper oxides) near the surface is also responsible for the failure. The EBSD IPF images clearly revealed that the SCu150 is a single grain of Cu (111) within the measured area. Identical EBSD images were obtained for other locations on the SCu150 sample surface, indicating the absence of large-angle grain boundaries, which is consistent with the X-ray pole figure results. From the EBSD data, we can infer the full epitaxial relationship between the SCu thin film and sapphire substrate,  $\langle 110 \rangle \text{Al}_2\text{O}_3 // \{111\} \text{Cu}$ , which persists over the entire measured area,  $\sim 20 \mu\text{m} \times 20 \mu\text{m}$ . The SCu150 thin film appears to have a surface quality similar to that of bulk single-crystal Cu grown by the Czochralski method.

Figure 4b shows a cross-sectional HR-TEM image taken along the  $\text{Al}_2\text{O}_3$  [01-10] zone axis. The periodic lattice image at the bottom and top correspond to the sapphire substrate and SCu150 film, respectively. The HR-TEM image of the SCu150 film exhibited a very regular, homogeneous lattice for the Cu thin film, without any trace of crystalline defects. Selected-area electron diffraction (SAED) from the film-substrate interface (Figure 4c) indicated not only the absence of secondary phases or precipitation, but also provided confirmation of epitaxial growth. The epitaxial relationship between the Cu film and  $\text{Al}_2\text{O}_3$  substrate was determined to be (0001)  $\text{Al}_2\text{O}_3 // (111) \text{Cu}$  and [01-10]  $\text{Al}_2\text{O}_3 // [011] \text{Cu}$ .

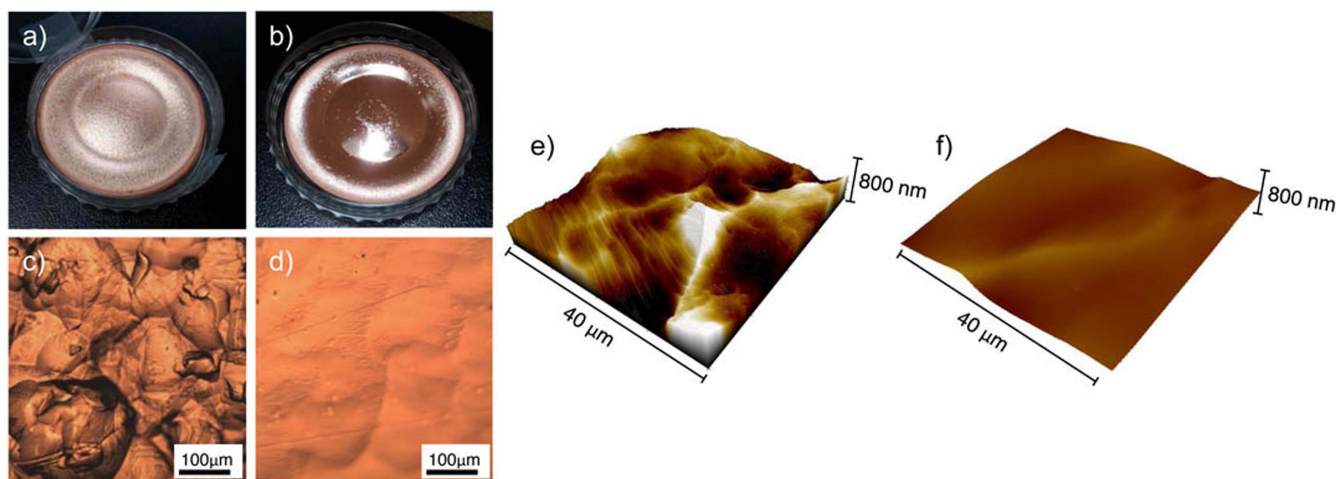
In an effort to identify the key mechanism for producing high-quality Cu thin films, we closely examined the surfaces of the two targets following the sputtering process. The two targets, polycrystalline Cu (Cu) and single-crystal Cu (SCu), exhibited very different surface conditions following the sputtering process (Figure 5). The surface of the polycrystalline target was very rough, whereas the surface of the single-crystal target was very smooth and shiny (Figure 5a and 5b, respectively). Microscope images (Figure 5c and 5d) and AFM images (Figure 5e and 5f) show these differences in greater detail.

The rough surface of the polycrystalline target suggested that the sputtering process was inhomogeneous due to the irregularity and larger size of the sputtered particles. Thus, irregular grain shape and orientation was expected in this case.

In contrast, the single-crystal target had a grain size on the order of a few millimeters; thus, few grain boundaries were evident. As a result, the interatomic bonding energy was homogeneous over the entire surface, which led to an energetically favorable homogeneous sputtering process. However, the sputtering deposition temperature of films fabricated using a single-crystal target must be optimized ( $150^\circ\text{C}$  in this study); our results indicated significant degradation in film quality for sputtering deposition at room temperature,  $100^\circ\text{C}$ , and  $200^\circ\text{C}$ . The finely sputtered specimen from a single-crystal Cu



**Figure 4** | (a) Electron backscatter diffraction (EBSD) orientation map image and (b) cross-sectional high-resolution transmission electron microscopy (HR-TEM) image of a SCu/ $\text{Al}_2\text{O}_3$  sample. (c) Selected-area electron diffraction (SAED) pattern for the interface area between Cu film and sapphire substrate of SCu/ $\text{Al}_2\text{O}_3$ .



**Figure 5** | Surface photograph images of (a) Cu and (b) SCu targets after sputtering. Surface microscope images of (c) Cu and (d) SCu targets after sputtering. Atomic force microscopy (AFM) surface images of (e) Cu and (f) SCu targets after sputtering.

target can be easily crystallized close to 150°C, enabling molecular level epitaxial growth, such as that observed for CVD or MBE processes. Moreover, under optimized deposition conditions, the sputtered specimen was chemically stable; this allowed the film to suppress oxidation, resulting in the fabrication of a high-purity sample, even under less than optimal vacuum conditions.

The result of achieving the best quality Cu films from a single-crystal target at a deposition temperature of 150°C can be explained as follows. It is well known that the sputtered material from the target during the general sputtering process is not necessarily a uniform atomic species, but instead, clusters of material having different sizes and kinetic energies<sup>18</sup>. It could be easily anticipated that the as-sputtered species from a polycrystalline Cu target may be nonuniform in size and energy for the given sputtering conditions due to the inhomogeneous microstructure of the target. In contrast, a single-crystal target should produce a more homogeneous as-sputtered species (atoms or clusters) having a more uniform size and energy. This was evidenced by the difference in the surface topography of the two targets after prolonged sputtering (Figure 5).

When the sputtered material reaches the substrate surface, it may migrate due to the kinetic energy acquired during the sputtering process. When the size and energy distributions of the sputtered materials are inhomogeneous (e.g., a polycrystalline target), irregular growth structures form that have random crystallographic orientations<sup>1,18</sup>. However, if the sputtered species reaching the film surface is uniform in size and energy, then an optimal structure (e.g., an epitaxial film) forms, even at low deposition temperatures, if the surface conditions allow it. Our results indicate that very low growth rates ( $\sim 0.1 \text{ nm s}^{-1}$ ) were capable of producing epitaxial growth given the appropriate sputtering power and substrate temperature. Another 10-nm-thick Cu film using the single crystal target was deposited with a higher growth rate ( $0.33 \text{ nm s}^{-1}$ ), and the film quality was confirmed to be as good as the one with the lower growth rate ( $0.1 \text{ nm s}^{-1}$ ) (data not shown). For another sputter-chamber geometry, which is optimized for high growth rate without sacrificing the metal film quality, a much higher growth rate could be obtained. The lower substrate temperatures (room temperature and 100°C) did not allow the sputtered species to move along the surface; thus, the resulting film was polycrystalline. A higher substrate temperature (200°C) may have accelerated film oxidation due to the residual oxygen in the chamber, which interferes with epitaxial growth.

The growth of an oxygen-free epitaxial Cu film for a deposition temperature of 150°C suggests an important aspect of metal film growth under relatively poor vacuum conditions. Because both targets have a much lower oxygen concentration than that shown in

Figure 3b, most of the oxygen must have been obtained from the atmosphere during the sputtering process. Although the size and energy distributions of the two cases were quite different, their oxidation potential may not be so different. The significant difference in the oxygen concentration for the two cases indicates that oxidation actually occurs on the film surface; in contrast, the sputtered species are transported through the atmosphere without being oxidized. This is reasonable because the transit times are quite short. The high kinetic energy that the gas-like sputtered species have in the plasma state corresponds to a very high temperature; this temperature may coincide with the non-oxidized state of Cu. Therefore, the sputtered species must become oxidized as it cools on the surface. At the same time, the Cu atoms or clusters initiate solid film formation; thus, the oxidation process is in competition with the solidification process. When the size and energy of the species are favorable for epitaxial growth, the oxygen atoms in the atmosphere have little chance to diffuse into the film and form oxide. However, under unfavorable conditions for epitaxial growth, the Cu films tend to form inhomogeneous polycrystalline films that have grain boundaries. Such grain boundaries provide the oxygen atoms with fast diffusion paths, allowing relatively high oxygen incorporation into the films.

It has been widely accepted that polycrystalline metal films could be under high stress due to the zipping effect of grains. This effect induces low adhesion to a chemically stable substrate, such as sapphire<sup>19</sup>. The absence of grain boundaries in the epitaxial film greatly decreases the risk of zipping-related stress, resulting in the high mechanical stability of the Cu film, even on an inert substrate.

The Cu thin film fabricated using a single-crystal Cu target has high crystallinity, high conductivity, and low roughness. Our findings meet industrial needs (e.g., mass production) due to the advantages offered by the proposed RF sputtering technique with a single-crystal Cu target.

In conclusion, we demonstrated that it is possible to grow single-crystal-quality Cu thin films on a sapphire substrate using RF sputtering techniques and a single-crystal Cu target, even under highly unfavorable film-growth conditions. XRD, pole figures, and EBSD identified the resulting Cu thin film as close to a perfect single crystal, with a highly oriented Bragg plane along the (111) direction. XPS verified that the single-crystal film contained almost no oxygen or oxygen-related species and had superior anti-oxidative characteristics. The surfaces of both target materials were examined closely after the sputtering process to better understand the key mechanism for high quality Cu thin film production. The realization of single-crystal-quality Cu thin-film fabrication via RF sputtering provides a key turning point in the thin-film production process, not only in



research fields but also in industries requiring large-area high-quality Cu thin films. Adopting a single-crystal Cu target resulted, unexpectedly, in a substantial improvement in film quality.

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## Acknowledgments

This research was supported by the Converging Research Center Program through the Ministry of Science, ICT and Future Planning, Korea (MSIP) (2013K000310). The authors are grateful to the KAIST Analysis center for Research Advancement for SEM, EBSD, FIB and TEM experiments.

## Author contributions

S.L. designed the experiment and wrote main manuscript. J.Y.K. prepared the samples for experiments. T.-W.L. contributed to experiments and analysis for SEM, TEM and EBSD. W.-K.K. contributed to AFM experiments. B.-S.K., J.H.P. and Y.C.C. assisted with sample characterization and manuscript preparation. J.-S.B. contributed to experiments and analysis for XPS. J.K. and M.-W.O. helped in writing and preparing the manuscript. S.-Y.J. and C.S.H. arranged and supervised all experiments as well as manuscript preparation. All authors reviewed the manuscript.

## Additional information

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Lee, S. *et al.* Fabrication of high-quality single-crystal Cu thin films using radio-frequency sputtering. *Sci. Rep.* **4**, 6230; DOI:10.1038/srep06230 (2014).



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