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The anti-oxidation effect of coating film prepared by He⁺ ion implantation on the Cu surface

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Abstract

The anti-oxidation effect of ion implantation by only introducing a shallow alloying layer is usually inadequate for many oxidizable metals, limiting the application of ion implantation in the anti-oxidation field. In this work, the feasibility of preparing an anti-oxidation coating film by using ion implantation is explored to enhance the anti-oxidation efficiency of ion implantation. The results show that a barrier coating film can be prepared on a Cu surface by using He⁺ ion implantation, and the prepared coating film presents an excellent anti-oxidation effect with a thickness of 10 nm by blocking the diffusion of Cu cations and enhancing the adhesion of oxide film to the substrate. The formation of this film is attributed to the bombardment effect of the ion implantation and ion beam scanning, which dissociates the bonds of coating material and drives the redistribution of

dissociated species on the Cu surface. This study demonstrates the feasibility of preparing an anti-oxidation film by using ion implantation, which could advance the application of Cu as well as the ion implantation in anti-oxidation technology.

Keywords: Copper; Ion implantation; Oxidation; TEM; Coatings.

1. Introduction

Copper (Cu) is one of the most important metals, and it is widely used in daily applications and industry. However, Cu is susceptible to oxidation after several working cycles, which degrades its performance and limits its applications [1–3]. For example, Cu could be an environmentally friendly and low-cost substitute for the (currently used) tin-lead or (promising) gold- and silver-based solder alloys in electronic packaging, if there was a way to prevent its oxidation [1]. Therefore, anti-oxidation technologies of Cu have attracted great interest [2,3]. Many widespread anti-oxidation techniques, such as alloying and electroplating, often degrade some of the physical properties, such as the thermal and electrical conductivities and color [2]. As an alternative, shallow ion implantation has been proposed and used to improve the oxidation resistance of Cu by forming a shallow layer with a high content of alloying species [4,5]. In particular, shallow implantation makes Cu capable of application in electronic device fabrication, because it can

effectively enhance the oxidation resistance of Cu and not notably affect the conductivity [6]. The barrier effect by applying a protective coating is also effective for preventing Cu oxidation and corrosion [2,3,7-9]. As an example, the deposition of graphene on a Cu surface can effectively prevent Cu oxidation under harsh conditions, which is also a candidate method that promotes the application of Cu in electronic device fabrication and other fields [2]. However, Cu could still be heavily oxidized in long-time applications even proceed by shallow ion implantation or graphene deposition [2,4]. It is necessary to explore more effective anti-oxidation techniques and methods.

Coating methods usually show an excellent anti-oxidation effect at the early period of oxidation by preventing oxidative or corrosive media from directly contacting the substrate. Once the coating is consumed or falls out, an accelerated oxidation of Cu usually occurs. Conversely, shallow alloying by ion implantation usually performs a conspicuous anti-oxidation effect at the later oxidation period by passivating the Cu diffusion. Thus, an anti-oxidation technology, which could combine shallow alloying and anti-oxidation coating, will further increase the oxidation resistance of Cu. The passivation effect of ion implantation on Cu oxidation has been widely reported by introducing a shallow alloying layer [4,6]. If a barrier film could be coated on Cu using ion implantation, it is capable of simultaneously introducing a shallow alloying layer and

an anti-oxidation film, providing a stronger anti-oxidation effect. However, coating using ion implantation to form a barrier film has rarely been reported. The properties of ion implantation, such as deposition, bombardment, and sputtering, will lead to a contradictory effect on the coating [10-12]. For example, high-energy ion implantation could deposit materials on the surface, but its sputtering effect would also destroy the surface. To date, the capability of ion implantation in preparing a coating film is not well understood, as well as the anti-oxidation effect of the prepared coating film.

In this study, the feasibility of making an anti-oxidation coating by using ion implantation is explored. The fabrication method of barrier film by using He^+ ion implantation was designed, and the anti-oxidation effect of the prepared coating film is well investigated by various microscopy methods. The results of this study pave the way to further enhance the anti-oxidation efficiency of ion implantation, such as simultaneously introducing a protective coating and a shallow implanted layer using ion implantation, which could not only markedly increase the oxidation resistance of Cu but also advance the application of ion implantation in anti-oxidation technology.

2. Material and methods

2.1 materials and ion implantation

A polished and clean surface of bulk polycrystalline Cu (Nilaco Corporation, Tokyo,

Japan, No.1054) with a size of 10 mm × 10 mm × 1.0 mm was prepared. The purity of Cu is 99.99%. Carbonaceous contamination is inevitable during ion implantation owing to the pump oil in the vacuum system [11,12], which is usually considered as a trouble. However, in this study, vacuum pump oil (ULVOIL R-7, ULVAC, Inc., Tokyo, Japan) was used as coating material, which mainly consisted of C and H with small amounts of O and Si (Fig. S1). To increase the source of the pump oil during ion implantation, we lightly painted the pump oil (liquid at room temperature) on a mask with an 8-mm-diameter hole in the center, which was covered on the Cu sample during subsequent ion implantation (as shown in Fig. 1(a)). To assess the anti-oxidation effect of the prepared coating film, the alloying effect of the implanted ion on the oxidation behavior of Cu should be eliminated. The inert gas ion He⁺ was selected, and He⁺-ion implantation in the Cu sample was performed using 100-keV He⁺ ions at room temperature to a fluence of $5 \times 10^{15} \text{ cm}^{-2}$. During implantation, the ion-implantation flux was maintained at $6.2 \times 10^{12} \text{ He} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, and beam raster scanning was performed to reach a homogeneous ion-implantation condition. As a result, selected-area He⁺ implantation was performed. More details about the selected-area ion-implantation procedure are provided in Refs. 13 and 14.

2.2. Cu oxidation

The samples prepared as in Section 2.1 were oxidized at 400 °C for 10 min, 30 min or

1 h in ambient air using a tube furnace (KDF-S70), after which each specimen was cooled in air. During these trials, the furnace was equilibrated at the target temperature for 30 min before the sample was transferred into the tube.

2.3. Characterization

Raman analysis was carried out with a Raman microscope (HORIBA XploRA), employing confocal Raman microscopy with a confocal aperture of 100 μm , a 532 nm laser, and a 2400 groove/nm grating. X-ray photoelectron spectroscopy (XPS) analysis (JEOL JPS-9200) was performed with a monochromatic Al $K\alpha$ X-ray source. In preparation for these assessments, the samples were fixed on a sample holder using Cu clamping piece. The prepared samples were stored in desiccator decompressed with a rotary pump prior to loading into the spectrometer. The base pressure during spectra acquisition was better than 5.0×10^{-7} Pa achieved by turbomolecular pump. The electron emission angle was 0° , and the size of sample analyzed area was 1.0 mm in diameter. XPS etching technique was used to remove the surface contamination prior to analysis with a 0.75 keV Ar^+ ion beam with incidence angle of 45° . The composition distribution in the depth direction was also detected using the XPS etching technique with 2 keV Ar^+ ion beam with incidence angle of 45° . The pressure during etching was better than 3.0×10^{-6} Pa. The etching area is at the center of the sample with an etching size of 3×3 mm. Charge

neutralizer was not used during the analysis. The binding energy values of the XPS spectra was calibrated by using the work function method [15-17]. The work function for Cu samples was reported to be 4.23 eV [15], thus the binding energy of C 1s peak (corresponding to the C-C/C-H bonds) was calibrated at 285.35 eV in the present work. A Shirley background subtraction was performed before curve fitting. Parallel beam X-ray diffraction (XRD) analyses were performed by a Smartlab diffractometer using Cu K α radiation (Rigaku, Tokyo, Japan) to investigate the oxidation products of different samples. The grazing incidence angle of 1° was applied to the analyses.

An optical microscope (Nikon Eclipse LV150) was used to record the surface color variation of the samples. The surface morphologies were observed by field emission scanning electron microscopy (FE-SEM; JEOL JSM-7001FA) using an accelerating voltage of 15 kV. A cross-section of the bulk samples was made by using gallium ions in a focused-ion-beam (FIB) system (JEOL, JEM-90320FIB) at an accelerating voltage of 30 kV, which was then observed by SEM at a tilt angle of 70°. The transmission electron microscopy (TEM) samples were prepared by FIB at an accelerating voltage of 30 kV, and the samples were thinned to a final thickness of about 100 nm. To prevent damage of the coating film during TEM sample fabrication by the FIB system, Au and/or C were deposited on the sample prior to TEM sample preparation. Microstructural observations

were carried out using a JEOL JEM-2000FX at 200 kV. High resolution TEM (HR-TEM) analysis and high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) analysis were performed with a Cs-corrected STEM (FEI, Titan G2 60-300) operating at 300 kV.

3. Results and discussion

3.1 Characterization of prepared coating film

After He⁺ implantation, the implanted and nonimplanted areas could be distinguished by the surface color (Fig. 1(b)) and scanning electron microscopy (SEM) image contrast (Fig. 1(c)). The surface compositions of the implanted and nonimplanted areas were determined by XPS. In the wide-scanning XPS spectrum of the nonimplanted area, the characteristic peaks of Cu, C, and O were observed (Fig. 2(a)). For the implanted area, the peaks of C and O were observed with a higher intensity than those in the spectrum of the nonimplanted area, and new peaks corresponding to Si element appeared. However, there was no characteristic peaks of Cu in this spectrum (Fig. 2(a), indicating that there is something covered on the Cu surface after ion implantation. The content profile at the center of the implanted area concerning to the depth measured by XPS etching is shown in Fig. 2(b). A film with a thickness of approximately 10 nm consisting of C, O, and Si

was present on the Cu surface. This agreed well with a TEM image of the surface (Fig. 3(a)) where a film with a thickness of about 10 nm was observed, suggesting that a solid film rather than liquid (pump oil) was coated on Cu by using He⁺ implantation. The microstructure of the prepared coating film is analyzed by HR-TEM technique as displayed in the Fig. 3(d). The fast Fourier transform (FFT) of the selected area in the coating film demonstrated that this film was amorphous. In addition, a thicker film (thickness of approximately 50 nm) was observed at the edge of the implanted area (Fig. 3(b)), and energy-dispersive X-ray spectroscopy (EDS) confirmed that this film mainly consisted of C, O, and Si (Fig. 3(b) and (c)). Note that because the pump oil mainly consisted of C_xH_y, H was also expected to be introduced into the coating film [7]. However, it is not shown in Figs. 2(a) and 3(c) owing to the detection limitations of XPS and EDS.

The organics polymer tends to decompose and reconstruct under high energy laser or particles beam scanning, such as the ceramic synthesis of organosilicon compound by high energy laser scanning [18], and dissociation and deposition of hydrocarbon molecules under the bombardment of high-energy particles [12,19,20]. In this study, a phase transformation (liquid to solid) was observed under He⁺ ion implantation. At the same time, the composition variation between the pump oil and coating film was also

recognized. In the pump oil, the content ratio of C, O and Si element is 48:1:1 (Fig. S1). Compared with the pump oil, the relative content of C element decreased, while that of O and Si elements increased in the coating film as shown in the Fig. 2(a) and 3(b). The phase transformation and composition variation implied that the chemical bond structures were changed between the pump oil and coating film. Figures 2(c-e) and 2(f-h) showed the C, O and Si XPS spectra of pump oil and coating film, respectively. In the pump oil, the C element was mainly in the forms of C-C (C-H), C-O, and C=O, the O element was mainly in the forms of C-O, C-O-Si, and the Si element is mainly in the form of the Si-O-C with slight Si-Si. In the pump oil, Si element is mainly in one chemical environment. After ion implantation, peaks corresponding to three different chemical environments appeared in the Si XPS spectrum of coating film (Fig. 2(h)), demonstrating the bond structure transition from the pump oil to the coating film due to the He^+ ion implantation. Especially, SiO_2 appeared as a new species, indicating that the pump oil had partly become inorganic ceramic by ion implantation [18]. For the O element, its chemical bond variation was agreed well with that of Si element. For example, the new peak, corresponding to the SiO_2 , appeared with the decrease of the relatively intensity of Si-O-C bond. This confirmed again the formation of SiO_2 and the bond structure changes during the ion implantation. The C element was almost in the same chemical forms in the

181 pump oil and coating film, but a decrease of the relatively intensity of C-O bond was
182 observed in the Fig. 2(f) than that in the Fig. 2(c). The break of chemical bonds depended
183 on their chemical bonding energy as scanning by high energy laser or particles beam. The
184 chemical bonding energy of C-O (326 kJ/mol), C-C (332 kJ/mol), C-H (414 kJ/mol), and
185 Si-O (460 kJ/mol) gradually increased [18]. Consequently, the chemical bonds that were
186 of lower bonding energy, such as the C-C, C-O, and other carbon-containing functional
187 groups, preferentially broke down into small hydrocarbon molecules and dissipated
188 during ion implantation, resulting in the decreased C content in the coating film and the
189 decreased relatively intensity of C-O, C-O-Si in the Fig. 2(f) and 2(g), respectively.
190 Owing to the higher bonding energy of Si-O bonds, the Si and O element combined, and
191 SiO₂ formed (Fig. 2(h)) after He⁺ ion implantation.

192 During ion implantation, desorption of dissociated species is expected due to the
193 sputtering effect of ion implantation. However, the kinetic energy of dissociated species
194 would also increase from the injected ions, making them possible to back stream to the
195 target surface [19]. In this study, the deposition of these new species on the substrate was
196 attributed to their increased kinetic energy from the injected He⁺ ions. In addition, the
197 beam scanning performed in this study contributed to enhance the delivery of dissociated
198 species from the mask to the Cu surface (Fig. 1(a)) and their redistribution on the Cu

surface. For example, a thicker coating film formed at the edge of the implanted area (Fig. 3(b)), where migration of dissociated species was blocked by the mask. Thus, the formation of this film can be attributed to the bombardment of ion implantation and ion beam scanning, which dissociated the bonds of the pump oil and drove the redistribution of dissociated species on the Cu surface. In Fig. 2(b), some C, O, and Si atoms seem to be penetrated the Cu substrate, forming a transition layer from the coating to the substrate. This is confirmed by the STEM-EDS mapping results in Fig. S3. A transition layer between the substrate and deposited carbon film was also reported in the case of plasma immersion ion implantation with hydrocarbon gas, which could lead to carbon implantation as the kinetic energy of ionic hydrocarbon is high enough [20]. The formation of the transition layer in this study confirmed the kinetic energy conversion from He^+ ions to dissociated species. In addition, it is reported that a mixture layer is expected to form at the interface of two substances due to the ion beam mixing by enhancing the atom motion [4,10,20]. This indicated that the ion beam mixing induced by high-energy He^+ ion implantation also contributed to the formation of this transition layer.

3.2 Anti-oxidation effect in the thermal condition

Using He^+ implantation with pump oil, an ultrathin coating film (10 nm thick) was

successfully prepared on the Cu surface. Its anti-oxidation effect was then investigated by heating samples at 400 °C for different times. After heating for 10 min, the Raman spectroscopy results showed that Cu₂O and CuO formed on both the pristine-Cu and coated-Cu (He⁺-implanted Cu) samples (Fig. 4(a)). However, the relatively lower intensity of Cu₂O and CuO peak for the coated-Cu sample suggested a lower oxidation state of this sample, which is in accord with the XRD results in the Fig. 5, that the higher intensity of CuO peaks (marked by arrow at the bottom) were observed in the XRD spectrum of pristine-Cu sample. After heating and cooling, the surface of the pristine-Cu sample became rugged, and many blisters formed (Fig. 4(b)) due to the mismatch between the oxide layer and Cu substrate in terms of thermal expansion and the surface stress introduced during heating and cooling [21–23]. However, the surface of the coated-Cu sample was planar and smooth (Fig. 4(c)), and few blisters were observed. After heating for 30 min, an oxide film with an average thickness of approximately 1 μm (Fig. 4(e)) was observed on the pristine-Cu sample, which increased to approximately 2.5 μm when the heating time was increased to 1 h (Fig. 4(h)). For Cu with the coating film, the oxide thickness was only approximately 0.2 μm after heating for 30 min (Fig. 4(g)), and it was still relatively thin (approximately 0.5 μm) after heating for 1 h. The coating film prepared by using He⁺ implantation showed a favorable anti-oxidation effect on Cu by retarding

the growth rate of oxide. Moreover, after heating for 30 min, the oxide film on the pristine-Cu sample became cracked and was almost exfoliated from the Cu substrate, resulting in a scale-like structure (Fig. 4(d)). However, the surface of the coated-Cu sample was still planar with few blisters (Fig. 4(f), which indicated that the oxide film formed on the coated-Cu sample showed stronger adhesion to the Cu substrate than that formed on the pristine-Cu sample.

To better understand the anti-oxidation effect of the coating film, the microstructures of the samples were analyzed. Using the TEM and TEM-EDS techniques, an oxide film with a thickness of approximately 100 nm was observed on the pristine-Cu sample heated at 400 °C for 10 min (Fig. 6(a)), which has partly separated from the Cu substrate. However, for the coated-Cu sample (Fig. 6(b)), a film with a thickness of only approximately 20 nm was observed, which is well fixed to the Cu surface. Analyzing by the HAADF-STEM technique, a nonuniform image contrast was observed for this top film formed on the coated Cu as shown in the Fig. 6(c). The HAADF-STEM image is sensitive to the atomic number that a higher atomic number present a brighter image contrast. The position 2 marked in the Fig. 6(c) showed a brighter image contrast, and the STEM-EDS results indicated that Cu particles present at this area, which is confirmed by the HR-TEM analysis in the Fig. 6(d). Different from the oxide film formed on the

pristine-Cu sample after heating for 10 min that is mainly consisted of Cu_2O and CuO , the top film formed on the coated Cu sample is not an absolute oxide film at this oxidation period with more Cu particles presented in it, suggesting a lower oxidation state of coated Cu sample, which is agreed well with the Raman and XRD results in Figs. 4(a) and 5. From HAADF observation of STEM in the Fig. 7(a), a layer with weaker bright contrast was observed between the top film and Cu substrate. The STEM-EDS mapping of O and Si (Fig. 7(c) and (d)) indicated that this layer originated from the coating film (Fig. 2), and the coincident distribution of Si and O elements as marked in Fig. 7(c) and (d) confirmed again the formation of SiO_2 (Fig. 2(h)). After heating at 400 °C, the coating film remained, suggesting a relatively high stability of this coating film. The oxide formed on the outside of the coating film, and some Cu particles were present in the top film and coating film after heating (Figs. 6(d) and 7(b)). It indicated that oxidation of this sample mainly proceeded via outward Cu diffusion through this coating film [24]. Compared with the pristine-Cu sample, on which the oxide thickness increased from approximately 100 nm to 2.5 μm as the heating time was increased from 10 min (Fig. 6(a)) to 1 h (Fig. 4(h)), the growth rate of the oxide on the coated-Cu sample was much lower (Figs. 6(b) and 4(i)). Outward diffusion of metal cations has also been observed in the oxidation of SiO_2 -coated FeCrAl foil at 1000 °C [25], and its oxidation rate was reported to be

effectively reduced by the SiO₂ coating, which acts as a diffusion barrier of Al cations. SiO₂ is also present in our coating film as shown in the Fig. 7(c) and 7(d). Therefore, the coating film existing between the top film and substrate after heating (Fig. 7) decreases the oxidation rate by blocking the outward diffusion of Cu.

It has been reported that a continuous and dense oxide film can decrease the oxidation rate in the later oxidation period by blocking direct contact between the Cu substrate and air [1,26]. However, the cracked oxide film observed on the pristine-Cu sample (Fig. 3(d)) cannot effectively protect Cu against further oxidation. For example, in Fig. 4(h), a new oxide film formed at the area where the oxide film cracked. Compared with the pristine-Cu sample, the oxide film formed on the He⁺-implanted Cu sample showed better adhesion, as shown in Fig. 4(c), (f), and (i). Considering the microstructure in which the coating film existed between Cu and the oxide film after heating for 10 min (Fig. 7), it is reasonable to ascribe the enhanced adhesion of the oxide film to the coating film at this oxidation period. Figures 8(a) and (b) showed the cross-sectional TEM images of pristine-Cu sample after being heated for 1 h. In the Fig. 8(a), a loose interface of the oxide and substrate was observed, and the cavity formed at the interface is attributed to the accumulation of Cu vacancies [27]. A loose interface possessed a relatively low adhesion ability for the oxide film to the Cu substrate, resulting in a separation of oxide film from

the substrate during cooling as shown in the Fig. 8(b). For the coated Cu, a relatively compact interface of oxide film and Cu substrate was observed (Fig. 8(c)). At this oxidation period, there is no silica or carbon-containing species at the interface as shown in the HR-TEM image of Fig. 8(d). Thus, the stronger adhesion of oxide film at this oxidation period is attributed to the compact oxide/substrate interface. Subsurface defect such as dislocation and point defect clusters could decrease the accumulation of Cu vacancies at the interface by enhance their annihilation [27]. Amounts of lattice defects were introduced in the Cu during He^+ implantation due to the cascade collision of high energy ions [13], which could account for the compact interface for the coated Cu prepared by He^+ ion implantation. As mentioned above, because the continuous oxide film can protect Cu against further oxidation, the enhanced adhesion of the oxide film to the substrate should also contribute to the passivated oxidation in the He^+ -implanted Cu sample. The enhanced adhesion of oxide film to the substrate highlights the advantage of this coating technology using ion implantation [28].

Generally, a thicker coating shows stronger protective ability. However, for thermal systems [8] or electronic devices [24-26], thick coatings are undesirable owing to the increased overall heat transfer stemming resulting from the thermal resistance of the added coating. Hence, the development of ultrathin coatings that show an excellent anti-

oxidation effect is of great interest. The above results show that the ultrathin coating (approximately 10 nm thick) prepared by using He^+ implantation showed a prominent anti-oxidation effect, which may pave a way for the application of Cu as interconnecting material in ultra-large-scale integration devices [1,29-31]. Besides, the enhanced adhesion of oxide film to the substrate makes this coating method suitable for application in the thermal cycle condition, where the oxide scale more frequently separates or exfoliates from the substrate during application [17]. Moreover, these results indicate the feasibility of simultaneously introducing a protective coating and a shallow implanted layer using ion implantation, which could further increase the oxidation resistance of Cu and other metals and advance the application of ion implantation in anti-oxidation technology.

4. Conclusion

The feasibility of introducing an anti-oxidation film using ion implantation was demonstrated in this study. The formation of this film is attributed to the bombardment and scanning effect of the ion beam, which dissociates the bonds of coating material and drives the redistribution of dissociated species on the Cu surface. The prepared coating film using the selected-area He^+ implantation with pump oil presents an excellent anti-

oxidation effect by enhancing the adhesion of oxide film to the substrate and blocking the diffusion of Cu cations. These results promote the understanding of Cu oxidation and advance the application of ion implantation in anti-oxidation technology.

CRedit author statement

Subing Yang: Conceptualization, Investigation, Data curation, Writing-Original Draft,

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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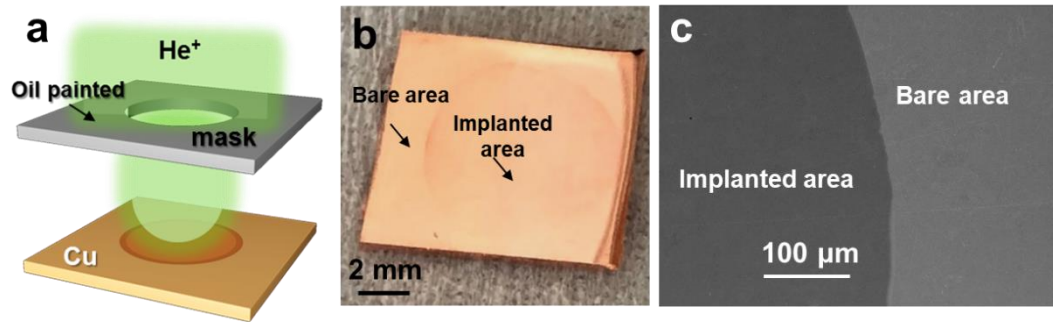
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450

451 **Figures**



452

453 Fig. 1. (a) Schematic image of selected-area He⁺ implantation using a mask painted with pump oil. (b)

454 Optical and (c) SEM images of the Cu sample after He⁺ implantation.

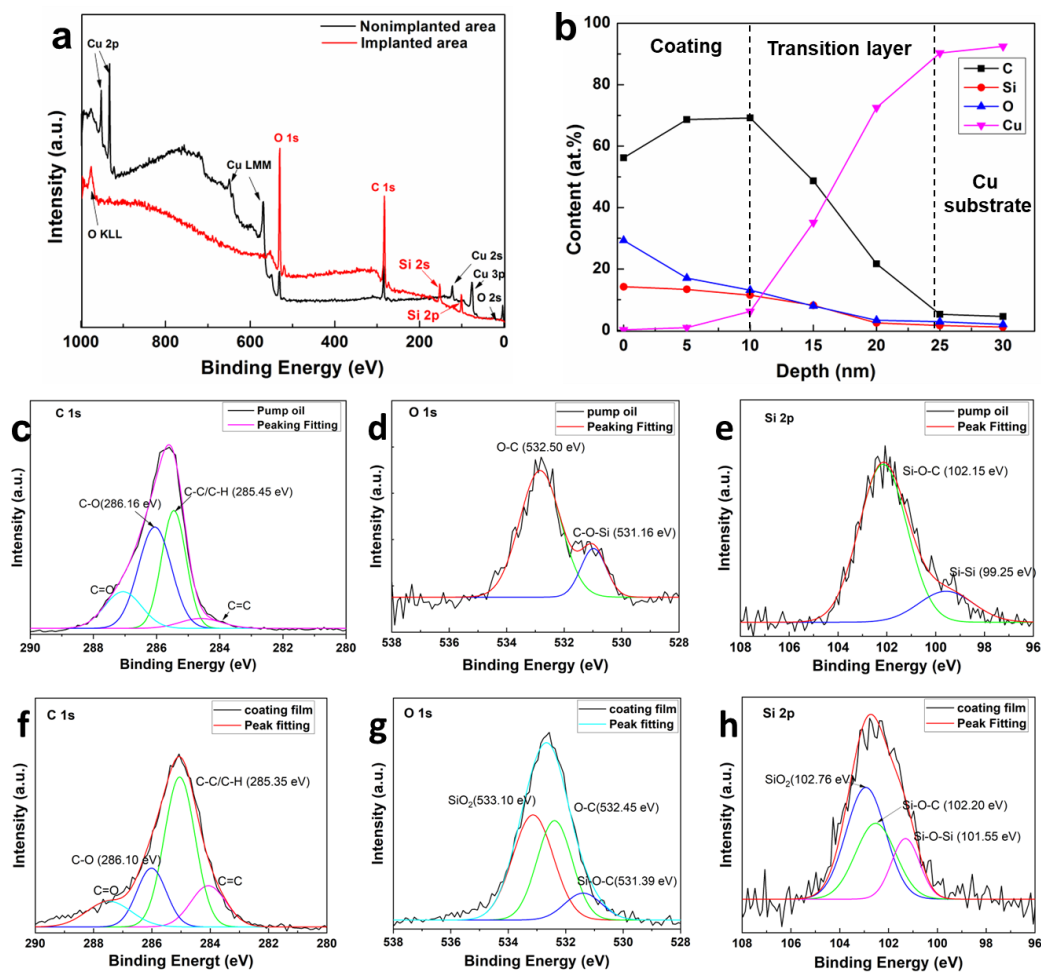


Fig. 2. (a) XPS wide-scanning spectra of different areas of selected-area He⁺-implanted Cu. (b) Composition distribution with respect to the depth of He⁺-implanted Cu measured by XPS etching, and XPS spectra at different depths is provided in the Fig. S2 of supplementary. (c-h) XPS narrow-scanning spectra of the (d)–(f) pump oil and (g)–(i) coating film.

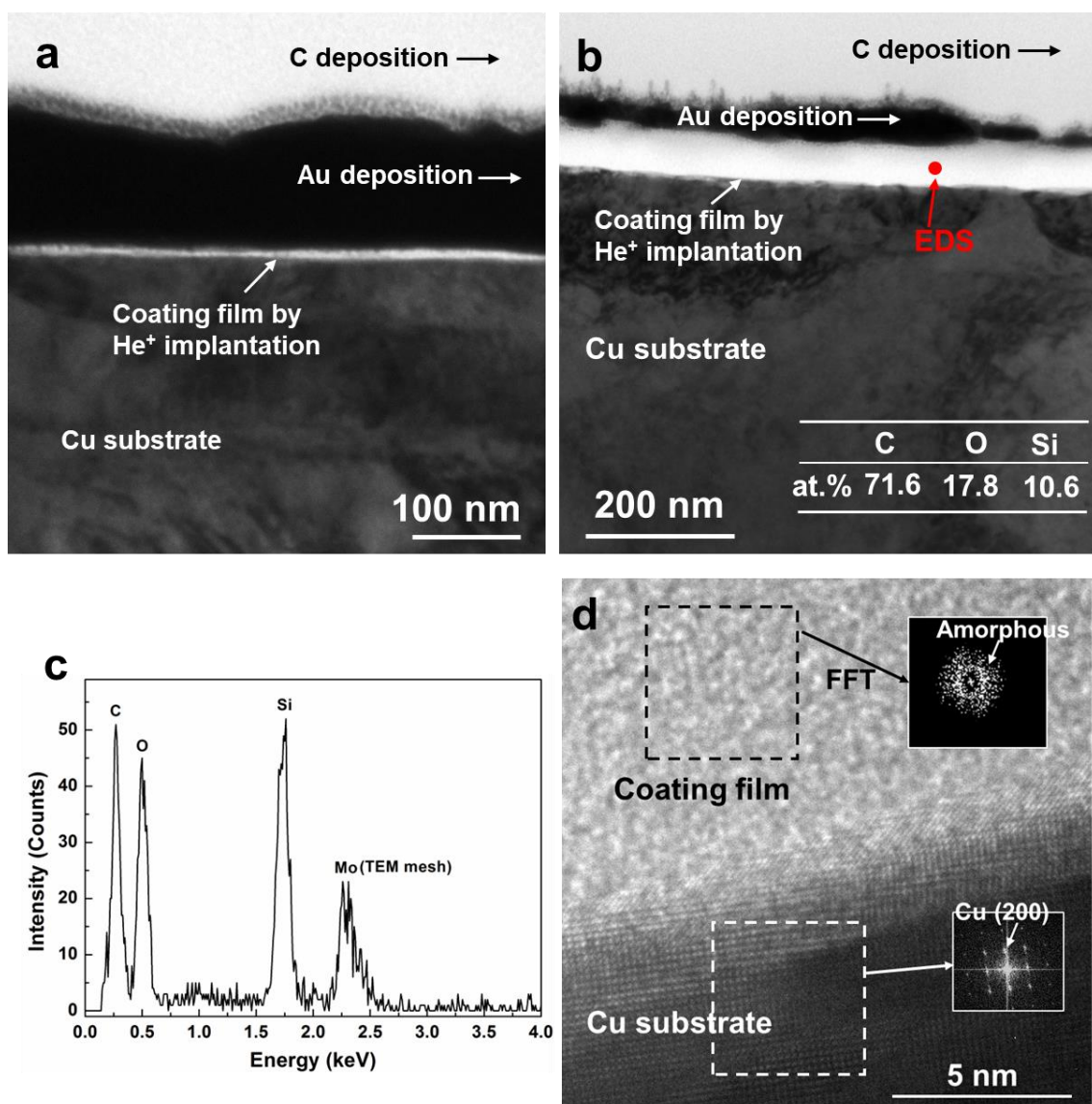
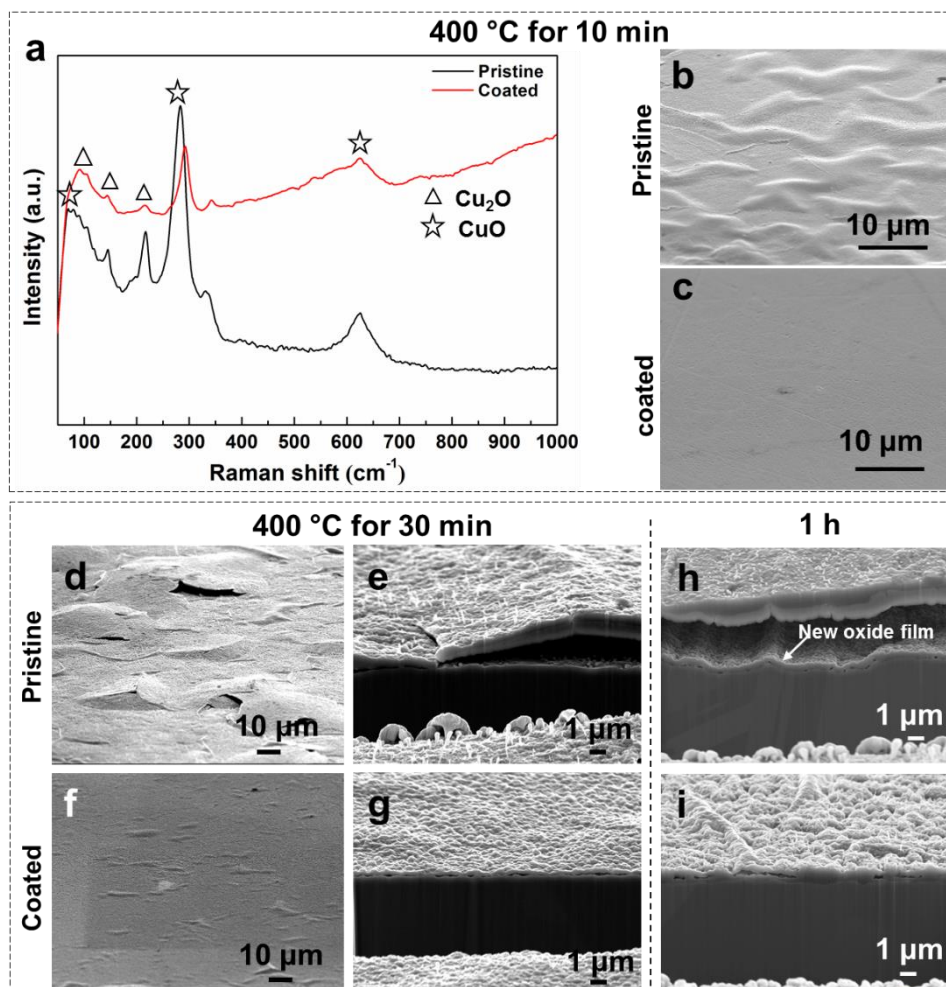


Fig. 3. Cross-sectional TEM images of the (a) center and (b) edge of the implanted area of He⁺-implanted Cu with a fluence of $5 \times 10^{15} \text{ cm}^{-2}$. The insert table shows the TEM-EDS results of the coating film. To prevent damage to the coating film during TEM sample fabrication by the focused-ion-beam system, Au and then C was deposited on the sample. (c) EDS spectrum of the coating film in (b). (d) High resolution TEM image of the interface of coating film and Cu substrate. The inserts are the FFT image of the corresponding areas.



469

470 Fig. 4. (a) Raman spectra and SEM images of (b) pristine Cu and (c) Cu coated with a film prepared
 471 by using He⁺ implantation heated at 400 °C for 10 min. SEM images of the (d), (e), and (h) pristine-
 472 Cu and (f), (g), and (i) coated-Cu samples heated at 400 °C for 30 min ((d)–(g)) and 1 h ((h) and (i)).
 473 All of the SEM images were observed by tilting the sample to 70°. The Raman spectra of the samples
 474 heated for 30 min and 1 h are shown in Fig. S4.

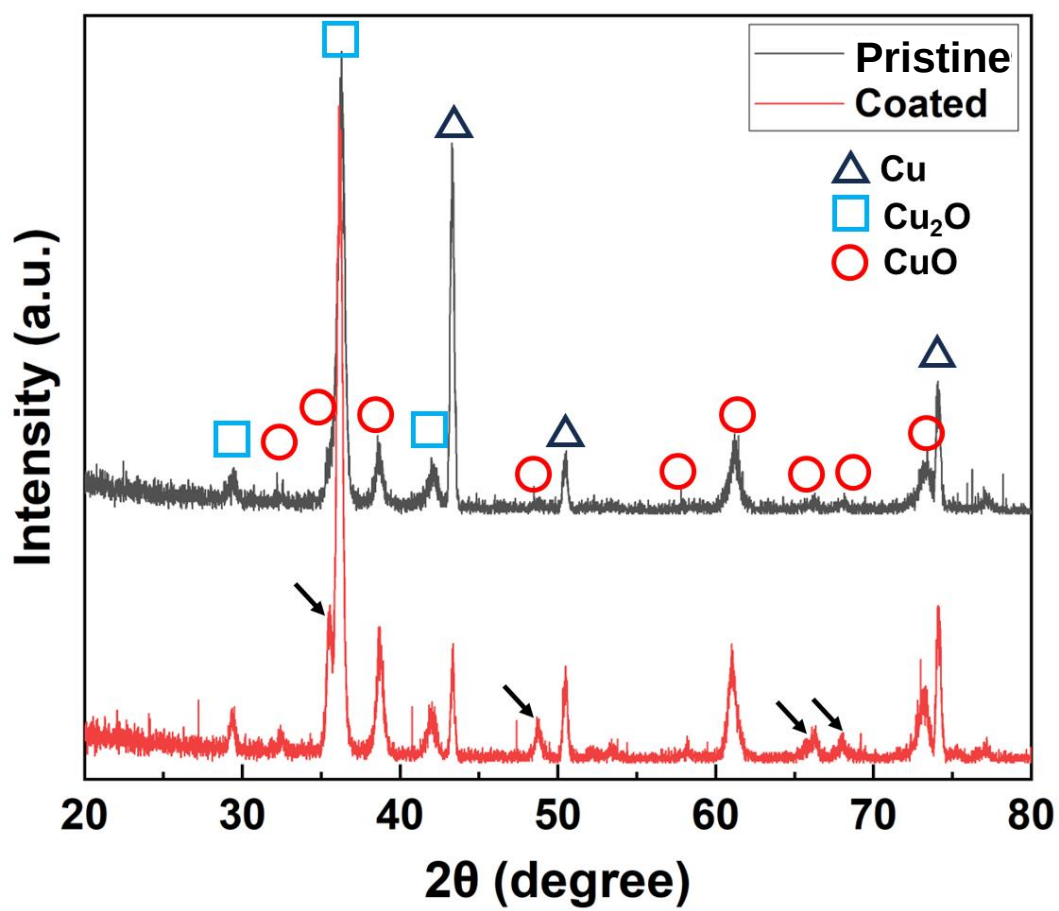
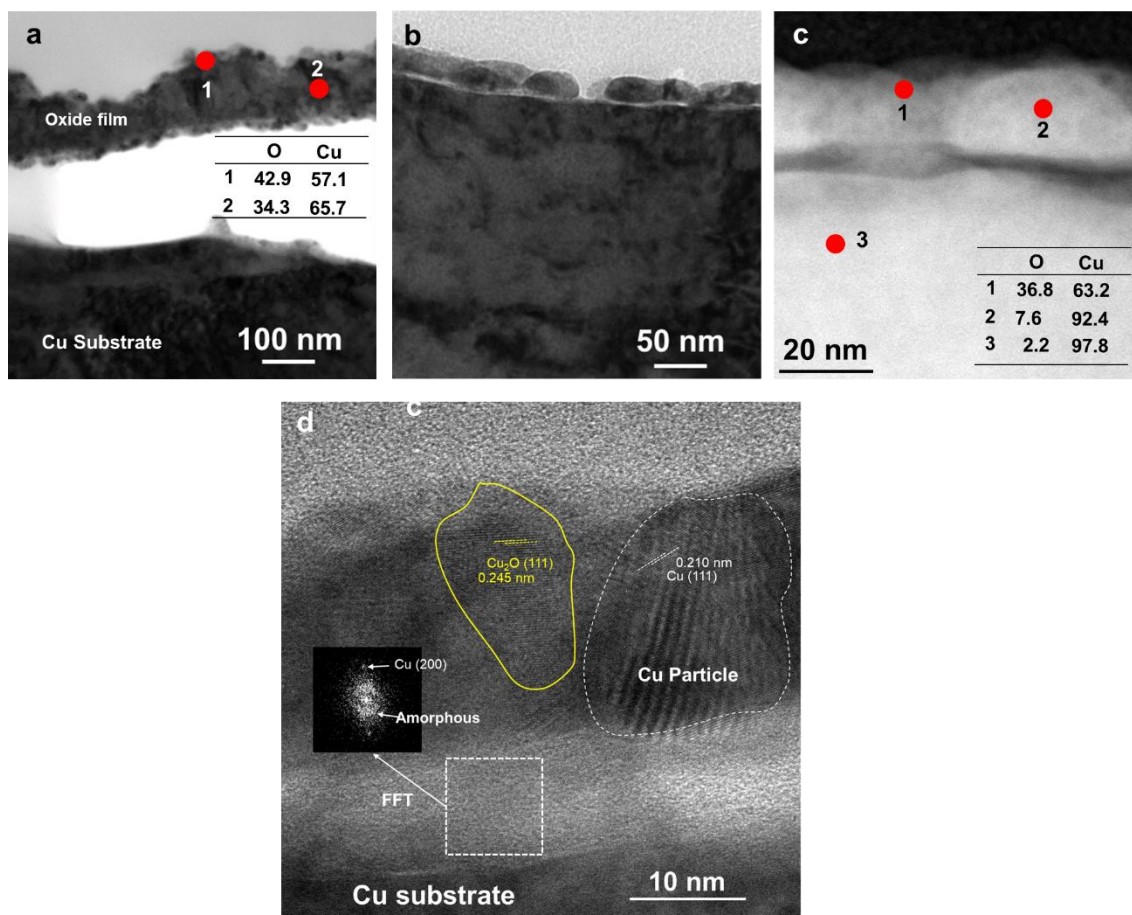


Fig. 5 XRD result of pristine Cu and coated Cu after being heated at 400 °C for 10 min.



477

478 Fig. 6. Cross-sectional TEM image of (a) pristine Cu and (b) coated Cu heated at 400 °C for 10 min.

479 (c) HAADF-STEM image of coated Cu heated at 400 °C for 10 min. The insert table shows the TEM-

480 EDS or STEM-EDS results of the corresponding point in (a) and (c). (d) HR-TEM image of the

481 interface of oxide and Cu substrate of coated Cu heated at 400 °C for 10 min. The inserts are the FFT

482 image of the corresponding areas.

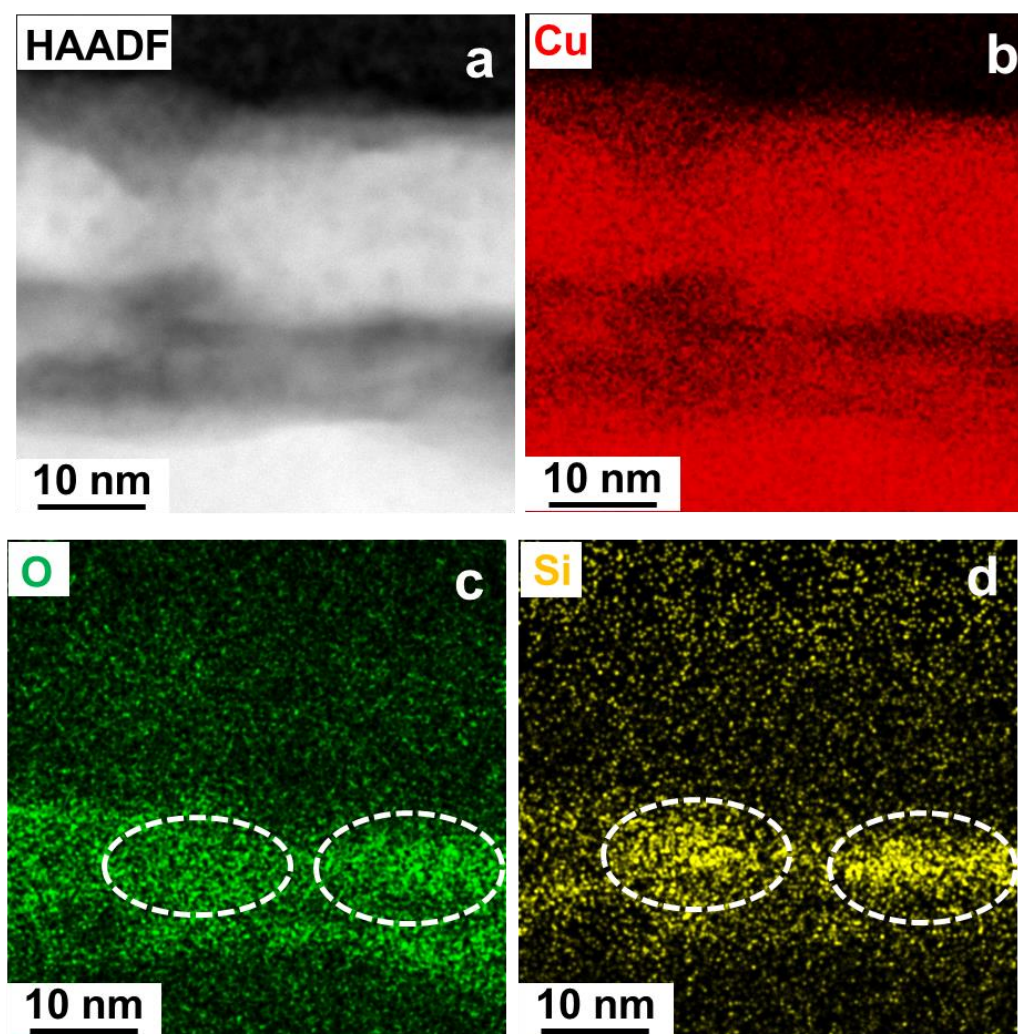
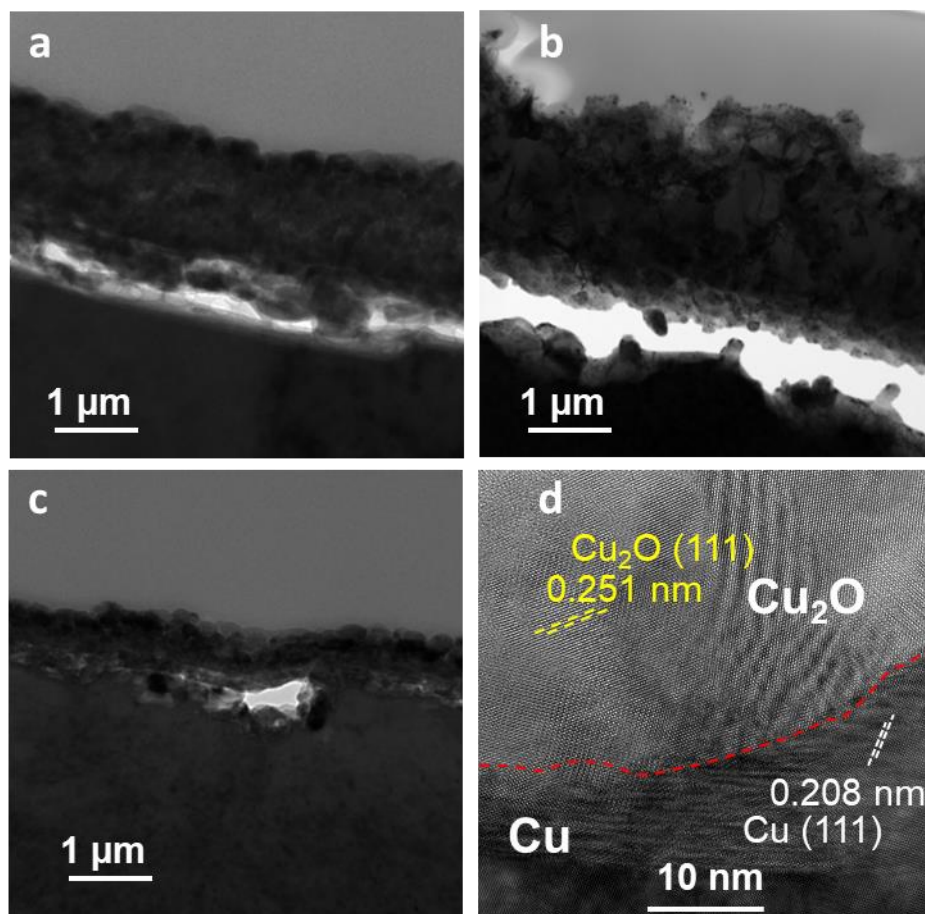


Fig. 7. (a) HAADF-STEM image, and STEM-EDS mapping of (b) Cu (c) O, and (d) Si of coated Cu after heating at 400 °C for 10 min.



487

488 Fig. 8. (a) and (b) Cross-sectional TEM image of different areas of pristine-Cu sample heated at 400 °C

489 for 1 h. (c) Cross-sectional TEM image of coated Cu sample heated at 400 °C for 1 h. (d) HR-TEM

490 image of the interface of oxide and Cu substrate of coated Cu heated at 400 °C for 1 h.