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Modified galvanic replacement using ethanol vapor-assisted vacuum ultraviolet (E-VUV) for enhanced Ag deposition

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ABSTRACT

To enhance the Ag coverage on the Cu surface in the galvanic replacement (GR) method, a two-step surface treatment was developed using Ar fast atom beam (Ar-FAB) bombardment followed by ethanol vapor-assisted vacuum ultraviolet (E-VUV) irradiation. Ar-FAB removed the native oxide from Cu, and E-VUV formed a protective layer that prevents Cu reoxidation in air and dissolves readily in $AgNO_3$ solution. Compared to the traditional GR method with acid etching, X-ray photoelectron spectroscopy (XPS) analyses showed an increased spectrum intensity in Ag 3d and a decrease in Cu-O and –OH, indicating better coverage of the Ag layer on the Cu surface. The Ag layer thickness grew by about 7 nm during immersion from 10 to 300 s, while the traditional GR film stopped growing after 60 s. Scanning electron microscopy (SEM) revealed minimal growth of large Ag dendrites.

1. Introduction

For wafer-scale Cu hybrid bonding, managing low process temperatures, ensuring compliance of Cu electrodes, and preventing surface oxidation are critical challenges [1]. Coating Cu with a soft Ag layer can improve mechanical conformity and electrical conductivity [2]. Galvanic replacement (GR) is commonly used to deposit Ag on Cu but often yields porous or dendritic films due to uncontrolled Ag^+ reduction [3]. Some pioneering studies used acid washing to remove Cu native oxide [4], but reoxidation during transfer can still disrupt nucleation and degrade film quality. Therefore, we propose a two-step surface modification to remove Cu native oxide and form a reoxidation-tolerant protective layer that easily dissolves in a silver nitrate solution. For these characteristics, the protective layer should be only a few nanometers thick. The surface modification method involves Ar fast atom beam (Ar-FAB) bombardment to eliminate native oxide, followed by ethanol vapor-assisted vacuum ultraviolet (E-VUV) irradiation in a nitrogen atmosphere [5,6] to develop a Cu carboxylate-containing protective layer. Afterwards, the Cu sample is immersed in a silver nitrate solution to deposit an Ag film. The coverage and chemical binding state of the Ag film are examined using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), compared to the Ag film formed solely through the conventional GR method with acid cleaning.

2. Experimental details

Cu plates (99.9 % purity, 10 mm diameter, and 500 μm thickness) were used as substrates to study the behavior of Ag nucleation. As shown in Fig. 1(a), the Ar-FAB was performed at 2.0 kV and 20 mA for 120 s at a background vacuum pressure of 1.0×10^{-3} Pa to remove the native oxide. The substrate was then transferred into a nitrogen environment for E-VUV irradiation. In the E-VUV method, the product of VUV irradiation time and ethanol density (defined as the injected weight divided by the chamber volume) was designated as Exposure ($s \cdot kg/m^3$) [6,7], serving as a process parameter. First, the chamber was evacuated to approximately 10^{-3} Pa, then ethanol was atomized and introduced into the chamber with nitrogen (99.9999 % purity) at a flow rate of 80 sccm until the total pressure reached about 0.9 atm, and VUV (172 nm) was irradiated. Exposure was adjusted by balancing between high-purity nitrogen and humidified nitrogen. In this study, an exposure of 2.4 $s \cdot kg/m^3$ was chosen as the process condition based on our previous work using isopropanol vapor as shown in Fig. 1(b) [7]. Although the solvent was different from this study, a similar basic structure, including Cu-OH, Cu-O-, C-OH, and C=O, could form due to CH radicals from dissociated low-grade alcohol. Therefore, the same growth saturation condition was used for the nonce. Next, the substrate was transferred in ambient air and immersed in a 0.1 mM $AgNO_3$ + 1 mM H_2SO_4 solution at room

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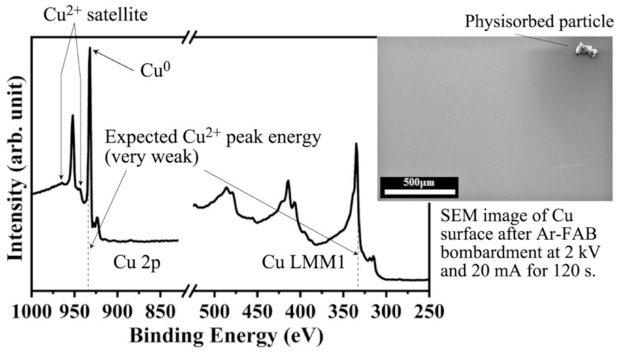
temperature (RT) for 10, 60, or 300 s. Low $AgNO_3$ was chosen to control nucleation and limit dendrite growth [8]. For comparison, the sample that was acid-washed with 3.6 wt% HCl for 10 s experienced the same immersion process. The surface chemical binding conditions were examined using XPS (ULVAC ESCA 1600). A Mg-Kα source with 400 W power was used to perform wide and angle-resolved scans (AR-XPS) with energy steps of 1 and 0.1 eV, respectively. Additionally, SEM (Hitachi SU5000) observations were conducted to compare the physical structures of the Ag films.



SEM image of Cu surface after Ar-FAB bombardment at 2 kV and 20 mA for 120 s.

Fig. 2. Wide-scan XPS spectra of Cu 2p and Cu LMM after Ar-FAB bombardment.

3. Results and discussion

Fig. 2 shows the XPS wide scan spectra (Cu 2p and Cu LMM) and the SEM image after Ar-FAB. The Cu^{2+} peak and its shake-up satellites are negligible compared to the main Cu $2p_{3/2}$ peak, and the Cu^0 signal dominates in the Cu LMM region, confirming native oxide removal and exposure of metallic Cu. The inset SEM image shows no noticeable increase in surface roughness, suggesting minimal mechanical disruption that could affect Ag nucleation. Then, the AR-XPS results after various immersion times are presented in Fig. 3. Spectra were calibrated using standard Cu and Ag binding energies [9]. Fig. 3(a)–(f) show Ag 3d and Cu 2p signals at 15°, 30°, and 45°, corresponding to increasing detection depth. The progressive rise in Ag 3d intensity and reduction in Cu 2p signals with time indicate enhanced Ag coverage. Figs. 3(g) and (h) compare O 1s spectra for the traditional GR and the current methods, respectively. While 3(g) exhibits an asymmetric shape indicative of the synthesis of Cu-O, –OH, and Ag-O peaks, likely due to a certain volume of Ag film defects, 3(h) shows a sharp Gaussian peak centered around 530.2 eV. Assuming this peak corresponds to Ag-O, the atomic concentration ratio in the O 1s spectrum exceeds 90 % with the current method, while the Cu-O and –OH ratios exceed 70 % in the traditional GR method. This indicates fewer defects in the Ag film using the current approach. Fig. 3(i) to (k) show the time evolution of the relative intensities of the Ag 3d, Cu LMM, and Ag 3p spectra in the current method, measured at the same detection depth, with spectra from the traditional GR film at 60 s immersion for comparison, illustrating the trend explained in 3(a) to (h). These findings are further supported by depth estimation using Eq. (1):

$$I_m = I_u \times \exp\{(-x/\lambda_m) \times \sin\Delta\theta\} \quad (1)$$

where I_m and I_u represent the peak area values at different angles, λ_m is the inelastic mean free path obtained from the database [9], Δθ is the angle difference, and x denotes the layer thickness. Using Cu 2p and O 1s spectra, it was found that the Ag film continuously grew during the immersion period from 10 s to 300 s in the current method, with a thickness increase of about 7 nm. In contrast, the traditional GR Ag film

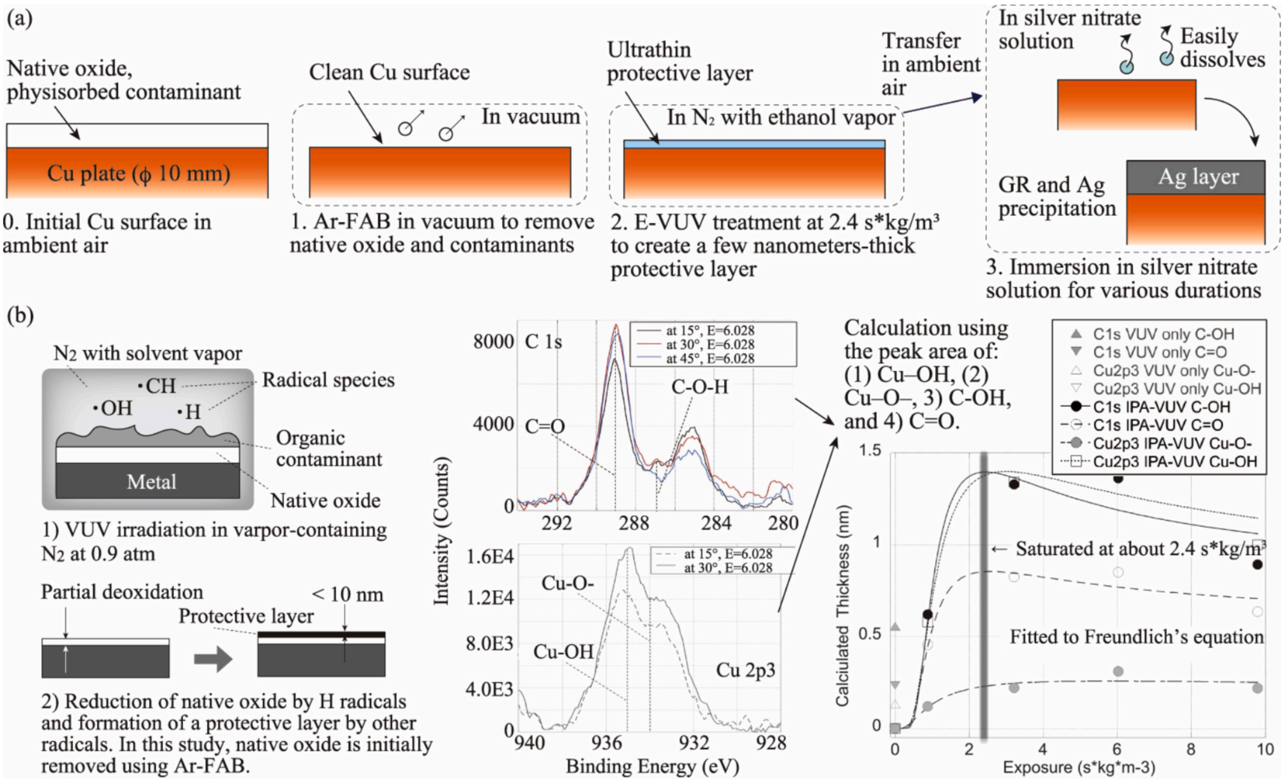


Fig. 1. (a) Outline of the modified GR process, (b) schematic of the E-VUV process, and an example of layer growth behavior on a Cu surface with Exposure, as measured in our previous study using isopropanol vapor [7].

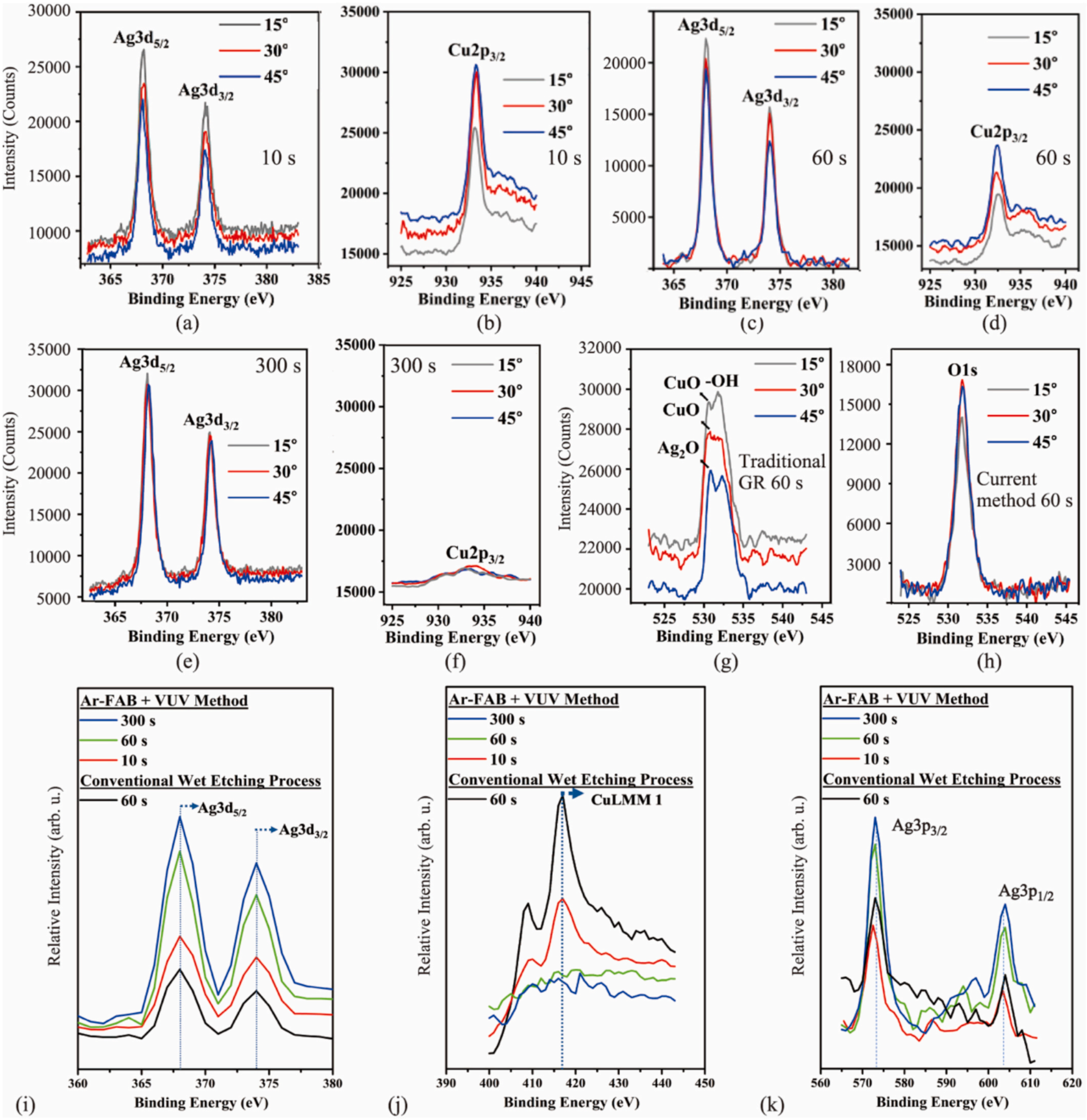


Fig. 3. Evolution of immersion time affecting chemical binding conditions on Cu surfaces in the current process. (a) to (f) show AR-XPS spectra of Ag 3d and Cu 2p, (g) and (h) compare the O 1s spectra of the traditional GR method and the current method, respectively. (i) to (k) present overlays of the Ag 3d, Cu LMM, and Ag 3p spectra from both the current and traditional methods (60-s immersion) for quick comparison.

stopped growing after 60 s, with an increase of around 3 nm.

The SEM results revealed clear differences in the physical structure of Ag films. Fig. 4(a) to (c) display images of Ag films formed using the current method, while those made with the traditional GR method are shown in Fig. 4(d). Figs. 4(a) to (c) demonstrate that a progressively uniform Ag film develops as the immersion time increases. In contrast, Fig. 4(d) shows many coarse dendritic Ag crystals, resulting in porous films with exposed Cu. These coarse dendritic crystals are typical of the traditional GR method, which is initiated by initial defects or residual oxides [10], promoting uncontrolled local Ag^+ reduction. In the current method, it is believed that forming a protective layer on the Cu surface effectively triggered Ag-Cu replacement across the entire surface. The improved film uniformity observed in the modified method can be interpreted using classical nucleation theory [11,12], as shown in Eq. (2):

$$J = A \times \exp(-\Delta G^{*}/kT) \quad (2)$$

where J represents the flux rate, A is the pre-exponential factor, ΔG^{*} is the Gibbs free energy of activation, k is the Boltzmann constant, and T is the temperature. A lower interfacial free energy, for example, through

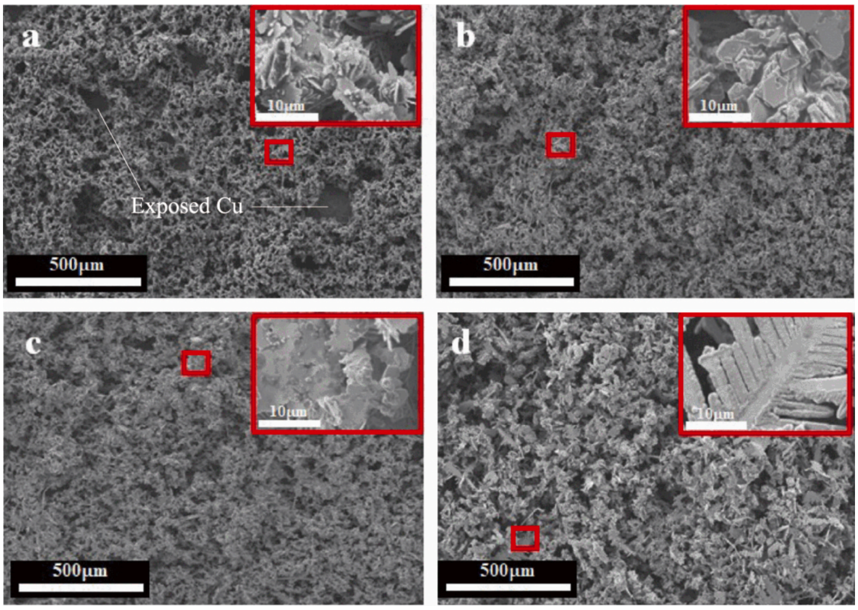


Fig. 4. SEM images of Ag-coated Cu. (a) to (c) show the samples after immersion times of 10, 60, and 300 s with the current method. (d) Displays the surface obtained by the traditional GR method with a 60-s immersion.

oxide suppression, is expected to reduce ΔG*, thereby enhancing nucleation rate (J). Combined with the expected growth mechanism of the protective layer on metal surfaces [6,7,13], the formation steps of the Ag film are summarized in the Graphical Abstract.

4. Conclusion

We achieved an enhanced deposition of Ag on the Cu surface compared to the traditional GR method with HCl oxide removal. A protective layer was formed on the Cu surface using a combination of E-VUV irradiation and Ar-FAB bombardment. The created surface layer prevented the re-oxidation of Cu in air and dissolved easily when immersed in $AgNO_3$ solution. XPS analyses confirmed the formation of an enhanced Ag layer, and SEM observations suggested that this was due to suppressed dendrite growth and uniform Ag precipitation. This method offers potential for future fabrication of Ag-capped Cu electrodes.

CRediT authorship contribution statement

Shubhayan Mukherjee: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Akitsu Shigetou:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Yu-Hao Chou:** Conceptualization. **Shih-Kang Lin:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Akitsu Shigetou reports financial support was provided by Grant Number JP J004596 and the Technical Research Aid provided by the JFE 21st Century Foundation. Shih-kang Lin reports financial support was provided by National Science and Technology Council (NSTC), Taiwan (113-2628-E-006-019, 112-2622-8-006-020). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2025.139482.

Data availability

The data that support the findings of this study, within the article or its supplementary materials, are available from the corresponding authors, upon reasonable request.

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