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Unintended Catalysis and Defect Formation in Electroless Metallization of Semiconductor Wafers

Phey Yee Foong[a,*], Nurhanani Zakaria[a], Theng Theng Tan[a], Zhi En Er[a], and Chaowei Du[b]

[a]*Failure Analysis, Quality Management Department, Infineon Technologies (Kulim) Sdn. Bhd., Kulim Hi-Tech Park, 09000 Kulim, Kedah, Malaysia*

[b]*Failure Analysis, Quality Management Department, Infineon Technologies Austria AG, Siemensstraße 2, 9500 Villach, Austria*

**Corresponding author. Tel.: +6-011-1638-3430; e-mail: PheyYee.Foong@infineon.com*

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ABSTRACT

Owing to the advantages like minimized material waste and green streamlined process, additive metallization has grown as an attractive technique in semiconductor fabrication. Still, reliability issues such as the formation of metallic nodules prevent its widespread use. To date, the formation mechanism of these metallic nodules remains unclear. In this study, a comprehensive formation mechanism of metallic nodules on electroless-plated wafers was investigated using a thorough physical failure analysis (PFA). Optical microscopy, field-emission scanning electron microscopy (FESEM), focused ion beam (FIB) cross-sectioning, and energy-dispersive X-ray spectroscopy (EDX) were among the analytic techniques used to reveal that the nodules (mainly composed of Ni and Pd) are loosely adhered to the passivation layer. Metal oxide residues were identified as potential catalytic sites for unintended metal deposition by EDX line scan after the delayering process. A formation mechanism of nodules is proposed, which includes the leftover of metal residue during the physical vapour deposition (PVD) etching process, oxidation of metal residue and autocatalytic deposition using electroless plating. A potential mitigation strategy, which is ultrasonic, was proven to be effective in dislodging the nodules upon formation. These results provide valuable insight into preventing defect formation and streamlining the electroless metallization for cutting-edge semiconductor applications.

Keywords: *Metallization, Electrochemical Deposition, Metal-Oxide Semiconductor, Failure Analysis, Advanced Characterization*

1. INTRODUCTION

When fabricating electronic components like printed circuit boards (PCBs), antennas and integrated circuits, metallization of non-conductive surface is an essential process, either by subtractive or additive approaches [1]. This process is necessary because the electrical signals were transmitted through this fabricated metal track when they were gapped with a non-conductive surface.

During wafer fabrication, subtractive metallization usually entails a blanket deposition of a metal layer across the whole wafer surface via physical vapor deposition (PVD) or chemical vapor deposition (CVD). Following, lithographic patterning was carried out by resist deposition, patterning and selective etching to remove the unwanted metal, until the desired designed metal interconnect was fabricated [2]. Although this method allows high-resolution patterning, it generates a lot of waste, such as etched metal and used chemical etchant. The process also necessitates a number of complex procedures under strict cleanroom protocol, which raises manufacturing costs and environmental burden. Despite the effort put into waste reduction and recycling, a comprehensive and economical solution to solve these drawbacks is still elusive [3].

In contrast with subtractive metallization, the additive metallization approach forms metal structures directly at the targeted structure, eliminating the repeated process of metal removal [4]. This approach requires the application of a catalytic seed such as palladium [6, 7] and other noble metals [8-10] to activate the non-conductive substrate surface before deposition. To develop a metal structure on a wafer through additive metallization, the catalytic site/precursor layer was first deposited at the targeted structure using inkjet printing, microcontact printing, or laser surface activation. After that, the wafer is subjected to an electroless plating bath to grow metal at the catalyzed site [5]. An appealing alternative for low-cost, flexible and environmentally friendly electronics manufacturing, the additive metallization approach reduces the material consumption and chemical waste while streamlining the entire process flow [11].

However, the additive approach has yet to completely supplant its subtractive counterparts in the semiconductor industry, especially for high-density applications. The main obstacles in replacing additive metallization are the concerns of reliability and consistency of the deposited metal layers. The performance of the product can be seriously compromised if defects such as poor adhesion, void formation and unwanted metallic defects happen [12]. The fundamental principles of all these defect formations are still not well understood, despite the great effort of research being done to improve electroless chemical deposition. For this reason, a comprehensive understanding of these failure mechanisms is crucial in order to achieve robust and defect-free metallization processes.

Several designs of experiments (DoE) were carried out to optimize the processing parameters of electroless-chemical deposition of metal in wafer fabrication. One failed wafer with nodules formation was reserved for a detailed analysis of its failure and formation mechanism. To determine its underlying root cause of the nodules, a comprehensive physical failure analysis (PFA) workflow was carried out. This workflow includes analytical techniques such as optical inspection, field-emission scanning electron microscopy (FESEM), focused ion beam (FIB) cross-sectioning, and energy-dispersive X-ray spectroscopy (EDX). Last but not least, to improve the reliability and process yield of additive metallization, a mitigation strategy was proposed if these nodules were observed during wafer fabrication.

2. CHARACTERIZATION

First of all, optical inspection using a digital high-power microscope (HPM, Keyence, Malaysia) was conducted to localize the defect. After that, the sample was manually cleaved out from the defective wafer. To avoid charging and drifting during FESEM inspection, a thin layer of AuPd was deposited on the cleaved sample using a sputter coater (Quorum, United Kingdom). After sputter coating, the sample was subjected to FESEM (Hitachi, Japan) to study the defect's morphology.

Other than top surface morphology, the cross-sectional microstructure of the nodules was also investigated. A FIB system (FIB, Thermo Fisher Scientific, United States) was employed for cross-sectioning the nodules. Meanwhile, FESEM imaging was conducted to progressively observe the cross-sectional microstructure. At the same time, the elemental composition at the cross-section was analyzed using EDX (Oxford Instrument, United Kingdom).

Chemical delayering was then conducted to delayer the top-most metal layers to visualize the catalytic seed. The sample was submerged in a beaker filled with 80 °C100% fuming nitric acid (HNO_3, SigmaAldrich, Germany) for 30 min to remove the Pd and Ni layer. Following, the sample was rinsed with distilled water to remove all the chemical waste. Next, optical inspection, FESEM imaging (Zeiss, Germany), as well as EDX analysis, was carried out on the delayed sample to study the underlying surface morphology and its elemental composition.

Lastly, ultrasonication was done utilizing an ultrasonic bath (Elma Transsonic, Germany) in order to study the removability and propose a mitigation strategy for these metallic nodules. The sample was subjected to 52 kHz ultrasonication for 15 minutes, followed by optical inspection using HPM.

3. RESULT AND DISCUSSION

The optical images shown in Figure 1(a) and (b) present the process control monitoring (PCM) structures and active die on the defective wafer, respectively. It can be noticed that numerous metallic nodules were observed adjacent to the metal pads and metal lines, which are not seen in other regions. The existence of a nodule and the metal structure has a location association, indicating that these defects most likely formed prior to or during the metal deposition process.

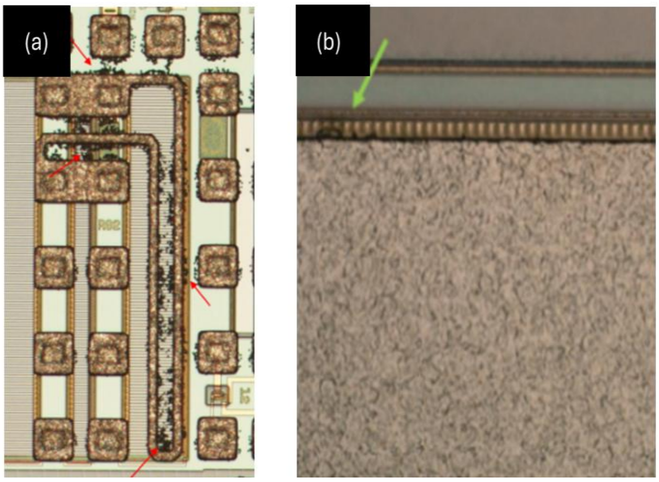

Figure 1. All the nodules (which are indicated by the arrows) are seated adjacent to the metal pad at both (a) the PCM and (b) the active die area.

SEM images in Figure 2(a) illustrate that clusters of nodules were formed near the metal features, at both the metal pad and the metal line. Figure 2(b) shows the tilted view of a high magnification FESEM image of the nodules at the bottom of the metal line. It can be seen that the nodules demonstrate partial detachment from the underlying non-conductive passivation layer. Furthermore, it was observed that every nodule appeared in the same size, regardless of whether it was in the PCM area or the active die area. The nodule surface, shown in Figure 2(c), exhibits a granular morphology that shows all the grain boundaries, suggesting it was composed of a crystalline metallic composition.

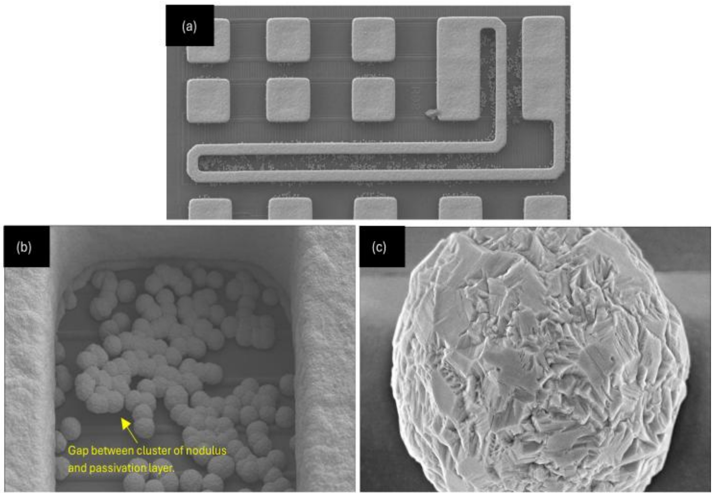

Figure 2. (a) Overview of the nodules between metal lines, (b) tilted view of nodules at the bottom of the metal line, and (c) surface morphology of the nodule at high magnification.

To understand the internal structure and elemental composition of the nodules, progressive FIB cross-sectioning was performed. As shown in Figure 3(a) and (c), EDX mapping showed that the nodules primarily consisted of a Ni layer, followed by a thin Pd layer. This finding corroborates the granular morphology observed in SEM imaging and supports the hypothesis that the nodules are metallic in nature, which is Pd in this case. Notably, Figure 3(b) shows a thin Pd layer making limited contact with the underlying passivation layer, suggesting weak adhesion at the interface.

Based on the observation, the presence of nodules adjacent to the metal pad, and not elsewhere, points to a process-related root cause. According to Danilova et. al. [13], electroless plating occurs selectively on conductive surfaces or catalytically active materials. Nevertheless, after several attempts at progressive FIB cross-section, we failed to detect any residual conductive material beneath the Ni and Pd layers at the nodule sites, likely due to the minute size of the residues, which may have been removed during FIB slicing.

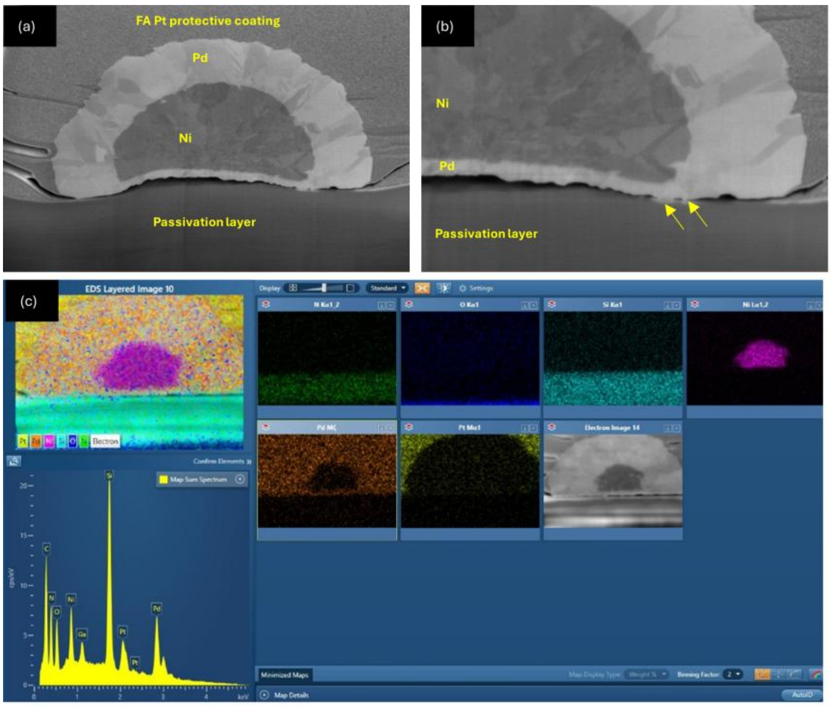

Figure 3. FIB cross-section of nodules at (a) low and (b) high magnification, as well as (c) 5 keV EDX elemental mapping.

To further probe the origin of the nodules, selective chemical delayering was conducted using fuming nitric acid (HNO_3), a known etchant for nickel. Figure 4(a) and (b) show the same region before and after HNO_3 treatment, confirming successful removal of the metal layers. Post-delayering SEM images Figure 4(c) and (d)) revealed the presence of numerous white residues adjacent to the former metal pads, located precisely at sites where nodules had previously formed. These residues are hypothesized to be the precursors or seeds of nodule formation.

The chemical composition of the residues was determined by the EDX line scanning at 15 keV. The presence of oxidized metallic residue was proved by the detection of two localized oxygen peaks along the EDX scan path, as illustrated in Figure 5. However, the specific elemental composition of the metal oxide could not be determined due to the limitation of EDX's detection. Yet, it is hypothesized that these residues may be leftover metallic oxides during the etching process, which further served as the unintended catalysts or nucleation sites during the electroless plating process.

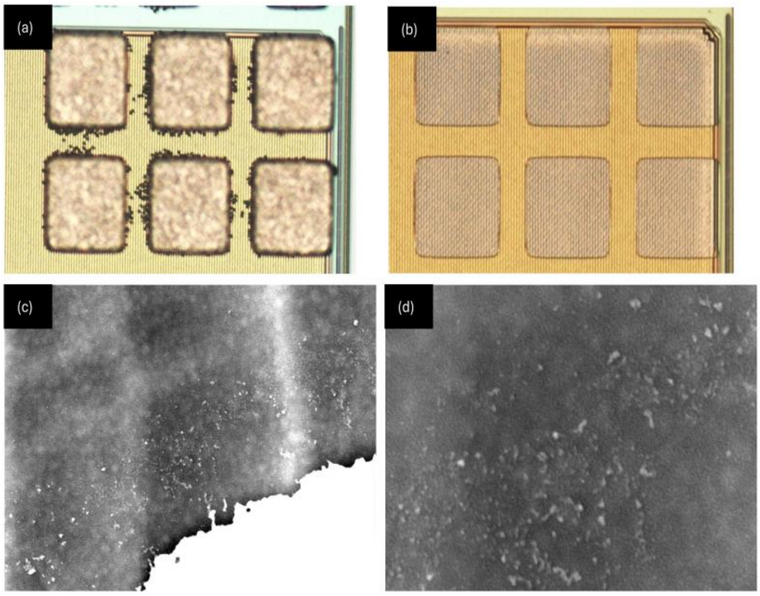

Figure 4. Optical images of the metal pad region (a) before and (b) after chemical delayering and the FESEM images of the post-delayering metal pad at (c) low and (d) high magnification.

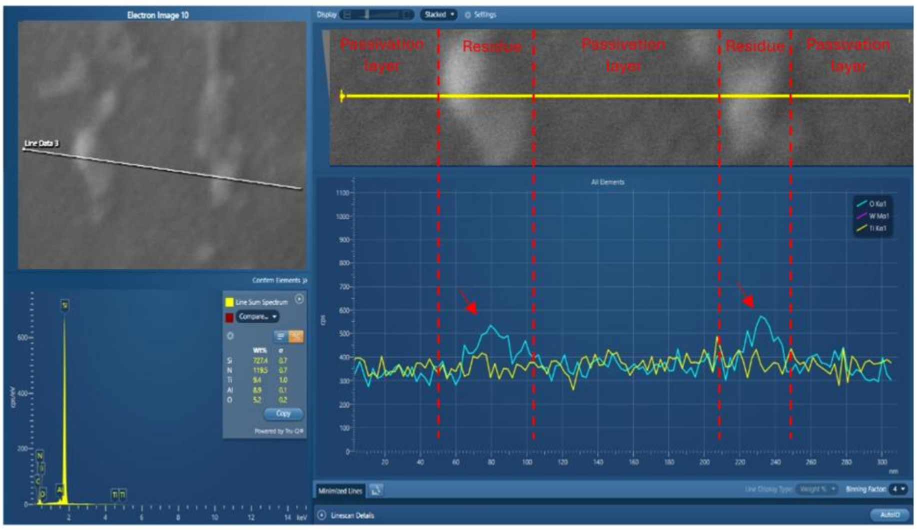

Figure 5. EDX linescan of the residue that seated adjacent to the metal pad after chemical delayering.

According to the FIB and FESEM findings, it is visible that the nodules are weakly attached to the non-conductive passivation layer, which makes them vulnerable to mechanical removal. Apparently, the majority of nodules were successfully removed after being subjected to 15 min of ultrasonication, with only a small number of nodules remaining firmly attached to the metal pads, as shown in Figure 6(a) and (b). Based on this observation, it can be suggested that ultrasonication can emerge as a useful and effective mitigation technique for reducing nodule-induced failure risks if they happen again in the future.

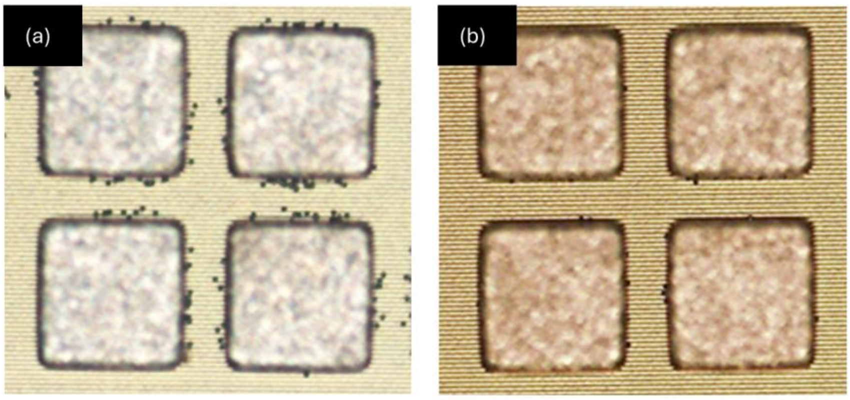

Figure 6. Nodules adjacent to the metal pad (a) before and (b) after ultrasonication.

4. FORMATION MECHANISM OF NODULE DEFECTS

According to the detailed PFA workflow that is supported by surface morphology, elemental mapping, and cross-sectional imaging, a formation mechanism for the observed metallic nodules after electroless chemical deposition, as presented in Figure 1, was proposed. Consistently found next to the metal features on the wafer, the nodules were hypothesized to originate from the process as opposed to random contamination. Therefore, it is assumed that the nodules were formed due to the unintended catalytic activation from the metallic residue leftover from metal etching, resulting in the metal deposition, which subsequently formed a nodule. Figure 7 shows the formation mechanism of the metallic nodules on the passivation layer. The entire mechanism can be categorized into four sequential steps:

(A) Cleaning
Wafer surface cleaning was the first step in every process block in wafer fabrication, which functions to eliminate all the organic, inorganic and particle contamination from the passivation layer process. Although the goal of this step was the surface preparation for metal deposition, insufficient cleaning might leave behind nanoscale metal residue on the surface, particularly in regions with complicated geometry and topography, such as metal sidewalls. Subsequently, these nanoscale residues may serve as the precursor or nucleation site for the metal deposition.

(B) Physical Vapor Deposition (PVD) of Metal Stack
To form a seed layer for the subsequent electroless plating process, a metal layer, commonly tungsten (W) or titanium-based (Ti) materials, was deposited via the physical vapor deposition (PVD) method. With PVD, the metal atoms are sputtered and condensed onto the wafer surface in a directed and line-of-sight direction. Nevertheless, a non-uniform PVD deposited layer can be observed, especially at the complex surface topographies such as steep sidewalls and deep trenches, due to its intrinsically low step coverage. In this case, the geometric shadowing of these complex topographic sites received significantly less material than a flat horizontal surface. As a result, the vertical surface often has a thin or irregular metal layer as compared to a flat horizontal surface.

This irregular coverage may lead to a number of problems during wafer fabrication. As an instance, it could retain chemicals or particles that are challenging to get rid of in the later process, which may further lead to device failure. Besides that, this non-uniform coated region may then undergo micro-masking during the subsequent etching process, in which residues shaded metal layer persist while other metal in the clean area is etched. As a result, the wafer surface is left with residual metallic fragments.

(C) Patterning and Etching
Following, the wafer was subjected to photolithographic patterning and an etching process to develop a metal interconnect structure. This phase involves the selective removal of the unwanted PVD metal layer. Yet, as can be seen in FESEM images in Figure 4, metallic residue (M) may still be present neighboring the metal features if the etching and cleaning process is not accurately optimized. When exposed to ambient environments, this residual metal can experience surface oxidation, as shown by the EDX linescan in Figure 5, forming a thin film of metal oxide ($M(OH)_n$ or MO that can further lead to unwanted metal deposition. Equation (1) and (2) shows the oxidation reaction of these metal residues under ambient conditions.

$$M \rightarrow M^{n+} + ne^{-} \tag{1}$$

$$M^{n+} + H_2O \rightarrow M(OH)_n \ or \ MO \tag{2}$$

Due to its nanoscale size, these metal oxide residues might not be detected during in-line inspection. For this reason, this nanoscale residue acted as the nucleation site when subjected to the following electroless-plating process.

(D) Electroless Plating
Electroless plating is an autocatalytic redox process, in which metal ions in solution are reduced and deposited onto a catalyzed surface without external electrical power required [14]. Instead, it depends on the presence of a

catalytic or conductive surface to initiate the redox reaction. The general mechanism involves a metal ion (N^{n+}) being reduced by a chemical reducing agent present in the solution, depositing metallic atoms (N^0) onto the substrate [10]:

$$N^{n+} + Reducing\ Agent\ \rightarrow\ N^0 + Oxidation\ Products \quad (3)$$

This surface-mediated reaction occurs only on conductive or catalyzed surfaces, such as exposed metal lines or surfaces seeded with catalytic metal. On insulating materials such as silicon oxide, electroless plating cannot proceed unless unintended conductive residues are present [10]. In semiconductor fabrication, residual metallic particles left behind after dry etching or incomplete cleaning can serve as unintended nucleation sites. In this case, the metallic oxide fragment, besides the metal pad, served as the nucleation site for the growth of metallic nodules. Owing to the undetectable size, the wafer was proceeded to the subsequent process, which is electroless plating of the following layer. When exposed to the reducing environment of the electroless plating bath, these sites promote unwanted metal growth, resulting in the localized formation of spherical or hemispherical protrusions—referred to as nodules adjacent to patterned metal features, as shown in Figures 1 and 2. These nodules can cause reliability issues such as short circuits or increased leakage current if not properly removed or prevented.

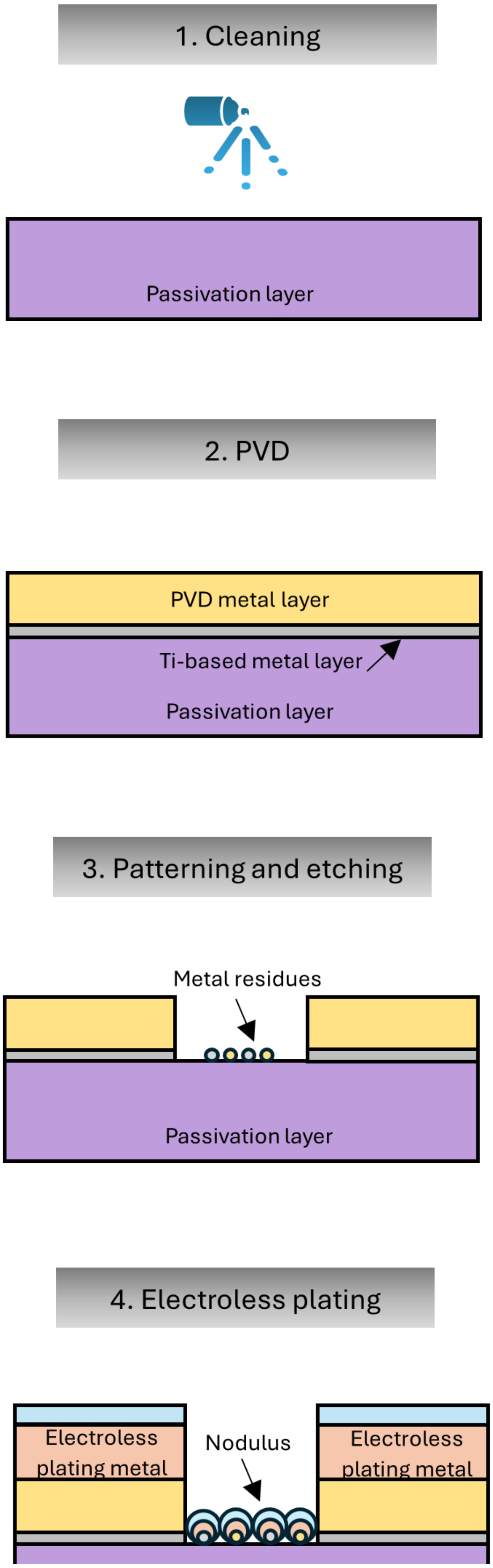

Figure 7. Formation mechanism of the nodules during the electroless plating process.

In this study, these nodules were observed to form exclusively adjacent to metal features, as confirmed by SEM and FIB analysis. They exhibit metallic grain structures and weak adhesion to the passivation layer, suggesting that they are a product of post-etch surface contamination activated during plating. Upon formation, these conductive metallic nodules have the potential to connect tightly those gapped metal features, resulting in the electrical shorting and current leaking.

Consequently, with the combination of various factors, including (1) incomplete residue removal during surface cleaning and etching process, (2) oxidation of metal residue and (3) autocatalytic deposition of metal layer on the unwanted region during electroless plating process, the area responsible for the formation of metallic nodules near metal features. Hence, enhancing the pre-plating surface cleanliness, optimizing the etching coverage, especially in complex geometries, and reducing the occurrence of metallic residue on the passivation layer should be the main goals to prevent the nodule formation and increased process yield.

CONCLUSION

As a conclusion, in this work, a thorough PFA workflow was conducted to study the formation of metallic nodules on semiconductor wafer after the electroless chemical deposition process. In brief, the nodules were identified to be metallic in nature and seated next to the metal pad and metal line. This suggests that these nodules were caused by the process rather than random contamination. Unintended catalytic activation from the metallic residue leftover during pre-plating processes such as PVD, etching, and cleaning was traced as the primary root cause. During electroless chemical deposition, these incomplete etched metallic residues served as the nucleation site for the metal deposition, leading to the formation of metallic nodules after a subsequent metal layer was grown on them. A formation mechanism was proposed, emphasizing the roles of incomplete metal residue etching, surface oxidation, and autocatalytic redox reactions in nodules initiation. Additionally, it has been demonstrated that ultrasonication can be a successful mitigation technique for eliminating those nodules that were poorly adhered to the non-conductive passivation layer. Future studies should focus on optimizing metal etching and surface cleaning process parameters, preventing the occurrence of unintentional catalytic activation on insulating substrates, which contributes to higher process reliability and yield.

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DATA AVAILABILITY DECLARATION

The FESEM images' scale bars and magnification, as well as the raw/processed data of this study, cannot be shared due to company confidentiality restrictions.

REFERENCES

[1] Rahman, M. A., Saleh, T., Jahan, M. P., McGarry, C., Chaudhari, A., Huang, R., Tauhiduzzaman, M., Ahmed, A., Mahmud, A. A., Bhuiyan, M. S. (2023). Review of intelligence for additive and subtractive manufacturing: Current status and future prospects. Micromachines. Volume: 14 Issue: 3. 508.

[2] Pandey, K., Sharma, A., Singh, A. K. (2022). Silicon wafers; its manufacturing processes and finishing techniques: An overview. Silicon. Volume: 14 Issue: 18. 12031-12047.

[3] Meese, A. F., Kim, D. J., Wu, X., Le, L., Napier, C., Hernandez, M. T., Laroco, N., Linden, K. G., Cox, J., Kurup, P. (2021). Opportunities and challenges for industrial water treatment and reuse. ACS EST Engineering. Volume: 2 Issue: 3. 465-488.

[4] Kim, S., Lee, I., Kim, H. (2021). Fabrication of parts with integrated circuits by selective electroless plating of additively manufactured plastic substrates. International Journal of Precision Engineering Manufacturing-Green Technology. Volume: 8. 1439-1447.

[5] Andreatta, G. A., Hendricks, N. R., Grivel, A., Billod, M. (2022). Grafted-to polymeric layers enabling highly adhesive copper films deposited by electroless plating on ultra-smooth three-dimensional-printed surfaces. ACS Applied Electronic Materials. Volume: 4 Issue: 4. 1864-1874.

[6] You, J.-L., Chang, C.-P., Pu, N.-W., Chen, Y.-S., Wang, L.-H., Pan, K.-H., Ger, M.-D. (2022). Electroless plating of a 5g copper antenna on polyimide patterned with laser-induced selective activation and curing of metal–organic catalyst. Applied Surface Science. Volume: 599. 153990.

[7] Huang, J., Gui, C., Ma, H., Li, P., Wu, W., Chen, Z. (2021). Surface metallization of pet sheet: Fabrication of pd nanoparticle/polymer brush to catalyze electroless nickel plating. Composites Science Technology. Volume: 202. 108547.

[8] Ababaii, M. A., Gilani, N., Pasikhani, J. V. (2024). Hydrogen evolution from nabh4 solution using cr-doped ni–b metallic catalyst deposited on rice husk via electroless plating. International Journal of Hydrogen Energy. Volume: 51. 648-662.

[9] Muench, F. (2021). Electroless plating of metal nanomaterials. ChemElectroChem. Volume: 8 Issue: 16. 2993-3012.

[10] Kim, N. K., Kang, S. M., Kim, T., Kim, S., Kim, G. H. (2025). Electroless plating on polymer surfaces: Comprehensive review of mechanism, process, analysis, and future applications. Advanced Materials Interfaces. 2400931.

[11] Kostrada, A. (2023). Effectiveness of metal coating using electroplating, electroless plating and hot dipping in the manufacture of weapons. International Journal of Social Service Research. 1494-1498.

[12] Zhang, Y., Zhang, T., Shi, H., Liu, Q., Shi, Y., Wang, T. (2021). Electroless plating cycle process for high-conductivity flexible printed circuits. ACS Sustainable Chemistry Engineering. Volume: 9 Issue: 35. 11991-12004.

[13] Danilova, S., Graves, J. E., Sort, J., Pellicer, E., Cave, G. W., Cobley, A. J. E. A. (2021). Electroless copper plating obtained by selective metallisation using a magnetic field (smmf). Volume: 389. 138763.

[14] Muraliraja, R., Selvan, R. A. S., Selvakumar, A., Franco, M., Tamilarasan, T., Sanjith, U., Sha, W., Sudagar, J. (2023). A review of electroless coatings on non-metals: Bath conditions, properties and applications. Journal of Alloys Compounds. Volume: 960. 170723.