applied sciences

MDPI

Article

In Situ Annealing Behavior of Cu Thin Films Deposited over Co-W Diffusion Barrier Layers

Bruno M. C. Oliveira [1,2,*,†], **Ruben F. Santos** [1,2,†] and **Manuel F. Vieira** [1,2]

[1] Department of Metallurgical and Materials Engineering, University of Porto, 4200-465 Porto, Portugal
[2] LAETA/INEGI—Institute of Science and Innovation in Mechanical and Industrial Engineering, 4200-465 Porto, Portugal
* Correspondence: up200803851@edu.fe.up.pt
† These authors contributed equally to this work.

Abstract: The development of new materials for the electronics industry has been in focus in recent years, as circuit miniaturization poses challenges for conventional solutions. Dewetting of Cu films over diffusion-barrier layers has fostered an interest in developing new solutions with lower interfacial energies, to withstand processing and service life. Co-W is a candidate material for seedless Cu-interconnect deposition, but its behavior during annealing is still not properly addressed. This study used an in situ scanning-electron-microscopy (SEM) approach to assess how heating rates affect dewetting behavior, as well as to determine the limits of annealing of 40 nm-thick Cu films deposited over this substrate. The 10 °C/min heating rate used showed copper dewetting starting at 450 °C, whereas the higher 30 °C/min rate induced dewetting at 400 °C. The Cu film deposited over Ta exhibited slightly different dewetting, with its onset starting earlier, but developing a slower progression throughout the temperature range analyzed in the annealing treatments.

Keywords: in-situ dewetting; cobalt tungsten; diffusion barrier; copper interconnects; thin film

check for updates

Citation: Oliveira, B.M.C.; Santos, R.F.; Vieira, M.F. In Situ Annealing Behavior of Cu Thin Films Deposited over Co-W Diffusion Barrier Layers. *Appl. Sci.* **2022**, *12*, 9778. https://doi.org/10.3390/app12199778

Academic Editor: Francesco Enrichi

Received: 1 September 2022
Accepted: 26 September 2022
Published: 28 September 2022

1. Introduction

The development of increasingly powerful central processing units (CPU) has been sustained by manufacturing advances in the semiconductor industry that enabled the fabrication of increasingly smaller features, such as the Cu interconnects used for electron flow throughout the circuitry. As the features progressively shrink to smaller dimensions, physical limits to the properties of the materials used start to pose challenges to proper wafer-processing during manufacture, which in turn inhibits the adequate functioning of the underlying devices.

One of the components whose performance has become an obstacle to the progress of circuit miniaturization is the diffusion-barrier layer used to prevent Cu from diffusing from the metallic interconnects to the adjacent dielectric layers. As the thickness of these structures enters the nanometric scale, the associated increase in the electrical resistivity of the TaN-based solutions commonly used adversely affects the efficiency of the circuit. Another issue affecting Cu interconnect development is the dewetting of the Cu layers during the annealing stage in manufacturing, due to the low thermal stability associated with the interface of very thin Cu films and the substrate onto which they are deposited [1]. Mullins [2] theorized that the thermal-grain boundary grooving, which has since become associated with dewetting, results from the evaporation and surface-tension-evolution interaction during annealing.

Different alternative systems of various chemical compositions have been tested over recent years to replace the Ta/TaN adhesion and diffusion barrier layers, respectively [3]. Solutions using conductive materials, such as Co and Ru, alloyed with other metals, such as Ta or W, to confer additional thermal stability have been explored so far [4–8]. These solutions not only solve the issue mentioned above but also attempt to suppress the need to use a Cu-seed layer before Cu electroplating for via filling, which limits the minimum thickness attainable by the most commonly used technology. Fillot et al. [9] claim that since Ta has a higher melting temperature than Cu, its surface energy should be higher. By this reasoning, both Co and W should exhibit a higher surface tension value than Cu, as both their melting temperatures are higher than Cu. Although several studies have been carried out regarding the properties of these materials, thin film dewetting or dewetting of Cu films, there is not currently any study concerning the phenomenology of the dewetting phenomenon of the Cu films deposited over these new alternative-barrier layer materials [10–13].

Using in situ microscopy enables investigation of the behavior involved in the thin film dewetting process. This type of study can prove instrumental in identifying the structural evolution of the Cu film over each of the materials under study during annealing, which in turn can help assess substrate viability as Cu-adhesion barrier layers. By using this technique, observation of the evolution of the surface of the films can be registered as the materials are submitted to high temperatures in real time. A recent in situ study of Cu films deposited over Si determined that Cu-film thickness was related to the shape in which dewetting occurs, with 20 nm thick films exposing the substrate through the expansion of fractal shapes. The same study found that hillocking of grains was the behavior registered for films of thickness higher than 55 nm [10,14]. In this work, we explore how a thin Cu film deposited over an equimolar Co-W substrate evolves at progressively higher temperatures via in situ scanning-electron-microscopy (SEM) analysis. A Ta substrate was also studied to compare its Cu-adhesion performance under identical processing conditions. By using this approach, we obtained real-time data of the surface of the stacks during annealing, and in this way were able to assess the associated surface stability of the systems as well as evaluate how Cu surface dewetting develops.

2. Materials and Methods

2.1. Thin Film Deposition

Co-W and Ta films, which will be used as substrates for Cu-film deposition, were produced by physical vapor deposition (PVD) over a p-type boron-doped single-crystal wafer piece of (100) oxidized silicon with a 4 mm diameter (Silicon Valley Microelectronics, Santa Clara, USA). A 27 nm thick Co-W film was created by co-sputtering separate Co and W targets (99.95%, Testbourne Ltd., Basingstoke, UK) at 40 W power each, for 600 s in a DC magnetron sputtering system (Kenosistec, Binasco, Italy) using a constant 20 sccm Ar flux. A 25 nm Ta film was used for comparison, after being deposited at 100 W for 380 s, (99.99%, Testbourne Ltd., Basingstoke, UK) at 6.9×10^{-3} Pa. The Cu film was deposited over both stacks at 40 W for 900 s at 6.9×10^{-3} Pa, forming a 40 nm thick film as detailed in a previous work [15]. The same Ar pressure during Cu deposition should allow for identical compressive-stress distribution from the deposition stage on the film [16].

2.2. In Situ SEM Heating

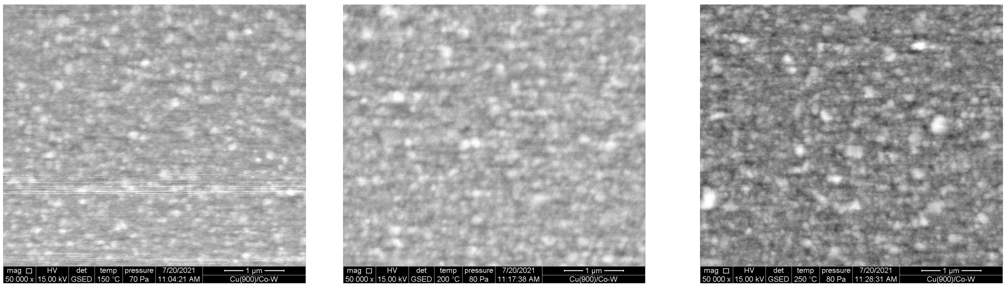
In situ SEM annealing was carried out using a hot stage mounted inside a Thermo Fischer Scientific Quanta 400FEG ESEM (Thermo Fischer Scientific, Waltham, MA, USA). The sample holder that allows heating requires the machine to be used in ESEM mode. Heating rates were uniformly applied and controlled from the user interface according to thermocouples placed near the crucible holding the samples. During these experiments, an Ar pressure of 70–80 Pa was applied, as use of the hot stage hampered operating conditions for a conventional vacuum-level-image acquisition for sample heating started from 150 °C and progressed until 550 °C using two distinct heating rates for both systems, namely 10 °C/min and 30 °C/min, to assess the effects of the heating rate on Cu dewetting behavior. The samples were left for 10 min at each target temperature for both heating rates, to allow for temperature homogenization throughout the surface of the films.

3. Results

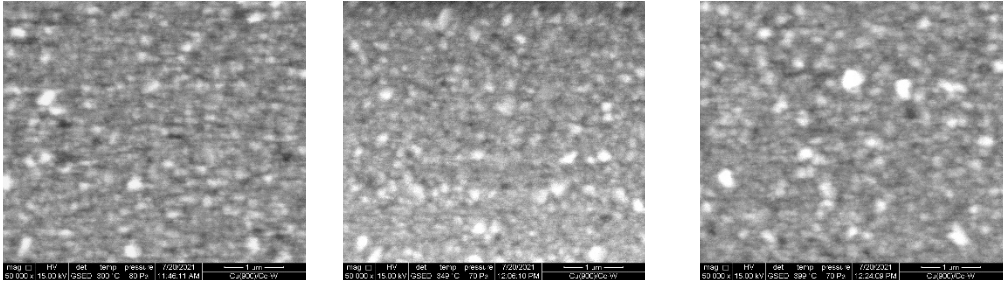
3.1. Cu/Co-W

3.1.1. 10 °C/min Heating Rate

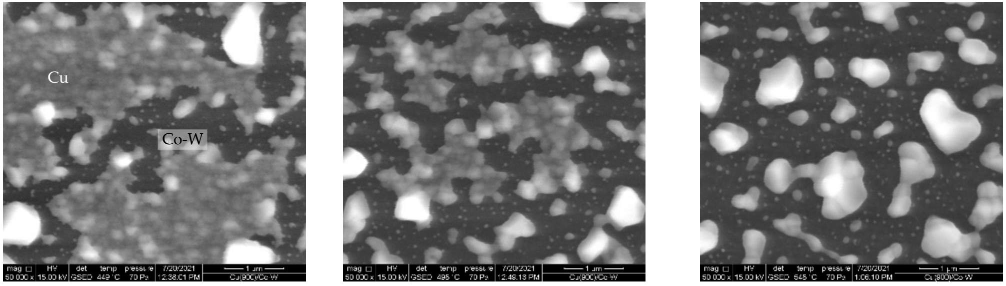
The surface of the Cu film starts exhibiting grain growth at 200 °C when a 10 °C/min heating rate is applied, as seen in Figure 1b. The onset of dewetting at this heating rate was found to be in the 400 and 450 °C range. At the end of the isothermal step of the latter temperature, the Cu film was retracting its coverage over the Co-W substrate. The rate at which this front retracts, consuming the Cu film, is very fast. As temperature rises, abnormal grain growth progresses until the stage seen in Figure 1i, where nearly all the Cu film has diffused to form mostly large islands. This type of island geometry has been calculated to present a lower energy state than a thin, continuous film, in line with total energy minimization [17]. The geometry of the large Cu grains present suggests that the dewetting process has not concluded, seeing as the particles are not yet completely round.



(**a**) 150 °C (**b**) 200 °C (**c**) 250 °C



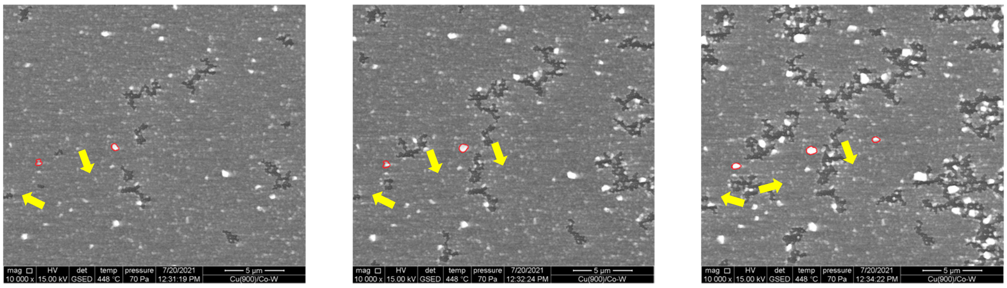
(**d**) 300 °C (**e**) 350 °C (**f**) 400 °C



(**g**) 450 °C (**h**) 500 °C (**i**) 550 °C

Figure 1. Surface of the Cu film deposited over a Co-W layer from 150 °C (**a**) to 550 °C (**i**), using a 10 °C/min heating rate. The figures illustrate the progressive microstructural variation with temperature increases of 50 °C.

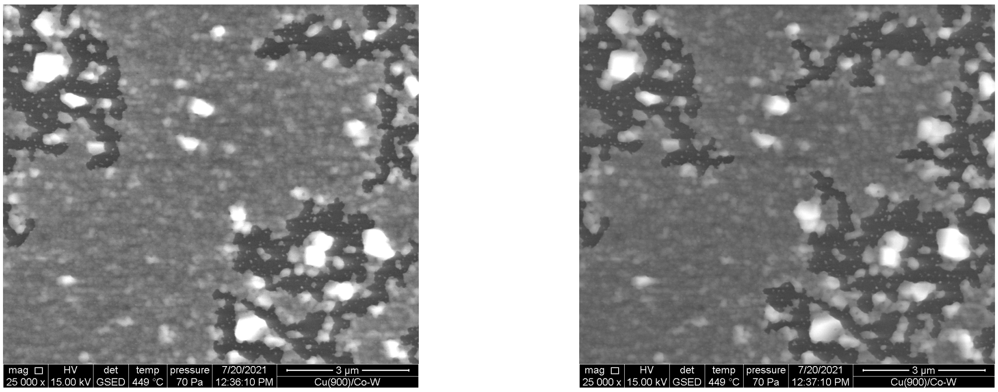
There were no visible indications of Cu dewetting under 400 °C, with Figure 2 showing dewetting of the Cu layer occurring quickly once conditions for its onset are met, during the 450 °C isothermal step. This sequence shows how abnormal grain formation and growth are stimulated by lateral diffusion of the Cu atoms disposed throughout the previously compact film, even at large distances from where the atoms are being displaced, as noted in the highlighted areas. This behavior suggests that lateral distance is not the main determining factor affecting Cu-atom diffusion throughout the film, with favorable crystallographic orientations exerting an important effect in determining which grains grow and which grains are consumed to foster the grain growth [18,19].



(**a**) (**b**) (**c**)

Figure 2. Dewetting progression at 450 °C of a Cu film with a Co-W substrate during a 3 min time-lapse, heated at 10 °C/min, with (**b**,**c**) being captured 1 and 3 min after (**a**), respectively. Yellow arrows and red outlines indicate abnormally large grains growing some distance from the developing dewetting front.

The evolution of an area of the film after one minute at 450 °C can be seen in Figure 3. It is observable that even in the initial stages of dewetting, the set of conditions for the formation of very small vestigial Cu grains has already been fulfilled. This observation is opposed to the hypothesis of these smaller grains being formed only during the final stages of the process, when most of the Cu film has already been consumed to feed the growth of the Cu islands at high temperatures.

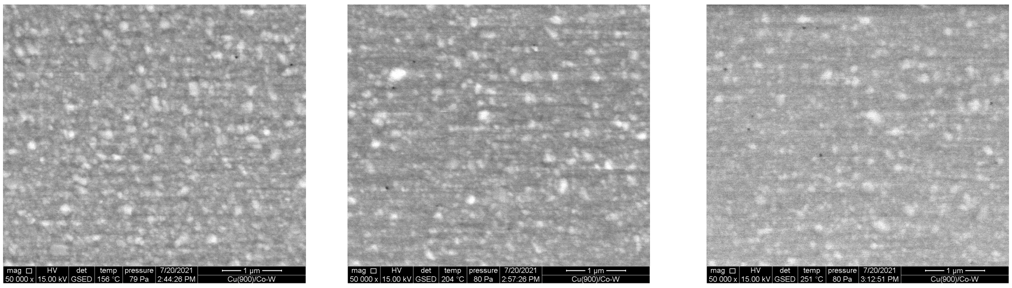


(**a**) (**b**)

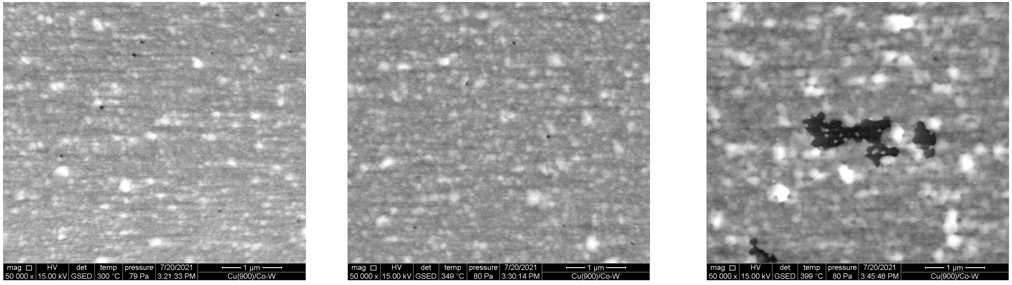
Figure 3. Dewetting progression of a Cu film with a Co-W substrate during a 1-min time-lapse, at 450 °C, heated at 10 °C/min (**a**) after 127 min. and (**b**) after 128 min. total annealing time.

3.1.2. 30 °C/min Heating Rate

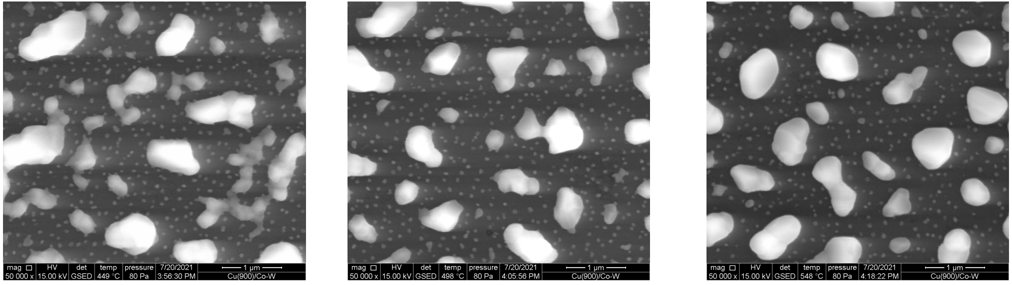
A higher heating rate of 30 °C/min was used to determine the effect on the dewetting resistance of the Cu films over the substrates under different thermal loads, as seen in Figure 4. Higher heating rates led to changes in dewetting resistance of the Cu film, triggering dewetting of the Cu for a temperature 50 °C lower than the lower heating rate studied. Furthermore, as seen in Figure 4i, the final temperature analyzed showed formation of more regularly shaped islands than the equivalent temperature for the lower heating rate. This indicates that a higher heating rate translates to an acceleration of total energy minimization of the Cu film studied, assuming identical initial interface energy conditions for the Cu/Co-W interface for both stacks used. The presence of pinholes can be seen from Figure 4a–e), with their dimensions remaining stable throughout the associated temperature range and no abnormally large grain appearing to form in their vicinity.



(**a**) 150 °C (**b**) 200 °C (**c**) 250 °C



(**d**) 300 °C (**e**) 350 °C (**f**) 400 °C



(**g**) 450 °C (**h**) 500 °C (**i**) 550 °C

Figure 4. Surface of the Cu film deposited over a Co-W layer from 150 °C (**a**) to 550 °C (**i**), using a 30 °C/min. heating rate.

3.2. Cu/Ta

3.2.1. 10 °C/min Heating Rate

The Cu/Ta stack annealed using the 10 °C/min heating rate exhibited the first signs of Cu-film dewetting as early as at the 200 °C stage, as seen in Figure 5. Contrary to what was observed for the Cu/Co-W system, however, dewetting did not seem to progress continuously after its onset under these experimental conditions. The area percentage of Ta substrate exposed remained rather uniform until the 450 °C stage, after which abnormal Cu-grain growth became more pronounced in association with the progression of dewetting. As the Cu atoms diffuse laterally to other grains to feed grain growth, the Cu-film thickness decreases leading to exposure of the substrate. The final 550 °C temperature exhibited a smaller exposed substrate area than any of the Co-W heating rate results, at roughly 60% of the area covered by Cu. Given that dewetting of the Cu film did not progress continuously as soon as the substrate was exposed, surface tension at the Cu film should be lower than observed for the Co-W systems, where dewetting progressed quickly once conditions for its onset were fulfilled. This difference in behavior between both systems may be attributed to different initial residual stresses in the Cu film, as a result of the PVD process of creating both the substrate and the Cu films. The results at each analyzed temperature also show considerable differences from those seen on the Co-W system, with the presence of only a few abnormally large Cu grains dispersed along a still visible Cu film covering the substrate.

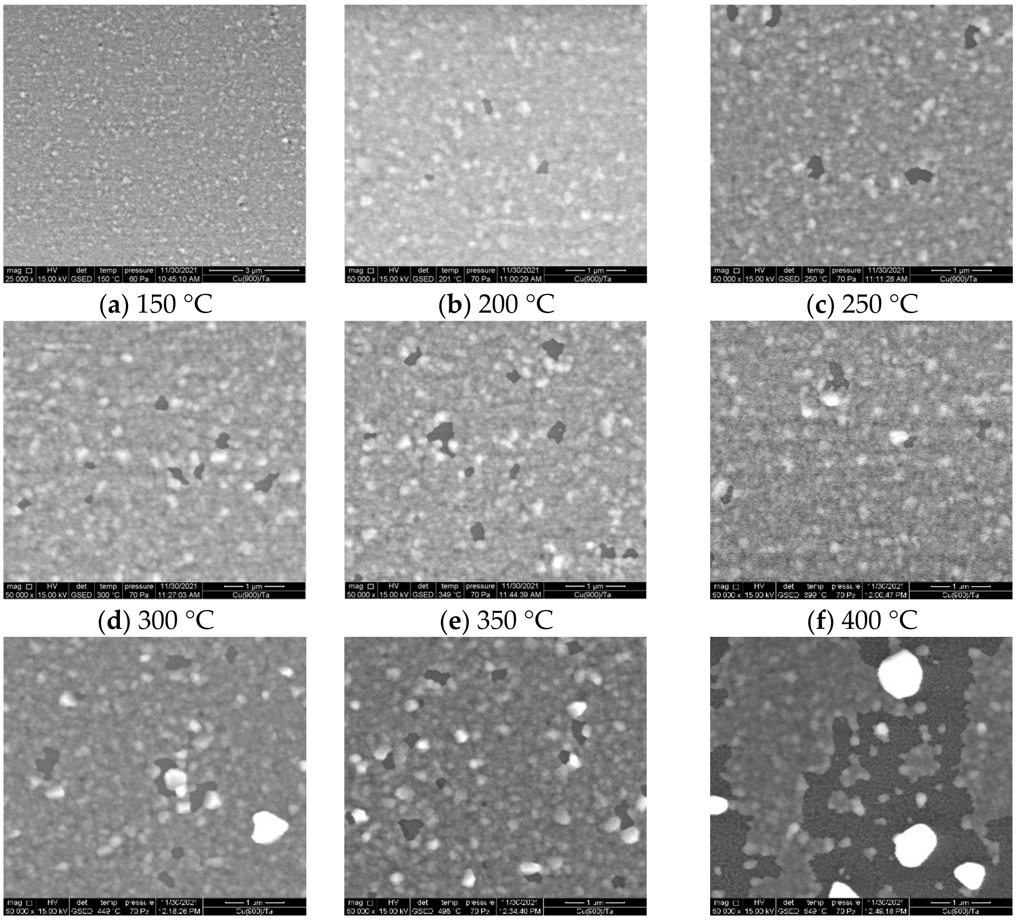
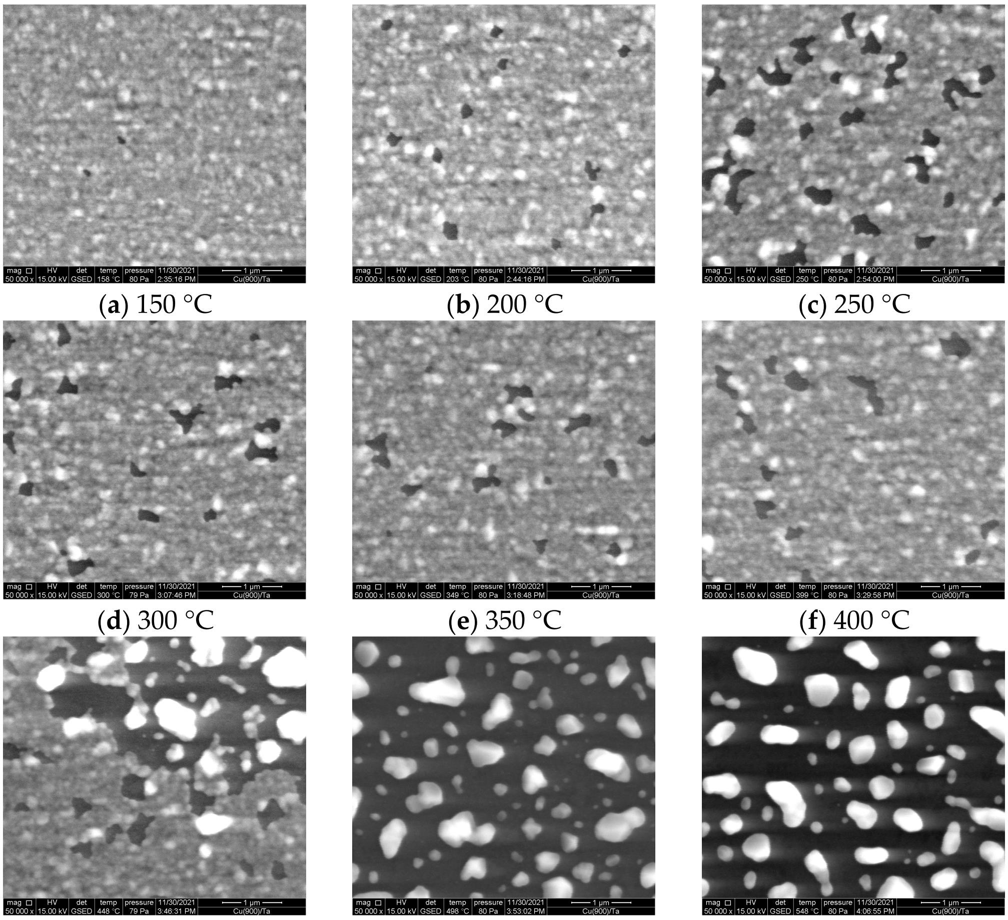

(**a**) 150 °C (**b**) 200 °C (**c**) 250 °C (**d**) 300 °C (**e**) 350 °C (**f**) 400 °C (**g**) 450 °C (**h**) 500 °C (**i**) 550 °C

Figure 5. Surface of the Cu film deposited over a Ta layer from 150 °C (**a**) to 550 °C (**i**), using a 10 °C/min. heating rate.

The higher heating rate used for the Cu/Ta stack exhibited an initial dewetting stage at 200 °C, which expanded slightly at 250 °C but remained mostly stable until 450 °C, at the end of which the area of exposed substrate was nearing 22%. The two highest isothermal stages used showed large Cu islands formed after completely consuming the Cu film, with no considerable differences between the 500 and the 550 °C temperatures, thus indicating Cu dewetting was already mostly complete at 500 °C.

3.2.2. 30 °C/min Heating Rate

The higher heating rate applied to the Cu/Ta stack did not significantly alter the Cu film surface behavior in regards to dewetting up until 450 °C, as seen in Figure 6. Even though the substrate area initially exposed was slightly superior to the one obtained at 10 °C/min., overall it remained mostly unaltered until reaching that temperature, as seen on all previously mentioned samples. The last isothermal stage, however, exhibited the largest portion of exposed substrate area of all the studied sets of systems and annealing conditions, with seemingly little difference between the results at 500 °C and 550 °C.



(**a**) 150 °C (**b**) 200 °C (**c**) 250 °C

(**d**) 300 °C (**e**) 350 °C (**f**) 400 °C

(**g**) 450 °C (**h**) 500 °C (**i**) 550 °C

Figure 6. Surface of the Cu film deposited over a Ta layer from 150 °C (**a**) to 550 °C (**i**), using a 30 °C/min. heating rate.

4. Discussion

Quantitative analysis of the evolution of the Cu surface coverage at the end of each isothermal stage is represented in Figure 7. Results show that both the lower and the higher heating rates induced Cu film dewetting at temperatures above 450 °C. As the temperature value for the onset of dewetting remained constant through different substrate materials and heating rates, it indicated Cu-film thickness to be the overall most influencing parameter that defined the dewetting behavior [1]. The Cu/Co-W surface remained relatively unaltered below the said stage, above which dewetting of the Cu film progressed very rapidly in the case of the 30 °C/min. heating rate. This behavior could be attributed to the energy release and different grain growth rates associated with different heating rates, which translate to different recovery kinetics for each condition [20].

This difference in dewetting progression rates suggests that the interfacial energy between the two films should not be the most determinant factor concerning thin-film dewetting behavior during thermal processing, as this initial value should be identical for both heating rates applied to each of the systems. The strain energy associated with different thermal expansion coefficients for the materials involved may also significantly contribute to the dewetting behavior of the Cu films [1].

The results regarding increased dewetting at high temperatures are in line with the findings of previous works [21]. The Cu/Ta results at 10 °C/min. heating rate indicate a considerably lower surface tension of the Cu film than the one observed for the Co-W alternative under equivalent annealing conditions, as evidenced by the earlier status of Cu agglomeration registered at 550 °C. Hillock formation can also lead to dewetting through thinning of the film near the hillock until the substrate is exposed [17]. The grain growth morphology registered in this work deviates slightly from the definition of hillock presented in other works, however, seeing as all Cu islands formed after the longer annealing times were round shaped, as opposed to exhibiting faceted surfaces [10]. Said work associated hillock formation with void presence near grain boundaries, with the present findings showing that hillock formation does not seem to necessarily occur before Cu-film dewetting and grain growth, assuming voids are inherently forming to foster grain growth. A previous work claims that strain relaxation during annealing may be responsible for the first stages of dewetting and Cu agglomeration, along with lattice mismatches between the different materials present in the stack [22].

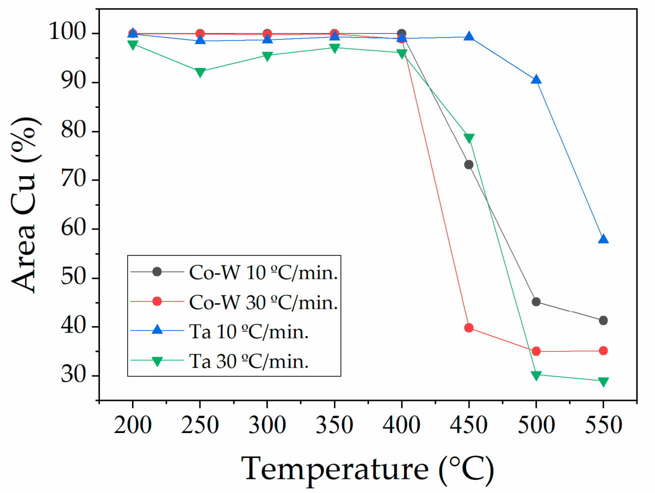


Figure 7. Percentage of sample surface covered by the Cu film as a function of temperature for all studied systems.

The behavior displayed by the Cu film during this study is consistent with the Ostwald ripening mechanism, where abnormally large grains grow through consumption of the atoms of smaller grains of neighboring regions [9]. It is worthy of note that Cu atoms can seemingly diffuse along considerably long distances, i.e., some micrometers, to feed said abnormal grain growth, as opposed to being restricted to their immediate vicinity.

Comparison of the behavior of both types of substrates used showed that the Cu film deposited over the Co-W substrate was more resistant to the onset of dewetting, but after the phenomenon had started it exhibited a more aggressive progression than over the Ta film. The dimensional stability of the pinholes present in the Co-W stack across a broad temperature range, when annealed at 30 °C/min, is an interesting result considering this type of defect is often depicted as being the precursor to solid-film dewetting. This behavior suggests the driving force for Cu-film dewetting is influenced by the defects at the surface of the material and, likely more prominently, by total energy minimization mechanisms as mentioned in previous works [1].

5. Conclusions

A thin Cu film covering a Co-W substrate was tested in situ to ascertain its behavior at high temperatures in order to evaluate its validity as a candidate material for a dual-purpose adhesion/diffusion barrier layer. Through comparison with a Ta layer representing a conventional adhesion layer, all studied systems exhibited comparable dewetting resistance below 400 °C, with a 30 °C/min heating rate leading to lower Cu surface coverage at 550 °C than a 10 °C/min rate.

The Co-W system presented a similar performance to the Ta adhesion layer at the temperature ranges associated with microelectronics processing, which typically remain below 400 °C. This result positions this material as a potential alternative for adhesion-barrier layer applications when annealed below 400 °C.

Author Contributions: Conceptualization, B.M.C.O., R.F.S. and M.F.V.; Data curation, B.M.C.O.; Formal analysis, M.F.V.; Funding acquisition, M.F.V.; Investigation, B.M.C.O., R.F.S. and M.F.V.; Methodology, B.M.C.O., R.F.S. and M.F.V.; Project administration, M.F.V.; Supervision, M.F.V.; Validation, M.F.V.; Writing—original draft, B.M.C.O. and R.F.S.; Writing—review and editing, R.F.S. and M.F.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Portugal 2020 through European Regional Development Fund (FEDER) in the frame of Operational Competitiveness and Internationalisation Programme (POCI) and in the scope of the project USECoIN with grant number PTDC/CTM CTM/31953/2017. The authors would also like to acknowledge funding from the PhD grant from the Fundação para a Ciência e a Tecnologia (FCT) of Portugal with the reference PD/BD/128419/2017.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Thompson, C.V. Solid-State Dewetting of Thin Films. *Annu. Rev. Mater. Res.* **2012**, *42*, 399–434. [CrossRef]
2. Mullins, W.W. Theory of Thermal Grooving. *J. Appl. Phys.* **1957**, *28*, 333–339. [CrossRef]
3. Li, Z.; Tian, Y.; Teng, C.; Cao, H. Recent Advances in Barrier Layer of Cu Interconnects. *Materials* **2020**, *13*, 5049. [CrossRef] [PubMed]
4. Wang, P.; Qu, X.-P.; Dordi, Y.; Joi, A. Investigation of RuZn alloy as barrier to Cu interconnect. *J. Mater. Sci. Mater. Electron.* **2022**, *33*, 6318–6328. [CrossRef]
5. Carbonell, L.; Volders, H.; Heylen, N.; Kellens, K.; Caluwaerts, R.; Devriendt, K.; Sanchez, E.A.; Wouters, J.; Gravey, V.; Shah, K.; et al. Metallization of sub-30 nm interconnects: Comparison of different liner/seed combinations. In Proceedings of the 2009 IEEE International Interconnect Technology Conference, Sapporo, Japan, 1–3 June 2009; pp. 200–202.
6. Kuo, T.-C.; Su, Y.-H.; Lee, W.-H.; Liao, W.H.; Wang, Y.-S.; Hung, C.-C.; Wang, Y.-L. A study on the plating and wetting ability of ruthenium-tungsten multi-layers for advanced Cu metallization. *Microelectron. Eng.* **2016**, *162*, 27–33. [CrossRef]
7. Santos, R.F.; Oliveira, B.M.C.; Savaris, L.C.G.; Ferreira, P.J.; Vieira, M.F. Seedless Cu Electroplating on Ru-W Thin Films for Metallisation of Advanced Interconnects. *Int. J. Mol. Sci.* **2022**, *23*, 1891. [CrossRef]
8. Zhang, J.; Hu, B.; Qiao, H.; Zhang, Y.; Du, Y. Thermodynamic Modeling of the Re-Ru, Ru-W and Re-Ru-W Systems. *J. Phase Equilibria Diffus.* **2021**, *42*, 489–498. [CrossRef]
9. Fillot, F.; Tőkei, Z.; Beyer, G.P. Surface diffusion of copper on tantalum substrates by Ostwald ripening. *Surf. Sci.* **2007**, *601*, 986–993. [CrossRef]
10. Sonawane, D.; Choudhury, A.; Kumar, P. New Insights into Dewetting of Cu Thin Films Deposited on Si. *Langmuir* **2020**, *36*, 5534–5545. [CrossRef]
11. Sonawane, D.; Kumar, P. Stability of Cu-islands formed on Si substrate via 'dewetting' under subsequent thermal cycling. *Nanotechnology* **2021**, *32*, 195703. [CrossRef]
12. Han, G.C.; Wu, Y.H.; Luo, P.; Qiu, J.J.; Chong, T.C. Dewetting observations of ultrathin metallic films. *Solid State Commun.* **2003**, *126*, 479–484. [CrossRef]
13. Soriadi, N.; Abdullah, M.F.; Md Yakin, F.S.; Mohamad Badaruddin, S.A.; Syono, M.I. Effect of Cu thickness and temperature on growth of graphene on 8-inch Cu/SiO2/Si wafer using cold-wall CVD reactor. *Mater. Today Proc.* **2021**, *42*, 2948–2952. [CrossRef]
14. Minenkov, A.; Šantić, N.; Truglas, T.; Aberl, J.; Vukušić, L.; Brehm, M.; Groiss, H. Advanced preparation of plan-view specimens on a MEMS chip for in situ TEM heating experiments. *MRS Bull.* **2022**, *47*, 359–370. [CrossRef] [PubMed]
15. Oliveira, B.M.C.; Santos, R.F.; Piedade, A.P.; Ferreira, P.J.; Vieira, M.F. Co-W Barrier Layers for Metallization of Copper Interconnects: Thermal Performance Analysis. *Nanomaterials* **2022**, *12*, 1752. [CrossRef]
16. Gadkari, P.R.; Warren, A.P.; Todi, R.M.; Petrova, R.V.; Coffey, K.R. Comparison of the agglomeration behavior of thin metallic films on SiO2. *J. Vac. Sci. Technol. A* **2005**, *23*, 1152–1161. [CrossRef]
17. Srolovitz, D.J.; Goldiner, M.G. The Thermodynamics and Kinetics of film agglomeration. *JOM* **1995**, *47*, 31–36. [CrossRef]
18. Ye, J.; Thompson, C.V. Anisotropic edge retraction and hole growth during solid-state dewetting of single crystal nickel thin films. *Acta Mater.* **2011**, *59*, 582–589. [CrossRef]
19. Bishara, H.; Lee, S.; Brink, T.; Ghidelli, M.; Dehm, G. Understanding Grain Boundary Electrical Resistivity in Cu: The Effect of Boundary Structure. *ACS Nano* **2021**, *15*, 16607–16615. [CrossRef]
20. Chen, W.; Chen, M.; Jin, X.; Zhang, P. Effect of heating rate during annealing on microstructure and texture evolution of AA8021 aluminum foil. *Mater. Res. Express* **2020**, *7*, 096514. [CrossRef]

21. Sudheer; Mondal, P.; Rai, V.N.; Srivastava, A.K. A study of growth and thermal dewetting behavior of ultra-thin gold films using transmission electron microscopy. *AIP Adv.* **2017**, *7*, 075303. [CrossRef]
22. De Los Santos, V.L.; Lee, D.; Seo, J.; Leon, F.L.; Bustamante, D.A.; Suzuki, S.; Majima, Y.; Mitrelias, T.; Ionescu, A.; Barnes, C.H.W. Crystallization and surface morphology of Au/SiO2 thin films following furnace and flame annealing. *Surf. Sci.* **2009**, *603*, 2978–2985. [CrossRef]