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Inorganic capping layers in RDL technologies: process advantages and reliability

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Abstract

Atomic layer-deposited (ALD) inorganic films were processed on top of copper metal lines in a polymer-based redistribution layer (RDL). The primary objective was to develop capping layers thinner than 15 nm to prevent copper oxidation. Due to their uniformity and high density, ALD layers are established permeation barriers. Nonetheless, owing to the presence of polymers in the final product, a low deposition temperature is required, resulting in an increased defect density and a greater susceptibility to degradation by moisture. In this study, various inorganic cappings, based on Al₂O₃, HfO₂ and TiO₂, deposited at 100 °C were integrated in an RDL stack. It is demonstrated that they impede the reaction of the polymer photo acid generator with copper, improving the lithography process, and ultimately allowing to print smaller critical dimensions. Additionally, capping layers built upon Al₂O₃ or HfO₂ are shown to fully block copper oxidation after reliability stress tests.

Keywords: Copper, Oxidation, Polymer, Redistribution layer, Capping layer, Atomic layer-deposited

1 Introduction

Customer wishes for faster electronic products with enhanced functionalities and smaller form factors, have pushed the industry toward advanced packaging technologies used in combination with heterogeneous integration. These advanced packages rely heavily on redistribution layers (RDL) to route the ever increasing number of connections between adjacent dice. To reduce the number of metal layers needed to achieve this complex routing, the critical dimensions of the RDL lines must be decreased [1]. Among the various options recently proposed [2–4], the most promising approach utilizes a dual damascene patterning with copper lines embedded in a high-resolution photo-sensitive polymer [1, 5]. Owing to the chemical-mechanical polishing (CMP) step of the damascene process, the flatness of the stack is guaranteed, enabling additional metal layers to be processed at resolution limit. Nonetheless, using a polymer as a dielectric presents serious reliability challenges as polymers are generally unable to block the diffusion of oxygen, resulting in copper oxidation even at temperatures below 200 °C [6–9]. Additionally, experimental evidence suggest that copper oxidation is not self-limiting [9–11]. As the critical dimensions of the lines are scaled down, high rates of oxidation are therefore a major reliability concern [8].

Over the last decades, various capping layers have been developed to mitigate reliability issues in CMOS technologies. For example, SiN has been extensively used to prevent corrosion of the metal lines [12–14], while SiCN, SiCO or MnSiO₃ were integrated as copper diffusion barrier [15–20]. Unfortunately, due to their high process temperature, these materials are not compatible with a polymer-based process. Consequently, the field of organic electronic devices has seen the development of low temperature atomic layer-deposited (ALD) thin films barrier coatings [21–26]. Using sequential and self-limiting surface chemical reactions, ALD results in pinhole-free, dense and highly conformal films [27, 28]. Owing to their low defect concentrations, these films are excellent gas and moisture permeation barriers [29–31].

Although deposition temperatures below 120 °C are now commonly achieved [23, 32–36], the resulting films generally present degraded barrier performances due to an increased defect density [29, 34] as well as an enhanced susceptibility to corrosion [30, 37, 38] leading to larger critical thicknesses. Consequently, state of the art Al₂O₃ capping layers, commonly used in the field of organic electronics are still around 50 nm thick [39, 40]. Since a decrease of the deposition temperature results in extended processing times, achieving thinner reliable capping layers is of primary importance.

In this study, thin inorganic films have been processed on top of copper RDL lines and their performance as potential capping layers have been assessed after oxidation and corrosion stress tests.

2 Experimental

This study was performed using polymer-based RDL samples manufactured on 300 mm wafers using a dual-damascene process. In this approach, the RDL lines are embedded in a negative tone phenol-based photosensitive polymer provided by JSR Corporation. The flow, summarized in Fig. 1, is initiated on top of an insulating layer to isolate the RDL stack from the silicon substrate. A first polymer layer is coated to a thickness of 2.8 μm . Metal trenches are opened using an i-line-based lithography process followed by development in a normal TMAH developer. The polymer is then cured using a multistep process with a maximum temperature of 200 °C (below the glass transition temperature, T_g). Metal line stack starts with the deposition of a 30 nm Ti thin film followed by a 100 nm Cu seed layer using a Physical Vapor Deposition (PVD) process. The Ti layer enhances the adhesion of copper on polymer and serves as a diffusion barrier layer. Electrochemically deposited (ECD) copper, grown on top of the seed layer is used to fill the line, while a chemical-mechanical polishing (CMP) process is performed to remove the excess copper and keep the stack flat. At the end of the process, the RDL lines are around 2.5 μm thick. At this point, in order to test multiple capping solutions, a wafer was diced into samples of around 2.0 by 2.5 cm.

ALD capping layers have been processed directly on top of the RDL layer in a Veeco Savannah[®] S300 chamber. All ALD films were deposited at 100 °C. The various films tested in this study as well as their deposition temperature are summarized in Table I. Al_2O_3 was obtained using trimethylaluminum (TMA), HfO_2 resulted from a tetrakis(dimethylamido) hafnium (TDMAHf) and TiO_2 was deposited from titanium tetrachloride. In all cases, water was used as co-reactant. Finally, an additional polymer layer is coated and cured on top of the stack to mimic the final product. Additional process details are available in [5].

The thicknesses of the capping layers were measured through ellipsometry using silicon substrates placed along the RDL samples in the ALD chamber. Al_2O_3 measurements were performed using wavelengths ranging from 275 to 885 nm (1.4–4.5 eV) at an incident angle of 70° using a Horiba Jobin Yvon UVISSEL ellipsometer. HfO_2 and TiO_2 characterizations were carried out in the wavelength range 350–1000 nm using a J. A. Woollam variable angle spectroscopic ellipsometer at three incident angles (65°, 70° and 75° with respect to the substrate normal) using a 5 s acquisition time. The silicon substrate and native oxide were represented by standard optical models. Al_2O_3 and HfO_2 were modeled using a Cauchy model while a “New Amorphous” model (which is a re-parameterization of a Tauc-Lorentz model) was used for TiO_2 .

Failure mechanisms of interest in capping layers were triggered using two different reliability stresses. Copper oxidation was induced in a nitrogen-rich dry air environment using a Thermo Scientific Heraeus UT6060 oven. The oxygen content in the oven during the oxidation process was 2 %. This high temperature storage (HTS) was performed at 150 °C for 1000 h. Susceptibility to degradation by water was characterized through a dual stage reliability

stress. The first step consisted of a temperature-humidity stress (TH) executed at 85 °C and 85 % RH in a climate chamber WEISS SB22 for 1000 h. This phase enabled moisture to reach the interface between the polymer and the capping layer, and to trigger a potential chemical reaction with the capping layer base material, ultimately resulting in the degradation of the barrier properties [30]. Copper oxidation is then induced by HTS stress performed at 150 °C for 1000 h. This second phase reveals the presence of potential pin holes in the capping layer since TH alone is insufficient to grow a significant copper oxide layer [8]. The combination of TH followed by HTS will be referred as corrosion stress test throughout this study. At the end of each stresses, cross-sections of the metal lines performed with focused ion beam (FIB) milling using a FEI Helios Dual Beam system were used to verify the presence of copper oxide on top of the lines.

Tests and stress conditions were selected in accordance with the AEC-Q100 standard [41].

3 Results and discussions

3.1 Protection against copper oxidation

Fig. 2 presents unprotected copper lines submitted to high temperature storage stress for 1000 h at 150 °C. In comparison to the reference unstressed sample (Fig. 2a), after stress, a thick oxide layer is present above the RDL lines as well as on the sidewalls (Fig. 2b). Additionally, the copper-oxide interface presents Kirkendall voids created by the difference in the diffusion rate of copper atoms within copper and inside the oxide ($\sim 10^{-25}$ cm²·s⁻¹ versus $\sim 10^{-20}$ cm²·s⁻¹ respectively at 150 °C) [42, 43]. On the other hand, as shown in Fig. 3, the oxidation is fully blocked by a 50 nm thick Al₂O₃ capping layer (Fig. 3a).

While ALD offers the advantages of dense, highly conformal and pinhole-free layers, its notoriously low deposition rate is detrimental for high throughput [44]. Additionally, electrical connections between RDL layers require openings in the capping film to properly land vias and allow for electrical connectivity. As a result, a simplification and minimization of the processing time calls for a radical reduction of the capping layer thickness. Fig. 3b presents a FIB cross-section performed on a sample protected by 15 nm of Al₂O₃ subjected to HTS. In this configuration, the oxidation of copper is still

Table I: Summary of the different capping materials, thicknesses and deposition temperatures used in the study.

#	Material	Temperature (°C)	Thickness (nm)
1	Al ₂ O ₃	100	50
2	Al ₂ O ₃	100	15
3	HfO ₂	100	12
4	TiO ₂	100	13

fully blocked confirming the potential of thin layers of Al_2O_3 to prevent the diffusion of oxygen toward the metal lines.

Unfortunately, prior studies have highlighted that Al_2O_3 is prone to corrosion upon exposure to water or moisture, quickly resulting in the loss of the barrier properties [22, 30, 31]. Thin HfO_2 and TiO_2 capping layers were therefore tested as mitigation solutions. As shown in Fig. 4, while a 12 nm thin HfO_2 film is able to prevent copper oxidation (Fig. 4a), the same thickness of TiO_2 results in the presence of a thick layer of copper oxide on top of the RDL lines and along the capping layer (Fig. 4b). Likely, due to the direct contact between TiO_2 and copper, a preferential diffusion path is created, allowing copper atoms to diffuse along the TiO_2 layer. The fast diffusion of copper in TiO_2 at low temperatures already suggested by Schubert et al. [45] is therefore confirmed. This phenomenon is most probably responsible for the increased oxide thickness observed on samples protected by TiO_2 (~ 440 nm versus ~ 350 nm on unprotected lines) and could explain the corrosion-promotion behavior of this material reported by Zhang et al. [46]. Samples protected with HfO_2 were additionally subjected to a corrosion stress test to assess the impact of moisture on the performances of this material. As shown in Fig. 5, the barrier properties of a 12 nm thin HfO_2 layer are not affected by the presence of moisture and the RDL lines remain free from oxidation after the stress. For this material, a critical thickness around 9 nm was previously reported by the authors [47]. While these results would suggest that HfO_2 is better suited than Al_2O_3 as an RDL capping layer, the manufacturability metrics favor the higher deposition rate of Al_2O_3 in the low temperature range. In this case, the corrosion issues are often mitigated by the utilization of nanolaminates [29, 37].

3.2 Impact on lithography process

Beside enhanced reliability, an additional benefit result from the presence of a capping layer in the RDL stacks. Chemically amplified photosensitive resists and polymers are known to interact with copper, leading to an uneven distribution of the photo acid generators in the material. Ultimately, this quenching effect results in undercuts profiles as shown in Fig. 6a and Fig. 6b, strongly limiting the minimum feature size achievable [48–51]. Furthermore, undercuts produce discontinuous Ti barriers, finally leading to reliability issues [8]. By physically isolating the photosensitive polymer from the copper lines, and offering a chemically stable surface, capping layers suppress quenching, allowing the patterning of straighter profiles and smaller feature sizes as laid out on Fig. 6c and Fig. 6d.

Additionally, in presence of a capping layer, a division by a factor 2 of the exposure dose was necessary to correctly print the via layer. While, Al_2O_3 , HfO_2 and TiO_2 are known to reflect and absorb differently the UV light around the i-line band (365 nm) [52–54], their sole presence in the stack cannot explain the correction needed in the exposure dose. Fig. 7 presents the simulated reflection at the interface polymer–capping layer (Fig. 7a) as well as the exposure dose absorbed in the polymer (Fig. 7b). The simulations were performed at

normal incidence, for a wavelength of 365 nm with OpenFilters (v, 1.1.1) [55]. The simulated stack consists of a copper substrate, a capping layer and 3 μm of uncured photosensitive polymer. The optical properties of the capping layers were collected from various sources [52–54] while JSR corporation provided the Cauchy coefficients of the photosensitive polymer. As shown in Fig. 7, while the reflection at the interface polymer–capping is strongly dependent on the capping composition, the exposure dose absorbed in the polymer remains mostly constant regardless of the capping layer. A slight decrease of the dose absorbed in the polymer, resulting from destructive interference, is observed in presence of a capping layer. The increase in the exposure dose, needed when the polymer layer is in direct contact with copper is therefore most likely another signature of photo acid generator quenching in the polymer [48, 50].

4 Conclusions

Thin inorganic ALD layers processed at low temperature have been utilized as protective layers against copper oxidation in a polymer-based RDL technology. Depending on the base material used in these layers, a film as thin as 12 nm on top of the copper lines can offer a full protection against oxidation when exposed to high temperature stresses or to corrosion stress tests. In comparison to previous state of the art capping layers, these films offer a drastic thickness reduction while retaining an extreme resistance against corrosion, making them ideal permeation barrier solutions for organic electronics products. Finally, by suppressing photo acid generator quenching, these layers allow to print smaller features in photosensitive polymers paving the road for the next generation of RDL technologies.

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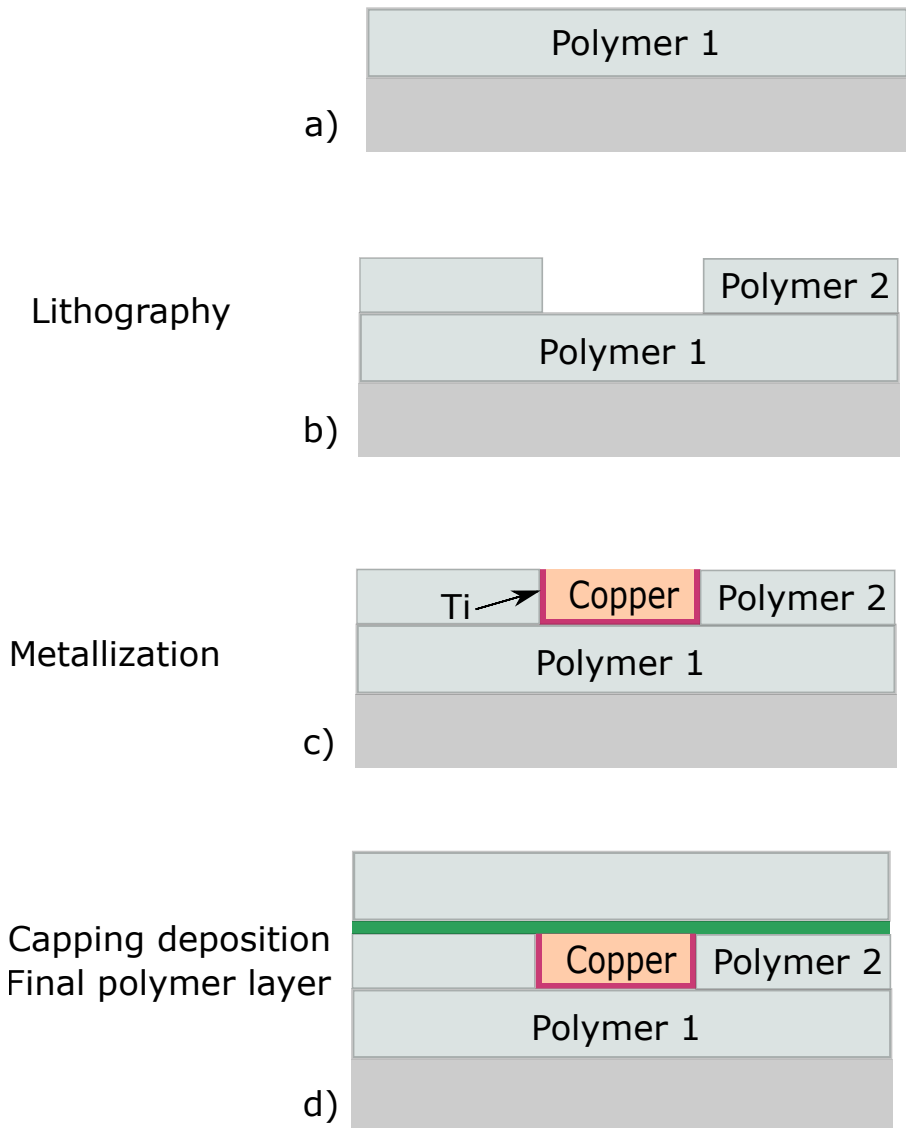


Fig. 1: Schematic representation of the dual damascene flow used to manufacture the samples used in the study.

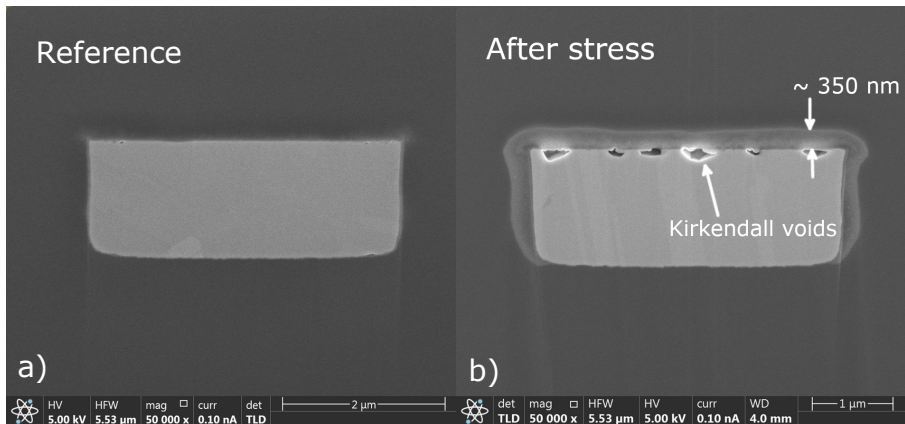


Fig. 2: FIB cross-sections of a polymer-based RDL. In this approach, copper wires are fully surrounded by polymer. a) Reference unstressed sample. b) After 1000 hours spent at 150 °C, a 350 nm thick oxide layer is present at the top of the metal line and Kirkendall voids appeared at the interface copper–oxide.

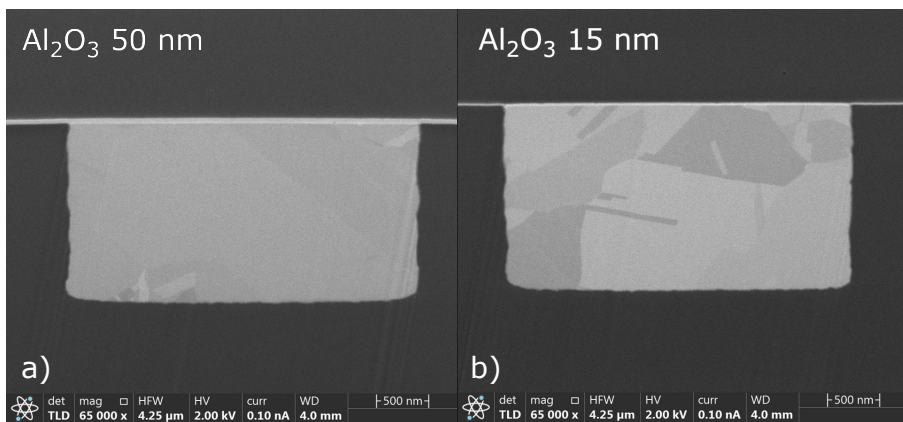


Fig. 3: RDL lines protected by an Al_2O_3 capping layer do not present traces of oxidation after HTS. a) 50 nm thick capping layer. b) Capping thickness reduced to 15 nm.

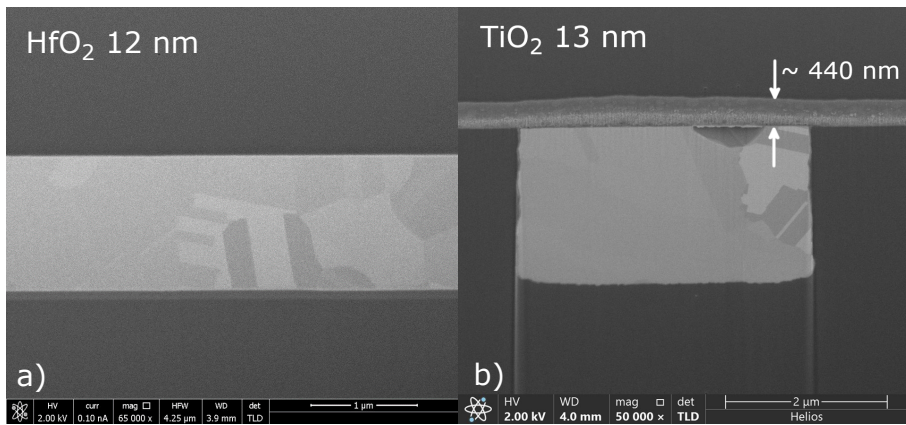


Fig. 4: RDL lines protected with thin layers of HfO₂ and TiO₂. a) 12 nm of HfO₂ fully blocks oxidation. b) On the other hand, 13 nm of TiO₂ is unable to prevent copper oxidation.

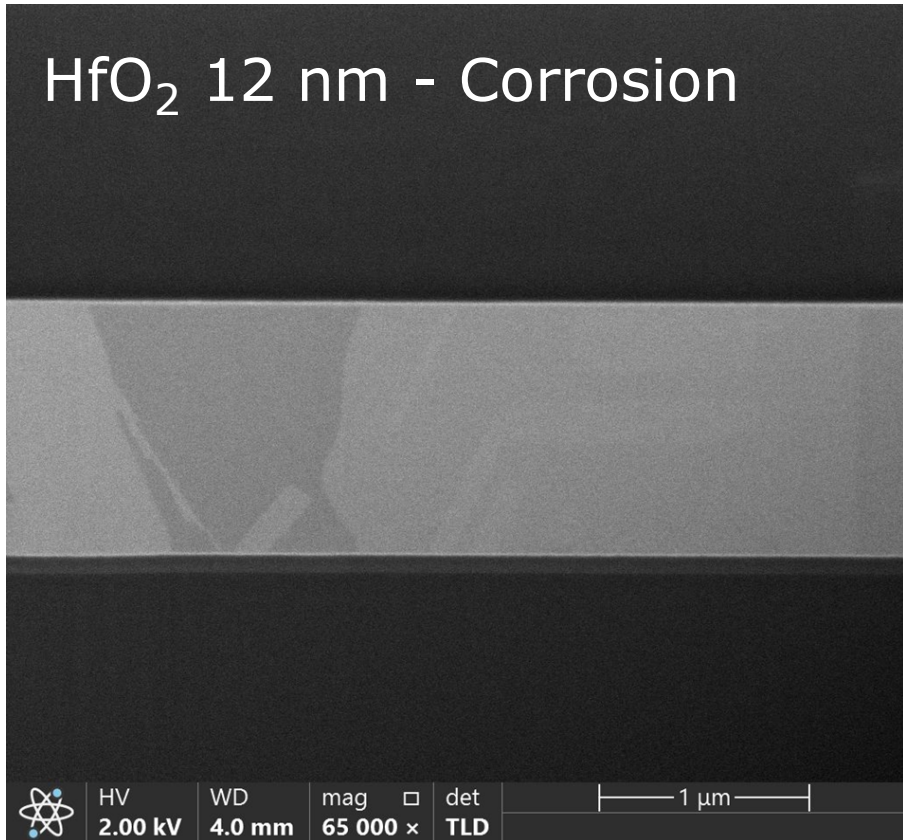


Fig. 5: A 12 nm thin HfO₂ capping layer is efficient at blocking copper oxidation after a corrosion stress test.

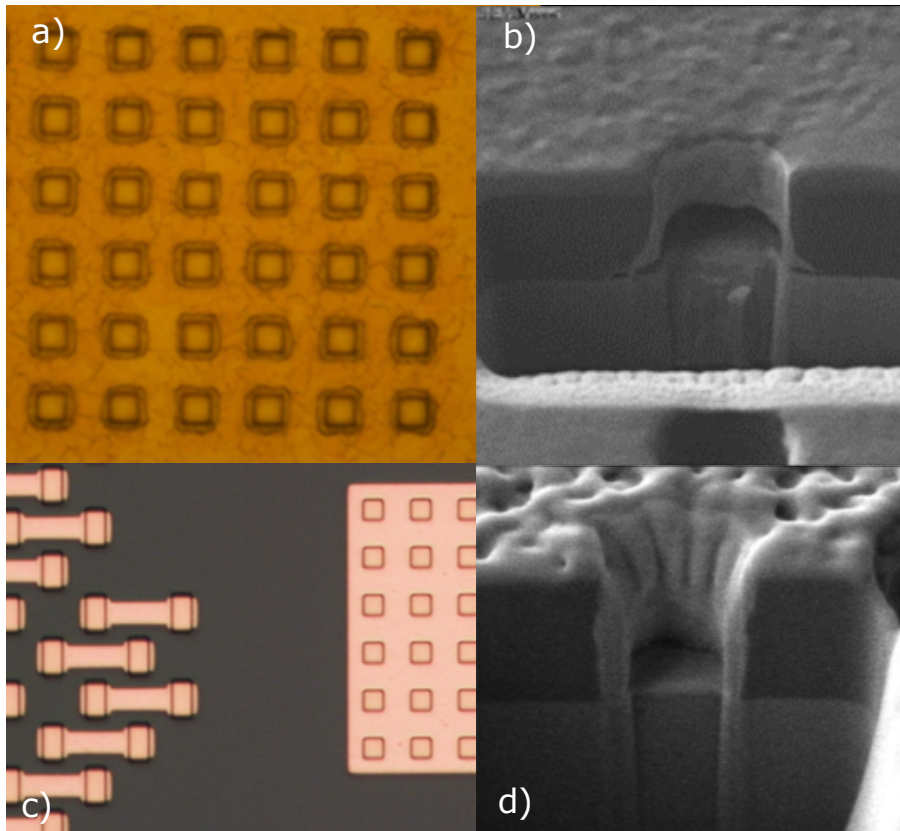


Fig. 6: a) and b) Quenching issues result in undercuts around the via opening. c) and d) In presence of a capping layer, vias are correctly printed.

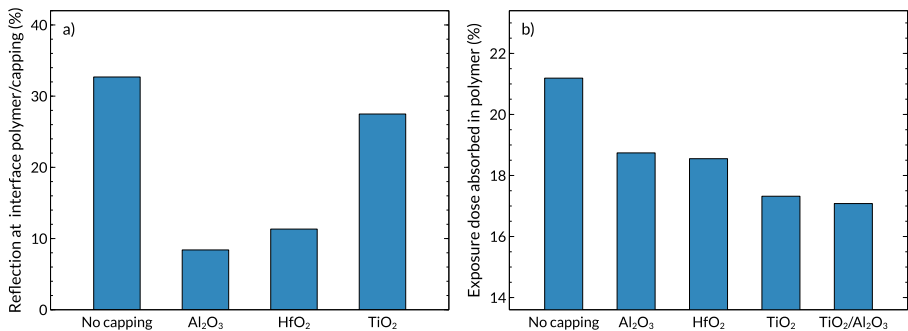


Fig. 7: a) Simulation of the reflection at the interface between the polymer and the capping layer and b) exposure dose absorbed in the polymer in presence of different capping layers for a copper-capping-polymer stack. Simulations were performed using OpenFilters.

Statements and Declarations

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Author contributions. E.C, A.B-B., R.B., S.A., J.S. and G.S. conceived and planned the experiments. E.C., A.B-B. and R.B. carried out the experiments. A.B-B., R.B., N.P. and J.S. contributed to sample preparation. E.C. took the lead in writing the manuscript. All authors provided critical feedback and helped shape the research, analysis and manuscript.

Availability of data and code. The data that support the findings of this study are available within the article.

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