Supercritical Fluid Deposition of Metals for Micro Electro Mechanical Systems

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Reduction of metalorganic compounds dissolved in supercritical carbon dioxide ($scCO_2$) has been used to deposit metal layers onto silicon wafers. Special attention was given to the applicability of this advanced metallisation method for the manufacturing of micro electro mechanical systems (MEMS). As a model material we chose copper as the preferred metal for forming interconnects. If a thick layer is needed, the layer grown by supercritical fluid deposition acts as the plating base for the following electro chemical deposition, in other cases it can be used directly during semiconductor manufacturing.

INTRODUCTION
In literature, most research groups working on metallization by supercritical fluids address applications in chemical engineering or advanced semiconductor manufacturing [1-5]. Similarly, the International Technology Roadmap for Semiconductors (ITRS)[1] refers several times to $scCO_2$ in conjunction with advanced metallization for interconnects, but this is only related to the manufacturing of integrated circuits (IC). During MEMS production, a lot of similar processes are used; therefore it is interesting to investigate the potential of supercritical fluid deposition for the MEMS industry. A good overview of $scCO_2$ applications in the whole microelectronic area is given by Weibel et al. [6]. Despite the similarities between IC and MEMS manufacturing, there are some differences as well. As well as the layer by layer approach in IC manufacturing, MEMS also sometimes require deposition inside cavities or micro channels. Depending on the application, the geometries vary between nanometres and millimetres, thus cover several orders of magnitude. Established metallization methods, which are used by both MEMS and IC manufacturing, can be distinguished between physical vapour deposition (PVD) and chemical vapour deposition (CVD). Each one affiliated with particular advantages and disadvantages discussed later in this document. A benefit for the integration of $scCO_2$ into MEMS manufacturing is the existence of a MEMS specific process called critical point drying, where delicate micro mechanical structures are released without stiction by the use of supercritical carbon dioxide. By adding $scCO_2$ metallisation to the process portfolio, the introduction of $scCO_2$ processing into MEMS manufacturing is more likely.

EXPERIMENTAL
The different metal complexes for the deposition experiments were obtained from ABCR and Sigma-Aldrich. CO_2 had a quality of 4.5 and was obtained from Air Liquide. The silicon

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[1] http://public.itrs.net (In particular 2005 edition interconnects available at
http://www.itrs.net/Links/2005ITRS/Interconnect2005.pdf)

substrates were standard 6"-wafers cleaved into smaller pieces. We chose different geometries to examine the potential of supercritical fluid deposition as an advanced metallization method for MEMS production. The largest features were deep trenches of up to 380 µm in depth with varying lateral dimensions between 15 µm and 100 µm whereas the smallest features were porous silicon layers with a thickness of 60 µm and an average pore diameter of 5 nm to 20 nm corresponding to a very high aspect ratio. Furthermore, surface pre-treatments with hydrofluoric acid, hydrogen peroxide, and oxygen plasma were investigated as well as the influence of different surface materials like copper and aluminium sputtered onto the silicon samples before processing.

The apparatus (see figure 1) has a modular configuration and consists of two parts; the first part contains pumps, valves, filters, and a storage vessel to provide the necessary pressure and flow while the second part of the system consists of the actual reaction chamber. According to the experiment, the chamber can be replaced. Both parts are connected to each other via flexible high pressure hoses and allow the use of different reaction chambers, while using the same infrastructure for pressure generation.

All depositions were conducted in a cold wall reactor with a resistively heated substrate holder. The whole system was kept at a constant temperature above the critical temperature of CO_2 (31.1 °C). Before closing the chamber, the powdery metal precursor was placed in a glass dish next to the samples onto the substrate heater. Once the desired CO_2 pressure was applied, the precursor was given a certain time period for dissolution. After adding the hydrogen from a high pressure manifold, the substrate heating was switched on in order to start the deposition reaction by reducing the dissolved metal precursor and depositing pure metal onto the heated surfaces.
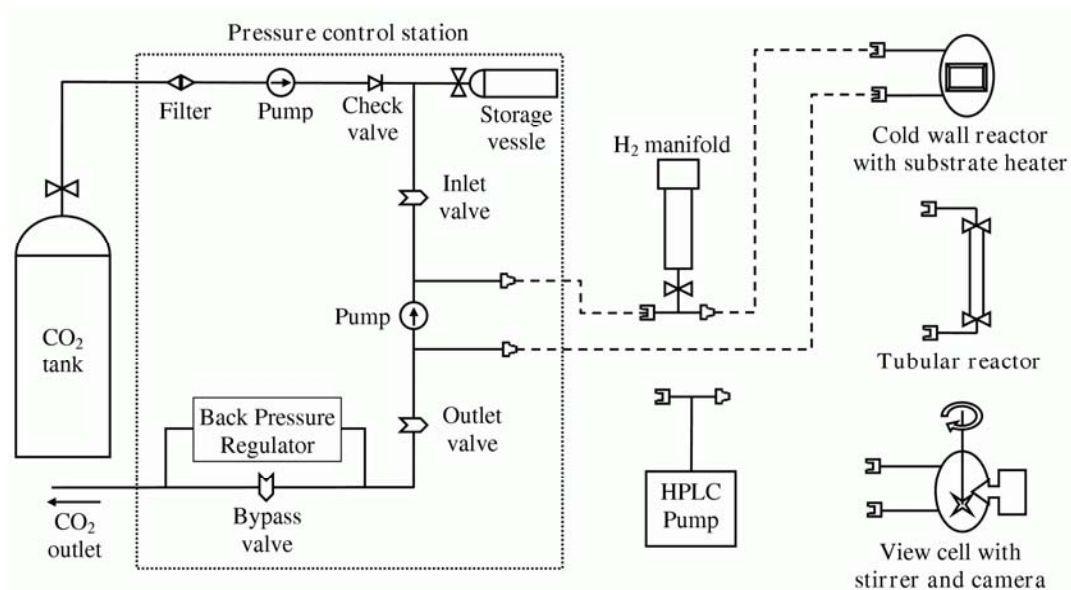

Fig. 1: Overview of scCO$_2$ system with different process chambers. For clarity, only one wiring configuration is shown.

After processing, all samples were photographed to document homogeneity and whether they were reflective or dull. Furthermore, micrographs were taken with a magnification up to 1000 and for more precise inspection, a scanning electron microscope was used which was also capable of EDX analysis. Finally, two more measurements were conducted in a clean room; a surface profile to determine the thickness and the surface roughness of the deposited metal layer, and a 4-point resistance measurement to quantify the sheet resistivity of the layer.

RESULTS AND DISCUSSION

Initially, we started to deposit copper onto flat silicon samples by hydrogen reduction of copper(II)tetramethyl-heptandionate [Cu(tmhd)$_2$] dissolved in scCO$_2$, comparable to the process described by Blackburn et al. [2]. For process development, we systematically alternated the following parameters: temperature, pressure, precursor mass, sample pre-treatment, and precursor material. The largest influence was observed with temperature, where we found a threshold temperature of 190 °C (see figure 2a). Below that temperature, no copper deposition was observed and at temperatures slightly above 190 °C, the deposition rate was very low, resulting in thin layers of approximately 100 nm even after 30 minutes of reaction. Above 250 °C, the deposition rate was fast enough to reduce the reaction time down to 10 minutes while achieving same layer thicknesses around 500 nm. In contrast to literature [1-3], we did not observe a strong dependence on substrate material or substrate pre-treatment. None of the treatments with oxygen plasma, hydrofluoric acid, or hydrogen peroxide caused a significant enhancement or suppression of the deposition rate. Even copper or an aluminium alloy sputtered onto the silicon, did not lead to a preferential growth on these samples. The amount of precursor showed a linear relationship (see figure 2b) with the layer thickness as expected and was varied between 0.06 wt% and 0.5 wt%.
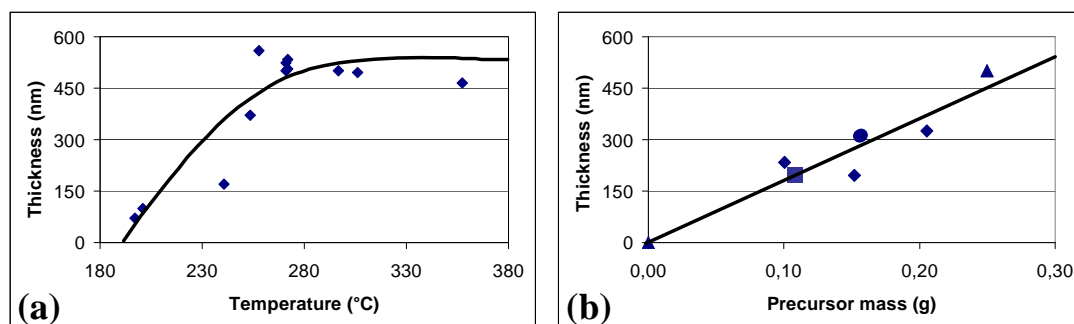

Fig. 2: Diagram (a) shows the threshold temperature of 190°C for copper deposition from Cu(tmhd)$_2$ and the saturation region above 270°C. Diagram (b) illustrates the linear relationship between precursor mass and layer thickness.

The pressure during the dissolution time was varied to attain CO$_2$ densities between 300 g/l and 600 g/l. The first value represents the lower limit due to insufficient solubility of the precursor, while 600 g/l forms the upper limit due to the pressure boundary of the chamber that was reached during heated deposition. Other precursors were investigated as well namely copper(II)trimethyl-octanedionate [Cu(tmod)$_2$], according to Zong et al. [7] and copper(II)heptafluoro-dimethyl-octanedionate [Cu(hfdmod)$_2$], which is a customary CVD precursor but was not reported for supercritical fluid deposition yet. Both precursors belong to the group of ß-diketonate copper complexes like Cu(tmhd)$_2$ and showed very similar behaviour. In figure 2b some points correspond to experiments with these two precursors, as indicated by the different shape of the data points.

The microscopic analysis showed significant differences in surface roughness and surface morphology (see figure 3). For all samples, we observed a pronounced granular growth with varying grain sizes. In general, we saw a direct relationship between layer thickness and surface roughness. Sheet resistivity of the layer depended primarily on layer thickness, but also a minor influence of layer granularity was measured. Samples of low temperature experiments that had no continuous copper layer showed the sheet resistivity of the silicon substrate, which was several orders of magnitude higher.

Established metallization methods for planar metal layers are sputtering and evaporation, both of which belong to the group of PVD processes. These methods lead to very smooth surfaces and show excellent conducting properties. PVD technology is very mature and versatile and allows deposition of a large variety of metals, but due to the line of sight characteristic, these vacuum processes have limited usage with uneven structures when conformal deposition is required.
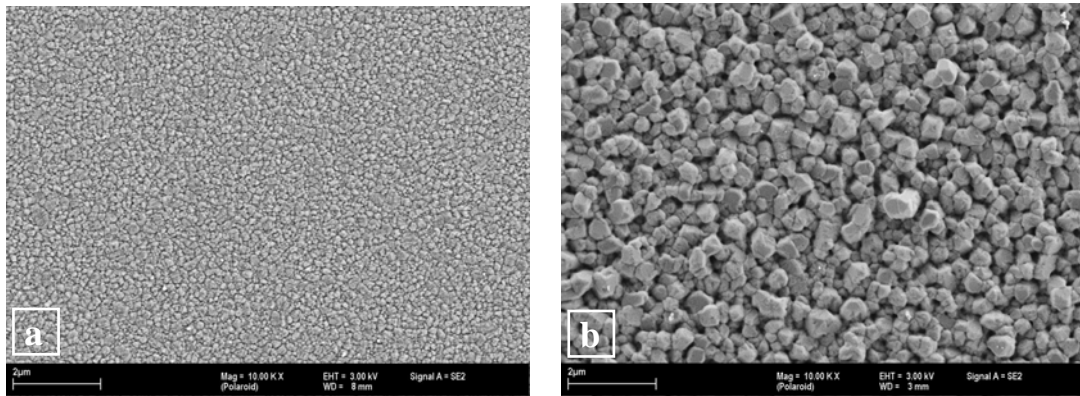

Fig. 3: SEM micrographs of two different copper depositions with Cu(tmhd)$_2$. Picture (a) is a 100 nm copper layer deposited at 200°C, while picture (b) shows a 465 nm copper layer grown at 350°C. Please note that the precursor material, amount of precursor, and substrate material, as well as the magnification of both pictures is identical.

A more challenging task is to cover vertical sidewalls with a conducting layer of metal. For this kind of application, CVD processes are used; however the selection of an appropriate precursor is problematic and the substrate temperature is usually very high. If supercritical fluid deposition can offer an advantageous solution for this challenge, this technology would find a great demand in the whole semiconductor industry.

To investigate the sidewall deposition inside of confined structures, we choose two different structures. First, trenches etched with a deep reactive ion etching (DRIE) process with varying lateral dimensions as mentioned above and second, porous silicon in two configurations - macro-porous silicon with average pore diameters of 1 µm to 2 µm and meso-porous silicon with 5 nm to 20 nm pore size. Figure 4 shows two of these structures after copper deposition. In both pictures, the granular growth as mentioned above is noticeable, forming a continuous film on the surface and even across the edge of the hole, as shown in picture 4a.
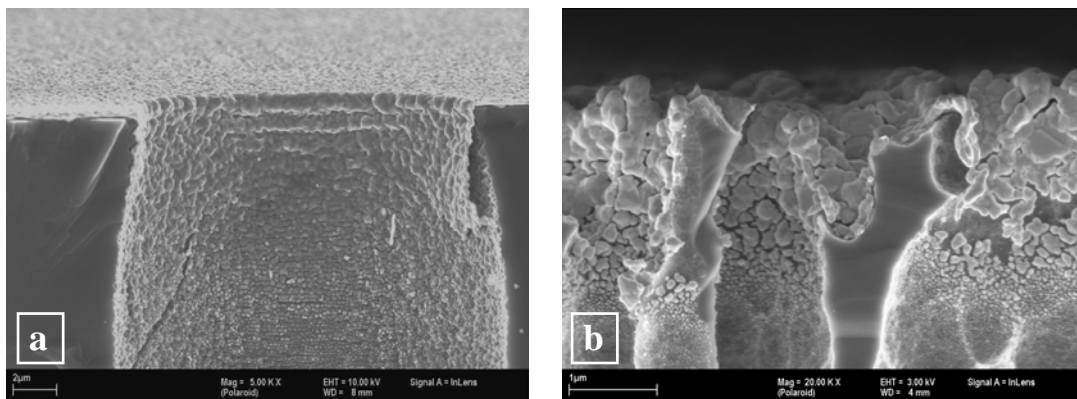

Fig. 4: Copper deposition into confined structures using Cu(tmhd)$_2$ at 270 °C and 250 °C, respectively. The dark areas are silicon, the light areas are copper. (a) Top edge of a 140 µm deep trench with a diameter of 15 µm and (b) macro-porous silicon with an average pore diameter of 1 µm – 2 µm.

Deeper inside the structure, the copper layer gets thinner and finally, becomes discontinuous after a few micrometers. The same effect is visible with the porous structure, as can be seen in figure 4b. It is noticeable, that even at the bottom of the trench a certain amount of copper is detectable by EDX (see figure 5) and very small copper nuclei are visible under large magnification SEM analysis.
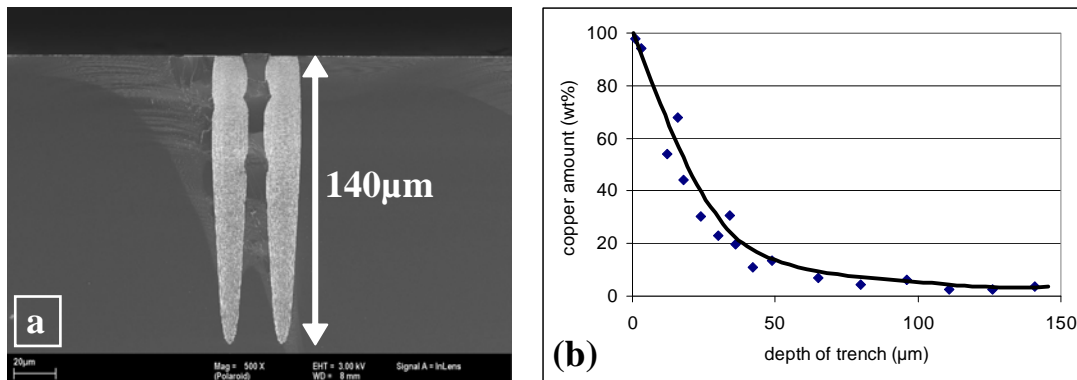

Fig. 5: Analysis of the copper amount inside of a deep structure. (a) 140 µm deep trench inside silicon with 15 µm diameter after deposition with Cu(tmhd)$_2$ at 270 °C. (b) Graph showing the copper amount in wt% according to EDX analysis.

An explanation for this effect could be a high reactivity of the deposition reaction. Before adding the reducing agent and heating the substrate, a homogeneous mixture of scCO$_2$ and metal precursor is present in the whole chamber and also inside of the voids of the substrate. After adding the hydrogen and reaching the threshold temperature, the deposition starts by forming small nucleation spots of copper on the entire surface. But when all metal precursor inside of a trenched structure is consumed, only a few small copper grains are present. To form a continuous film, these grains need to grow by adding more copper which is present in the rest on the chamber. By means of diffusion, the metal complex needs to be transported into the structure. We believe the reactivity of the complex is too high, which leads to a reaction within the first few micrometers inside of the structure. In our opinion, another type of precursor and reduction material needs to be developed or a chemical suppresser that reduces the reactivity should be used. This approach is similar to electro chemical deposition, where so called levelers and suppressors are added to the electrolyte and yield in bottom up filling of confined structures.

CONCLUSION
Supercritical fluid deposition has proven applicability as a metallization method for MEMS production and future semiconductor processing, but still some progress needs to be achieved. For planar and anisotropic deposition PVD methods offer a mature and versatile solution. A larger demand for advanced metallization exists for methods to replace CVD processes; thus, supercritical fluid deposition has to prove its applicability in this field. It certainly has potential to become an advanced metallization method in the future, but one major drawback is the introduction of a complete new infrastructure of high pressure processes. Traditional metallization processes use vacuum and plasma technology and the manufacturers have a lot of know-how in this field. They will try to retain these technologies, since they have proven production feasibility. Nevertheless, if a crucial manufacturing step requires scCO$_2$ treatment, the way for supercritical fluid deposition into semiconductor manufacturing is open.

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