Project: I. 4

THIN FILMS by CHEMICAL VAPOR DEPOSITION (CVD)

Project leader: D. Davazoglou
PhD students: G. Papadimitropoulos
Master students: L. Zambelis (Master Programme: Microsystems)
Undergraduate students: M. Delihas, G. Aspiotis
Collaborating scientists: Dr. M. Vasilopoulou**,** Dr. T. Speliotis**,** Dr. D, Kouvatsos**,** N. Vourdas

Objectives:
The objectives of this group include research and development in the following:
a) Process and material development
b) Characterization of CVD films
c) Applications

Funding:
- Copper nano-electrodes and novel transistors based on tungsten oxides nano-rods CONECTOR
- Optical Smoke Detectors (PAVET)

RESEARCH RESULTS

A. Metal-Organic Hot-Wire Chemical Vapor Deposition (MOHWCVD) of Cu films

G. Papadimitropoulos

Copper films were deposited on Si substrates covered with W, TiN and SiLK® using a novel chemical vapor deposition reactor in which reactions were assisted by a heated tungsten filament (hot-wire CVD, HWCVD). Liquid at room temperature hexafluoroacetylacetonate Cu(I) trimethylvinylsilane (CupraSelect®) was directly injected into the reactor with the aid of a direct-liquid injection system using N_2 as carrier gas. The deposition rates of HWCVD Cu films obtained on W and TiN covered substrates were found to increase with filament temperature (65 and 170 ^{o}C were tested) as seen in Fig. 1. Moreover, high quality Cu films were deposited on SiLK®, which cannot be done by conventional thermal CVD (see Fig.s 2 and 3).

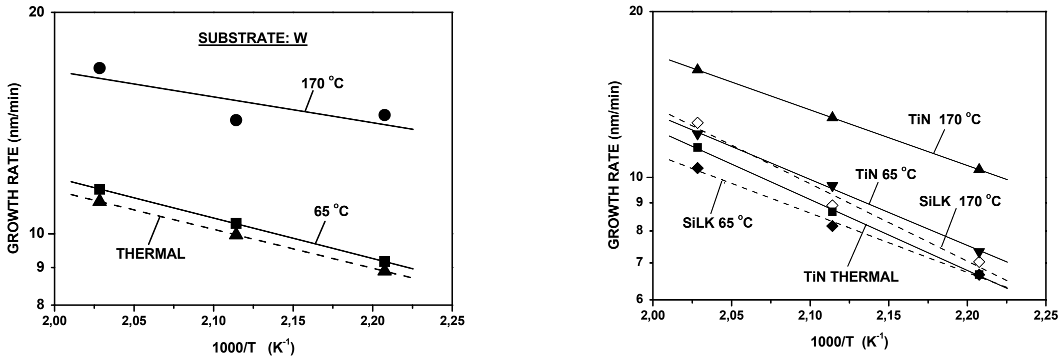

Fig. I.4.1. (Left) Growth rate dependence on substrate temperature for HWCVD Cu films deposited on W-covered Si substrates (left) and on TiN and SiLK®-covered Si substrates (right). The corresponding dependences for thermally grown films are also reported in figure.

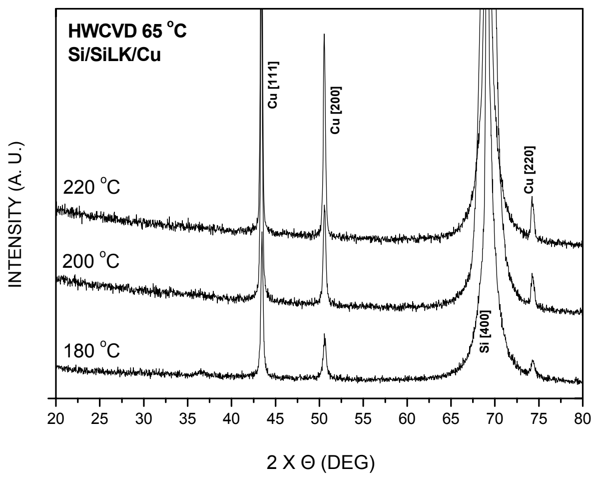

Fig. I.4.2. XRD patterns recorded on HWCVD Cu films deposited on SiLK® at various substrate temperatures. Peaks corresponding to Cu only are observed.

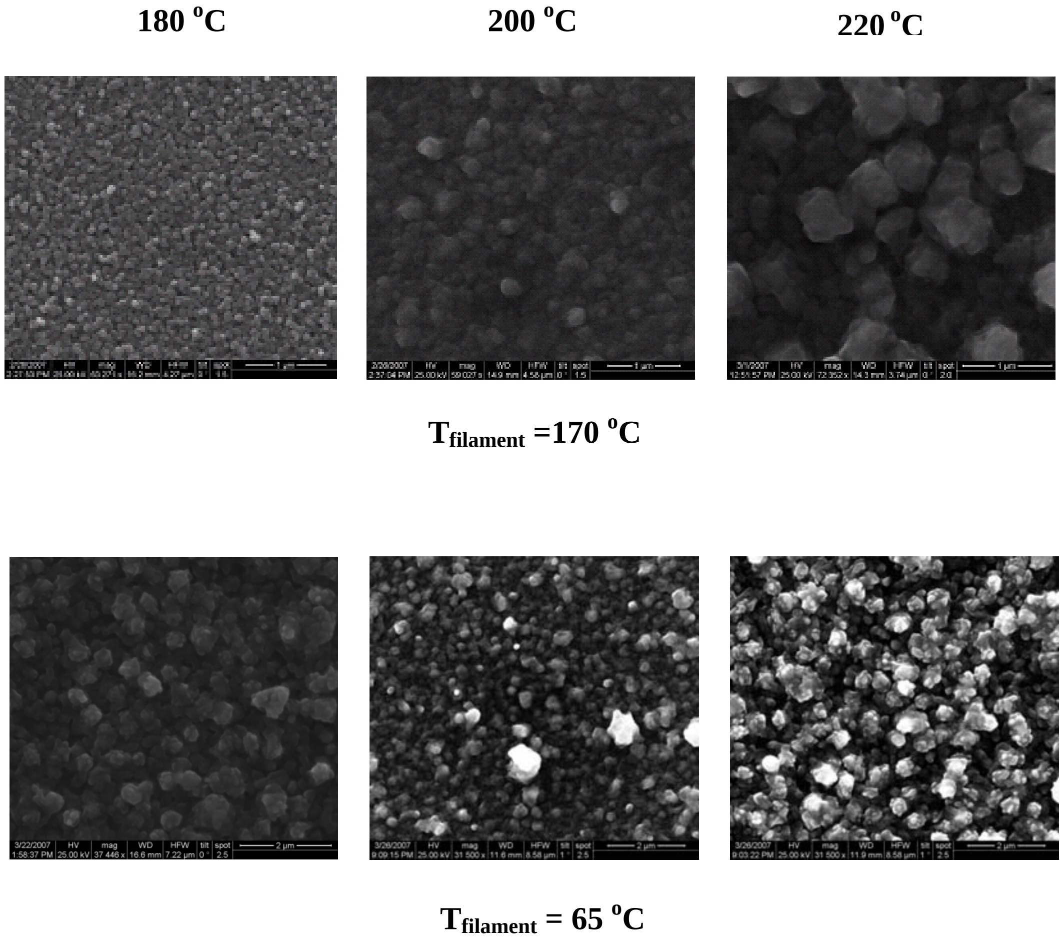

Fig. I.4.3. SEM micrographs taken on the surface of HWCVD Cu films deposited on SiLK®-covered Si substrates at various filament and substrate temperatures (please note the changes in scale).

Independent of the nature of the substrate, resistivities of HWCVD Cu films were higher than for thermally grown films (see Fig. 4) due to carbon and oxygen contamination resulting from the incomplete dissociation of the precursor (see Fig. 5).

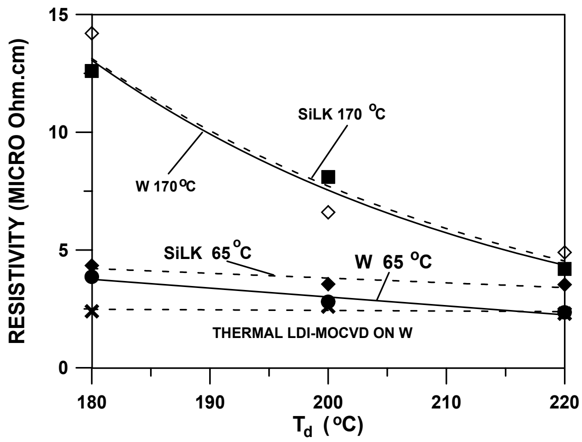

Fig. I.4.4. *Dependence of the Cu film resistivity on the temperature of deposition for HWCVD and thermal CVD films deposited on W and SiLK® substrates. Resistivities for films grown on TiN were always slightly lower than those for W*

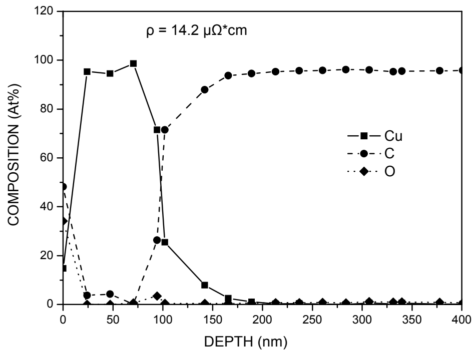

Fig. I.4.5. *Compositional depth profile of a 150 nm thick HWCVD Cu sample deposited on SiLK®.*

W impurities were detected in the HWCVD Cu films confined near the interface Cu film/substrate due to the presence of the filament. Their presence does not, however, degrade catastrophically film conductivity.

B. Colloidal Lithography

L. Zambelis

Monodispersed spheres of submicrons to microns in size can readily self-assemble into highly ordered and close-packed arrays, so-called colloidal crystals. By using the ordered interstitial arrays within colloidal crystals as masks, one can succeed in sculpturing hexagonal arrays of monodisperse nanoparticles with the shape of a pyramid, ring, or rod on planar substrates, paving a colloidal lithography way. This enables rather facile and cheap fabrication of periodic nanostructures over large areas as compared to conventional lithography. In Fig. 6 arrays of hexagonally arranged Cu nano-dots with dimensions of 65 (left) and 50 nm (right) are shown. These arrays can be used as templates for the subsequent chemical vapor deposition of other materials (see next section).

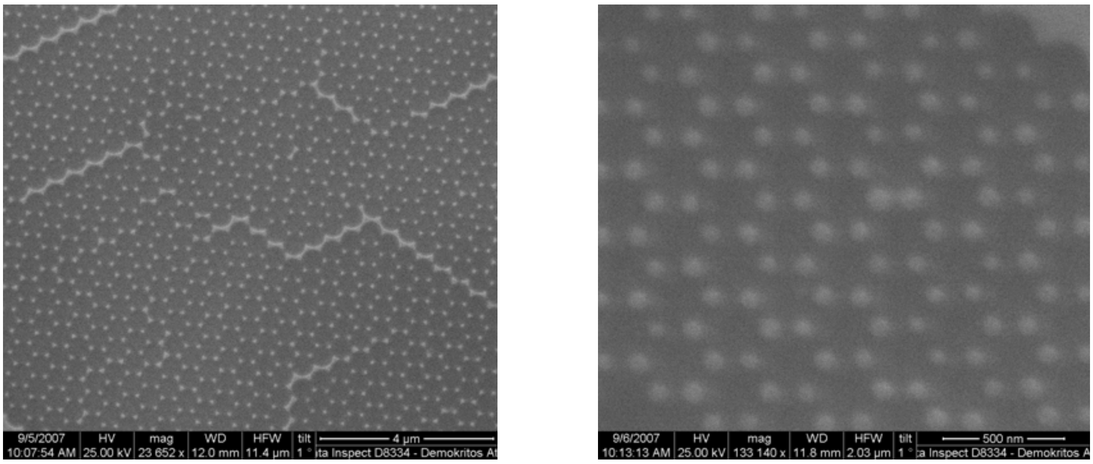

Fig. I.4.6. *(Left) SEM image of hexagonally arranged Cu nano-dots with dimensions of 65 nm obtained using PS spheres with diameter of 500 nm. (Right) a periodic arrangement of Cu nano-dots obtained using PS spheres with diameter of 280 nm. The dimensions of Cu dots are near 50 nm.*

C. Selective CVD of Vanadium oxide films

L. Zambelis

Vanadium oxide films were selectively deposited on Cu by atmospheric pressure chemically vapor deposition (APCVD) by oxidizing Vanadium (V) tri-i-propoxy oxide ($OV(OC_3H_7)_3$) vapors with water vapor. Depositions were carried out at atmospheric pressure and at temperatures varying between 135 and 175 ^oC and were selectively made on Si substrates on which Cu nano-patterns, such as those seen in Fig. 6 were formed. In Fig. 7 to 9 the effect of the deposition temperature on the selectivity is shown. It is observed that this improves as the deposition temperature increases

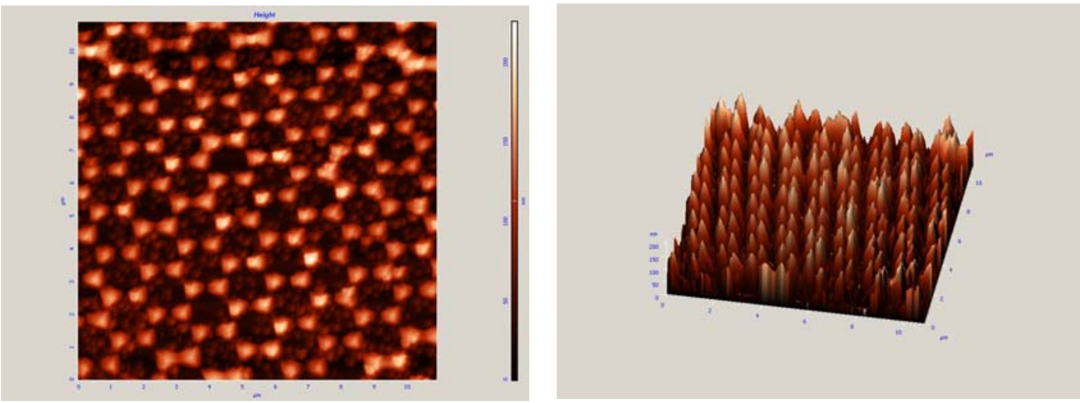

Fig. I.4.7. *Selective chemical vapour deposition of VO_x on hexagonally arranged Cu nano-dots (as shown in Fig. 6) with dimensions of 500 nm deposited at 135 ^oC. Most of the deposition occurs on the Cu dots but some deposition is also observed between them.*

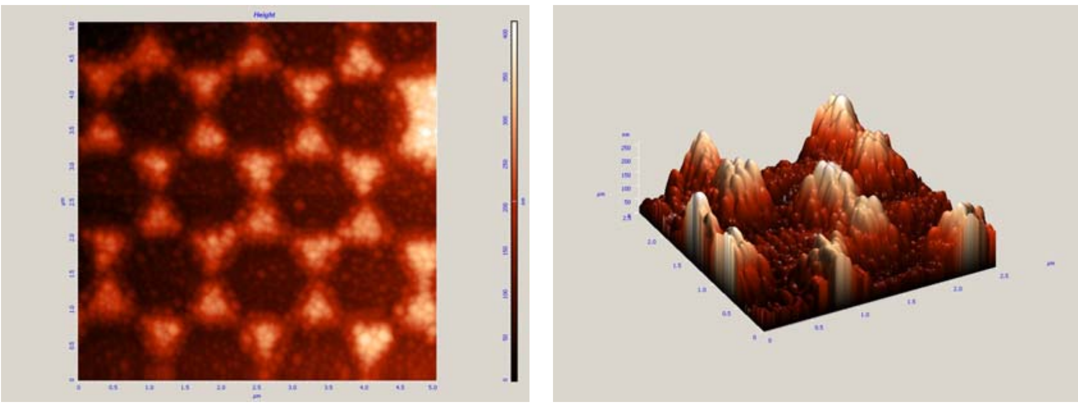

Fig. I.4.8. *Selective chemical vapour deposition of VO_x on Cu nano-dots at 150 ^oC. Some deposition is observed on the substrate between the Cu dots.*

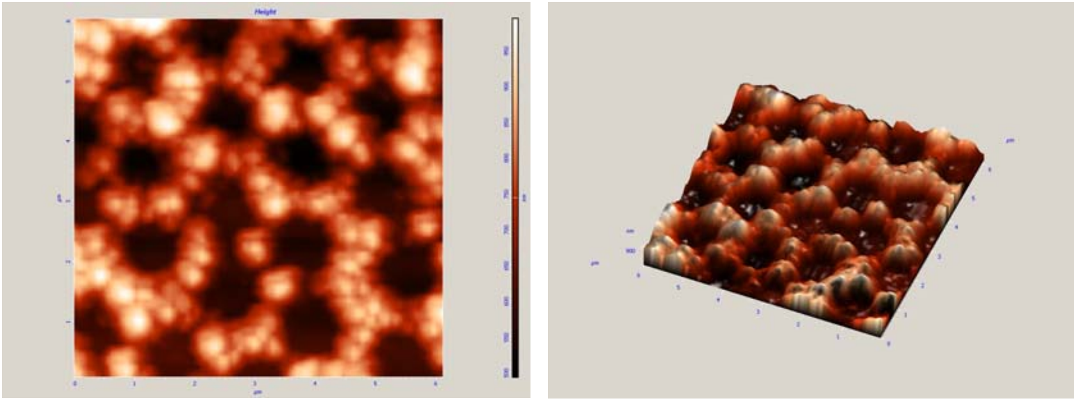

Fig. I.4.9. *At deposition temperature of 175 ^{o}C the growth rate is very fast. The height of the features shown is approximately 1 μm. The selectivity of deposition is impressive since no deposition occurs between dots is spite of the fact that the maximum distance between them is 500 nm.*

PROJECT OUTPUT in 2007

Publications in International Journals and Reviews

1. “Copper metallization based on direct-liquid-injection hot-wire CVD”, G. Papadimitropoulos, D. Davazoglou Microelectronic Engineering 84 1148–1151 (2007).
2. “Hot-wire assisted chemical vapor deposition of Cu by direct-liquid-injection of CupraSelect”, G. Papadimitropoulos, D. Davazoglou Surface & Coatings Technology 201, 8935 (2007)
3. “Selective chemical vapor deposition of vanadium oxides by of Vanadium tri-i-propoxy oxide vapors”, L. Kritikos, L. Zambelis, G. Papadimitropoulos and D. Davazoglou Surface & Coatings Technology 201, 9334 (2007)
4. “Copper films deposited by hot-wire chemical vapor deposition and direct-liquid-injection of CupraSelect”, G. Papadimitropoulos and D. Davazoglou Chemical Vapor Deposition 13, 656 (2007)

Publications in Conference Proceedings

1. “Mirrors based on tal reflection for concentration PV panels”, E. Karvelas, A. Papadopoulos, D. Dousis Y. P. Markopoulos E. Mathioulakis, G. Panaras, V. Vamvakas and D. Davazoglou, 4Th International Conference on Solar Concentrators for the Generation of Electricity or Hydrogen, San Lorenzo de El Escorial, Spain, March 12-16, 2007.
2. “Crystalline Silicon solar cell design optimized for concentrator applications”, K. Kotsovos, V. Vamvakas, D. Davazoglou, K. Misiakos, V. Paschos and E. Skouras, 4Th International Conference on Solar Concentrators for the Generation of Electricity or Hydrogen, San Lorenzo de El Escorial, Spain, March 12-16, 2007.

Conference Presentations

1. “Hot-wire assisted chemical vapor deposition of Cu by direct-liquid-injection of CupraSelect”, G. Papadimitropoulos, D. Davazoglou Proceedings of the 16th European Conference on Chemical Vapor Deposition EUROCVD-16, The Hague, The Netherlandsm September 16-21 (2007)
2. “Selective chemical vapor deposition of vanadium oxides by of Vanadium tri-i-propoxy oxide vapors”, L. Kritikos, L. Zambelis, G. Papadimitropoulos and D. Davazoglou Proceedings of the 16th European Conference on Chemical Vapor Deposition EUROCVD-16, The Hague, The Netherlandsm September 16-21 (2007)

Conference Participation

1. EUROCVD-16 The Hague, The Netherlandsm September 16-21 (2007)