Project: I. 4: THIN FILMS by CHEMICAL VAPOR DEPOSITION (CVD)

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Objectives:

The objectives of this group include research and development in the following:

- Process and material development
- Characterization of CVD films
- Applications

MAIN RESULTS in 2009

A. Hot-Wire Atomic Layer Deposition System

I. Kostis, G. Papadimitropoulos

An atomic layer deposition (ALD) system was designed and developed. The system is equipped with a hot wire (HW-ALD) permitting the separate heating of the gas phase in order to create activated species with special characteristics such as, for example, high surface mobility on the substrate, etc.

Fig. 1. Photo of the HWALD system that was developed. The reactor and various electronic sub-systems are shown left while on the right a part of the gas line.

Except of “classical” depositions, heating of the wire only at a pressure of the order of 0,1-1 Torr, under certain conditions, gives deposits composed of oxides of the metallic wire. More precisely, a native oxide is grown on the surface of every wire. If the vapor pressure of this oxide is higher than that of the metal, heating of the wire produces a vapor of oxides which is deposited on a cold substrate. Typical examples are W and Mo whose oxides have much higher vapor pressures than that of the corresponding metals.

In Fig. 2 SEM micrographs taken on the surfaces of a tungsten oxide (left) and a molybdenum oxide (right) film deposited in the HW-ALD system are shown. It can be observed that the obtained films are porous. As shown by spectroscopic ellipsometry measurements their porosity being near 60%. As shown by TEM measurements (Fig. 3), films

are composed by grains with dimensions of the order of 10 nm. The stoichiometry of films depends on the gas phase composition during deposition: in a nitrogen ambient stoichiometric oxide films were obtained while when hydrogen was added into the reactor reduced films with optical constants very near to those of the corresponding metals were obtained. The last were easily crystallized by heating at temperatures of the order of 150 ^{o}C to give films composed by well crystallized grains with dimensions of the order of 5 nm as shown in Fig. 3 (right).

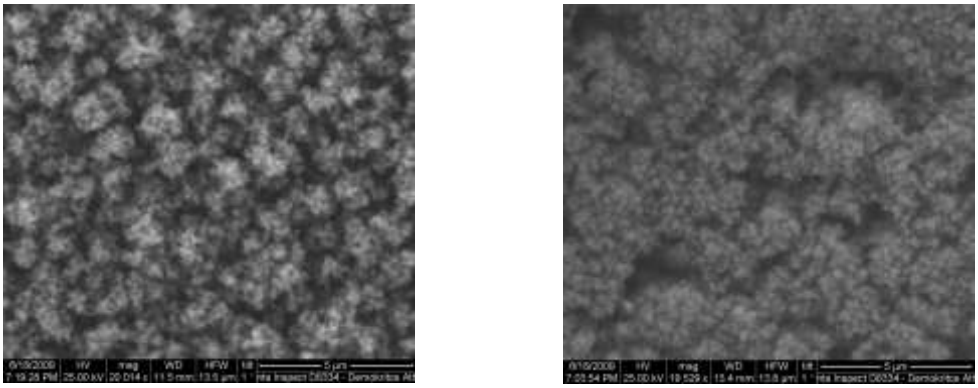

Fig. 2. SEM micrographs taken o the surface of porus WO_3 (left) and MoO_3 (right) thin films deposited by heating the corresponding wires in a vacuum of 0,1 Torr. Grains with dimensions of the order of 30-40 nm are shown, which are composed by smaller ones with dimensions near 5 nm (see Fig. 3).

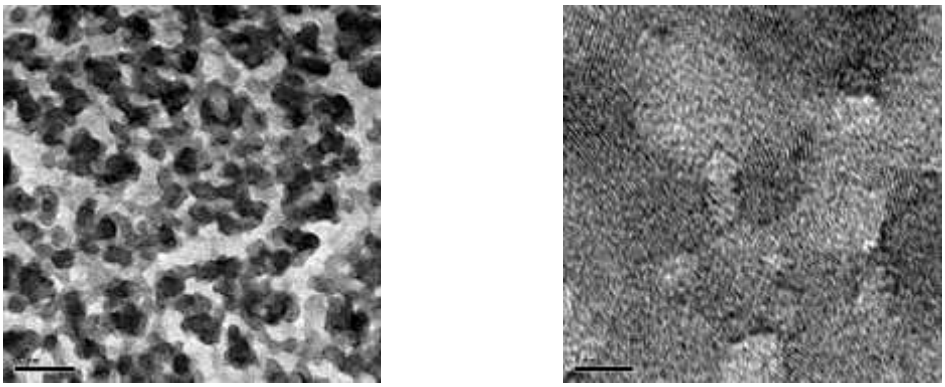

Fig. 3. TEM micrographs taken o porous WO_3 films deposited in a vacuum of 0,1 Torr of oxygen (left) and hydrogen (right) at a substrate temperature of 100 ^{o}C.

The above films were used in organic light emitting diodes (OLEDs) and organic photovoltaic devices (see Project I 1, Functional molecular materials for lithography and organic-molecular electronics).

B. Miniature Concentration Silicon Solar Cells

G. Rokadakis

Miniature photovoltaic (PV) cells with dimensions of 0,5X0,3 cm^2 were formed on Si (Fig. 4). After an initial run it turned out that only 50% approximately of PV cells were operating after dicing saw and cutting form the Si wafer. This was attributed to the poor passivation of the edges. After these initial efforts, a second run was made introducing a passivating oxide between cells so sawing was done on this oxide. The introduction of this oxide increased yield to 100 %.

Fig. 4. Miniature PV Silicon cells with dimensions of 0,15 (0,5X0,3) cm^2 before (left) and after cutting (right).

Miniature cells were operated under a moderate concentration (X20) of sun light packed to form modules and panels as seen in Fig. 5. The optical parts of modules have been fabricated by poly-dimethyl siloxane (PDMS), which is an advanced material with optical properties conformal with the operation of Si PV cells. Moreovefr, this material is easily cast to form semi-spherical lenses. It is noted that because of the hemispherical shape of these concentration lenses an accurate sun tracking is not necessary for the proper operation of modules; an accuracy of ±1 degree from the vertical is enough. Cells, modules and panels were tested at real conditions yielding efficiencies of 16%.

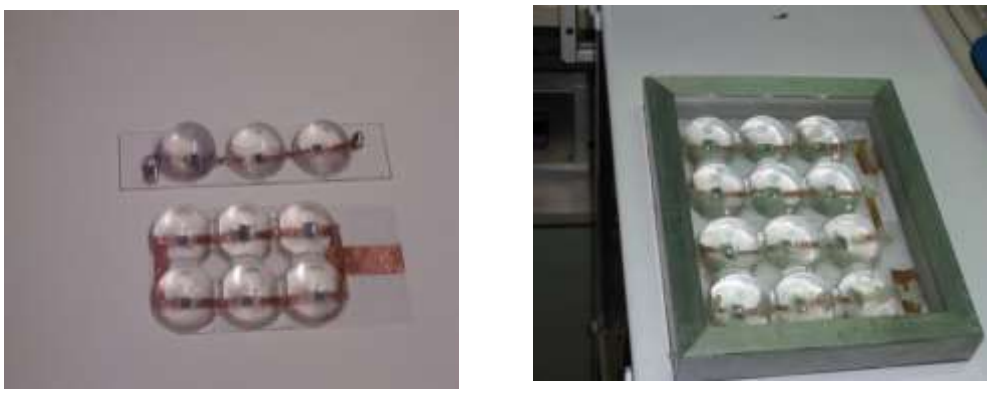

Fig. 5. Modules (left) and a panel (right) made of miniature concentration Si cells.

PROJECT OUTPUT in 2009

Publications in Refereed Proceedings

1. Initial Stages of Thermally and Hot-Wire Assisted CVD Copper on SiLK® and LTO Substrates Activated with Mercaptopropyl Triethoxysilane Self-Assembled Monolayers G. Papadimitropoulos, T. Speliotis, A. Arapoyianni and D. Davazoglou, **EUROCVD 17**, ECS Transactions. V25, No 8, p 893 (2009)
2. Memory Structures Based on the Self-organization of Cu Nanoparticles Deposited by Hot-Wire CVD on Polythiophene Layers P. Dimitrakis, G. Papadimitropoulos, L.C. Palilis, M. Vassilopoulou, P. Normand, P. Argitis and D. Davazoglou, **EUROCVD 17** ECS Transactions. V25, No 8, p 893 p. 1073 (2009)
3. Fabrication of Micro- and Nano-Electrodes by Selective Chemical Vapor Deposition of Cu on Si Substrates Patterned with AZ5214™ and PMMA, G. Papadimitropoulos, S. Cibella, R. Leoni, A. Arapoyianni and D. Davazoglou, **EUROCVD 17** ECS Transactions, 25 (8) 1285-1292 (2009)

Conference Presentations

1. "Inorganic metal oxides as cathode interfacial layers for polymer electronic devices", M. Vasilopoulou, L. C. Palilis, D. G. Georgiadou, P. Argitis, I. Kostis, G. Papadimitropoulos, N. A. Stathopoulos, A. Iliadis, N. Konofaos and D. Davazoglou, 2nd International Symposium on Flexible Organic Electronics, 8-10 July 2009, Halkidiki Greece
2. Initial Stages of Thermally and Hot-Wire Assisted CVD Copper on SiLK® and LTO Substrates Activated with Mercaptopropyl Triethoxysilane Self-Assembled Monolayers G. Papadimitropoulos, T. Speliotis, A. Arapoyianni and D. Davazoglou, EUROCVD 17, ECS Transactions. V25, No 8, p 893 (2009)
3. Memory Structures Based on the Self-organization of Cu Nanoparticles Deposited by Hot-Wire CVD on Polythiophene Layers P. Dimitrakis, G. Papadimitropoulos, L.C. Palilis, M. Vassilopoulou, P. Normand, P. Argitis and D. Davazoglou, EUROCVD 17 ECS Transactions. V25, No 8, p 893 p. 1073 (2009)
4. Fabrication of Micro- and Nano-Electrodes by Selective Chemical Vapor Deposition of Cu on Si Substrates Patterned with AZ5214™ and PMMA, G. Papadimitropoulos, S. Cibella, R. Leoni, A. Arapoyianni and D. Davazoglou, EUROCVD 17 ECS Transactions, 25 (8) 1285-1292 (2009)

Ph.D Thesis

1. "Development and characterization of thin films of Cu and copper oxides and application in electronic devices", G. Papadimitropoulos, University of Athens

Master Theses

1. "Selective chemical vapor deposition of vanadium oxides on Cu features made by colloidal lithography", L. Zambelis, NTUA
2. "Micrographic concentration silicon photovoltaic cells", G.L. Rokadakis, Univ. Of Athens