

PROJECT: I. 4

THIN FILMS by CHEMICAL VAPOR DEPOSITION (CVD)

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Funding:

- CONECTOR, "Copper nano-electrodes and novel transistors based on tungsten oxides nano-rods", (GSRT project) 2005-2008
- FOCUS, 2006-2007 (Contract with Industry)

RESEARCH RESULTS

A. Metal-Organic Chemical Vapor Deposition (MOCVD) of Cu films

a₁ Cu thermal deposition over patterned surfaces

G. Papadimitropoulos, D. Renesis

Cu films were deposited by metal-organic chemical vapor deposition (MOCVD) in a newly installed MOCVD reactor with direct liquid injection (DLI) of CupraSelect® (hfacCu¹VTMS) vapors. Cu films were deposited on patterned low temperature SiO₂ (LTO) lines 0,5 μm wide and 0,5 μm deep (see Fig. I.4.1). The LTO features were first covered with an LPCVD W film by pyrolysis of W(CO)₆ vapors.

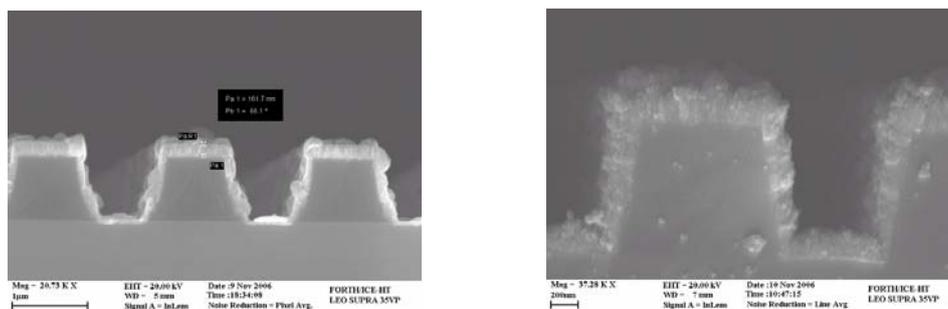


Fig. I.4.1: LTO features 0,5 μm wide 0,5 μm deep covered with a W/Cu sandwich of films

a₂ Hot-Wire CVD of Cu - Patterning of Cu films

G. Papadimitropoulos

In Fig. I.4.2a SEM micrograph is shown where Cu is selectively deposited on a patterned insulating WO₃ film at 120 °C, (see also below). The deposited film is composed by grains with dimensions of the order of 1 μm. Moreover, it has a resistivity several orders of magnitude higher than that of the bulk metal. When assisted by hot-wire (HWCVD), copper can be easily deposited by CVD on insulating surfaces as shown in Fig. I.4.2 (b,c).

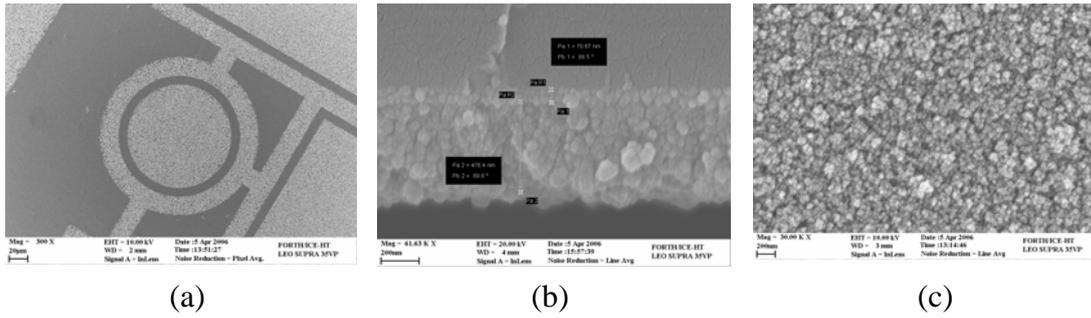


Fig. I.4.2: (a) Cu deposited selectively on a patterned WO₃ film. (b) A sandwich WO₃/hot-wire CVD Cu deposited on a Si substrate. (c) Top view of the Cu film. It is observed that it has a resistivity slightly higher than that of bulk Cu and is fine-grained

Based on the above a Cu metallization scheme can be proposed within which a WO₃ film is deposited first on a surface patterned with negative-tone photoresist, followed by the deposition of a HWCVD Cu film. The sandwich WO₃/HWCVD Cu is patterned by “lifting-off” the photoresist and the Cu film thickness is increased further by selective CVD (SCVD) of Cu. The HWCVD Cu layer has low resistivity and smooth surface. A pattern made with this method is shown in Fig. I.4.3.

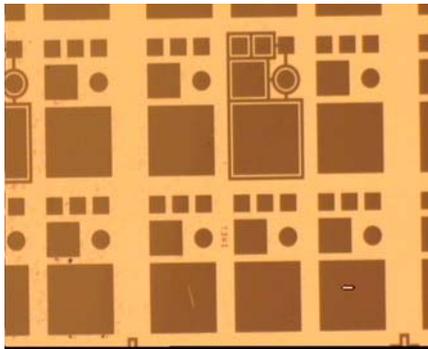


Fig. I.4.3: Patterns obtained by SCVD of Cu on a lift-off patterned WO₃/HWCVD Cu “sandwich”.

B. Nano-structured WO₃ thin films of high porosity

b₁ Characterization

G. Papadimitropoulos, N. Vourdas, K. Giannakopoulos

Nano-structured WO₃ films were deposited on quartz substrate by heating a tungsten filament in a vacuum chamber at temperatures of 650, 750 and 800 °C (hot-wire tungsten oxide, hw-TO). Hw-TO films exhibit a very high transmission due to their high porosity. As shown by spectroscopic ellipsometry measurements, porosities above 50% may be obtained (see Fig. I.4.4). TEM measurements have shown that hw-TO films were composed of grains with dimensions of the order of 5 nm. Very small, crystallized regions with dimensions of the order of 3 nm, were also detected.

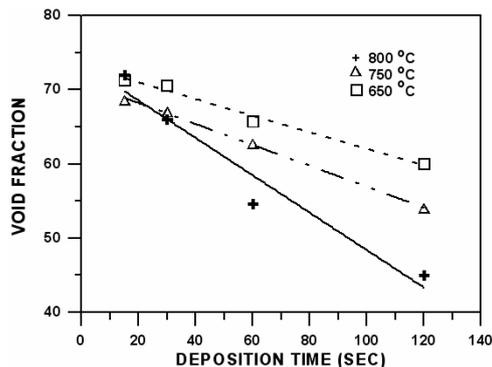


Fig. I.4.4: Dependence of the porosity of hw-TO films on deposition time for three different filament temperatures.

b₂ Electrochromic Displays based on WO₃ nano-structured films

M. Vasilopoulou, G. Papadimitropoulos and G. Aspiotis

The above described hw-TO films may be deposited on plastic substrates since their deposition takes place at room temperature. In Fig. 8 a polyurethane (PET) sheet covered with a transparent-conductive SnO₂:F layer on which a hw-To layer was deposited is shown. Electrochromic displays were formed by depositing on the PET/SnO₂:F/hw-TO sandwich organic electrolytes and adding a counter electrode of Al. The organic electrolytes were based on poly(methyl methacrylate) (PMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) into which phospho-11 dodecatungstic acid (H₃PW₁₂O₄₀) was added at various concentrations.

The electrochromic configurations formed exhibited high coloration efficiency, near 80 cm²/Cb as compared to 40 cm²/Cb for devices based on LPCVD WO₃ films. Moreover, they started to color at 0,8 V as compared to 1,5 V and were much faster than devices based on LPCVD WO₃ films.

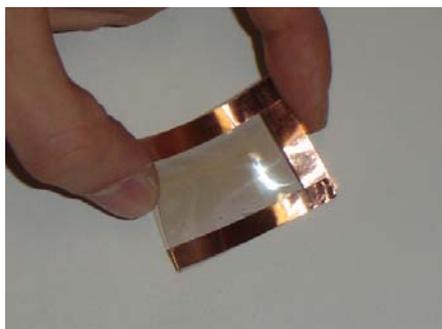


Fig. I.4.5: A hw-TO film deposited on a PET substrate covered with a SnO₂:F layer.

C. Colloidal Lithography

L. Zambelis

Monodispersed spheres of submicron to micron sizes can 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. I.4.6 (left) an array of hexagonally closely packed polystyrene (PS) spheres with dimensions of 0,9 μm is shown. This array can be used as template for the subsequent vacuum deposition of metal nano-dots as shown in Fig. I.4.6 (right) where periodically arranged Cu nano-dots with dimensions of the order of 200 nm are shown.

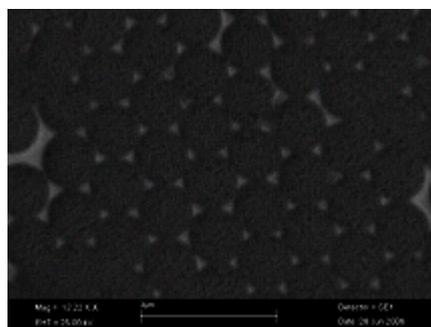
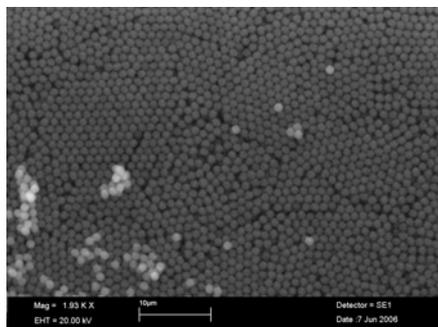


Fig. I.4.6: (Left) SEM image of hexagonally packed PS spheres with dimension of 0,9 μm. (Right) a periodic arrangement of Cu nano-dots with dimensions of 200 nm produced after vacuum evaporation of the metal through a mask such as that shown left and etching of the PS spheres (the diameter of PS spheres was 1,3 μm).

D. Selective CVD of Vanadium oxide films

E. Kritikos, L. Zambelis

Vanadium oxide films were deposited by atmospheric pressure chemical vapor deposition (APCVD) on Si substrates covered with Cu films by oxidizing Vanadium (V) tri-i-propoxy oxide ($\text{OV}(\text{OC}_3\text{H}_7)_3$) vapors. Selective deposition on Cu was carried out at atmospheric pressure and at temperatures varying between 135 and 350 °C. The Vanadium oxide films were characterized by X-ray diffraction and electrical resistance measurements at various temperatures.

Electrical resistance measurements made at temperatures varying between 25 and 80 °C have shown that APCVD VO_x films exhibit an insulator to metal transition at 68 °C. The exact point of this transition depends on the temperature of deposition, which, as shown by XRD measurements, implies changes in the stoichiometry of films.

Selective APCVD of VO_x combined with colloidal lithography yields ordered features in the nano-scale as shown in Fig. I.4.7.

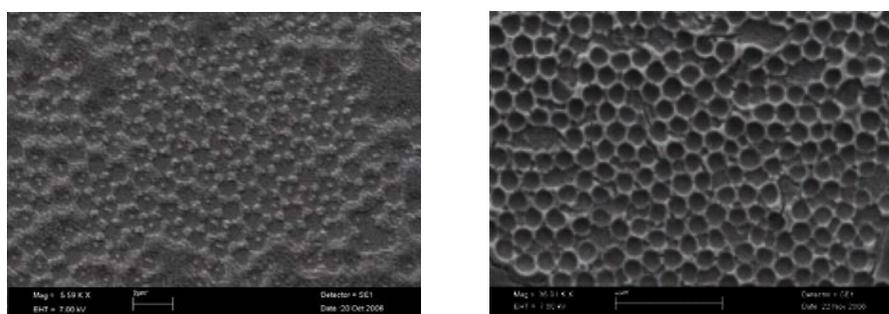


Fig. I.4.7: Nano-scale features obtained by selective APCVD of VO_x on Cu patterned with colloidal lithography.

PROJECT OUTPUT in 2006

Publications in International Journals

1. “Optical and structural properties of copper oxide thin films grown by oxidation of metal layers”, G. Papadimitropoulos, N. Vourdas, V. Em. Vamvakas and D. Davazoglou, *Thin Solid Films*, 515, 2428 (2006)
2. “Polymeric electrolytes for WO_3 -based electrochromic displays”, M. Vasilopoulou, I. Raptis, P. Argitis, I. Aspiotis and D. Davazoglou *Microelectronics Engineering* 83 (4-9 SPEC. ISS.), pp. 1414-1417, (2006)

M.Sc. theses

1. E. Kritikos, “Structure and electrical properties of CVD vanadium oxide films”, UOA July 2006
2. D. Renesis, “Deposition of W/Cu layers on patterned LTO surfaces. Study of the dependence of step coverage on the deposition conditions”, UOA Dec. 2006