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Collaborating scientists: Dr. D. Kouvatsos, Dr. M. Vasilopoulou

Funding:

- EU STREP IST PROTEAS PV System, Contract N^{o} ENK6-CT-2002-00674, 1/1/2003-31/12/2005

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

Main results in 2005

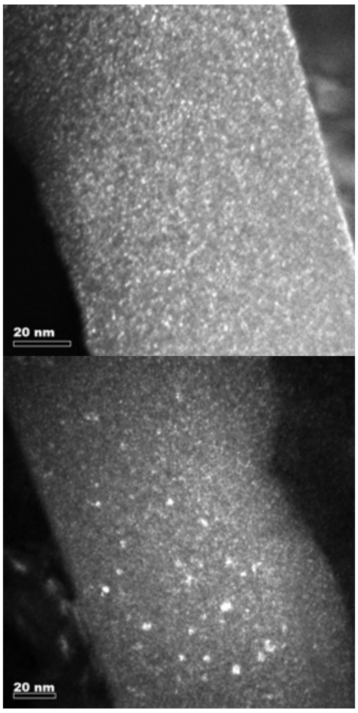
The main results obtained in 2005 within the different tasks of the project are given below.

Task 1 Characterization of Si rich Silicon nitride films prepared by LPCVD

V. Vamvakas

Si rich silicon nitride films were deposited by chemical vapor deposition at low pressures (LPCVD) from SiH_2Cl_2 (DCS) and NH_3 gas mixtures. Films stoichiometry was controlled by the DCS/NH_3 flow ratio.

The as deposited films were found to be homogeneous by transmission electron microscopy (TEM) measurements. After annealing at 950 ^{o}C Si nano-crystals (Si nc) were observed with size ranging between 1,0 and 1,5 nm (fig. I.4.1). Annealed at 1100 ^{o}C for 1h induced the formation of Si nc with dimensions of 4,5 to 5 nm (fig. I.4.1).



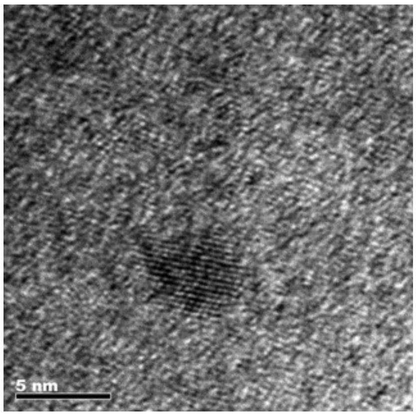


Fig. I.4.1: *TEM images of Si rich silicon nitride films prepared with a DCS/NH_3 ratio equal to 10 after annealing at 950 ^{o}C for 30 minutes (left top) and 1100 ^{o}C for 1h (left bottom). High resolution TEM image of a Si nc with size of 5,0 nm (upper).*

Fourier Transform Infrared Spectroscopy (FTIR) has shown that Si rich LPCVD silicon nitride films have a main transmission band near 830 cm $^{-1}$ corresponding to the stretching mode of vibration of the Si – N bond. As seen in fig. I.4.2, the increase of the Si content in films implies a slight shift towards higher wavenumbers of this absorption band.

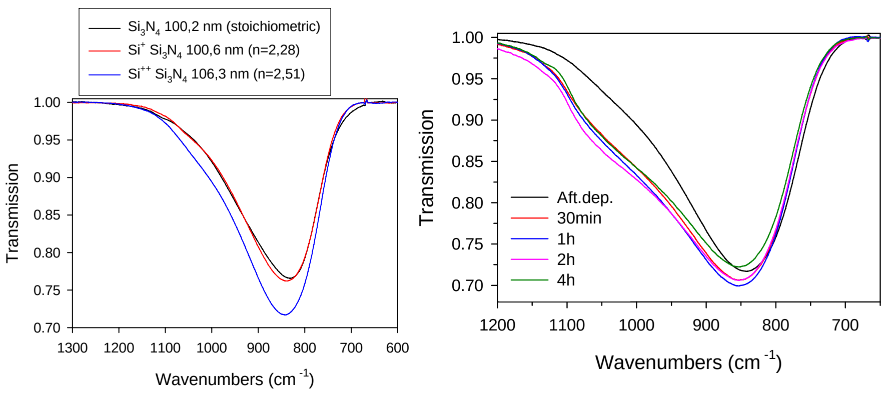


***Fig. I.4.2:*.** *(left) FTIR Transmission spectra of three Si-rich silicon nitride films with different Si content. (Right) FTIR spectra of Si rich silicon nitride films annealed at 1100 ^{o}C for several time periods.*

Annealing Si rich LPCVD silicon nitride films causes the appearance of an extra absorption band near 1075 cm $^{-1}$ (fig. I.4.2) probably connected to the presence of oxygen in films.

Task 2 Metal and metal oxide films

a. Metal-Organic Chemical Vapor Deposition (MOCVD) of Cu films – Selective deposition

G. Papadimitropoulos

A new MOCVD reactor for the deposition of Cu was installed (see figure). CupraSelect® vapors, which is the industry standard, are directly injected in the reactor in the liquid phase. The reactor operates within the temperature range 90 to 250 ^{o}C and pressures ranging between several mTorr to 10 Torr. The reactor is equipped with a hot filament for several purposes: 1) Heat the reactant gases during deposition and accelerate the growth rate and 2). W filaments when heated at high temperatures and at pressures of 10^{-2} Torr emit nano-particles of WO_x, which form films with a nano-columnar morphology (see fig. I.4.6). Morphology and composition of these films depend on the temperature of the filament during deposition. Such films may find applications as adhesion promoters for Cu deposition, templates for nano-particle deposition, nano-devices, gas sensors, etc. Other may be considered applications based on the combination of the two materials (Cu and WO_x) in the same reactor.

Fig. I.4.3: *MOCVD system developed in 2005. Left, a view of the MOCVD system. The electronics, the DLI system and the stainless steel reactor are shown. On the right, a photo of the interior of the reactor is shown. The ring-like injector, the W filament and the substrate are distinguished.*

Cu films were deposited by metal-organic chemical vapor deposition (MOCVD) using the installed MOCVD reactor with direct liquid injection (DLI) of CupraSelect® (hfacCu^{I}VTMS). Uniform films were obtained on 3 in. Si wafers covered with LPCVD W by pyrolysis of $W(CO)_6$ vapors, at temperatures ranging between 100 and 180 ^{o}C.
The roughness of Cu films was found to increase with temperature as shown by AFM measurements (see fig. I.4.4).

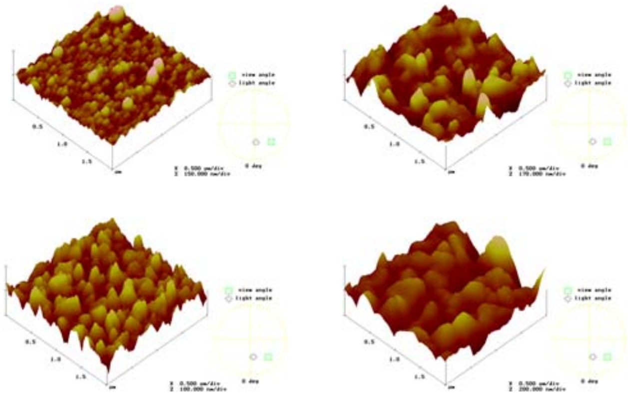


Fig. I.4.4: *AFM images taken on the surface of MOCVD Cu films deposited at 100 (upper left), 120 (upper right), 150 (lower left) and 180 ^{o}C (lower right).*

Under specific conditions selective deposition of Cu has been achieved on oxidized Si wafers covered by an LPCVD W layer and patterned with AZ5214 photoresist. Selective CVD has been performed on the entire surface of 3 in Si wafers.

b. Cu oxide films

G. Papadimitropoulos, N. Vourdas

Copper oxide films were grown by oxidation of vacuum evaporated copper layers on silicon substrates. Oxidation was made at atmospheric pressure, in a nitrogen-oxygen mixture 10% in oxygen and at temperatures varying between 185 and 450^{o}C. X-rays diffraction (XRD) patterns showed that, dependent on oxidation temperature, films were entirely composed either of Cu_2O, at 225 ^{o}C, or of CuO above 350 ^{o}C and of mixtures of these oxides and Cu silicide at other temperatures. The optical properties of films were studied with spectroscopic ellipsometry measurements within the energy range 1 to 3,5 eV (see fig. I.4.5). The band gap, as defined by the Tauc model, was found equal to 2.3 eV for the Cu_2O and between 1,05 and 1,2 eV for CuO. It was shown that the gap of the Cu_2O films was free of localized states (see fig. I.4.5), which was not the case for the gap of CuO.

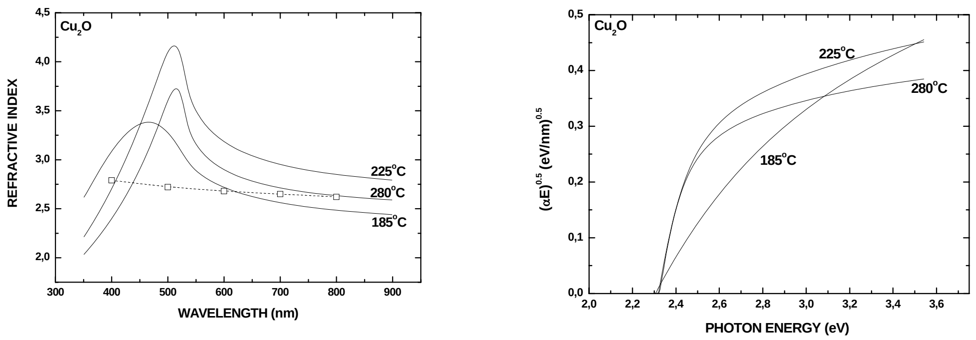


***Fig. I.4.5: (Left)** Dispersion of the real part of the refractive index of Cu_2O films grown at various temperatures. Data for single-crystalline material are also shown. **(Right)** Tauc' s plots for the above films.*

c. W oxide nano-structured films

G. Papadimitropoulos

Films composed of tungsten sub-oxides (WO_x, x<3) are deposited into the reactor used for Cu deposition by heating a W filament at a moderate vacuum of the order of 10^{-2} Torr. These films are composed of nano-rods with diameter of 10-40 nm, high porosity and are amorphous when currents between 25 and 35 A pass through the W filament. At higher currents they become crystalline. In fig. I.4.6 SEM and AFM micrographs taken on the surface of such a film are shown and the high film porosity is observed. These nano-structured films may find many applications such as barriers against Cu diffusion, nano-rod transistors, gas sensors, etc.

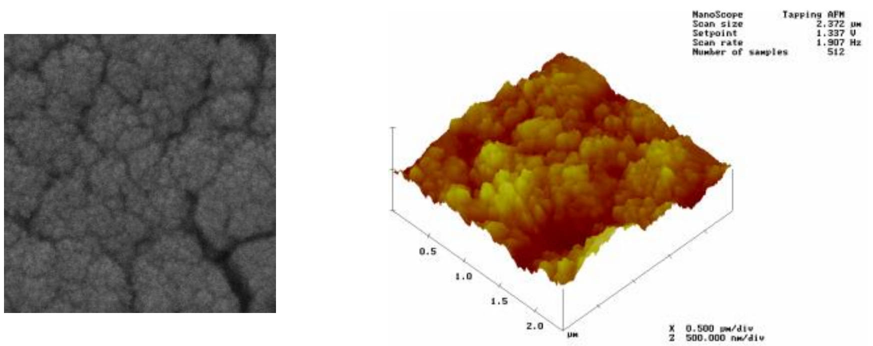


***Fig. I.4.6: (Left)** SEM micrograph taken on a $1x1\mu m^2$ area on the surface of a nano-structured WO_x film. **(Right)** AFM micrograph taken on the surface of the same film.*

Task 3

a. Gas sensors-Electrochromic Displays

M. Vasilopoulou, D. Economou, C. Favre, G. Aspiotis

SnO_2 films were deposited on Si and glass substrates by atmospheric pressure chemical vapor deposition (APCVD) using a reactor entirely made of quartz and Teflon by oxidizing $SnCl_4$ vapors. Deposition was carried out at atmospheric pressure and at temperatures varying between 350 and 450 ^{o}C. The SnO_2 films were characterized by X-ray diffraction, FTIR spectroscopy, AFM and spectroscopic ellipsometry measurements.

Gas sensors were fabricated using SnO_2 films (see fig. I.4.7) and their electrical and sensing properties were tested in H_2. Reversible changes of electric conductance of films were observed when activated with Pt.

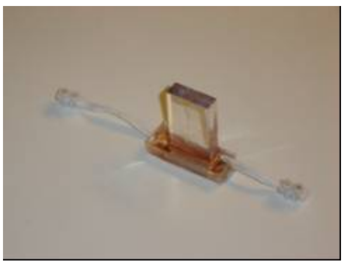
All solid-state electrochromic displays (see fig. I.4.7) were fabricated by tungsten oxide films on SnO_2:F covered glass substrates and using solid or gel-like organic electrolytes. These ionically conductive and electronically insulating electrolytes were based on poly (methyl methacrylate) (PMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) into which phospho-11 dodecatungstic acid ($H_3PW_{12}O_{40}$) was added at various concentrations. It was found that the degree of coloration does not depend on acid concentration.

Fig. I.4.7: *An all solid-state electrochromic display*

b. Packaging of concentration solar cells

V. Vamvakas

This activity focuses on the encapsulation of concentration solar cells used on PROTEAS, which is a hybrid solar system able to produce electric power, heat (hot water) and cooling power. In order to be economically viable, solar systems must have a long life (20 years or more) under extreme conditions. To insure the long life of the concentration solar cells used on PROTEAS a special encapsulation scheme, based on the use of poly-dimethyl siloxane (PDMS), was conceived (see fig. I.4.8).



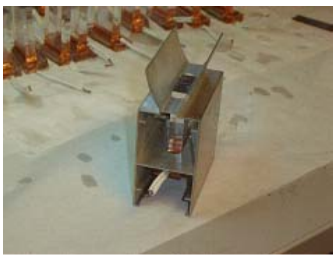


Fig. I.4.8: (Left) *Photo of an encapsulated concentration solar cell. A prism ensuring the even distribution of energy on its surface and the current leads are integrated on the encapsulation.* ***(Right)*** *Photo of a cell ready to be positioned on PROTEAS.*

PROJECT OUTPUT in 2005

PUBLICATIONS in INTERNATIONAL JOURNALS and REVIEWS

1. “Influence of the annealing temperature on the IR properties of SiO_2 films grown from SiH_4+O_2”, V. Em. Vamvakas and D. Davazoglou, Miroelectronics Reliability, 45 (2005) 986–989
2. “Characterization of various insulators for possible use as low-k dielectrics deposited at temperatures below 200 ^{o}C”, M. Vasilopoulou, A. M. Douvas, D. Kouvatsos, P. Argitis and D. Davazoglou, Miroelectronics Reliability, 45 (2005) 990–993
3. “Influence of the growth temperature on the atomic distribution of TEOS deposited SiO_2 films”, V. Em. Vamvakas and D. Davazoglou, Journal of Vacuum Science and Technology B, Vol. 23, 1956 (2005)

PUBLICATIONS in CONFERENCE PROCEEDINGS

1. “Simulation of FTIR spectra in non-normal incidence”, K. Zogopoulos, V. Vamvakas and D. Davazoglou, J. Phys.: Conf. Ser. Vol. 10. p. 194 (2005)
2. “Doping dependence of the adsorption of proteins on proton doped WO_3 films”, V. Asimakopoulos, C. Mastichiadis, S. Kakabakos and D. Davazoglou, J. Phys.: Conf. Ser. Vol. 10. p. 321 (2005)
3. “Fabrication of WO_3 –based electrochromic displays using solid or gel-like organic electrolytes”, M. Vassilopoulou, G. Aspiotis and D. Davazoglou, J. Phys.: Conf. Ser. Vol. 10. p. 329 (2005)
4. “Deposition and characterization of copper oxide thin films”, G. Papadimitropoulos, N. Vourdas, V. Em. Vamvakas and D. Davazoglou J. of Phys. Conf. Ser. Vol 10 (2005) 182-185.
5. “Calculation of the Infrared optical constants of LPCVD and thermally grown SiO2 films by measurements of reflection in non-normal incidence”, K. Zogopoulos, V. Vamvakas and D. Davazoglou, Electrochemical Society Proc. Vol. 2005-09, p. 291 (2005).
6. “Chemically vapor deposited SnO_2 films by oxidation of $SnCl_4$ vapors. Films characterization and application in gas sensors”, C. Favre, N. Vourdas, E. Pimienta V. Em. Vamvakas and D. Davazoglou, Electrochemical Society Proc. Vol. 2005-09, p. 952 (2005).
7. "Characterization of various low-k dielectrics for possible use in applications at temperatures below 160 C", M. Vasilopoulou, S. Tsevas, A.M. Douvas, P. Argitis, D. Davazoglou and D. Kouvatsos, Journal of Physics: Conference Series, 10, 218, October 2005.
8. “PROTEAS: a hybrid device for the production of electricity, heat and cooling power”, A. Papadopoulos, K. Chrysagis, S. Karvelas, D. Dousis, J. Lutz, Y. Spanoudakis, Y. Aspiotis, I. Luque-Heredia, J. M. Moreno, P. H. Magalhaes V. Emm. Vamvakas, M. Mathioulakis and D. Davazoglou, Proceedings of the 20th European Photovoltaic Solar Energy Conference, pp.2242-2245, Barcelona, 2005

CONFERENCE PARTICIPATION

1. “Chemically vapor deposited SnO_2 films by oxidation of $SnCl_4$ vapors. Films characterization and application in gas sensors”, C. Favre, N. Vourdas, E. Pimienta V. Em. Vamvakas and D. Davazoglou, 15th European Conference on Chemical Vapor Deposition (EUROCVD 15), Bochum, Germany, 5-9 Sept. 2005.

M.Sc. THESES

1. “Study of the adsoprion of proteins on tungsten oxide (WO_3) thin films”, V. Asimakopoulos
2. “Fabrication of an electrochromic display based on tungsten oxide thin films”, D. Oikonomou

DIPLOMA THESES

1. “Chemical vapor deposition of SnO_2 films. Application of these films in the fabrication of gas sensors.”, C. Favre