Digest Journal of Nanomaterials and Biostructures Vol. 7, No 1, January-March 2012, p. 393 – 397

POROUS Al_2O_3 FILMS OBTAINED BY PLD ON COPPER TEMPLATES

D. TENCIU, C.R. IORDANESCU*, R. SAVASTRU, I.D. FERARU, A. KISS, C.N. ZOITA, R. NOTONIER[a], A. TONETTO[a], M. EYRAUD[b], O. MONNEREAU[b], L. TORTET[b], C. E. A. GRIGORESCU, S. ANTOHE[c]

National Institute R&D Optoelectronics INOE 2000, 409 Atomistilor, PO Box MG-5, Magurele, 77125 Romania

[a]Service Commun de Microscopie, Universite de Provence, Site Saint Charles, Case 26, Marseille, France

[b]Laboratoire MADIREL, Universite de Provence, Faculte de Saint Jerome, Marseille, France

[c]Faculty of Physics, University of Bucharest, Magurele, 77125 Romania

Porous Al_2O_3 films were deposited on copper thin film templates onto silicon substrates by means of pulsed laser deposition (PLD) technique using a KrF excimer laser. The copper films have been first deposited in vacuum on Si substrates at room temperature, with a particular distribution of Cu droplets to favour pores formation. Alumina deposition has been done following ablation of a pure Al target at 10^{-3} Torr oxygen pressure at different substrate temperatures: room temperature, 600 °C and 650 °C. The characterization of samples involved micro-Raman spectroscopy, FTIR spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive x-ray spectroscopy (EDS) to reveal structural and morphological properties. FTIR and Raman spectroscopy results corroborated with EDS analyses confirm the presence of alumina in the Al_2O_3/Cu/Si structures. SEM images show ~300 nm ordered pores in films deposited at room temperature.

(Received March 9, 2012; Accepted March 13, 2012)

Keywords: PLD, Alumina, Plasmon resonance

1. Introduction

The specific nature of a porous oxide layer on aluminum has received a great deal of attention over several decades, and determined fully the present applications of anodized aluminum in nanotechnology [1]. Because of the immense surface-to-volume ratio and the abundant void fraction, very high sensitivities can be obtained with porous ceramics in the gas sensor field. Porous Al_2O_3 has proven to be stable at elevated temperatures and at high humidity levels. The quality of the Al_2O_3 layers and consequently the sensor behaviour (sensitivity, humidity range, response time, stability etc.) strongly depend on the thickness of the porous layer and the density and size of the pores [2]. As a simple and versatile method for producing thin films, PLD is widely used in obtaining of various materials, complex oxides among others. Its advantage lies in the possibility to make ultrathin films from materials that are difficult to shape under normal conditions. It has the particular potential of producing films with controlled morphology, density, crystalline phase and grain size, because it offers various leverages to control the size, chemistry and kinetic energy of the elementary 'building blocks' being deposited [3]. An orientation of the pores is very difficult to obtain with usual PLD film-forming parameters. However, by controlled PLD [4] zirconia oriented porous membranes made of uniform nanoparticles and nanochannels deposited on porous alumina substrates have been obtained [5]

*Corresponding author: iorda85@yahoo.com

The experiment that generated this work has been an attempt to obtain porous alumina with embedded copper particles using the PLD technique. Copper cluster related materials have been already reported [6-13] mainly in connection with the sol gel technique that requires annealing of copper oxide particles under reducing atmosphere. Formation of metallic copper or copper oxide particles by PLD has been shown to strongly depend on the residual oxygen pressure during the deposition [14, 15]. The study of Celep et al [6] on optical properties of copper clusters embedded in alumina considers codeposition of Cu clusters (formed by laser vaporisation of a copper rod) and transparent alumina (evaporated using an electron gun). This study underlines that the metallic character of the copper clusters has been preserved owing to the substrate temperature held at 400°C.

In our work, thin alumina films were deposited on Cu/Si substrates through ablation of a pure aluminum target, controlling the oxygen pressure in the chamber of a PLD workstation. The copper films with a controlled distribution of droplets [16] have been used as “templates” to favour pores formation in the alumina film.

2. Experimental

We employed a PLD 2000 workstation (PVD Products Ltd) to run Cu and Al_2O_3 depositions using. The rotating target holder permitted switching from Cu to Al target according to the growth sequence. Copper droplet templates were first deposited in vacuum. It has been our choice to use Cu due to its high thermal and electrical conductivities, the interesting results on surface plasmon resonance obtained previously [6] and also its low cost. The copper films were deposited on Si substrates at room temperature using a KrF laser (CompexPro 201 - Coherent) λ=248 nm, τ= 20 nsec/pulse at a repetition rate of 10 Hz [16] and 30.000 pulses. Alumina was then deposited with 50.000 laser pulses, at a fluence of ~ 2 J/cm^2. The preliminary pressure in the chamber was 2×10^{-6} Torr and the oxygen pressure during deposition was 1×10^{-3} Torr. The substrates were held at 20°C, 600 °C and 650 °C respectively for alumina deposition to find an optimal value for pores formation.

The structural properties were investigated by XRD, micro-Raman spectroscopy, FTIR and EDS, whereas morphological aspects were extracted from SEM. The SEM-EDS investigations were performed with a PHILIPS ESEM 30 microscope. AFM operated in ac mode was done in order to investigate the surface topology. Raman spectra were taken with a LABRAM HR 800 micro-Raman spectrometer (Horiba Scientific), at room temperature, with a 632 nm laser source, 0.5 cm^{-1} resolution. The FTIR spectra were acquired by means of a Perkin Elmer spectrophotometer Spectrum 100, using an UATR accessory, with 32 scans and the measuring error ± 0.1%.

3. Results and discussion

The XRD measurements performed with a Rigaku MiniFlexII indicate a fully amorphous material at all deposition temperatures.

The main Raman lines for alumina are found around 383 cm^{-1} and 420 cm^{-1}[17], shifts being also possible [18]. The samples in this work show the A_{1g} around 410 cm^{-1} and 633 cm^{-1} respectively and the E_g mode shifted to 785 cm^{-1} (fig.1., where the x-axis has a break at 520 cm^{-1}, i.e. the Si Raman line).

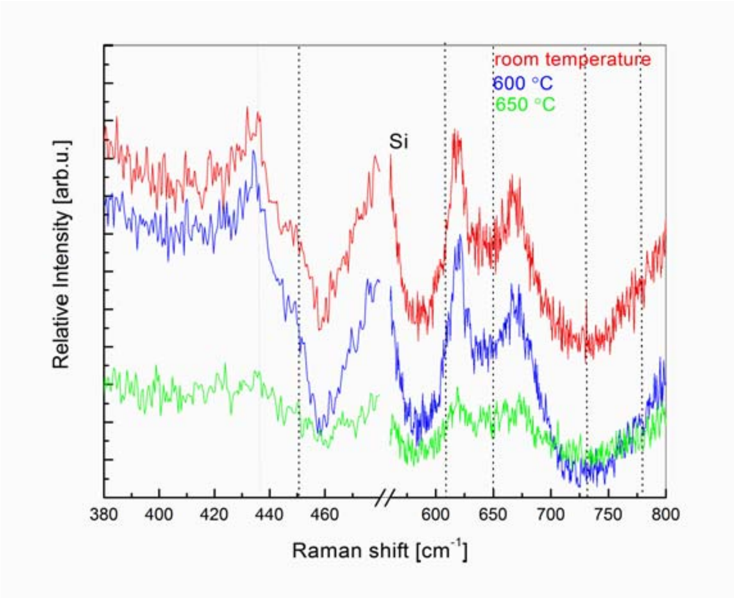


Fig. 1 Raman spectra of PLD alumina films with specific Raman modes. The break on the x-axis removes the too intense Si Raman line.

The FTIR absorption spectra of our samples feature a broad absorption maximum in the 900-925 cm^{-1} region, which can be associated with vibrations of Al-O bond accounting for a ~20 cm^{-1} shift. This shift may originate in the porosity of the films [19].

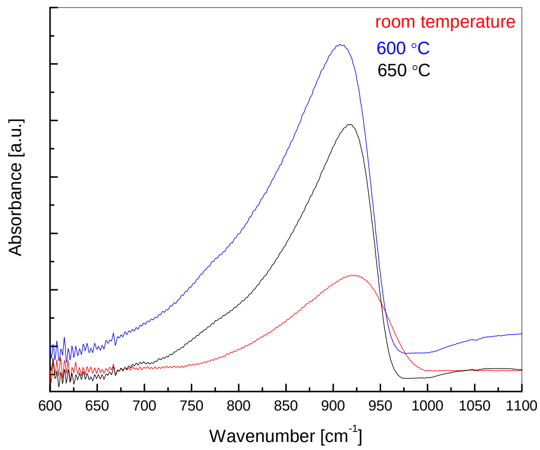
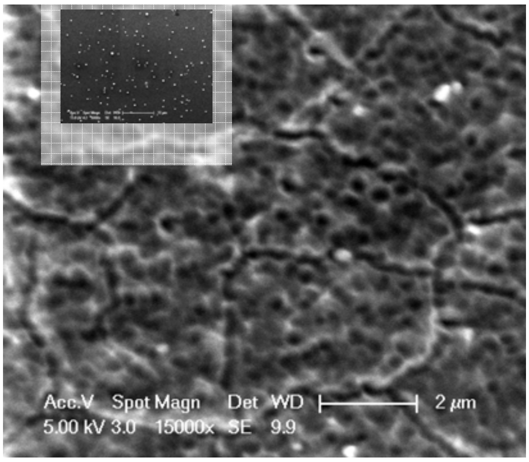


Fig. 2 FTIR-UATR absorption spectra of Al_2O_3/Cu/Si samples. The absorption band around 920 cm^{-1} corresponds to Al-O bond vibration.

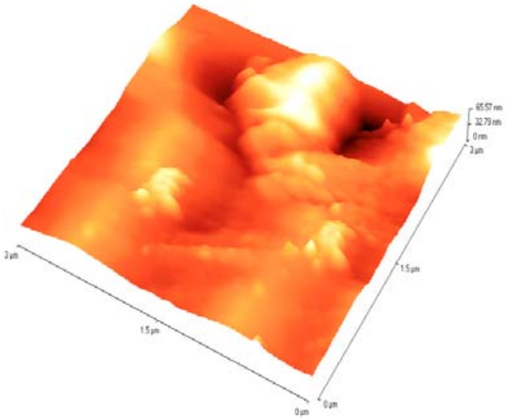
From the SEM images of the alumina films obtained in this study (fig. 3a, b, c) and the SEM image of a PLD copper oxide film [16, *and also inset in fig.3a*] a comparison can be made between the sizes of alumina pores and copper droplets. The average diameter of pores in films deposited at room temperature (~300nm) is about half size of the droplets' average diameter (~650 nm). Cracks also show up in these films, which are undoubtedly caused by the fast heat transfer and consequent thermal stress at the alumina/copper interface.

EDS analyses confirm the 2Al-3O proportion in all samples no matter the substrate temperature. An excess of 6% at. oxygen in the Al_2O_3 films deposited at room temperature could be attributed to copper oxide supposed to form at the Al_2O_3/Cu interface, most likely around the pores' edges. Holding the substrate temperature above 400°C [6] prevents Cu oxide formation. Since CuO forms around 300°C and Cu_2O around 700°C, it is expected that alumina films grown on copper at substrate temperatures between 400°C and 650°C are Cu_xO_y free.

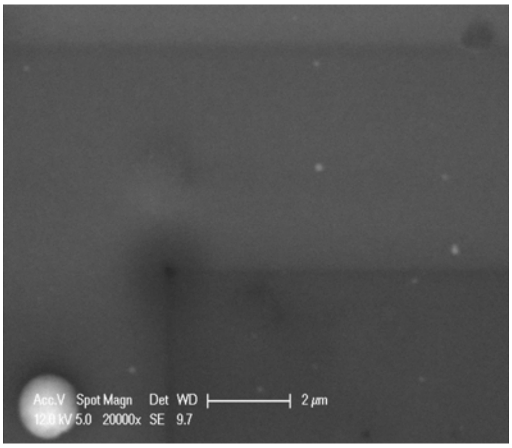
The pores' size reduces with increasing substrate temperature, as it can be remarked from SEM images in fig. 3 (a, b, c) and corresponding AFM images (fig. 3 d, e, f). The smoothest surface is associated with 600°C deposition temperature (RMS 0.36 nm) and not with 650°C. This result concerns rather the pore density than the pore size judging at least from the AFM images of the corresponding films (fig3 e) and f).



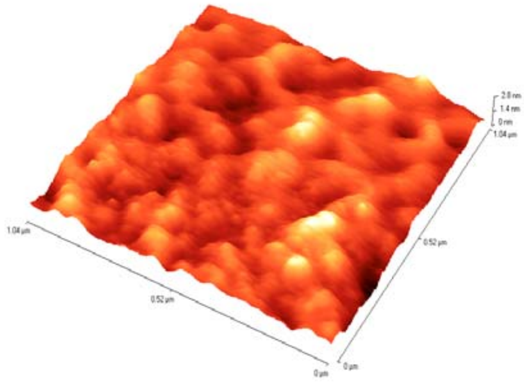
a)



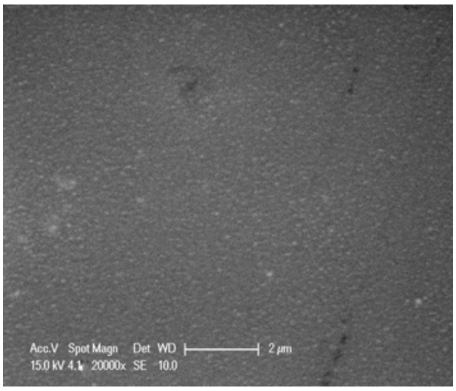
d) RMS (nm) 6.48



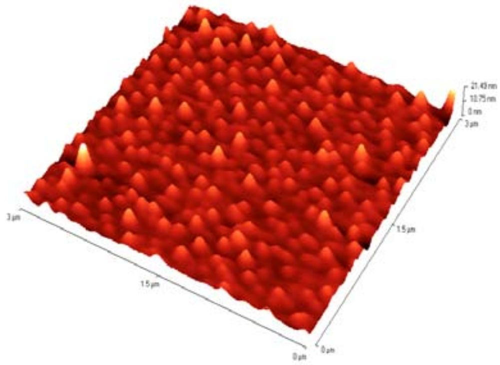
b)



e) RMS (nm) 0.36



c)



f) RMS (nm) 1.82

Fig. 3 SEM images of PLD alumina films deposited at room temperature (a), 600 °C(b), 650 °C (c), and corresponding AFM images (d, e, f).

4. Conclusions

Porous Al_2O_3 films were obtained by PLD on Cu droplets "templates". The pore size diminishes and their density increases with increasing substrate temperature.

The films grown at room temperature exhibit pores whose dimensions are half size of the Cu droplets of the "template".

Porous alumina films grown by PLD at substrate temperatures of $600^{O}C$ and $650^{o}C$ are Cu_xO_y free and also cracks free.

Further work will be devoted to the relation between the Cu droplets diameter and the dimensions of the pores in alumina PLD films with a focus to their surface plasmon resonance properties.

Acknowledgments

This work has been supported from project SENSGLASS, contract No. 7-031/04.04.2011, MNT-ERANET

References

[1] Grzegorz D. Sulka, Highly Ordered Anodic Porous Alumina Formation by Self-Organized Anodizing Nanostructured Materials in Electrochemistry. Edited by Ali Eftekhari, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008.
[2] Veronika Timár-Horváth, László Juhász, András Vass-Várnai, Gergely Perlaky, DTIP of MEMS&MOEMS, Stresa, Italy, 25-27 April 2007
[3] F. Di Fonzo, D. Tonini, A. Li Bassi, C.S. Casari, M.G. Beghi, C.E. Bottani, D. Gastaldi, P. Vena, R. Contro, Appl Phys A **93**: 765, (2008).
[4]T. Venkatesan et al, MRS Bull 1992, 17, 54.
[5] Balagopal N. Nair et al, Advanced Materials, **17**, 1136, (2005).
[6] G. Celep, E. Cottancin, J. Lermé, M. Pellarin, L. Arnaud, J. R. Huntzinger, J. L. Vialle, M. Broyer, B. Palpant, O. Boisron, P. Mélinon, Phys. Rev. B **70**, 165409 (2004)
[7] M. Nogami et al, J Mater Res **10**, 2648 (1995)
[8]D. Kundu, et al, J. Am. Ceram. Soc.**77**, 1110 (1994)
[9] G. De, et al, J. Appl. Phys. **80**, 6734 (1996)
[10] J. Manzanares-Martinez et al, Thin Solid Films **365**, 30 (2000)
[11] J. F. Perez et al, J. Phys. Chem. Solids **60**, 1729 (1999)
[13]T. Lutz, et al, J. Alloys Compd. **262-263**, 438 (1997)
[14] R. Serna et al, Phys Rev B **66**, 205402 (2002).
[15] J. Gonzalo et al, Appl. Surf. Sci.**154-155**, 449 (2000)
[16] C. R. Iordanescu, D. Tenciu, I. D. Feraru, A. Kiss, M. Bercu, D. Savastru, R. Notonier, C. E. A. Grigorescu Digest Journal of Nanomaterials and Biostructures, **6**(2), 863 (2011)
[17] S. Cava, S.M. Tebcherani, I.A. Souza, S.A. Pianaro, C.A. Paskocimas, E. Longob, J.A. Varela, Materials Chemistry and Physics **103**, 394, (2007)
[18] J.-A. Xu, E. Huang, J.-F. Lin, and L. Y. Xu, Handbook of Raman Spectra, Am.Mineral., **80**, 1157 (1995).
[19] Valeri P. Tolstoy, Irina V. Chernyshova, Valeri A. Skrishevsky, Handbook of infrared spectroscopy of ultrathin films, Wiley –Interscience, John Wiley & Sons, Inc., 227 (2003)