[Ide@s CONCYTEG 7 (87), Septiembre, 2012]
ISSN: 2007-2716

Como citar: Ramírez-Meneses E., Cervantes-Sodi F., Hernández-Pérez M.A., Vázquez-Olavarrieta J.L., Aguilar-Morales A., Martínez-Guerrero R. (2012), "Low temperature one-step synthesis of molybdenum oxide films", *Ide@s CONCYTEG*, 7 (87), 1083-1090pp.

Low temperature one-step synthesis of molybdenum oxide films.

Ramírez-Meneses E. [1], **Cervantes-Sodi F.**[2], **Hernández-Pérez M.A.** [3] **Vázquez-Olavarrieta J.L.**[1], **Aguilar-Morales A.**[1], **Martínez-Guerrero R.**[2]

Resumen

Entre los metales de transición, el óxido de molibdeno (MoO_3) exhibe propiedades estructurales, químicas, eléctricas y ópticas interesantes. Películas de MoO_3 son materiales *switchables*, teniendo aplicaciones en dispositivos electrocrómicos y ventanas inteligentes. En este artículo, películas de MoO_3 han sido obtenido por deposición química de vapores en sustratos de cuarzo a 350, 425 y 550°C utilizando acetilacetonato de dióxido de molibdeno ($MoO_2(acac)_2$, acac = CH_2COCH_2COCH) como precursor y O_2 como gas reactivo y de transporte. Las películas depositadas fueron caracterizadas por difracción de rayos X y microscopía de fuerza atómica, mostrando que a la baja temperatura de 425°C se deposita una película delgada de α-MoO_3 policristalino.

Palabras películas de molibdeno, deposición química de vapores, acetilacetonato de dióxido de molibdeno.

Abstract

Among the transition metal oxides, molybdenum oxide (MoO_3) exhibits interesting structural, chemical, electrical and optical properties. MoO_3 films are switchable materials having applications in electrochromic devices and smart windows. MoO_3 were obtained by atmospheric pressure chemical vapor deposition on quartz substrates at 350, 425 and 550 °C using molybdenum dioxide acetylacetonate ($MoO_2(acac)_2$, acac = CH_2COCH_2COCH) as precursor and O_2 as transport and reactive gas. Deposited films were characterized by X-ray Diffraction and Scanning Probe Microscope finding that in this single step process polycrystalline α-MoO_3 films were accomplished at low temperature (425 °C).

Keywords: molybdenum oxide films, chemical vapor deposition, molybdenum dioxide acetylacetonate.

---

[1] Departamento de Ingeniería y Ciencias Químicas, Universidad Iberoamericana, Prolongación Paseo de la Reforma 880, Lomas de Santa Fe, 01219, D.F., México.

[2] Departamento de Física y Matemáticas, Universidad Iberoamericana, Prolongación Paseo de la Reforma 880 Lomas de Santa Fe, 01219, D.F., México

[3] Departamento de Ingeniería en Metalurgia y Materiales. ESIQIE, Instituto Politécnico Nacional, UPALM Zacatenco, 07738, D.F., Mexico

* Corresponding autor: esther.ramirez@ibero.mx

Introduction

Transition metal oxides have gain attention in the recent years due to their technological applications as catalysts (Gellings & Bouwmeester, 1992), cathodic material in lithium batteries (García, Farcya, Pereira-Ramos, Perichon & Baffier, 1995), in gas sensors (Ferroni, Guidi, Martinelli, Nelli, Sacerdoti & Sberveglieri, 1997, Rossinyol et al., 2005, Rahmani, 2010) and in electronic and electrochromic devices (Granqvist, 2000, Brezesinski, Wang, Tolbert, Dunn, 2010). Numerous techniques are currently used for the deposition of nanostructured MoO_3 thin films, such as thermal evaporation (Siciliano, Tepore, Filippo, Micocci & Tepore, 2009, Kalantar-zadeh 2010), sputtering (Mohamed & Venkataraj, 2007), electrodeposition (Patil, Uplan & Patil, 2008, Zach, Ng, Penner, 2000), sol-gel (Shih-Yuan, Chih-Ming, Kuo-Sheng, Ying-Chung & Chan-Chih, 2010), flash evaporation (Julien, El-Farh, Balkanski, Hussain & Nazri, 1993), pulsed laser deposition (Bhosle, Tiwari & Narayan, 2005, Al-Kuhaili, Durrani & Bakhtiari, 2010), evaporation-induced self-assembly (Brezesinski, Wang, Tolbert, Dunn, 2010, Brezesinski, Groenewolt, Pinna, Amenitsch, Antonietti & Smarsly, 2006) and chemical vapor deposition (CVD) (Ivanova, Surtchev & Gesheva, 2002, Gesheva, Surtchev & Ivanova, 2003, Martínez Guerrero, Vargas García, Santes & Gómez, 2007). Among these techniques, CVD is a widely used one due to its versatility for the production atlow processing temperatures, of single layer, multilayer, doped, nanostructured, and functionally graded coating materials, with well controlled dimensions and unique structures (Ivanova, Surtchev & Gesheva, 2002, Gesheva, Surtchev & Ivanova, 2003, Martínez Guerrero, Vargas García, Santes & Gómez, 2007, Choy, 2003). In this context, a two-step process has been used for the synthesis of polycrystalline MoO_3 films by atmospheric CVD using carbonyl precursors (e.g. $Mo(CO)_6$) (Bhosle et al., 2005, Ivanova et al., 2002). Amorphous and crystalline molybdenum oxide coatings from $Mo(CO)_6$ have also been obtained using low pressure CVD (Gesheva et al. 2003). A more advantageous single step process was developed by metal-organic CVD using molybdenum dioxide acetylacetonate ($MoO_2(acac)_2$, acac = CH_2COCH_2COCH) precursor (Martínez Guerrero et al., 2007), obtaining crystalline α-MoO_3 at 560 °C with nitrogen as carrying gas in an horizontal hot-wall reactor (Martínez Guerrero et al. 2007). In this paper, we report the deposition of α-MoO_3 thin films with a single step process using oxygen as carrying and reactive gas and more importantly, at the low temperature of 425 °C. Our CVD is performed at atmospheric pressure with three different temperatures and under two flow rates. Experimental results revealed that the temperature deposition and the gas flow rate determine the surface morphology of the obtained films as observed by a Nanoscope Scanning Probe Microscope (SPM). The advantage over previous works (Bhosle et al., 2005, Ivanova et al., 2002, Gesheva et al., 2003, Martínez Guerrero et al., 2007) resides on the reduction of processing temperature by ~140 °C and the simplicity of obtaining the films by a one-step CVD process without the need of a post-deposition thermal treatment (Ivanova et al., 2002, Gesheva et al., 2003).

Experimental

Synthesis of the precursor

$MoO_2(acac)_2$; precursor was synthesized as previously described (Martínez Guerrero et al., 2007). Molybdenum was synthesized from MoO_3 powder (Aldrich, 99.99%) and acetylacetone (Fluka, 99.5%) used as received. 50 mL of acetylacetone were added to 10 g of MoO3 powder to react under reflux for 30 h. The resulting solution was added to 250 mL of toluene at room temperature for the precipitation of unreacted MoO_3, which was separated by filtering. The solution was heated under nitrogen atmosphere leading to the evaporation of toluene and the precipitation of $MoO_2(acac)_2$. The obtained product was analyzed by infrared spectroscopy analysis, shown in Fig. 1, to confirm the formation of $MoO_2(acac)_2$.

Films deposition

Deposition of the films was done at atmospheric pressure in a tubular hot wall reactor. $MoO_2(acac)_2$ precursor was placed in a glass crucible inside the chamber at 180-220 °C. Oxygen (INFRA extra dry, 99.5%) was used as transport and reactive gas at flow rates of 200 and 300 sccm. Quartz substrates, previously sonicated in deionized water and ethanol and rinsed in acetone, were positioned in a downflow direction from the precursor. The experiment was developed at three substrate temperatures: 350, 425 and 550 °C. After 30 minutes of deposition the reactor was cooled down to room temperature and the substrates extracted for characterization.

Analysis of the films

Fourier transform-infrared spectroscopy (FT-IR) was carried out with a Spectrum One Perkin Elmer instrument; the precursor sample was measured in a KBr pellet. X-ray Diffraction (XRD) analysis was carried out on a Bruker D8 Focus diffractometer with Cu-kα radiation. A Nanoscope Scanning Probe Microscope (SPM) (Digital Instruments) was used for surface and profile characterization.

Results and discussion

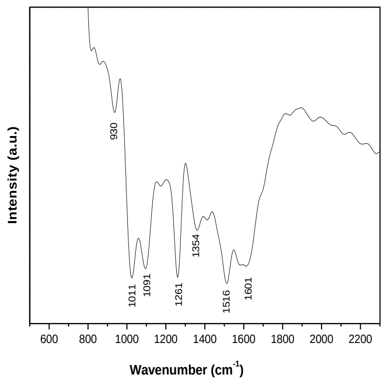

Fig1.FT Y-R spectrum. As synthesized $MoO_2(acac)_2$ precursor’s FTIR (KBr pellet) with bands corresponding to the Mo=O symmetric vibration (930 cm^{-1}) and asymmetric stretching of the C-O-C bonds (1200-1000 cm^{-1}).

Infrared spectroscopy, shown in Fig. 1, was performed in order to verify the formation of the $MoO_2(acac)_2$ precursor. The bands located at 930 cm-1 corresponds to Mo=O symmetric vibration. The set of bands around 1200-1000 cm-1 are assigned to the asymmetric stretching of the C-O-C bonds (Socrates, 2001), confirming the bonds in $MoO_2(acac)_2$.

Fig. 2 shows SPM surface micrographs of the deposited films at a substrate temperature of 350 °C and under two different flow rates. The morphology of the deposited film is highly dependent on the O_2 flow rate; at 200 sccm the film is formed by irregular particles with a broad distribution of sizes dispersed on the substrate. In contrast, the deposition at 300 sccm generates a highly homogeneous distribution of particles with an averagediameter in the order of 100 nm. X-ray analysis of both samples corresponds to amorphous structure and/or very thin films (not shown).

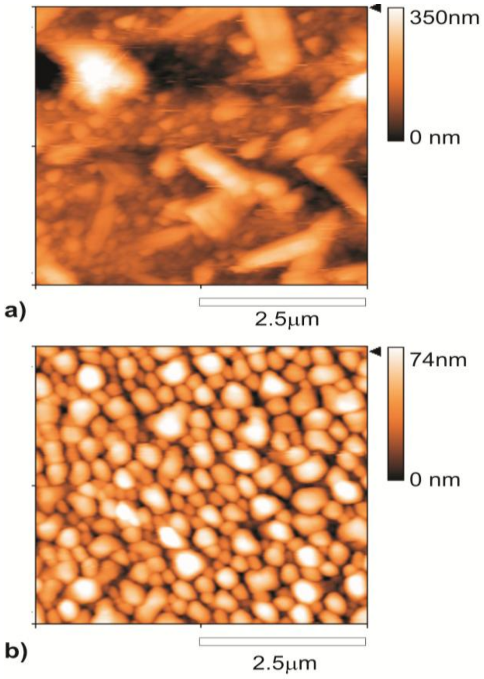

Fig. 2. SPM surface micrographs of the films MoO_3 films, deposited at the substrate temperature of 350 °C using a gas flow rate of O_2 of (a) 200 and (b) 300 sccm, respectively.

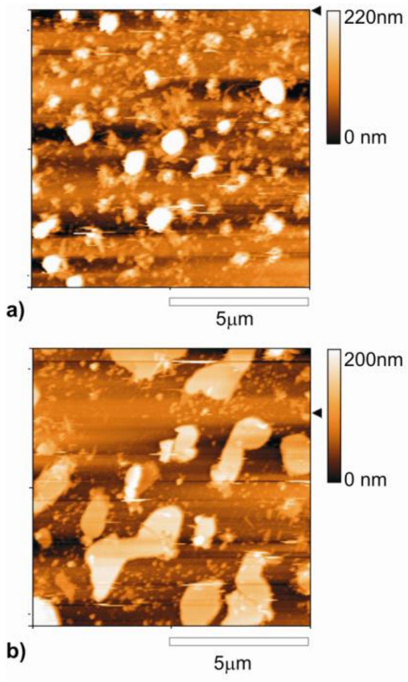

Fig. 3. XRD patterns of MoO_3 films, deposited at the substrate temperature of 425 °C using a gas flow rate of O_2 of (a) 200 and (b) 300 sccm.

XRD patterns in Fig. 3 correspond to the samples deposited at the substrate at a temperature of 425º C. In contrast to the amorphous deposition at 350 °C, the samples deposited at 425 °C present the typical XRD pattern of polycrystalline orthorhombic α-MoO_3 (JCPDS reference card No. 05-0508) with preferential growth in the 010 direction (Brezesinski et al., 2006, 2010). In addition to the three dominant planes of MoO_3; (020), (040) and (060) at (13.1, 26.0, and 39.3°, respectively), minor signals corresponding to (110) and (130) planes were also observed. These XRD patterns are in agreement with those reported by Brezesinski et al, (2006, 2010) for iso-oriented α-MoO_3 obtained by evaporation-induced self-assembly process at 400 and 450 °C (Al-Kuhaili et al., 2010, Socrates, 2001).

Fig. 4 shows the SPM images of the samples obtained at 425 °C using a gas flow rate of O_2 of 200 and 300 sccm. Dispersed particles relatively homogeneous in shape and size (~1 μm) are observed. In contrast, the deposition with 300 sccm of O_2 presents an irregular surface covering, consisting of non-uniform MoO_3 islands.

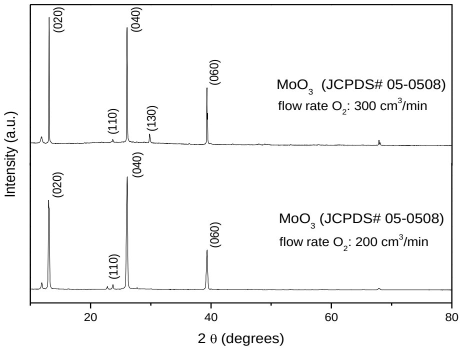

Fig. 4. SPM surface micrographs of CVD MoO_3 films, deposited at the substrate temperature of 425 °C using a gas flow rate of O_2 of (a) 200 and (b) 300 sccm.

Finally, the deposition of films at 550 °C (substrate temperature) using a gas flow rate of O_2 of 200 sccm were carried out. At this temperature, polycrystalline films were expected (Brezesinski et al., 2006, 2010). However, the XRD patterns (not shown) reveals the amorphous-semicrystalline nature of the film as for the case of the deposition at 350 °C.

Fig. 5(a) reveals that the amorphous-semicrystalline nature of the film is provoked by a dense surface, covered by some well-defined, randomly-dispersed small crystals (1 – 2.5 μm).

When gas flow rate of O_2 increases, irregular particles, in shape and size (0.5 – 1 μm), are obtained on a non-homogeneous distribution (Fig. 5b).

The best experimental conditions in structural terms, size homogeneity and dispersion of particles, are the films obtained at substrate temperature of 425 °C under 200 sccm as confirmed by X-ray diffraction.

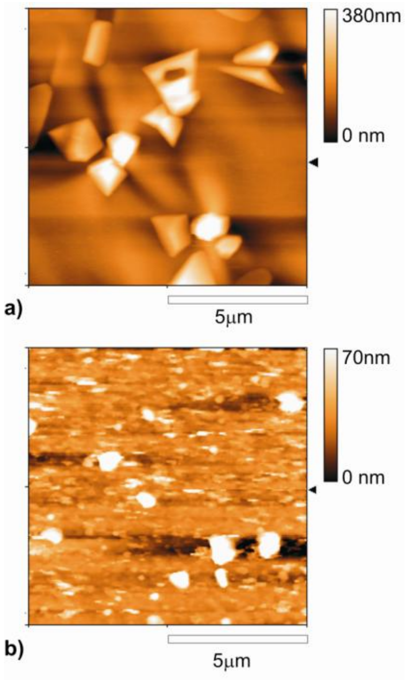

Fig. 5. SPM surface micrographs of the MoO_3 films, deposited at the substrate temperature of 550 °C using a gas flow rate of O_2 of (a) 200 sccm and (b) 300 sccm.

From Fig. 2,3&5 we notice that when temperature increases, non-uniform coating thickness occur, this seems to indicate that the deposition is performed in the mass transport controlled regime that take place in thermal CVD and other types of CVD systems such as the metallorganic assisted CVD due to the depletion of precursor (Choy, 2003). This situation is clearly observed when a gas flow rate of O_2 of 300 sccm is used.

Conclusions

Molybdenum trioxide thin films were successfully deposited in a one-step deposition process at 425 °C using a gas flow rate of O_2 of 200 and 300 sccm. It was seen that the crystallization process begins with the formation of α-MoO_3 phase at 425 °C. However, XRD diffraction analysis, showed amorphous nature of the films at the substrate temperature of 350 °C (not showed) and semicrystalline nature at 550 °C. When temperature changes from 350 to 550 °C and gas flow rate from 200 to 300 sccm, an increase on the grain size was observed. The use of O_2 instead of N_2, as reported by Martínez-Guerrero et al. (2007), allows a considerable drop in deposition temperatures in atmospheric pressure CVD.

Acknowledgements

This work was supported by UIA, Dirección de Investigación projects No. 054 and 057, FISMAT programs 00L3 & 0033, and Research Project CONACyT 59921. The authors would like to thank Samuel Macias Bravo and Miguel Sanchez Rayas for their technical support.

References

Al-Kuhaili, M.F., Durrani, S.M.A., Bakhtiari, I.A. (2010). "Pulsed laser deposition of molybdenum oxide thin films". *Appl. Phys. A. Mat. Sci. & Procc.*, 98, 609-615.

Bhosle, V., Tiwari, A., Narayan, J. (2005). "Epitaxial growth and properties of MoO_x ($2<x<2.75$) films". *J. Appl. Phys.*, 97, 083539.

Brezesinski, T., Groenewolt, M., Pinna, N., Amenitsch, H., Antonietti, M., Smarsly, B. (2006). "Surfactant-Mediated Generation of Iso-Oriented Dense and Mesoporous Crystalline Metal-Oxide Layers". *Adv. Mater.*, 18, 1827-1831.

Brezesinski, T., Wang, J., Tolbert, S.H., Dunn, B. (2010). "Ordered mesoporous α-MoO_3 with iso-oriented nanocrystalline walls for thin-film pseudocapacitors". Nature Mater., 9, 146-151.

Choy, K.L. (2003). "Chemical vapour deposition of coatings". *Prog. in Mater. Sci.*, 48, 57-170.

Ferroni, M., Guidi, V., Martinelli, G., Nelli, P., Sacerdoti, M., Sberveglieri, G. (1997). "Characterization of Molybdenum Oxide Sputtered Thin Film as a Gas Sensor". *Thin Solid Films*, 307, 148-151.

García, B., Farcya, J., Pereira-Ramos, J.P., Perichon, J., Baffier, N. (1995). "Low-temperature cobalt oxide as rechargeable cathodic material for lithium batteries". *J. Power Sources*, 54, 373-377.

Gellings, P.J., Bouwmeester, H.J.M. (1992). "Ion and mixed conducting oxides as catalysts". *Catal. Today*, 12, 1-101.

Gesheva, K., Surtchev, M., Ivanova, T. (2003). "Optical properties of chemical vapor deposited thin films of molybdenum and tungsten based metal oxides". *Solar Energy Mater. & Solar Cells*, 76, 563.

Granqvist, C.G. (2000). "Electrochromic tungsten oxide films: Review of progress 1993–1998". *Solar Energy Mater. & Solar Cells*, 60, 201-262.

Ivanova, T., Surtchev, M., Gesheva, K. (2002). "Investigation of CVD molybdenum oxide films". *Mat. Lett.*, 53, 250-257.

Julien, C., El-Farh, L., Balkanski, M., Hussain, O.M., Nazri, G.A. (1993). "The growth and electrochemical properties of metal-oxide thin films: lithium intercalation". *Appl. Surf. Sci.*, 65-66, 325-330.

Kalantar-zadeh, K., Tang, J., Wang, M., Wang, K.L., Shailos, A., Galatsis, K., Kojima, R., Strong, V., Lech, A., Wlodarskib, W., Kaner, R.B. (2010). "Synthesis of nanometre-thick MoO_3 sheets". *Nanoscale*, 2, 429-433.

Patil, R.S., Uplan, M.D., Patil, P.S. (2008). "Electrosynthesis of Electrochromic Molybdenum Oxide Thin Films with Rod-Like Features". *Int. J. Electrochem. Sci.* 3, 259-265.

Martínez Guerrero, R., Vargas García, J.R., Santes, V., Gómez, E. (2007). "Preparation of molybdenum oxide thin films by MOCVD". *J. Alloys and Comp.*, 434, 701-703.

Mohamed, S.H., Venkataraj, S. (2007). "Thermal stability of amorphous molybdenum trioxide films prepared at different oxygen partial pressures by reactive DC magnetron sputtering". *Vacuum*, 81, 636-643.

Rahmani, M. (2010). “Gas sensing properties of thermally evaporated lamellar MoO_3”. *Sensors and Actuators B Chemical*, 145, 13-19.

Rossinyol, E., Arbiol, J., Peiro, F., Cornet, A., Morante, J.R., Tian, B., Bo, T., Zhao, D. (2005). “Nanostructured metal oxides synthesized by hard template method for gas sensing applications”. *Sensors and Actuators B Chemical*, 109, 57-63.

Shih-Yuan, L., Chih-Ming, W., Kuo-Sheng, K., Ying-Chung, C., Chan-Chih, L. (2010). “Electrochromic properties of MoO_3 thin films derived by a sol-gel process”. *J. Sol-Gel Sci. Technol.*, 53, 51-58.

Siciliano, T., Tepore, A., Filippo, E., Micocci, G., Tepore, M. (2009). “Characteristics of molybdenum trioxide nanobelts prepared by thermal evaporation technique”. *Mater. Chem. and Phys.*, 114, 687-691.

Socrates, G. (2001) *Infrared and Raman Characteristic Group Frequencies Tables and Charts*, 3rd ed., England, John Wiley & Sons.

Zach, M.P., Ng, K.H., Penner, R.M. (2000). “Molybdenum Nanowires by Electrodeposition”. *Science*, 290, 2120-2123.