Revista Mexicana de Física S **58** (2) 253–257 DICIEMBRE 2012

Preparation and magnetic behavior of molybdenum oxide and neodymium thin films grown by spray pyrolysis technique

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Recibido el 25 de junio de 2010; aceptado el 30 de noviembre de 2010

In this work we analyze the morphology, crystallographic and magnetic behaviors of molybdenum oxides doped with Nd thin films grown onto glass slide, through spray pyrolysis technique. The films were subjected to thermal treatments, after the fabrication, in oxygen from 2 to 20 hours. These were structurally analyzed by X-ray Diffraction (XRD), its chemical composition was determined by Energy Dispersive X-ray Analysis (EDX), and morphological evolution was evaluated through Scanning Electron Microscopy (SEM.The magnetic response was studied by DC magnetic susceptibility The XRD results show that the films obtained in different dissolution volumes and substrate temperatures of 300 °C present triclinic phases of molybdenum trioxide, deficient of oxygen (Mo_9O_{26}, $Mo_{18}O_{52}$). The films with thermal treatment have deficient oxygen phases and stoichiometric phases of MoO_3. SEM results show that morphology of films changes with thermal treatment; the EDX study indicates that the films incorporate the Nd to the crystalline structure of the molybdenum oxide. Finally, films with 5% of Nd showed a paramagnetic response.

Keywords: Spray pyrolysis; molybdenum oxide; morphology; stoichiometry; magnetic susceptibility.

En el presente trabajo se analizan la morfología, la cristalografía y el comportamiento magnético de películas delgadas de óxidos de molibdeno dopados con Nd, crecidos en portaobjetos de vidrio mediante la técnica de rocío pirolítico. Las películas fueron sometidas a tratamientos térmicos, después de la fabricación, en oxígeno durante 2 a 20 horas. Las muestras fueron analizadas estructuralmente mediante difracción de rayos X (DRX), su composición química se determinó mediante análisis de espectroscopia de dispersión de energía de rayos X (EDX), la evolución morfológica se evaluó mediante microscopía electrónica de barrido (SEM). La respuesta magnética se estudió mediante susceptibilidad magnética DC. Los resultados de DRX muestran que las películas obtenidas en diferentes volúmenes de disolución y temperaturas de sustrato de 300 ° C presenten fases triclínicas de trióxido de molibdeno, deficiencia en oxígeno (Mo9O26, Mo18O52). Las películas con tratamiento térmico tienen fases deficientes en oxígeno y fases estequiométricas de MoO3. Los resultados de SEM muestran que la morfología de las películas cambia con el tratamiento térmico, el estudio de EDX indica que las películas incorporarel Nd a la estructura cristalina del óxido de molibdeno. Por último, las películas con un 5% de Nd mostraron una respuesta paramagnética.

Descriptores: Rocío Pirolitico; oxido de molibdeno; morfología; estequiometricas; susceptibilidad magnética.

PACS: 75.70.AK; 75.20.CK

1. Introduction

Molybdenum trioxide is a transition material with optical properties such as photochromism, which allows applications such as displays manufacture, optical smart windows, and high-density memory devices [1, 2, 3, 4]. In addition, the incorporation of ions as Li to the crystalline structure of the molybdenum oxide, has allowed the manufacture of batteries in which the molybdenum oxide acts as a cathode [5, 6, 7] and in recent years Jinshu Wang *et al.* [8] studied the emission property of new kinds of rare earth oxide-molybdenum cermet cathode made by powder metallurgy. Wang showed that adding either single rare-earth oxides La_2O_3, Y_2O_3, and Gd_2O_3 or a mixture of these rare-earth oxides into molybdenum oxide can improve the secondary emission coefficient of the cathode. Additionally, some works have stated that MoO_3improves the sensitivity for detection of gases like NH_3 when coated with Ti thin films [9] and CO when doped with SnO_2 nano-particles [10].

The previous applications can be explained from crystalline structures in which MoO_3 grows; α-MoO_3 and β-MoO_3, the former is orthorhombic, formed by MoO_6octahedral chains that share edges with two similar chains and form the stoichiometric MoO_3. These layers are stacked in a staggered arrangement and are held together by weak Van der Waals forces.The β-MoO_3 has a Perovskite-type (ReO_3) monocyclic structure and can be seen as an infinite thin octahedral chain of $MoO_6$with shared edges, each with a Mo atom surrounded by six equidistant oxygen atoms. These octahedra are extended tunnels that can be used as conduits and intercalation sites for mobile ions. Taking advantage of the crystal structure of the molybdenum oxide, this work has grown thin films of molybdenum oxides doped with Nd by spray pyrolysis method to produce optically and magnetic active devices.

2. Experimental

Thin films of molybdenum and neodymium oxide, $Mo_{1-x}Nd_xO_3$, were prepared from ammonium molybdate tetrahydrate ($(NH_3)_6Mo_7O_{24..}4H_2O$ Merck analytical re-

active) and neodymium nitrate via spray pyrolysis method. Dissolutions of molybdate ammonium and neodymium nitrate in water were atomized on glass substrates between 300°C and 400°C; air at 2.0 atm pressure (2.026×10^5 Pa) was used as gas transport. The thickness of the films was varied by atomizing volumes of dissolution between 5.0 and 20.0 mL.

Neodymium nitrate was prepared by adding nitric acid dissolution on oxide Nd_2O_3 neodymium (Aldrich) under continuous magnetic stirring. The cation concentration Mo^{6+} and Nd^{3+} in the atomized dissolution is of 0.1 M (Mo^{6+} 0.095 M and Nd^{3+} 0.05M). The heat treatments were done in a furnace with heating slope of 5°C/min until obtaining 500°C and with oxygen flows of 4 mL/min.

The glass substrates of $2.58 \times 3.00 \times 1.0$ cm^3 were previously cleaned with detergent, sulfochromic dissolution, distilled water, and acetone and then warmed in a furnace to 500°C, removed to apply approximately 0.5 mL of dissolution equivalent aerosol, and again introduced into the furnace for 2 min and the procedure was repeated until obtaining the desired volume.

The X-ray diffraction (XRD) patterns were taken with Panalytical X-pert Pro MPD equipment working at 45 kV and 40 mA, emitting in line Kα of Cu, in steps of 0.2 degrees and exposure times of 20 seconds. Studies of the morphology and chemical composition of the films were done with an electron microscope, Quanta FEI 200, working with 20kV. The analyses of the X-ray diffraction patterns were made via DRXWIN software. Measurements of DC magnetic susceptibility as a function of temperature were performed by using a MPMS Quantum Design SQUID.

3. Results and discussion

The XRD patterns presented in Fig. 1 show the results obtained in the growth of molybdenum oxide thin films, as a function of the volume of dissolution of ammonium molybdate tetra-hydrate ($(NH_3)_6Mo_7O_{24}.4H_2O$) and neodymium nitrate with an atomic percentage of 5% of Nd, the substrate temperature was set at 300°C. The XRD patterns allowed finding that the crystallographic behavior of the films is very similar among them. Basically, only the triclinic phases (Mo_9O_{26}, $Mo_{18}O_{52}$) appear; they have very low crystalline structure and display oxygen deficiency with respect to the MoO_3 Stoichiometric phase.

To analyze the incorporation of oxygen on the crystalline lattice of the molybdenum oxide thin films doped with neodymium, thermal treatments were done for 2 and 20 h in controlled oxygen atmospheres and temperature at 500 °C to samples prepared atomizing 10 mLof dissolution of ($(NH_3)_6Mo_7O_{24}.4H_2O$) and 5% of the Nd A sample of molybdenum oxide without neodymium was introduced as a control of the process; the results of these treatments are presented in Fig. 2a and 2b, respectively. Figure 2a allowed determining that Nd-doped samples treated during 2 h periods display crystallographic behavior similar to the films grown without Nd, since both films showed the planes (020), (040), (110) and the (220) plane of the orthorhombic phase of the MoO_3 (PDF 350609).

On the other hand, the two films present the planes (240), (520), (620) (910), and (461) with low intensities with re-

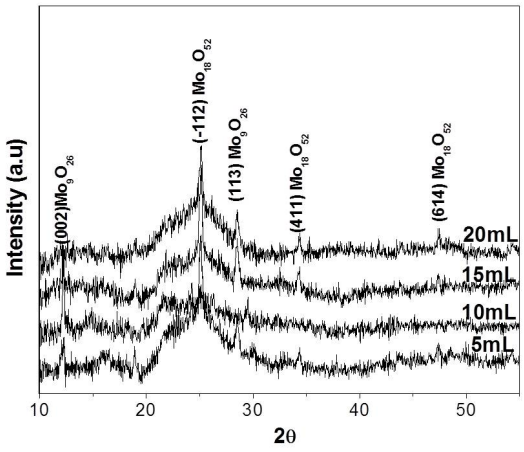

FIGURE 1. XRD pattern of the Molybdenum oxides doped as function of the volume dissolution.

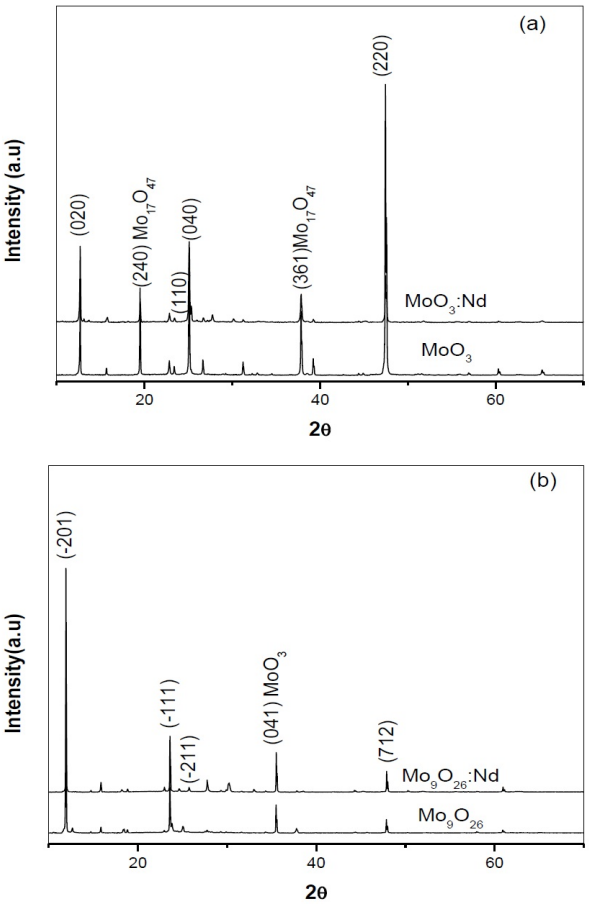

FIGURE 2. XRD patterns of the Molybdenum oxides doped with Nd a)thermal treatment 2hs in oxygen and b)thermal treatment 20hs in oxygen.

spect to the former information, associated to the orthorhombic phase of $Mo_{17}O_{47}$ (PDF710566). In the XRD pattern associated to the Nd-doped film, the presence of planes associated to molybdates or neodymium oxides were not demonstrated.

The previous results indicate that the molybdenum oxide films without being doped have a stable crystallographic phase; Stoichiometric composition has grown in texture along the (220) plane. The films, to which Nd was added, have a less textured growth and, most likely, have incorporated Nd onto the crystalline lattice of the molybdenum oxides present in the film.

The XRD pattern of the films warmed up in oxygen atmospheres for 20 h (Fig. 2a), allowed determining that the orthorhombic phase of the undoped molybdenum oxide film, with previous heat treatment, decreased substantially and in its place appeared the monoclinic Mo_9O_{26} phase (PDF 050441) growth with a high degree of texture throughout the plane (-201). Other planes associated to the same phase are (-111), (-211), and (712); other planes with lower intensities than the one appearing in the XRD pattern belong to the MoO_3 phase, but the most relevant plane is (041). The film that grew with the neodymium oxide (Fig. 3b) reproduces the crystallographic behavior of the film without Nd, except for values of intensity, since the intensity of the plane (-201) is 1.5 times with respect to the same plane of the Nd-doped film. In this case, planes belonging to Nd oxides or molybdates were not determined.

The results obtained suggest that thermally treated films, during 20 h, present transition phase with respect to those treated for 2 h. The orthorhombic phase is transformed into monoclinic and there is no efficient incorporation of oxygen to the crystalline lattice; this may due to oxygen diffusion to the surface of the film, which causes the growth of nonstoichiometric molybdenum oxide phases. The absence of Nd oxide suggests the incorporation of the Nd to the crystallographic lattice of molybdenum oxides grown in the films.

Figure 3a shows the morphology of a molybdenum oxide film without Nd, the film is formed by slabs with average area of approximately 16 μm^2; this sample was thermally treated for approximately 20 h in oxygen atmosphere. After the thermal treatment, the film showed morphological changes to extended structures superposed over a granulated surface (Fig. 3b).

Moreover, the molybdenum oxide film doped with Nd presents a coralline morphology (Fig. 3c). This film treated with the same conditions as the film shown in Fig. 3b presents a morphology formed by slabs grown in transverse direction to the substrate (Fig. 3d). Magnification on one of the slabs (Fig. 3e) reveals that the slabs are formed by hemispherical granular structures. The films heated for 2 h in oxygen (Fig. 3f) showed morphology formed by needles, grown in different directions, approximately 15 μm long and sheets that retain the structure the molybdenum oxide without being doped. These results indicate that thermal treatments and the incorporation of Nd have strong influence on the morphology

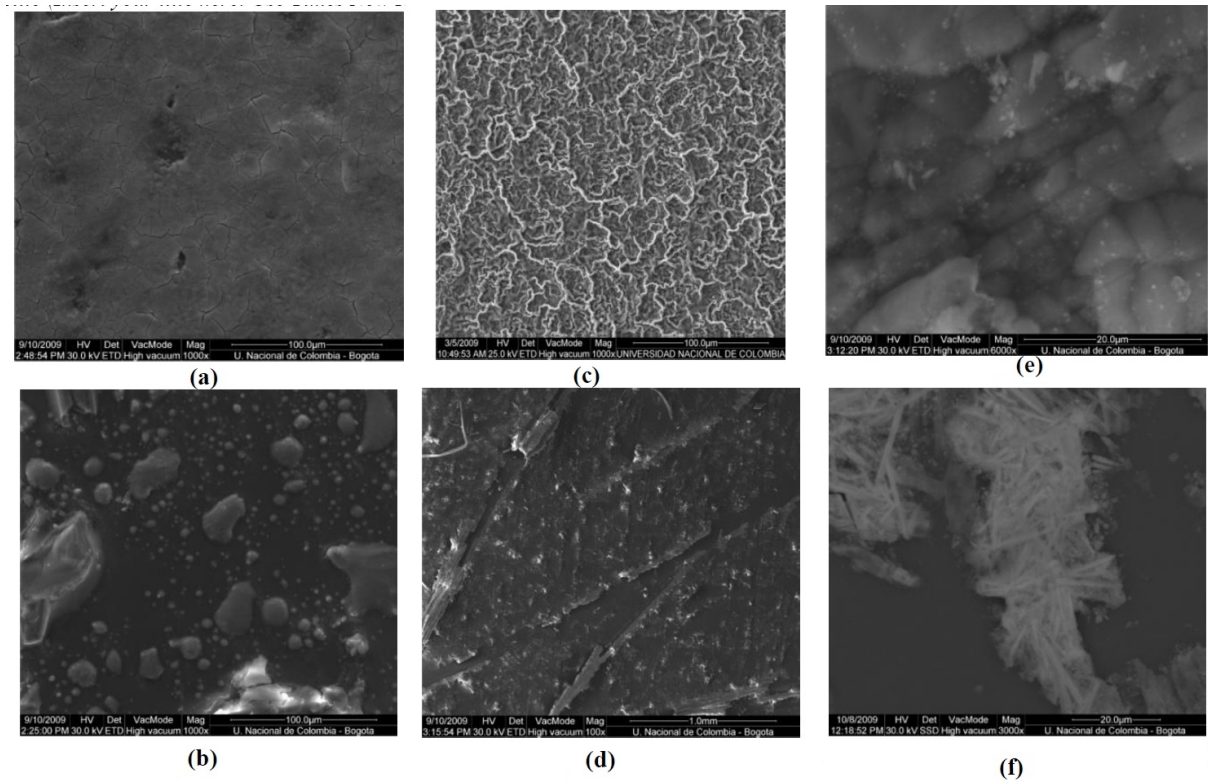

FIGURE 3. Molybdenum oxide films a) film without Nd ;b)film without Nd with thermal treatment 20hs in oxygen; c)film doped without thermal treatment; d)film doped with thermal treatment 20hs in oxygen and e) amplification of the granular zone of the film c and f) film doped with thermal treatment 2hs in oxygen.

of the films, because they transform from simple structures to complex structures.

EDX results are shown in Table 1. Basically it shows the composition and relationship of %at of Mo and % at Nd of the films fabricated at different experimental conditions.

As from the compounds used in the preparation of the films, and taking into account the electro- neutrality, we found that its chemical formula is $Mo_{0.95}Nd_{0.05}O_{2.925}$ with a theoretical elemental composition as shown in Table 1. Moreover, by making the relationship between the percentage of atoms of Mo/ Nd and taking into account XRD results was established that most likely is that in all cases Nd, was incorporated to the crystallographic lattice of the MoO_3 and the decreasing of the Mo/Nd relation when increase the time of heat treatment may indicate sublimation of MoO_3. However, the way the Nd replaces Mo can not be established with the analytical techniques used in this study.

Figure 4 exemplifies the DC susceptibility response of thin film with 5% of Nd and without heat treatment as a function of temperature, measured in a field cooling procedure. As observed in picture, the material evidences a paramagnetic-like behavior. The Curie Weiss formalism $\chi = \chi_0 + C/T$, where χ_o represents the susceptibility independent of temperature and C is the Curie Weiss constant was applied to adjust experimental data to the paramagnetic characteristic. The line in Fig. 4 shows an excellent adjusts of susceptibility with the Curie Weiss feature. In order to determine the effective magnetic moment of material, from fitting we obtain $C = 1.185$ emu.K/mol and $\chi_o = -3.64 \times 10^{-3}$ emu/mol. A magnetic moment $\mu = 3.075\mu_B$ was calculated from $C = N\mu^2/k_B$, where N is the Avogadro number and k_B represents the Boltzmann constant. We notice that the effective magnetic moment of material is close to the known value $P_{eff} = 3.62$ of an isolated Nd^{+3} calculated by the Hund's rule, where $P_{eff} = g\sqrt{J(J+1)}$ [11]. This result is expected because contribution of Mo^{+6} cations to magnetic susceptibility is significantly shorter (1.2 %) when compared with Nd^{+3} ions [12].

TABLE I. Concentration average of elements (at%) in films of molybdenum oxide doped with Nd.

Film	Mo	O	Nd	Mo/Nd
MoO_3:Nd without heat treatment	25.08	73.90	1.52	16.50
MoO_3:Nd with 2-h heat treatment	32.86	65.12	2.02	16.27
MoO_3:Nd with 20-h heat treatment	28.50	69.18	2.32	12.28
Theorical composition	24.20	74.52	1.27	19.06

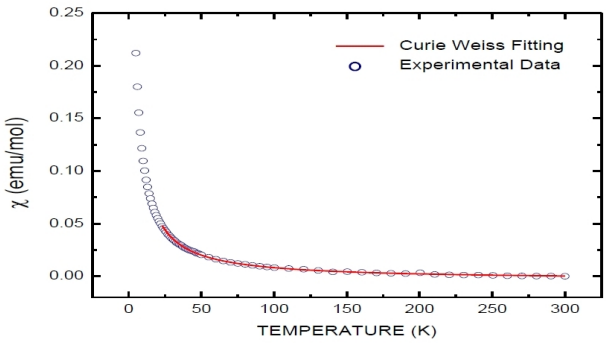

FIGURE 4. DC magnetic susceptibility as a function of temperature on the application of H=10^{-2} T. Symbol represents experimental data and line is the fitting result.

4. Conclusions

In this work, we managed to grow films of various oxides of molybdenum-doped with Nd by the spray pyrolysis method under different thermodynamic conditions, and assessed their morphological, crystallographic and magnetic behavior. Basically, it has been established that moderate thermal treatments produce films with textured orthorhombic structures, predominantly of MoO_3, and prolonged thermal treatment to monoclinic structures changes with oxygen-deficient phases the molybdenum oxide. Concurrently, it has been established that molybdenum oxide films incorporate the Nd crystallographic lattice and in some cases have magnetic response. The importance of this work is have presented by the first time results of molybdenum oxide films doped with Nd, which involves new possibilities in the development of magnetic and optically active materials more economic and less harmful from an environmental point of view.

Acknowledgements

The authors gratefully acknowledge the financial support from the Research Division of "Universidad Nacional de Colombia (DIB)". And Professor Julio Evelio Rodriguez by the colaboration with thermal treatments.

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