INVESTIGACIÓN REVISTA MEXICANA DE FÍSICA **52** (5) 409–412 OCTUBRE 2006

Cobalt nitride films produced by reactive pulsed laser deposition

W. De La Cruz, O. Contreras, G. Soto, and E. Perez-Tijerina*,**
Centro de Ciencias de la Materia Condensada, UNAM,
Apartado Postal 2681, 22800 Ensenada B.C., México.
** Laboratorio de Nanociencias y Nanotecnología, FCFM-UANL,*
Av. Universidad s/n, Cd. Universitaria. San Nicolas de los Garza, N.L., México.

Recibido el 27 de febrero de 2006; aceptado el 26 de septiembre de 2006

The nitrides of magnetic metal are becoming important due to their potential technological applications. In this work cobalt nitride thin films are deposited by reactive pulsed laser deposition (nitrogen environments) on silicon substrates at room temperature. The resultant films are characterized *in-situ* by Auger, X-Ray Photoelectron and Electron Energy Loss Spectroscopies. The chemical bond of the CoN_x is strongly linked to the stoichiometry, and it can be controlled by the N background pressure. We conclude that this deposition method offers a means for fine-tuning the properties of cobalt nitride.

Keywords: Cobalt nitride; X-ray photoelectron spectroscopy; electron energy loss spectroscopy; thin films; laser ablation.

Los Nitruros de metales magnéticos han tomado gran importancia debido a sus potenciales aplicaciones tecnológicas. En este trabajo se han depositado capas delgadas de Nitruro de Cobalto usando la técnica de ablación láser pulsado reactivo en ambiente de nitrógeno. Se han usado sustratos de silicio a temperatura ambiente. Las capas resultantes se caracterizaron *in situ* por espectroscopias Auger, de foto-emisión de rayos X y de pérdida de energía. El enlace químico y la estequiometría están fuertemente correlacionados, y ambos son controlados simultáneamente por la presión durante el depósito. Concluimos que este método de síntesis permite tener un control muy fino de las propiedades de capas delgadas de Nitruro de Cobalto.

Descriptores: Nitruro de Cobalto; espectroscopia de electrónes fotoemitidos; espectroscopia de perdidas de energía; capas delgadas; ablación láser.

PACS: 79.60-i; 75.70-i; 77.84.Bw

1. Introduction

Since the fabrication of the first magnetic data storage devices, thin films of magnetic materials have been of considerable interest. Reducing the dimensions of the magnetic domains that store the minimal element of information is the key issue to increasing the capabilities of any magnetic storage device. Thus, a suitable control of chemical and physical properties of magnetic thin films might permit the enhancing of the storing capacity of present storage devices. Nitrides of magnetic metals are receiving special attention in this research field. Magnetic-nitrides are catalogued as new materials for high performance magnets because of their strong uniaxial anisotropy and high saturation magnetization [1].

A wide range of thin films are produced mostly by reactive sputter methods; however, it is known that highly ferromagnetic materials are difficult to produce by this technique when a magnetron-type source is employed. Using a ferromagnetic material as a sputtering target gives an unpredictable magnetic flux in front of the magnetron target surface [2], resulting in of poor-quality, inhomogeneous films. Therefore, alternative deposition techniques for magnetic thin films need to be developed.

One technique that has emerged promisingly for the film deposition of magnetic materials is pulsed laser deposition (PLD). PLD has been used advantageously to deposit many different materials ranging among metals, dielectrics, ferroelectrics and superconductors [3]. Unlike sputtering technique, PLD does not depend on magnetic fields to deposit thin films, being thus advantageous for magnetic film processing (for a review, see [4]). In recent times, PLD has been observed to be the preferred method in manufacturing magnetic homogeneous films [5] or heterostructured films [4]. Nowadays, the technology associated with PLD has been developed in such a way that PLD is now considered a reliable and predictable technique. Although much work has aimed at understanding the laser deposition process, transference of PLD technology to industry has been slow [3, 6].

The purpose of this work is to show that PLD is a reliable technique for magnetic-nitride film deposition. In order to accomplish this goal, cobalt nitride thin films were prepared by ablating a high purity Co target in the presence of molecular nitrogen.

2. Experimental

All films were deposited at room temperature in a laser ablation system, Riber LDM-32, with *in-situ* Auger electron spectroscopies (AES), electron energy loss (EELS) and x-ray photoelectron (XPS) spectroscopies facilities. The deposition was accomplished by ablating a cobalt target at 99.9% in a background of high-purity molecular nitrogen. Nitrogen pressures, P_N, were in the $1\times10^{-9} \leq \mathrm{P}_N \leq 1.2\times10^{-1}$ Torr range (1 Torr = 1.33×10^{2} Pa). Layers were deposited on as-received (111) n-doped silicon wafers, *i.e.* without any cleaning process. Target ablation was accomplished by means of a KrF excimer laser (λ = 248 nm) focused on a target at 50° off the surface normal. Laser energy, deposition time and pulse repetition rate were fixed at 400 mJ, 10 minutes and 10 Hz, respectively, for a total of 6,000 laser pulses for each film. Considering the loss at one laser window, the energy density at the target surface is estimated to be 2 J cm^{-2}.

AES and EELS spectra were collected using an electron beam with incident energy of 3 and 1 KeV, respectively. XPS measurements were collected using the Mg Kα line of an x-ray source with energy of 1253.6 eV. The energy scale was calibrated against the $Cu_{2p3/2}$ and $Ag_{3d5/2}$ references, at 932.67 and 368.26 eV, respectively.

X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and perfilometry was carried out on every film to determine crystalline status, thickness, roughness, particulate density and in general, film surface quality.

3. Results and discussion

The XRD analysis does not show any noticeable peak, except those related to the substrate. The only exception was for the film processed at P_N = 0 mTorr, showing a notorious peak at 2θ = 51.8°. This peak was identified as the (111) plane of cubic cobalt, powder diffraction file # 15-0806. The film thickness was kept on average near 90 nm (± 10 nm), enough to obtain a good signal if the rest of films were crystalline; thus we conclude that the cobalt films processed at room temperature in a nitrogen environment are habitually amorphous.

The film surfaces are very smooth, near the limits of SEM resolution, as can be appreciated in Fig. 1 for a typical film. The splashing-density was relatively low for this deposition technique, except for the film growth at P_N = 0 mTorr, which shows large melt-shaped droplets on the film's surface. The AFM image, Fig. 2, shows that the films are composed of a granular structure. The films have roughness typically on the order of 10% of the film's thickness (RMS values, $\sim$10 nm).

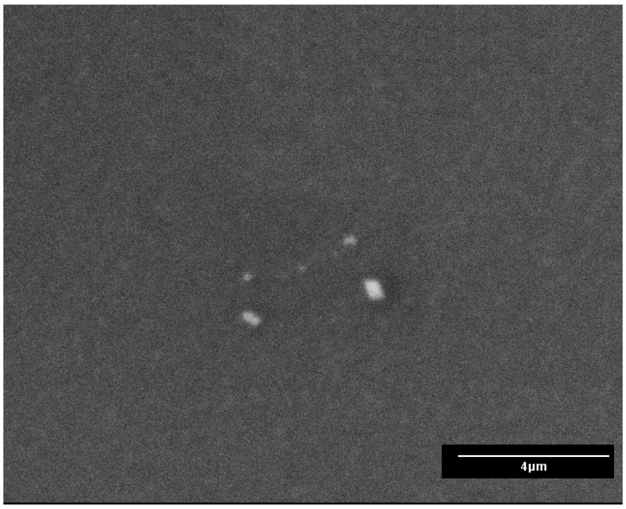

FIGURE 1. Typical SEM micrograph of a CoN_x layer deposited by laser ablating a cobalt target in a nitrogen environment. In this case it corresponds to a film grown at P_N = 40 mTorr.

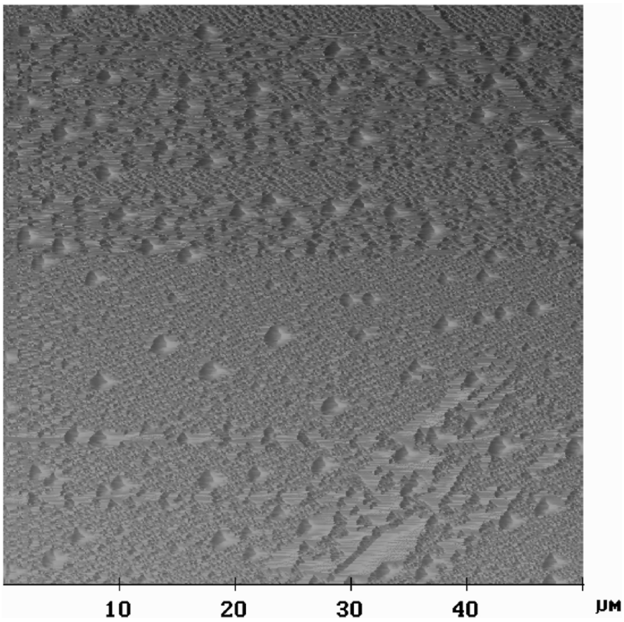

FIGURE 2. AFM image of the film grown at P_N = 40 mTorr.

XPS and AES analyses performed on the ablated films revealed cobalt nitride compounds that are free of contaminants to the limits of detection of these techniques (close to 1% atomic). Figure 1 shows a typical XPS spectrum of the cobalt nitride films, where only photoelectron emissions from Co and N are observed. Relative atomic concentrations of Co and N are calculated from the areas under the $Co_{2p3/2}$ and N_{1s} peaks after Touggard background subtraction. The sensitivity factors were calculated using the same procedure described in a previous report [7].

Atomic concentration of Co and N plotted as a function of nitrogen pressure is illustrated in Fig. 2. This graph shows a monotonic increase of N concentration in the films with the N pressure. Nitrogen incorporation into the ablated Co is almost linearly bore in the range of 25-120 mTorr of N pressure. The linear behavior of the N curve allows fine-tuning of the cobalt nitride stoichiometry by simple control of the nitrogen pressure. Stoichiometry of films produced by PLD has been established to depend on the total gas pressure [8]. Co_2N, CoN and Co_2N_3 stoichiometries are estimated to take place at P_N of 40, 90 and 120 mTorr, respectively.

Monitoring the peak positions of $Co_{2p3/2}$ and N_{1s} lines can reveal any chemical state change that Co and N might suffer during the ablation process. Plotting the positions of maximum intensity of the Co and N lines as a function of the relative nitrogen concentration, x = [N]/[Co], in the films shows a gradual shifting of the $Co_{2p3/2}$ and N_{1s} peaks (Fig. 3). These relative displacements are not a consequence of charge-induced artifacts because the difference in Co and N energy levels does not shows a constant value as a function of x. Thus the peak shifts must be related to changes in the chemical state.

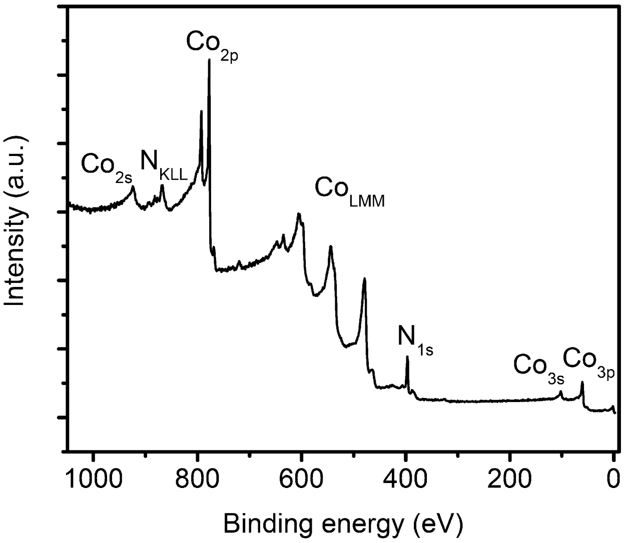

FIGURE 3. XPS spectrum of a film grown by reactive ablating a cobalt target at P$_N$ = 120 mTorr.

The change in position of the peaks is the result of a charge-transference between the Co and N atoms. Cobalt atoms acquire an ionic character as x is increased, slowly shifting the binding energy of Co$_{2p3/2}$ electrons from a neutral state at 777.8 eV, towards a state with a certain ionic character, at 778.3 eV. In the case of nitrogen atoms, these are incorporated into the films with a higher ionic character, observing a change in the binding energy of N$_{1s}$ electrons from 398.5 to 396.8 eV in the entire $x$regime analyzed. The shift to lower binding energies of the N$_{1s}$ electrons is related to an electron gain of the N atoms at the expense of the Co atoms. This tendency is observed as more nitrogen atoms are incorporated into the films. In particular, the measured binding energies for the nominal stoichiometries of Co$_2$N, CoN and Co$_2$N$_3$, were 778.0, 778.2 and 778.4 eV for Co$_{2p3/2}$ electrons, and 398.0, 397.4 396.8 eV for the N$_{1s}$electrons, respectively (Fig. 4).

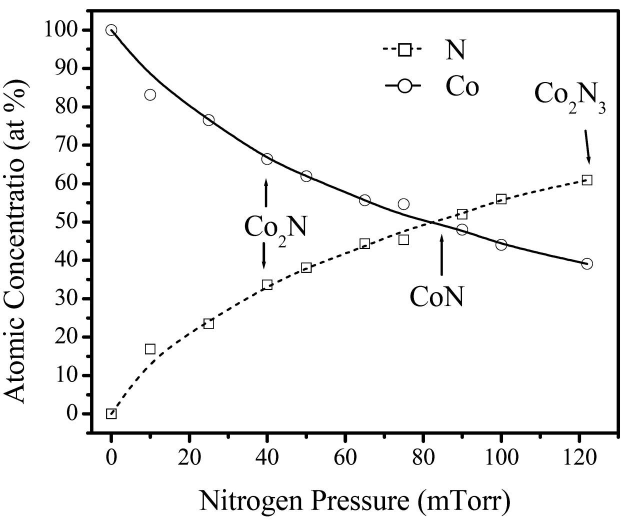

FIGURE 4. Atomic concentration determined by XPS as a function of the nitrogen pressure.

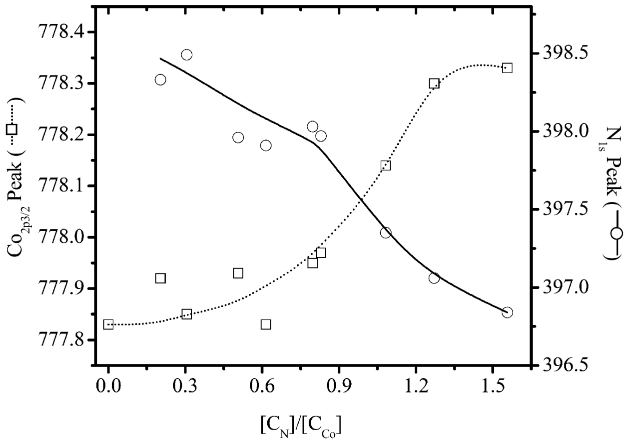

FIGURE 5. Co$_{2p3/2}$ (squares) and N$_{1s}$ (circles) peak positions determined from XPS as a function of relative nitrogen concentration in the film,x= [C$_N$]/[C$_{Co}$].

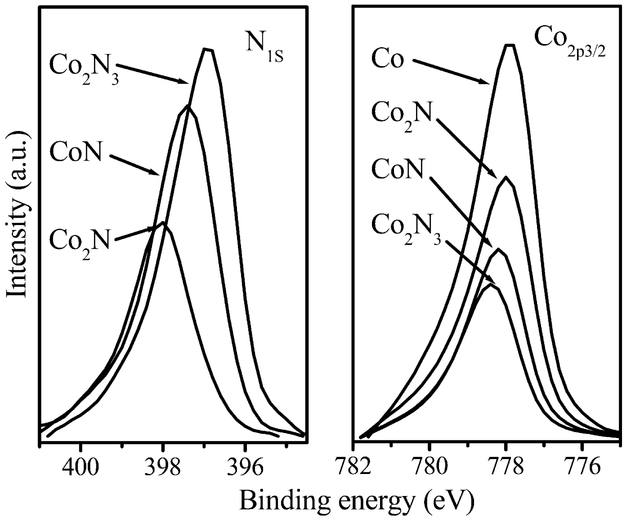

FIGURE 6. Comparison of the N$_{1s}$ and Co$_{2p3/2}$ XPS peaks determined for Co, Co$_2$N, CoN and Co$_2$N$_3$.

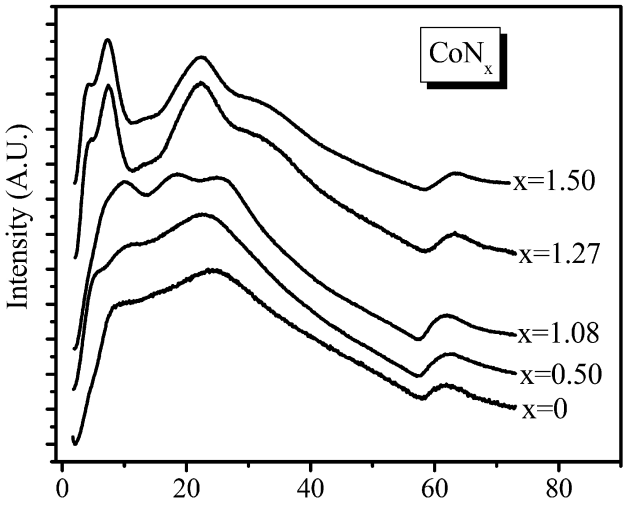

FIGURE 7. EELS spectra of CoN$_x$ films with different nitrogen concentrations.

EELS can provide information more directly about changes in the electronic state in solids. A modification in the electronic structure leads to strong modifications in the EELS spectrum. There are many papers focused on the loss spectra of transition metals [9], with Co among them. Although the theoretical background of this field has been extensively discussed in other papers [10-15], the interpretation of loss spectra remains unclear for Co. Figure 5 shows the EELS spectra taken to several films prepared at the following values: P_N = 0, 40, 90, 100 and 120 mTorr. The loss spectrum of metallic Co shows a main peak at 25 -27 eV which has been catalogued by Barbier *et al.* [16] as the volume plasmon (ω_v) even though ω_v is smaller than the value expected from dielectric theory (34 eV). The less intense peak at 8 - 9 eV is cataloged as a peak with a volume-type behavior. The surface plasmon $\omega_s = \omega_v/\sqrt{2}$ that should appear at $\sim$18-19 eV is not observed in the spectrum. It is important to note that the $\omega_s = \omega_v/\sqrt{2}$ rule is valid only for atomically flat surfaces. In this case the films are terminated in distributed spherical-like particles of variable size; accordingly, this is a possible reason to justify the disappearance of the surface plasmon. In the case of CoN_x films, the energy-loss structure in the 5-30 eV range changes drastically, and each cobalt nitride stoichiometry presents its own characteristic loss structure. As the nitrogen concentration is increased in the nitride, the ω_v peak shifts to lower energies. This fact indicates a reduction in the electronic density of the nitride phases [17].

4. Conclusions

In summary, cobalt nitride thin films have been grown by ablating a cobalt target in an N_2 atmosphere at different background pressures. The difference of 0.5 and 1.5 eV in the binding energy of $Co_{2p3/2}$ and N_{1s} electrons, respectively, is evidence that the reaction between nitrogen and cobalt was effectively made. The stoichiometry can be adjusted by varying the nitrogen pressure, it being feasible to produce the nominal stoichiometries of Co_2N, CoN and Co_2N_3. At higher pressures the stoichiometry seems to remain practically unchanging. PLD can be a very valuable method for depositing nitrides of ferromagnetic materials, offering a means of tuning the properties of the material produced.

Acknowledgments

The authors wish to thank V. Garcia, J. Díaz H., J. Peralta, and P. Casillas for their valuable technical assistance, and CONACYT project 40183-F and DGAPA-UNAM IN120306 for financial support.

$**$ Corresponding Author: Tel: +52 8183294030, e-mail: egperez@fcfm.uanl.mx

1. S.T. Oyama In *The chemistry of Transition Metal Carbides and Nitrides*, S.T. Oyama (ed) (Blackie Academic & Professional: London, 1996) 107.
2. H. Asahara, T. Migita, T. Tanaka, and K. Kawabata, *Vacuum* **62** (2001) 293.
3. *Pulsed Laser Deposition of Thin Films*, Chrisey DB, Hubler GK (eds) (John Wiley: New York, 1994).
4. J. Shen, Zheng Gai, and J. Kirschner, *Surf. Sci. Rep.* **52** (2004) 163.
5. A.G. Jenner, J.P. Hayes, L.A. Stone, H.V. Snelling, and R.D. Greenough, *Appl. Surf. Sci.* **138-139** (1999) 408.
6. H. Sankur, J.T. Chueng, and W.J. Gunning. *J. Appl. Phys. A* **47** (1988) 271.
7. G. Soto, J.A. Díaz, R. Machorro, A. Reyes-Serrato, and W. de la Cruz, *Mat. Letters* **52** (2002) 29.
8. A. Perrone, *Jpn. J. Appl. Phys.* **41** (2002) 2163.
9. D.L. Misell and A.J. Atkins, *Phil. Mag.* **27** (1973) 95.
10. K.L. Ngai, E.N. Economou, and M.H. Cohen, *Phys. Rev. Let.* **24** (1970) 61.
11. J.W. Gadzuk, *Phys. Rev. B* **1** (1970) 1267.
12. D.M. Newns, *Phys. Lett. A* **28** (1972) 341.
13. R.H. Ritchie, *Phys. Rev.* **106** (1957) 874.
14. R.A. Ferrell, *Phys. Rev.* **111** (1958) 1214.
15. E.A. Stern and R.A. Ferrell, *Phys. Rev.* **120** (1960) 130.
16. A. Barbier, P. Ohresser, V. Da Costa, B. Carriere, and J.-P. Deville, *Surf. Sci.* **405** (1998) 298.
17. G. Soto, W. De La Cruz, F.F. Castillón, J.A. Díaz, R. Machorro, and M.H. Farías, *Appl. Surf. Sci.* **214** (2003) 58.