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Magnetic behavior of cobalt oxide films prepared by pulsed liquid injection chemical vapor deposition from a metal-organic precursor

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Abstract

Thin films of cobalt oxide were prepared by the pulsed liquid injection chemical vapor deposition technique from metal-organic precursor. By using a β-diketonate complex of cobalt, namely cobalt (II) acetylacetonate ($Co(acac)_2$) as the precursor, oxygen as the reactant and argon as the carrier gas, cobalt oxide films 100 nm in thick were deposited onto Si (100) substrates at 650 °C in about 40 min. According to the characterization by X-ray diffraction and atomic force microscopy, smooth and polycrystalline films, consisting exclusively of the Co_3O_4 phase, were deposited. Magnetic properties, such as saturation magnetization, the remanence, the coercivity, the squareness ratio and the switching field distribution, were extracted from the hysteresis loop. Cobalt oxide films with coercivities of 6.61 mT, squareness ratio of 0.2607 and saturation magnetization of 12.17 nA m^2, corresponding to a soft magnetic material, were achieved.

Keywords: Chemical vapor deposition (CVD); Cobalt oxide; Magnetic properties and measurements

1. Introduction

Co-based alloys have been employed for many years for fabricating permanent magnets. Magnetic properties of different Co-doped films have been investigated recently, as well as those of Co nanoparticle films obtained by a number of techniques [1–5]. High quality magnetic films of Co-based alloys are currently used in magnetic heads and magnetic random access memory. For example, simple binary alloys, such as Co–Sm, produce high quality films for the magnetic recording industry [1]. On the other hand, cobalt oxide-based ceramics have attractive magnetic properties and their films and multilayers have been studied for decades and still motivate serious research and development efforts [6–10].

In general, magnetic oxides containing transition elements such as cobalt, manganese or ruthenium exhibit most fascinating magnetic properties. Among these transition metal oxides, the cobalt oxide is one of the most versatile ceramic materials, since it is a p-type antiferromagnetic oxide semiconductor with the highest Curie temperature, T_c = 1123 °C. Cobalt forms two stable oxides: CoO and Co_3O_4, being Co_3O_4 the stable one at lower temperatures. Co_3O_4 has the normal spinel structure of the type AB_2O_4, where Co^{2+} ions occupy the tetrahedral 8a sites and Co^{3+} occupy the octahedral 16d sites. Thin films of cobalt oxide have been prepared from various deposition techniques such as spray pyrolysis, sputtering, chemical vapor deposition (CVD), pulsed laser deposition, sol–gel process, electrophoretic deposition (EPD), etc., on a variety of substrates [6–11]. Each deposition technique offers different advantages, for example EPD is an effective, fast and controllable process for depositing various thin film layers on curved or cylindrical shaped substrates. On the other hand, the CVD provides uniform deposition over large areas, good coverage and selective deposition. Moreover, the pulsed-injection metal organic chemical vapor deposition (MOCVD) technique has the possibility to produce and controlling the film composition, microstructure and morphology, through a suitable choice of the substrate, precursor and reactant, as well as the deposition conditions [12]. Accordingly, the main goal of this investigation is to deposit cobalt oxide films, to study their structure, morphology and magnetic response, as well as to demonstrate the potential of pulsed-injection MOCVD as an alternative technique to traditional ceramic film deposition methods.

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2. Experimental

A vertical pulsed-injection MOCVD reactor was used for the cobalt oxide film deposition. The reactor allows the formation of oxide layers and multilayers by using small micro-doses of precursors mixed in an organic solvent. The precise micro-doses of such solution are injected through a computer-driven system into the evaporation zone, where they instantly evaporate (flash evaporation), so no chemical changes of the precursors are allowed. The resulting vapor mixture is transported by a carrier gas into the high temperature reaction chamber, where the reactant gas flows and the decomposition reaction and film growth on the hot substrate temperature occurs. The reactant and carrier gases are regulated by electronic mass flow controllers. The reaction chamber is a fused quartz tube surrounded by a resistive furnace, which can heat the substrate up to 900 °C. Substrates, as large as 2 in. in diameter, can be mounted easily on the holder.

Five small pieces of a mirror polished Si (100) wafer were used as substrates, placed adjacent to one another and fixed to the holder by using a DUPONT 4929 conductor paste. A mass of 0.2134 g of commercially available cobalt (II) acetylacetonate was used as precursor, mixed in 30 ml of toluene to form a liquid solution. To avoid the precipitation of the precursor, the solution container was maintained at ~40 °C during the injection process. The pressure in the system was kept at 10 Torr with the Ar gas as the carrier and O_2 gas as the oxidation source flowing at 0.8 and 0.4 l/h, respectively. The substrate temperature was maintained at T_s=650 °C meanwhile, the temperature in the evaporation zone and along the vapor transport line was set to $T_e=T_v$=280 °C, respectively.

A computer-driven system was used for the control of the injector frequency through a computer program. The time interval between pulse injection was t_I=0.5 s, since the resulting injection frequency was 2 pulses per second. The initial volume of the solution was 30 ml and the deposition took about 40 min. 4800 pulses were applied during the film deposition and then a micro-dose of 6.25×10^{-3} ml per pulse was injected. The solution concentration involved in the deposition process was 7.1133×10^{-3} g/ml, so the resulting solution amount injected per pulse was 4.4458×10^{-5} g. It must be noticed that this micro-dose can be accurately controlled by adjusting the injection frequency, through the computer program.

The film composition was analyzed by a Rigaku D/max-2100 (Cu, 1.5406 Å) diffractometer equipped with a thin film attachment. Atomic force microscopy (AFM) study was achieved using an AFM-STM Park Scientific equipment, model Autoprobe CP, operating in the contact mode at 0.2 MHz. The magnetic measurements were performed in an alternate gradient magnetometer Micro Mag Model 2900 system, which allows to measure with high sensitivity the magnetic properties of a vast range of materials, including thin solid films. All magnetic measurements were made at room temperature and longitudinally, with the magnetization parallel to the plane defined by the substrate/film surface.

3. Results and discussion

3.1. X-ray difraction analysis

The X-ray difraction (XRD) patterns of the cobalt oxide films grown by pulsed-injection MOCVD are shown in Fig. 1. The films are crystalline and formed exclusively by the Co_3O_4 phase. The XRD patterns display, in the 2θ range between 10° to 80°, a clear preference for the (311) orientation, which is a characteristic reflection in polycrystalline Co_3O_4 films, being over five times stronger than the (111) reflection [7,13]. Since the (111) plane is the most densely packed one in Co_3O_4, the films deposited here grew also along this orientation. In Fig. 1 the reflections corresponding to the (111), (220), (400) and (440) planes are also observed. In general, the formation of a preferred orientation on thin films of oxides grown by MOCVD is due basically to complex process in which different physicochemical reactions take a place at substrate surface, and wherein the use of β-diketonate complexes as precursors and oxygen as oxidation source plays an important role at a molecular level. Moreover, the reactivity of the oxygen may be affecting the formation of oxygen sub-lattice with cobalt, which may be responsible for formation of the Co_3O_4 phase. The preferred orientation of MOCVD cobalt oxide films may also be due to the details of the growth process occurring at the substrate surface, such as the energy associated to the surface of the thin film, which is highly orientation-dependent. On the other hand, although the substrate temperature was high enough as to produce high mobility, no epitaxial growth was observed. However, this is not surprising due to the large difference in the lattice mismatch of the Si substrate (0.543 nm) and the Co_3O_4 (0.808 nm) film. In particular, it may be noticed that, as the film grows thicker, the influence of the substrate decreases and then, relaxation of the strain due to the poor lattice mismatch occurs, through the nucleation of misfit dislocations. Therefore, since to the strain relaxation is enhanced as the growth temperature is increased, the higher mobility at 650 °C facilitates the formation of misfit dislocations, improving the strain relaxation in the film. Additionally, the cobalt oxide films were found to be stable at room temperature after the deposition. No changes in the phase composition of any of the films reported here, even after several months in storage, were detected, suggesting that they may be useful for practical applications. One problem associated to the use of β-diketonates as precursor is that they

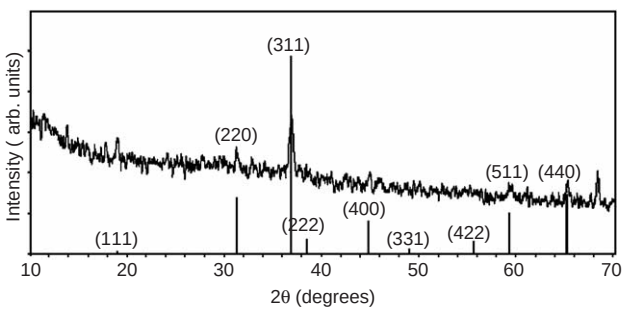

Fig. 1. XRD pattern of the Co_3O_4 films.