DEPOSITION OF COBALT FILMS AND COBALT/ZINC OXIDE MULTILAYERS BY MOCVD

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Abstract - Thin layers of cobalt and Co/ZnO multilayers have been deposited by metal-organic chemical vapour deposition and characterized by a range of structural and magnetic techniques. In general, the samples exhibited an overall in-plane magnetic anisotropy, the strength of which decreased with decreasing cobalt layer thickness. A buffer layer of ZnO was found to decrease the strength of the anisotropy with respect to a film of the same thickness deposited onto glass.
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INTRODUCTION

Magnetic multilayers show great promise for a wide range of technological applications including magneto-optic (MO) data storage media and magnetoresistive and magnetostrictive sensors. The most favoured systems for MO applications are Co/Pt [1,2] and Co/Pd [2] multilayer stacks with the individual ultrathin Co layers around 5 Å thick. In this case the multilayers must be hard magnets at room temperature and possess perpendicular magnetic anisotropy. Research into ultrathin Co films on a variety of underlayer materials has shown that the latter can be achieved by use of Au [3,4], Ir [4], or Ni [4] as well as Pt and Pd. Multilayers of Co/W have also been shown to exhibit perpendicular anisotropy [5].

The predominant production technique for magnetic multilayers is sputtering, although molecular beam epitaxy (MBE) has often been used to produce small numbers of high quality samples for research purposes. An alternative technique for production of multilayers is by use of metal-organic chemical vapour deposition (MOCVD). This has been used to good effect for many years in the semiconductor industry for production of III-V and II-VI semiconductor multilayer stacks. Deposition of cobalt has previously been reported, as well as iron films from Fe(CO)₅ [6]. However, MOCVD has not been used to any great extent for deposition of magnetic multilayer systems. This paper concerns a programme which focused on the development of a viable MOCVD process for the deposition of Co-based multilayers.

We report here the results of investigations into the growth mode and magnetic properties of MOCVD deposited Co thin films and multilayers. As part of this work we have been producing Co/ZnO multilayers. This is with a view to evaluating the potential of Co-based metal/dielectric magnetic multilayers, a system which

has been proposed to allow the magnetic and optical properties of MO media to be decoupled [7]. However, this kind of multilayer has not yet been extensively investigated experimentally.

The work has been carried out as a collaboration between Epichem Limited, who developed the precursors, Metals Research Semiconductors Limited (MRSL), who designed and built a dedicated MOCVD reactor for the project, and Keele University, where most of the film deposition and evaluation has taken place.

FILM DEPOSITION

The deposition of cobalt by MOCVD has been carried out previously using a variety of sources, including dicobalt octacarbonyl [8] and cyclopentadienylcobalt dicarbonyl (CpCo(CO)₂) [8]. Zinc oxide deposition has also been reported, from precursors including dimethylzinc tetrahydrofuran adduct (DMZ.THF) with an alcohol [9]. The main task in terms of precursor development was the matching of optimum parameters for the two layers in the stack. We discuss here the results of film deposition using DMZ.THF together with tertiary butanol (tBuOH) for the zinc oxide and CpCo(CO)₂ for the cobalt.

All depositions were carried out at atmospheric pressure and a substrate temperature of 350 °C, using hydrogen as the carrier gas. The bubbler temperatures were 12.7, 10 and 17 °C, and the gas flow rates 70, 21 and 84 sccm for the CpCo(CO)₂, DMZ.THF and tBuOH, respectively. The total gas flows to the cell were maintained at 2000 sccm during Co deposition and 329 sccm for the ZnO. A vent-run system was employed on the reactor and gas flow switching during multilayer

deposition was computer controlled, using MRSL software.

FILM PROPERTIES

Film thickness and crystallographic texture were determined by low-angle and high-angle x-ray diffraction respectively, in reflection geometry in-house at Keele and using Station 2.3 of the synchrotron radiation source at the CCLRC Daresbury Laboratory. In addition, transmission high energy electron diffraction (THEED) was performed on specially prepared samples. The microstructure was determined by use of a Hitachi field emission scanning electron microscope (FESEM) and the composition by energy-dispersive x-ray analysis (EDS), Auger electron spectroscopy (AES) and Rutherford backscattering (RBS). Magnetic anisotropy was investigated by use of ferromagnetic resonance spectroscopy, magneto-optic magnetometry and vibrating sample magnetometer measurements. The magnetic properties are described in detail elsewhere [10].

The ZnO films were found to be homogeneous and amorphous for a deposition temperature of 250 °C, with a gradual increase in the number of ellipsoidal crystalline grains with increasing temperature, until highly crystalline films were produced at 350 °C. Although the number of grains increased with temperature, their size remained approximately constant with lengths of 100 - 200 nm and aspect ratios of around 5:1. Figure 1 is an FESEM micrograph of a film deposited at 350°C.

Films deposited at 350 °C had a strong preferred orientation with the c-axis normal to the film plane, the only Bragg reflection observed in $\theta/2\theta$ x-ray diffraction patterns being the (00.2). Figure 2 gives the high angle diffraction pattern for such a film. These higher temperature depositions (350 °C) led to slightly non-stoichiometric films with a composition of $\text{ZnO}_{0.93}$, as determined by AES. The excess Zn was in the form of metallic zinc grains with dimensions of around 80 nm. These led to a brown tint. The initial deposition rate at 350 °C was $18 \text{ \AA min}^{-1}$, gradually falling to around $1.1 \text{ \AA min}^{-1}$ for thicker films, above 220 Å.

The CpCo(CO)_2 precursor led to deposition of pure Co at an initial rate of $3.3 \text{ \AA min}^{-1}$. No contamination was found from EDS measurements. However, the EDS was not able to detect light elements and RBS was used to confirm that there was no carbon, hydrogen or oxygen present. Thicker films were found to have a uniform granular microstructure (see figure 3) and a close-packed crystal structure with a strong preferred orientation. The close-packed planes were perpendicular to the film plane, even on bare glass substrates, there being only one

Figure 1 FESEM micrograph of a ZnO film deposited at 350°C

Figure 2 High angle x-ray diffraction pattern from a ZnO film deposited at 350°C, showing the ZnO (00.2) peak and 2 impurity peaks

ZnO Bragg peak present in the $\theta/2\theta$ x-ray diffraction patterns (figure 4). This corresponded to the hcp (00.2) or fcc (111) planes; both phases were found to be present in Co films deposited on carbon grids for THEED analysis, although this may not be representative of the structure of films grown on glass or ZnO. The thinnest films (less than 20 Å) were found from x-ray reflectivity to have an average density of one third that of bulk

Figure 3 FESEM micrograph of a 250 Å thick Co film.

Figure 5 FESEM micrograph of a thin Co film, showing island microstructure

Figure 2 High angle x-ray diffraction pattern from a thick Co film, showing a broad hump from the amorphous substrate and the Co (00.2) Bragg peak

cobalt. This was due to island growth, as determined from FESEM images (figure 5). The island size varied between 20 and 200 nm depending upon the exact deposition conditions. The overall anisotropy was in-plane in all samples, but there was a perpendicular anisotropy field component, the strength of which was inversely proportional to the film thickness [10].

Use of the $\text{CpCo}(\text{CO})_2$ for Co deposition and DMZ.THF with $^t\text{BuOH}$ for the ZnO has allowed us to produce Co/ZnO bilayers and multilayers with minimum mismatch of conditions. We have deposited a range of Co/ZnO and ZnO/Co bilayers with different thicknesses of both ZnO and Co. The overall trend is again that the perpendicular magnetic anisotropy component decreases with increasing thickness of the constituent Co layers [10]. However, we have not yet been able to analyse single layers with thicknesses of less than 17 Å.

We have deposited ZnO/Co multilayers with different thicknesses of Co and ZnO. The first of these had relatively thick Co layers (50 - 200 Å) separated by thin (~ 6 Å) ZnO layers. This has enabled us to determine the effects of multilayering and use of buffer layers on samples with readily measurable magnetic signals. The magnetic behaviour of the multilayers was similar to that of the single films. One set of optimum conditions involves use of a fairly thin (~ 90 Å) ZnO buffer layer. A sample of the form $\text{ZnO}(90 \text{ Å})/[\text{Co}(50 \text{ Å})/\text{ZnO}(6 \text{ Å})]_{10}/\text{ZnO}(90 \text{ Å})$ was found to have good specular optical reflectivity in addition to promising magnetic behaviour. By increasing the DMZ.THF and $^t\text{BuOH}$ concentrations in the carrier gas it was found to be possible to produce equally good quality films without a ZnO buffer layer at all.

DISCUSSION

We have found that it is possible to produce Co/ZnO multilayers with well matched deposition conditions. The fact that the in-plane anisotropy decreases as the films become thinner augers well for the production of films with perpendicular anisotropy. In addition, the optical properties of the multilayers are suitable for MO applications.

We have made use of ZnO for the buffer layer. This has been used by other workers to induce texture in Co/Pt stacks [11]. This approach also avoids the need for a further precursor for a different material. Since it was a (00.2) texture that was found useful as the buffer layer for texturing Co/Pt multilayers, in order to attempt to produce perpendicular magnetic anisotropy we have continued to deposit the ZnO at 350 °C. This may well remain the optimum approach for the buffer layer and the multilayer stacks themselves. The clear amorphous ZnO films deposited at 250 °C may ultimately be advantageous for optical overlayers because of their lower optical absorption and scatter.

CONCLUSIONS

We have successfully produced Co/ZnO multilayers by use of MOCVD with well matched deposition conditions for the 2 materials. The magnetic properties are similar to those of sputtered samples. Use of 90 Å thick layers of ZnO as the buffer and overlayer leads to good magnetic behaviour and reasonable optical properties. Further research is required to obtain overall perpendicular anisotropy and reduced laser scatter.

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