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COMPOSITION AND STRUCTURE OF SPUTTER DEPOSITED ERBIUM HYDRIDE THIN FILMS

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ABSTRACT

Erbium hydride thin films are grown onto polished, a-axis α Al_2O_3 (sapphire) substrates by reactive ion beam sputtering and analyzed to determine composition, phase and microstructure. Erbium is sputtered while maintaining a H_2 partial pressure of 1.4×10^{-4} Torr. Growth is conducted at several substrate temperatures between 30 and 500°C. Rutherford backscattering spectrometry (RBS) and elastic recoil detection analyses after deposition show that the H/Er areal density ratio is approximately 3:1 for growth temperatures of 30, 150 and 275°C, while for growth above ~430°C, the ratio of hydrogen to metal is closer to 2:1. However, x-ray diffraction shows that all films have a cubic metal sublattice structure corresponding to that of ErH_2. RBS and Auger electron spectroscopy confirm that sputtered erbium hydride thin films are relatively free of impurities.

INTRODUCTION

Rare earth metal hydride thin films are currently used for industrial applications such as down-hole, oil-logging devices. Recently, certain metal hydride thin films have attracted a great deal of added attention, for these materials exhibit interesting optical and magnetic properties. Extensive work by Griessen et. al.[1-3] and others[4] investigates the growth of yttrium and lanthanum hydrides, while demonstrating feasibility for use as switchable mirrors. Additional work[5-8] researches the effects of hydrogen loading on metal film structure and phase formation. In previous studies, metal hydride thin films are fabricated by a two-step process involving ultra-high vacuum evaporation of metal and post-growth, ex-situ loading of hydrogen through a protective Pd overlayer.

In this study, we examine reactive deposition of erbium hydride. The erbium / hydrogen material system has been studied in the past. This includes investigations of erbium hydride thin films grown on various substrates.[9,10-] Two well-characterized erbium hydride phases, having different crystal lattice structures, are identified. Similar to Tb, Dy, Ho, Y, Lu and Tm, erbium forms a cubic dihydride phase and a hexaganol trihydride phase.[11] The thermodynamically-stable ErH_2 structure is that of fluorite (CaF_2). ErH_3 is shown to have a 'HoH$_3$ type structure'[12] with a space group $P\bar{3}cl$ (D^4_{3d}). This can be envisioned as a hexagonal close-packed metal lattice with H atoms situated in positions that are slightly displaced from the tetrahedral and octahedral interstitial sites.[11]

In the current study, the composition and structure of erbium hydride thin films deposited by reactive sputtering are investigated. Metal hydride thin films are grown by

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'co-deposition' in order to avoid large stresses that may develop during ex-situ loading of an initially well-adhered metal film. It is expected that reaction of a pre-deposited metal layer could lead to film blistering or buckling. Furthermore, sputtering may ultimately be useful for tailoring metal hydride thin film stress.[13] Reactive sputtering has been used in the past to deposit numerous two-component thin films, including various metal nitrides.

DEPOSITION AND ANALYTICAL TECHNIQUES

Films are deposited in a cryopumped sputter apparatus having a base pressure of 9 x 10^{-9} Torr, as indicated by a stable ion gauge. A static sputter deposition geometry is employed for film growth. Samples are fixed 23 cm from the surface of a 10 cm-diameter, high purity (99.95%) Er sputter target. The angle of incidence of the deposition flux is 20° off substrate normal. A Kaufmann ion source is used for argon sputtering of erbium. The ion source is oriented so that Ar ions impinge at a 48^{0} incidence angle relative to target normal. Ultra-high purity (99.999%) Ar is used for sputtering, with the pressure regulated by a mass flow controller. Ultra-high purity H_2 (99.999%) is introduced into the chamber for reactive deposition after passing through a SAES getter filter and a mass flow controller.

Films are deposited onto a-axis α Al_2O_3 (sapphire). Samples are initially diced into 12mm x 50mm rectangles and wet-chemically cleaned before loading. Cleaning involves sequential rinsing in acetone, deionized H_2O, hot hydrogen peroxide and deionized H_2O. Samples are blown dry with filtered nitrogen after rinsing. In the vacuum system, samples are mounted vertically in a molybdenum holder. After sample loading and pumpdown to 10^{-9} Torr, substrates are outgassed using a backside, noncontact heater. Outgassing consists of a programmed 'ramp and hold' sequence including anneals at 50, 150, 300 (2 hours) and 500°C (15 minutes). Thereafter, substrates are equilibrated at a desired growth temperature for 1.5 hours. The heater and accompanying thermocouples are contained inside a metal housing having a single window opening on the front side for deposition.

Immediately prior to deposition, the Er target is sputtered for 10 minutes with a shutter covering the sample. A presputter is necessary to remove contaminants at the surface, particularly oxygen that attaches during system openings. Sputter deposition parameters include a 1200eV beam energy (exiting source) and a 45mA beam current. Growth rates are approximately 0.5 Å/sec. A stable ion gauge measures chamber pressure during sputtering, equal to 8.0 x 10^{-4} Torr. In separate experiments, the same gauge is used to estimate the hydrogen partial pressure present during deposition, equal to 1.4 x 10^{-4} Torr. After deposition, the heater supply and the mass flow controllers are turned off. The chamber pressure rapidly decreases, attaining 1.0×10^{-6} Torr in 2 minutes.

Films are analyzed using a number of techniques. A Physical Electronics PHI 660 Scanning Auger system is used to probe film composition. A 5keV electron beam is employed with a ~400nA beam current. Sputtering for depth profile analysis involves 3keV Ar. A custom built micro-diffractometer system having a Siemens Hi-Star area detector is used to collect x-ray diffraction data. With this instrument, we scan from 20-

50° 2θ, while probing a range of χ between –20 to $+20^{\circ}$ about the surface normal. This system employs a Rigaku 12kW rotating anode (Cu) as the x-ray source, and the x-ray beam is collimated using a 100 μm diameter pinhole. A nickel foil attached to the front surface of the area detector filters K_{β} radiation. Elastic recoil detection (ERD) and Rutherford backscattering spectrometry (RBS) are used to determine the H/Er ratio of thin films. ERD analysis determines the areal density of H. Experiments involve a 24 MeV Si^{5+} beam, a 75° incidence angle (relative to sample normal) and a 12 μm thick Mylar range foil. RBS is used to measure the areal density of Er using a 2.0 MeV beam of ^{4}He, an incidence angle of 10° from sample normal, and a backscatter (detector) angle of 164°. Both beams are obtained via an EN tandem Van de Graaff.

RESULTS AND DISCUSSION

A number of erbium hydride thin films are sputter deposited onto sapphire to thicknesses of ~1600 Å and analyzed. This includes deposition at various growth temperatures, T_g, between 30 and $500^{\circ}C$. In general, several techniques show that sputtered metal hydride thin films are relatively free of impurities. RBS and ERD demonstrate that films consist mostly of Er and H. RBS spectra, such as the one shown in Figure 1.a., indicate the presence of Er in the film and Al and O contained within the substrate. Most importantly, RBS spectra indicate no large amount of oxygen in the bulk of films. The presence of oxygen within films would be indicated by higher backscatter yield at energies greater than that corresponding to the displayed oxygen front edge (channel 200). A challenge in growing films containing Er is the extreme sensitivity of this metal to oxidation. RBS spectra do reveal small amounts of Ar throughout films. Ar is most likely incorporated during sputtering. Measurements made by high-energy ion beam analysis are consistent with Auger electron spectroscopy depth profiles performed

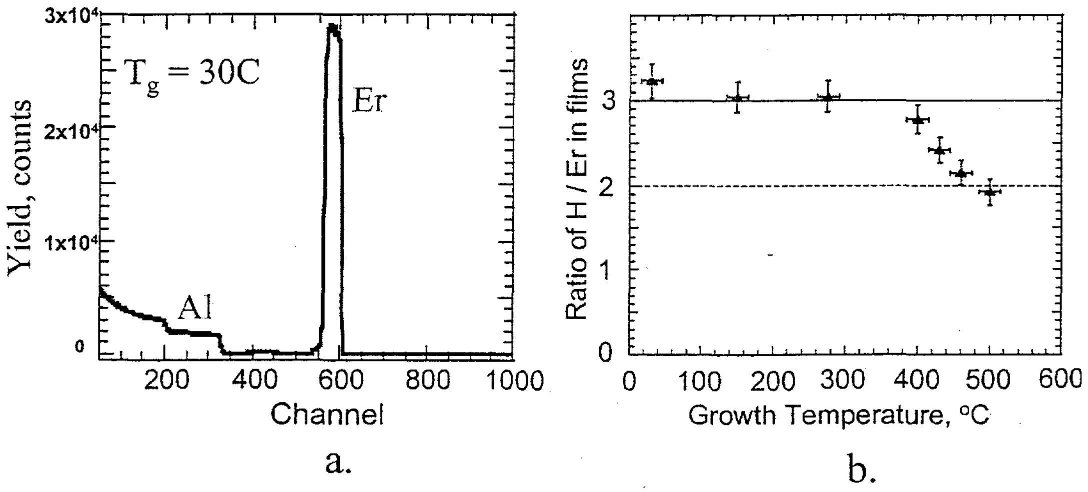

Figure 1. RBS spectra (a.) taken from a film grown at 30°C.
Plot (b.) of H/Er areal density ratio as determined by ERD and RBS.

on the same samples. Auger electron spectroscopy indicates that the bulk of films consist of Er with relatively little oxygen (H is not detected by Auger spectroscopy).

Rutherford backscattering spectrometry and elastic recoil detection analyses show that the H/Er ratio in films depends on growth temperature. As indicated in Figure 1.b., the ratio of measured areal densities, η_H/η_{Er}, is 3:1 for films grown at 30, 150, 275°C. Above 275°C the ratio of H/Er decreases, and at growth temperatures above 460°C, η_H/η_{Er} is approximately 2:1. Error bars indicated in the plot for the H/Er ratio reflect the uncertainty of measurements. Accurate measurements of H areal density by ERD are made possible with a silicon nitride standard that contains 5.77×10^{21} H/cm^3, or ~6.0 at.%. Note, erbium hydride films are initially probed 1-3 weeks after growth, but several are re-analyzed six months after deposition. No change in the H/Er ratio is detected after long times relative to initial measurements. It is expected that the oxide layer at the film surface protects against hydrogen desorption / absorption.

X-ray diffraction shows that, over the entire range of observed H/Er ratios, films have a cubic metal sublattice. Area detector patterns indicate that films are textured and oriented ~10° from the substrate normal. Integrating a small slice through the area detector maps, generates the 1-D diffraction scans shown in Figure 2. Although scans cover a large range of 2θ, only a portion of scans is plotted about the sole diffraction peak detected. As shown in the figure, a single Bragg reflection is found at 2θ=29.7° for films grown at 30, 150 and 275°C. The diffraction peak centroid is located at slightly larger 2θ for growth at 400 and 430°C. The single diffraction peak in each scan is consistent with a {111} reflection for the cubic ErH_2-type structure having a d-spacing of 3.00 Å at low T_g and 2.98 Å at higher T_g. The predicted ErH_2 {111} lattice spacing is 2.96 Å based on a unit cell dimension of 5.12 Å. Note, calculated lattice spacings for the di- and trihydride phases are consistent with previous analysis of both phases by electron diffraction.[9]

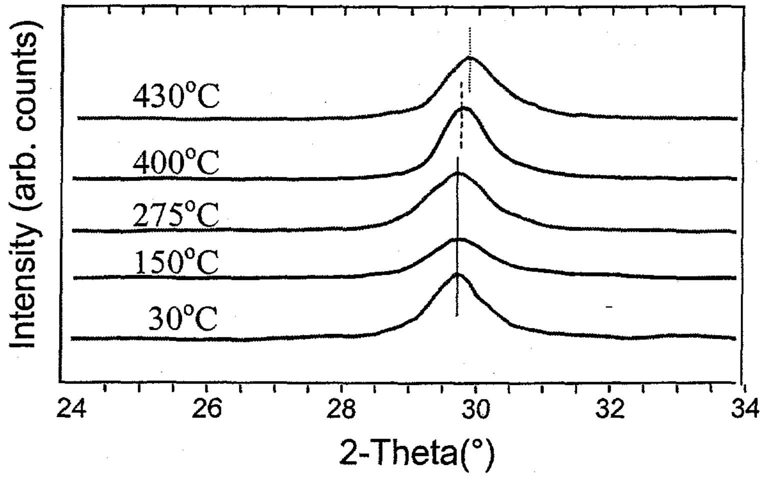

Figure 2. Plot of x-ray diffraction scans for several metal hydride thin films. Temperatures shown are 'growth temperatures'.

X-ray pole figure techniques are employed to probe over a larger range of reciprocal space in an attempt to detect the hexagonal phase. In these experiments 2θ is varied incrementally by 0.25° between 25-36°, and a complete pole figure to $\chi = 80^{\circ}$ is scanned *for each* θ. Potential ErH_3 reflections are calculated to be at $2\theta = 27.3^{\circ}$, 28.4° and 31.6° for CuK_{α} radiation ($\lambda = 1.54$ Å). Interestingly, no evidence of a hexagonal ErH_3 crystal structure is found. All detected Bragg reflections are consistent with a single-phase, cubic structure. In addition to the {111} reflection indicated in Figure 2, diffracted radiation is detected at $2\theta = 35.0^{\circ}$. A representative pole figure for this 2θ is shown in Figure 3. This reflection originates from the {200} lattice planes of the cubic phase. Note, sapphire reflections are also displayed in this pole figure. Using these as a reference, it is apparent that the film is tilted off wafer normal.

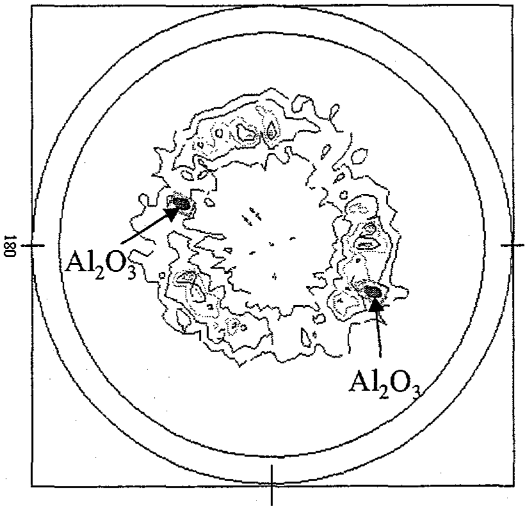

Figure 3. X-ray Pole figure for $2\theta = 35.0^{\circ}$, corresponding to the {200} reflection of cubic erbium hydride. Two reflections from sapphire are superposed.

The observation of a cubic structure for all films is contrary to published Er-H phase diagrams.[14] Under equilibrium conditions, single-phase ErH_2 having a fluorite structure forms over a small range of compositions between $ErH_{1.9}$ to $ErH_{2.2}$ for $T < 400^{\circ}C$. For ErH_x compositions such that $x > 2.1$, a large two-phase region exists composed of both the cubic dihydride and hexagonal trihydride. At $T = 350^{\circ}C$, the two-phase region boundaries correspond to compositions of $ErH_{2.14}$ and $ErH_{2.97}$. The two-phase region is bounded at compositions of $ErH_{2.1}$ and $ErH_{3.0}$ at $30^{\circ}C$. Comparing measurements of sputtered film composition to structural observations provided by XRD, it is apparent that films studied in this work have a stable, cubic ErH_2-type structure despite large relative amounts of H. No evidence of a hexagonal trihydride phase is found even though several films have a H/Er ratio equal to 3:1.

CONCLUSIONS

In summary, erbium hydride thin films are reactively sputtered onto single crystal, α-Al_2O_3 {11.0} substrates at various temperatures, and analyzed for composition and crystal structure. Rutherford backscattering and elastic recoil detection analyses reveal that the H/Er ratio is 3:1 at temperatures $\leq 275^{\circ}C$ and approaches 2:1 at higher growth temperatures. Interestingly, all films consist of a single-phase, cubic ErH_2-type crystal structure despite large differences in the relative amounts of H and Er. A single peak is found in x-ray diffraction scans utilizing an area detector, consistent with a {111} out-of-plane texture.[15] X-ray pole figures and area detector scans show no evidence for the hexagonal trihydride phase. Future work will explore the stability of various hydride phases and the influence of strain energy, substrate/film lattice matching, and kinetics.

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