

PERPENDICULAR MAGNETIC ANISOTROPY IN IRON FILMS PRODUCED BY LASER CHEMICAL VAPOUR DEPOSITION OF $\text{Fe}(\text{CO})_5$

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Abstract - Uniform thin films of polycrystalline α -iron are obtained by decomposing a stream of $\text{Fe}(\text{CO})_5$ in a flow reactor using 193 nm ArF excimer laser pulses. The films are optically flat and 2.6 μm thick, but have a spiculate columnar microstructure with a mean column width of 0.2 μm . The films show perpendicular magnetic anisotropy. The Mössbauer spectra of the surface and bulk can be fitted by assuming an angle of 37° between the magnetization direction and the normal to the film.

INTRODUCTION

Laser chemical vapour deposition (LCVD) of metals is a process whereby laser light is used to decompose an organometallic compound in order to deposit a thin metal film on a substrate. The decomposition may be photolytic, through absorption of the light by the organometallic, or thermal, via laser heating of the substrate. LCVD of metal films using ultraviolet (UV) lasers and has been known for about a decade and is the subject of much investigation [1]. Interest in the process is mainly due to the possibility of direct writing of conducting features on microcircuitry without the need for a mask.

There are several reports of iron films prepared by UV photolysis of $\text{Fe}(\text{CO})_5$ in the gaseous phase. It is possible to condense a thin layer of carbonyl on a cooled substrate and decompose it in situ [2]. This avoids the difficulty that arises in the gas phase of the film tending to form on the inside of the entrance window limiting the film thickness to less than 0.1 μm [3]. The iron films obtained by LCVD are reported to contain varying amounts of oxygen and carbon [4], but there is little information about their structural or magnetic properties. Iron deposition from $\text{Fe}(\text{CO})_5$ has also been demonstrated by both conventional pyrolytic chemical vapour deposition and electron beam induced deposition [5].

Here we report on the preparation of uniform thin films of polycrystalline α -Fe on quartz substrates. The films are investigated using scanning electron microscopy, x-ray diffraction and Mössbauer spectroscopy. The results show that the films exhibit perpendicular magnetic anisotropy which is related to their columnar microstructure.

EXPERIMENT

The flow reactor used for the deposition is shown in figure 1. Deposition takes place on a quartz substrate placed in front of the exit window, and the partial pressure of the carbonyl is ≈ 0.1 Torr. A continuous flow of helium gas bathes the entrance window in order to avoid deposition there. The pressure of the helium in the deposition chamber is 2 Torr. A 193 nm ArF excimer laser with a pulse duration of 20 ns was used. The laser beam was weakly focussed to give a fluence of 14 mJ cm^{-2} at the substrate. The laser repetition rate was 50 Hz and 2×10^4 shots were found to give a film 2.6 μm thick with an area of 0.65 cm^2 . Approximately 1 g of $\text{Fe}(\text{CO})_5$ was used per run, which means that 0.5 % of the carbonyl used contributes to the film.

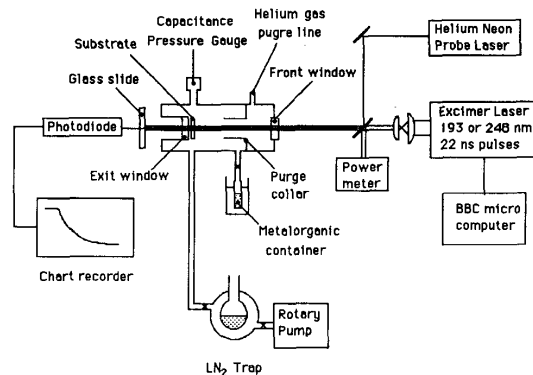


Figure 1 Experimental set-up

The ArF excimer laser was chosen because the photon energy (6.42 eV) exceeds the binding energy of the iron in $\text{Fe}(\text{CO})_5$ (6.07 eV)[6]. A blue-green fluorescence is observed in the beam path near the substrate; which may be due to the de-excitation of Fe^* produced by the photolytic decomposition of $\text{Fe}(\text{CO})_5$.

The first stages of the deposition were monitored by recording the transmission of a He-Ne laser (632.8 nm) through the growing film. The transmission was found to decrease exponentially as $I(n) = I_0 \exp(-n/n_0)$ where n is the number of laser shots; which implies that a constant thickness is deposited per shot. The ultimate film thickness was measured by direct observation of the cross-section

in a scanning electron microscope (SEM). It follows that about one half of a monolayer is deposited per shot. The laser fluence required to decompose the corresponding amount of $\text{Fe}(\text{CO})_5$ is about 1 mJ cm^{-2} , which is 7 % of the fluence used. The LCVD process for preparing metal films is about 100 times more efficient than laser ablation deposition, where typically 10^6 pulses of 100 mJ are required to deposit a comparable film on an area of about 5 cm^2 .

RESULTS AND DISCUSSION

The area of the film was defined by the shape of the laser beam on the substrate. Films usually adhered and had a smooth metallic appearance except near the edge. A cellular surface structure with a scale of $0.2 \mu\text{m}$, is clearly visible in the SEM photographs, shown in figure 2. This is due to a spiculate columnar microstructure extending throughout the depth of the film, which was revealed by fracturing the substrate and film.

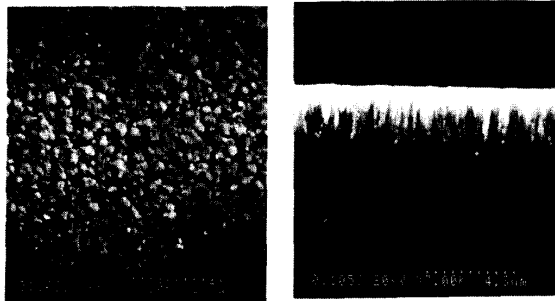


Figure 2. SEM of surface and edge.

The columns are more numerous near the quartz interface, and taper towards that interface. The film thickness is uniform to within 5% over the central region, but decreases towards the edge of the film where the fluence was lower. When both the film and the substrate were coated with an opaque layer of gold it was found that the specular reflectivity of the coated LCVD film, at near normal incidence, was 80% of that for the coated substrate. This implies a value of 25 nm for the rms surface roughness of the LCVD film which is consistent with the SEM images of the cross-section.

X-ray diffraction ($\text{Cu K}\alpha$) from the films, figure 3, shows a series of broadened peaks due to $\alpha\text{-Fe}$. Assuming the line broadening is to particle size rather than lattice strain, an effective crystallite diameter of 8 nm is obtained from the (110) peak using the Scherrer formula.

Room-temperature Mössbauer spectra, shown in figure 4, confirm that the films are polycrystalline $\alpha\text{-Fe}$. The direction of the γ -ray is perpendicular to the film surface. A transmission Mössbauer spectrum,

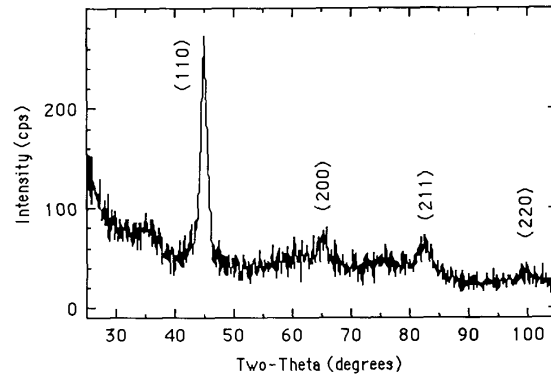


Figure 3. XRD of LCVD thin film

which examines the bulk of the sample, reveals a magnetic split pattern with a hyperfine field of 33.1 T, typical of pure $\alpha\text{-Fe}$. The top $0.3 \mu\text{m}$ layer is sampled using conversion electron Mössbauer (CEMS) and the spectrum is similar to the bulk, except for 25% of a paramagnetic impurity phase.

The most striking feature of the Mössbauer spectra is the reduced intensity of the $\Delta m = 0$ transitions, (lines 2 and 5). Their ratio R relative to the $\Delta m = 1$ transitions, (lines 1 and 6) is given by

$$R = \frac{4 \sin^2 \theta}{3(1 + \cos^2 \theta)} \quad (1)$$

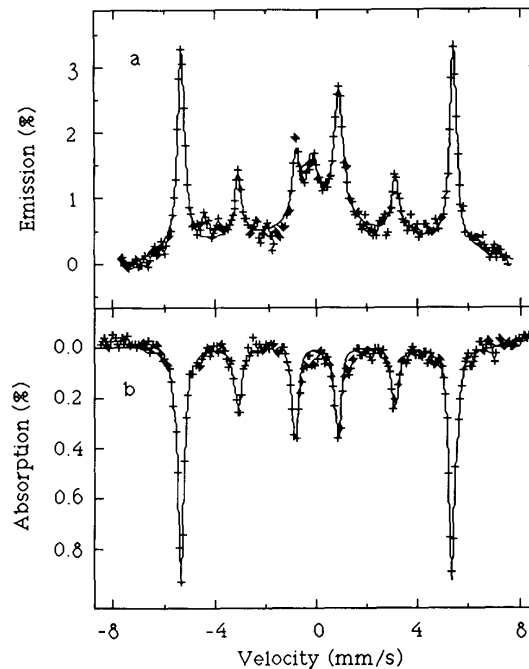


Figure 4. Mössbauer spectra of LCVD film (a) surface (CEMS) and (b) bulk (transmission).

where θ is the angle between the γ -ray and the magnetization direction. The Mössbauer data are fitted with $\theta = 37^\circ$, indicating a strong preference for the iron magnetization to lie perpendicular to the film plane.

Bulk magnetization of the thin film was measured with the field applied parallel and perpendicular to the film plane using a vibrating sample magnetometer, figure 5. An estimate can be made for the perpendicular anisotropy constant K_{\perp} from the perpendicular magnetization vs. field data. A uniform and homogeneous ferromagnetic film will exhibit in-plane anisotropy due to the demagnetizing field $D\mu_0 M$ where $D = 1$. (i.e. 2.2 T for α -Fe). This in-plane shape anisotropy will be reduced by any contribution to the perpendicular anisotropy in the film. The measured anisotropy field B_a will be

$$B_a = \frac{2K}{M_s} \quad (2)$$

where K is the sum of the shape anisotropy caused by demagnetization and the perpendicular anisotropy

$$K = \frac{1}{2} \mu_0 M_s^2 + K_{\perp} \quad (3)$$

For $B_a = 0.65$ T, and assuming the full saturation magnetization of iron, $M_s = 1.7 \times 10^6$ J T⁻¹ m⁻³, yielding $K_{\perp} = -1.3 \times 10^6$ J m⁻³.

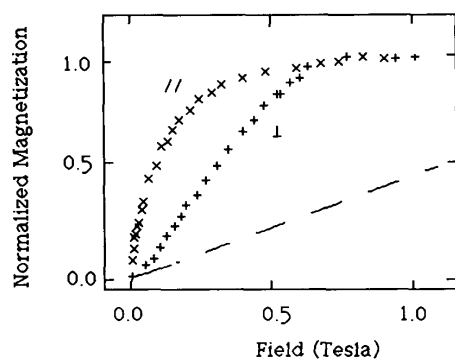


Figure 5. Magnetization vs. field. The dashed line represents the case for a thin iron film with no perpendicular anisotropy.

The origin of the perpendicular anisotropy in the LCVD iron films is attributed to their columnar microstructure. Columnar microstructure is thought to arise from self-shadowing during film growth, when atoms arrive at nearly normal incidence to the substrate [7] and has been known for some time to be responsible for perpendicular anisotropy in vacuum deposited permalloy films [8]. The ratio of K_{\perp} to the shape anisotropy for columnar microstructure has been shown to depend on the factor δ/d , where δ is the gap between the columns and d is the columnar width [9].

The two mutually perpendicular contributions to the anisotropy will result in the magnetization lying either parallel or perpendicular to the film, yet the Mössbauer data show that, on the average, the magnetic moment is tilted at 37° to the normal. The SEM micrographs in figure 2 showing the spiculate structure indicate a distribution of the column widths and spacings which may explain the Mössbauer fitting angle of 37° .

CONCLUSIONS

Large area iron films of optical quality have been deposited on quartz substrates by LCVD of iron carbonyl while avoiding the problem of deposition on the entrance window of the deposition chamber. These films exhibit a perpendicular magnetic anisotropy due to columnar microstructure with columns about 0.2 μm wide. If the LCVD process can be extended to alloys, there may be a prospect of producing films with sufficient anisotropy to be used for perpendicular magnetic recording. Such films might be intrinsically more stable than the amorphous films currently employed.

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