

An investigation of the growth of nickel ferrite films on magnesium oxide substrates

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Nickel ferrite films have been prepared by chemical vapour deposition and by the oxidation of sputtered and vacuum deposited films at high temperature. The interaction of magnesium oxide substrates with these films has been investigated using a wide range of electron optical techniques. Considerable interdiffusion is observed, which is likely to alter the magnetic properties of these films.

1. Introduction

The structure and composition of ferrimagnetic films such as nickel ferrite films is an important parameter in device efficiency. The choice of a suitable substrate that will not produce strain leading to crystal defects at the film-substrate interface and will not interact chemically with the film is important in preserving the magnetic properties. Single crystal magnesium oxide is believed to be a suitable substrate for epitaxial growth of single crystal ferrite films and (100) ferrite films have been grown on the (100) faces of MgO single crystals [1, 2]. For most ferrites the (100) interplanar spacing is almost exactly twice the (100) spacing in MgO, however, the misfit f [3, 4, 5] between ferrites and MgO has been shown to have a magnitude that will result, in most cases, in its accommodation by interfacial dislocations [6]. Although detailed studies have been made of the microstructure of ferrite thin films grown on MgO and the composition of these films has been studied by energy dispersive X-ray microanalysis, a detailed analysis of the influence of the MgO substrate on film composition has not been made until the present study.

The aims of the present investigation have been to study the composition of nickel ferrite films, prepared by three preparation techniques, and to study the interaction of these films with the single crystal MgO substrate. The three preparation techniques were: chemical vapour deposition of nickel ferrite films; d.c. sputtering of nickel ferrite films from a nickel ferrite cathode; and oxidation of NiFe₂ (Invar alloy) films obtained by sputtering and by vacuum evaporation using an electron beam source. Films sputtered in both argon and oxygen have been studied.

2. Experimental procedures

Ferrite films prepared by chemical vapour deposition were prepared using a method first described by Mee *et al.* [1] using a T-reactor system. The sputtered nickel ferrite films were prepared in a high vacuum system (ultimate pressure 10^{-4} Pa) and were d.c. sputtered at a pressure of 20 Pa onto the MgO single crystal substrates. Films sputtered from an NiFe₂ cathode were also deposited on the MgO substrates at

this pressure. NiFe₂ films prepared by means of an electron beam source were deposited at a pressure of 10^{-4} Pa. The single crystal magnesium oxide substrates were polished prior to film deposition using the procedure described by Fitzgerald and Engin [7].

The structure and microstructure of these films were examined by electron microscopy and electron diffraction in an AEI EM6G transmission electron microscope, a JEOL 100C scanning transmission electron microscope, and the Cavendish Laboratory 750 kV high voltage electron microscope. The bulk composition was examined by energy dispersive X-ray microanalysis in the transmission instruments and in a JEOL T300 SEM. The surface composition of the films was examined by means of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) in a VG Microscope HB100 UHV-SEM fitted with a CLAM 100 electron spectrometer. Throughout this work the Au4f_{7/2} peak centre was located at a binding energy of 83.9 eV. Specimen charging effects were checked by flashing specimens with a thin gold film.

3. Electron diffraction

Thin films prepared from both nickel ferrite and Invar alloy cathodes in argon and oxygen were found to be polycrystalline when examined in the transmission instruments. With the exception of films sputtered from the Invar alloy cathode in argon, where electron diffraction patterns indicated the possible presence of NiO, FeO and nickel-iron alloy, electron diffraction patterns from each film were identified as nickel ferrite (Fig. 1) before oxidation at high temperature. Oxidized films of NiFe₂ deposited in vacuum from an electron beam source have also been identified by electron diffraction as polycrystalline nickel ferrite [8].

Because of the nature of the preparation technique, films prepared by chemical vapour deposition could only be examined by electron diffraction after ion etching through the MgO substrate and film to a thickness suitable for electron penetration. The films were found to have the ferrite crystal structure and grew epitaxially in the (100) orientation on the (100) single crystal MgO substrate [9].

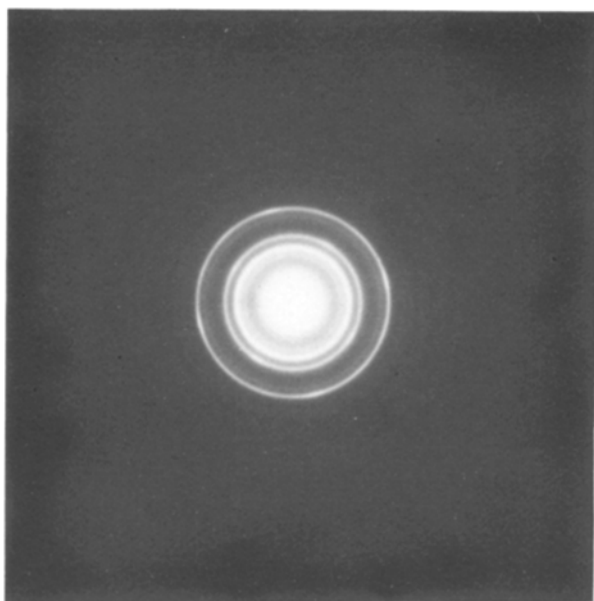


Figure 1 Electron diffraction pattern obtained from a thin film sputtered from a nickel ferrite cathode in argon.

4. X-ray photoelectron spectroscopy studies

X-ray photoelectron spectroscopy studies are important in determining the nature of the chemical bonding and therefore the particular metal oxides formed on the surface of films produced by the various preparation techniques. In conjunction with a light argon ion etch the nature of chemical bonding below the surface can also be investigated. Sputtered and vacuum deposited films have been examined before high temperature oxidation to determine the extent of oxidation that occurs before annealing in air.

The structure of the O 1s peak in X-ray photoelectron spectra has been investigated for each film because this could give a clue to the nature of the oxides on the surface. In some instances the O 1s peak in films sputtered in argon or oxygen was found to have a shoulder at the high binding energy side at the position of oxygen in the hydroxyl groups in FeO(OH) [10, 11], Ni(OH)₂ [12, 13] and NiO(OH) [14] (Fig. 2a, b). This shoulder was removed or reduced by subjecting the films to a light argon ion etch. The remaining component of this peak after ion etching was sited at the position of the O 1s peak in nickel ferrite.

The structure of the O 1s peak from NiFe₂ films vacuum deposited using an electron beam source has also been examined before oxidation (Fig. 2c). The shoulder associated with hydroxide formation was not observed.

For films prepared by chemical vapour deposition, without exception, in each film examined, a broad O 1s peak was observed that was reduced by a light argon ion etch (Fig. 2d, e). The components of this peak that are reduced upon argon ion etching lay in the range of binding energies from 531 to 534 eV, suggesting that the surface layer also contains the hydroxides described above. A similar broad O 1s peak has been observed in films of vacuum evaporated

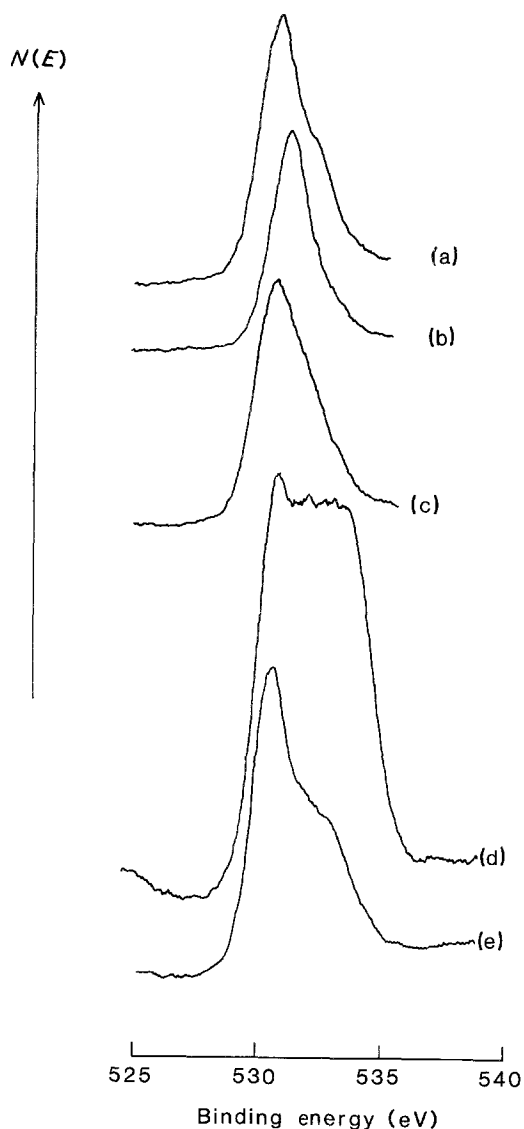


Figure 2 The structure of the O 1s X-ray photoelectron peaks from (a) a film sputtered in oxygen from an Invar alloy cathode, (b) a film sputtered in argon from an Invar alloy cathode, (c) a film deposited in vacuum using an electron beam source, (d) a film prepared by chemical vapour deposition, and (e) the film in (d) after a 30 sec argon ion etch.

iron exposed to controlled pressures of water vapour in a high vacuum reaction chamber [13].

Fe 2p peaks in the X-ray photoelectron spectrum from each type of film have also been studied. For sputtered films and films deposited by the electron beam source in vacuum, the Fe 2p_{3/2} peak was found to be broad, suggesting that it is the superposition of Fe 2p_{3/2} peaks from FeO(OH), Fe₂O₃ and NiFe₂O₄ (Fig. 3a, c). A small satellite peak observed in spectra from sputtered films (Fig. 3a) at 8 eV above the Fe 2p_{3/2} position confirmed the presence of Fe₂O₃ [11]. This satellite peak was removed in each case by a short argon ion etch (Fig. 3b). After more extensive argon ion etching a small Fe 2p_{3/2} peak situated at the position of this peak in uncombined iron was observed in argon sputtered films from the Invar alloy cathode. A similar peak appeared after only a light etch in NiFe₂ films vacuum deposited using the electron beam source (Fig. 3d).

A narrow Fe 2p_{3/2} peak was obtained from films

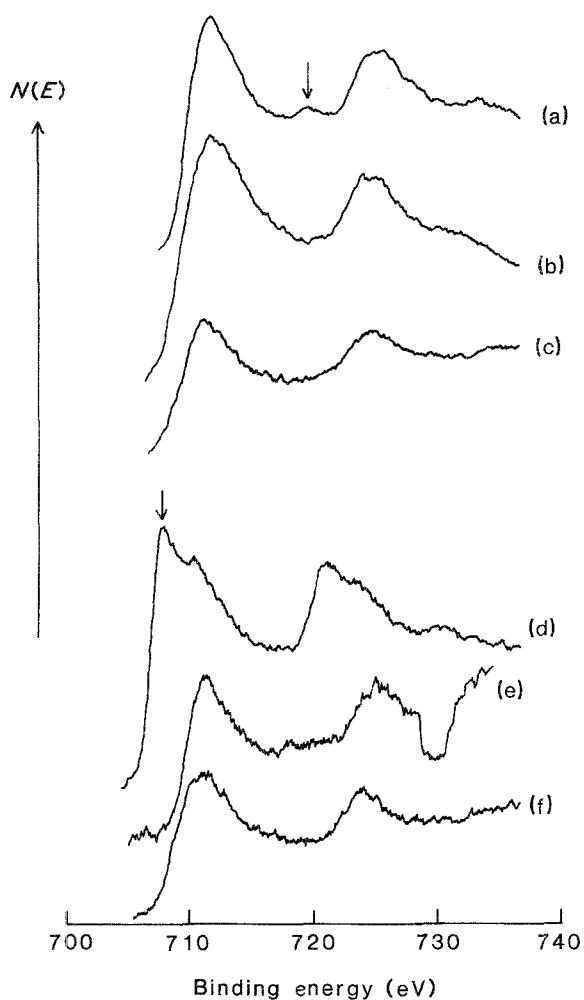


Figure 3 The structure of the Fe 2p X-ray photoelectron peaks from (a) a thin film sputtered in argon from a nickel ferrite cathode (arrow indicates the position of the satellite peak associated with Fe_2O_3), (b) the film in (a) after a 60 sec argon ion etch, (c) a thin film deposited in vacuum using an electron beam source, (d) the film in (c) after 60 sec argon ion etch (arrow indicates the position of the peak associated with uncombined iron), (e) a thin film deposited by chemical vapour deposition, and (f) the film in (e) after a 30 sec argon ion etch.

deposited by chemical vapour deposition. The peak was situated at 710.7 eV, the accepted position for nickel ferrite [11]. Ion etching of these films led to peak broadening (Fig. 3e, f).

Similar effects were also observed with the Ni 2p peaks. The position of the Ni $2p_{3/2}$ peak in X-ray photoelectron spectra from sputtered films indicated the presence on the surface of one or both of the hydroxides, $\text{Ni}(\text{OH})_2$ and $\text{NiO}(\text{OH})$ (Fig. 4a), and for films prepared by sputtering from an Invar alloy cathode in argon the complex structure of this peak indicated the presence also of NiO and higher oxides of nickel such as Ni_2O_3 . When each of these sputtered films was argon-ion etched the structure of the Ni $2p_{3/2}$ peak was modified in a similar manner to the Fe $2p_{3/2}$ peak. The peak was split with the appearance of a component at lower binding energy (Fig. 4b). This lower binding energy peak is probably the Ni $2p_{3/2}$ peak associated with pure nickel [13] and is probably produced by reduction of the sputtered ferrite films in the argon ion beam. For films sputtered in argon it is likely, as demonstrated from electron diffraction,

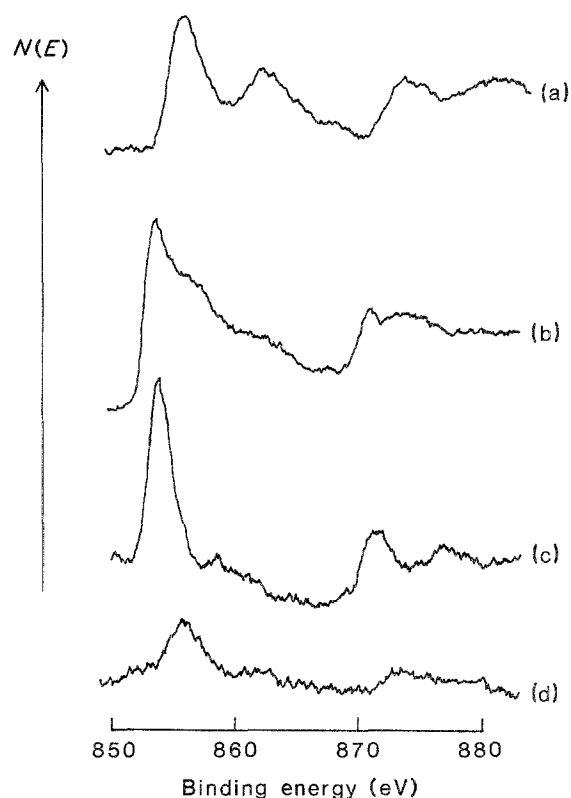


Figure 4 The structure of the Ni 2p X-ray photoelectron peaks from (a) a film sputtered in argon from a nickel ferrite cathode, (b) the film in (a) after a 300 sec argon ion etch, (c) a film vacuum deposited using an electron beam source followed by an argon ion etch of 180 sec, and (d) a film prepared by chemical vapour deposition followed by a 30 sec argon ion etch.

that some uncombined nickel metal exists below the surface.

In films prepared by evaporation from the electron beam source the Ni $2p_{3/2}$ peak was found to have a low intensity, however, after a light argon ion etch, a more intense peak was obtained that was situated at the position of this peak in nickel metal (Fig. 4c) [13].

Films prepared by chemical vapour deposition before ion etching also had a low intensity. After a light argon ion etch a more intense Ni $2p_{3/2}$ was obtained (Fig. 4d) that was situated at the position of this peak in nickel ferrite [13]. In addition to oxygen, iron and nickel photoelectron peaks, magnesium photoelectron peaks were also obtained from the surface of films prepared by chemical vapour deposition.

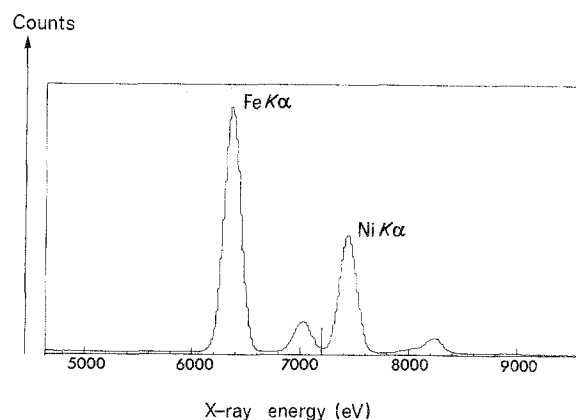


Figure 5 Energy dispersive X-ray microanalysis spectrum obtained in the transmission electron microscope from a thin film prepared by sputtering from a nickel ferrite cathode in oxygen.

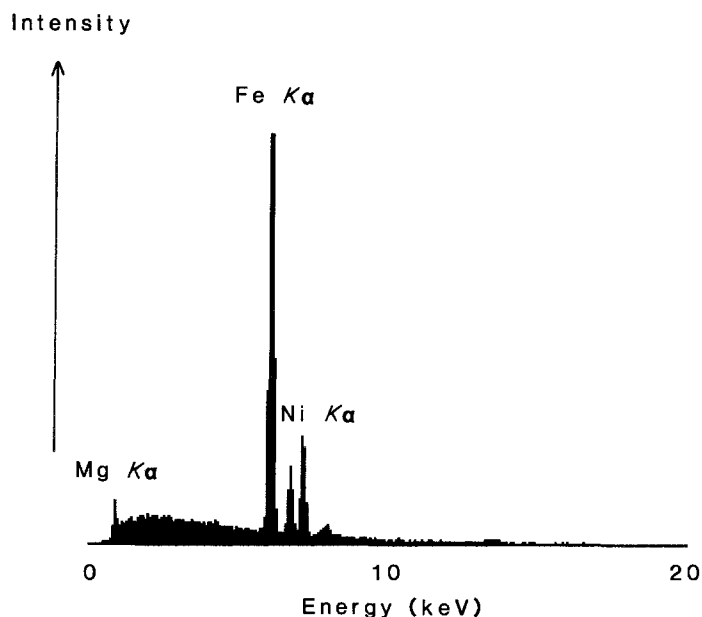


Figure 6 Energy dispersive X-ray microanalysis spectrum obtained in the scanning electron microscope from a film prepared by chemical vapour deposition.

5. X-ray microanalysis

Energy dispersive X-ray (EDX) microanalysis studies in the transmission electron microscope, from sputtered films identified by electron diffraction as nickel ferrite, indicated that the nickel:iron atomic ratio in each film was 1:2 as expected (Fig. 5). Thin films of Invar alloy evaporated using the electron beam source were also found to have a nickel:iron ratio of 1:2. Films sputtered from the Invar alloy cathode in argon were found in some cases to be nickel rich.

EDX spectra have been obtained in the SEM and in the TEM from films prepared by chemical vapour deposition. These spectra were found to contain magnesium peaks (Fig. 6). In previous investigations the appearance of these peaks had been attributed to a contribution from the underlying magnesium oxide substrate [6]. In some instances, dependent upon the

chemical vapour deposition conditions, the nickel and magnesium content of the films were observed to vary with position in the film.

6. Transmission electron microscopy

Previous transmission electron microscope studies of nickel ferrite films grown by chemical vapour deposition on magnesium oxide substrates [9] have shown that extensive arrays of stacking faults occur in these films (Fig. 7). These faults have been found to lie on (110) type planes with $1/4 [110]$ type fault vectors. It

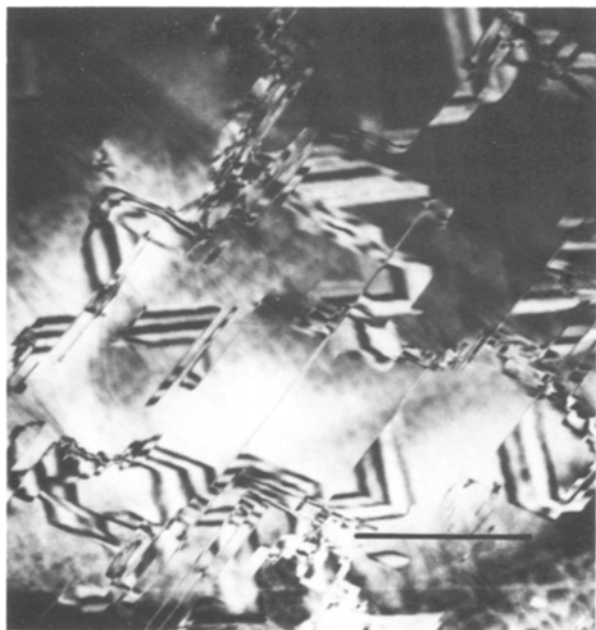


Figure 7 Electron diffraction contrast from stacking faults on (110) planes in films prepared by chemical vapour deposition. The micrograph was recorded at 100 keV accelerating voltage in the transmission electron microscope. Scale bar, $0.3 \mu\text{m}$.

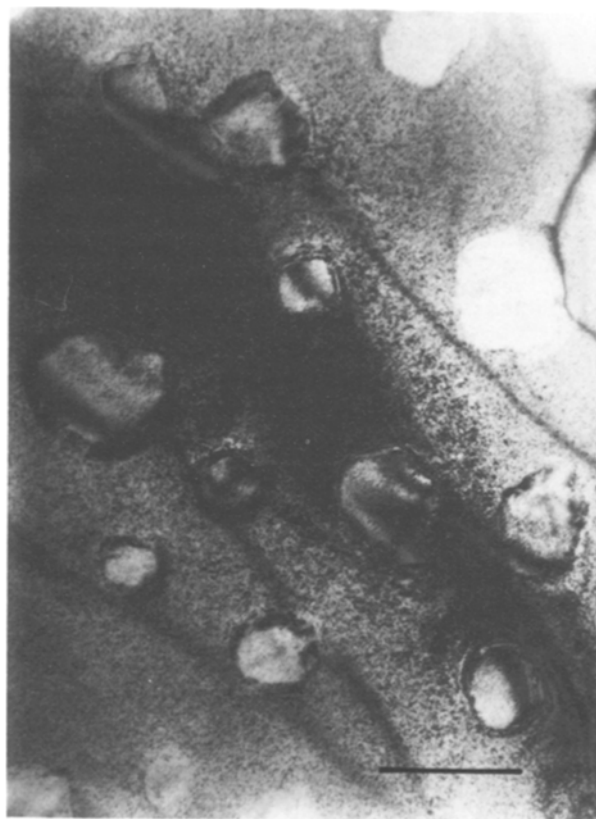


Figure 8 Electron diffraction contrast from ferrite precipitates in films prepared by chemical vapour deposition. The micrograph was recorded at 750 keV accelerating voltage in the transmission electron microscope. Scale bar, $1 \mu\text{m}$.

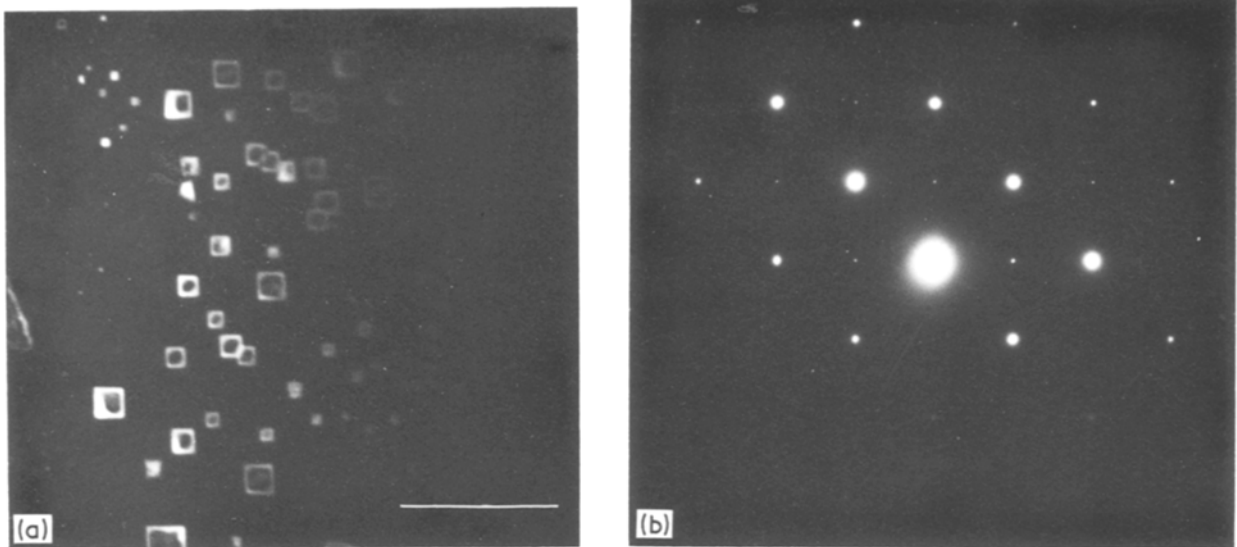


Figure 9 (a) Dark field electron micrograph of ferrite precipitates in a magnesium oxide single crystal obtained using a (2 2 0) ferrite reflection. The material was prepared by oxidizing an Invar alloy film deposited on the magnesium oxide. Scale bar, 0.2 μm . (b) Electron diffraction pattern from the area shown in (a); the fainter spots are associated with the ferrite inclusions. The electron diffraction pattern indicates that MgO and ferrite inclusions are in the (1 0 0) orientation.

has also been found that the composition of these nickel ferrite films is dependent on growth conditions. Under certain conditions high voltage transmission electron microscope observations (Fig. 8) and energy dispersive X-ray microanalysis measurements show areas where the ferrite crystal structure has intergrown with nickel oxide [15].

Films prepared by sputtering from NiFe_2O_4 and Invar alloy cathodes onto single crystal MgO substrates, and films deposited in vacuum onto these substrates using an electron beam source, have been examined after annealing in air at 1000°C. Observations of the oxidized Invar alloy films on MgO confirm earlier studies [16]. Small inclusions with the ferrite crystal structure (Fig. 9) are observed in the magnesium oxide matrix.

7. Auger electron spectroscopy

Auger electron spectra have been obtained from NiFe_2 films oxidized on the single crystal magnesium oxide substrate. Fig. 10 shows Auger electron spectra obtained before and after oxidation. The nickel, iron and oxygen present on the surface before oxidation were found to be replaced by magnesium and oxygen with traces of iron. The Auger spectra obtained from the unoxidized surface prior to argon ion etching confirm XPS observations: the concentration of nickel on the surface is lower than in the bulk of the film. Similar results have been obtained from sputtered films when oxidized (Fig. 11).

These observations suggest that there is considerable diffusion of the constituents of a nickel ferrite film into the magnesium oxide substrate at high oxidation temperatures. Chemical vapour deposition of ferrite films onto magnesium oxide substrates occurs at temperatures greater than 1000°C and it is likely that similar diffusion effects occur during deposition. Fig. 12 shows a series of Auger electron spectra obtained from a nickel ferrite film prepared by chemi-

cal vapour deposition after argon ion etching for increased periods of time. It is clear that magnesium is detected with nickel, iron and oxygen on the surface of the film and is present, with these elements, through the complete film.

8. Conclusions

The nature of the oxides formed on the surface of films prepared by sputtering, chemical vapour deposition and by vacuum deposition using an electron beam source has been examined by X-ray photoelectron

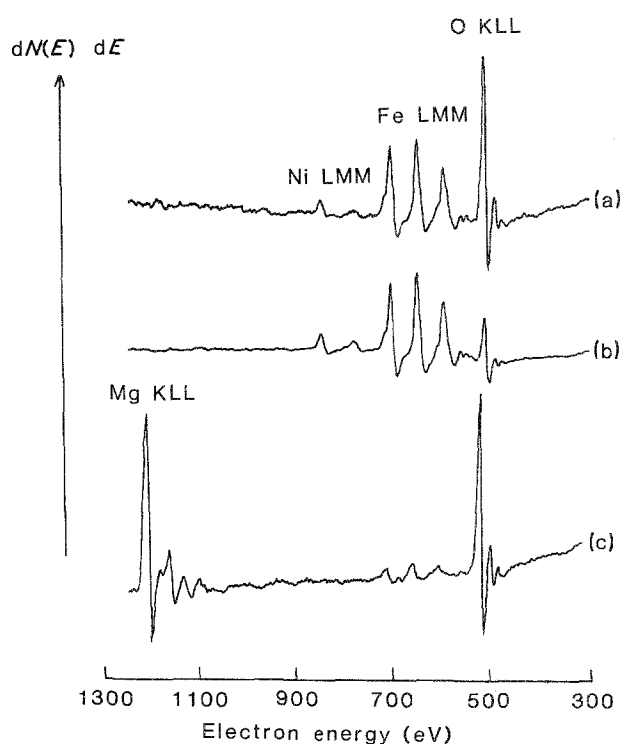


Figure 10 Auger electron spectra obtained from an Invar alloy film deposited using an electron beam source onto single crystal magnesium oxide (a) immediately after deposition, (b) after argon ion etching for 30 sec and (c) after annealing for 24 h at 1000°C.

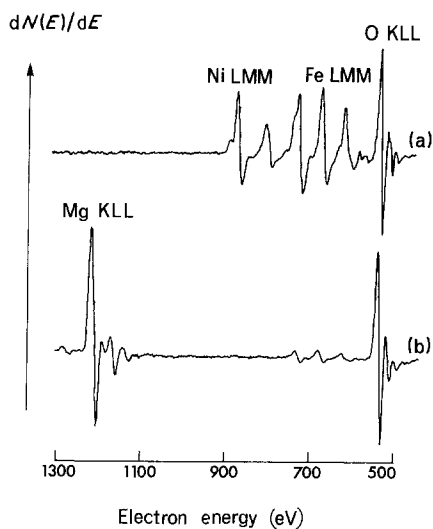


Figure 11 Auger electron spectra obtained from a film sputtered in argon from a nickel ferrite cathode and deposited onto single crystal magnesium oxide (a) immediately after deposition and (b) after annealing for 24 h at 1000°C.

spectroscopy. Chemical vapour deposited films have been identified as nickel ferrite films with traces of magnesium. Films sputtered from a nickel ferrite cathode prior to annealing in air have been found to contain a variety of oxides and hydroxides on the surface. For films sputtered from the Invar alloy cathode in argon, and films prepared by electron beam evaporation from this material, a light argon ion etch reveals the existence of unoxidized iron and nickel below the surface. The oxides and hydroxides detected on the surface of argon sputtered films and vacuum deposited films probably occurs mainly on contact with the atmosphere. However, calculation of the likely partial pressure of oxygen during the deposition process suggests, especially during sputtering, that a good proportion of oxygen is incorporated during deposition.

Electron microscopy and electron diffraction studies confirm these results. Chemical vapour deposited films have been identified as having the ferrite crystal structure and are found to grow epitaxially on the MgO substrate. Apart from films sputtered in argon from an Invar alloy cathode the sputtered films before annealing in air have been identified as having the ferrite crystal structure.

Energy dispersive X-ray microanalysis has confirmed that the Ni:Fe atomic ratio is 2:1 for sputtered and electron beam deposited films apart from the Invar alloy films sputtered in argon, where films were found to be nickel rich. EDX spectra obtained from chemical vapour deposited films were found to contain magnesium peaks. The composition distribution with depth in these chemical vapour deposited films has been studied by Auger electron spectroscopy in conjunction with argon ion etching. It is found that magnesium is distributed uniformly through the films.

Auger spectra obtained from sputtered films and electron beam deposited films after annealing in air show that nickel and iron diffuse into the magnesium oxide substrate. These observations are supported by transmission electron microscope observations of

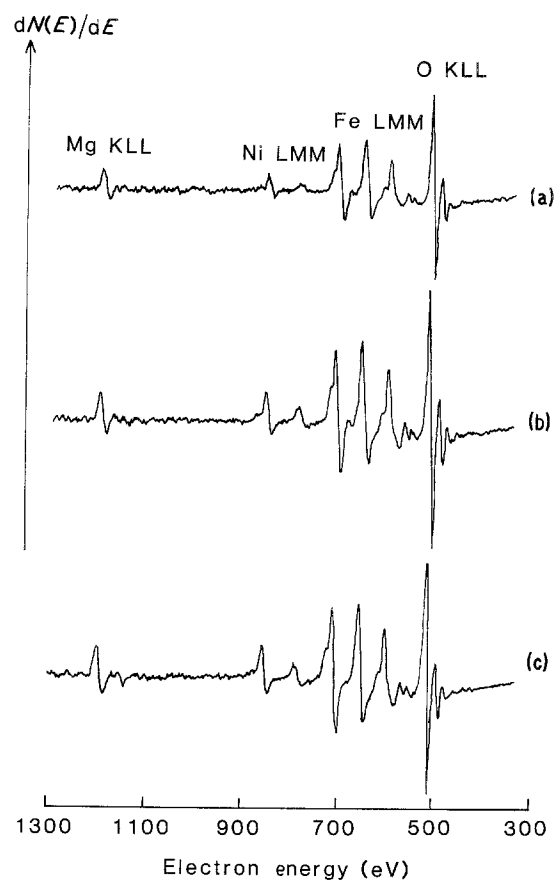


Figure 12 Auger electron spectra obtained from a film prepared by chemical vapour deposition, as-deposited and after argon ion etching for the periods of time indicated. $t =$ (a) 0 sec; (b) 30 sec; (c) 259 min.

oxidized films on magnesium oxide. Ferrite inclusions have been detected.

It is clear that there is considerable interdiffusion between nickel ferrite films and magnesium oxide substrates when these films are deposited or annealed at high temperatures. These effects must be taken into account in any thin film device applications of ferrite films.

It is likely that the incorporation of magnesium from the substrate in chemically deposited nickel ferrite films leads to a lower misfit between film and substrate, since magnesium ferrite has a slightly larger lattice parameter than nickel ferrite. Magnesium ferrite also has a thermal expansion coefficient that is closer in magnitude to that of the magnesium oxide substrate [17]. It is probable that the incorporation of magnesium in nickel ferrite films is conducive to the growth of films with a lower misfit and therefore lower strain on the magnesium oxide substrate by comparison with pure nickel ferrite films.

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