CHAPTER FIVE

BUFFER LAYERS

This chapter describes the development of three types of buffer layers on the Ni-based substrates detailed in chapter 4. The deposition of metallic buffers based on Pd and Ag is discussed and modelled and the properties of such layers are investigated. Then the development of a native cube-textured oxide layer on NiFe substrates by a novel two-stage process is outlined. Finally, the properties of CeO$_2$ and YSZ deposited on both the bare Ni-based substrates and native oxide buffers is reported.

5.1 Metallic Buffer Layers

5.1.1 Deposition of silver

Silver was deposited onto (100) Ni films by sputtering at temperatures ranging from 150°C to 300°C. Because of the high mobility of silver, this relatively low temperature is thought to be sufficient to establish a favourable epitaxial relationship. As with the Ni films, the initial deposition rate of silver is slow (around 0.3 nm/min) in order to allow time for the depositing atoms to arrange themselves on the substrate surface.

In all experiments, the preferred orientation of the Ag layer was found to be (111). The fact that this is epitaxial growth, i.e. determined directly by the crystallography of the underlying substrate rather than just an anisotropic growth mode which favours (111) growth, is demonstrated by figure 5.1, which is a $\phi$ scan showing the positions of the (200) poles of Ag at $\psi=55^\circ$. 
Epitaxy is achieved through matching of the (111) plane of Ag, which has 3-fold symmetry with the (100) plane of Ni, having 4-fold symmetry. The positions of the twelve (200) poles in the $\phi$ scan show that the $<110>$ directions of Ni are parallel to the $<110>$ directions of Ag, leading to four different in-plane orientations. Deposition of Ag onto cube textured NiFe tape under similar conditions produces the same (111) texture in the Ag as demonstrated by the $\theta$-$2\theta$ scan of figure 5.2.
The fact that the (100) orientation of Ag on either (100) Ni or (100) NiFe is not favourable is to be expected if one considers the lattice matching. The mismatch, defined as \(2(a_1-a_2)/(a_1+a_2)\) between Ag and 4 other FCC metals, Ni, NiFe, Pd and Pt is shown in table 5.1. It would appear that to achieve cube textured growth in the Ag layer, the deposition of a layer such as Pt or Pd, with an intermediate lattice parameter would be favourable.

<table>
<thead>
<tr>
<th>Lattice Parameter (Å)</th>
<th>Mismatch with Ag (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>3.52</td>
</tr>
<tr>
<td>NiFe</td>
<td>3.58</td>
</tr>
<tr>
<td>Pd</td>
<td>3.89</td>
</tr>
<tr>
<td>Pt</td>
<td>3.92</td>
</tr>
</tbody>
</table>

### 5.1.2 Palladium/Silver

The \{100\} nature of Pd and Ag films deposited on Ni is demonstrated in figure 5.3. Only peaks of type \{h00\} are apparent in each of the layers deposited and the excellent texture is confirmed by the rocking curves, though these do show a small deterioration in the out-of-plane alignment of subsequent layers. However, the FWHM of the Ag layer is still less than \(2^\circ\), and also \(\phi\) scans produce curves whose width is determined by the resolution of the machine (around \(1.8^\circ\)) confirming that good in-plane alignment is also produced.

![Fig. 5.3. a) \(\theta-2\theta\) scan of a MgO/Ni/Pd/Ag sample, with (h00) peaks only, b) (200) rocking curves of i) Ni, ii) Pd and iii) Ag showing slight broadening in subsequent layers.](image)

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Figure 5.4a demonstrates that the cube texture in Pd and Ag is also produced when they are deposited onto NiFe tape. However in this case, there is a clear improvement in the texture for both the Pd and Ag layers which is also seen in the \{111\} pole figures, shown in figure 5.5. A further feature of figure 5.4b is that the rocking curves for Pd and Ag are smoother than that of NiFe due to the smaller grain size.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_4.png}
\caption{a) $\theta$-2$\theta$ scan of a NiFe/Pd/Ag sample, demonstrating that again only (h00) peaks are present. b) (200) rocking curves of i) NiFe, ii) Pd and iii) Ag showing improving alignment in each layer}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_5.png}
\caption{$\{111\}$ pole figures of a) NiFe tape b) Pd layer and c) Ag layer}
\end{figure}
Table 5.2 FWHM of \{111\} poles in the metallic layers
(corrected for instrumental broadening)

<table>
<thead>
<tr>
<th></th>
<th>Single crystal substrate</th>
<th>Polycrystalline substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta\psi(\degree)$</td>
<td>$\delta\phi(\degree)$</td>
</tr>
<tr>
<td>Ni/NiFe</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Pd</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Ag</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Results obtained from EBSD measurements also demonstrate the significant improvement in texture when Pd and Ag are deposited on NiFe. By comparison with the EBSD measurements of the NiFe substrate detailed in section 4.2, the Ag layer can be seen to have a much better degree of alignment. Figure 5.6 shows that most boundaries are the lightly shaded 2°-4° type and there are very few at angles above 10°. Boundaries of 1° or less are not shown in the maps due to the fact that they become confused with the noise arising from the uncertainty in angular measurements of neighbouring pixels within the same grain. Figure 5.7 shows that in the Ag layer, there is now percolation through the measured region below an angle of 4°.

![Figure 5.6 a) Grain boundary misorientation map of an area of the Ag buffer layer, and b) corresponding histogram showing the frequency of grain boundaries up to 15°](image-url)
The EBSD measurements also give a good indication of the grain size of the samples if one examines a low angle percolation map. In this case an estimate may be obtained from the 2° map, where many grains have an area of only a few pixels. It is thus apparent from that the grain size in the Ag film is significantly smaller than that in the NiFe tape, confirming the result indicated by X-Ray measurements.

There is a clear difference in the development of texture on the different Ni based surfaces. The degree of alignment becomes progressively poorer for films on the single crystal, but improves significantly for both Pd and Ag deposited onto the rolled textured tapes. For the Pd layer, this could be explained by the better matching with NiFe, which has a larger lattice parameter than Ni. However, the Ag is in both cases deposited onto a Pd layer with $a=3.89$ Å and thus it is more likely that there is some other explanation, possibly that there is an equilibrium level of texture for growth of the films under these conditions. It should be noted that the significant change in texture is in the out-of-plane component with the changes in $\delta\phi$ accounted for by this alone. Thus it is possible that for films deposited onto NiFe tape, the lower surface energy involved in having (100) planes parallel to the tape surface favours the better oriented grains and the texture improves. This is limited by the fact that depositing atoms have a finite time to rearrange on the substrate surface and thus an initially perfect texture may worsen. The significance is that this implies that producing a very well textured substrate may be a wasted effort if the deposition process leads to poorer alignment in the buffers.
The conditions under which the films are deposited are also extremely important in determining the texture of a thin film. It is found that if the Ag deposition temperature is increased to 300°C, it grows with an additional in-plane orientation, rotated by approximately 18.5° relative to the cube texture, which may be described as {001} Ag // {001} Pd, <100> Ag // <310> Pd. This occurs when Ag is deposited onto Pd on NiFe, as shown in figure 5.8 and also on Pd on thin film Ni.

![Figure 5.8](image)

*Figure 5.8 {111} pole figure of Ag deposited on Pd at 300°C, showing a second in-plane orientation rotated by approximately 18.5°.*

### 5.1.3 Diffusion of metallic buffer layers

A potential problem with a metallic buffer layer system such as Ni/Pd/Ag is that there may be significant inter-diffusion at the elevated temperatures at which the superconductor is deposited. As demonstrated by figure 5.9, there is complete solid solution across the composition range for both the Ni-Pd and Pd-Ag binary systems, which makes it rather likely that the three layers will be able to inter-diffuse with atoms of varying sizes being accommodated in the FCC crystal structure.
Figure 5.9 Phase diagrams of the Ni-Pd and Ag-Pd systems showing complete solid solubility across the composition range [224].

Two NiFe tapes, each coated with a (100) Pd layer approximately 20 nm thick and a (100) Ag layer approximately 200 nm thick were annealed in vacuum at temperatures of 550°C and 650°C in order to assess the inter-diffusion of the films and substrate. Figure 5.10 shows an X-Ray θ-2θ scan of the as-deposited film (a) and the results of annealing at 550°C (b) and 650°C (c).

Figure 5.10 X-Ray θ-2θ scans of Ag deposited onto NiFe tape with a thin intermediate Pd layer a) as deposited b) after annealing at 550°C for 15 minutes and c) after annealing at 650°C for 15 minutes.
After annealing at 550°C for 15 minutes as shown in (b), the intensity of the silver peak is obviously decreased and the Pd peak which can only just be identified in the as-deposited trace has disappeared completely, indicating that some inter-diffusion has occurred. Much more information may be extracted by examining the peak profiles and positions. The (200) NiFe peak clearly develops a shoulder on the low angle side, which indicates that some Pd and/or Ag has diffused into the tape. Also the (200) Ag peak has moved to a slightly higher angle, indicating that Ni has diffused into the film. Thus after diffusion there are probably three regions, the Ag film which contains Ni, Fe and Pd in solution, a NiFe-rich region with some Ag and Pd in solution and at a greater depth the original NiFe.

The average lattice parameters of these layers can be calculated from the X-Ray peak positions and using Vegard’s law (which predicts that the lattice parameter of a solid solution changes linearly with composition) we can estimate the composition of the regions, as detailed in table 5.3. Note that as the Pd layer is quite thin, and in order to simplify the analysis, the effect of Pd has not been considered.

<table>
<thead>
<tr>
<th>Lattice parameter (Å)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe</td>
<td>3.58 NiFe</td>
</tr>
<tr>
<td>Ag (initial position)</td>
<td>4.07 Ag</td>
</tr>
<tr>
<td>NiFe (shoulder)</td>
<td>3.65 NiFe - 14%Ag</td>
</tr>
<tr>
<td>Ag (shifted position)</td>
<td>4.03 Ag - 8%NiFe</td>
</tr>
</tbody>
</table>

The amount of Ag remaining on the surface of the tape as a function of annealing time at the two temperatures is indicated in figure 5.11. The presence of silver is measured by the intensity of its X-Ray peak and therefore whilst this may not necessarily be an accurate measure of the layer’s thickness, it is still a useful qualitative estimate of its presence.
At 550°C, the Ag appears to diffuse into the substrate approximately linearly with time and a reasonable amount still remains after an hour. At a higher temperature, the process is much quicker, which is clearly problematic for the practical use of such buffer layers. At 650°C, a 200 nm thick layer completely diffuses into the substrate in less than 15 minutes and although the situation is much better at 550°C, the shifting of the Ag X-Ray peak seen in figure 5.10b) suggests that Ni may have diffused to the surface, reaching the solid solubility limit in the first 15 minutes.

There are two ways in which this problem may be addressed. A very thick Ag layer could be used and indeed a 2 µm thick film has been deposited without any loss of texture, but as this is done by sputtering, the deposition takes several hours and would be impractical for large scale tape production. Alternatively as Pd probably plays a role in facilitating the easy inter-diffusion of the layers due to its intermediate lattice parameter, if just a few atomic layers of Pd were used, the diffusion rate may be slowed. It has recently emerged that the Pd layer may in fact not be necessary to obtain the cube texture and if this is the case, its elimination may help [181].
5.1.4 Modelling epitaxial growth

The mechanisms underlying epitaxial growth are not generally well understood, though a simple prediction of whether growth in a particular orientation is likely is often made by considering lattice parameter match. As previously discussed, since Ni, Pd and Ag all have the same FCC structure, “square on square” (100) growth is expected if the lattice parameter mismatch is small enough that the strain produced at the interface is not too large.

However, for growth in other orientations, or when the two materials are not isostructural, some other model of matching is needed. Lattice match must involve low interface strains, though this may not be possible for the most simple lattice configurations, which have all or a large fraction of lattice sites matching across the boundary. It may be that through some relative rotation of the lattices in the plane of the interface, a configuration can be found that introduces a lower strain though this will in general cause some atoms, which are not matching, to lie in high energy sites. Therefore, these lower strain configurations are most likely to be seen if they have a high fraction of near-matching sites. This approach is known as the near coincidence site lattice (NCSL) model [186, 225].

A model has been developed [226] to find possible low energy in-plane orientations of an epitaxial film on a single crystal by examining the two-dimensional lattice of each material in the plane of the interface. Two criteria are used in finding good matches, that a large fraction of sites are matching and also that the strain required to bring the lattices into perfect coincidence is small. In the model, a non-primitive cell with lattice points at each corner, and with basis vectors \( \mathbf{A} \) and \( \mathbf{B} \), which are linear combinations of the primitive unit cell vectors (\( \mathbf{a} \) and \( \mathbf{b} \)) is identified for the substrate such that \( \mathbf{A} = k \mathbf{a} + l \mathbf{b} \) and \( \mathbf{B} = p \mathbf{a} + q \mathbf{b} \). For the film, a cell will have \( \mathbf{C} = m \mathbf{c} + n \mathbf{d} \) and \( \mathbf{D} = r \mathbf{c} + s \mathbf{d} \). A large number of these non-primitive cells may be examined in the lattices of the film and substrate materials and the matching between them assessed. In order to consider whether two cells match well, the parameters calculated are the linear strains along each cell edge, \( \varepsilon_1 \) and \( \varepsilon_2 \) and also the angular strain, \( \gamma \). Also, the inverse of the fraction of matching sites is calculated - this is referred to as \( \sigma \) and is calculated for each lattice.
All cells generated with \( k,l,m,n,p,q,r,s \) running independently from -4 to +4 have been compared and for each, the strains involved in cell matching and the fraction of coincidence sites calculated. NCSL matches are described by the relative orientation of the two lattices (\( \alpha \)). The criteria which have been used in assessing lattice match are that the cells must have linear strain not exceeding 10\% and angular strain not more than 5\%. Also, at least 10\% of sites must be matching in both the film and substrate lattices i.e. \( \sigma_f, \sigma_s \leq 10 \).

The (111) growth mode of Ag on Ni indicates that the configuration of atomic positions at the interface is that shown in figure 5.12. Table 5.4 shows the results generated by the model for growth of Ag on (100) Ni, demonstrating that there are no very low strain or fully matching orientations for (100) growth. There are also no configurations for (111) growth which exhibit both low strain and good matching, but the orientation observed in the deposited film at \( \alpha=15^\circ \) does at least correspond to a low strain NCSL.

![Figure 5.12 NCSL positions for (111) Ag on (100) Ni. Atoms marked M match exactly.](image)

**Table 5.4 NCSL model results for Ag on (100) Ni**

<table>
<thead>
<tr>
<th>(100)</th>
<th>( \alpha(\circ) )</th>
<th>( \gamma(%) )</th>
<th>( \sigma_f )</th>
<th>( \sigma_s )</th>
<th>( \varepsilon_1(%) )</th>
<th>( \varepsilon_2(%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>8.1</td>
<td>0</td>
<td>4</td>
<td>3</td>
<td>-1.8</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>11.3</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>-1.7</td>
<td>-9.7</td>
</tr>
<tr>
<td></td>
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<td>3</td>
<td>-8.9</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
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<td>5</td>
<td>4</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>33.6</td>
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<td>8</td>
<td>6</td>
<td>-3.8</td>
<td>4.2</td>
</tr>
<tr>
<td>(111)</td>
<td>10.9</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>5.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Ag</td>
<td>11.4</td>
<td>0.8</td>
<td>7</td>
<td>6</td>
<td>-3.8</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>14.7</td>
<td>1.9</td>
<td>6</td>
<td>5</td>
<td>-3.2</td>
<td>0.2</td>
</tr>
<tr>
<td>*</td>
<td>15.0</td>
<td>2</td>
<td>8</td>
<td>7</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>
The difference in lattice parameter between Ni and Pd is somewhat smaller and hence for (100) Pd films on (100) Ni, the straightforward square on square growth, shown in figure 5.13, is more favourable. However this does involve a strain of nearly 10%. Another favourable orientation predicted by the model as detailed in table 5.5 is for $\alpha=26.6^\circ$, though this was not observed in the Pd films, which were deposited at 300°C. It may be that at a different deposition temperature, this would be present.

![Figure 5.13 Atomic matching for Pd on Ni](image)

<table>
<thead>
<tr>
<th>$\alpha$ ($^\circ$)</th>
<th>$\gamma$ (%)</th>
<th>$\sigma_s$</th>
<th>$\sigma_f$</th>
<th>$\varepsilon_1$ (%)</th>
<th>$\varepsilon_2$ (%)</th>
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<tbody>
<tr>
<td>(100) Pd</td>
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<td>1</td>
<td>1</td>
<td>-9.9</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>0</td>
<td>3</td>
<td>4</td>
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</tr>
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<td></td>
<td>* 26.6</td>
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<tr>
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<td>8</td>
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</tr>
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<tr>
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<td>2</td>
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<tr>
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<td>2</td>
<td>-4.5</td>
</tr>
</tbody>
</table>

Ag and Pd also have well matched lattice parameters and so the desired square on square growth mode is again favourable. The two in-plane orientations observed are both predicted by the NCSL model to be of low energy, as outlined in table 5.6. The $\alpha=0^\circ$ orientation corresponds to a complete matching of all the lattice points, but with a significant strain in each direction, whereas the $18.4^\circ$ rotation is one in which the lattices can be matched with only 0.5% strain, though a smaller fraction of the sites are matching. The $\alpha=0^\circ$ orientation is
similar to that for Pd on Ni, shown in figure 5.13, but with slightly less strain, and the \(\alpha = 18.4^\circ\) orientation is shown in figure 5.14.

![Figure 5.14 Atomic matching for Pd on Ag](image)

**Figure 5.14 Atomic matching for Pd on Ag**

<table>
<thead>
<tr>
<th>(\alpha^\circ)</th>
<th>(\gamma)</th>
<th>(\sigma_1)</th>
<th>(\sigma_2)</th>
<th>(\varepsilon_1)</th>
<th>(\varepsilon_2)</th>
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<tr>
<td>(100) Ag</td>
<td>0.0</td>
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<td>1</td>
<td>1</td>
<td>4.7</td>
</tr>
<tr>
<td>* 14.0</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>1.7</td>
<td>7.8</td>
</tr>
<tr>
<td>* 18.4</td>
<td>0</td>
<td>10</td>
<td>9</td>
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</tr>
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<td>-9.7</td>
<td>-4.7</td>
</tr>
</tbody>
</table>

The NCSL model is useful in justifying the in-plane orientations that are observed in epitaxially deposited films but it is difficult to arrive at a method of predicting accurately which in-plane configuration will have the lowest energy. It appears that low strain and a high number of matching sites are both important, though the relative influence of each is unclear. For the isostructural materials studied in this work it is apparent that the configuration with all sites matching is low energy, despite the fact that strains up to 10% may be involved. Also, orientations are seen which indicate that if the strains are very low, then site matching is not then so important. The configurations that exhibit quite low strain (several per cent) and quite good matching \((\sigma = 4)\) seem not to be so favourable. Also the configurations that are unfavourable under a certain set of deposition conditions may become
apparent upon changing the growth temperature. Whilst the model is rather useful, it may not work for materials which have very different structures and different bonding types i.e. metal/ceramic interfaces. More in-depth studies of epitaxy should examine such factors as graphoepitaxy, kinetics and local chemical bonding in order to provide a better estimate of the interfacial energy.

5.2 Surface Oxidation Epitaxy

5.2.1 Introduction
Oxidation of the substrate is usually to be avoided as the oxide which grows is often of an unsuitable orientation or lattice match for deposition of buffer layers. However by controlling the conditions in which the substrate is oxidised it may be possible to produce an adherent epitaxial oxide with the cube texture. Any further buffer layers can then be deposited using an oxidising environment and also substrate oxidation will not be a problem in the superconductor deposition stage. Indeed it may even be the case that if the oxide acts as a diffusion barrier it may remove the requirement for further buffer layers, in which case the surface oxidation epitaxy technique may serve as a fast and inexpensive buffer layer route.

5.2.2 Tape oxidation procedure
In order to systematically study this high temperature oxidation process, a number of tapes were oxidised using O₂ and Ar/O₂ mixtures in a UHV chamber, tapes being heated resistively using a direct current [227]. There are two methods of carrying out the oxidation which turn out to show important differences. One way is to preheat the tape in vacuum, then introduce the Ar/O₂ gas mixture, or alternatively to introduce the required pressure of gas into the chamber, then ramp up the current from zero. The thicknesses of the resulting oxide layers were estimated using two methods. By monitoring the resistance of the tape in-situ, as the oxide is grown, it is possible to calculate the rate at which metal is consumed. Also when the oxide spalls from the surface, an ex-situ method may be used, where the mass of oxide spalled from a tape is measured directly.
As there is a window in the flange used the oxidising tape can be viewed and in principle, the temperature of the tape can be measured using the infra-red pyrometer. When the tape is preheated under vacuum, the emmisivity of the metal is known quite accurately and the temperature of the tape, which glows bright red above around 600°C, can be measured. Upon the introduction of oxygen into the chamber, the surface becomes progressively duller over several seconds (depending on the oxygen pressure). This is associated with a significant increase in emmisivity of the oxide compared with the bare metal and so during this stage the temperature can no longer be measured accurately. Also, as the emmisivity is a function of temperature and has not been widely studied for nickel or iron oxides, there is no reliable way to measure the temperature using the pyrometer during the oxidation. However as the emmisivity of most oxides is above 0.5, it is probably significantly higher than that of bare NiFe. Appendix B shows in detail how this is likely to affect the temperature, but if the emmisivity of the oxide is 0.7, the absolute temperature will fall to about 70% of its original value. This is significant as it suggests that tapes which originally are heated to 900°C may actually undergo most of the oxidation at around 600°C. A number of other pieces of experimental evidence confirm that this temperature decrease does occur. The first is that there is a drop of voltage across the tape when the oxidation begins, indicating a fall in the resistivity of the tape of a few per cent, which is consistent with a drop in temperature. Unfortunately, as the resistivity variation with temperature is not very strong except at low temperatures, this technique cannot be used to accurately measure the temperature. A further piece of evidence is that currents up to 17 A have been passed through the tapes during oxidation. For the bare tape, this would cause secondary recrystallisation and grain growth to occur, but in tapes oxidised under these conditions, no secondary recrystallisation of the NiFe bulk is evident.

In order to make a quantitative measure of the temperature decrease, a tape was oxidised in a different vacuum chamber with a thermocouple attached to the surface. As the heat capacity of the tape is quite low due to the fact that it is very thin, it is likely that the presence of the thermocouple substantially lowered its temperature. However, the measured temperature decreased from 620°C for a bare tape to 500°C for an oxidised tape.
5.2.3 Results

Oxidation experiments were carried out at temperatures between 500°C and 1100°C, in each case preheating the tape before introducing the oxidising atmosphere. Note that the temperature quoted is the initial temperature of the bare NiFe tape, and will be reduced when the surface is oxidised. Below around 950°C a continuous oxide is grown, which is dark grey in appearance at sufficient thicknesses. At higher temperatures however, macroscopic oxide grains become visible on the surface due to secondary recrystallisation and abnormal grain growth.

Figure 5.15 shows X-Ray θ-2θ traces for the bare NiFe substrate and a typical sample oxidised at around 850°C for 60 minutes. The peaks may be indexed as labelled, with the systematic absences indicating that the oxide is cubic and the lattice parameter is calculated as $a=(8.352\pm0.010)$ Å. The important thing to note about the texture of the oxide is that it is a combination of (100) and (111), rather than being randomly oriented. The (311) and (440) peaks which should have high intensities in the powder pattern do not appear in the θ-2θ scan.

*Figure 5.15 a) X-Ray θ-2θ trace showing that oxidation of the NiFe leads to the formation of a mixed (100) and (111) oxide. The ratio in which these textures are present as a function of temperature is shown in b).*
Table 5.7 Candidate oxides of Ni and Fe.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Lattice type</th>
<th>Lattice parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>Cubic – P</td>
<td>8.350 Å</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Cubic – F</td>
<td>8.396 Å</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>Cubic – F</td>
<td>8.339 Å</td>
</tr>
</tbody>
</table>

The oxides detailed in table 5.7 are the possible candidates and whilst Fe₂O₃ has the best match in terms of lattice parameter, the fact that no (110) reflection can be detected at 45° to the surface indicates a face-centred structure. It is therefore likely that the oxide is neither entirely NiFe₂O₄ nor Fe₃O₄, but has some intermediate composition, best described as (NiₓFe₁₋ₓ)²⁺Fe³⁺₂O₄. This oxide has the structure known as spinel, each unit cell consisting of 32 oxygen atoms, 16 Fe³⁺ in octahedral interstices and 8 Ni²⁺ or Fe²⁺ atoms in tetrahedral interstices as shown in figure 5.16.

A further feature of figure 5.15a) is the fact that after oxidation, a large shoulder is produced on the high angle side of the (200) NiFe peak. This indicates that there is an excess of Ni over Fe in the remaining alloy, consistent with the formation of the iron-rich oxide detailed above. Figure 5.15b) demonstrates that although a mixed (111) and (100) layer is usually evident, the degree of (100) nature varies with temperature, with no (100) oriented material at low temperatures, a maximum around 800°C, and then less at higher temperatures.
The oxidation of nickel-iron alloys is reasonably well documented. Scully [229] reports that for any alloy of two metals with differing affinities for oxygen, the one with lower oxygen affinity, in this case Ni, tends to concentrate at the oxide/metal interface. A series of iron oxides is formed with nickel cations substituted in them and any nickel oxide that forms either in the film or at the interface will be reduced by the iron. This results in a matrix of iron oxide containing nickel cations with small islands of nickel and a metal layer at the interface rich in nickel. A section of the ternary phase diagram at 1000°C is shown in figure 5.17 which shows how a series of different oxides may be formed depending on the relative amounts of the two metals.

For oxidation of a Ni_{42}Fe_{58} alloy Foley et al. [231] found evidence of Fe_{2}O_{3} and ferrite (which includes NiFe_{2}O_{4} and Fe_{3}O_{4}), but not FeO (Wustite). The Fe_{2}O_{3} is the outer layer, but is likely to be quite thin as electron diffraction (beam penetration \approx 25 \text{ nm}) also identified the spinel oxide. Brabers et al. [232] found an FeO layer when oxidising Ni_{36}Fe_{64} sample oxidised at 1100°C, but as oxidation progressed and the alloy became richer in Ni, its presence was no longer observed. It seems clear from the phase diagram of 5.17 and the literature that the partial pressure of oxygen will be crucial in determining whether the FeO phase is observed. Greco et al. [233] have studied oxidation of a (100) single crystal of a
Chapter Five  Buffer Layers

Ni$_{50}$Fe$_{41}$ alloy. They observed that the initial layer, with an interplanar spacing consistent with Fe$_2$O$_4$, grew with a (111) orientation, which agrees well with the observations of this work.

Other experiments have also been carried out using slightly different conditions. One variation is to fill the vacuum chamber with the oxidising gas before passing the heating current through the tape. This change in initial oxidation conditions results in very different oxide films for an otherwise identical oxidation process. The most striking difference is the physical appearance of the film. Instead of being dark grey in colour, these oxides are reddish brown but the θ-2θ scans show that the oxide phase is still the nickel-ferrite spinel. The main difference is that the oxide is polycrystalline in nature, the (311) and (440) reflections now appearing in the trace as shown in figure 5.18. As the only difference in the oxidation conditions for this film is the initial oxidation temperature as the temperature is ramped up, the conclusion is that polycrystalline oxides are favoured at low temperatures. This was confirmed by performing an oxidation at a temperature of just 500°C. The tape has the same appearance and as can be seen in figure 5.18 has a polycrystalline texture. The figure also shows an example of a tape oxidised at a relatively low pressure, which also has evidence of the (311) and (440) peaks indicative of random textured growth.

![Figure 5.18 The effect of oxidising at a lower temperature or O$_2$ partial pressure](image)

*Figure 5.18 The effect of oxidising at a lower temperature or O$_2$ partial pressure*
One other experiment carried out was to oxidise the tapes in air using similar heating currents to those used previously. The temperatures are likely to be significantly lower due to cooling by convection and the experiment has only been carried out with the temperature being ramped up with the oxidising gas (air) present. The resulting oxide is significantly different from those obtained in controlled atmospheres, with a significant (polycrystalline) Fe₂O₃ phase being evident as shown by the peaks at 33.2° and 49.5° in figure 5.19. The much higher oxygen partial pressure is consistent with the formation of the phase with the higher oxygen content as indicated in the phase diagram of figure 5.17.

![Figure 5.19 Comparison between tapes oxidised in air and a controlled atmosphere. Lines mark the positions of the peaks of the spinel phase.](image)

5.2.4 Spalling and re-oxidation

The fact that a layered structure is produced by high temperature oxidation, rather than a single continuous oxide seems to be very important. In addition to the layers varying in oxygen stoichiometry, it is possible that they also vary in crystallographic texture. Hence it may be that the mixed (100) and (111) texture seen in a goniometer scan such as that of figure 5.15 represent the orientations of different layers. Evidence of this is that tapes from which the oxide has visibly spalled show much larger proportions of the (100) texture.
In order to study this, a sample was intentionally made to spall after the oxidation. This is done by rapidly quenching the oxidising tape by turning off the heating current suddenly. Complete spalling happens reliably only if the oxide layer is sufficiently thick, which is probably associated with the elastic strain produced in the film due to the large volume change. As the oxide spalls in large pieces, it is possible to X-Ray both the oxide flakes and the underlying tape. These θ-2θ scans are shown in figure 5.20 and clearly show that the oxide which was removed has a (111) texture whilst the remaining tape is covered with an oxide which is (100) oriented.

![Graph showing X-ray diffraction patterns](image)

*Fig. 5.20 The (111) oxide (c) may be completely removed from the oxidised tape (a) to leave behind a NiFe tape which has a cube textured oxide layer (b).*

Figure 5.21 shows how the resistance changes during a typical tape oxidation, at 800°C. The initial fall is attributed to a fall in temperature as the emissivity increases. Subsequently as the resistivity of the oxide is much larger than that of the metal, we can assume that the increase in resistance represents loss of metal.
Figure 5.21 The change in electrical resistance of the tape as the oxidation progresses

The data has been plotted in figure 5.22 to indicate the oxide thickness as a function of time. Note that as shown in table 5.8, the volume of oxide produced by a given amount of metal is more than double the original volume. Hence the oxidation of 1 µm of metal produces an oxide layer more than 2 µm thick.

Figure 5.22 Oxide thickness vs oxidation time

The growth rate of an oxide layer is often such that the square of the thickness is proportional to the time. Whilst figure 5.22 does not exactly match this relationship, it is qualitatively similar with the oxidation rate gradually decreasing as the layer thickens. The $t^2$ dependence arises in situations where the oxidation rate is controlled by diffusion processes and has been observed in other NiFe oxidation experiments. In this case, there are probably 2 diffusion processes occurring. Assuming that the reaction between Fe and O occurs at the metal-oxide interface, Fe has to diffuse through the Ni rich region just below the surface and O has to
diffuse through the oxide layer. The slowest of these two processes will determine the overall oxidation rate and it may be that this changes during the oxidation process.

The mass spalled from 3 tapes oxidised together under the same conditions was measured as 
(0.007 ± 0.001) g. Using the density values of table 5.8 results in an estimate of (400 ± 100) nm for the film thickness after 40 minutes. The most likely reason that this is significantly different from that predicted by the resistance measurements is that the spalled layer does not represent the entire thickness of the oxide, although from X-Ray measurements and optical microscopy, it appears that the oxide which remains on the tape surface is rather thin.

| Table 5.8 Properties of NiFe and its spinel oxides |
|--------------------------------------|----------|----------|----------|----------|----------|
| NiFe       | 3.590    | 46.3     | 229      | 8280     | 11.6     |
| Fe₃O₄      | 8.396    | 580      | 1852     | 5230     | 24.2     |
| NiFe₂O₄    | 8.339    | 592      | 1875     | 5400     | 24.7     |

This fact that a thin (100) layer remains on the surface may be utilised to consistently produce cube textured oxides on the surface of the NiFe tape. If the tapes are further oxidised they maintain the cube texture, and the rocking curve of figure 5.23 demonstrates the excellent alignment.

![Figure 5.23](image)  
*Figure 5.23 {400} rocking curve showing excellent alignment after re-oxidation*
Optical micrographs of these surfaces are shown in figure 5.24. The continuous (111) oxide layer is shown in a), whilst b) demonstrates that upon removal, the grain structure of the underlying metallic tape is revealed.

![Figure 5.24 Optical micrographs of a) the upper (111) oxide layer and b) the (100) oxide which remains on the NiFe surface after spalling.](image)

The atomic force microscope images of figure 5.25 indicate that the oxide layer is rough, which could be a problem for subsequent superconductor deposition. The (111) layer which is produced initially is very rough, but when removed, it leaves a much smoother cube textured oxide layer. Unfortunately, the re-oxidation process results in a rough surface again.

![Figure 5.25 Atomic force micrographs of a 10 x 10 µm² region of the surfaces of the oxide layers. a) is the (111) oxide, b) the surface (100) oxide and c) the thicker (100) oxide obtained after re-oxidation.](image)
5.3 Ceramic Buffer Layers

5.3.1 Cerium oxide films

CeO$_2$ was deposited onto Ni from an oxide target originally by DC sputtering from a well conducting target. Films were deposited at 600°C and figure 5.26 shows θ-2θ scans for films where the CeO$_2$ layer was deposited in Ar/O$_2$ and in Ar/H$_2$.

![Graph showing θ-2θ scans for CeO$_2$ films deposited in Ar/O$_2$ and Ar/H$_2$.]

Figure 5.26 θ-2θ scan of CeO$_2$ layers deposited onto Ni on MgO in O$_2$ and forming gas.

The oxidising atmosphere leads to the development of a (111) NiO layer, on which the CeO$_2$ grows epitaxially. Figure 5.27 shows however that the film deposited in forming gas however is cube textured. The unusual aspect is that a direct cube on cube orientation is seen, rather than being 45° rotated as is usually found for CeO$_2$ on Ni [115].

![Pole figure showing {111} pole figure and {111} φ scan of CeO$_2$ film on Ni/MgO.]

Figure 5.27 {111} pole figure and {111} φ scan of CeO$_2$ film on Ni/MgO.
As ceramic sputtering targets are very brittle, they are subject to cracking upon repeated thermal cycling. This occurred to the target initially used and a further set were produced in-house. These targets are more porous than that initially used and have a higher electrical resistance. Therefore it was no longer possible to produce a DC discharge and RF sputtering was employed for further depositions. The initial aim was to reproduce the predominantly (100) CeO\textsubscript{2} film from the new targets. The traces of figure 5.28 show the CeO\textsubscript{2} (111) and (200) peaks of films grown at various temperatures. Forming gas (4%H\textsubscript{2} in Ar) was used for the first 10 minutes of the deposition, followed by pure Ar.

![Figure 5.28 Section of the θ-2θ scans showing the (111) and (200) peaks for CeO\textsubscript{2} films deposited at various temperatures](image)

At room temperature, the texture is uniquely (111) – at a higher temperature, it is mixed and the film deposited at 650°C has the best out-of-plane texture, though there is still a small (111) component. The (111) φ scans of figure 5.29 indicate that there is also a rather strong in-plane alignment, though for the 650°C deposited film, there are two in-plane orientations. Note that the 720°C φ scan actually demonstrates a single, 45° rotated orientation as the sharp intermediate peaks are from the underlying MgO single crystal. The texture of this CeO\textsubscript{2} layer is quite good, having a FWHM of around 4.5°.
After deposition the target appears blackened, particularly in the racetrack region. To investigate this X-Ray traces of the target surface before and after deposition were measured and are shown in figure 5.30. It appears that the lattice parameter is increased in places, which is consistent with de-oxygenation caused by the reducing atmosphere.

Initial depositions of CeO$_2$ onto NiFe tape carried out alongside depositions onto Ni on MgO proved unsuccessful. The texture of the buffer layer was consistently (111), with no evidence
of (h00) peaks in the θ-2θ scan. Given that the NiFe is more likely to have an oxide layer present on the surface, this could be a factor in the failure to produce cube textured epitaxial growth. Therefore a series of experiments were undertaken in which the tape was annealed for several hours in a reducing environment before starting the CeO\textsubscript{2} deposition. The θ-2θ scans in figure 5.31 are for CeO\textsubscript{2} films deposited in forming gas at 620°C and in both cases the tape was annealed for 2 hours beforehand. The difference was that one tape was annealed at 620°C and another at 820°C. The significant difference in the relative intensities of the (111) and (200) peaks demonstrate that the annealing is an important feature and explains the failure to obtain (100) oriented films previously.

![X-Ray θ-2θ scans of CeO\textsubscript{2} films deposited onto NiFe tapes pre-annealed at 620°C and 820°C.](image)

Depositions were then carried out at a range of temperatures after a high temperature forming gas anneal of the NiFe tape had been carried out. X-Ray θ-2θ traces of these films are shown in figure 5.32.
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Figure 5.32 θ-2θ scans of CeO$_2$ films deposited onto NiFe at various temperatures

Figure 5.33 shows a typical pole figure for the CeO$_2$ with mixed texture. This film was deposited at 620°C and in addition to displaying a (111) component normal to the surface, has a (100) orientation which is rotated in-plane by approximately 26.5°. This corresponds to a NCSL orientation with a smaller lattice mismatch, \{001\}<100>\text{CeO}_2 // \{001\}<310>\text{Ni}.

Figure 5.33 \{111\} pole figure of CeO$_2$ film deposited onto NiFe. Apart from the cube textured buffer layer, there is an in-plane rotated component and also some \{111\} material.
Figure 5.32 indicates that the optimum temperature for the CeO$_2$ deposition on NiFe is around 620°C. At lower temperatures the texture is more predominantly (111) and at higher temperatures, two effects are noticeable. A number of new peaks appear in the trace and also the NiFe (200) peak begins to develop a shoulder on the high angle side. Both these features are consistent with oxidation of the tape to form an Fe-rich oxide layer, as described in section 5.2.

5.3.2 Yttria-stabilised zirconia

A target of ZrO$_2$-8%Y$_2$O$_3$ (YSZ) target was produced from a powder of purity 99.9%. The positions of the X-Ray peaks in the scan of the target surface (figure 5.33) indicate that the lattice parameter is 5.177Å.

![Figure 5.33 θ-2θ scan of a polycrystalline YSZ sputter target](image)

YSZ films were deposited onto NiFe in the same temperature range as was used for CeO$_2$ deposition. The forming gas anneal step was also used, the tapes being annealed in 5 Pa Ar/5%H$_2$ at 720°C for 20 minutes. Figure 5.34 shows θ-2θ scans for three different temperatures.
The scans show a mixed texture, though the degree of (100) orientation appears to increase with increasing temperature. As there is a temperature gradient along each sample, each was measured in 6 places along its length, but no systematic variation of texture was seen. The pole figures measured in the centre of each of the three samples are shown in figure 5.35.

The ‘mixed texture’ is confirmed by these \{111\} pole figures which have two distinct sets of poles. The peaks at $\psi=0^\circ$ and $70^\circ$ arise from the (111) oriented grains. The 12-fold symmetry is consistent with the texture of a (111) material being determined by an underlying (100) texture, as described for the deposition of Ag on Ni. The poles at $\psi=55^\circ$ arise from (100) oriented YSZ. The predominant epitaxial orientation is YSZ \{001\}<110> // NiFe \{001\}<100>, although there is a second (cube-on-cube) in-plane orientation present in each case.
This series of experiments demonstrates that YSZ films which are predominantly cube textured can be deposited by sputtering onto NiFe, though there is still a (111) component of texture present over the range of deposition temperatures used. The (111) component is smaller when the deposition temperature is raised to 820°C, but this could be caused by the fact that this allows the tape to anneal at a higher temperature for a couple of minutes before the deposition begins. Hence in order to remove the remaining (111) texture it may be necessary to increase the annealing temperature. It is less clear how it might be possible to prevent the two in-plane orientations of (100) grains forming. The lattice mismatch with NiFe could be reduced from 2% for growth in the {100}<110> orientation by reducing the lattice parameter of the YSZ, but this would produce a buffer layer less favourable for matching with YBCO.

In order to compare the quality of the texture obtained in these films, two samples deposited on NiFe at the University of Birmingham have been characterised. These buffer layers were deposited by PLD with the CeO$_2$/YSZ/CeO$_2$ architecture. The θ-2θ scans (fig. 5.36) show that these layers also have some degree of (111) texture although less than has been managed by sputtering. The pole figures of the CeO$_2$ and YSZ layers are shown in figure 5.37 and demonstrate that whilst the texture is more exclusively of a {100} nature, the peaks are somewhat broader than achieved for the sputtered films.

*Figure 5.36* θ-2θ scans of the CeO$_2$/YSZ/CeO$_2$/NiFe PLD sample compared with typical sputtered single buffer layers
5.3.3 Deposition onto the native oxide

As the surface of the oxide described in section 5.2 may not be compatible with HTS growth [234], the use of YSZ as a cap layer has been investigated. YSZ was deposited onto thin and thick oxide layers using a heating current of 9 A. Note that because of the higher emissivity of the surface, the temperature is likely to be significantly less than for the same current passing through a clean NiFe tapes and is estimated to be only 500°C at the tape centre. The θ-2θ scans of the resulting tapes are shown in figure 5.38.
For the film on the thin NiFe\textsubscript{2}O\textsubscript{4} layer, there are hints of the YSZ (111) and (200) peaks, though they are barely detectable. For the thicker oxide layer, a (200) Ni peak has split off the NiFe peak, suggesting that a significant amount of Fe has been removed from the sub-surface region. The YSZ peaks are now far more obvious, and the fact that there is a significant (200) peak suggests that the film may be textured. Heating currents up to 15 A have been used and the relative intensities of (111) and (200) peaks are similar throughout this range. Despite the (111) component, the pole figure does show excellent alignment, with an in-plane FWHM less than 9\textdegree. Figure 5.39 is a pole figure measured at 2\theta=30.2\textdegree, which is the Bragg angle for the (111) YSZ reflection, and also happens to coincide with the (220) reflection of NiFe\textsubscript{2}O\textsubscript{4}. Thus the pole figure shows that the epitaxial growth mode is <100>Y\textsubscript{SZ} // <100> NiFe\textsubscript{2}O\textsubscript{4}, and also shows that the YSZ (111) poles (at \psi=54\textdegree) are approximately as sharp as the (220) NiFe\textsubscript{2}O\textsubscript{4} poles (at \psi=45\textdegree), having a FWHM of 9\textdegree.

![Pole figure at 2\theta=30.2\textdegree, showing {111} YSZ poles and {220} NiFe\textsubscript{2}O\textsubscript{4} poles](image)

**5.4 Summary**

The deposition of cube textured Ag by including an intermediate Pd layer was successful on both Ni and NiFe substrates. The degree of orientation of the layers deposited onto the NiFe
tapes improves such that the Ag film is very sharply textured indeed. Use of the near coincidence site lattice indicates why other in-plane orientations may be found, though these can easily be avoided by optimising the deposition conditions. The main limitation of such buffer layers would appear to be the fact that they inter-diffuse rather rapidly at elevated temperatures.

Under all conditions studied the NiFe substrate oxidises to produce an uppermost oxide layer which has a (111) texture, unsuitable for coated conductor development. However the layer develops such that the oxide closest to the tape surface has the desired cube texture. This layer has the spinel structure and is a solid solution of NiFe$_2$O$_4$ and Fe$_3$O$_4$, and importantly remains adherent to the tape upon removal of the overlayer of (111) oriented material. Also on further oxidation, the (100) oriented oxide layer grows thicker and maintains the favourable cube texture at the surface. Thus such an oxide can be developed with a texture which replicates that of the underlying metal.

The popular oxides CeO$_2$ and YSZ have been deposited on Ni, NiFe and NiFe$_2$O$_4$ with varying degrees of success. A very well textured layer of CeO$_2$ is obtained on the Ni film on single crystal MgO by DC sputtering at 600°C, but attempts to replicate this resulted in 2 in-plane orientations. By increasing the temperature to 720°C, a single in-plane orientation has been produced although curiously, the in-plane orientation is different to that produced by DC sputtering, being rotated by 45°. The only significant difference in deposition conditions other than the higher temperature is that the deposition rate by RF sputtering is significantly lower. Producing the cube-texture on NiFe tapes proved more difficult, probably due to formation of a (111) textured native oxide on the surface. By introducing a pre-deposition anneal in forming gas, films of both CeO$_2$ and YSZ have been produced which are predominantly cube textured, yet in both some (111) material is present. Deposition of YSZ onto NiFe$_2$O$_4$ as a cap layer has proved successful. As there is no need to avoid substrate oxidation in this case the deposition is carried out in pure oxygen and if the native oxide layer is thick the YSZ can be grown with a single cube orientation.
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