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The Antiferromagnetic Domain Structure of Epitaxial Nickel Oxide

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Epitaxially grown nickel oxide single crystals (thickness 10 to 200 μm) have been examined below the Néel temperature (523° K) by optical and X-ray diffraction topographic techniques. The antiferromagnetic domain structure in the as-grown crystals is extremely complex and sensitive to crystal thickness. Annealing simplifies the domain structure, but the presence of the magnesium oxide substrate is shown to inhibit the formation of the large domains observed in well-annealed Verneuil-grown crystals. The misorientation between adjacent domains has been measured by a direct technique and shown to be consistent with the theoretical value.

1. Introduction

Nickel oxide is an antiferromagnetic material with a Néel temperature of 523° K [1]. Above this temperature, the oxide is paramagnetic and has the sodium chloride structure, while below, an antiferromagnetic ordering of atomic magnetic moments occurs with an associated lattice distortion. The spin structure is such that one family of (111) planes has a ferromagnetic arrangement of spins, the spin direction being approximately along $<11\bar{2}>$ [2]. Adjacent sheets have antiparallel spin arrangements leading to a three-dimensional antiferromagnetic array. This magnetic ordering gives rise to a slight contraction along the [111] axis normal to the ferromagnetic sheets, and the antiferromagnetic crystal structure is rhombohedral with a rhombohedral angle of 90° 4.2′ [3]. This distortion allows the possibility of a twinned structure where each twin domain has a different $<111>$ contraction axis. The spin direction in adjacent twinned regions will be twin-related and the twin planes, called T-walls by Roth [4], may also be considered to define a type of antiferromagnetic domain structure.

This twin domain structure has been investigated in Verneuil-grown crystals both optically and topographically by several workers [4-6]. In all cases, the as-grown crystals contain a complex domain structure, which is relatively stable and difficult to move on application of mechanical stresses or magnetic fields. After annealing at 1500° C, the domain structure is drastically simplified, and the application of a slight stress along [111] can produce crystals which are 99% single domain. Using the Schulz method [7] to measure the misorientation between reflecting planes in adjacent domains, Saito [5] obtained approximate agreement between his measured values and the values calculated on the basis of a rhombohedral angle of 90° 4.2′.

The work presented in this paper is confined to observations in thin NiO crystals grown epitaxially onto MgO substrates and was undertaken to explain the extremely complex domain structure observed in these thin crystals and the influence of the substrate.

2. Experimental

Single crystals of NiO were grown epitaxially onto (001) cleavage surfaces of MgO using a method similar to that of Cech and Allessandrini [8], the thickness varying between 10 and 200 μm. The domain structure was usually examined while the NiO was still attached to the MgO substrate, but in some cases the NiO was removed prior to examination by dissolving the substrate in 20% sulphuric acid held just below its boiling point.

Optical studies were performed using transmitted polarised light, and X-ray topographs were taken of the (001) growth faces with CuKα radiation, using the {420} or {311} reflections and the Berg-Barrett technique [9]. Owing to the minute distortion from the cubic structure, particular {420} and {311} planes are almost parallel in adjacent domains, and in order to obtain sharp detail on the topographs the experimental arrangement must have sufficient angular resolution to avoid simultaneous reflection from such planes. To achieve this, the specimen was placed 750 mm from the target of a Hilger microfocus generator, which had an effective focal spot of 40 × 4 μm, thus keeping the resolution to less than 15″ of arc. Ilford nuclear emulsion plates (L4 and G5, emulsion thickness 10 μm) were placed close to the specimen, giving a resolving power of 1 or 2 μm.

After the initial examination, the crystals were annealed at 1450° C in a low-pressure argon atmosphere for a few hours and then cooled very slowly (1° C/min), when the domain structure was again examined by both optical and X-ray methods.

3. Observations on As-Grown Crystals

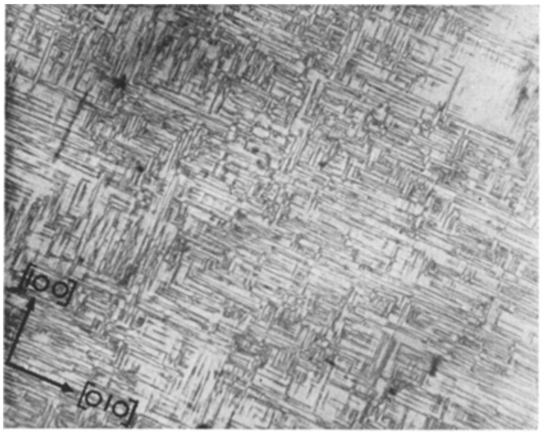
3.1. Optical Examination

The domain structure in the as-grown crystal is extremely complex, although the vast majority of domains consist of thin lamellar loops parallel to [100] or [010] (fig. 1a). Since all the domains observed were separated by sharply defined walls, the plane of the walls must be parallel to the incident beam and hence normal to the surface [10]. Lamellae normal to one another either terminate abruptly on approaching one another or unite to form a "T"- or "L"-shaped domain. Occasionally, lamellae parallel to <110> were observed, and, although these domains generally appeared to be independent of the {100} domains, isolated instances of {110} walls crossing {100} domains were observed (fig. 1b). An unusual feature of all these crystals was that {100} walls could be seen without polarised light, whereas {110} walls required critical alignment of the crystal between crossed polars, when the complete domain pattern was revealed.

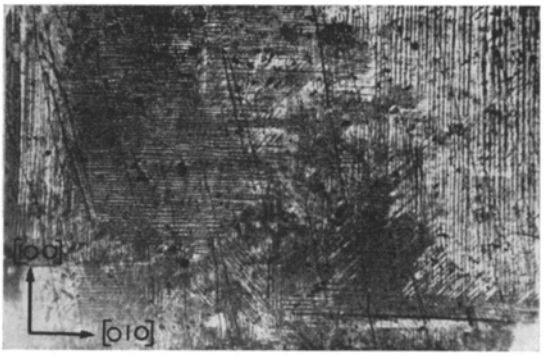
The width of the individual domains increased with the thickness of the crystal, from much less than 1 μm, at a thickness of 10 μm, to 3 to 5 μm, at a thickness of 120 μm. Increasing the thickness beyond this did not widen the domains; in fact, it made the structure more complicated as more {110} domains became visible and the structure began to break up into two layers parallel to the growth surface. Although the domain width was approximately the same in different crystals of comparable thickness, the length and distribution varied markedly.

On cleaving the crystal normal to the growth surface, the domain pattern altered such that a region about 50 μm wide alongside the cleavage edge became very uniform with thin domains running normal to the edge.

This fundamental domain structure was unchanged by simply removing the substrate,



(a)



(b)

Figure 1 (a) Complex domain pattern in an as-grown crystal (×126). (b) Complex region of {110} domain walls superimposed on the basic {100} walls (×115).

although the domains became more mobile. Some lamellar domains grew at the expense of others on application of a magnetic field of 7000 G in the (1 1 1) plane, whereas fields much higher than this had no effect when the crystal was still on the substrate.

3.2. X-ray Examination

The small individual domains on the as-grown specimens could not be resolved topographically, but considerable detail was revealed on a much larger scale than that observed optically. Every topograph revealed the fact that the deposited NiO was not quite parallel to the MgO and was slightly concave. This curvature almost exactly matched the divergence of the incident X-ray beam, and the Kα_1 reflection was about 1 mm wide instead of the expected 5 to 10 μm if the crystal had been perfectly flat. The radius of curvature was calculated to be about 50 cm and enabled a large region to be examined at any one time without having to traverse the crystal and the photographic plate as in the Lang technique. The curvature was relatively consistent and independent of crystal thickness.

Topographs taken from several MgO substrates proved that this gross curvature was not present in the substrate, but did show that these surfaces were far from perfect and contained numerous small-angle boundaries.

4. Observations on Annealed Crystals

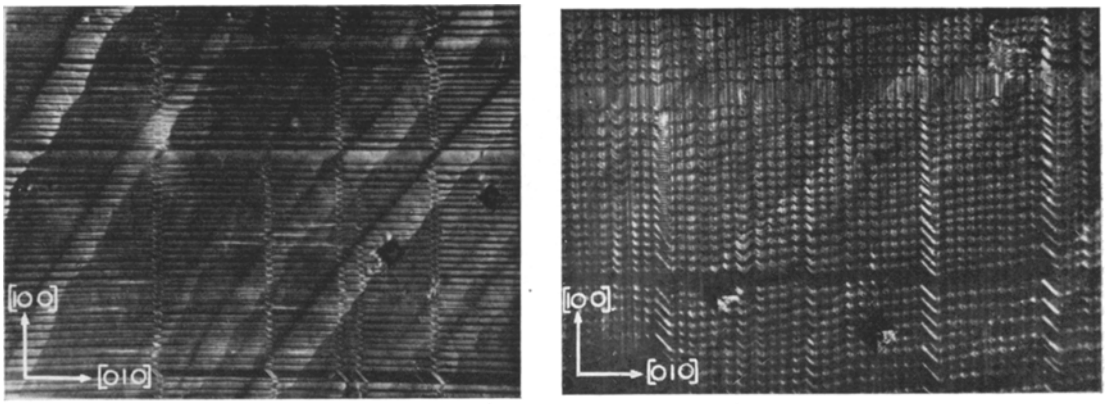
4.1. Optical Examination

Specimens were annealed at 1450° C in the manner described by Roth [4]. In all cases, the domain pattern became much less complex, and the crystal was split up into quite large regions, in each of which the domain structure was extremely regular. These regions contained either narrow lamellar domains parallel to [1 0 0] or [0 1 0] (width 5 μm or less, depending on the crystal thickness) (fig. 2a), or complex arrays of four-wall patterns in which the domains were less than 1 μm square (fig. 2b). Regions of lamellar domains parallel to < 1 1 0 > have never been observed in any of the crystals investigated. Usually, uniform regions were separated by irregular boundaries, and in a few instances the pattern was further broken up by a larger-scale rectangular network of slightly wider domains (fig. 3).

Specimens removed from the substrate showed considerable changes after annealing, and the subsequent domain pattern consisted of very large domains (dimensions of millimetre compare with micrometre) reminiscent of bulk-grown specimens. Immediately after annealing, large fir-tree patterns often appeared where the macroscopic {1 1 0} twin walls formed wedge-shaped domains, similar to those reported in barium titanate [11]. These domain walls were very mobile and only a slight stress was necessary to remove the {1 1 0} walls.

4.2. X-ray Examination

Annealing had no effect on the gross curvature of specimens still on the substrate, and topographs of large regions could still be taken with excellent resolution. The domain structure was now large enough for many of the individual domains to be resolved, and confirmation that



(a) (b)

Figure 2 (a) Regular (1 0 0) domain walls on an annealed crystal with the complete domain pattern revealed in polarised light (×82). (b) A region of complex four-wall pattern in an annealed crystal (×100).

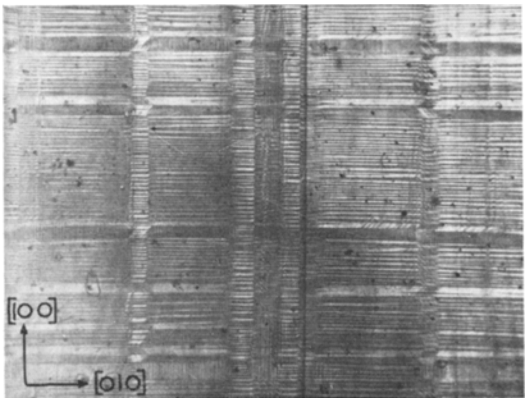


Figure 3 Large-scale rectangular domain network superimposed on basic pattern in an annealed crystal (×52).

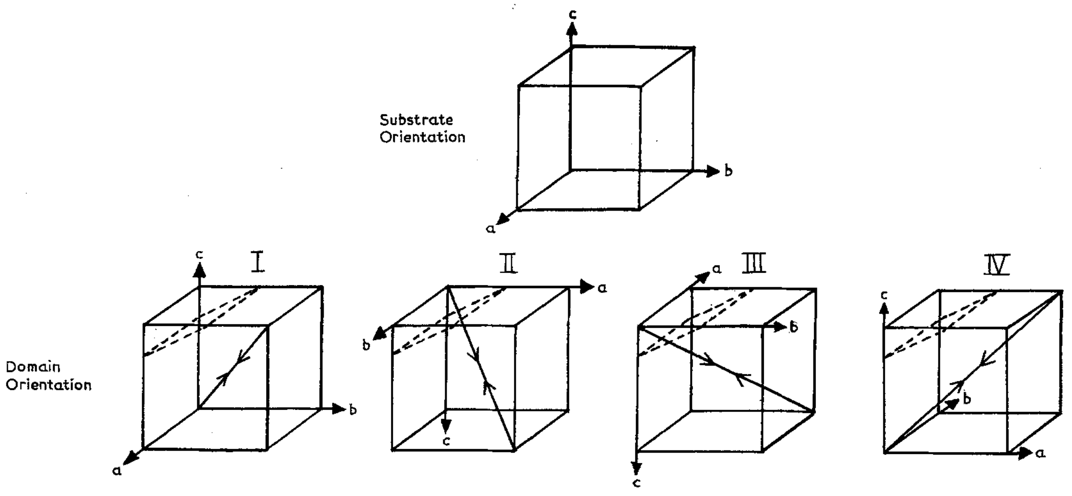
the domain walls were normal to the growth surface was obtained by taking topographs from cleavage surfaces normal to the growth surface.

The type of domain can be identified unambiguously both optically and topographically by observation of a four-wall region. If the four contraction axes in domains designated I, II, III, and IV (after Roth [4]) are [111], [11$\bar{1}$], [1$\bar{1}$1], and [$\bar{1}$11], respectively (with common reference axes [100] and [010] in the growth surface, all indices referring to the cubic unit-cell), there is only one possible configuration for each of the two types of four-wall pattern which can be taken in order to maintain crystallographic continuity. Using the table of possible domain walls from Blech and Meieran [6], only the following domain walls are observed in our epitaxial crystals.

Domains	I-II	I-III	I-IV
Twin walls	110	010	100
Domains	II-III	II-IV	III-IV
Twin walls	100	010	$\bar{1}$10

Most topographs were taken with the specimen mounted on a goniometer with [100] vertical using the (02$\bar{4}$) reflection, but these indices define a single plane, and it should be pointed out that, owing to the rhombohedral nature of the twinned structure, the indices of the reflecting plane change from domain to domain. This in turn leads to a possible change in "d" spacing and Bragg angle, a point not emphasised quantitatively by previous workers. If we now consider the structure in its true rhombohedral form, and index the reflecting planes on their rhombohedral axes, always taking [111] as the contraction axis, and domain I as indicated in fig. 4, we obtain the reflecting planes and Bragg angles as shown.

The theoretical misorientation between these reflecting planes across a (100) or (010) twin wall of 6.6′ (assuming a rhombohedral angle of 90° 4.2′) is partially compensated by the change in Bragg angle ($\delta\theta = 4'$), and a rotation of 2.6′ about [100] should be necessary to produce



	I	II	III	IV
Reflecting Plane (dotted plane in diagram)	02$\bar{4}$	204	024	20$\bar{4}$
Bragg Angle	55° 37·5′	55° 41·5′	55° 41·5′	55° 37·5′

Figure 4 Relative orientation of rhombohedral unit-cell in different domains. (The [111] contraction axis is marked with a double arrow.)

reflection from adjacent I-III or II-IV domains, provided the substrate does not restrict the magnitude of the rhombohedral distortion. In order to investigate this experimentally, regions of I-III and II-IV domains were examined and topographs were taken at intervals of 20″ of arc as the specimen was rotated about [100]. An average rotation of approximately 2′ was necessary to produce a complete reversal of domain pattern (fig. 5). The very complex four-wall region contained individual domains which were so small that no positive reversal of the pattern could be detected topographically. Measurements taken on {113} reflections using the direct rotation technique gave a value for the misorientation consistent with the expected theoretical value of 6′.

The topographs revealed that all specimens contained several small-angle boundaries with a misorientation of 3 to 10′ across the boundary. The domain pattern was unaffected by these boundaries and the walls passed straight across them.

Specimens freed from the MgO substrate were grossly distorted and it was impossible to obtain topographs of large areas with the microfocus tube. It proved extremely difficult to produce a complete reversal of the domain pattern with these topographs, but, from the few observations made, a rotation of about 2′ of arc about [100] was intimated in common with the specimens on the substrate. A more positive investigation of this misorientation was attempted using the Schulz technique with a larger focal spot (target area 1 × 1 mm at a distance of 25 cm), which reduced the resolution but increased the exposure area (see fig. 6). Using {420} and {113} reflections, the measured misorientation in both cases varied between 12 and 16′, which is much higher than the expected theoretical values of approximately 3 and 6′ respectively. Saito [5] obtained very high values with the Schulz technique using {113} reflections in Verneuil-grown crystals, and it appears that this method is not particularly accurate owing to the divergence of the incident and reflected X-ray beams, and the difficulties in measuring the specimen-to-plate distance accurately. These anomalies are due partly to the technique and the fact that the crystals are grossly distorted, rather than being a fundamental difference between the relative misorientations of adjacent domains in specimens on the substrate and those freed from it.

5. Discussion

On cooling through the Néel temperature, NiO changes from a cubic to a rhombohedral structure owing to the contraction along one of the <111> axes. This distortion may result in the formation of twins or antiferromagnetic domains to relieve internal strains in the crystal. During the epitaxial growth, various crystal defects such as dislocations and impurities will be incorporated into the lattice and their presence will disturb the crystallographic structure and spin-ordering in the resulting crystals. Although the formation and stabilisation of the twin domains must be related to the presence of these defects, the presence of the substrate will also

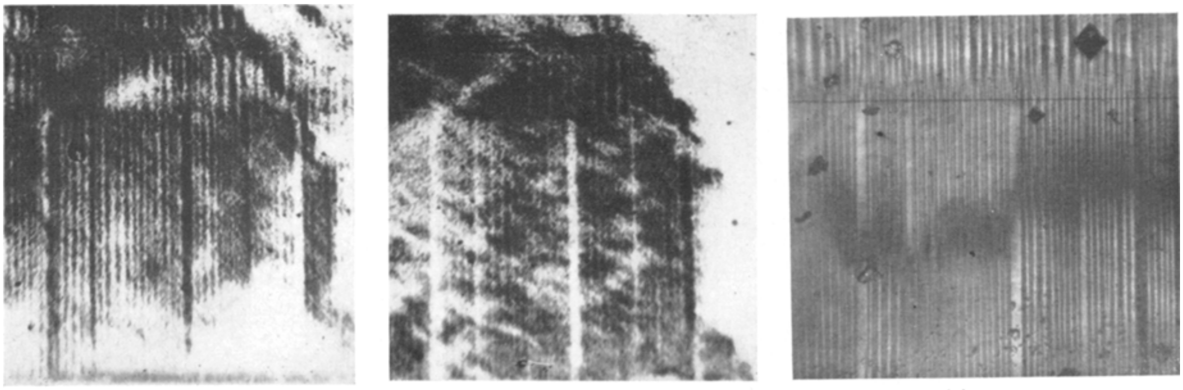
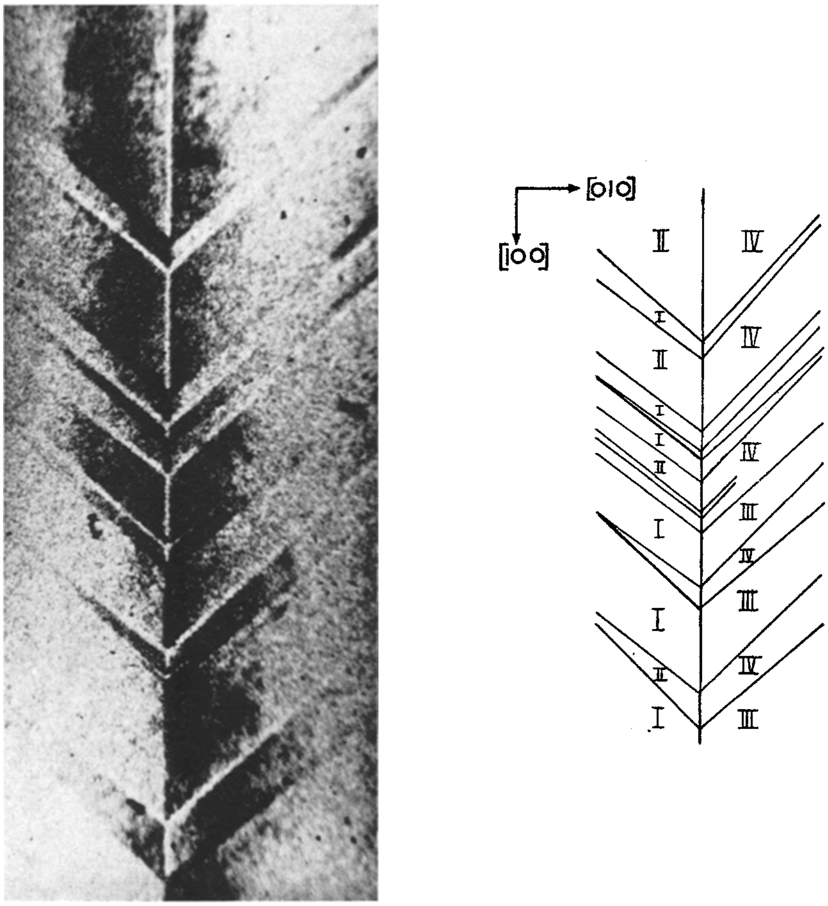

(a) (b) (c)

Figure 5 (a) Topograph of regular (100) domains in an annealed crystal (×95). (b) Same as (a), crystal rotated about [010] through 2′ of arc (×95). (c) Optical photograph of same region as seen in (a) and (b) (×95).



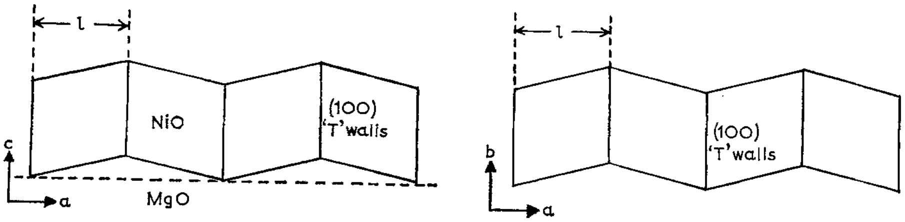
(a)

(b)

Figure 6 Schulz topograph showing fir-tree pattern in an annealed crystal removed from the substrate (×30). (b) Schematic diagram of (a) with the domains labelled.

affect the domain structure whether the crystal be perfect or not. Initially, therefore, the effect of the substrate will be considered irrespective of any other crystalline imperfections.

Basically narrow domains are observed with "T" walls parallel to [100] and [010] and it can be demonstrated quite simply why wide domains are unlikely in epitaxial crystals. For a {100} "T" wall, the amount of strain due to the rhombohedral distortion at a substrate interface will depend on the width of the domain (*l* in fig. 7). The only way to reduce this strain would be



(a)

(b)

Figure 7 Diagram representing the strain associated with the rhombohedral distortion (exaggerated for effect) at the substrate interface, viewed (a) parallel and (b) normal to the interface.

minimising the width, as is observed. The strain has components normal and parallel to the MgO surface, and the normal component can be removed by introducing $(10\bar{1})$ walls into the structure (fig. 8). It may seem surprising that these walls have never been observed. However, the energy associated with $(10\bar{1})$ walls is greater than that associated with (100) walls [12] and it is probable that this extra energy of formation is not compensated for by the decrease in strain energy at the interface. In annealed and unannealed crystals, the domain width increases regularly with thickness. For very thin crystals, the stress field set up in the NiO owing to the interfacial strain will be a maximum, resulting in the formation of very narrow domains to lower the energy of the system. As the crystal thickness increases, the matrix of the crystal will be less influenced by the interfacial strain, and slightly wider domains will be permitted; although the overall distribution of these domains will be governed by the internal strain in the bulk of the crystal. The domain width of approximately 5 μm does not increase as the crystal thickness increases beyond 120 μm and it is probable that this is the limit due to the overall influence of the substrate.

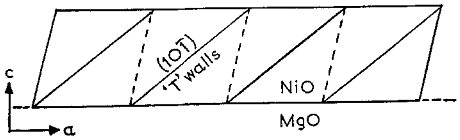


Figure 8 View parallel to the substrate interface showing possible removal of one strain component by the introduction of $(10\bar{1})$ "T" walls.

Returning now to the role played by crystal imperfections in the formation and stabilisation of the domain structure, evidence suggests that the relationship is rather indirect in the case of domain formation, but may be more direct as regards stabilisation. In going across a "T" wall, the directions of the individual spins in the two domains must be different owing to the twin relationship between the ferromagnetic layers; but, because of the strong magnetic interactions, this change in magnetic order cannot be sharp. Thus these "T" walls must have a finite thickness (a theoretical calculation by Yamada [12] gives a value of 80 Å for the width of an $\{001\}$ wall) and will not generally be as sharp as ordinary crystallographic twin boundaries. Dislocation etch-pit studies on well-annealed Verneuil-grown crystals by Takeda and Kondoh [13] showed no arrays of etch pits in the region of twin walls and no creation of fresh pits on their displacement. Furthermore, although the formation and motion of the twins are basically mechanical in nature, it is highly unlikely that twinning dislocations are involved owing to the extremely small shear magnitude of 0.003 (calculated from the rhombohedral distortion) along both $\langle 001 \rangle$ and $\langle 011 \rangle$ for $\{110\}$ and $\{100\}$ walls respectively. The formation of "T" walls, therefore, does not seem to be directly influenced by individual dislocations, or even dislocation networks or arrays accompanied by short-range stresses, but only by the overall strain in the crystal associated with the total density of structural and magnetic imperfections. However, it is likely that, once formed, "T" walls may be stabilised by interaction with regions of high local stress.

The epitaxial crystals used in this investigation would be expected to have numerous crystal imperfections and a high dislocation density, in common with all crystals grown by this technique on foreign substrates. The majority of these dislocations are incorporated into the crystal during the final stages of coalescence prior to the formation of a continuous "hole-free" film. This process seems to be complete in these NiO crystals when the thickness is a few microns (as evidenced by optical examination at various stages of growth), and these dislocation arrays may play an important role in stabilising the extremely complex domain pattern observed in all crystals approximately 10 μm thick. The minute domains and large number of "T" walls present in these thin crystals indicate a high degree of strain throughout the crystal.

Further growth takes place strictly by "autoepitaxy", and fewer dislocations are introduced as the crystal thickness increases. In fact, it is possible that the dislocation density could diminish owing to dislocation interaction and annihilation [14]. The optical photograph (fig. 9) taken of a cleavage face normal to the interface indicates that the crystal perfection improves as the thickness increases. All crystals examined with thicknesses greater than 20 μm had considerably fewer "T" walls than the very thin crystals, indicating that the overall strain in the crystal due to imperfections and interfacial strain is a maximum at a crystal thickness of a

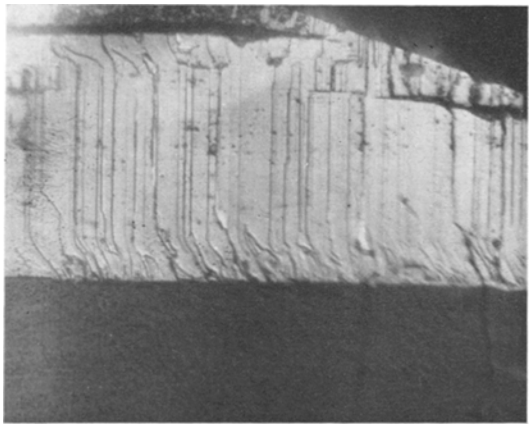


Figure 9 Cross-section of NiO/MgO interface (×236).

few microns. In all as-grown crystals, there are numerous examples of closed "L"- and "T"-shaped lamellar domains (see fig. 1a) and, since these cannot be separated from the surrounding domain by simple "T" walls without some lattice misfit, the stabilisation of such energetically unfavourable structures may well be associated with regions of high localised strain.

During growth at 640° C, there will be little tendency to anneal out many of the growth imperfections, but the high-temperature annealing at 1450° C will obviously allow many imperfections to diffuse out of the crystal thus reducing the overall strain (dislocation-density measurements on Verneuil-grown crystals [13] indicate a reduction factor of about 100). On cooling back through the Néel temperature, single domain crystals have been obtained in Verneuil-grown crystals, but in our epitaxial crystals only narrow laminar domains are observed. Thus, in these annealed crystals, the domain formation must be predominantly influenced by interfacial strain as described previously, and, because of the overall reduction in strain and regions of local stress, the resulting domain pattern should be much more regular than in as-grown crystals, with all domains bounded by "T" walls with no lattice misfit (see fig. 2). In all crystals examined after annealing, the structure consisted of regions of two domains separated by {010} walls, or regions of all four domains separated by regular four-wall boundaries, and these are the two lowest energy configurations possible [15]. The irregular boundaries between these regular regions and the rectangular network of slightly wider domains may well be stabilised by accumulation of imperfections following the high-temperature annealing.

In all these observations, the misorientation between adjacent twin domains is approximately the same, both in crystals on the substrate and those removed from it, and consistent with the quoted rhombohedral distortion of Slack [3]. The substrate merely constrains the domain size in such a way that it prevents the formation of wide domains and, although annealing makes the structure more regular, and may increase the domain length drastically, the width is unaltered. The mere removal of the specimen from the substrate does not remove the bulk strain or the stress field set up in the lower layer of the NiO by the interfacial strain, and the domain pattern is unchanged. Annealing removes a large proportion of this strain, and large mobile domains similar to those in Verneuil crystals are formed on cooling back to room temperature, since there is no substrate to constrain the domain width.

6. Conclusion

The complex twin structure in epitaxial crystals of antiferromagnetic NiO has been shown to be directly associated with the influence of the MgO substrate. The rhombohedral distortion is unaffected by the substrate and the associated strain energy is accommodated by the formation of narrow domains, as proved by the direct method of measurement of misorientation. This misorientation is consistent with the rhombohedral distortion measured in NiO by other methods.

Large domains are only formed in epitaxial NiO when the specimens have been removed from the substrate and subsequently annealed, the rhombohedral distortion remaining the same as in crystals on the substrate.

The domain structure has been shown to be dependent on the perfection, thickness, and conditions of growth of the crystals and in a unique way has revealed the strain associated with NiO crystals grown epitaxially.

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