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Quality Assessment of MgO Substrate Materials for High T_c Superconductor Thin Films using Cathodoluminescence Microscopy

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Abstract

Cathodoluminescence (CL) microscopy has been used to investigate the luminescence response of MgO single crystal substrates intended for high T_c *superconductor applications. Wavelength resolved CL spectra have been collected from both the surface and the bulk of the MgO single crystals, under different preparatory treatments. It was found that annealing the MgO resulted in the reduction of luminescent surface defect states present in the as-received and ion milled samples and at sites of surface damage. The surface treatment given to MgO single crystals can significantly affect the electrical properties of high* T_c *superconducting thin films deposited on them.*

Introduction

$YBa_2Cu_3O_{7-\delta}$ high T_c superconducting thin films, produced by laser ablation or sputtering, are frequently grown in an epitaxial relationship on MgO single crystals. The substrate/film lattice mismatch, however, will give rise to coherent or semi-coherent heterophase boundaries that can affect the performance of the thin film. In this respect the surface quality of the substrate is an important parameter in the construction of good epitaxial thin films as any disturbance in the substrate will ultimately be incorporated in the film structure.[1,2] Optimisation of deposition parameters maximises the number of *c*-axis oriented grains.

In a previous study, the observation of CL in the scanning electron microscope (SEM) and the light microscope was applied to the problem of locating and determining the nature of impurity phases within YBCO polycrystalline pellets.[3] Here the technique has been applied to the study of MgO single crystals intended as substrates for the production of superconducting thin films. MgO has a band gap of 7·7 eV[4] which is too big for direct CL emission, but the presence of impurities at parts per million (ppm) levels, local deformation, or defect structures can give rise to extra states in the band gap that allow a number of luminescent emissions to be observed in the visible range via electron beam excitation.

Slip planes in deformed and compressed single crystals display bright contrast in CL emission.[5–8] Datta *et al.*[5] recorded blue emission from the slip planes with a CL band at 466 nm; the undeformed crystal containing two CL bands at 425 nm and 488 nm. Changes in the slip plane luminescence intensity can be brought about by annealing, causing some planes to appear in dark contrast.[8] An excitation peak at 500 nm[7] in compressed crystals is attributed to the generation of F centres.

Vickers indentations in MgO have also been analysed in CL[8–10] and luminescence variations attributed to differences in the density of point defects. Piqueras *et al.*[9] observed CL intensity variation across indentations which appeared dark at the centre and bright at the edge of the deformation band. The dark CL contrast was attributed to a high density of defects at the centre, quenching the CL emission. Annealing caused the centre of the indent to luminesce as a result of the diffusion and annihilation of these point defects.[8] A broad band of emission at 400–420 nm was observed from some of the dislocation etch pits due to the impurities or point defects that surrounded them.[6] Away from the dislocations, two CL peaks were present at 400 and 430 nm. Frictional damage of MgO by 2 mm tungsten carbide balls gave rise to a non-luminescent region within the track with luminescence at the edges due to the highly distorted layer beneath the surface containing defects.[11]

Impurities contained within the MgO, particularly iron, have been shown to play a role in defining both the overall CL intensity and spectral response. Emissions in the red region have been found to increase with higher Fe doping in some cases[5] but not others.[6] Without knowing the precise overall impurity levels within the MgO crystals, correlation between workers'[1] sets of results for the band structure can only be speculative. This occurs because some impurities act to increase luminescence, whilst others can 'quench' or 'kill' emissions. In fact, a non-linear relationship of CL intensity versus concentration can be seen with some impurity atoms where increasing concentrations at first increase CL intensity, but then at some critical defect density, the introduced states interact and CL can be lost.

Other luminescence techniques such as fluorescence, radioluminescence, photoluminescence, thermoluminescence (TL), and gamma irradiation[12–19] have also been used to attempt to correlate the occurrence of certain impurities in MgO with observable peaks in the visible region. Ni^{2+} doping has been related to the emissions at 478, 482, 486, and 491 nm.[12] This idea has been supported by Delgado[14] who proposed the $^1T_{2g}$–$^3A_{2g}$[14,17,19] transition in substitutional Ni^{2+} ions. Chromium ions have been associated with the peaks in the 700 nm region.[15–19] However, there is some controversy about the role of the iron impurities and some suggest[18] that this impurity gives rise to red luminescence as well as chromium. However, Sathyamoarthy *et al.*[19] found in his samples that Fe acts to quench the observed TL intensity. Other impurity elements such as cobalt and copper also reduce the luminescence from MgO, whereas manganese has been seen to increase luminescence with a band at about 600 nm.[19]

For superconducting thin film fabrication, some workers[1,21,22] have considered pre-treatments before deposition. Of these, the most successful has been annealing the MgO at 1273–1473 K either in air or in oxygen. Awaji *et al.*[21] reported the removal of CL spots by annealing suggesting that any contamination layer on the MgO was removed. Moeckly *et al.*[22] concluded that films on annealed MgO substrates produced the higher T_c and J_c response. This finding has also been reproduced in previous work.[23] The reason is connected to improved surface crystallinity in the substrate.

The effect of substrate defects on thin films has been studied by Barkay *et al.*[24] They determined that cleavage slip steps in the substrate, observable by CL, disrupted the thin film. The step defects that they observed were of the order of microns in height and hence should be observable by normal optical microscopy.

This paper describes the CL technique as a method for assessing the surface structure quality of the MgO single crystals prior to superconducting film deposition and addresses the problem of characterising defects too small to be seen by light microscopy, but which are believed to affect the film microstructure.[23]

Experimental Method

MgO single crystals, 99·99% purity, were obtained from PI-KEM. The major impurity was ~5 ppm iron, with all other elements at lower levels than this. A piece of single crystal MgO was cleaved into three strips for each of the following surface treatments:

— annealed at 1273 K for 10 h in O_2 then cooled to RT in oxygen,
— ion milled for 30 h using argon,
— as-received (the control sample).

Using strips from the same MgO sample was necessary to obtain samples with identical impurity contents. This allowed the effect of the treatments on the CL emission to be compared. The samples were cleaned in ethanol using an ultrasonic bath and then rinsed with acetone. A light carbon coat was applied to eliminate charging in the SEM.

Panchromatic CL images of the samples were recorded in colour using a Technosyn Cold Cathode Luminescence stage, model 8200MK11, fitted to a light microscope. This was operated at 15 keV and 200 μA load current, illuminating approximately 1 cm^2 of the sample surface.

Collection of the CL emissions was carried out using an Oxford Instruments CL detector and wavelength resolved by a Bentham monochromator with a slit width of 0·4 mm. The MgO samples were cooled to 77 K which reduced band broadening and increased the overall CL intensity. Higher order diffraction peaks were eliminated by the use of two optical filters at 400 and 700 nm respectively. A linear response GaAs solid state detector with a useful wavelength range of 400–900 nm amplified any emissions. Noise output from the detector was reduced by cooling to 273 K. The secondary electron and CL images were generated in a Jeol JSM 840A scanning electron microscope. For each analysis, the CL collection mirror was optimally focused and accurate beam currents were measured using a Faraday cage. The electron beam conditions ranged from 5 to 20 keV and 3 to 9 nA.

Results

Some variability in CL emission (both chemically and mechanically induced) was noted between as-received MgO crystals from different batches and so obtaining single crystals from the same melt and to a good polished quality is very important in any comparative work.

The colour micrographs in Fig. 1(a) (transmitted light optical) and Fig. 1(b) (CL) demonstrate the benefits of CL microscopy over optical for observing fine surface damage in MgO single crystals. Figure 1(b) clearly shows sharply defined blue lines in CL at the surface of the substrate. No surface damage can be seen in the optical image of Fig. 1(a).

Figure 2(a–c) illustrates the effects on the CL images of ion milling and annealing MgO single crystals. The micrograph in Fig. 2(a) shows dark red lines, possibly at the sites of subgrain boundaries, running throughout the as-received sample. Ion milling the surface (Fig. 2(b)) resulted in a pronounced increase in the light blue excitations generated from the surface layer. Annealing decreased the intensity of these CL excitations which resulted in the sample having strong luminescent emission in the red region. The dark red lines are now unresolved.

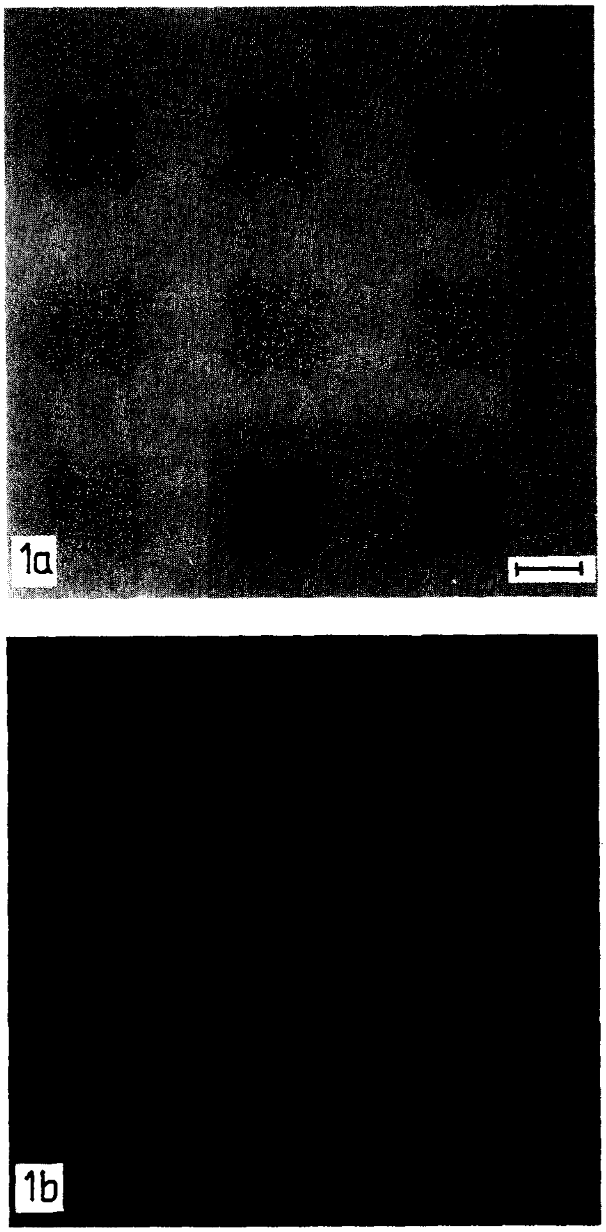

Fig. 1. Optical micrographs of the surface of an MgO single crystal: (a) normal mode and (b) CL mode (scale bar = 200 μm).

Wavelength resolved CL examination of the substrates in the SEM is illustrated in Fig. 3(a–d). The luminescence response generated from the bulk and from the surface were determined by using accelerating voltages of 5 and 20 keV. Using the Kanaya equation[25] 5 keV corresponded to 0·07 μm penetration depth and 20 keV to 0·78 μm depth, for the surface and bulk analysis respectively. On comparing Fig. 3(a) and (c), sharp peaks are observed from the bulk but not the surface around the 480 nm region. The spectra collected at 20 keV in Fig. 3(c) all display sharp peaks at 477, 481, 486 and 490 nm. The low CL emission at 5 keV meant that spectral resolution was poor, and hence no peaks could be resolved in Fig. 3(a).

Comparison of Fig. 3(a) with the colour micrographs (Fig. 2(a–c)), indicate good CL correlation between the systems. Ion milling the surface results in the highest proportion of luminescent defect states at wavelengths above 500 nm, with bands at 540, 560 and 630 nm. The annealed sample had the lowest CL intensity. Consideration of Fig. 3(b) and (d), analysing the surface and bulk luminescence generation respectively, illustrate similar spectra between the ion milled and as-received samples. Several peaks are present in the red region, between 696 and 740 nm. One unusual feature is the presence of a broad excitation band stretching from 750–850 nm. However, the annealed spectrum differs in one major respect from the as-received and ion milled samples, as the peak intensity at 867 nm is greatly reduced.

The wavelength resolved data in Fig. 4(a) and (b) show the effect of surface damage. Using spot mode at 10 keV and 6 nA resulted in the CL signal to noise ratio being sufficient for data collection without appreciable sample damage. In Fig. 4(a), the spectrum collected from the scratch has around 10 times the CL intensity of that from an undamaged area. Numerous luminescent states are generated throughout the visible range demonstrating that the electronic band structure is greatly disrupted. The 540, 560 and 630 nm bands are all clearly visible. However annealing the surface damage (Fig. 4(b)) returns the spectrum close to that of the undamaged surface.

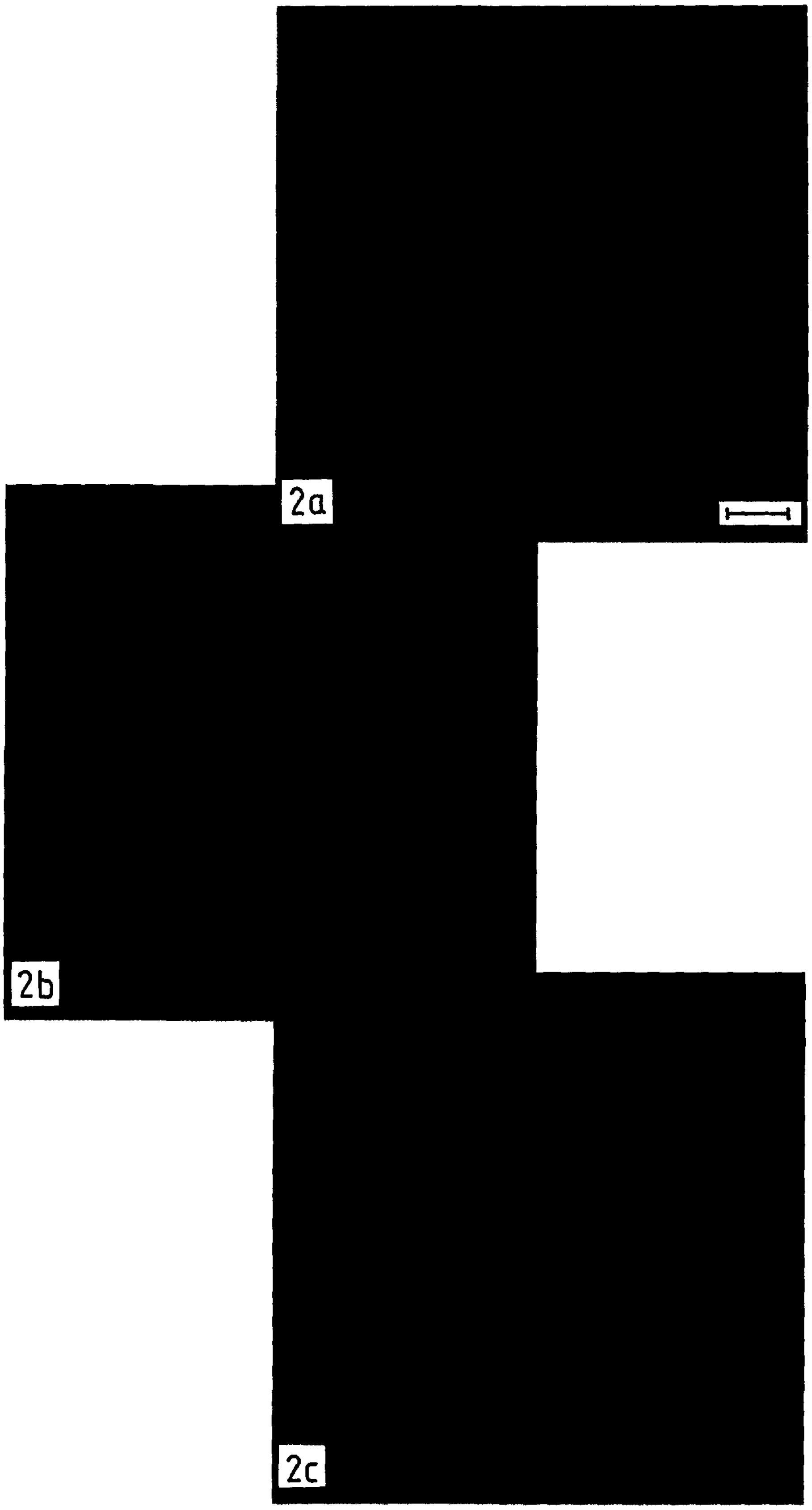

Fig. 2. CL micrographs showing the luminescent emissions of the MgO under the surface treatments of: (a) as-received, (b) ion milled and (c) annealed (scale bar = 200 μm).

Discussion

Assessment of the quality of MgO substrates, suitable for high T_c thin film deposition, can be carried out quickly by optical CL. Surface damage, which greatly affects the quality of epitaxial thin film growth, is easily observed due to local disruption of the electronic band structure at the site of flaws giving rise to bright CL contrast. However, other workers have reported the CL intensity to

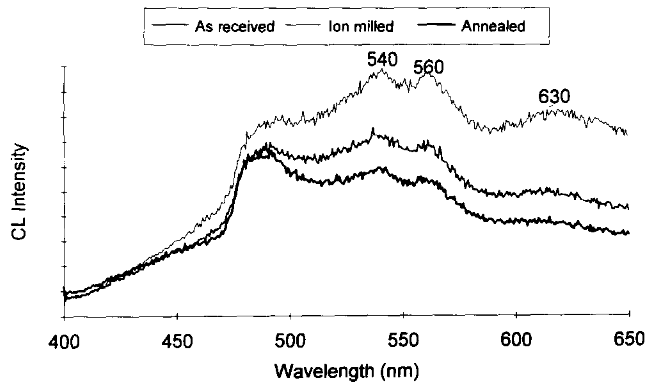

Fig. 3(a). CL intensity versus wavelength for the three surface treatments collected under the conditions of 5 kV, 9 nA in the SEM at 77 K using spot mode.

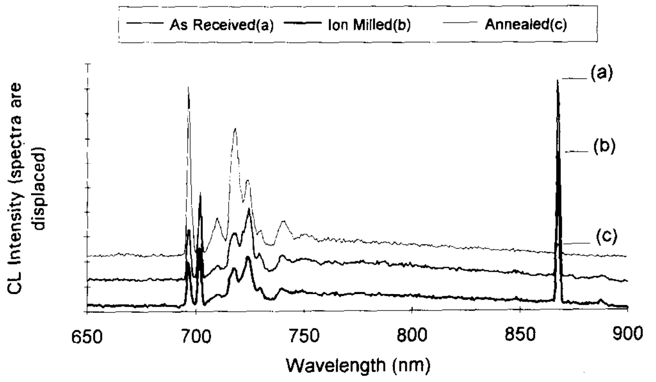

Fig. 3(b). CL intensity versus wavelength for the three surface treatments collected under the conditions of 5 kV, 9 nA in the SEM at 77 K using spot mode.

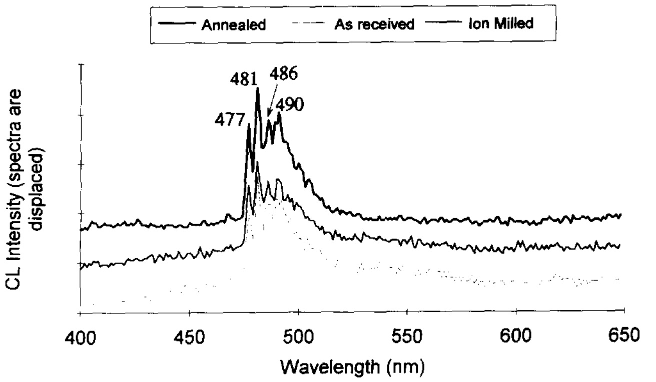

Fig. 3(c). CL intensity versus wavelength for the three surface treatments collected under the conditions of 20 kV, 3 nA in the SEM at 77 K using spot mode.

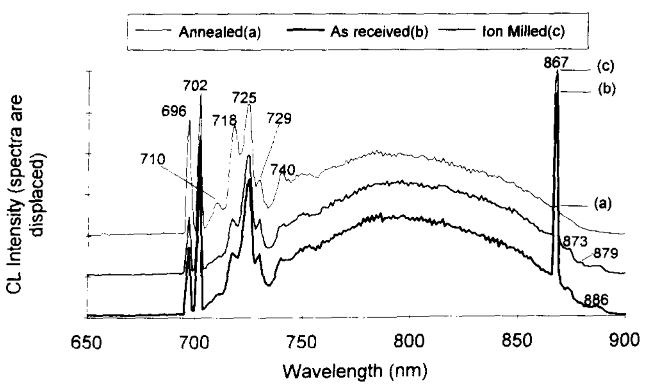

Fig. 3(d). CL intensity versus wavelength for the three surface treatments collected under the conditions of 20 kV, 3 nA in the SEM at 77 K using spot mode.

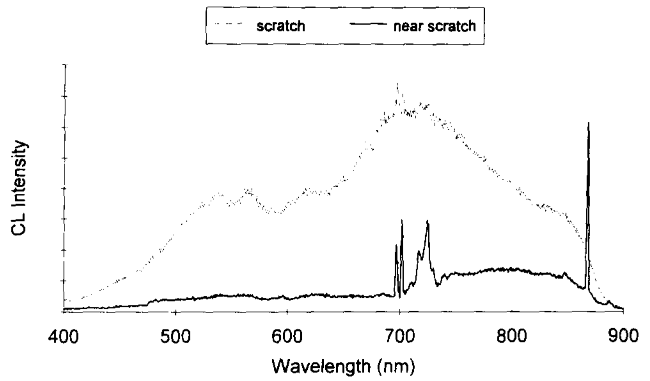

Fig. 4(a). CL wavelength analysis near and at a surface scratch in the as-received MgO. Conditions: 10 kV, 6 nA, spot mode.

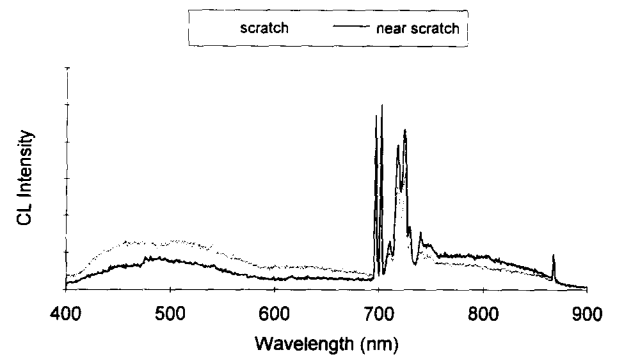

Fig. 4(b). CL wavelength analysis near and at a surface scratch in the annealed MgO. Conditions: 10 kV, 6 nA, spot mode.

be dependent upon the density of defect sites, with a high density giving rise to low CL emission.[8] Analysis of other single crystals, with optically visible surface flaws, confirmed that the surface damage displays a characteristic luminescence emission. Hence, in this study, the sharp blue lines in MgO single crystals are concluded to be due to fine surface flaws, that cannot be resolved using normal light microscopy. The damage observed by CL and described in this paper is much finer than that previously studied[24] and is generally not observable by normal light microscopy. Other researchers have also observed dislocations in CL contrast,[6,24] but were not able to correlate them with red luminescence. It is well documented that substitional Cr^{3+} ions are responsible for the red peaks between 696 and 701 nm. The direct transition is believed to be ^2E–$^4A_2$.[13,18] From the data presented here, it is not easy to judge the true position of the direct electronic transition as no system response correction was made to the data, but it is reported to lie at 698 nm.[13]

The peaks at 710, 718 and 724 nm resemble a direct transition with vibrational side bands. These could be connected to Fe^{3+} ions, but there is no evidence of this in the literature, although it has been suggested that Fe^{3+} gives rise to red luminescence.[18]

The broad blue emissions, in the colour micrographs of the as-received and ion milled samples occur uniformly within the samples. The spectroscopic analysis reveals four distinct excitations (476, 481, 486 and 490 nm), from the bulk (20 kV), which correlate very well with the TL data of Ralph *et al.*[12] for substitutional Ni^{2+} ions undergoing the $^1T_2$–$^3A_2$ transition.[14,17,19] Monochromatic CL imaging in the SEM at 480 and 700 nm was not able to identify the dislocations, because of the detector's small area of focus, hence any differences in the CL excitation spectra at the dark red lines, believed to be sub-grain boundaries, could not be determined.

Spectroscopic analysis of the surface at 5 keV beam energy, however, showed the band attributed to the Ni^{2+} ions together with luminescent transitions giving rise to bands at 540, 560 and 630 nm. The intensity of these emissions was found to be dependent upon the surface treatment suffered by the MgO, with the ion milled surface showing an increased CL intensity compared with the other two. Figure 3(a) shows that the as-received sample also has some defect band transitions. Residual lattice strain in the surface, caused by mechanical polishing prior to their supply, would be expected to alter the electronic band structure. This may be connected to the three luminescent bands. Ion milling appears to have enhanced these defects. The CL spectrum from the annealed specimen shows some recovery of the surface deformation and elimination of defects resulting in the CL intensity of the defect bands being much lower. These bands at 540, 560 and 630 nm are possibly connected to surface defect states associated with atomic scale surface roughness, as the bulk spectra displayed no such bands above noise levels. Annealing would result in the reconfiguration of the surface layers, reducing the density of defect states, thus giving a reduced CL intensity for these bands.

The spectra in Fig. 3(b) and (d) contain two peaks that have not been previously described. The emission at 867 nm is dominant in both, but annealing reduces its intensity considerably. Associated with this are four small peaks at 873, 880 and 886 nm, all of which are removed during annealing. The narrow width of the peak at 867 nm suggests a direct transition, with the small peaks being vibrational side bands. This could possibly be the result of surface contamination, as MgO suffers degradation when exposed to the atmosphere through chemisorption of H_2O and CO_2[20], but for the presence of peaks at 20 keV in the as-received and ion milled samples. Presumably, either the electronic configuration of the MgO is being affected by the anneal, which acts to remove vacancy sites, or an impurity ion is diffusing through the sample.

The presence of surface flaws in the MgO substrate greatly affects the local electronic band structure. Similar defects, albeit larger, from cleavage steps, have been described by Barkay *et al.*[24] However, their use of large excitation volumes (beam energies of 30 keV) meant that CL collection was predominately from the bulk and not from the surface. The spectra in Fig. 4(b) show that the CL intensity is reduced by annealing the substrate. The CL emissions from an annealed flaw are now very similar to that of the undamaged substrate. However, the gross flaws that can be seen optically are not removed by the anneal; only the luminescent defect states associated with the flaw have been removed, whilst the flaw itself remains.

Superconducting thin films of YBCO have been grown onto similarly treated MgO substrates which contain defects, and the film morphologies determined.[23] At the site of a defect, porosity was observed in the film microstructure. For example, the defect width in an YBCO film deposited on an annealed substrate was about 200 nm. Hence it is seen that fine defects in the substrate, not easily observable by optical methods can affect the thin film nucleation and growth processes, resulting in unwanted defects in the final microstructure. This is undesirable for electronic device applications.

Conclusions

The preparation of MgO single crystals has been successfully monitored by the CL technique. The optical and spectroscopic CL systems have enabled the identification of both Ni and Cr impurities, and the assessment of surface quality, with respect to treatment. Annealing has resulted in the removal of surface defect states, which are responsible for the luminescence in both the untreated and ion milled samples. Also luminescent defects states associated with surface scratches are virtually removed on annealing. It is concluded that, with respect to high T_c thin films, the process of annealing results in a marked improvement in the thin film electrical properties.

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