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LETTER TO THE EDITOR

Ca²⁺ and ¹⁸O²⁻ diffusion in ultrapure MgO

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Abstract. We have grown ultrapure MgO from multiply distilled Mg and pure gaseous O₂, using molecular beam epitaxy to prepare high-quality crystals with levels of trivalent cation impurities reduced by a factor of $\sim 10^2$. From studies of Ca and ¹⁸O tracer diffusion on the respective sublattices we infer that the active impurity level during diffusion is a factor of 10 below that of high-quality commercial MgO. In a temperature range where it is insensitive to impurity content the anion diffusion appears consistent with theoretical predictions that anion jumps occur largely by motion of bound vacancy pairs.

For several decades the diffusion in oxides has remained poorly understood [1, 2]. The experimental results have differed widely among laboratories, and for various measurement techniques. Even for a simple oxide such as MgO, the measurements have disagreed markedly with the predictions of theoretical calculations that provide values for the relevant defect energies and entropies [3, 4]. The measured diffusion rates on the cation sublattice of MgO have typically taken reasonable values, dominated by excess cation vacancies introduced by trivalent cation impurities. The measured anion diffusion has been the origin of the problem. In a recent paper [5] we report measurements on samples grown by molecular beam epitaxy (MBE). The diffusion was detected by the broadening of tracer layers grown 0.1 μm or more below the final surface. In these new materials the observed anion diffusion is smaller by several orders of magnitude than in earlier bulk measurements. For both sublattices the entire data set is in good agreement with the theoretical predictions, given an assumed concentration of about 30 ppm trivalent cation impurities. This impurity level appears reasonable but has not been measured directly. In the present paper we report two significant new results. First, we have successfully employed MBE to grow 'superpure' MgO with greatly reduced levels of trivalent cations. Specifically, the level of active impurity during diffusion runs is reduced to about 3 ppm. Second, we have made diffusion measurements on the pure material, and the results prove to lie in satisfactory agreement with the earlier interpretation. By supporting the interpretation of the MBE results published earlier, they also reflect the accuracy of the theory.

MgO can be grown from the vapour phase either by evaporation of MgO onto a suitable substrate or by the simultaneous deposition of Mg and O₂ from separate sources [6]. The latter method was employed in the present research in order to prepare single crystals of MgO much purer than those previously available. To this purpose we used special distilled Mg of 99.9999% purity (apart from Zn), kindly prepared and supplied by Dr J L Pastol, and described in earlier publications [7]. The evaporating Mg, together with standard 99.9999% pure bottled O₂ from a nozzle, was allowed to fall onto a cleaned (001) face of an epitaxial grade MgO substrate crystal at 400 °C in an ultrahigh-vacuum system, as described previously [6]. The growth temperature was higher than convenient, given the low

sticking probabilities [6], in order to mitigate a problem concerning crystal growth described below. Typical samples contained several tenths of a micrometre of fresh epitaxial growth. For diffusion measurements, CaO or Mg^{18}O tracer was introduced in a manner described elsewhere [8], after establishing $0.2\ \mu\text{m}$ epitaxial growth on the substrate. The tracer was usually in two 5 nm layers separated by $\sim 0.1\ \mu\text{m}$, followed by further growth of normal MgO to buffer the diffusion zone from the crystal surface.

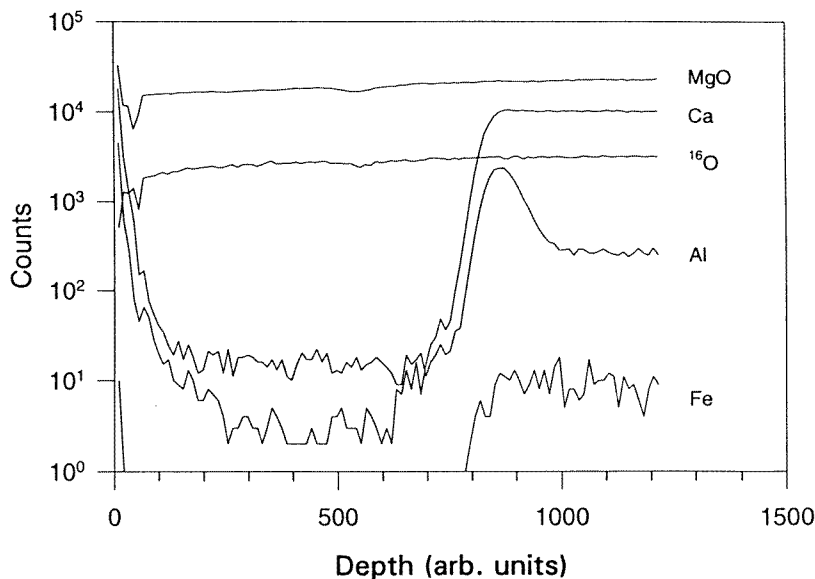


Figure 1. The depth profile of ultrapure MgO and its less pure MgO substrate obtained by secondary-ion mass spectroscopy. The concentrations of Al, Ca and Fe impurities decrease by two orders of magnitude at the interface with the bulk substrate.

The effectiveness of these procedures may be judged from the sample analysed in figure 1. There the concentration profile determined by secondary-ion mass spectrometry (SIMS) is shown for ^{16}O , Mg, Ca, Fe and Al. Only the relative levels throughout the sample are meaningful because the impurity counts shown have poorly known sensitivity factors that vary by orders of magnitude from one species to the next. The interface between the pure substrate crystal and the ultrahigh-purity epitaxial MgO is nevertheless clearly marked by decreases of the impurity concentrations by two or more orders of magnitude. Fe and Al are believed to be the main cation impurities that cause extrinsic diffusion, so the improvements are quite encouraging.

Diffusion profiles were determined by SIMS after diffusion anneals in a Brew furnace. It is important that dual samples were annealed face to face in a Ta enclosure packed with MgO powder. Failure to do so resulted in surfaces roughened on the $0.1\text{--}1\ \mu\text{m}$ length scale by excessive sublimation during high-temperature annealing. Satisfactory Gaussian profiles of the type reported in [5] are observed in the buried marker layers of epitaxially grown MgO using these doping and annealing methods.

Figure 2 compares the Ca and ^{18}O diffusion coefficients D thus determined for the present ultrapure MgO with those obtained earlier using commercial high-purity MgO. Lines drawn near the cation results represent predictions [5] for different levels of trivalent cation

impurities. These predictions employ vacancy formation, migration and binding energies and frequency factors calculated using the Harwell HADES codes [9]. While not exact, the fits of the cation diffusion to theory are quite satisfactory. They indicate that the present materials give close to an order of magnitude improvement in effective purity over the commercial material.

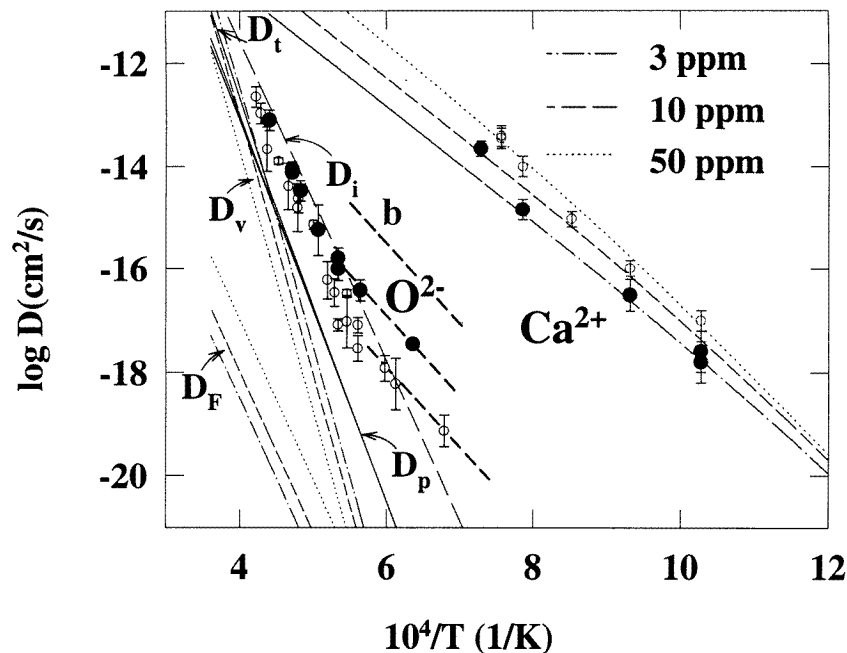


Figure 2. Measured diffusion coefficients in single-beam epitaxial MgO (open symbols) compared with present results for ultrapure MgO. The faint lines are predictions for different impurity levels, with D_t the anion total derived for these impurity levels from D_F , Frenkel defects, D_v , single vacancies, and D_p , neutral vacancy pairs, and with D_i the predicted intrinsic diffusion. The heavy broken line marked b shows best data for the bulk material.

Turning now to the anion diffusion, we note in general that impurity-induced changes of diffusion on the two sublattices of strongly ionic crystals normally appear as reciprocal factors caused by the suppression of vacancies on one sublattice and their increase on the other sublattice by the same factor. This happens because the product of the vacancy concentrations is constrained by the law of mass action (see e.g. [10]). According to the modelling that leads to the predictions in figure 2, the levels of cation impurities in the ultrapure samples remain sufficiently large to suppress the anion vacancies below the level of detection. The anion diffusion that remains to cause the observed marker broadening then arises from the motion of bound vacancy pairs that comprise one vacancy from each sublattice, rather than from free single vacancies. Being electrically neutral the pairs are independent of impurity doping. This is the origin of the predictions for anions in figure 2.

At the highest temperatures, the new results for anion diffusion merge with those for the less pure crystal, in agreement with the belief that only vacancy pairs contribute. It is nevertheless apparent from figure 2 that the anion diffusion at low temperatures in the present pure samples grown from two molecular beams is larger than that in the less pure

material grown from a single beam, even though no increase is expected. An explanation is therefore needed for this departure from theory at low temperatures.

There is strong evidence that the increased diffusion is an extrinsic effect caused by poor crystal quality. Indicated by a bold broken line and marked 'b' in figure 2 is the anion diffusion rate typical of the best bulk measurements [1,2]. It is now apparent that the three sets of anion data show a common systematic trend at the lowest temperatures, indicated by the three parallel bold broken lines. The single-beam (less pure) MBE material deviates from an Arrhenius plot at low temperature in much the same way as the two-beam (ultrapure) material deviates at an order of magnitude faster diffusion. This trend strongly suggests that the diffusion curve for the bulk material (the broken line marked b) reflects the same extrinsic behaviour but with a still larger magnitude. We infer that the anion diffusion at low temperature is sensitive to some structural defect that is present to differing degrees in the various samples. We have not been able to identify the defect responsible for the problem, nor have we determined why the two-beam procedures cause a tenfold deterioration of the crystal quality obtained using a single beam. A specific indication of poorer quality is, however, also evident in channelling spectra that show twice the backscattering rate for the two-beam material. Since channelled atoms backscatter from structural defects this evidence is consistent with the diffusion observations. The structural defects become more numerous as the growth temperature is reduced, and for this reason we chose to prepare the ultrahigh-purity materials at about 400 °C.

With this interpretation of the extrinsic effects, the composite of all the available diffusion results for MgO grown by MBE forms a consistent picture. There is an extrinsic defect that spoils bulk measurements of anion diffusion, and interferes more with MBE material grown from separate Mg and O₂ than by evaporation of MgO. When the MBE material is purified, the cation diffusion is reduced as predicted. Anion diffusion in the ultrapure material shows no complementary increase in the high-temperature region where the extrinsic effects are negligible. This establishes that the anion diffusion occurs mainly by neutral point defects even in the high-temperature regime where the pairing effects are weakest. With the exception of the systematic deviations caused by extrinsic behaviour, this is just what the theory predicts.

We note finally that the full impurity reduction of $\sim 10^2$ suggested by SIMS results of figure 1 fails to emerge in the cation diffusion data, which correspond to an average improvement only by a factor of ~ 10 . This happens because fast-diffusing anion impurities from the bulk substrate flood into the tracer regions during diffusion anneals at high temperature, and in this way degrade the ultrapure material. Efforts to suppress this process by buffer layers grown from immobile dopants were not successful. The diffusion conditions used here required a difficult compromise between the suppression of impurities diffusing in from the substrate and the need for long enough anneals to give adequate broadening of the marker layers. This explains why the diffusion results indicate higher levels of impurity than present in the as-grown ultrapure crystal. Some part of the scatter of the tracer diffusion coefficients reported here is undoubtedly caused by variations of the effective impurity levels among samples.

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