Intrinsic Diffusion Properties of an Oxide: MgO

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(Received 7 March 1994)

We use molecular beam epitaxy to grow MgO of high structural quality with buried tracer layers for diffusion measurement. The diffusion observed on both sublattices is in good accord with predictions for the existing impurity content; on the anion sublattice the rates slightly exceed the theory for bound Schottky pairs alone. The results provide new and substantial support for the application to oxides of theories that determine the energy and entropy of the nonlinear dielectric relaxation fields near charged defects in ionic crystals.

PACS numbers: 61.72.Ji, 66.30.Hs, 77.84.Bw

Ionic solids such as wide gap oxides exhibit a unique response to the formation of charged defects. In these materials the electric fields surrounding fixed charges are screened by dielectric relaxation which includes optic mode displacements, so that the ionic positions are modified [1,2]. The relaxation causes large nonlinear reductions (by $\frac{1}{2}$ to 1 order of magnitude) in the formation energy of such defects as vacancies in oxides [3]. The temperature and volume dependences of this relaxation produce characteristic large entropies and volumes of formation, which are mainly anharmonic in character, related to electrostriction [4–6]. Whatever theory is employed to treat the unrelaxed energy, realistic predictions for the equilibrium lattice configuration require accurate modeling of this ionic displacement field. A means to calculate the displacement fields self-consistently is provided by the Mott-Littleton method in various computerized forms [7]. By these means defect formation energies accurate to 10% or better have been calculated for alkali halides [1,2]. Applications have also extended to the treatment of oxides [3,8–11]. In the latter case, however, the justification is much less certain, because the oxygen orbitals are poorly localized, and it is then no longer clear that the concepts of ionic charge and polarization remain useful. Unfortunately, the application to oxide materials has also lacked quantitative practical assessment owing to parallel experimental difficulties [12]. Even in the most favorable case of MgO, cation impurities at the 30+ ppm level, together with extended defects from surface preparation, result universally in measured anion diffusion energies ~3–5 eV, in the face of predicted values > 6 eV for Schottky defects [3]. Thus the experimental facts and the effectiveness of the theory both remain uncertain for oxides. A resolution of the difficulties bears on the utility of these important materials in structural, electrical, and electronic applications, and in high temperature and irradiation environments.

In this Letter we report anion and cation diffusion in high quality MgO grown with buried tracer layers by molecular beam epitaxy. For the first time the activation energies are in the range predicted for Schottky defects. Indeed, the observed diffusion on both sublattices falls into remarkable quantitative agreement with theory for the existing impurity concentration. To this extent the application of self-consistent lattice calculations to oxide materials finds substantial new support. The diffusion shows no depth dependence at the surface, to a resolution of 250 Å, also in accordance with theoretical predictions of the Debye-Huckel screening length. Finally, we observe a trapping effect at the interface between the substrate MgO and the molecular beam epitaxy (MBE) grown material that suggests surface damage at the polished surface may be one main source of the misleading anion diffusion results obtained in all earlier studies.

The diffusion measurements reported here employed the spread of tracer elements through MgO grown by molecular beam epitaxy. New crystal typically 2000–5000 Å thick was grown on conventional polished substrates (from ESPI) of high purity $Mg^{16}O$ after a prolonged anneal for 12 h at 1100 K. Single crystal $Mg^{18}O$ and $(Ca_{0.01}Mg_{0.99})O$ layers typically 50 Å thick were incorporated at depths between 300 and 2500 Å by methods described in earlier publications [13,14] and overgrown with high quality crystal by evaporation of MgO chips. Diffusion anneals at temperatures in the range 1000–2400 K were conducted in a Brew furnace, using twin samples clamped face-to-face and packed in MgO powder, in order to inhibit sublimation from the active surfaces. Diffused tracer distributions were then studied by secondary ion mass spectrometric (SIMS) depth profiling. No significant differences were observed in alternative uses of vacuum or argon furnace environments. The temperature was calibrated in the relevant range by observations of melting for several metals.

In Fig. 1, diffusion coefficients determined in this research are compared with a representative display of earlier results [15,16]. Best fits to the present data are presented as heavy lines. They represent the equations

$$D_{\mathrm{Ca}} = (1.04 \times 10^{-4}) \exp(-2.52\ \mathrm{eV}/k_B T)\,\mathrm{cm}^2/\mathrm{s};$$

$$D_{\mathrm{O}} = 76 \exp(-6.91\ \mathrm{eV}/k_B T) + 10^{-10}\exp(-2.66\ \mathrm{eV}/k_B T)\,\mathrm{cm}^2/\mathrm{s}.$$

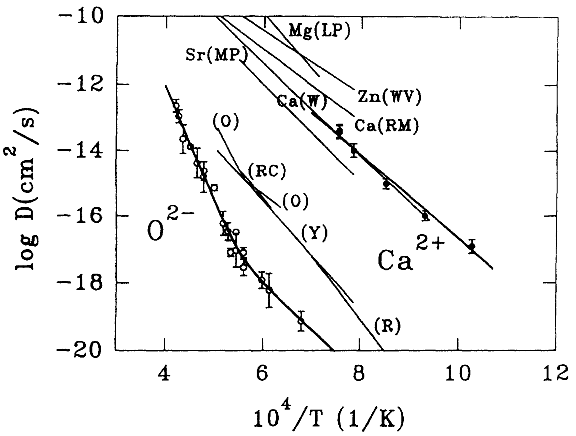

FIG. 1. Measured diffusion coefficients for ^{18}O and Ca in MBE grown MgO. Dark solid lines represent the fits to the data reported in the text. The lighter lines refer to the earlier studies (see Refs. [15] and [16]).

The fitted activation energies of 6.9 and 2.5 eV on the anion and cation sublattices agree generally well with predictions of 7.3 eV for intrinsic vacancy pair activation [3], and extrinsic Ca activation with energy 2.29 eV [10]. The large anion D_0 indicates that entropy contributes a factor $\gtrsim 10^2$, which is the expected result of anharmonic dielectric relaxation, as a characteristic of ionic crystals (see above). A matter of particular note in our later discussion is that the anion data generally fall 2 orders of magnitude below earlier results, while the cation data exhibit smaller departures. Also, the anion diffusion becomes less activated at the lowest temperatures, with a slope resembling that of earlier studies. Studies of loop annealing yield D values close to the present results [17].

The experimental facts are clarified by the typical ^{18}O diffusion profiles, determined by SIMS, and provided in Fig. 2. Both the as-grown profiles and those taken after substantial added diffusion fit the Gaussian curves very well, with squared widths that increase linearly with diffusion time as expected (Fig. 2 inset). An increase $>10^2$ for diffusion in the bulk would give Gaussians much wider than the entire Fig. 2. Also the 10 K uncertainty of the temperature is negligibly small compared to the 350 K shift required for equal bulk and film diffusion rates at 1800 K. Therefore our results afford convincing proof that the anion diffusion in MBE materials is slower than values reported for the bulk by this large factor. A pertinent point is that spurious contributions from imperfect sample geometry (Fig. 3 inset), and added diffusion paths from flaws, all *broaden* a distribution and cannot possibly explain the *narrower* profiles in the MBE material reported here. We conclude that ^{18}O diffusion in the MBE samples is indeed slower by at least the observed large factor.

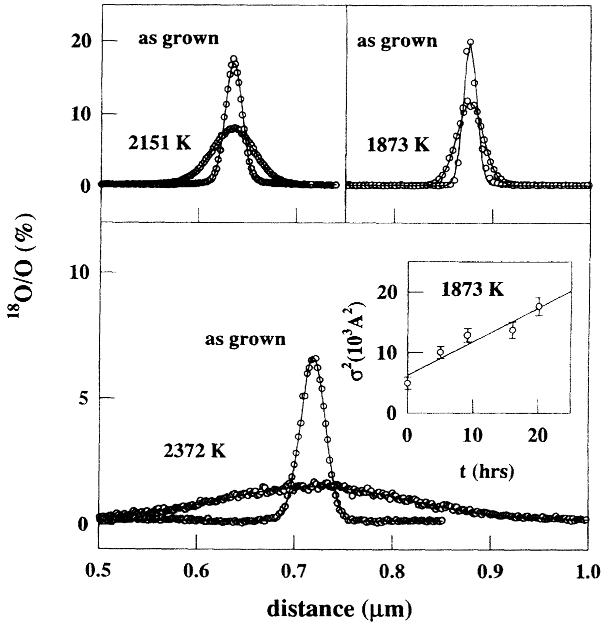

FIG. 2. Typical ^{18}O diffusion profiles at several different temperatures are shown. Profiles (circles) for both the as grown and the diffusion annealed samples are fitted very well by Gaussian curves (lines). Inset shows that the square of the Gaussian width (σ^2) increases lineally with diffusion time (t) as expected.

More comprehensive comparisons between our experiment and theoretical prediction reveal a still greater degree of accord. Figure 3 shows data points graphed with model predictions. Trivalent impurity concentration

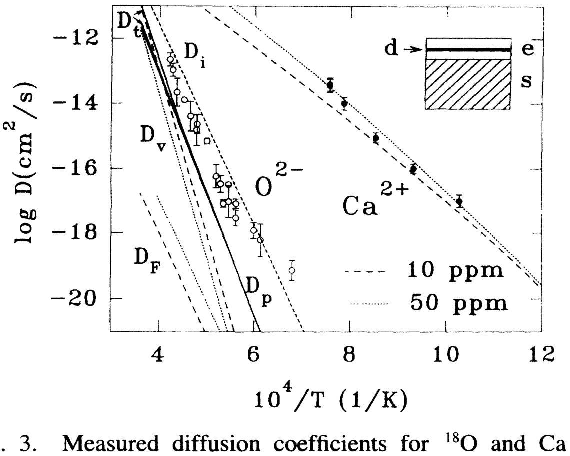

FIG. 3. Measured diffusion coefficients for ^{18}O and Ca in MgO, compared with values predicted by theory, for the cation impurity levels indicated. Inset is a sketch showing the sample geometry with substrates, epilayer e and doped layer d. The quantities entering into the predictions are described in the text. For anion diffusion, the contributions of pairs (D_p), free vacancies (D_v), Frenkel pairs (D_F), and the totals (D_t) are shown separately. The predicted intrinsic diffusion, common to both sublattices, is indicated by the broken line marked D_i.

of 10 and 50 ppm are employed, consistent with the characteristics of the MgO source material and substrate. Diffusion on the cation sublattice is very fast owing to the large cation vacancy population required to neutralize the trivalent impurities. The predicted Ca diffusion rates, obtained using the theoretical migration and binding parameters for the selected impurity levels, and indicated by the solid line in Fig. 3, are within a small numerical factor of the experimental rates.

As remarked by Ando, Kurokawa, and Oishi [18], the internal potential produced by the positively charged impurities suppresses free anion vacancies. Anion diffusion then proceeds in part by the migration of vacancy pairs. Bound pairs comprising one anion and one cation vacancy, being electrically neutral, remain unaffected by the impurity-induced potential. The line in Fig. 3 marked D_p represents the theoretical prediction for diffusion of anions promoted by vacancy pairs alone. According to theory it represents the smallest possible anion diffusion rates, for complete suppression of free vacancies. These predictions fall only just below the measured anion diffusion coefficients, which in turn lie below the broken line, marked D_i, indicating the predicted intrinsic diffusion. The curves marked D_v are the added rates due to free vacancies for the assumed impurity levels, which sum with the pair term to yield the total anion rates marked D_t. Predicted contributions D_F from Frenkel disorder are much smaller.

In deriving the predictions we have simply taken the calculated Schottky pair energy and entropy of $E_S = 7.65$ eV and $S_S = 4.5k_B$ from Mackrodt [3], together with the calculated pair binding energy of $B = 2.65$ eV [10,11]. The binding entropy was not available and was assumed to be $S_B = 1.54k_B$ in order that $S_S/E_S = S_B/B$. The entropies are mainly volume dependences of the dielectric relaxation energies and should therefore fall in a similar ratio. The cation and anion migration energies and entropies of 2.26 eV, $2.48k_B$, 2.30 eV, and $2.7k_B$ similarly were taken from Sangster and Stoneham [8] and Mackrodt [3], respectively. The frequency factor 23 THz was calculated for Mg vacancy migration explicitly by Sangster and Stoneham [8] and is assumed here to be the same for the vacancy pair migration. The binding of cation vacancies to trivalent impurities is calculated to be $B_i = 0.8$ eV [8,10]; their small binding to Ca ions in MgO is predicted as $B_{\mathrm{Ca}} = 0.09$ eV [10], and the activation energy for Ca migration is calculated at 2.29 eV [10]; these values were therefore adopted in the analysis shown.

In assessing the predictions it is appropriate to note that a change of the net activation energy by 0.25 eV typically modifies the predicted diffusion rates by $\frac{1}{2}$ to 1 order of magnitude. As predictions with this precision present a considerable challenge to the theory, it is our assessment that the high degree of numerical agreement in Fig. 3 may in part be fortuitous; it nevertheless remains highly impressive. The predictions generally lie below the observed values as if the migration rates are slightly underestimated.

Given this straightforward explanation of the diffusion results, in terms of available models and long standing predictions, we have performed certain auxiliary measurements to explore the differences between the present and earlier samples. By creating marker layers at different depths below the surface we have measured the depth dependence of the observed mixing rate. Care was taken to eliminate spurious effects from temperature irreproducibility and gradients. Tracers were grown at progressively greater buried depths along a substrate and two halves clamped face-to-face with opposing depth sequences. The way this exposes the effects of residual small gradients is illustrated for our worst case in Fig. 4. Measurements made using these methods between 1700 and 2100 K failed to reveal any depth dependence of the anion diffusion rate to within 250 Å of the surface. This is consistent with Debye-Huckel screening length κ^{-1} of surface sinks for the high prevailing densities of charged defects ($\kappa^{-1} \sim 55$ Å for $c = 30$ ppm at 2000 K).

The diffusion data provide striking indications that the differences between these and less explicable earlier results arise from the quality of the near-surface material rather than from an improvement in its purity. Specifically, the present anion diffusion is a factor up to 10^2 less than that observed in other research, yet the cation diffusion undergoes no significant enhancement but, rather, appears in the lower range of the scattered earlier results. Any effect of impurities from either sublattice, acting through the interior potential, must cause equal but opposite effects on the vacancies of the two sublattices,

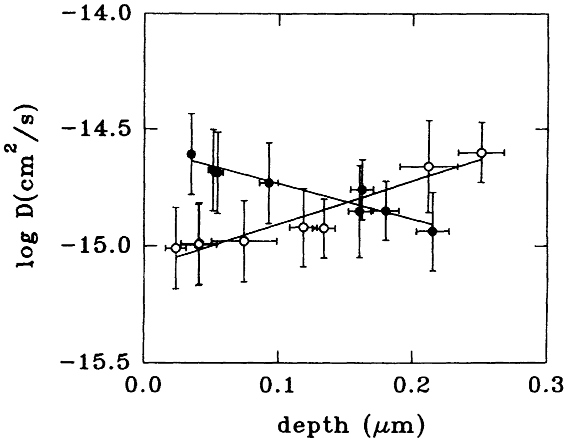

FIG. 4. Opposing trends of the measured diffusion coefficient are shown as functions of the buried layer depth from paired samples at a nominal temperature of 1990 K. This method is used to eliminate the temperature gradient effect across the samples. The temperature gradient inferred from the data is about 2 K/mm. No net depth dependence was observed between 1700 and 2100 K.

and hence on the diffusion rates. From the lack of comparable increase of cation diffusion it therefore appears *certain* that the reduced anion diffusion observed here does not arise from modified doping alone.

The tail visible on the anion diffusion rate at low temperature is reminiscent in slope of earlier high temperature anion diffusion data in bulk samples. It suggests that alternative migration paths exist in the bulk materials and are greatly reduced but not completely eliminated in the MBE crystal, merely lowered by some 2 orders of magnitude [19]. Even if these processes were equally effective on the two sublattices, they could not affect diffusion on the cation sublattice, where diffusion by impurity-induced vacancies is overwhelming. Improved crystal quality of the MBE samples would therefore have its main effect on anion diffusion alone, just as is observed. One likely candidate mechanism for such enhanced low-temperature diffusion involves the damage caused by surface preparation. Extended defects associated with the damage near the surfaces of polished crystals may possibly provide fast diffusion paths that exceed the suppressed anion mixing at all accessible temperatures. This may be the origin of the spuriously high anion diffusion rates observed in "bulk" samples.

Further evidence that the substrate surface causes diffusion problems comes directly from secondary-ion-mass spectroscopy (SIMS) profiles of impurity diffusion. The Ca profiles in Fig. 5 show the initial distribution broadening with progressive annealing and the interface with the substrate made visible by the concentration discontinuity. Note that an anomaly occurs in the Ca concentration where the diffusant reaches the interface, indicating apparent trapping. We have observed larger effects in the concentrations of higher valence impurities such as Al. The detailed origins of these surface effects remain still to be explored.

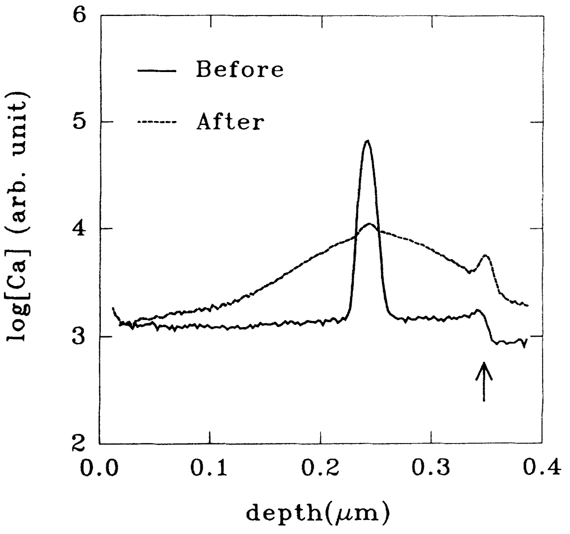

FIG. 5. Ca diffusion profiles in MgO showing the initial discontinuity at the interface (as indicated by the arrow) and the interfacial peak probably due to subsequent trapping by defect structure.

In summary, we have measured diffusion on both sublattices of MgO grown by molecular beam epitaxy. For the first time in any oxide material, the diffusion energies and entropies are in quantitative accord with theoretical expectation. The results provide striking support for the theoretical models employed to simulate the anharmonic displacement fields that surround charged defects in ionic oxides. The procedures employed here appear to open the path to a comprehensive future understanding of intrinsic defect behavior in a variety of oxide materials. Measurements of a similar type are, for example, currently in progress on Y_2O_3, which supports Frenkel disorder.

We wish to thank R. L. Averback for helpful and stimulating discussions. This research was supported in part by the University of Illinois MRL Grant No. DE-FG0291ER45439 from the Department of Energy.

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