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Low-temperature growth of MgO by molecular-beam epitaxy

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We have explored the epitaxial growth of MgO single crystals using separate O_2 and Mg beams and also *e*-beam-evaporated MgO. The latter method is preferred as the incorporation efficiency of O_2 turns out to be $\sim 10^{-3}$ even at 200 °C in the former method. Excellent MgO grows by *e*-beam evaporation at temperatures down to 140 K ($T_m/20$), in agreement with expectations of Yang and Flynn. Good surface quality is achieved in heteroepitaxy, even for the first few monolayers.

Simple, strongly ionic oxides represent an interesting new class of materials for thin-film studies. They are wide-gap insulators, sufficiently tough and unreactive for potential applications as single-crystal insulators, and suitable for use as single-crystal tunnel barriers.[1] Their growth behavior is also of considerable scientific interest. It has recently been suggested that fast diffusion on the neutral cleavage planes of strongly ionic systems can make epitaxial growth possible down to remarkably low temperatures $\sim 0.1 T_m$, with T_m the melting temperature.[2] Here we report successful initial studies of MgO growth by molecular-beam epitaxy (MBE). MgO is a prototypical simple oxide. It is highly ionic, with the rock-salt structure, and a melting temperature near 3000 °C. The temperature range over which this compound grows well and the perfection with which ultrathin films can be prepared are of particular interest.

A good deal of recent effort has focused on the growth of fairly complicated oxide structures from molecular beams.[3-5] This has been driven largely by interest in single-crystal films of high-T_c superconductors. The earlier pioneering research of Bando and co-workers on NiO, CoO, Fe_3O_4, and certain superlattices, using "activated" oxygen beams, predates the recent effort by several years.[6-9] No comparable effort has been directed to the growth characteristics of simple metal oxides like MgO by molecular-beam methods.[10] A recent attempt to grow BaO on W(110) resulted in three-dimensional crystals of marginal quality, possibly owing to interfacial reactions.[11] It has nevertheless long been known[12] that MgO "smoke" grows as fine cubes with excellent (001) faces from the vapor phase, so the prospects for epitaxial growth of single crystals appear good. Recent studies by Yang and Flynn[2,13] are closely related, in which excellent single crystals of alkali halides were grown by MBE. They discovered that single-crystal growth persisted even at low temperatures, ~ 100 K for crystals that melt at 1000–1200 K. Their explanation is that the corrugated electrostatic potential due to the ions decays exponentially outside a neutral ionic surface to leave only weak barriers impeding the mobility of surface species. The same conditions recur for MgO, which is also strongly ionic and has the NaCl structure, with low-energy (001) cleavage planes. The present research on MgO was undertaken to explore growth characteristics of a simple ionic oxide and to determine whether or not the (001) terraces offer unusually high surface mobility.

MgO may be grown from separate beams of Mg and O_2 (which can be activated if necessary) or directly from a beam of evaporated MgO. As the binding energy of the ionic molecule exceeds 10 eV, one may expect the latter method to mainly involve a beam of Mg^+O^- molecules. This has been confirmed by experiments in which a deflecting field is placed across the beam path, with no observable effect on the composition of the molecular-beam flux. We have successfully grown single-crystal MgO with flat (001) terraces by both methods. These results are described briefly in what follows, starting with the case of separate Mg and O_2 beams.

Mg was evaporated from an effusion cell and O_2 obtained from a 0.2-mm nozzle at a pressure of 10–100 torr.[14] Differential pumping between successive baffles refined the O_2 flux into a molecular beam, so that the background O_2 in the growth chamber remained below 10^{-6} torr even for 100 torr at the nozzle. The MBE chamber was equipped with a quadrupole mass spectrometer and a quartz-crystal thickness monitor to follow the intensities of the beams. Reflection high-energy electron diffraction (RHEED) was used to study the growing surface *in situ*. Substrate temperatures could be varied between room temperature and 1000 °C in this arrangement.

By these means we have grown MgO on cleaved MgO(001) surfaces and on various cuts of epitaxial-grade sapphire. RHEED patterns for the [100] and [110] azimuths of a MgO(001) surface grown at 250 °C are shown in Fig. 1. The growth characteristics are dominated by the small sticking coefficients of the ions on terraces, somewhat as in studies of II-VI chalcogenides.[15] We have made preliminary studies of the kinetics by the following method. An O_2 beam flux and a Mg deposition rate were selected and growth started. Beginning at high temperature, the substrate temperature was progressively lowered and the RHEED pattern monitored. At a certain critical temperature T_c new structure that corresponds to crystalline Mg in its (0001) orientation appeared in the RHEED pattern. For the case of zero O_2 flux this occurred when the rate of Mg thermal desorption from an almost complete monolayer precisely equaled the Mg adsorption from the molecular beam. The excess Mg readily desorbed

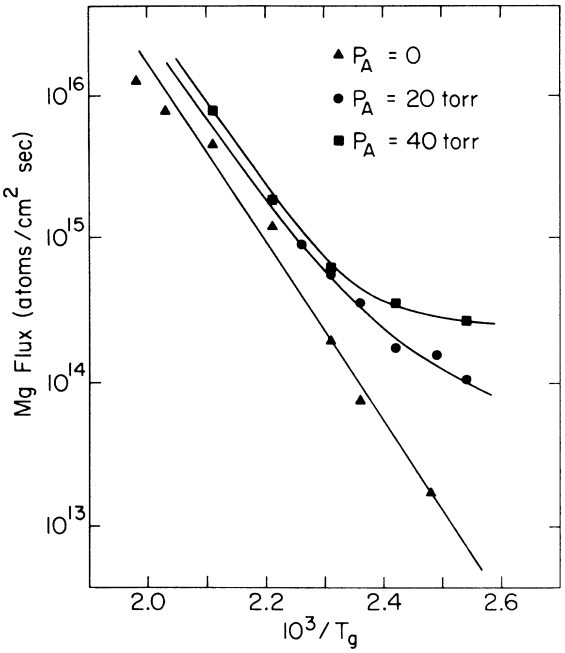

FIG. 1. Fluxes for Mg nucleation in the growth of single-crystal MgO at various temperatures and O_2 pressures.

again if the temperature was raised, so that a protracted series of observations could be undertaken. For higher O_2 fluxes the Mg nucleation was observed to occur at a lower growth temperature because a fraction of the Mg was captured by O_2 to form MgO, leaving less to desorb. Figure 2 shows how the critical temperature for Mg nucleation varied with Mg flux for several O_2 fluxes. A straight line through the data for zero O_2 flux indicates an activation energy of 1.25 ± 0.1 eV. This energy is comparable with the cohesive energy of ~ 1.56 eV for pure Mg metal.

It proved possible to obtain approximate estimates of the sticking coefficients for O_2 and Mg. From the source geometry we calculate for 20-torr driving pressure an O_2 flux of $\sim 10^{20}$ cm^{-2}sec^{-1}. This would correspond to 160 Å/sec of MgO growth, whereas 0.24 Å/sec was observed at $T_g = 200\,^\circ$C by α step thickness measurements. Evidently the O_2 incorporation efficiency was $\sim 10^{-3}$ at 200 °C. From the observed Mg flux under these same circumstances the incorporation efficiency was found to be $\sim 20\%$. These experiments establish clearly that two-beam growth is limited by problems of O_2 incorporation that most probably arise from weak sticking of O_2 on the (001) MgO terraces.

High-quality MgO single crystals were grown by molecular-beam epitaxy most conveniently using a flux of MgO evaporated from an *e*-beam hearth. In this way stoichiometric proportions of the two species are supplied automatically. Moreover, as the beam mainly consists of Mg^+O^- molecules, the O_2 pressure in the chamber is 2 orders of magnitude lower than that observed when using separate molecular beams of Mg and O_2. The *e*-beam work employed a chamber in which the substrate temperature could be maintained at selected temperatures in the range 140–1300 K. Excellent growth was observed for (001) oriented MgO throughout this range at modest growth rates ~ 0.5 Å/sec, even though the lowest temperatures were only $\sim 0.05 T_m$, with T_m the melting temperature. For comparison, Si and Ge require temperatures $\geq 0.5 T_m$ to grow well at rates ~ 1 Å/sec. No effort was made to perfect the proportions of Mg and O actually sticking at the substrate. Probably as a consequence of this deficiency we observed by RHEED that during protracted low-temperature growth an increasing fraction of the surface became overgrown with poor-quality crystal, the rest remaining excellent. We believe that this problem arose from successive nucleation events associated with nonstoichiometry or impurity condensation, and might well be corrected by a more appropriate balancing of incident species. No such problems arose for growth temperatures above 200 K. X-ray diffraction studies of *e*-beam MgO films reveal excellent structural coherence. Figure 2 shows as an example the Bragg scan and rocking curve for the (002) reflection of MgO grown 2000 Å thick on V(001) at 650 °C with a growth rate of 0.4 Å/sec.

In further experiments, we have grown MgO on (0001) sapphire as (111)-oriented good single crystals but with rough three-dimensional surfaces, as seen by RHEED. On $(11\bar{2}0)$ epitaxial-grade sapphire MgO grows in the (011) orientation with a reasonably smooth surface but not so good as (001)-oriented growth. In addition, we have grown excellent (001) single crystals on vanadium (001) (see Fig. 3) and niobium (001) single-crystal surfaces. RHEED patterns indicate that fairly smooth single crystals grow even from the first few monolayers. These systems have a variety of potential applications to tunnel barriers and device structures. Details of the latter results will be reported in a separate publication.

The research reported here may be summarized by

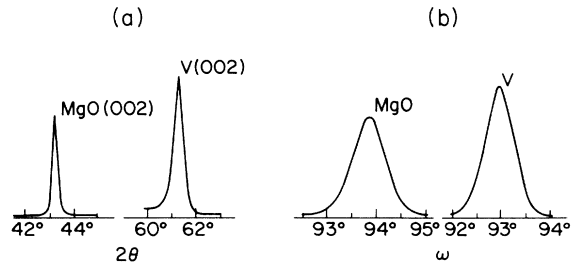

FIG. 2. (a) X-ray Bragg scans and (b) rocking curves of the V buffer layer and 2000-Å-thick MgO epilayer.

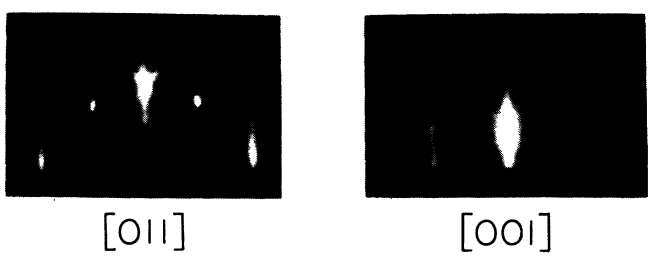

FIG. 3. RHEED patterns of MgO(001) after 300-Å regrowth.

three main results. First, high-quality MgO single crystals may be grown from molecular beams at temperatures down to $\sim T_m/20$, in agreement with earlier expectations for strongly ionic crystals.[1] Second, an *e*-beam source is preferred, owing to the low sticking probability of O_2 on the smooth (001) terraces. Third, relatively smooth two-dimensional growth can be achieved even for the first few monolayers on several types of substrates including metals and oxides. These characteristics establish MgO as a candidate single-crystal electrical barrier in applications to device structures.

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[1]A. I. Braginski, J. R. Gavaler, M. A. Janocko, and J. Talvacchio, in *New Materials for Refractory Tunnel Junctions: Fundamental Aspects; Squid '85–Superconducting Quantum Interference Devices and their Applications* (Walter de Gruyter & Co., Berlin, 1985).

[2]M. H. Yang and C. P. Flynn, Phys. Rev. Lett. **62**, 2476 (1989).

[3]J. Kwo, M. Hong, D. J. Trevor, R. M. Fleming, A. E. White, R. C. Farrow, A. R. Kortan, and K. T. Short, Appl. Phys. Lett. **53**, 2683 (1988).

[4]V. Paserin, M. A. Rashti, and D. E. Brodie, Appl. Phys. Lett. **53**, 624 (1988).

[5]D. D. Berkely, D. H. Kim, B. R. Johnson, and A. M. Goldman, Appl. Phys. Lett. **53**, 708 (1988).

[6]Y. Bando, S. Horii, and T. Takada, Jpn. J. Appl. Phys. **17**, 1037 (1978).

[7]T. Shigematsu, H. Ushigome, Y. Bando, and T. Takada, J. Cryst. Growth **50**, 801 (1980).

[8]T. Terashima and Y. Bando, J. Appl. Phys. **56**, 3445 (1984).

[9]T. Terashima and Y. Bando, Thin Solid Films **152**, 455 (1987).

[10]T. Koyano, Y. Kuroiwa, E. Kita, N. Saegusa, K. Ohshima, and A. Tasaki, J. Appl. Phys. **64**, 5764 (1988).

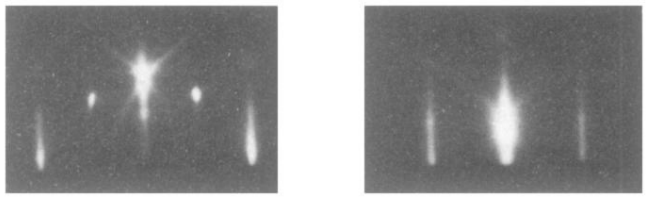
[11]D. A. Gorodetskii, Yu. P. Mel'nik, V. K. Sklyar, and A. A. Yas'ko, Kristallografiya **31**, 367 (1986). [Sov. Phys. Crystallogr. **31**, 216 (1986)].

[12]A. F. Moodie and C. E. Warble, J. Cryst. Growth **10**, 26 (1971).

[13]M. H. Yang and C. P. Flynn, Phys. Rev. B (to be published).

[14]Details of the oxygen source will be published elsewhere.

[15]J. P. Faurie, J. Cryst. Growth **81**, 483 (1987).



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