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Perspective: Oxide molecular-beam epitaxy rocks!

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Molecular-beam epitaxy (MBE) is the "gold standard" synthesis technique for preparing semiconductor heterostructures with high purity, high mobility, and exquisite control of layer thickness at the atomic-layer level. Its use for the growth of multicomponent oxides got off to a rocky start 30 yr ago, but in the ensuing decades, it has become the definitive method for the preparation of oxide heterostructures too, particularly when it is desired to explore their intrinsic properties. Examples illustrating the unparalleled achievements of oxide MBE are given; these motivate its expanding use for exploring the potentially revolutionary states of matter possessed by oxide systems. [http://dx.doi.org/10.1063/1.4919763]

Molecular-beam epitaxy (MBE) is a vacuum deposition method in which well-defined thermal beams of atoms or molecules react at a crystalline surface to produce an epitaxial film. It was originally developed for the growth of GaAs and (Al,Ga)As,[1] but due to its unparalleled ability to control layering at the monolayer level and compatibility with surface-science techniques to monitor the growth process as it occurs, its use has expanded to other semiconductors as well as metals and insulators.[2,3] Epitaxial growth, a clean ultra-high vacuum deposition environment, *in situ* characterization during growth, and the notable absence of highly energetic species are characteristics that distinguish MBE from other thin film methods used to prepare epitaxial oxides. These capabilities are key to the precise customization of oxide heterostructures at the atomic layer level. In addition to molecular beams emanating from heated crucibles containing individual elements, molecular beams of gases may also be introduced, for example, to form oxides or nitrides. This variant of MBE is known as "reactive MBE"[4] in analogy to its similarity to "reactive evaporation," which takes place at higher pressures where well-defined molecular beams are absent.

The use of reactive MBE to grow multicomponent oxides dates back to 1985, when Betts and Pitt used it to grow $LiNbO_3$ films.[5] Although these authors succeeded in achieving epitaxial $LiNbO_3$ films, after publishing two papers,[5,6] they left the field they had started, never to return. This has perhaps more to do with their choice of compound—$LiNbO_3$ is notoriously difficult to grow[7]—than oxide MBE itself. Spurred by the discovery of high-temperature superconductivity,[8,9] oxide MBE has since been used to grow the oxide superconductors $DyBa_2Cu_3O_{7-\delta}$,[10–13] $YBa_2Cu_3O_{7-\delta}$,[14,15] $NdBa_2Cu_3O_{7-\delta}$,[16] $SmBa_2Cu_3O_{7-\delta}$,[17] $(La,Sr)_2CuO_4$,[18–20] $(Pr,Ce)_2CuO_4$,[19] $(Nd,Ce)_2CuO_4$,[20] $(Ba,K)BiO_3$,[21,22] $(Ba,Rb)BiO_3$,[23,24] and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ for n = 1–11.[25–30] It has also been used to grow ferroelectrics beyond $LiNbO_3$,[5,6,31] including $LiTaO_3$,[31] $BaTiO_3$,[32–34] $PbTiO_3$,[35,36] and $Bi_4Ti_3O_{12}$;[37,38] the incipient ferroelectric $SrTiO_3$;[33,39] the ferromagnets $(La,Sr)MnO_3$,[40,41] $(La,Ca)MnO_3$,[40,42] and EuO;[43–46] the ferrimagnet Fe_3O_4;[47] the magnetoelectric Cr_2O_3;[47] the multiferroics $BiFeO_3$,[48–50] $YMnO_3$,[51,52] and $LuFeO_3$;[53] and superlattices of these phases.[26,29,30,34,54–66]

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The configuration of a MBE system for the growth of multicomponent oxides differs in several important ways from today's more conventional MBE systems designed for the growth of semiconductors. The major differences are the required presence of an oxidant species, more stringent composition control, and more pumping to handle the oxidant gas load.

To oxidize the elemental species reaching the substrate to form the desired multicomponent oxide, a molecular beam of oxidant is used. The tolerable pressure of this oxidant is limited so as not to destroy the long mean free path necessary for MBE. The maximum pressure depends on the MBE geometry, the element to be oxidized, and the oxidant species used, but oxidant pressures lower than about 10^{-4} Torr are typically required for MBE.[29] While molecular oxygen has been used for the growth of oxides that are easily oxidized,[5,6,32,33,43–47,51,58–60] oxidants with higher activity are needed for the growth of ferroelectrics or superconductors containing species that are more difficult to oxidize, e.g., bismuth-, lead-, or copper-containing oxides. For this purpose, purified ozone[13,14,17,25–27,29,30,35–39,49,50,54,62–66] or plasma sources[7,10–12,15,21–24,31,34,47,48,52] have been successfully employed. Distilled ozone is explosive, but distillation utilizing a silica gel can contain it relatively safely.[67] Indeed, this has become the technique[25] used by all commercial MBE companies to supply distilled ozone for their oxide MBE systems.

Composition control is another significant challenge for oxide MBE;[29] improvements in composition control have led to significant progress in customizing oxide structures, perfecting superlattices, and achieving improved properties. The use of atomic absorption spectroscopy for oxide MBE composition control has allowed fluxes to be measured with an accuracy of better than 1%.[68–75] *In situ* RHEED oscillations during the shuttered MBE growth of multicomponent oxides has also been shown to provide a means to accurately calibrate fluxes.[76] A particularly powerful means of composition control utilizes thermodynamics to provide an adsorption-controlled regime in which excess volatile species are supplied and reevaporte to yield automatic composition control. Such growth conditions are analogous to the way in which III-V and II-VI compound semiconductors are routinely grown by MBE.[77–84] Adsorption-controlled growth conditions for oxide MBE have been identified for numerous complex oxides containing volatile constituents including $PbTiO_3$,[36] $Bi_2Sr_2CuO_6$,[85] $Bi_4Ti_3O_{12}$,[37,38] $BiFeO_3$,[49] $BiMnO_3$,[86] $BiVO_4$,[87] EuO,[88] and $LuFe_2O_4$.[89] Another approach to achieving adsorption control at MBE-amenable growth temperatures is the use of volatile metalorganic precursors, i.e., oxide MOMBE.[90,91] This approach has yielded adsorption-controlled growth regimes for $SrTiO_3$,[92] $GdTiO_3$,[93] and $BaTiO_3$.[94]

Oxide MBE has yielded films with the highest structural quality and most precise layering control at the atomic-layer level. A few examples are (1) the growth of oxide thin films with the narrowest x-ray rocking curves ever reported for any oxide film grown by any technique,[95–98] (2) the growth of $A_{n+1}B_nO_{3n+1}$ Ruddlesden-Popper phases with n as high as 10 (Ref. 99; the highest that has been reported using any other technique is $n = 6$ (Refs. 100 and 101)), (3) the growth of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ phases with n as high as 11 (Refs. 27 and 28; the highest that has been reported using any other technique is $n = 8$ (Ref. 102)), (4) the growth of high-quality $SrTiO_3$ on (100) Si,[103–105] enabling the incredible properties of oxides to be expitaxially integrated with the backbone of semiconductor technology. On this last point, the superior structural perfection of $SrTiO_3$ achieved on silicon by oxide MBE is reflected in its rocking curves being 85× narrower (full width at half maximum of 0.008° vs. 0.68°) than the best $SrTiO_3$/Si layers made by other techniques.[106,107]

Due to the absence of highly energetic species during deposition, oxide MBE is the method of choice when it comes to achieving the intrinsic properties of sensitive materials. For example, $EuTiO_3$ is an antiferromagnet on the verge of becoming ferromagnetic. To date, the only technique that has succeeded in achieving this antiferromagnetic ground state in as-grown films is oxide MBE.[108,109] $EuTiO_3$ made by other techniques is ferromagnetic[110,111] and must be post-annealed, which presumably anneals out some defects, to bring it into the antiferromagnetic ground state.[112]

An excellent way to assess a growth technique is via electrical transport measurements on films made by it, which can be extremely sensitive to impurities and disorder. Table I shows such a direct comparison between films grown by oxide MBE vs. the best report in the literature for the same material grown by other techniques. As is evident from Table I, when it comes to growing *oxide* films with high purity, high mobility, superb perfection, and exquisite control of layer thickness at the atomic-layer level, nothing comes close to oxide MBE![125]

TABLE I. Comparison of the best transport properties reported on films made by oxide MBE vs. other thin film growth techniques.

Material	Best MBE figure of merit	Best non-MBE figure of merit	References
ZnO	$\mu_e = 770\,000\ \mathrm{cm^2/(V\cdot s)}$ at 0.4 K	$\mu_e = 5500\ \mathrm{cm^2/(V\cdot s)}$ at 1 K	113–115
$SrTiO_3$	$\mu_e = 53\,200\ \mathrm{cm^2/(V\cdot s)}$ at 2 K	$\mu_e = 6600\ \mathrm{cm^2/(V\cdot s)}$ at 2 K	116 and 117
$SrRuO_3$	$R_{300\,K}/R_{1.8\,K} = 45$	$R_{300\,K}/R_{4\,K} = 8.4$	118–120
$SrVO_3$	$R_{300\,K}/R_{5\,K} = 222$	$R_{300\,K}/R_{5\,K} = 2$	121–123
EuO	Metal-insulator transition $\Delta R/R = 10^8$	Metal-insulator transition $\Delta R/R = 5\times10^4$	46 and 124

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