Physics of Transition Metal Oxides

Lecture 14
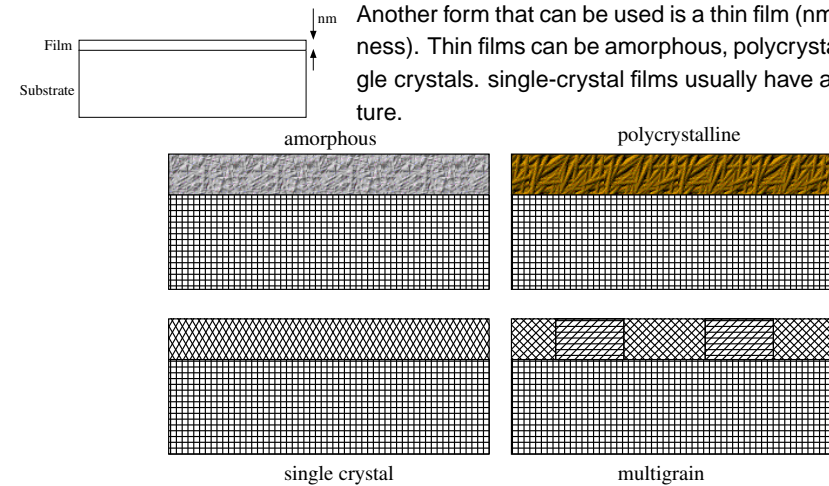
Oxide thin films

Thin films:

So far, we have looked at results that are obtained from bulk samples. Bulk means powder, pressed powder (*pellet*), or single crystals.

Another form that can be used is a thin film (nm order thickness). Thin films can be amorphous, polycrystalline, or single crystals. single-crystal films usually have a grain structure.

amorphous   polycrystalline

single crystal   multigrain

Why are thin films useful?

- Strain control: Lattice distortions can change the electronic structure of oxides

- Strain may also stabilize otherwise metastable crystal phases (similar to high-pressure synthesis)

- It is possible to grow very thin layers and superlattices

- Artificial lattices can be grown by combining two or more different materials

- Nanostructures can form during thin film growth

- Thin films are necessary for building electronic devices.


Oxide thin film growth methods:

Thin films can be grown various reactions:

- *solid-solid* sol-gel synthesis

- *liquid-solid* liquid-phase epitaxy, similar to crystal pulling

- *gas-solid* Most common method, includes

  - Physical vapor techniques (MBE, sputtering, PLD, thermal evaporation, etc.)
    Most useful for materials science and physics experiments

  - Chemical vapor techniques (CVD, ALE)
    Industrial use

Molecular beam epitaxy (MBE):

MBE is done in an ultra-high vacuum chamber. Several evaporation sources point at a heated substrate. Each element has a separate source.

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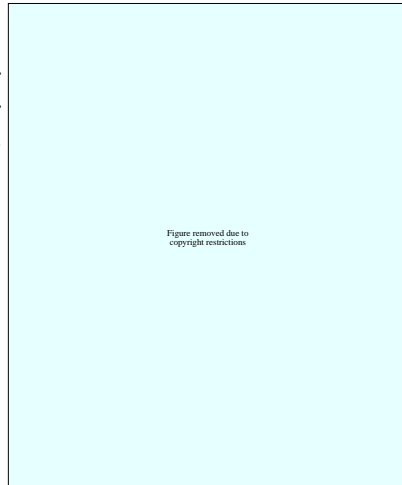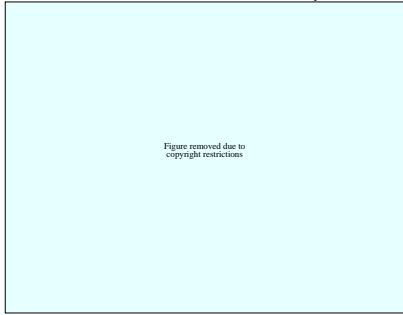
Herman96 p.7,61

A thermal evaporation cell containing a liquid metal is one common source, called a *Knudsen cell*, or a *K cell* for short. Evaporation rate can be adjusted by changing the source temperature. Other evaporation sources can also be used, e.g. e-beam.

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An MBE chamber can have very many sources. The system shown here has 16 sources. The pressure has to be low enough in the chamber for the mean free path of atoms to be longer than the source-to-sample distance. In practice the pressure has to be below 10^{-5} Torr and often much better than that.

Advanatages of MBE:
- Large area can be covered with a film
- Very high-quality crystals can be grown
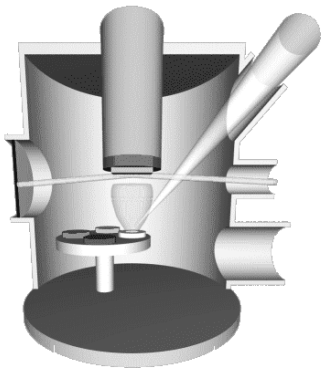- Any composition can be created by adjusting evaporation rates

Oxxel

Disadvantages:
- Deposition must be done at low pressure, cannot use background oxygen.
- Adjusting the precise stoichiometry can be difficult
- Many different sources must be maintained (complicated instrument)

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Pulsed laser deposition (PLD):

Evaporation in PLD is done with a high-power laser. A gas laser, such as KrF excimer, is commonl used. Short wavelength is more efficient. Typical numbers are 248 nm for KrF, 193 nm for ArF, 355 nm for 3ω Nd:YAG laser. Evaporation is momentary and usually happens at a rather low pulse rate, 1..10 Hz. The substrate is also heated. Many different target materials can be used. Targets are simple ceramic pellets or single crystals. Operating pressure can be as high as 1 Torr.
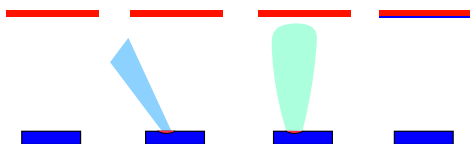
Laser pulse length is about 20 ns. Energy density at the target 1 to 10 J/cm^2. Power density 250 MW/cm^2 to 2 GW/cm^2. Temperature 10^4 K.

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Advantages of PLD:

- Can be used at a high background pressure (usually oxygen). Depositions at around 100 to 500 mTorr are common for Cu oxides, for example.

- Easy to prepare targets (traditional ceramic process)

- Technically simple

- Temperature at the target surface during the laser pulse is so high that stoichiometric evaporation occurs (usually).

- Easy to control film stoichiometry

Problems with PLD:

- Useful deposition area is very small (mm scale)

- Growth is very slow

- No easy way of correcting for nonstoichiometric evaporation

- Does not wotk for low melting point elements

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Sputtering:

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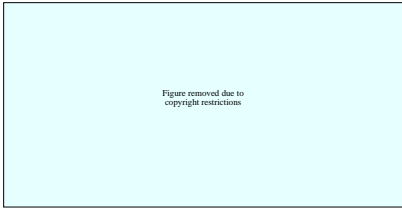
Sputtering uses a stream of energetic ions to re-move atoms from a target. These atoms can then be deposited on a substrate. Ions can come from a separate ion gun (ion beam sputtering) or be created with a radio-frequency field. Required ion energy is in the 10 eV to 10 keV range.
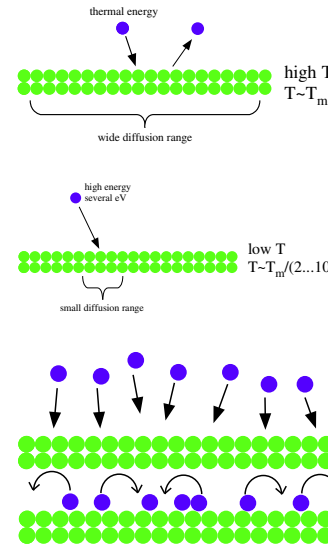
Advanatages:

- Can be used to cover very large areas
- Fast growth is possible
- Can be used even when volatile elements are present (Pb oxides)

Problems:

- Sputtering rate is dependent on the element (atomic weight)
- Process involves a sputtering gas

Thin film growth

Bulk crystals (single crystals) are grown close to the melt-ing point. Atoms have a long time to find a good crystal-lization site.

Thin film growth is done far below the melting point. Growth is controlled by kinetics.

Film growth involves two types of processes:
- deposition of atoms to the surface (MBE, sputtering, PLD pulse)
- Surface relaxation, i.e. surface diffusion of newly-deposited atoms. (between PLD laser pulses)

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The main processes are

- adsorption of adatoms on the film surface
- surface migration and surface reactions
- incorporation of adatoms into the growing lattice
- thermal desorption of some adatoms

For adatoms we have a sticking coefficient

$$s = \frac{N_{\mathrm{adh}}}{N_{\mathrm{tot}}},$$

which shows how many atoms (of particular type) actu-ally stay on the surface. This is one of the main sources of nonstoichiometry in oxide film growth. At first, the adatoms are *physisrobed*, i.e. only van der Waals forces are active. After thermalization e get *chemisrob-tion*, when actual bonds form between atoms.

Surface structures:
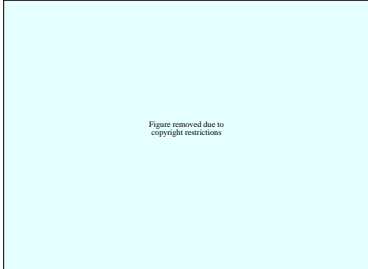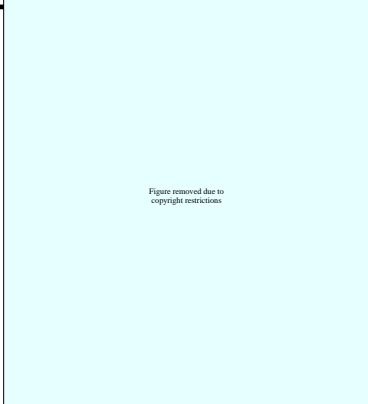
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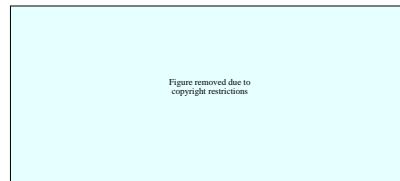
Thin films are grown on single-crystal substrates. Substrates are cut from large single crystals and pol-ished. This cutting is never (or hardly ever) exact, which means we have a *vicinal* surface. The miscut angle is usually of 0.1° order.

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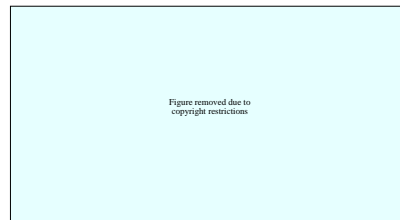
Surface migration occurs on flat terraces or along the step edges (faster). Kink sites are the least sta-ble sites in a lattice.

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Herman96 p.13

The basic growth modes for epitaxial films are
- *Layer-by-layer* or Frank van der Merve
- *Layer plus islands* or Stranski-Krastanov
- *island growth* or Vollmer-Weber

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Oxide thin films are also affected by structural changes of the surface layer. Possible changes include
- Lattice spacing changes (surface normal direction)
- Surface reconstruction (in-plane direction)
- Missing row reconstruction

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Strain effects in $La_{1-x}Sr_xMnO_3$

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We look at the magnetic ordering in $La_{1-x}Sr_xMnO_3$. The phase diagram shows a complex magnetix structure that depends on the doping level and temperature.

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The e_g levels are, in principle degenerate. In a real crystal, the oxygen octahedra surrounding the Mn ions are distorted (the Jahn-Teller distortion). This also lifts the degeneracy of the e_g levels, which also changes the bonding between Mn $3d$ and O $2p$ orbitals.

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Substrate A

Film

Substrate B

compressive strain

tensile strain
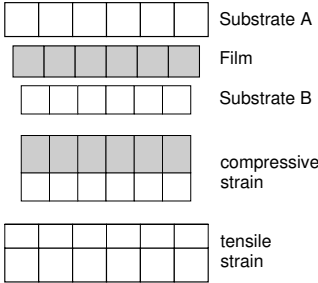
The Jahn-Teller distortion can be changed by stretching or compressing the lattice. This is possible by growing thin films on substrates that have different lattice constants.

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Here we see x-ray diffraction images of two films, grown on a $LaAlO_3$ substrate and a $SrTiO_3$ substrate. LSAT is $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$.

JPSJ 68 (1999) 3790

Slide 16

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We can now compare the resistivity and magnetization in films with different lattice strain. Strain is parametrized as a c/a ratio, which varies from 0.98 to 1.06. These chages correspond to pressures of -5 GPa to +11 GPa. The results can be summarized in one figure

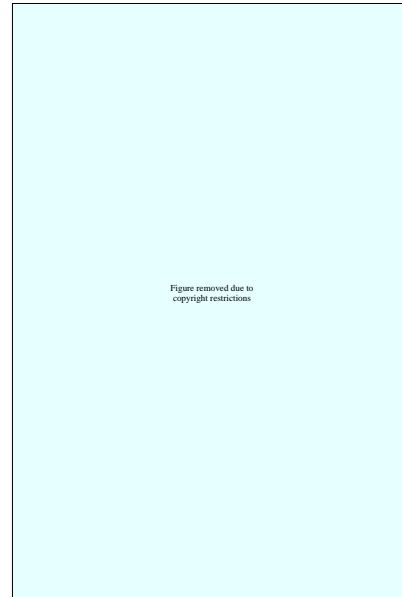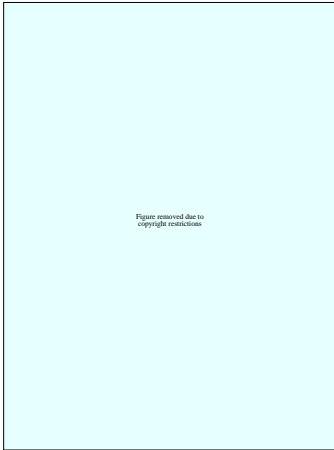Figure removed due to copyright restrictions

JPSJ 68 (1999) 3790

Another example of strain effects in thin films: La$_{1.9}$Sr$_{0.1}$CuO$_4$ superconductor

The critical temperature can be parametrized in terms of lattice pressure or strain

$$T_c = T_c(0) + 2\frac{\delta T_c}{\delta P_{ab}}P + \frac{\delta T_c}{\delta P_c}P$$
$$= T_c(0) + s\frac{\delta T_c}{\delta \epsilon_{ab}}\epsilon_{ab} + \frac{\delta T_c}{\delta \epsilon_c}\epsilon_c,$$

where strain $\epsilon = (d_{\text{bulk}} - d_{\text{strained}})/d_{\text{bulk}}$.
Usually, ϵ_{ab} and ϵ_c have opposite signs under hydrostatic pressure and therefore the pressure effect is small.
In films, the ϵ values can be quite different.
The lattice constants and temperature dependence of lattice parameters are shown in the plot.

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The pressure on the lattice in this example is about 5 GPa, corresponding to a lattice strain of $\epsilon_{ab} = -\epsilon_c = 0.7\%$. the critical temperatures are 10 K under tensile strain (grown on SrTiO$_3$), 37 K in a bulk crystal, which is strain free, and 49 K in a compressively strained lattice, grown on SrLaAlO$_4$.

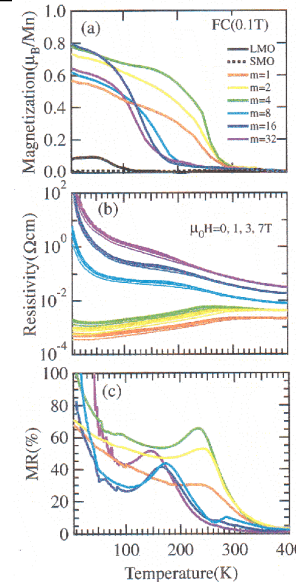Nature 39 (1998) 453

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Superlattices:

d_0 − superlattice period
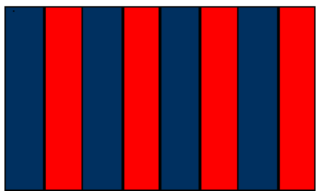
Superlattices consist of two or more different materials, arranged in layers. It forms a lattice with a much larger 'lattice constant' than either (or any) of the constituent layers.
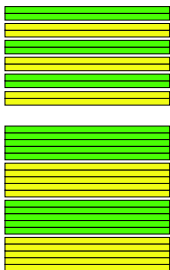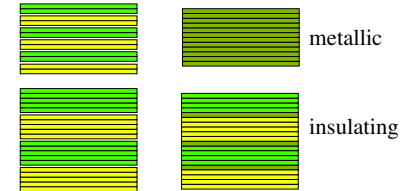
We look what happens if we combine two antiferromagnetic insulators in a superlattice: LaMnO$_3$ and SrMnO$_3$. We can change the layer thicknesses in the superlattice.

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Surprisingly, we see a ferromagnetic response in the superlattices. The superlattices are also metallic, not insulating.

metallic

insulating

We thus have effective interface layer doping. The interfaces are conducting and metallic due to a transfer of charge across the LaMnO$_3$ / SrMnO$_3$ interface. Effectively we get a La$_{1-x}$Sr$_x$MnO$_3$ behavior within about 2 unit cells of the interface without actually mixing La and Sr ions.

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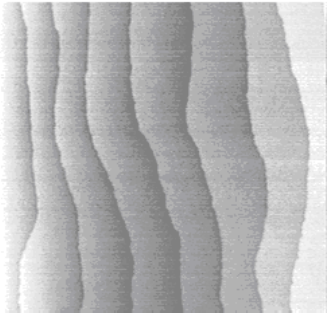
Nanostructures:

Atomically flat surfaces can be used for growing various nanostructures. First we need a flat surface. in oxides, this can often be obtained by simple annealing. Chemical etching is sometimes used as well. This STM image shows a $SrTiO_3$ surface.
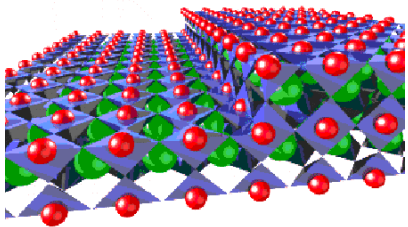

This is what an ideal surface would look like on an atomic scale. In case of $SrTiO_3$, the TiO_2 layer is more stable. All of the steps on the vicinal surface have a single unit cell height. Terraces are atomically smooth.

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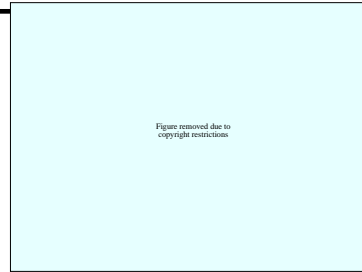
Branham01 p.8

The easiest form of nanostructures to grow is a random collection of nanodots. This is simply the initial stage of thin film growth (any mode).
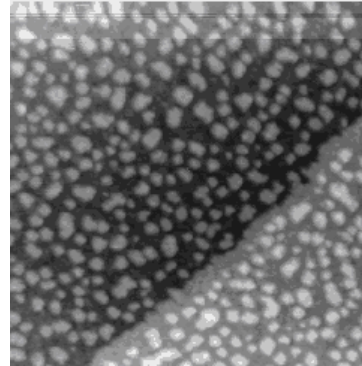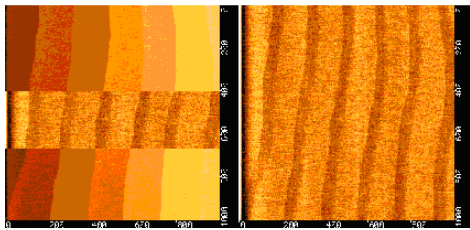

This is what a surface looks like after the growth of about half a monolayer of $LaFeO_3$ on $SrTiO_3$. Lots of small islands form and grow. The average diameter is about 4 nm. the height of islands is just one unit cell.
the shape and sixe of the nanodots depends on the temperature and the rate of surface diffusion.

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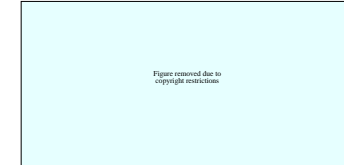
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If temperature is high, surface migration is fast and the formation of small nuclei on the surface is not energetically favorable. Migration continues until adatoms find step edges. These are always stable crystallization sites. At the beginning of heteroepitaxial growth we therefore get a nanowire along the existing step edges.
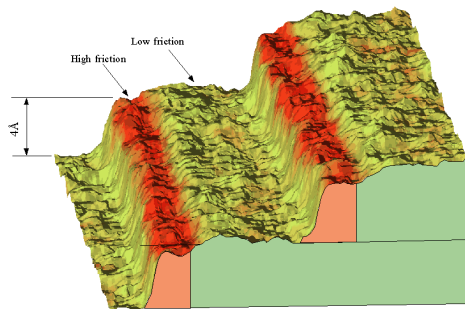
A three-dimensional view of $La_{0.6}Sr_{0.4}MnO_3$ nanowires on a vicinal $SrTiO_3$ surface. Note that the vertical and horizontal scales are very different. The step height is only 4 Å, while the terrace width is around 1000 Å.

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References:

Herman96 M. A. Herman, H. Sitter, "Molecular Beam Epitaxy", Springer, Berlin, 1996.

Branham01 K. Branham D. Vvedensky, "Low-Dimensional Semiconductor Structures", Cambridge University Press, 2001.

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