Lecture 7
Metal Oxide Semiconductors

Announcements
Homework 1/4:
• I will return it next Tuesday (October 16th).
Homework 2/4:
• Will be online on later today.
• Due Thursday October 18th at the start of the lecture (10:00am).
• I will return it on the day of the midterm (October 25th).
• Homework 2 will consist of content covered in Lectures 5, 6 and 7.
Additional Information

- The course textbook (Brotherton) – Chapter 9 covers this subject quite well.
- This is an active area of research, so there are plenty of reviews on the subject.
  - [https://www.nature.com/articles/nmat4599](https://www.nature.com/articles/nmat4599).
- One of John Wager’s (just retired from EECS) talks is available on YouTube:
  - [https://www.youtube.com/watch?v=yalJI9SpO9s](https://www.youtube.com/watch?v=yalJI9SpO9s).

Lecture 7

- Chemistry of Metal Oxides.
- Metal Oxide TFT Fabrication Process.
- Binary Oxides.
- Mixed Oxides.
Chemistry of Metal Oxides

Oxides

- Let’s start by asking **what is an oxide**?
- It is a compound that contains at least one oxygen and one other element.
- Normally the term is applied to compounds in an oxidation state of -2.
- So carbon dioxide is an oxide:
  \[ \text{O=C=O} \]
- Metal oxides are, unsurprisingly, oxide compounds containing a metal element.
Metal Oxides

- Probably the metal oxide you are most familiar with is iron(III) oxide: Fe$_2$O$_3$.

- Almost all metallic elements easily form stable bonds with oxygen, meaning that most metals have a corresponding oxide.
- Platinum and gold are prized because this does not happen naturally in air.

Metal Oxides

- It turns out that certain metal oxides can be used for electronics.
- There are no metal oxide integrated circuits.
- So why are we interested in metal oxides for large-area electronics?
- The answer is due to the nature of bonding in metal oxides.
Ionic Bonding

- Ionic bonding involves the transfer of one or more electrons between atoms.
- The most common example is NaCl (table salt):

![Diagram of Sodium and Chlorine forming Sodium chloride]

Metal oxides also formed through ionic bonding.
- Oxygen has 6 electrons in the outer shell.
- So 2 electrons are transferred to the oxygen atom.
- For a Group 2 or Group 12 atom this would look like:

![Diagram of Metal and Oxygen forming Metal Oxide]

- E.g. zinc oxide: ZnO.
Ionic Bonding

- For other groups, different combinations are required to fill all shells:
- For Group 4 or 14, we could have one metal and two oxygens:

  ![Diagram of ionic bonding between a metal and two oxygens]

  - E.g. tin oxide: $\text{SnO}_2$.

Ionic Bonding

- More complex oxides require more atoms:

  ![Diagram of ionic bonding between a metal and three oxygens]

  - E.g. indium oxide: $\text{In}_2\text{O}_3$. 
Ionic Bonding

- For the correct combination, s-electrons will participate in bonding.
- As an example, let’s consider zinc.
- Zinc has the following electronic structure:

\[
\text{Zn} = [\text{Ar}]3d^{10}4s^2
\]

- So, notice, the two outer electrons are in the 4s state.

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Ionic Bonding

- So what happens when these 4s electrons are transferred when bonding with oxygen?

\( M^0 \) denotes generic metal

\( M^{2+} \) denotes a general state. For ZnO this would be a 4s state.

\( O^{2-} \) denotes the metal oxide orbitals

- We have 2 empty ns electron states, which form the conduction band.

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S-Orbitals

- S-orbital are spherical in nature:

  ![S-Orbital Diagram](https://www.example.com/s-orbital.png)


- The higher the $n$, the larger the orbital.
  - I.e. the radii of $1s < 2s < 3s < \cdots$

Silicon

- Recall for silicon, transport occurs through hybridized $sp^3$ orbitals.

  ![Silicon Structure](https://www.example.com/silicon.png)

  (https://youtu.be/ApqFLv600s?t=9m10s)

- These are highly directional.
- The situation is similar for most covalent semiconductors.
Orbital Overlap

• The following images are routinely used to explain why this is important:

**Crystalline Silicon**

**Amorphous Silicon**


Directional $sp^3$ orbitals

Orbital Overlap

• The following images are routinely used to explain why this is important:

**Crystalline Metal Oxide**

**Amorphous Metal Oxide**


Oxygen $2p$ orbitals

Metal ns orbitals
Orbital Overlap

• The large, spherical, $ns$ orbitals that form the conduction band states in metal oxides, are much less dependent on order than directional orbitals.

• In some cases the electron mobility may be only 50% of the value in crystalline form.
• The electron mobility in amorphous silicon is $\sim 0.1\%$ ($1/1000^{th}$) of its value in the crystalline form.

This means that for large-area deposition, where we expect the film to be disordered, we should still get similar electron transport.

• We can get up to $\mu_e \sim 20 - 100 \text{ cm}^2/\text{Vs}$.

Notice the filled oxygen $2p$ states are highly isolated.
• This means there is very little overlap between hole-transporting states.
• $\mu_h \sim 10^{-3} \text{ cm}^2/\text{Vs}$. 

Environmental Stability

- We didn’t cover environmental stability in the last lecture, but it is important to mention it here.
- Silicon is highly reactive, and will not be found in its elemental form naturally.
  - Normally silicon dioxide, SiO$_2$, (sand) is naturally occurring.
  - Silicon-based transistors are encapsulated with an insulator during processing.

Oxides on the other hand are, by definition, already oxidized.

- Which means they are a lot more stable than many other semiconductor systems, as they will not change state due to oxygen exposure.
- So in air they are generally more stable.
  - However, if they are soluble in water, they will still degrade due to humidity in the air.
  - This is beneficial for manufacturers, as they can be more versatile with product design, and are not constrained by finding an appropriate encapsulant.
Metal Oxide TFT Fabrication Process

Metal Oxide TFTs

- Metal Oxide TFTs are not widely commercially employed (yet).
- There are no universally agreed-upon procedures for TFT development.
- And there are many (different) experimental procedures used in laboratories.
- The architecture shown here is an "emerging trend", as described by Brotherton.
**Substrate and Gate**

- Commercial TFT backplanes are produced on glass.
- To ensure the back (gate electrode) is very flat, a buffer layer is applied to the surface of the glass.
  - This is insulating (e.g. SiN).
- As with a-Si:H, the metal gate electrode in then deposited.
- This will be sputtered and then patterned as described in the previous lecture.

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**Substrate and Gate**

- There have been many demonstrations of flexible metal oxide transistors.
- They use a plastic as a substrate.
  - E.g. PET = Polyethylene terephthalate.
  - Commercial prototypes have also been demonstrated.
Gate Dielectric

- The dielectric is then deposited onto gate / substrate.
- In demonstration displays (where details are made public), SiO$_2$ is usually used as a gate dielectric.
- Silicon nitride (SiN$_x$) or silicon oxynitride (SiO$_x$N$_y$) are also used.
- These layers are also deposited by PECVD.
- Process temperatures ~ 300°C.
- Not suitable for plastic substrates

Alternative Dielectrics

- If we wish to use plastic substrates, then we require dielectrics that can be processed at lower temperatures.
- Luckily there are many options, and dielectrics for TFTs is an intense area of research (see Lecture 10).
- Many oxides are insulators.
  - Silicon dioxide (SiO$_2$) is the best known.
  - But there are many others to choose from. E.g. alumina (Al$_2$O$_3$), titania (TiO$_2$), zirconium dioxide (ZrO$_2$), hafnium dioxide (HfO$_2$).
Solution-Processed Dielectrics

- These dielectrics can be deposited from solution.
- Precursor of dielectric material is dissolved or suspended in a solvent.
- Solution / suspension deposited onto substrate at room-temperature.
- Samples may then need to be thermally annealed to convert precursor into the dielectric material.
- Annealing at < 200°C is possible – plastic compatible.

https://www.youtube.com/watch?v=bzAhGLo20

Solution-Processed Dielectrics

- There are examples of low-temperature (< 150°C) solution deposition of SiO₂.
- This would be very useful as SiO₂ dielectrics are widely employed and well understood.
- The process is still cumbersome at present.

Metal Oxide Deposition

• Next is the deposition of the metal oxide semiconductor itself.
• Normally this is carried out by DC sputtering.
• This is because DC sputtering is already employed industrially to deposit materials over large areas.
• Substrate temperature is normally quite low during deposition.
• Compatible with flexible substrates.

Metal Oxide Deposition

• As with dielectrics, many metal oxide semiconductors are solution-processable.
• One challenge is conversion.
• Most metal oxide solutions are actually formed of precursors.
• After deposition, they typically need treatment (normally thermal) to convert from a precursor to a semiconductor.

https://www.youtube.com/watch?v=crAugjXG3QA
Spray Coating

- Spin coating is fine for laboratory testing, but is clearly not suited for large-area deposition.
- Researchers are interested in developing scalable techniques such as spray-coating.

- This is still an emerging area of research.

Currently surface roughness is a lot higher for spray-coated vs spin-coated films.

\[ \text{Spray Cast In}_2\text{O}_3 \quad \text{Spin Cast In}_2\text{O}_3 \]

Faber et al., ACS Appl. Mater. & Int. 7 (2015) 782.
Conversion Temperature

- Probably the biggest issue with solution-processed metal oxides is the conversion temperature.
- Normally above plastic-compatible temperatures are required for optimum performance.
- This is a big area of research.

Faber et. al., ACS Appl. Mater. & Int. 7 (2015) 782.

Low Temperature TFTs

- Recently progress has been made to get the conversion temperatures down to acceptable values.
- But a lot of work remains to be done on this subject.

Electrodes

- Finally, the electrodes are deposited.
- The procedures are similar to a-Si:H, but an etch stop is used.
- This is an insulator, designed to protect the semiconductor during the etch process.
- SiO\textsubscript{2} or TiO\textsubscript{2} is often used. SiNx can cause charge to leak into the channel, causing on/off ratio to drop.

Binary Oxides
Different Oxides

- Unlike silicon, we are now faced with a choice as to which oxide(s) do we use for our semiconductor?

Let’s start by getting rid of the lanthanides and Actinides. They are too rare to be useful.
Different Oxides

• Let’s get rid of heavy atoms, as they are normally poisonous or radioactive.

Different Oxides

• We can also get rid of the noble gases, since they will not react.
Different Oxides

- We want elements that have a lot of s-type character to their outer electrons.

- So, when the atoms are transferred, they leave spherical s-type conduction band states for transport.
- There is still a lot of choice.

Binary Oxides

- We will start by restricting ourselves to two elements in our compound: one is oxygen, and one is a metal.
  - We call such compounds binary oxides.
  - In contrast to indium tin oxide (ITO), which is a ternary oxide, for example.
  - The first reported oxide transistor was based on tin oxide: SnO$_2$.[1]
  - No mobility given in the paper, but if the drain voltage was ~10V, the value should be: 0.5 cm$^2$/Vs.
  - Not too bad, for the first oxide TFT ever!
  - No one really looked at oxides again until 2003.

Zinc Oxide

- Probably, the most famous metal oxide semiconductor is zinc oxide: ZnO.
- There are plenty of review articles on the material:
  - E.g: [http://dx.doi.org/10.1088/0034-4885/72/12/126501](http://dx.doi.org/10.1088/0034-4885/72/12/126501).
- John Wager here at OSU played a big role in its development.

Zinc Oxide

- A few properties of ZnO:
  - Crystallizes into Wurtzite crystal structure:
  - It is a direct band gap semiconductor:
Zinc Oxide

• When deposited as a film it is polycrystalline.

![Image of Zinc Oxide film with a thickness of 6-7 nm](image)


• Recall from the previous lecture that polycrystallinity can lead to significant device-to-device variation.

Zinc Oxide

• When sputtered, devices can reliably exhibit electron mobilities up to $\mu_e = 10 \text{ cm}^2/\text{Vs}$.

• From solution $\mu_e = 1-5 \text{ cm}^2/\text{Vs}$ is normal.

![Graphs showing mobility vs. voltage](image)


• Device-to-device variation is however significant.
Zinc Oxide

- What about optical properties?
- Conduction band minimum: ~3.8 eV
- Valence band maximum: ~7.05 eV
- Band Gap ≈ 3.25 eV.
  - 381nm. (i.e. ultraviolet)
  - i.e. It is optically transparent!

Transparent Electronics

- The idea of transparent electronics has led to a lot of excitement.
John Wager on ZnO

- A talk given by John Wager (OSU) in 2013:
  - https://www.youtube.com/watch?v=yalJI9SpO9s.
  - 7mins 20sec to 10mins 40sec.

Other Binary Oxides

- What about other oxides?
- Indium oxide (In$_2$O$_3$) is very similar to ZnO.
  - Band gap (3.6eV) is slightly larger than ZnO.
    - →Lower off current.
  - Mobility, and device-to-device variation similar.
Other Binary Oxides

- Gallium oxide (Ga$_2$O$_3$) has a very wide band-gap (~4.9eV).
- Generally considered an insulator.
- However, with the correct electrodes, TFTs can be fabricated.

Thomas et al., APL 105 (2014) 092105.

Mixed Oxides
Multiple Oxides

- So far we have just restricted ourselves to compounds consisting of oxygen and one metal.
- However, it turns out that most of these simple semiconductors are polycrystalline when processed as thin films.
- What happens if mix oxides?

John Wager on Mixed Oxides

- A talk given by John Wager (OSU) in 2013:
  - [https://www.youtube.com/watch?v=yalJl9SpO9s](https://www.youtube.com/watch?v=yalJl9SpO9s).
  - 10mins 41sec to 12mins 49sec.
Multiple Oxides

- We won’t go into details, but this has been widely observed.
- E.g. Indium zinc oxide (IZO) in solution:

![Graph](image)


IGZO

- But IGZO is the current standard, and has been commercialized.
- Formed of 3 metals and oxygen:
  - Indium.
  - Gallium.
  - Zinc.

[YouTube Video](https://www.youtube.com/watch?v=kDXF54cy9b8)
IGZO

• What is so special about IGZO?
• The field is new, and it is the best combination found.
  • The combination **frustrates crystallization**.
• But also consider the electron configuration of the three relevant atoms:

\[
\text{In} = [\text{Kr}]4\text{d}^{10}5\text{s}^25\text{p}^1
\]

\[
\text{Ga} = [\text{Ar}]3\text{d}^{10}4\text{s}^24\text{p}^1
\]

\[
\text{Zn} = [\text{Ar}]3\text{d}^{10}4\text{s}^2
\]

• We have contributions from 5s and 4s orbitals to electron transport.
• Recall, the \( n \) of the orbitals determines their size (5s > 4s etc.).

IGZO

• We could picture an amorphous film of overlapping 5s orbitals (from In\(_2\)O\(_3\)) as:

• We would expect electrons to percolate through the shortest pathway.
IGZO

- If we also add smaller 4s orbitals, then the theory is that the gaps between orbital should be smaller.

- We would expect the percolation pathway to be more optimized.

IGZO Mobility

- The electron mobility in IGZO is highly dependent on composition.
IGZO TFT Performance

- The electron field effect mobility for IGZO is reliably $\mu_e = 20-30 \text{ cm}^2/\text{Vs}$.
- $\gg 10 \times$ better than a-Si:H.
- Highly optically transparent.
- Highly amorphous.
- Low device-to-device variation.
  - High yield.

Off Current

- Because the band gap is so large in IGZO, the off-current is extremely low.
- There is no competitor to metal oxides when it comes to off-current.
John Wager on Off-Current

- A talk given by John Wager (OSU) in 2013:
  - https://www.youtube.com/watch?v=yaiJl9spO9s. 27mins 54sec to 29mins 37sec.

IGZO Deposition.

- Industrially, large-area DC sputtering is used to deposit IGZO.
- Solution deposition is also possible, but it is still experimental.
Bias Stress Instability

- A major downside to IGZO (and oxides generally) is their threshold-voltage instability.
- This is not found to effect mobility or subthreshold slope, just threshold voltage.
- But this is still a problem.
- This is due to a large density of electron traps at the IGZO/dielectric interface.

Fig 9.21. Brotherton

Bias Stress Instability

- We will cover dielectrics in more detail in Lecture 10.
- But briefly, upon application of a constant bias, traps are filled, leading to a charging of the dielectric.
- This acts as a constant negative voltage, that needs to be overcome before the device can turn on.
- I.e. a positive $V_T$. 
Bias Stress Instability

- This can be overcome through high temperature (~400°C) post-deposition anneals.
- Believed to remove organic contaminants (H and C).
- **Passivation** can be used to remove traps at the interface.
- More on this in Lecture 10.

![Fig 9.21. Brotherton](image)

NBIS

- One problem that needs to be overcome for IGZO to be commercially ubiquitous is **negative bias illumination stress** (NBIS).
- This is a change in the electrical behavior of TFTs under illumination.
NBIS

- This is a particular problem for **transparent electronics** applications.
- Because the characteristics change with sub-band gap radiation, the effect is due to trap states.
- This has been attributed to photo-ionization of neutral oxygen vacancies.
- It is a persistent effect.
- It requires further study to be understood fully.

![Fig 9.23. Brotherton](image)

John Wager’s Summary

- A talk given by John Wager (OSU) in 2013:

  - https://www.youtube.com/watch?v=yalJI9SpO9s.
  - 18mins 33sec to 20mins 55sec.
Next Time…

- Organic Semiconductors