Lecture 7
Metal Oxide Semiconductors

Announcements

Homework 3/10:

• Is online now.
• Due Tuesday October 19th at the start of the lecture (2:00pm).
• I will return it one week later (October 26th).
• Homework 3 will consist of content covered in Lectures 5 and 6.
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 (retired from EECS) talks is available on YouTube:
  • [https://www.youtube.com/watch?v=yalJI9S09s](https://www.youtube.com/watch?v=yalJI9S09s).

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:

\[
\text{O=\text{C}=\text{O}} 
\]

• 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 ions forming sodium chloride](image)

**Metal Oxide Formation**

- 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 ions forming zinc oxide](image)

- 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:

• E.g. tin oxide: SnO$_2$.

Ionic Bonding
• More complex oxides require more atoms:

• E.g. indium oxide: In$_2$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 \textbf{4s state}.

Ionic Bonding

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

- We have 2 empty \( n_s \) electron states, which form the conduction band.
**S-Orbitals**

- S-orbital are spherical in nature:

  ![Image](https://i.imgur.com/3Q5Q5Q.jpg)


- 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.

  ![Image](https://i.imgur.com/4Q5Q5Q.jpg)

  https://youtu.be/ApqFLVd0XaI?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**

![Crystalline Silicon Image]

**Amorphous Silicon**

![Amorphous Silicon Image]


Directional sp^3 orbitals

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

**Crystalline Metal Oxide**

![Crystalline Metal Oxide Image]

**Amorphous Metal Oxide**

![Amorphous Metal Oxide Image]


Metal ns orbitals

Oxygen 2p 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.

Orbital Overlap

- 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 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 is then deposited.
- This will be sputtered and then patterned as described in the previous lecture.

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 \(\sim 300^\circ\text{C}\).
- 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.

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.

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.
- SiO₂ or TiO₂ is often used. SiNx can cause charge to leak into the channel, causing on/off ratio to drop.
Different Oxides

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

- 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.

- 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: \( \text{SnO}_2 \).\(^1\)
- No mobility given in the paper, but if the drain voltage was \(~10V\), the value should be: \(0.5 \text{ cm}^2/\text{Vs}\).
- Not too bad, for the first oxide TFT ever!
- No one really looked at oxides again until 2003.

\(^1\)Klaisentz, Sol. State. Electron. 7 (1964) 701

**Zinc Oxide**

- Probably, the most famous metal oxide semiconductor is zinc oxide: \( \text{ZnO} \).
- There a 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 (normally) into Wurtzite crystal structure:
  - It is a direct band gap semiconductor:

When deposited as a film it is polycrystalline.

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

- Device-to-device variation is however significant.

Zinc Oxide

- What about optical properties?
- Conduction band minimum: $\sim 3.8 \text{ eV}$
- Valence band maximum: $\sim 7.05 \text{ eV}$
- Band Gap $\approx 3.25 \text{ eV}$.
  - 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](https://www.youtube.com/watch?v=yalJI9SpO9s).
  - 7mins 20sec to 10mins 40sec.
Other Binary Oxides

- What about other oxides?
- Indium oxide ($\text{In}_2\text{O}_3$) is very similar to $\text{ZnO}$.

- Band gap (3.6eV) is slightly larger than $\text{ZnO}$.
  - $\rightarrow$ Lower off current.

- Mobility, and device-to-device variation similar.

Other Binary Oxides

- Gallium oxide ($\text{Ga}_2\text{O}_3$) has a very wide band-gap (~4.9eV).
- Generally considered an insulator.
- However, with the correct electrodes, TFTs can be fabricated.
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:
  
  ![Image of John Wager's talk](https://www.youtube.com/watch?v=yalJI9SpO9s)
  
  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 showing mobility vs In\(_2\)O\(_3\) fraction](https://example.com/graph.png)

IGZO

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

https://www.youtube.com/watch?v=KXF54ctY3g8

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:
  \[ \text{In} = [\text{Kr}]4d^{10}5s^25p^1 \]
  \[ \text{Ga} = [\text{Ar}]3d^{10}4s^24p^1 \]
  \[ \text{Zn} = [\text{Ar}]3d^{10}4s^2 \]
  - 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.

![Fig 9.2. Brotherton](image)

**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=yalJI9SpO9s](https://www.youtube.com/watch?v=yalJI9SpO9s).
  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.

![Diagram of IGZO Deposition](image)

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.
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 a constant negative voltage, that needs to be overcome before the device can turn on.
- I.e. a positive $V_T$.

- 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.
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.

\[ \text{Fig 9.22. Brotherton} \]

\[ \text{Dark} \quad V_{dd} = 10V \]
\[ 3.4eV (> \text{Band Gap}) \]
\[ 2.7eV (< \text{Band Gap}) \]

- 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.

\[ \text{Fig 9.23. Brotherton} \]
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