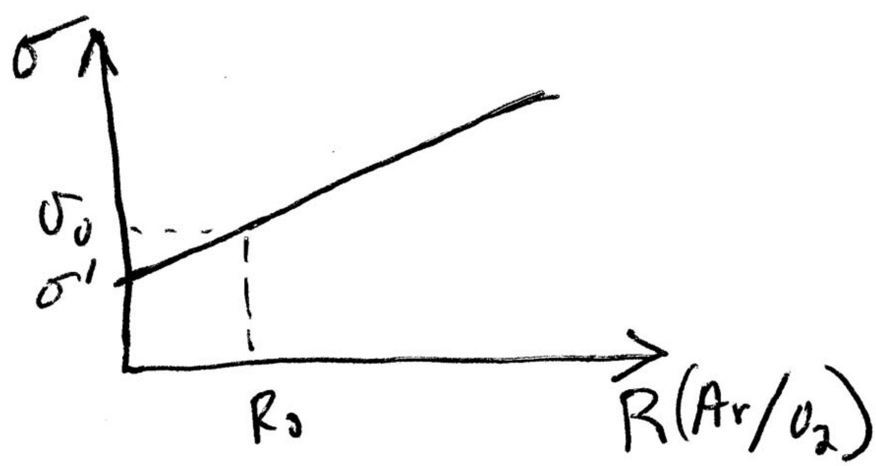
**Chapter 2**
**Electrochemical Sensors**
**Solutions**

1. In a metal oxide semiconducting sensor, the electrodes are metallic. If the metal is a non noble one, an oxide layer is formed between the metal and metal oxide forming a metal insulator semiconductor (MIS) contact.

2. A semiconducting metal oxide is n-type due to oxygen vacancies. Oxygen vacancies in semiconducting metal oxides act as donors which results in free electrons moving to the conduction band making the oxide n type. Electrons come from the metal ions which normally would be shared with the electrons associated with the oxygen ion.

3. Initially, you must experimentally determine in the RF magnetron sputtering system the relationship between the conductivity (σ) and argon/oxygen ratio (R). In most all cases, this relationship is linear as shown. Next, determine the equation for the linear variation shown and using this equation, determine the Ar/$O_2$ ratio necessary to get a film conductivity of $10\sigma_0$. In this case, the Ar/$O_2$ ratio is the following:

$$\left[\frac{10\sigma_0 - \sigma'}{\sigma_0 - \sigma'}\right] R_O$$




4. The mobility varies as $T^{-3/2}$ while the carrier concentration varies as $e^{-Eg/2kT}$. For a given increase in temperature, $e^{-Eg/2kT}$ varies significantly more than $T^{-3/2}$.

5.

$$\mu \propto T^{-3/2}$$

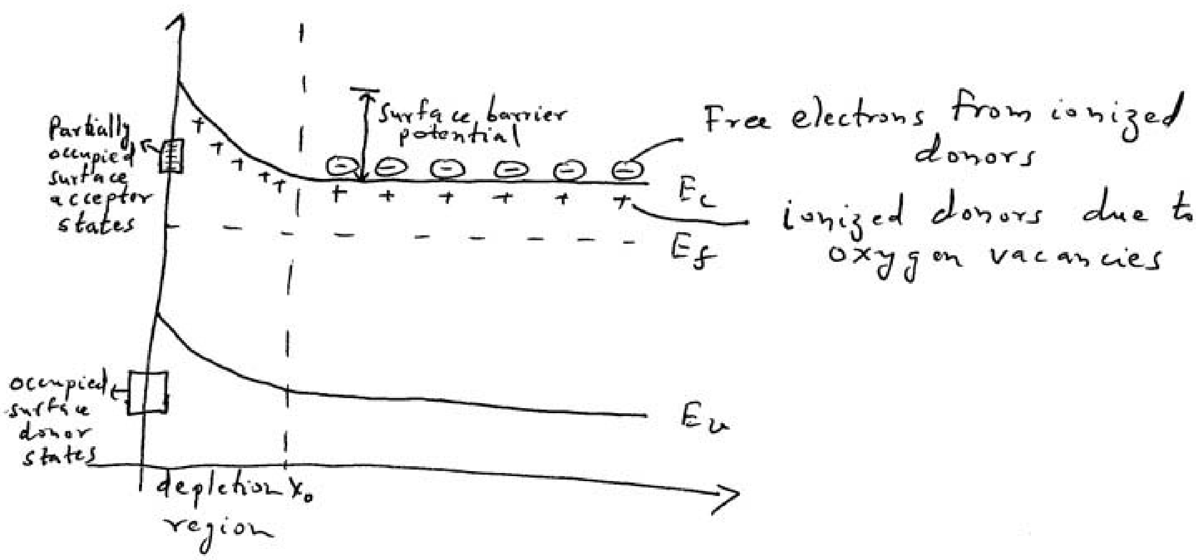
$$\mu \propto (24)^{-3/2}$$

$$\mu_{200} \propto (200)^{-3/2}$$

$$\frac{\mu}{\mu_{200}} = \frac{(24)^{-3/2}}{(200)^{-3/2}}$$

$$\mu_{200} = \left[\frac{3}{25}\right]^{3/2} \mu$$

6.




7. Polycrystalline films are more stable. Amorphous films sorb and desorb water causing the film electrical properties to change. Amorphous films can be made polycrystalline by heat treating (annealing).

8.

Consider Poisson's equation

$$\frac{d^2\phi}{dx^2} = -\frac{qN_D}{\epsilon} \qquad -(1)$$

where $\epsilon$ = metal oxide dielectric constant

$N_D$ does not vary with x as we assume doping is homogeneous.

Lets define a parameter, V, as follows

$$V(x) = \phi(x) - \phi(b) \qquad -(2)$$

$\phi_b$ = potential in the metal oxide bulk

Solving equation 2 for $\phi(x)$ and substituting into eqn 1

$$-\left.\frac{dV}{dx}\right|_{x}^{x_0} = -\int_{x}^{x_0} \frac{qN_D}{\epsilon}\, dx \qquad -(3)$$

$$\frac{dV}{dx} = 0 \text{ at } x = x_0$$

∴ Eqn 3 becomes

$$\frac{dV}{dx} = \frac{qN_D}{\epsilon}(x - x_0) \qquad -(4)$$

Integrating Eqn 4 gives

$$V = \frac{qN_D}{\epsilon}(x - x_0)^2 \qquad -(5)$$

Surface barrier potential then becomes

$$V_s = V|_{x=0} = \frac{qN_D}{2\epsilon} x_0^2 \quad - (6)$$

Now seperation of charge occurs near the surface of the metal oxide and thus a space charge exists. This region is approximated as parallel plate capacitance as follows

$$C = \frac{\epsilon A}{X_0} \Rightarrow C^2 = \frac{\epsilon^2 A^2}{X_0^2} \quad - (7)$$

$$V_s = \frac{qN_D}{2\epsilon} \cdot X_0^2 \quad - (8) \quad [\text{From } 6]$$

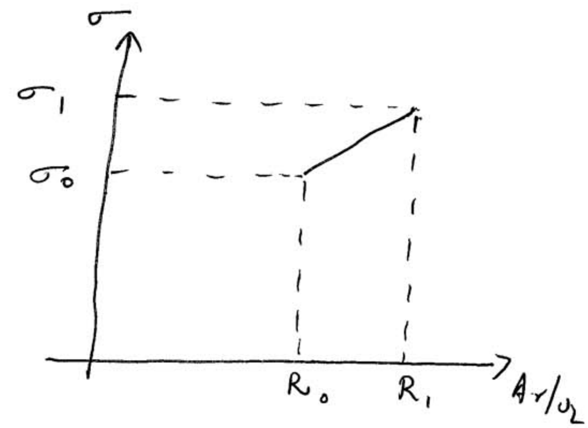
$$X_0^2 = \frac{2 \epsilon V_s}{q N_D}$$

$$C^2 = \frac{\epsilon^2 A^2}{2 \epsilon V_s} \cdot q N_D \Rightarrow \frac{1}{C^2} = \frac{2V_s}{\epsilon A^2 q N_D}$$

9.

$\sigma = n e \mu$

$n \downarrow$ oxygen vacancies




$y = mx + b$

$\sigma = mR + b$

for $(\sigma_0, R_0)$

$n_0 e \mu = m R_0 + b \qquad - (1)$

for $(\sigma_1, R_1)$

$n_1 e \mu = m R_1 + b \qquad - (2)$

$n_0 e \mu = m R_0 + b$

$\dfrac{n_0 e \mu - b}{R_0} = m \qquad - (3)$

$n_1 e \mu = \left(\dfrac{n_0 e \mu - b}{R_0}\right) R_1 + b$

$n_1 e \mu = \dfrac{n_0 e \mu R_1}{R_0} - b\dfrac{R_1}{R_0} + b$

$\dfrac{\left(n_1 e \mu - n_0 e \mu \dfrac{R_1}{R_0}\right)}{\left(1 - R_1/R_0\right)} = b \qquad - (4)$

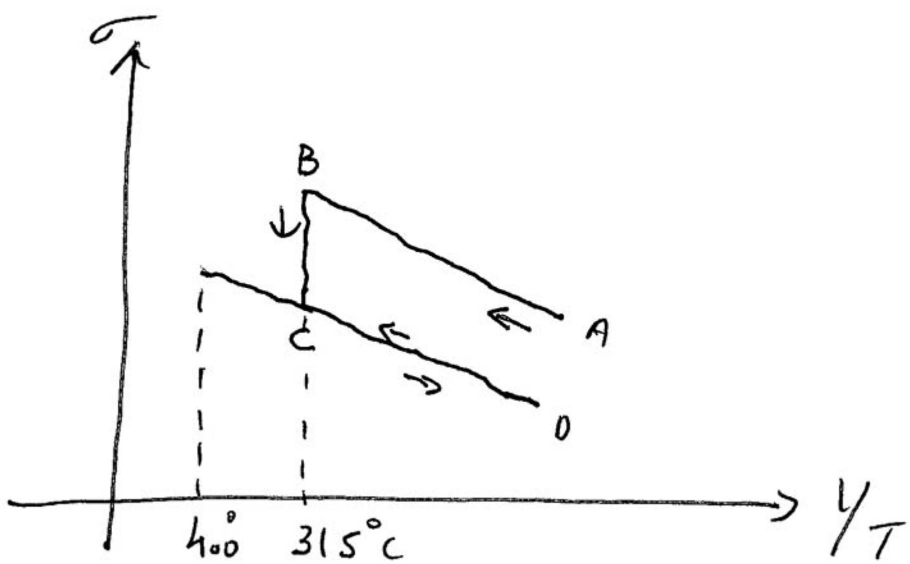
$$n e \mu = m R + b$$

$$n = \frac{m R + b}{\mu e}$$

where $m$ & $b$ are given by eqn (3) and (4)

10. Impedance based sensor gives both the real and imaginary parts ($Z_r$ and $Z_I$) of the impedance while resistance based sensor will only give the real part. Another advantage of impedance based sensors is that we can choose the frequency of operation (f). The 3 main parameters of $Z_R$, $Z_I$ and f can be used in an impedance based sensor while in the resistance based only R can be used for determining target gas type and concentration level.

11.




From A → B, $WO_3$ film is in amorphous state. From B → C, $WO_3$ film is transitioning to polycrystalline. From C → D, $WO_3$ film is in polycrystalline state. It is irreversible. Once the film is polycrystalline, it cannot go back to being amorphous. $WO_3$ becomes polycrystalline at 315° C.

12. Oxidation takes place. Oxygen (ionosorbed) exists as $O_2^-$ and $O^-$. They increase the surface barrier potential ($O_2^-$ and $O^-$ augment the surface states). Thus, resistivity increases and conductivity decreases.

13. Hydrogen combines with oxygen to form water. Barrier potential decreases, free electrons appear, resistance decreases and conductivity increases.

$$H_2 \rightarrow 2H$$
$$4H + 2\bar{O} \rightarrow 2H_2O + \bar{e}$$

14.

$$\bar{e} + O_2 \rightarrow O_2^-$$
$$O_2 \rightarrow 2O$$
$$\bar{e} + O \rightarrow \bar{O}$$

15. $CH_4$ is a reducing agent.

$$CH_4 \rightarrow C + 4H$$
$$C + 4H + 3\bar{O} \rightarrow CO + 2H_2O + 3\bar{e}$$

This results in free electrons and thus conductivity increases.

16.

$NO_x$ can be either $NO$ or $NO_2$

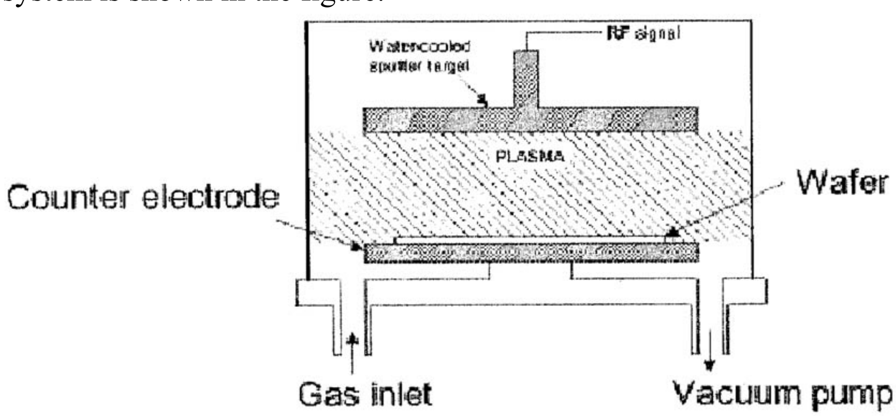
$$2NO \rightarrow N_2 + O_2$$
$$O_2 \rightarrow 2O$$
$$O + e^- \rightarrow O^-$$

$$2NO_2 \rightarrow N_2 + 2O_2$$
$$2O_2 \rightarrow 4O$$
$$O + e^- \rightarrow O^-$$

$NO_x$ is an oxidizing agent. Resistance increases, barrier potential increases due to formation of $O^-$ and as a result conductivity decreases.

17. Metal oxide films are doped with noble metals so that they act as reaction centers. They attract target gases to the surface and lower the energy necessary to break the gas into individual atomic components, thus allowing them to react with metal oxide film. Thus it imparts more selectivity and reduces the response time. Examples of noble metals are palladium, gold, and iridium.

18. Sputtering is a technology in which material is released from a source at much lower temperature than evaporation. The substrate is placed in a vacuum chamber with the source material, named a target, and an inert gas (such as argon) is introduced at low pressure. A gas plasma is struck using an RF power source, causing the gas to become ionized. The ions are accelerated towards the surface of the target, causing atoms of the source material to break off from the target in vapor form and condense on all surfaces including the substrate. As for evaporation, the basic principle of sputtering is the same for all sputtering technologies. The differences typically relate to the manner in which the ion bombardment of the target is realized. A schematic diagram of a typical RF sputtering system is shown in the figure.



19. In an IDT electrode configuration, the net resistance is much lower as the electrodes are in parallel. When used as a sensor, changes can be monitored more easily if the base resistance is lower.

20. Gold is a perfect conductor. But when gold is used to detect Hg above 10 ppm, it goes from being a perfect conductor to an insulator. Thus it has a very limited range of detection.

21. 1) Thickness increases as the polymer absorbs gas (swelling).

$$t \rightarrow t + \Delta t$$

2) Dielectric constant changes

$$\varepsilon \rightarrow \varepsilon \pm \Delta\varepsilon$$

22. Recently there has been considerable interest in using polymer based capacitive arrays for gas sensing. In contrast to the single MOS capacitor sensors, the novel use of the electrodes and the selective properties of polymer coatings have resulted in the fabrication of multiple capacitors in a single substrate. One of the major obstacles in a capacitor based sensor is the exposure of the target gas to the chemi-selective layer. One such capacitor array configuration is shown in Figure 2.40 and 2.41 (book). This type of arrangement can accommodate many capacitors and the perforated top conductor plate allows the target gas to diffuse into the polymer layer.